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## QUANTUM ELECTRODYNAMICS IN MATERIAL MEDIA

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## Synopsis

The canonical quantum theory of an electromagnetic field within an isotropic, nondispersive dielectric body in motion is developed. The quantization of the free field is carried out in two different ways, both by basing the canonical procedure directly on the field Lagrangian in the medium in a conventional way, and by using a new transformation procedure which maps the results from the vacuum field into those of the medium field. In the latter case, we also permit the existence of a family of covariant gauges. Covariant polarization vectors are introduced which are convenient for the relativistic appearance of the theory; in particular, the GuptaBleuler procedure will thereby involve only Lorentz invariant operator components and state vectors.

## 1. Introduction

The classical electromagnetic radiation field within a transparent medium may conveniently be described by a phenomenological theory, so that the influence of the medium is taken into account by means of a refractive index $n$ which in general is a function of both position and frequency. It should be expected that this approximative kind of description is good if the wavelength of the radiation is considerably greater than the interatomic distances in the material. This is however the case for a solid or liquid medium in the visible part of the spectrum. Further, in considering field quantities like energy and momentum one should employ Minkowski's energy-momentum tensor for the field, since this divergence-free tensor provides the simplest and most efficient description of the various optical phenomena. In this connection we may refer to the Jones-Richards experiment ${ }^{(1)}$ involving a measurement of the electromagnetic radiation pressure exerted on a metal plate immersed in a dielectric liquid at rest. Minkowski's tensor leads also to a straightforward explanation of various experiments involving the propagation of light through media in motion, such as the Fizeau experiment ${ }^{(2)}$ for rectilinear motion and the Sagnac-type experiment due to Heer, Little and Bupp ${ }^{(3)}$ for rotational motion. (An extensive classical treatment of various aspects of the alternative electromagnetic energy-momentum tensors has recently been given by one of the authors ${ }^{(4)}$.) The theory can readily be extended to the case where extraneous charges or currents are present. A typical example of such a situation is the Čerenkov effect; also in this case it has turned out that the agreement between the phenomenological theory and the experiments is remarkable ${ }^{(5)}$.

The intention of the present paper is to give, still within the phenomenological kind of approach, a quantal description of the electromagnetic field within an infinite medium in interaction with charged particles in the general case where the medium moves with uniform velocity. Since the field equations can readily be obtained from a Lagrangian, it is natural
to make use of the canonical formalism to construct the quantum theory. It can be verified that the results one obtains with the canonical procedure are closely connected with the results obtained with Minkowski's tensor. In this quantum theory the refractive index will of course appear as a parameter. Of earlier works on the relativistic phenomenological quantum electrodynamics the best known seems to be the extensive and excellent, but now somewhat old, treatment by J. M. Jauch and K. M. Watson ${ }^{(6)}$. Related treatments have been given by V. L. Ginzburg ${ }^{(7)}$, R. T. Cox ${ }^{(8)}$, K. Nagy ${ }^{(9)}$, M. I. Riazanov ${ }^{(10)}$, C. Muzikar ${ }^{(11)}$, R. Dobbertin ${ }^{(12)}$, V. N. Tsytovich ${ }^{(13)}$ and others. We shall occasionally refer to some of these works later on. As regards the classical phenomenological theory of radiating particles within a dielectric medium, this theory has been extensively studied by several authors concerned mainly with the relativistic theory ${ }^{(14)}$, while other authors have concentrated on the microscopic non-relativistic quantal description ${ }^{(15)}$.

Let us next enunciate the physical assumptions inherent in the following calculations. The medium is taken to be isotropic and infinite, so that the spatial dispersion is zero, but we shall also neglect the spectral dispersion and simply put the refractive index $n$ equal to a real constant. While the influence from the medium on the photons is thus described by means of the refractive index, we shall on the other hand neglect any influence from the medium on the wave function for an electron and simply describe the latter by the usual Dirac equation. This is a reasonable assumption since the Compton wave length for the electron is $\mathrm{h} /(\mathrm{mc})=0.024 \AA$, which is much smaller than the interatomic distances (see also the discussion by $\operatorname{Cox}{ }^{(8)}$ ).

Now we know that a charged particle, when passing through matter, ionizes the atoms (or excites them to discrete energy levels) and thereby loses energy. As a consequence of the retardation, the particle emits bremsstrahlung. By working with heavy particles, the latter effect can be made very small. We shall however exclude the ionisation loss from the consideration, in accordance with our previous assumption about complete transparency (real $n$ ) so that the medium is not allowed to absorb photons. The only interaction between particle and medium that we shall consider is the interaction connected with emission or absorption of real or virtual "phenomenological" photons. Thus the only kind of dragging force (or stopping power) with which we shall be confronted in the case of a particle travelling through homogeneous matter is the force arising from the Čerenkov radiation. The Čerenkov loss only amounts to a small fraction of the total energy
loss. Jelley ${ }^{(5)}$ reports that in a typical situation the actual ratio will be of the order of $1^{0} / 00$ (see also Ch. XII of Landau and Lifshitz's book ${ }^{(16)}$ ).

It is known that in the usual cases the modification introduced by the quantum theory is very small, owing to the smallness of the photon energy in comparison with the particle energy. * There are some situations however, in which the quantum theory may be of greater numerical importance: If we calculate higher order corrections to the S-matrix for general physical processes, particle collisions say, which take place in the medium, we have to integrate over the momenta of the virtual photons and have thus to include the long wavelength region for which the medium properties are important ${ }^{(10)}$. Apart from this, the phenomenological quantum electrodynamics represents from a formal point of view an interesting generalization of the conventional vacuum quantum electrodynamics.

We start in section 2 by developing the relativistic phenomenological theory in the configuration space of a free radiation field. The field is quantized according to the canonical scheme, and we base the calculation upon a Lagrangian density which represents the appropriate generalization of the Lagrangian density of conventional Fermi gauge vacuum quantum electrodynamics. The Lorentz covariance of the theory is examined by comparing the operators for momentum and angular momentum with the generating operators for translations and rotations in four-space.

In section 3 we go into Fourier space considerations. The four-potential is expanded in a form which is convenient for the relativistic appearance of the theory. The gauge condition is handled in a way which represents a generalization of the Gupta-Bleuler method for the vacuum field case. We find also in our case that there remain only two physically independent polarization directions of a photon of momentum $\boldsymbol{k}$; these polarization directions are however only orthogonal to the vector $\boldsymbol{k}$ in some special cases, viz. when $\boldsymbol{k}$ is parallel or antiparallel to the medium velocity $\boldsymbol{v}$ (or $\boldsymbol{v}=0$ ). We close the section with some remarks upon the literature, especially in connection with the works of JaUCH and Watson ${ }^{(6)}$.

Section 4 is devoted to classical considerations. We introduce a new method by which the phenomenological theory of the medium field can be obtained from the vacuum field theory simply by a mapping procedure. Thereafter the gauge condition is examined. We find the interesting result that the polarization vectors $e_{\mu}^{(\lambda)}$, introduced earlier in section 3 for the

[^0]medium field, stand in intimate connection with the simplest gauge condition one can impose on the transformed vacuum field. Further, we make use of the fact that the rest frame of the medium represents a distinguished system of reference, to introduce a set of new covariant vectors $e_{\mu}^{(\lambda)}$.

In section 5 we make use of the mapping method from section 4 and construct the quantum theory of the medium field simply by transforming the results from the vacuum field theory. Besides, in the construction of the commutation rules in configuration space, we also permit a wider class of covariant gauges than the single Fermi gauge which is ordinarily used. With the use of the new covariant polarization vectors $e_{\mu}^{(\lambda)}$ the quantum theory is found to take a completely covariant form, both with respect to Lorentz transformations and with respect to the transformation medium-vacuum. In particular, the Gupta-Beuler method in this formulation only involves Lorentz invariant operator components and state vectors. Finally we write down the Feynman rules for the medium field.

The final section 6 contains some supplementing remarks to the foregoing. The possibility of dividing the total field angular momentum into an orbital part and a spin part is discussed. It is stressed that, although the canonical formalism is intimately connected with Minkowski's energymomentum tensor, it does not thereby exclude the legitimacy of other expressions for the electromagnetic energy-momentum tensor. A proposal of a new experiment is put forward, consisting in a detection of spin in an electromagnetic wave travelling through a dielectric liquid. Such a detection would represent a further critical test of Minkowski's theory, in addition to the tests mentioned in the beginning of this section.

## 2. The Pure Radiation Field

It is convenient to start with a consideration of the pure radiation field. If we use units for which $c=1$, Maxwell's equations can be written in any reference frame as

$$
\begin{align*}
\nabla \times \boldsymbol{E}=-\frac{\partial \boldsymbol{B}}{\partial t}, & \nabla \cdot \boldsymbol{B}=0  \tag{2.1a}\\
\nabla \times \boldsymbol{H}=\frac{\partial \boldsymbol{D}}{\partial t}, & \nabla \cdot \boldsymbol{D}=0 . \tag{2.1~b}
\end{align*}
$$

In this paper we shall employ the real coordinates $x_{\mu}=\left(x_{0}, x_{1}, x_{2}, x_{3}\right)=$ $(t, \boldsymbol{x})$, the diagonal components of the metric tensor $g_{\mu \nu}$ in the form $(1,-1$,
$-1,-1$ ), and shall put also $\hbar=1$. If the antisymmetric field tensors $F_{\mu v}$ and $H_{\mu \nu}$ are defined by

$$
\begin{aligned}
\left(F_{10}, F_{20}, F_{30}\right) & =\boldsymbol{E}, \quad\left(F_{23}, F_{31}, F_{12}\right)=-\boldsymbol{B} \\
\left(H_{10}, H_{20}, H_{30}\right) & =\boldsymbol{D}, \quad\left(H_{23}, H_{31}, H_{12}\right)=-\boldsymbol{H},
\end{aligned}
$$

we can write the field equations as

$$
\begin{gather*}
\partial_{\lambda} F_{\mu \nu}+\partial_{\mu} F_{\nu \lambda}+\partial_{v} F_{\lambda \mu}=0  \tag{2.2a}\\
\partial^{v} H_{\mu \nu}=0 \tag{2.2~b}
\end{gather*}
$$

where $\partial^{v} \equiv \partial / \partial x_{v}$. If the uniform four-velocity of the medium is denoted by $V_{\mu}=\left(V_{0}, \boldsymbol{V}\right)=\gamma(1, \boldsymbol{v})$, where $\gamma=\left(1-v^{2}\right)^{-1 / 2}, V^{2}=V_{\mu} V^{\mu}=1$, the connection between the field tensors $F_{\mu \nu}$ and $H_{\mu \nu}$ can be written as

$$
\begin{equation*}
\mu H_{\mu \nu}=F_{\mu \nu}+\varkappa\left(F_{\mu} V_{\nu}-F_{\nu} V_{\mu}\right) \tag{2.3}
\end{equation*}
$$

where $x \equiv \varepsilon \mu-1, F_{\mu} \equiv F_{\mu \varrho} V^{\varrho}$. The relation (2.3) can be brought into a compact form by making use of the following matrix

$$
\begin{equation*}
b_{\mu v}=g_{\mu \nu}+(n-1) V_{\mu} V_{\nu}, \tag{2.4}
\end{equation*}
$$

where the refractive index $n=\sqrt{\varepsilon \mu}$. We first note that this matrix has the remarkable property that its $p^{\prime}$ th power is obtained by replacing $n$ by $n^{p}$ :

$$
\begin{equation*}
\left(b^{p}\right)_{\mu \nu}=g_{\mu \nu}+\left(n^{p}-1\right) V_{\mu} V_{\nu} \tag{2.5}
\end{equation*}
$$

This is even true for negative integers $p$ as well as for $p=0$, i.e. for all integers. We can now write eq. (2.3) as

$$
\begin{equation*}
\mu H_{\mu \nu}=\left(b^{2}\right)_{\mu}^{o}\left(b^{2}\right)_{\nu}^{\sigma} F_{\varrho \sigma} \tag{2.6}
\end{equation*}
$$

By introducing the four-potential by the relation $F_{\mu \nu}=\partial_{\mu} A_{\nu}-\partial_{\nu} A_{\mu}$ and exploiting the freedom in the choice of the potential components to impose the subsidiary condition in the conventional form (Lorentz gauge):

$$
\begin{equation*}
\Lambda^{F}(x) \equiv\left(b^{2}\right)^{\mu v} \partial_{\mu} A_{v}=\partial \cdot A+\varkappa \partial \cdot V A \cdot V=0 \tag{2.7}
\end{equation*}
$$

where $\partial \cdot A \equiv \partial_{\mu} A^{\mu}$, we can insert (2.6) into (2.2b) to obtain

$$
\begin{equation*}
\left(b^{2}\right)^{\varrho \sigma} \partial_{\varrho} \partial_{\sigma} A_{\mu}=\left[\square+\varkappa(\partial \cdot V)^{2}\right] A_{\mu}=0 \tag{2.8}
\end{equation*}
$$

( $\square \equiv \partial_{\mu} \partial^{\mu}$ ). Eq. (2.2 a) is automatically satisfied.

It can be verified that the field equations (2.8) also follow from a variational principle in which the Lagrangian density has the form

$$
\begin{equation*}
L=-\frac{1}{4} F_{\mu \nu} H^{\mu \nu}-\frac{1}{2 \mu}\left(\Lambda^{F}\right)^{2} \tag{2.9}
\end{equation*}
$$

Note, however, that the variational equations obtained from this Lagrangian are equivalent to Maxwell's equations (2.2b) only when we impose the subsidiary condition $\Lambda^{F}=0$.

In order to quantize the field we may apply the canonical procedure and take the expression (2.9) as the starting point. The canonically conjugate momenta $\pi^{\mu}$ are defined by

$$
\begin{equation*}
\pi^{\mu}=\frac{\partial L}{\partial \partial_{0} A_{\mu}} \tag{2.10}
\end{equation*}
$$

which mean that in the present case

$$
\begin{equation*}
\pi^{\mu}=H^{\mu 0}-\frac{1}{\mu}\left(b^{2}\right)^{\mu 0} \Lambda^{F} \tag{2.11}
\end{equation*}
$$

In the quantum theory the field variables become operators satisfying certain commutation rules, which are constructed without regard to the subsidiary condition. It is thus clear from (2.11) and (2.9) that because of the $\left(\Lambda^{F}\right)^{2}$ term in the Lagrangian density we avoid the result $\pi^{0}=0$, as we must in order to be able to apply the canonical quantization scheme to the case $\mu=0$. Accordingly, in quantum theory $\Lambda^{F}$ must be considered as a nonvanishing operator. The canonical commutation rules are postulated as

$$
\begin{gather*}
{\left[\pi^{\mu}(x), A_{v}\left(x^{\prime}\right)\right]_{x_{0}=x_{0}^{\prime}}=-i g_{v}^{\mu} \delta\left(\boldsymbol{x}-\boldsymbol{x}^{\prime}\right)}  \tag{2.12a}\\
{\left[\pi^{\mu}(x), \pi^{v}\left(x^{\prime}\right)\right]_{x_{0}=x_{0}^{\prime}}=0, \quad\left[A_{\mu}(x), A_{v}\left(x^{\prime}\right)\right]_{x_{0}=x_{0}^{\prime}}=0} \tag{2.12b}
\end{gather*}
$$

corresponding to the interpretation of the field as a mechanical system of infinitely many degrees of freedom.

The Hamiltonian is found as

$$
\begin{gather*}
\mathscr{H}=\int\left(\pi^{\mu} \partial_{0} A_{\mu}-L\right) d V=\int\left[H^{\mu 0} \partial_{0} A_{\mu}+\frac{1}{4} F_{\mu \nu} H^{\mu \nu}+\right. \\
\left.\quad+\frac{1}{\mu} \Lambda^{F}\left(-\left(b^{2}\right)^{\mu 0} \partial_{0} A_{\mu}+\frac{1}{2} \Lambda^{F}\right)\right] d V \tag{2.13}
\end{gather*}
$$

where $\partial_{0} A_{\mu}$ can be eliminated by means of (2.11), so that $\mathscr{H}$ becomes a function of $\partial_{k} A_{\mu}, \pi^{\mu}$ and $V_{\mu}$. Now it can be shown in general (cf. for instance Källén's article ${ }^{(17)}$, p. 174), that the quantal equations of motion in the Heisenberg picture are formally in agreement with eqs. (2.11) and (2.8), when the latter are looked upon as operator equations.

The relativistic invariance of the canonical quantization procedure is conveniently shown by means of the covariant commutator for the components of the four-potential at arbitrary space-time relative distances, and we shall return to this topic in the next section in connection with momentum space considerations. Let us, however, here notice the following point: The relativistic invariance of the quantization procedure for a closed system is often ascertained by verifying that the operators for linear four-momentum $P_{\mu}$ and angular momentum $M_{\mu \nu}$ are constants of motion, and moreover that they can be identified, respectively, with the Hermitian operator $\mathscr{P}_{\mu}$ generating infinitesimal translations and the Hermitian operator $\mathscr{M}_{\mu \nu}$ generating infinitesimal rotations (Lorentz transformations) in four-space. The latter operators satisfy the relations

$$
\begin{gather*}
i\left[\mathscr{P}_{\mu}, A_{\nu}(x)\right]=\partial_{\mu} A_{v}(x)  \tag{2.14a}\\
i\left[\mathscr{M}_{\mu \nu}, A^{\sigma}(x)\right]=x_{\mu} \partial_{\nu} A^{\sigma}(x)-x_{\nu} \partial_{\mu} A^{\sigma}(x)+I_{\mu \nu}^{\sigma \rho} A_{\varrho}(x), \tag{2.14b}
\end{gather*}
$$

where $I_{\mu \nu}^{\sigma O}=g_{\mu}^{\sigma} g_{\nu}^{o}-g_{\mu}^{o} g_{\nu}^{\sigma}$. Here $\mathscr{P}_{\mu}$ and $\mathscr{M}_{\mu \nu}$ may be time-dependent operators and should be taken at the time $t=x_{0}$, where $x_{0}$ is the time argument appearing in $A_{\nu}(x)$.

Let us now compare eqs. (2.14) with the equations one obtains by replacing $\mathscr{P}_{\mu}$ and $\mathscr{M}_{\mu \nu}$ by the field operators $P_{\mu}$ and $M_{\mu \nu}$. We have

$$
\begin{equation*}
P_{\mu}=\int S_{\mu 0} d V \tag{2.15}
\end{equation*}
$$

where $S_{\mu \nu}$ is the canonical energy-momentum tensor

$$
\begin{equation*}
S_{\mu \nu}=-g_{\mu \nu} L+\frac{\partial L}{\partial \partial^{v} A_{\alpha}} \partial_{\mu} A_{\alpha} . \tag{2.16}
\end{equation*}
$$

The four-momentum $P_{\mu}$ is a constant of motion in virtue of the field equations, and by means of (2.15) and (2.16) we readily find that (2.14 a) remains valid when $P_{\mu}$ is present.

The study of angular momentum is somewhat more complicated; characteristic ambiguities in the formalism are shown very explicitly. By using

Noether's theorem for an infinitesimal Lorentz transformation under which we know how the field entities transform, we obtain

$$
\begin{gather*}
\partial^{\sigma} M_{\sigma \mu \nu}+\frac{\partial L}{\partial V^{\sigma}} I_{\mu \nu}^{\sigma \varrho} A_{\varrho}=0  \tag{2.17}\\
\text { where } \quad M_{\sigma \mu \nu}=x_{\mu} S_{\nu \sigma}-x_{v} S_{\mu \sigma}+\frac{\partial L}{\partial \partial^{\sigma} A^{\alpha}} I_{\mu \nu}^{\alpha \beta} A_{\beta} \tag{2.18}
\end{gather*}
$$

Hence it is natural to define the angular momentum of the field as

$$
\begin{equation*}
M_{\mu \nu}=\int M_{0 \mu \nu} d V \tag{2.19}
\end{equation*}
$$

since this expression is in formal agreement with the angular momentum expression for an electromagnetic field in the vacuum. It should be noted, however, that according to (2.17) (considered as an operator equation), the angular momentum defined in this way is not a constant of motion. The present feature of the theory is a direct consequence of the fact that we are considering a non-closed physical system; the Lagrangian (2.9) describes the field and its interaction with the medium but not the medium itself. Ambiguities in the formalism should therefore be expected. (In the classical theory, where one can establish the correspondence with the Maxwell field simply by putting $\Lambda^{F}=0$, it can readily be shown that $P_{\mu}$ given by (2.15) and $M_{\mu \nu}$ given by (2.19) are equal respectively to the total four-momentum and the angular momentum calculated with the use of Minkowski's energymomentum tensor $S_{\mu \nu}^{M}$ :

$$
\begin{equation*}
\left.S_{\mu \nu}^{M}=-F_{\mu \alpha} H_{\nu}^{\cdot \alpha}+\frac{1}{4} g_{\mu \nu} F_{\alpha \beta} H^{\alpha \beta} .\right) \tag{2.20}
\end{equation*}
$$

Going back to quantum theory, we can now also verify the validity of the commutator relation $(2.14 \mathrm{~b})$, when $\mathscr{M}_{\mu \nu}$ is replaced by $M_{\mu \nu}$ determined by (2.18) and (2.19). We have thus found that the linear momentum and the angular momentum operators can be identified with the corresponding generators for infinitesimal transformations in four-space, exactly as for conventional vacuum quantum electrodynamics. It must be borne in mind, however, that the angular momentum is no longer a constant of motion.

## 3. Transition to Momentum Space

We now write the four-potential in the form of a four-dimensional Fourier integral

$$
\begin{equation*}
A_{\mu}(x)=(2 \pi)^{-\frac{3}{2}} \int d k \delta\left(k^{2}+\varkappa(k \cdot V)^{2}\right) e^{-i k \cdot x} A_{\mu}(k) \tag{3.1}
\end{equation*}
$$

where $d k \equiv d k_{0} d \boldsymbol{k}$ and the delta function has been introduced because of the field equations (2.8), which lead to the condition

$$
\begin{equation*}
k^{2}+\varkappa(k \cdot V)^{2}=0 . \tag{3.2}
\end{equation*}
$$

Solving this equation with respect to $k_{0}$ we obtain two solutions $k_{0}=k_{a}$ and $k_{0}=k_{b}$, where

$$
\begin{equation*}
k_{a, b}=\frac{\varkappa V_{0} \boldsymbol{k} \cdot \boldsymbol{V} \pm \sqrt{\left(1+\varkappa V_{0}^{2}\right) \boldsymbol{k}^{2}-\varkappa(\boldsymbol{k} \cdot \boldsymbol{V})^{2}}}{1+\varkappa V_{0}^{2}} . \tag{3.3}
\end{equation*}
$$

Here $k_{a}$ refers to the upper sign, which corresponds to the positive solution in the case of a vacuum field. Note that the expression (3.3) is always real, and that $k_{a, b}(\boldsymbol{k})=-k_{b, a}(-\boldsymbol{k})$. Owing to the space-like character of the four-vector $k_{\mu}$, there exists a class of inertial systems in which $k_{a}$ may be negative. This is the class for which $\varkappa V^{2}>1$, i. e. $n^{2} v^{2}>1$. In such a system there is a half cone with opening angle $2 \alpha$ around the opposite direction of $v$ on which $k_{a}=0$; inside the cone $k_{a}$ is negative and outside it is positive. The behaviour is illustrated in Fig. 1. The opening angle is determined by

$$
\begin{equation*}
\cos \alpha=\frac{1}{\sqrt{x}|\boldsymbol{V}|} \tag{3.4}
\end{equation*}
$$

Let us also choose the coordinate axes so that $V_{1}=|\boldsymbol{V}|, V_{2}=V_{3}=0$, and use eq. (3.2) to derive the following equation for a surface $k_{0}=$ const in $\boldsymbol{k}=$ space:
$\frac{\left[k_{1}+\varkappa k_{0} V_{0}|\boldsymbol{V}|\left(1-\varkappa \boldsymbol{V}^{2}\right)^{-1}\right]^{2}}{n^{2} k_{0}^{2}\left(1-\varkappa \boldsymbol{V}^{2}\right)^{-2}}+\frac{k_{2}^{2}}{n^{2} k_{0}^{2}\left(1-\varkappa \boldsymbol{V}^{2}\right)^{-1}}+\frac{k_{3}^{2}}{n^{2} k_{0}^{2}\left(1-\varkappa \boldsymbol{V}^{2}\right)^{-1}}=1$.
when $\varkappa \boldsymbol{V}^{2}<1$ this is the equation of an ellipsoid; when $\varkappa \boldsymbol{V}^{2}>1$ it is the equation of a two-sheet hyperboloid such that the left hand sheet (the sheet extending towards $k_{1} \rightarrow-\infty$ ) corresponds to the relation $k_{0}=k_{a}(\boldsymbol{k})$ and the right hand sheet corresponds to the relation $k_{0}=k_{b}(\boldsymbol{k})$. When $x \boldsymbol{V}^{2}=1$ the surface $k_{0}=$ const in $\boldsymbol{k}$-space degenerates into an elliptic paraboloid.


Fig. 1.

We now write the delta function in (3.1) as a sum of two terms involving the delta functions of $\left(k_{0}-k_{x}\right)$ and $\left(k_{0}-k_{b}\right)$, and carry out the integration over $k_{0}$. The result is conveniently written as

$$
\begin{gather*}
A_{\mu}(x)=  \tag{3.6}\\
\frac{1}{(2 \pi)^{3 / 2}} \cdot d \boldsymbol{k}\left[\frac{\mu}{\left(1+\varkappa V_{0}^{2}\right)\left(k_{a}-k_{b}\right)}\right]^{\frac{1}{2}}\left(b^{-1}\right)_{\mu}^{v}\left(e^{-i k \cdot x} a_{\nu}(\boldsymbol{k})+e^{i k \cdot x} a_{\nu}^{\dagger}(\boldsymbol{k})\right),
\end{gather*}
$$

where $k_{0}=k_{a}(\boldsymbol{k})=-k_{b}(-\boldsymbol{k})$. The reason for writing the expansion in the particular form (3.6) is that we thereby obtain the usual commutation rules for the components $a_{\mu}$ :

$$
\begin{gather*}
{\left[a_{\mu}(\boldsymbol{k}), a_{v}^{\dagger}\left(\boldsymbol{k}^{\prime}\right)\right]=-g_{\mu \nu} \delta\left(\boldsymbol{k}-\boldsymbol{k}^{\prime}\right)}  \tag{3.7a}\\
{\left[a_{\mu}(\boldsymbol{k}), a_{\nu}\left(\boldsymbol{k}^{\prime}\right)\right]=\left[a_{\mu}^{\dagger}(\boldsymbol{k}), a_{v}^{\dagger}\left(\boldsymbol{k}^{\prime}\right)\right]=0,} \tag{3.7~b}
\end{gather*}
$$

after an insertion into eqs. (2.12).
Let us now transform the commutation rules to a symmetrical four-dimensional form. We obtain from (3.6) and (3.7), when $x$ and $x^{\prime}$ are arbitrary space-time points,

$$
\begin{gather*}
{\left[A_{\mu}(x), A_{v}\left(x^{\prime}\right)\right]=-\frac{i \mu}{n}\left(b^{-2}\right)_{\mu \nu} D^{M}\left(x-x^{\prime}\right)}  \tag{3.8}\\
\text { where } D^{M}(x)=-\frac{i n}{(2 \pi)^{3}} \int d k e^{-i k \cdot x} \delta\left(k^{2}+x(k \cdot V)^{2}\right) \varepsilon(k \cdot V) \tag{3.9}
\end{gather*}
$$

and $\varepsilon$ is the step function, $\varepsilon(t)= \pm 1$ for $t \geq 0$. It is apparent that $D^{M}(x)$ is a Lorentz invariant, so that eq. (3.8) is a covariant equation. The invari-
ance of the quantization procedure can now be verified on the basis of eq. (3.8), by using this equation plus eq. (2.11) to recover the commutation relations (2.12). This procedure has been carried through by Jauch and Watson, so we need not enter into this. Jauch and Watson also gave an integral representation of the invariant commutator function (it should be mentioned that the expression (3.9) is equal to $-n$ times the $D$-function defined by these authors). It is instructive to carry out the integrations in the expression (3.9) in the inertial rest frame $\stackrel{\circ}{K}$ to obtain

$$
\begin{equation*}
D^{M}(x)=D^{M}(\dot{x})=-\frac{1}{2 \pi} \delta\left(\dot{\boldsymbol{x}}^{2}-\frac{1}{n^{2}} \dot{x}_{0}^{2}\right) \varepsilon\left(\dot{x}_{0}\right) \tag{3.10}
\end{equation*}
$$

where we have added a superscript zero above symbols pertaining to $K \circ$. From (3.10) it is apparent that $D^{M}\left(x-x^{\prime}\right)$ is nonvanishing only when $x$ and $x^{\prime}$ can be connected by light signals, similarly as in the case $x=0$.

Let us now make use of the expansion (3.6) to calculate the four-momentum $P_{\mu}$ defined by (2.15) and (2.16). By inserting (2.9) we find after some calculation the compact expression

$$
\begin{equation*}
P_{\mu}=-\frac{1}{2} \int d \boldsymbol{k} k_{\mu}\left\{a_{\nu}(\boldsymbol{k}), a^{\nu \dagger}(\boldsymbol{k})\right\}, \tag{3.11}
\end{equation*}
$$

where $P_{0}=\mathscr{H}$ (cf. (2.13)) and the curly bracket denotes the anticommutator.

Instead of using (3.6), it is sometimes convenient to employ an expansion which runs over discrete values of $\boldsymbol{k}$. A discrete and covariant expansion can be constructed in the following way. We imagine that the field is enclosed within a box with linear extensions $\dot{L}_{x}, L_{y}, L_{z}$ in the rest frame $\stackrel{\circ}{K}$ and impose the usual periodicity conditions at the walls. Hence

$$
\begin{equation*}
\dot{k}_{x} \grave{L}_{x}=2 \pi m_{x}, \grave{k}_{g} \mathscr{L}_{y}=2 \pi m_{y}, \grave{k}_{z} \stackrel{L}{L}_{z}=2 \pi m_{z} \tag{3.12}
\end{equation*}
$$

where the $m^{\prime} s$ are integers. The volume of the box is $\mathscr{\mathscr { V }}=\dot{L}_{x} \dot{L}_{y} \dot{L}_{z}$. It is obvious that after the transition to another inertial frame $K$, with respect to which $\check{K}$ moves with the velocity $\boldsymbol{v}$, the above periodicity conditions at the walls of the box are in general lost. Instead, each Fourier component of the field is periodic at corresponding points of the fictitious boundaries of a "box" whose volume is determined by the properties of propagation of the field component. This topic is discussed in detail elsewhere, both in a statistical treatment ${ }^{(18)}$ and in an exposition upon coherence theory of black-body radiation ${ }^{(19)}$. Here we recall that the plane wave component with wave vector $\check{\boldsymbol{k}}$ in $\stackrel{\circ}{K}$ corresponds in $K$ to a fictitious box with the volume

$$
\begin{equation*}
\mathscr{V}_{k}=\frac{n \dot{\mathscr{V}}}{\gamma(n+\boldsymbol{v} \cdot \dot{\boldsymbol{k}} /|\dot{\boldsymbol{k}}|)}, \tag{3.13}
\end{equation*}
$$

where $\gamma=\left(1-v^{2}\right)^{-\frac{1}{2}}$. The four-potential is expanded as

$$
\left.\begin{array}{l}
A_{\mu}(x)=  \tag{3.14}\\
{[]_{k}^{\frac{1}{2}}\left(b^{-1}\right)_{\mu}^{v}\left(e^{-i k \cdot x} a_{\nu}(\boldsymbol{k})+e^{i k \cdot x} a_{v}^{\dagger}(\boldsymbol{k})\right) .}
\end{array}\right\}
$$

By inserting the expression (3.14) into the commutation rules (2.12) we can verify that the nonvanishing commutator (3.7a) is now changed into

$$
\begin{equation*}
\left[a_{\mu}(\boldsymbol{k}), a_{\nu}^{\dagger}\left(\boldsymbol{k}^{\prime}\right)\right]=-g_{\mu v} \delta_{\boldsymbol{k \boldsymbol { k } ^ { \prime }}} \tag{3.15}
\end{equation*}
$$

while eqs. (3.7b) remain unchanged. To this end we take into account that, in the limit of a large normalization volume $\mathscr{\mathscr { V }}$, the sum over discrete $\boldsymbol{k}$ can be replaced by an integral over the $m^{\prime}$ 's such that $d m=d m_{x} d m_{y} d m_{z}=$ $=\partial(m) / \partial(\boldsymbol{k}) d \boldsymbol{k}$, and from ref. 19 we recall that

$$
\begin{equation*}
d m=(2 \pi)^{-3} \mathscr{V}_{k} d \boldsymbol{k} \tag{3.16}
\end{equation*}
$$

## The Subsidary Condition

Let us now turn our attention to the subsidiary condition which, as was pointed out already in connection with eq. (2.9), must be imposed in order to maintain the connection with Maxwell's equations. First, let us consider for a moment the classical case, and notice that the Lorentz condition (2.7) leads to the following equations in Fourier space*:

$$
\begin{gather*}
l(\boldsymbol{k}) \cdot a(\boldsymbol{k})=0, \quad l(\boldsymbol{k}) \cdot a^{*}(\boldsymbol{k})=0,  \tag{3.17a}\\
\text { where } \quad l_{\mu}(\boldsymbol{k}) \equiv b_{\mu}^{v} k_{v}, l^{2}=0 . \tag{3.17b}
\end{gather*}
$$

In conformity with usual practice let us decompose the potential by means of a $\boldsymbol{k}$-dependent basis

$$
\begin{equation*}
a_{\mu}(\boldsymbol{k})=\sum_{\lambda=0}^{3} e_{\mu}^{(\lambda)}(\boldsymbol{k}) a^{(\lambda)}(\boldsymbol{k}) \tag{3.18}
\end{equation*}
$$

so that

$$
\begin{equation*}
g^{\mu \nu} e_{\mu}^{\left(\lambda^{\prime}\right)} e_{\nu}^{\left(\lambda^{\prime}\right)}=g^{\lambda \lambda^{\prime}}, \sum_{\lambda, \lambda^{\prime}=0}^{3} g_{\lambda \lambda^{\prime}} e_{\mu}^{(\lambda)} e_{\nu}^{\left(\lambda^{\prime}\right)}=g_{\mu \nu} \tag{3.19}
\end{equation*}
$$

* The star denotes complex conjugate.

Let us choose the components $e_{\mu}^{(\lambda)}$ in the following form

$$
\begin{gather*}
\boldsymbol{e}^{(1)}=\frac{\boldsymbol{l}}{l_{0}}, \quad \boldsymbol{e}^{(2)}=\frac{(\boldsymbol{V} \times \boldsymbol{l}) \times \boldsymbol{l}}{|(\boldsymbol{V} \times \boldsymbol{l}) \times \boldsymbol{l}|} \\
\boldsymbol{e}^{(3)}=\frac{\boldsymbol{V} \times \boldsymbol{l}}{|\boldsymbol{V} \times \boldsymbol{l}|}, \quad \boldsymbol{e}^{(0)}=0, \quad e_{0}^{(\lambda)}=\delta_{\lambda 0} \tag{3.20}
\end{gather*}
$$

Thereby eqs. (3.19) are satisfied, and the classical Lorentz condition (3.17) takes on the simple form

$$
\begin{equation*}
a^{(1)}-a^{(0)}=0, \quad a^{(1) *}-a^{(0) *}=0 . \tag{3.21}
\end{equation*}
$$

In quantum theory the subsidiary condition cannot be taken over as a set of operator equations corresponding to eqs. (3.21) since this would lead to the relation

$$
\begin{equation*}
\left[a^{(1)}, a^{(1)^{\dagger}}\right]=\left[a^{(0)}, a^{(0)^{\dagger}}\right] \tag{3.22}
\end{equation*}
$$

which contradicts the relation $\left[a^{(\lambda)}, a^{\left(\lambda^{\prime}\right) \dagger}\right]=-g^{\lambda \cdot \lambda^{\prime}}$ following from (3.15). This is evidently a consequence of the fact that we have quantized the field according to the canonical procedure on the basis of the Lagrangian (2.9), without regard to the Lorentz condition. Nor should (3.21) be postulated valid when acting on a state vector $|\Psi\rangle$ (Fermi’s method), since (3.22) would then remain as a relation between the expectation values. Instead, we shall employ the method due to S. Gupta and K. Bleuler (cf., for instance, ref. 17) with the modifications that are necessary because of the presence of the medium.

Just as in the case $\chi=0$ we introduce a Hermitic and unitary metric operator $\eta$ :

$$
\begin{equation*}
\eta=\eta^{\dagger}=\eta^{-1} \tag{3.23}
\end{equation*}
$$

and define the expectation value of an operator $F$ as $\bar{F}=\langle\Psi| \eta F|\Psi\rangle$. The metric operator is further required to satisfy the usual commutation and anticommutation relations

$$
\left.\begin{array}{l}
{\left[\eta, a^{(\lambda)}(\boldsymbol{k})\right]=0 \quad(\lambda=1,2,3)}  \tag{3.24}\\
\left\{\eta, a^{(0)}(\boldsymbol{k})\right\}=0
\end{array}\right\}
$$

Both in the commutator (3.15) and in the expansion (3.14) $a_{\nu}^{\dagger}(\boldsymbol{k})$ is replaced by $\tilde{a}_{v}(\boldsymbol{k})$, where

$$
\begin{equation*}
\tilde{a}_{v}(\boldsymbol{k}) \equiv \eta a_{v}^{\dagger}(\boldsymbol{k}) \eta . \tag{3.25}
\end{equation*}
$$

By decomposing into the polarization directions, the commutation relations can then be written as

$$
\begin{equation*}
\left[a^{(\lambda)}(\boldsymbol{k}), a^{\left(\lambda^{\prime}\right) \dagger}\left(\boldsymbol{k}^{\prime}\right)\right]=\delta_{\lambda, \lambda^{\prime}} \delta_{\boldsymbol{k} \boldsymbol{k}^{\prime}} \tag{3.26}
\end{equation*}
$$

and $a^{(\lambda)}$ and $a^{\left(\lambda_{2} \dagger\right.}$ can be interpreted as annihilation and creation operators for the "phenomenological" photons. The potential components $A_{\mu}(x)$ become complex quantities; the simple Hermitic property of $A_{i}(x)$ and the anti-Hermitic property of $A_{0}(x)$ which hold in the case $x=0$ are in general lost. However, the expectation values of the potential components must satisfy the same reality conditions as the classical fields, i. e. $\langle\Psi| \eta A_{\mu}(x)|\Psi\rangle=$ $=\langle\Psi| A_{\mu}^{\dagger}(x) \eta|\Psi\rangle$, or

$$
\begin{equation*}
A_{\mu}(x)=\eta A_{\mu}^{\dagger}(x) \eta \tag{3.27}
\end{equation*}
$$

By means of (3.24) it can actually be verified that the relation (3.27) is satisfied, so that the reality properties are correct. The subsidiary condition is written as

$$
\begin{equation*}
\left(a^{(1)}-a^{(0)}\right)|\Psi\rangle=0, \tag{3.28}
\end{equation*}
$$

which involves absorption operators only. Hence the conflict (3.22) is avoided, yet (3.28) is sufficient to yield the relation

$$
\begin{equation*}
\langle\Psi| \eta \Lambda^{F}|\Psi\rangle=0 \tag{3.29}
\end{equation*}
$$

which expresses the correspondence with the classical Lorentz condition. When the expectation values are taken, the field equations (2.8) are thus equivalent to Maxwell's equations. Similarly we find that $\langle\Psi| \eta \Lambda^{F 2}|\Psi\rangle=0$, and that the influence of the $\Lambda^{F}$-dependent term in the Lagrangian (2.9) on the field-dependent part of $P_{\mu}$ vanishes, so that the correspondence with the classical field is established also for the conserved quantities $P_{\mu}$. In fact, by omitting the zero point contributions we can write $P_{\mu}$ as

$$
\begin{gather*}
P_{\mu}=\sum_{k} k_{\mu} \sum_{\lambda=0}^{3} a^{(\lambda) \dagger} a^{(\lambda)}  \tag{3.30a}\\
\text { and }\langle\Psi| \eta P_{\mu}|\Psi\rangle=\sum_{k} k_{\mu}\left(N^{(2)}+N^{(3)}\right), \tag{3.30b}
\end{gather*}
$$

where $N^{(2)}, N^{(3)}$ mean the numbers of photons polarized in the transversal directions. It should be noted that, as a characteristic difference from the case $x=0$, the phrase "transversal" refers to the directions which are transversal to the vector $\boldsymbol{l}=\boldsymbol{k}+(n-1) \boldsymbol{V} k \cdot V$.

From (3.30) it follows that the energy of a photon is equal to $k_{0}=k_{a}$ which, according to the remarks in the beginning of this section, may be negative in the inertial systems for which $\chi \boldsymbol{V}^{2}>1$. The space-like character of the four-momentum $k_{\mu}$ is a direct consequence of the fact that Minkowski's momentum density in the rest frame is put equal to $(\boldsymbol{D} \times \boldsymbol{B})$, and hence includes also a contribution from the moving constituent particles of the medium. The classical aspects of this subject have been treated elsewhere ${ }^{(4)}$.

We may write an arbitrary state vector $|\Psi\rangle$ as

$$
\begin{equation*}
|\Psi\rangle=\left|\Psi_{T}\right\rangle \prod_{\boldsymbol{k}}\left|\Phi_{\boldsymbol{k}}\right\rangle, \tag{3.31}
\end{equation*}
$$

where $\left|\Psi_{T}\right\rangle$ contains transversal photons only and $\Phi_{k}$ contains a mixture of longitudinal and scalar photons which is arbitrary apart from the fact that it must be compatible with the condition (3.28). A certain mixture corresponds to a certain value for the gauge and has no influence on the physical quantities. The argument proceeds similarly as for an electromagnetic field in vacuum ${ }^{(17)}$, so we abstain from a detailed exposition.

As regards the Lorentz invariance of the theory it should first be noted that by choosing the expansion of the four-potential in the form (3.14) we obtain a convenient relativistic behaviour of the Fourier components. For by observing that $\left[\left(1+x V_{0}^{2}\right)\left(k_{a}-k_{b}\right)\right]^{-1} d \boldsymbol{k}$ is a Lorentz invariant and that $d m$ given by (3.16) also is a Lorentz invariant so that $\mathscr{V}_{k} d \boldsymbol{k}=\mathscr{\mathscr { V }} d \stackrel{\circ}{\boldsymbol{k}}$ (cf. ref. 19), we see that

$$
\begin{equation*}
\frac{\mu}{\left(1+x V_{0}^{2}\right)\left(k_{a}-k_{b}\right) \mathscr{V}_{k}}=\frac{\mu}{2 n|\dot{\boldsymbol{k}}| \mathscr{\mathscr { V }}}=\text { invariant. } \tag{3.32}
\end{equation*}
$$

Thus the expectation value of the Fourier component $a_{\mu}(\boldsymbol{k})$ will simply transform like a four-vector. Consequently, the Lorentz invariance of the total photon number $N(\boldsymbol{k})$ corresponding to some wave vector $\boldsymbol{k}$ (i.e. the expectation value of $-g^{\mu \nu} \tilde{a}_{\mu} a_{\nu}=\sum_{\lambda=0}^{3} a^{(\lambda) \dagger} a^{(\lambda)}$ ) follows in a very natural way.

## Remarks

We finish this section with a few remarks related to earlier works on the subject. The only works we are aware of in which the method of decomposing the potential by means of the unit vectors (3.20) has been employed, are the two papers by C. Muzikář̌ ${ }^{(11)}$. He developed a covariant theory based on the Coulomb gauge in the rest frame and found, similarly as above, that the physically important polarization directions are the directions trans-
verse to $\boldsymbol{l}$. . On the other hand, the result $(3.30 \mathrm{~b})$ is in disagreement with the result obtained by JaUch and $\mathrm{Watson}^{(6)}$; they found that the physically important polarization directions were the directions transverse to the vector $\boldsymbol{k}$. It can be checked that (for $\varkappa, V \neq 0$ ) the unit vector $\boldsymbol{e}^{(1)}$ defined by (3.20) is equal to $\boldsymbol{k} /|\boldsymbol{k}|$ when, and only when, $\boldsymbol{k}$ is parallel or antiparallel to $\boldsymbol{V}$. We think that it is desirable to go into some detail and give the reason for this rather essential discrepancy. Thus, by transforming the formalism to our notation, let us introduce a new basis $\varepsilon_{\mu}^{(\lambda)}(\boldsymbol{k})$ where the differences from (3.20) are contained in the following terms:

$$
\begin{equation*}
\boldsymbol{\varepsilon}^{(1)}=\boldsymbol{k} /|\boldsymbol{k}|, \boldsymbol{\varepsilon}^{(2)}=\frac{(\boldsymbol{V} \times \boldsymbol{k}) \times \boldsymbol{k}}{|(\boldsymbol{V} \times \boldsymbol{k}) \times \boldsymbol{k}|}, \boldsymbol{\varepsilon}^{(3)}=\frac{\boldsymbol{V} \times \boldsymbol{k}}{|\boldsymbol{V} \times \boldsymbol{k}|} . \tag{3.33}
\end{equation*}
$$

These unit vectors were essentially chosen by Jauch and Watson. Further, the Fourier expansions (of the Schrödinger operators) chosen by these authors are equivalent to the following Fourier expansions of the Heisenberg operators:

$$
\begin{align*}
A_{\mu} & =(2 \pi)^{-\frac{3}{2}} \int d \boldsymbol{k} \sum_{\lambda=0}^{3} \varepsilon_{\mu}^{(\lambda)} \alpha^{(\lambda)}\left(e^{-i k \cdot x} c^{(\lambda)}+e^{i k \cdot x} c^{(\lambda) \dagger}\right)  \tag{3.34a}\\
\pi_{\mu} & =i(2 \pi)^{-\frac{3}{2}} \int d \boldsymbol{k} \sum_{\lambda=0}^{3} \varepsilon_{\mu}^{(\lambda)} \beta^{(\lambda)}\left(e^{-i k \cdot x} c^{(\lambda)}-e^{i k \cdot x} c^{(\lambda) \dagger}\right) \tag{3.34b}
\end{align*}
$$

where $\alpha^{(\lambda)}$ and $\beta^{(\lambda)}$ are numerical factors. The expansions (3.34) are inserted into the Hamiltonian in its reduced form after the subsidiary condition has been imposed, so that only physically important terms are left. In this way the authors find that only the polarization directions $\lambda=2$ and $\lambda=3$ (based on (3.33)) remain, and that the Hamiltonian takes the desired form involving $k_{a} \sum_{\lambda=2}^{3}\left\{c^{(\lambda)}, c^{(\lambda) \dagger}\right\}$ if the pertinent factors $\alpha^{(\lambda)}, \beta^{(\lambda)}$ in (3.34) are assigned the following values

$$
\begin{gather*}
\alpha^{(2)}=\frac{1}{2 n|\boldsymbol{k}|}\left[\mu\left(1+\varkappa V_{0}^{2}\right)\left(k_{a}-k_{b}\right)\right]^{\frac{1}{2}}, \alpha^{(3)}=\sqrt{\mu}\left[\left(1+\varkappa V_{0}^{2}\right)\left(k_{a}-k_{b}\right)\right]^{-\frac{1}{2}} \\
\beta^{(2)}=\frac{1}{2 \alpha^{(2)}}, \quad \beta^{(3)}=\frac{1}{2 \alpha^{(3)}} . \tag{3.35}
\end{gather*}
$$

By letting $\beta^{(\lambda)}=1 /\left(2 \alpha^{(\lambda)}\right)$ also for $\lambda=0$ and $\lambda=1$ one finds that the commutation rules (2.12) are satisfied if $\left[c^{(\lambda)}(\boldsymbol{k}), c^{\left(\lambda^{\prime}\right) \dagger}\left(\boldsymbol{k}^{\prime}\right)\right]=-g^{\lambda \lambda^{\prime}} \delta\left(\boldsymbol{k}-\boldsymbol{k}^{\prime}\right)$.

It should be pointed out, however, that the expansions (3.34) are in-
compatible with the definition equation (2.11) for the canonical momentum. In fact, if we make use of (3.34 a) and (2.11) we can write

$$
\begin{gather*}
\pi_{\mu}=-\frac{i}{\mu}(2 \pi)^{-3 / 2}\left[\left(b^{2}\right)_{\mu}^{\varrho}\left(b^{2}\right)_{0}^{\sigma}-\left(b^{2}\right)_{\mu}^{\sigma}\left(b^{2}\right)_{0}^{\varrho}-\left(b^{2}\right)_{\mu 0}\left(b^{2}\right)^{\varrho \sigma}\right]  \tag{3.36}\\
\cdot \int d \boldsymbol{k} k_{\varrho} \sum_{\lambda=0}^{3} \varepsilon_{\sigma}^{(\lambda)} a^{(\lambda)}\left(e^{-i k \cdot x} c^{(\lambda)}-e^{i k \cdot x} c^{(\lambda) \dagger}\right),
\end{gather*}
$$

which shows a more complicated behaviour than Jauch and Watson's expression ( 3.34 b ). If we consider the various polarization directions separately, we find however that the contributions to ( 3.34 b ) and (3.36) from the direction $\lambda=3$ are equal for any $\boldsymbol{k}$. For $\lambda=2$ we find a disagreement, except in the special cases $\boldsymbol{k} \times \boldsymbol{V}=0$ or $\varkappa=0$. In the limiting cases $\boldsymbol{k} \times \boldsymbol{V} \rightarrow 0$ or $\varkappa \rightarrow 0$ the unit vectors (3.33) tend to coincide with the unit vectors (3.20).

The next point that we shall consider, is the possibility of using instead of (2.9) the following expression for the Lagrangian density :

$$
\begin{equation*}
L_{1}=-\frac{1}{2 \mu}\left(\partial_{v} A_{\mu}\right) \partial^{v} A^{\mu}-\frac{\varkappa}{2 \mu}\left(V \cdot \partial A_{\mu}\right)\left(V \cdot \partial A^{\mu}\right) . \tag{3.37}
\end{equation*}
$$

(It is well known that in the vacuum case $x=0$ either of the expressions (3.37) and (2.9) can be used.) Actually, R. Dobbertin ${ }^{(12)}$ has worked out a covariant theory on the basis of (3.37). The theory so constructed appears to have some attractive, simple properties: The variational equations obtained from (3.37) are the same as our previous (2.8) or (3.2); moreover, one can employ the Fourier expansion (3.6), simplified in the sense that $\left(b^{-1}\right)_{\mu}^{\nu}$ is replaced by $g_{\mu}^{\nu}$, in order to obtain an expression for the total fourmomentum in the form (3.30a). The photon four-momentum thus also becomes equal to $k_{\mu}$.

However, the following essential feature of the theory should be pointed out: The canonical four-momentum calculated from (3.37) does not correspond to the classical canonical four-momentum $P_{\mu}^{\text {Maxw. of the Maxwell }}$ field calculated from the Lagrangian density

$$
\begin{equation*}
L^{\text {Maxw. }}=-\frac{1}{4} F_{\mu \nu} H^{\mu \nu}, \tag{3.38}
\end{equation*}
$$

even if the comparison is made after the application of the subsidiary condition. Let us consider the Hamiltonian as an example: By using (3.37) and (3.38) to establish the relation

$$
\left.\begin{array}{rl}
L^{\text {Maxw. }}- & L_{1}=-\frac{\varkappa}{2 \mu}\left(\partial_{v} V \cdot A\right) \partial^{v} V \cdot A-\frac{\varkappa^{2}}{2 \mu}(V \cdot \partial V \cdot A)^{2}+\frac{1}{2 \mu}\left(\Lambda^{F}\right)^{2}+ \\
& +\partial^{\mu}\left[\frac{\varkappa}{\mu} V \cdot A\left(V \cdot \partial A_{\mu}-V_{\mu} \partial \cdot A\right)+\frac{1}{2 \mu}\left(A \cdot \partial A_{\mu}-A_{\mu} \partial \cdot A\right)\right] \tag{3.39}
\end{array}\right\}
$$

and disregarding the divergence term, we find

$$
\left.\begin{array}{c}
\mathscr{H}^{\text {Maxw, }}-\mathscr{H}_{1}=\frac{1}{\mu} \int\left[-\frac{1}{2}\left(\Lambda^{F}\right)^{2}+\Lambda^{F}\left(b^{2}\right)^{0 \mu} \partial_{0} A_{\mu}-\right. \\
\left.-\chi\left(b^{2}\right)^{0 \mu}\left(\partial_{0} V \cdot A\right)\left(\partial_{\mu} V \cdot A\right)+\frac{\varkappa}{2}\left(b^{2}\right)^{\mu \nu}\left(\partial_{\mu} V \cdot A\right)\left(\partial_{v} V \cdot A\right)\right] d V \tag{3.40}
\end{array}\right\}
$$

This relation shows that $\mathscr{H}^{\text {Maxw, }}$ and $\mathscr{H}_{1}$ are in general not equivalent, even when the terms containing $\Lambda^{F}$ are disregarded. This behaviour is restricted to the case where $x \neq 0$; in a vacuum field it follows that $\mathscr{H}^{\text {Maxw, }}$ and $\mathscr{H}_{1}$ are equivalent.

The above feature represents a serious restriction on the applicability of the Lagrangian density $L_{1}$ in the description of the electromagnetic field. One should rather employ a Lagrangian, as for instance $L$ given by (2.9), which maintains the connection with the Maxwell field in virtue of the subsidiary condition.

## 4. A Transformation Procedure applied to the Classical Field

Up till now we have considered the simple case of a pure radiation field from a conventional point of view in the sense that all the analysis has been carried out in the actual physical situation, i.e. in the presence of a uniformly moving transparent medium. Instead of going on using this method, we shall in the following present another, rather unconventional, method to construct the phenomenological theory, namely, to start from the well known expressions in the vacuum field case and then obtain the corresponding expressions in the medium field case simply by a transformation procedure. In this section we shall restrict ourselves to the classical case.

We first show how the Maxwell equations in matter, in the presence of external charges,

$$
\begin{equation*}
\partial^{v} H_{\mu v}=-j_{\mu}, \tag{4.1}
\end{equation*}
$$

where $j_{\mu}=(\varrho, \boldsymbol{j})$, can be mapped into the vacuum field equations. The transformation is accomplished in two steps. First we define the $B$-potentials

$$
\begin{equation*}
B_{\mu}(x)=b_{\mu \nu} A^{\nu}(x) \tag{4.2}
\end{equation*}
$$

and the differential operator

$$
\begin{equation*}
D_{\mu}=b_{\mu \nu} \partial^{\nu} \tag{4.3}
\end{equation*}
$$

The "field strengths" corresponding to the $B$-potentials are

$$
\begin{equation*}
G_{\mu \nu}(x)=b_{\mu}^{\varrho} b_{v}^{\sigma} F_{\varrho \sigma}(x)=D_{\mu} B_{v}(x)-D_{\nu} B_{\mu}(x) . \tag{4.4}
\end{equation*}
$$

The Maxwell equations (4.1) can then be written

$$
\begin{equation*}
D^{v} G_{\mu v}=-D^{2} B_{\mu}+D_{\mu} D_{\nu} B^{v}=-J_{\mu}, \tag{4.5}
\end{equation*}
$$

where $J_{\mu}=\mu\left(b^{-1}\right)_{\mu}^{v} j_{\nu}$ is the "current" of the $B$-field satisfying the "continuity equation"

$$
\begin{equation*}
D^{\mu} J_{\mu}=0 \tag{4.6}
\end{equation*}
$$

The resemblance of eqs. (4.4-6) with the equations of the Maxwell field in vacuum is striking. Gauge invariance, which can be expressed as the invariance of the equations of motion under the transformation

$$
\begin{equation*}
A_{\mu} \rightarrow A_{\mu}+\partial_{\mu} \chi, \tag{4.7}
\end{equation*}
$$

is in terms of the $B$-field expressible as the invariance under the transformation

$$
\begin{equation*}
B_{\mu} \rightarrow B_{\mu}+D_{\mu} \chi, \tag{4.8}
\end{equation*}
$$

and it immediately follows that a natural choice of gauge condition corresponding to the Lorentz condition of vacuum electrodynamics is

$$
\begin{equation*}
D^{\mu} B_{\mu}=\partial \cdot A+\varkappa V \cdot \partial V \cdot A=0 . \tag{4.9}
\end{equation*}
$$

This is the same gauge condition as our previous eq. (2.7) and it implies, as we have seen, that the Maxwell equations take on the form (2.8).

We are now in a position to complete the transformation to the Maxwell equations in vacuum by defining the vacuum field

$$
\begin{gather*}
A_{\mu}^{\mathrm{vac}}(x)=\varrho B_{\mu}(y)=\varrho b_{\mu \nu} A^{\nu}(y),  \tag{4.10}\\
\text { where } \quad y_{\mu}=b_{\mu \nu} x^{\nu}  \tag{4.11}\\
\text { and } \varrho=(n / \mu)^{\frac{1}{2}} . \tag{4.12}
\end{gather*}
$$

It will be clear later on that the factor $\varrho$ in (4.10) is necessary in order that the vacuum field shall acquire the correct commutation relations of a free
field (cf. also the momentum space considerations below). A consequence of the definition (4.11) is that $D_{\mu}^{y}$ can be replaced by $\partial_{\mu}^{x}$, and so the equations of motion for $A_{\mu}^{\mathrm{vac}}(x)$ can be written as

$$
\begin{equation*}
-\square A_{\mu}^{\mathrm{vac}}(x)+\partial_{\mu} \partial^{v} A_{v}^{\mathrm{vac}}(x)=-j_{\mu}^{\mathrm{vac}}(x) \tag{4.13}
\end{equation*}
$$

where the "vacuum current" is given by

$$
\begin{equation*}
j_{\mu}^{\mathrm{vac}}(x)=\varrho J_{\mu}(y)=\varrho \mu\left(b^{-1}\right)_{\mu}^{v} j_{\nu}(y) \tag{4.14}
\end{equation*}
$$

This current also satisfies the continuity equation

$$
\begin{equation*}
\partial^{\mu} j_{\mu}^{\mathrm{vac}}(x)=0 \tag{4.15}
\end{equation*}
$$

These considerations show that there is an intimate connection between the equations of motion of the Maxwell field in isotropic matter and in the vacuum; the Maxwell field in matter can be mapped uniquely into the Maxwell field in the vacuum. This feature is not so surprising as it might seem at first. For if we consider the equations of motion in the rest frame they will essentially consist of the differential operator $\Delta-n^{2} \partial^{2} / \partial t^{2}$ acting on the potentials. If we then redefine time by putting $t^{\prime}=\frac{1}{n} t$ this operator will be transformed into the usual d'Alembertian operator and the equations of motion will look like the free equations of motion. What we have done in this section is just to carry out such a procedure in a manifestly covariant way.

As an example of the application of the developed formalism it is instructive to go into momentum space considerations. We may expand the vacuum field in a form similar to (3.14):

$$
\begin{equation*}
A_{\mu}^{\mathrm{vac}}(x)=\sum_{\boldsymbol{l}} \frac{1}{\left[2 l_{0} \mathscr{V}_{l}\right]^{1 / 2}}\left(e^{-i l \cdot x} e_{\mu}(\boldsymbol{l})+e^{i l \cdot x} e_{\mu}^{*}(\boldsymbol{l})\right), \tag{4.16}
\end{equation*}
$$

where $l_{\mu}$ is the four-momentum of a vacuum "photon" and the normalization volume $\mathscr{V}_{l}$ transforms according to eq. (3.13) (with $n=1$ ). With the use of (4.10) and (4.11) it follows that

$$
\begin{equation*}
k_{\mu}=\left(b^{-1}\right)_{\mu}^{v} l_{\nu} . \tag{4.17}
\end{equation*}
$$

In view of the invariance property (3.32) the normalization volumes $\mathscr{V}^{\circ}$ in the expansions (3.14) and (4.16) can be put equal, whereby

$$
\begin{equation*}
a_{\mu}(\boldsymbol{k})=e_{\mu}(\boldsymbol{l}) \tag{4.18}
\end{equation*}
$$

Note that the factor $\varrho$ appears automatically in the transformation formula. The equations of motion for a radiation field imply that $l^{2}=0$, whereas the Lorentz condition implies that $l \cdot e=0$. If the volume $\mathscr{V}_{l}$ contains only one "photon", the vector $e_{\mu}$ in (4.16) fulfils the normalization condition

$$
\begin{equation*}
e_{\mu}^{*} e^{\mu}=-1 \tag{4.19}
\end{equation*}
$$

It is however convenient to change the normalization conditions in such a way that the "one-photon" potential of a vacuum photon (with four-momentum $l_{\mu}$ ) takes the form

$$
\begin{equation*}
A_{\mu}^{\mathrm{vac}}(x)=e^{-i l \cdot x} e_{\mu}(\boldsymbol{l})+e^{i l \cdot x} e_{\mu}^{*}(\boldsymbol{l}) \tag{4.20}
\end{equation*}
$$

Here $e_{\mu}$ still fulfils eq. (4.19), but the volume corresponding to one "photon" is now not $\mathscr{V}_{l}$ but instead $v_{l}$, where $v_{l}=1 /\left(2 l_{0}\right)$.

The corresponding equation for one "photon" in the medium is

$$
\begin{gather*}
A_{\mu}(x)=\frac{1}{\varrho}\left(e^{-i k \cdot x} f_{\mu}+e^{i k \cdot x} f_{\mu}^{*}\right)  \tag{4.21a}\\
f_{\mu}=\left(b^{-1}\right)_{\mu}^{v} e_{\nu} \tag{4.21~b}
\end{gather*}
$$

and the "one-photon" volume is now $v_{k}$, where

$$
\begin{equation*}
v_{k}=\frac{n}{\left(1+x V_{0}^{2}\right)\left(k_{a}-k_{b}\right)} \tag{4.22}
\end{equation*}
$$

cf. eq. (3.32). The vacuum field equations $l^{2}=0, l \cdot e=0$ and the condition (4.19) then lead to the equations

$$
\begin{gather*}
k^{\mu} k^{v}\left(b^{2}\right)_{\mu \nu}=k^{2}+\varkappa(k \cdot V)^{2}=0  \tag{4.23a}\\
k^{\mu} f^{v}\left(b^{2}\right)_{\mu v}=k \cdot f+\varkappa(k \cdot V)(f \cdot V)=0  \tag{4.23~b}\\
f^{\mu^{*}} f^{v}\left(b^{2}\right)_{\mu v}=f^{*} \cdot f+\varkappa\left(f^{*} \cdot V\right)(f \cdot V)=-1 . \tag{4.23c}
\end{gather*}
$$

## Gauge Considerations

It is instructive to make use of the above transformation method in a study of the gauge condition. We first observe that the gauge invariance of the vacuum field, which means $e_{\mu}$ and $\left(e_{\mu}+c l_{\mu}\right)$ are equivalent polariza-
tion vectors, implies that in the case of the medium field eqs. (4.23) are invariant under the transformation $f_{\mu} \rightarrow f_{\mu}+c k_{\mu}$. Normally one imposes one extra gauge condition on the polarization vector in the vacuum, namely the transversality condition $e_{0}=0$. This result can always be obtained by a gauge transformation since $l_{0}$ is different from zero. However, the corresponding condition $f_{0}=0$ in matter is not always possible, because $k_{0}$ can be zero in certain inertial frames due to the space-like character of $k_{\mu}$ (cf. eq. (3.4)). In fact, in the zero frequency case $k_{0}=0$ it is possible to show that one cannot find two independent solutions of $f_{\mu}$, both with $f_{0}=0^{*}$. Hence the requirement $f_{0}=0$ is in general not a legitimate gauge condition.

In order to obtain a general description we must find another gauge condition than $f_{0}=0$. Let us examine the possible choice $e_{0}=0$. By means of (4.21 b) and (4.17) we then see that

$$
\begin{equation*}
f_{0}+(n-1) V_{0} f \cdot V=0 \tag{4.24}
\end{equation*}
$$

and

$$
\begin{equation*}
\boldsymbol{l} \cdot \boldsymbol{e}=(\boldsymbol{k}+(n-1) \boldsymbol{V} k \cdot V) \cdot \boldsymbol{e}=0 \tag{4.25}
\end{equation*}
$$

It is clear that as two independent solutions of the latter equation we can choose the vectors $\boldsymbol{e}^{(2)}$ and $\boldsymbol{e}^{(3)}$ given by (3.20). Notice that hereby the condition (4.19) will be satisfied. The corresponding f's can be found from ( 4.21 b ). We have thus obtained the interesting result that our earlier choice (3.20) of unit vectors stands in intimate connection with the natural solutions of the equations of the "one-photon" problem in the transformed vacuum field case.

It is however apparent that the above gauge condition suffers from the usual drawback of vacuum electrodynamis that it is non-covariant. As we shall see now it is possible to improve this feature and make the whole theory covariant, by making use of the transformation procedure and the fact that the rest frame of the medium represents a distinguished system of reference. In this frame the frequency is always different from zero so that we can put $\dot{f}_{0}^{\circ}=0$. This condition can be expressed in covariant fashion as

$$
\begin{equation*}
f \cdot V=0 \tag{4.26}
\end{equation*}
$$

and we shall seek to make the whole theory covariant by introducing new covariant polarization vectors which are in conformity with (4.26). First

[^1]it should be noted that the condition (4.26) can always be obtained by a suitable gauge transformation $f_{\mu} \rightarrow f_{\mu}+c k_{\mu}$, since $k \cdot V$ is always different from zero. It can readily be verified that for polarization vectors $f_{\mu}$ satisfying (4.26) we also have $f_{\mu}=e_{\mu}$.

Now let $e_{\mu}^{(2)}$ be an arbitrary polarization four-vector satisfying

$$
\begin{gather*}
V \cdot e^{(2)}=l \cdot e^{(2)}=0  \tag{4.27}\\
e^{(2) *} \cdot e^{(2)}=-1 . \tag{4.28}
\end{gather*}
$$

Then we can define the vector*

$$
\begin{equation*}
e_{\mu}^{(3)}=-\frac{\varepsilon_{\mu \nu \varrho \sigma} l^{\nu} V^{\varrho}\left(e^{(2) *}\right)^{\sigma}}{l \cdot V} \tag{4.29}
\end{equation*}
$$

This vector also satisfies

$$
\begin{gather*}
V \cdot e^{(3)}=l \cdot e^{(3)}=0  \tag{4.30}\\
e^{(3) * \cdot} \cdot e^{(3)}=-1 \tag{4.31}
\end{gather*}
$$

and furthermore

$$
\begin{equation*}
e^{(2) *} \cdot e^{(3)}=0 \tag{4.32}
\end{equation*}
$$

Another important property is

$$
\begin{equation*}
\varepsilon_{\mu \nu \varrho \sigma}\left(e^{(2)}\right)^{\varrho}\left(e^{(3)}\right)^{\sigma}=-\frac{l_{\mu} V_{\nu}-l_{\nu} V_{\mu}}{l \cdot V}, \tag{4.33}
\end{equation*}
$$

which in the rest system implies

$$
\begin{equation*}
\dot{\boldsymbol{e}}^{(2)} \times \dot{\boldsymbol{e}}^{(3)}=\check{\boldsymbol{l}} /|\check{\boldsymbol{l}}|=\stackrel{\circ}{\boldsymbol{k}} /|\boldsymbol{k}| . \tag{4.34}
\end{equation*}
$$

For the following it is convenient to introduce two four-vectors more. These can however not be interpreted as polarization vectors for plane waves. Let us define

$$
\begin{gather*}
e_{\mu}^{(0)}=V_{\mu}, \quad e^{(0)} \cdot e^{(0)}=1  \tag{4.35}\\
e_{\mu}^{(1)}=\frac{l_{\mu}-V_{\mu} l \cdot V}{l \cdot V}, \quad e^{(1)} \cdot e^{(1)}=-1 . \tag{4.36}
\end{gather*}
$$

Then we can verify that our new covariant basic vectors $e_{\mu}^{(\lambda)}, \lambda=0,1,2,3$, satisfy eqs. (3.19) (with one of the vectors replaced by its complex conjugate). It is appropriate at this place to recall that the $e_{\mu}^{(\lambda)}$ defined by (3.20) are not four-vectors.

[^2]Mat. Fys. Medd. Dan.Vid. Selsk. 38, no. 1.

Thus, according to this new description in which both the field equations and the gauge condition are covariant, it follows that $e_{\mu}^{(2)}$ and $e_{\mu}^{(3)}$ can be taken as the two independent physical solutions describing the "one-photon" situation in the vacuum field case. The corresponding solution in the medium field case is obtained by means of eq. (4.21b).

Let us finally make use of eq. (3.19) to calculate the polarization sum

$$
\begin{equation*}
\sum_{\lambda=2,3} e_{\mu}^{(\lambda)} e_{\nu}^{(\lambda) *}=-g_{\mu \nu}-\frac{l_{\mu} l_{\nu}}{(l \cdot V)^{2}}+\frac{l_{\mu} V_{\nu}+l_{\nu} V_{\mu}}{l \cdot V}, \tag{4.37}
\end{equation*}
$$

which can be expressed in terms of $f$ and $k$ :

$$
\begin{equation*}
\sum_{\lambda=2,3} f_{\mu}^{(\lambda)} f_{\nu}^{(\lambda) *}=-\left(b^{-2}\right)_{\mu \nu}-\frac{k_{\mu} k_{v}}{n^{2}(k \cdot V)^{2}}+\frac{k_{\mu} V_{\nu}+k_{\nu} V_{\mu}}{n^{2} k \cdot V} . \tag{4.38}
\end{equation*}
$$

## 5. Quantization of the Electromagnetic Field by Means of the Transformation Method. Use of Covariant Gauges in Configuration Space

In this section we shall make use of the transformation method introduced in the previous section and shall construct the quantum theory of the electromagnetic field in the medium by starting from the expressions of vacuum quantum electrodynamics. Besides, we shall permit the presence of general covariant gauges in the construction of the commutation rules in configuration space. (We recall that in the sections 2 and 3 a single gauge was permitted, namely the Fermi gauge.) The family of covariant gauges that we shall assume has been studied (in the case $\varkappa=0$ ) by one of the authors elsewhere ${ }^{(20)}$. It corresponds to the Lagrangian density

$$
\begin{equation*}
L^{\mathrm{vac}}(x)=-\frac{1}{4} F_{\mu \nu}^{\mathrm{vac}} F^{\mu \nu \mathrm{vac}}-\Lambda^{\mathrm{vac}} \partial^{\mu} A_{\mu}^{\mathrm{vac}}+\frac{a}{2}\left(\Lambda^{\mathrm{vac}}\right)^{2}, \tag{5.1}
\end{equation*}
$$

where $A^{\text {vac }}$ is a Lagrange multiplier field which is introduced to take care of the gauge condition, and where $a$ is the gauge parameter. The Fermi gauge is obtained by putting $a=1$. The field equations are obtained from eq. (5.1) as

$$
\begin{equation*}
-\square A_{\mu}^{\mathrm{vac}}+\partial_{\mu} \partial^{v} A_{\nu}^{\mathrm{vac}}=\partial_{\mu} A^{\mathrm{vac}}, \tag{5.2}
\end{equation*}
$$

while the gauge condition emerges after variation with respect to $\Lambda^{\text {vac }}$ :

$$
\begin{equation*}
\partial^{\mu} A_{\mu}^{\mathrm{vac}}=a \Lambda^{\mathrm{vac}} \tag{5.3}
\end{equation*}
$$

The commutation rules become

$$
\begin{equation*}
\left[A_{\mu}^{\mathrm{vac}}(x), A_{\nu}^{\mathrm{vac}}\left(x^{\prime}\right)\right]=-i g_{\mu \nu} D\left(x-x^{\prime}\right)-i(1-a) \partial_{\mu} \partial_{\nu} E\left(x-x^{\prime}\right) \tag{5.4}
\end{equation*}
$$

where $D(x)$ is the well known singular function

$$
\begin{equation*}
D(x)=-\frac{i}{(2 \pi)^{3}} \int d l \varepsilon(l) \delta\left(l^{2}\right) e^{-i l \cdot x}=-\frac{\varepsilon(x)}{2 \pi} \delta\left(x^{2}\right) \tag{5.5}
\end{equation*}
$$

and (20)

$$
\begin{equation*}
E(x)=\frac{i}{(2 \pi)^{3}} \int d l \varepsilon(l) \delta^{\prime}\left(l^{2}\right) e^{-i l \cdot x}=\frac{\varepsilon(x)}{8 \pi} \theta\left(x^{2}\right), \tag{5.6}
\end{equation*}
$$

where the delta function is differentiated with respect to its argument.
Let us now use eqs. (4.10-12) to define the fields $B_{\mu}(y)$ and $A_{\mu}(y)$ from the vacuum field $A_{\mu}^{\text {vac }}(x)$. We obtain immediately from (5.2) and (5.3) the equations of motion and gauge-condition for the $B$-field

$$
\begin{gather*}
-D^{2} B_{\mu}(y)+D_{\mu} D^{v} B_{v}(y)=D_{\mu} \Lambda(y)  \tag{5.7}\\
D^{\mu} B_{\mu}(y)=a \Lambda(y) \tag{5.8}
\end{gather*}
$$

where $\Lambda(y)=\varrho^{-1} \Lambda^{\text {vac }}(x)$. In the Fermi gauge $(a=1)$ eq. ( 5.7 ) reduces to the well known equations of motion. The commutation relations for the $B$-field become

$$
\left.\begin{array}{c}
{\left[B_{\mu}(y), B_{\nu}\left(y^{\prime}\right)\right]=}  \tag{5.9}\\
=\frac{1}{\varrho^{2}}\left\{-i g_{\mu \nu} D\left(b^{-1}\left(y-y^{\prime}\right)\right)-i(1-a) D_{\mu}^{y} D_{\nu}^{y} E\left(b^{-1}\left(y-y^{\prime}\right)\right)\right\}
\end{array}\right\}
$$

where $\left(b^{-1}\left(y-y^{\prime}\right)\right)_{\mu}=\left(x-x^{\prime}\right)_{\mu}$. At last we obtain the commutation relations for the $A$-field

$$
\left.\begin{array}{c}
{\left[A_{\mu}(y), A_{v}\left(y^{\prime}\right)\right]=}  \tag{5.10}\\
=\frac{1}{\varrho^{2}}\left\{-i\left(b^{-2}\right)_{\mu \nu} D\left(b^{-1}\left(y-y^{\prime}\right)\right)-i(1-a) \partial_{\mu}^{y} \partial_{v}^{y} E\left(b^{-1}\left(y-y^{\prime}\right)\right)\right\} .
\end{array}\right\}
$$

In order to cast (5.10) into a more conventional form we apply the transformation (4.17) to the expression (5.5), whereby we get

$$
\begin{equation*}
D\left(b^{-1} y\right)=-\frac{i n}{(2 \pi)^{3}} \int d k \varepsilon(k \cdot V) \delta\left(k^{2}+x(k \cdot V)^{2}\right) e^{-i k \cdot y} \tag{5.11}
\end{equation*}
$$

Here we have used the connections $\varepsilon(l)=\varepsilon(k \cdot V)$, $\operatorname{det}\left\{b_{\mu}^{\nu}\right\}=n$. Similarly

$$
\begin{equation*}
E\left(b^{-1} y\right)=\frac{i n}{(2 \pi)^{3}} \int d k \varepsilon(k \cdot V) \delta^{\prime}\left(k^{2}+\varkappa(k \cdot V)^{2}\right) e^{-i k \cdot y} \tag{5.12}
\end{equation*}
$$

Putting $a=1$ and comparing with our earlier eqs. (3.8) and (3.9) it is thus apparent that $D\left(b^{-1} y\right)=D^{M}(x)$ and that the commutation relations (5.10) and (3.8) are identical. We recall that the relations (3.8) were calculated on the basis of the Lagrangian density (2.9), corresponding to the Fermi gauge for the medium field. It should also be noted that in the case $a=1$ it follows from (4.10-12) that $L^{\mathrm{vac}}(x)=n L(y)$.

Let us now consider the four-momentum operator for the free radiation field. Since the energy of the field is diagonalizable in the Fermi gauge only ${ }^{(20)}$, we shall for the sake of convenience limit ourselves to this case. However, as has been shown in ref. 20, the corresponding results in the other gauges $(a \neq 1)$ can be obtained from the Fermi gauge results by a gauge transformation. The fact that the vacuum operators satisfy the relation

$$
\begin{equation*}
i\left[P_{\mu}^{\mathrm{vac}}, A_{\nu}^{\mathrm{vac}}(x)\right]=\partial_{\mu} A_{\nu}^{\mathrm{vac}}(x) \tag{5.13}
\end{equation*}
$$

immediately tells us that the operators

$$
\begin{gather*}
P_{\mu}=\left(b^{-1}\right)_{\mu}^{v} P_{v}^{\mathrm{vac}}  \tag{5.14}\\
\text { satisfy } \quad i\left[P_{\mu}, A_{v}(y)\right]=\partial_{\mu}^{y} A_{v}(y) \tag{5.13a}
\end{gather*}
$$

(cf. eq. (2.14a)), and hence should be interpreted as the four-momentum operators for the medium field.

## Momentum Space Considerations in the Fermi Gauge

We shall now show that interesting features of the theory are exhibited when we make use of the new covariant polarization vectors in the Fourier expansions. We shall limit ourselves to the Fermi gauge case. The fourpotential is expanded in the form

$$
\begin{equation*}
A_{\mu}(x)=\frac{1}{\varrho} \sum_{\boldsymbol{k}, \lambda}\left(b^{-1}\right)_{\mu}^{v} e_{\nu}^{(\lambda)}\left(e^{-i k \cdot x} a^{(\lambda)}(\boldsymbol{k})+e^{i k \cdot x} \tilde{a}^{(\lambda)}(\boldsymbol{k})\right) \tag{5.15}
\end{equation*}
$$

where the $e_{v}^{(\lambda)}$ (now assumed to be real) are introduced in eqs. (4.27-36). It must be borne in mind that this simple expansion of the potential corresponds for each $\boldsymbol{k}$ to the effective normalization volume $v_{k}$ given in eq. (4.22). Note also that in the rest frame the spatial vectors $\boldsymbol{e}^{(\lambda)}, \lambda=1,2,3$,
form an orthogonal set normalized to unity, so that the components $a^{(\lambda)}$ give the magnitudes of the potential operator $\boldsymbol{a}$ along each of the orthogonal directions $\lambda$. In other inertial frames the vectors $\boldsymbol{e}^{(\lambda)}$ are in general neither orthogonal nor of unit magnitude. The relativistic covariance of the theory is now expressed by requiring $a_{\mu}$ to transform like a four-vector, just as in the classical case. Because of the transformation properties of $e_{\mu}^{(\lambda)}$ the components $a^{(\lambda)}$ then become Lorentz invariant quantities. If we introduce the metric operator $\eta$ with the properties (3.24) we find, similarly as before, that the total photon number operator for each $\boldsymbol{k}$ is equal to $N_{\text {op }}=-g^{\mu v} \tilde{a}_{\mu} a_{v}$ $=\sum_{\lambda=0}^{3} a^{(\lambda) \dagger} a^{(\lambda)}$. It is clear that the operator $N_{\text {op }}$, as well as the photon number operators for each polarization direction $\lambda$ separately, $N_{\mathrm{op}}^{(\lambda)}=$ $a^{(\lambda) \dagger} a^{(\lambda)}$, are Lorentz invariants. Further, it turns out that not only the operator components $a^{(\lambda)}$, but also the state vector $|\Psi\rangle$ in the Hilbert (Fock) space, may be assigned a Lorentz invariant meaning. For the Hilbert space in some frame $K$ is spanned by the orthogonal unit vectors $\left|N^{(\lambda)}(\boldsymbol{k})\right\rangle$, one vector for each degree of freedom $(\boldsymbol{k}, \lambda)$ and a definite value for the occupation number $N$. In another frame $K^{\prime}$ we let the Hilbert space be spanned by just the same vectors, but replace each label $N^{(\lambda)}(\boldsymbol{k})$ by a new label $N^{(\lambda)}\left(\boldsymbol{k}^{\prime}\right)$, where $N$ and $\lambda$ are the same and where $\boldsymbol{k}^{\prime}$ is connected with $\boldsymbol{k}$ by a Lorentz transformation. Since both the partial photon number operators $N_{\text {op }}^{(\lambda)}(\boldsymbol{k})$ and the basic vectors $\left|N^{(\lambda)}(\boldsymbol{k})\right\rangle$ in the Hilbert space thus have an invariant meaning it follows that the state vector $|\Psi\rangle$ itself also is a Lorentz invariant.

From the above it is clear that with the use of the new covariant vectors $e_{\mu}^{(\lambda)}$ we obtain a very convenient description: The Gupta-Bleuler method can be carried through in a completely covariant way in the sense that it involves only Lorentz invariant operator components and state vectors. In forming the expectation value of the four-momentum operator of the field we see that the net contribution from the polarization directions $\lambda=0$ and $\lambda=1$ vanishes, while the contributions from the directions $\lambda=2$ and $\lambda=3$ survive. In any inertial frame the Gupta-Bleuler procedure runs exactly in the same way as in $K$, although it should be borne in mind that the direction of the spatial vector $\boldsymbol{e}^{(\lambda)}$, for a fixed value of $\lambda$, depends on the frame $K$ in which the vector is considered. Note that the invariance property of the occupation numbers for each polarization direction $\lambda$ depends on the use of the covariant vectors $e_{\mu}^{(\lambda)}$; with our old non-covariant vectors defined by (3.20) the invariance property of each $N^{(\lambda)}(\boldsymbol{k})$ is in general lost although also in that case the total number $N(\boldsymbol{k})$ remains an invariant.

It should be emphasized that the invariance property of the state vector $|\Psi\rangle$ implies the separate invariance of the state vector $\left|\Psi_{T}\right\rangle$, containing only "transversal" photons for which $\lambda=2,3$, and the state vectors $\left|\Phi_{k}\right\rangle$ containing "longitudinal" and "scalar" photons for which $\lambda=1,0$, cf. (3.31). In this context we recall that in the cases $\lambda=1,0$ the occupation numbers are arbitrary except for the single restriction imposed by the gauge condition. Let us elucidate this point by the following simple calculation. A state vector $\left|\Phi_{\boldsymbol{k}}\right\rangle$ giving the mixture of longitudinal and scalar photons can be written as ${ }^{(17)}$

$$
\begin{equation*}
\left|\Phi_{\boldsymbol{k}}\right\rangle=\left|\Phi_{\boldsymbol{k}}^{(0)}\right\rangle+\sum_{N \neq 0} c^{(N)}(\boldsymbol{k})\left|\Phi^{(N)}(\boldsymbol{k})\right\rangle \tag{5.16}
\end{equation*}
$$

where the coefficients $c^{(N)}(\boldsymbol{k}), N=N^{(0)}+N^{(1)}$, are arbitrary quantities. According to the above these coefficients should be Lorentz invariants, as we actually shall verify in the case $N=1$ by calculating the expectation value of the potential $A_{\mu}(x)$. Assuming that no photon with $\lambda=2,3$ is present, we get

$$
\begin{equation*}
\langle\Psi| \eta A_{\mu}(x)|\Psi\rangle=\frac{1}{\varrho} \sum_{k}\left(b^{-1}\right)_{\mu}^{v}\left(e_{\nu}^{(0)}+e_{\nu}^{(1)}\right)\left[e^{-i k \cdot x} c^{(1)}(\boldsymbol{k})+e^{i k \cdot x} c^{(1) *}(\boldsymbol{k})\right] . \tag{5.17}
\end{equation*}
$$

By inserting the expressions (4.35) and (4.36) we find

$$
\begin{gather*}
\langle\Psi| \eta A_{\mu}(x)|\Psi\rangle=\partial_{\mu} \chi(x)  \tag{5.18a}\\
\chi(x)=\frac{i}{n \varrho} \sum_{k} \frac{1}{k \cdot V}\left[e^{-i k \cdot x} c^{(1)}(\boldsymbol{k})-e^{i k \cdot x} c^{(1) *}(\boldsymbol{k})\right] \tag{5.18b}
\end{gather*}
$$

Eq. (5.18a) tells us that $\chi(x)$ plays the role of a Lorentz invariant gauge function, and eq. ( 5.18 b ) requires the expansion coefficients also to be invariants, $c^{(1)}(\boldsymbol{k})=c^{(1)}(\dot{\boldsymbol{k}})$, as claimed above. So far only the case $N=1$ has been considered, but we can verify the invariance of also the other coefficients $c^{(N)}$ by calculating the expectation value of a product of potential components.

It should be said explicitly that the metric operator $\eta$ itself is an invariant because of the invariance of the individual occupation numbers for ezch $\lambda$. In the conventional theory with non-covariant $e_{\mu}^{(\lambda)}$ this invariance property is lost due to the non-invariance of the scalar photon numbers. The transformation properties of the conventional theory for the vacuum field have been discussed by F. J. Belinfante ${ }^{(21)}$.

We are now in a position to return to a study of the relation (5.14),
connecting the four-momenta of the medium field and the vacuum field, in the light of the above developments in Fourier space. To this end let us expand the vacuum field in the form corresponding to (5.15), where $e_{\mu}^{(\lambda)}$ is the same and where $a^{(\lambda)}(\boldsymbol{k})$ is replaced by $a^{(\lambda)}$ vac $(\boldsymbol{l})$. By means of eq. (4.10) it follows however that $a^{(\lambda)}(\boldsymbol{k})=a^{(\lambda) \text { vac }}(\boldsymbol{l})$ for each pair of $\boldsymbol{k}, \boldsymbol{l}$ that are connected by eq. (4.17). Hence $N_{\mathrm{op}}^{(\boldsymbol{\lambda})}(\boldsymbol{k})=N_{\mathrm{op}}^{(\lambda) \mathrm{l})}$ vac $(\boldsymbol{l})$, and we recover the relation (5.14) by taking into account eq. (4.17). Now it turns out that the equivalence of the medium field and the vacuum field with respect to the operator components applies also with respect to the state vectors. For we may use the same Hilbert (Fock) space in the vacuum case as in the medium case, simply replacing the label $N^{(\lambda)}(\boldsymbol{k})$ of each basic vector $\left|N^{(\lambda)}(\boldsymbol{k})\right\rangle$ spanning the Hilbert space by the corresponding label $N^{(\lambda) \text { vac }}(\boldsymbol{l})$. Thus we conclude that the state vector $|\Psi\rangle$ of the physical system remains unchanged under the transformation medium field $\rightarrow$ vacuum field, just in the same way as above where we found that $|\Psi\rangle$ remains unchanged under a Lorentz transformation. In particular, the mixture of longitudinal and scalar photons in the medium field is just the same as the mixture in the transformed vacuum field, as expressed by the following property of the expansion coefficients appearing in (5.16): $c^{(N)}(\boldsymbol{k})=c^{(N) \text { vac }}(\boldsymbol{l})$.

We shall finally write down the Feynman rules for the medium field, by starting from the vacuum field case. The propagator in Fourier space for the vacuum field is given by

$$
\begin{equation*}
D_{\mu \nu}^{\mathrm{vac}}(l)=-i \frac{g_{\mu \nu}}{l^{2}+i \varepsilon} . \tag{5.19}
\end{equation*}
$$

We shall now see that the propagator in configuration space for the medium field can be transformed as

$$
\begin{gather*}
D_{\mu \nu}\left(y-y^{\prime}\right)=\langle 0| T\left(A_{\mu}(y) A_{\nu}\left(y^{\prime}\right)\right)|0\rangle  \tag{5.20a}\\
=\varrho^{-2}\left(b^{-1}\right)_{\mu}^{\varrho}\left(b^{-1}\right)_{\nu}^{\sigma}\langle 0| T\left(A_{\varrho}^{\mathrm{vac}}(x) A_{\sigma}^{\mathrm{vac}}\left(x^{\prime}\right)\right)|0\rangle . \tag{5.20b}
\end{gather*}
$$

First, it is clear from the remarks above that the ket vector $|0\rangle$ does not change under the transformation from the medium to the vacuum field. Next, we shall see that no difficulty arises from the fact that the time-ordering in (5.20 a) refers to $y_{0}$ and $y_{0}{ }^{\prime}$ while the time-ordering in ( 5.20 b ) refers to $x_{0}$ and $x_{0}{ }^{\prime}$. For by means of the relation

$$
\begin{equation*}
T\left(A_{\mu}(y) A_{v}\left(y^{\prime}\right)\right)=\frac{1}{2}\left\{A_{\mu}(y), A_{v}\left(y^{\prime}\right)\right\}+\frac{1}{2} \varepsilon\left(y_{0}-y_{0}^{\prime}\right)\left[A_{\mu}(y), A_{\nu}\left(y^{\prime}\right)\right] \tag{5.21}
\end{equation*}
$$

it follows that we can verify eq. ( 5.20 b ) by verifying the equation

$$
\begin{equation*}
\varepsilon\left(y_{0}\right) D\left(b^{-1} y\right)=\varepsilon\left(x_{0}\right) D(x) \tag{5.22}
\end{equation*}
$$

where now the relative distances have been denoted simply by $y$ and $x$. Because of the $D$-function in (5.22) the four-vector $x_{\mu}$ must lie on the light cone, i.e. $x^{2}=0$, and then it immediately follows that the vector $y_{\mu}$ is time-like, i. e. $y^{2}=\left(b^{2}\right)_{\mu \nu} x^{\mu} x^{\nu}>0$. Thus the sign of $x_{0}$, as well as the sign of $y_{0}$, are invariants under a Lorentz transformation, and $x_{0}$ and $y_{0}$ have the same sign in any frame since they have the same sign in the rest frame. This justifies eq. (5.22), and hence also eq. (5.20 b).

By means of eqs. (5.19) and (5.20) we now obtain the propagator in momentum space:

$$
\begin{equation*}
D_{\mu \nu}(k)=\int d x D_{\mu \nu}(x) e^{i k \cdot x}=-i \mu \frac{\left(b^{-2}\right) \mu \nu}{k^{2}+x(k \cdot V)^{2}+i \varepsilon} . \tag{5.23}
\end{equation*}
$$

Each internal photon line of four-momentum $k_{\mu}$ in a Feynman diagram may thus be associated with a factor $D_{\mu \nu}(k)$, defined by eq. (5.23).

External photon lines can be handled similarly. We know that an external photon line of four-momentum $l_{\mu}$ and polarization $\lambda$ in the vacuum case is associated with a factor $e_{\mu}^{(\lambda)}$; this must be so also in the present case where the $e_{\mu}^{(\lambda)}$ mean the covariant vectors defined by eqs. (4.27-36). Thus we conclude that the corresponding line in the medium case is associated with a factor $\varrho^{-1}\left(b^{-1}\right)_{\mu}^{\nu} e_{\nu}^{(\lambda)}=\varrho^{-1} f_{\mu}^{(\lambda)}$.

The remaining Feynman rules are the same as in the case of a vacuum field. In the practical calculation of transition probabilities it is usually convenient to let the normalization volume $\mathscr{V}$ tend to infinity, in which case the sum over $\boldsymbol{k}$ can be replaced by an integral. An expression for the integration element $d m$, based upon the expansion (3.6), was given already in eq. (3.16). Now we have in the present section made use of the simple expansion (5.15), which must be associated with the effective normalization volume $v_{k}$ given by (4.22). This means that we must use the following expression for the integration element $d m$ :

$$
\begin{equation*}
d m=\frac{n d \boldsymbol{k}}{(2 \pi)^{3}\left(1+\varkappa V_{0}^{2}\right)\left(k_{a}-k_{b}\right)} . \tag{5.24}
\end{equation*}
$$

The above results are consistent with the results obtained by Riazanov ${ }^{(10)}$. If we choose to carry through the analysis directly in terms of the medium field, without leaning upon the results from vacuum quantum electrodynamics, we can for instance connect the interacting fields with the noninteracting, incoming fields by means of a unitary transformation (the

U-matrix) in a well known way, and thereby verify the existence of the propagator (5.20 a) in the $S$-matrix.

The Čerenkov effect represents a typical example for an application of the above formalism. We may construct the matrix element for the first order transition and calculate the emission probability in the rest frame of the emitting particle, and will then find agreement with the result obtained by Jauch and Watson ${ }^{(6 b)}$ except for a factor $\mu$. The extra factor $\mu$ in their expression is connected with the fact that their Lagrangian density is defined as $\mu$ times the usual Lagrangian density that we have used (cf. eq. (2.9) in the free field case). Consequently, $\mu$ will appear also in the Hamiltonian; for instance, their Hamiltonian density in the rest frame $\stackrel{\circ}{K}$ for a free field becomes equal to $\mu$ times the usual expression $\frac{1}{2}(\dot{\boldsymbol{E}} \cdot \boldsymbol{D}+' \boldsymbol{H} \cdot \check{\boldsymbol{B}})$.

## 6. Final Remarks

We have seen that the vacuum relations (5.13) are convenient to use in order to find the connection (5.14) between the four-momentum operators. However, the corresponding procedure is not readily performed for the angular momentum operators. This is evidently connected with the fact that the angular momentum for the medium field is not a conserved quantity. Correspondingly, the quantities $M_{\mu \nu}$ do not form a tensor. This last result can be seen most easily by observing that the quantities $M_{\mu \nu}$ defined by (2.19) are physically equivalent to Minkowski's angular momentum based on the tensor expression (2.20), and the latter quantities do not form a tensor since the expressions

$$
\begin{equation*}
\partial^{\sigma}\left(x_{\mu} S_{\nu \sigma}^{M}-x_{\nu} S_{\mu \sigma}^{M}\right)=S_{\nu \mu}^{M}-S_{\mu \nu}^{M} \tag{6.1}
\end{equation*}
$$

in general do not vanish.
Let us divide the expression (2.18) into two parts and integrate over the volume ( $\sigma=0$ ) :

$$
\begin{align*}
L_{\mu \nu} & =\int\left(x_{\mu} S_{\nu 0}-x_{v} S_{\mu 0}\right) d V  \tag{6.2a}\\
\Sigma_{\mu \nu} & =\int \pi_{\alpha} I_{\mu \nu}^{\alpha \beta} A_{\beta} d V \tag{6.2~b}
\end{align*}
$$

By inserting the Fourier expansion of the field in these expressions it can be verified that the time-dependence of the spatial components $M_{i k}$ is contained entirely in the part (6.2 a), not in the part (6.2b).

For an electromagnetic field in the vacuum ${ }^{(17)}$ it is known that $L_{i k}$ is independent of the polarization possibilities of the photons, except for a term containing the potential component $A_{0}$ which is cancelled by a corresponding term in $\sum_{i k}$. We thus get a natural division of the total angular momentum into an orbital part and a spin part. For the medium field the situation is complicated and a corresponding division cannot readily be carried through in the general case. However, the situation of main physical interest arises when the electromagnetic wave runs parallel or antiparallel to the medium velocity (or $\boldsymbol{v}=0$ ). In this case $L_{i k}$ and $\sum_{i k}$ are conserved separately; $L_{i k}$ is polarization independent and is interpreted as orbital angular momentum while $\sum_{i k}$ is interpreted as the spin part. In this case we obtain for the constant spin term

$$
\begin{equation*}
\sum_{23}=\sum_{k}\left(a_{+}^{\dagger} a_{+}-a_{-}^{\dagger} a_{-}\right), \tag{6.3}
\end{equation*}
$$

where as usual

$$
\begin{equation*}
a_{+}=\frac{1}{\sqrt{2}}\left(a^{(2)}-i a^{(3)}\right), \quad a_{-}=\frac{1}{\sqrt{2}}\left(a^{(2)}+i a^{(3)}\right) \tag{6.4}
\end{equation*}
$$

The photons in the medium thus carry spin of unit magnitude.
The next point that we shall comment upon is the connection between the canonical procedure that we have used throughout, and the electromagnetic energy-momentum tensors. We have noted that both the canonical linear momentum and the canonical angular momentum are equivalent to the expressions we obtain by using Minkowski's energy-momentum tensor from the outset. A further illustration of the close connection between Minkowski's tensor and the canonical procedure is provided by eqs. (5.13) and (5.14). This tensor seems on the whole to be the most appropriate one in a quantal treatment, also because of the fact that it corresponds simply to the four-momentum $k_{\mu}$ of a photon in the medium.

It is, however, well known that also other tensor forms have been proposed ${ }^{(4)}$. It should be emphasized that the above formalism does not exclude the legitimacy of other tensor expressions. The best known alternative is due to M. Abraham ${ }^{(2,4)}$. This tensor is, however, not divergence-free even for a radiation field, and, as K. NAGY ${ }^{(9)}$ has pointed out, the energy and the momentum cannot be diagonalized simultaneously. From a quantal point of view a more interesting example is the so-called radiation tensor $S_{\mu \nu}^{S}$ introduced by G. Marx et al. ${ }^{(22)}$, since this tensor is divergence-free and hence implies a conserved four-momentum. We find

$$
\begin{equation*}
P_{\mu}^{S}=\frac{1}{n^{2}} \sum_{k}\left(b^{2}\right)_{\mu}^{v} k_{v} \sum_{\lambda=0}^{3} a^{(\lambda) \dagger} a^{(\lambda)}, \tag{6.5}
\end{equation*}
$$

so that the radiation tensor claims the four-momentum of a photon to be given by $n^{-2}\left(b^{2}\right)_{\mu}^{v} k_{v}$. As this is a time-like four-vector, the photon energy preserves its sign under proper Lorentz transformations.

When $\boldsymbol{k} \times \boldsymbol{V}=0$ the spin component corresponding to (6.3) is

$$
\begin{equation*}
\sum_{23}^{S}=\frac{1}{n^{2}} \sum_{\boldsymbol{k}}\left(a_{+}^{\dagger} a_{+}-a_{-}^{\dagger} a_{-}\right) . \tag{6.6}
\end{equation*}
$$

It has however turned out ${ }^{(4)}$ that the radiation tensor is unable to give a simple explanation of the Jones-Richards experiment mentioned in section 1. Now it appears from eqs. (6.3) and (6.6) that an experimental detection of the spin possessed by an electromagnetic wave in a dielectric liquid should yield a further critical test of the phenomenological theory. For instance, if we let a circularly polarized wave be absorbed by a screen immersed in the liquid and then measure the torque exerted on the screen, we may be able to distinguish between the expressions (6.3) and (6.6). Alternatively, instead of letting the incoming wave be absorbed by the screen, we may arrange the equipment so that the screen merely changes the state of polarization of the wave. Such an experiment will thus be a modification of the Carrara experiment ${ }^{(23)}$. In this context we should also refer to the papers by Toraldo di Francia (ref. 24 with further references therein). As far as we know, this kind of experiment has not been performed. It must be expected that disturbances from the fluid will be an essential difficulty for accurate measurements.

Finally we add some words on the Čerenkov effect. This case exhibits a further characteristic difficulty for the radiation tensor: By calculating the emission angle of a photon in the rest frame $\stackrel{\circ}{K}$ by means of the balance equations for energy and momentum we find, by assigning the spatial momentum $\stackrel{\circ}{\boldsymbol{k}} / n^{2}$ to the emitted photon in accordance with (6.5), that the emission angle takes a complex non-physical value ${ }^{(4)}$. Thus the use of the radiation tensor is beset with essential difficulties also from a theoretical point of view.

At the end of the previous section we mentioned that, when applied to the Čerenkov radiation in the rest frame of the emitting particle, the canonical formalism employed in this paper yields a result which is in essential agreement with the Jauch-Watson result. The reason for this agreement
does not seem to be straightforward. In the first place, we noted in section 3 some difficulties concerning the Fourier expansions used by JaUch and Watson. In the second place, the authors employ a rather complicated Hamiltonian method involving the elimination of the longitudinal field (an extension of the method presented in Wentzel's book ${ }^{(25)}$ ), while our method can be considered to be based upon the application of a unitary transformation connecting the incoming and the outgoing fields. (Whether we choose to transform the results pertaining to the vacuum field or to work directly in terms of the medium field, is immaterial in this context.) These two procedures are apparently rather different and it is not evident that they yield equivalent results in the rest frame of the emitting particle. However, we shall not here pursue this subject further.

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# THE $t$-REPRESENTATION OF THE GENERAL DEBYE FUNCTION 

Det Kongelige Danske Videnskabernes Selskab

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## Synopsis

The $t$-representation of the system function $S(p)=\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{-\beta}$, i.e. the general Debye function, has been determined in the general case of $0 \leqq \alpha, \beta \leqq 1$ and $0<\tau_{0}$ as an infinite $(\mathrm{C}, 1)$ summable series of Riesz distributions,

$$
B_{t}=\sum_{n=0}^{\infty} \frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} \operatorname{Pf} \frac{\left(t / \tau_{0}\right)_{+}^{(1-\alpha)(\beta+n)-1}}{\Gamma[(1-\alpha)(\beta+n)]}
$$

It is established that a transformation $T$ characterising a physical system and mapping an excitation $f$ into a response $r$ by $r=T[f]=B * f$ in spite of the singularities of the system function $S(p)$ possesses the six properties of (i) single valuedness, (ii) linearity, (iii) stationaryness, (iv) continuity, (v) passivity, and (vi) causality.

The main results required from the theory of distributions are presented in the text.

## 1. Introduction

In the present paper the transformation of an excitation $f$ into a response L $r, T: f \rightarrow r$, as effected by a physical system, is considered from a general, mathematical point of view. Only linear systems are treated.

Often, rather than describing the transformation directly, i.e. by giving the $t$-representation, an integral transformation (Laplace transformation) may be carried out, whereby the equivalent $p$-representation is obtained.

Whereas in the $t$-representation the information about the transformation is inherent in the mathematical properties of the transformation, in the $p$-representation this information is contained in the properties of the system function $S(p)$, a complex valued function of a complex variable $p$.

As particular instances of a system function $S(p)$ are discussed the Debye function, $\frac{1}{1+p \tau_{0}}$, and the general Debye function, $\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}$, where $p \in \boldsymbol{C}^{1}, \alpha, \beta, \tau_{0} \in \boldsymbol{R}^{1}, 0 \leqq \alpha, \beta \leqq 1$, and $0<\tau_{0}$. Inspection shows that whereas the Debye function in the complex $p$-plane as its sole singularity has one simple pole, viz. $p=\frac{-1}{\tau_{0}}$, the general Debye function may possess branch point singularities which may be greater than one in number and which may be dense on the circle $|p|=\frac{1}{\tau_{0}}$. Furthermore, the general Debye function may have a branch point at $p=0$.

Rather than as functions the excitations $f$ and the responses $r$ are treated as distributions, i.e. as elements of a topological, linear vector space $\mathscr{D}^{\prime}$ (over $\boldsymbol{C}^{1}$ ) of continuous, linear mappings from a space of test functions into the field $\boldsymbol{C}^{1}$ of the complex numbers.

In section 2 the main results required from the theory of distributions ${ }^{1)}$
${ }^{1}$ ) For a full treatment of the theory of distributions see ref.s (5), (14), (15), (16), and also ref.s (2), (6), and (13).
are indicated. In sections 3 and 4 the relationships between the properties of a transformation $T$ and the properties of the corresponding system function $S(p)$ are studied. Section 5 treats the properties of the general Debye function as system function and the properties of the transformation $T$ corresponding to it. In section 6 the $t$-representation of the general Debye function as system function is determined.

The main results of the treatise are the theorems 5.1 and 6.1 .

## 2. Distributions

Distributions ${ }^{2)}$ are essentially defined as elements of topological vector spaces $\Phi^{\prime}$ which are dual to certain other topological vector spaces $\Phi$, the elements of which are termed test functions $\varphi$. The vector spaces $\Phi$ and $\Phi^{\prime}$ are defined over the field $\boldsymbol{C}^{1}$ of the complex numbers. The test functions $\varphi$ are defined pointwise on sets of points, e.g. $\boldsymbol{R}^{1}, \boldsymbol{C}^{n}$, but only complex valued functions defined on $\boldsymbol{R}^{1}$ will be required.

In what follows some important function spaces and their duals will be treated.

Let the vector space $\mathscr{C}(K)$ be the space of all continuous, complex valued functions, $\varphi_{K}: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, of one real variable, which have their supports contained in the one compact set $K, K \subset \boldsymbol{R}^{1}, \operatorname{supp} \varphi_{K} \subseteq K$. The vector space $\mathscr{C}$ of all continuous functions $\varphi$ with compact support is generated as the union of all the vector subspaces $\mathscr{C}(K)$ as the compact set $K$ varies over $\boldsymbol{R}^{1}$. By defining the seminorms $p\left(\varphi_{K}\right)=\sup _{x \in K}\left|\varphi_{K}(x)\right|$ in the subspaces $\mathscr{C}(K)$ a topology of compact convergence is introduced on the spaces $\mathscr{C}(K)$. A topology on $\mathscr{C}$ is now defined as a set of neighbourhoods in $\mathscr{C}$ such that for each $K$ the intersection of each neighbourhood and the space $\mathscr{C}(K)$ is a neighbourhood in $\mathscr{C}(K)$ under the above topology of compact convergence. As $K$ varies over $\boldsymbol{R}^{1}$ this topology becomes the inductive limit topology of compact convergence, and the space $\mathscr{C}$ with this topology is the inductive limit of the spaces $\mathscr{C}(K)$.

Definition 2.1 $\mathscr{C}=\mathscr{C}_{x}$ is the topological vector space over $\boldsymbol{C}^{1}$ of all continuous, complex valued functions, $\varphi: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, of one real variable, $x \in \boldsymbol{R}^{1}$, which have compact support. The topology on $\mathscr{C}$ is the inductive limit topology of compact convergence.
${ }^{2}$ ) For a full treatment of the theory of distributions see ref.s (5), (14), (15), (16), and also ref.s (2), (6), and (13).

Theorem 2.1 A sequence $\left\{\varphi_{\nu}\right\}$ of functions in $\mathscr{C}, \varphi_{v} \in \mathscr{C}, v=1,2,3, \ldots$, converges to a limit $\varphi$ in $\mathscr{C}, \varphi \in \mathscr{C}$, if and only if (i) there exists a space $\mathscr{C}(K)$ such that $\varphi, \varphi_{v} \in \mathscr{C}(K), v=1,2,3, \ldots$, and (ii) the sequence $\left\{\varphi_{\nu}\right\}$ converges to $\varphi$ in the topology on $\mathscr{C}(K)$.

Likewise, let the vector space $\mathscr{D}(K)$ be the space of all infinitely differentiable, complex valued functions, $\varphi_{K}: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, of one real variable, $x \in \boldsymbol{R}^{1}$, which have their supports contained in the compact set $K, K \subset \boldsymbol{R}^{1}$, $\operatorname{supp} \varphi_{K} \subseteq K$. The vector space $\mathscr{D}$ of all infinitely differentiable functions $\varphi$ with compact support is generated as the union of all the vector subspaces $\mathscr{D}(K)$ as the compact set $K$ varies over $\boldsymbol{R}^{1}$. By proceeding in a manner quite analogous to the above a topology of compact convergence is defined on the vector subspaces $\mathscr{D}(K)$ by defining the seminorms $p_{j}\left(\varphi_{K}\right)=\sup _{x \in K}$ $\left|\varphi_{K}^{(j)}(x)\right|, j=0,1,2,3, \ldots$, in the spaces $\mathscr{D}(K)$. Again it is possible to define in $\mathscr{D}$ a set of neighbourhoods such that for each $K$ the intersection of each neighbourhood in $\mathscr{D}$ with the space $\mathscr{D}(K)$ is a neighbourhood in $\mathscr{D}(K)$ under the above topology of compact convergence, and the space $\mathscr{D}$ is thus generated as the inductive limit of the spaces $\mathscr{D}(K)$.

Definition 2.2 $\mathscr{D}=\mathscr{D}_{x}$ is the topological vector space over $\boldsymbol{C}^{1}$ of all infinitely differentiable, complex valued functions, $\varphi: \boldsymbol{R}^{\jmath} \rightarrow \boldsymbol{C}^{1}$, of one real variable, $x \in \boldsymbol{R}^{1}$, which have compact support. The topology on $\mathscr{D}$ is the inductive limit topology of compact convergence.

Theorem 2.2 A sequence $\left\{\varphi_{\nu}\right\}$ of functions in $\mathscr{D}, \varphi_{v} \in \mathscr{D}, v=1,2,3, \ldots$, converges to a limit $\varphi$ in $\mathscr{D}, \varphi ; \in \mathscr{D}$, if and only if (i) there exists a space $\mathscr{D}(K)$ such that $\varphi, \varphi_{v} \in \mathscr{D}(K), v=1,2,3, \ldots$, and (ii) the sequence $\left\{\varphi_{\nu}\right\}$ converges to $\varphi$ in the topology on $\mathscr{D}(K)$.

Finally is introduced the space $\mathscr{S}$ of test functions of rapid decrease.
Definition 2.3 $\mathscr{S}=\mathscr{S}_{x}$ is the topological vector space over $\boldsymbol{C}^{3}$ of all infinitely differentiable, complex valued functions, $p: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, of one real variable, $x \in \boldsymbol{R}^{1}$, with the property that $|x|^{k} \cdot\left|\varphi^{(l)}(x)\right| \leqq C_{k l}, k, l=0,1,2, \ldots$, with $C_{k l}$ a positive, real constant. The topology on $\mathscr{S}$ is introduced by defining the seminorms $p_{m n}(\varphi)=\sup _{x \in \boldsymbol{R}^{1}}\left|x^{m} \varphi^{(n)}(x)\right|, m, n=0,1,2,3, \ldots$

If $\Phi$ is a topological vector space over the field $\boldsymbol{C}^{1}$ of the complex numbers, the set of all continuous, linear mappings $\varphi^{\prime}$ of $\Phi$ into $\boldsymbol{C}^{1}, \varphi^{\prime}: \Phi \rightarrow \boldsymbol{C}^{1}$, constitutes a vector space called the dual of $\Phi$ and denoted by $\Phi^{\prime}$. The
value of the mapping $\varphi^{\prime} \in \Phi^{\prime}$ at the point $\varphi \in \Phi$ is denoted by $\varphi^{\prime}(\varphi)=$ $\left\langle\varphi^{\prime}, \varphi\right\rangle \in \boldsymbol{C}^{1}$.

To introduce a topology on $\Phi^{\prime}$ let a topology be defined on $\Phi$, and let $\mathscr{A}$ be a family of bounded subsets of $\Phi$ with the properties
(i) if $A \in \mathscr{A}$ and $B \in \mathscr{A}$ then there exists a $C \in \mathscr{A}$ such that $A \cup B \subseteq C$,
(ii) if $A \in \mathscr{A}$ and $\lambda$ is a complex number then there exists a $B \in \mathscr{A}$ such that $\lambda A \subseteq B$.

A topology on $\Phi^{\prime}$ now is determined by defining a set of seminorms in $\Phi^{\prime}$ by $p^{\prime}\left(\varphi^{\prime}\right)=\sup \left|\left\langle\varphi^{\prime}, \varphi\right\rangle\right|, A \in \mathscr{A}$. In particular, two topologies on $\Phi^{\prime}$ are $\varphi \in A$
of importance. If $\mathscr{A}$ is the set $\mathscr{A}_{f}$ of all finite subsets of $\Phi$, the topology defined on $\Phi^{\prime}$ is called the weak dual topology $\sigma\left(\Phi^{\prime}, \Phi\right)$. If $\mathscr{A}$ is the set $\mathscr{A}_{b}$ of all bounded subsets of $\Phi$, the topology defined on $\Phi^{\prime}$ is called the strong dual topology $\beta\left(\Phi^{\prime}, \Phi\right)$. As $\mathscr{A}_{f} \subseteq \mathscr{A}_{b}$ it follows that $\sigma \subseteq \beta$, i.e. that the strong topology is essentially finer than the weak topology.

Definition 2.4 The dual space $\mathscr{C}^{\prime}$ of the space $\mathscr{C}$ is the topological vector space of all continuous, linear, complex valued functionals, $\varphi^{\prime}: \mathscr{C} \rightarrow \boldsymbol{C}^{1}$, defined on $\mathscr{C}$. This is the space of Radon measures on $\mathscr{C}$. The topologies on $\mathscr{C}^{\prime}$ are the weak dual topology $\sigma$ and the strong dual topology $\beta$.

An important element in the space $\mathscr{C}^{\prime}$ is the Dirac measure, the delta functional.

Definition 2.5 The continuous, linear mapping $\delta: \varphi \rightarrow \varphi\left(x_{0}\right)$ of $\mathscr{C}$ into $\boldsymbol{C}^{1}$ is the delta functional at the point $x_{0} \in \boldsymbol{R}^{1}$.

The weak topology $\sigma$ on the dual space $\Phi^{\prime}$ is the topology of pointwise convergence in $\Phi$. A sequence of functionals $\left\{\varphi_{\nu}^{\prime}\right\}, v=1,2,3, \ldots$, converges in the $\sigma$-topology to the limit $\varphi^{\prime}$ if and only if the sequence of complex numbers $\left\{\left\langle\varphi_{\nu}^{\prime}, \varphi\right\rangle\right\}$ converges to the complex number $\left\langle\varphi^{\prime}, \varphi\right\rangle$ for every $\varphi \in \Phi$.

The strong topology $\beta$ on the dual space $\Phi^{\prime}$ is the topology of uniform convergence on every bounded subset of the space $\Phi$. A sequence of functionals $\left\{\varphi_{\nu}^{\prime}\right\}, \nu=1,2,3, \ldots$, converges in the $\beta$-topology to the limit $\varphi^{\prime}$ if and only if the sequence of complex numbers $\left\{\left\langle\varphi_{\nu}^{\prime}, \varphi\right\rangle\right\}$ converges to the complex number $\left\langle\varphi^{\prime}, \varphi\right\rangle$ uniformly on every bounded subset of $\Phi$.

If a sequence of functionals converges in the strong $\beta$-topology then it also converges in the weak $\sigma$-topology.

Definition 2.6 The dual space $\mathscr{D}^{\prime}$ of the space $\mathscr{D}$ is the topological vector space of all continuous, linear, complex valued functionals, $\varphi^{\prime}: \mathscr{D} \rightarrow \boldsymbol{C}^{1}$, defined on $\mathscr{D}$. This is the space of distributions on $\mathscr{D}$. The topologies on $\mathscr{D}^{\prime}$ are the weak dual topology $\sigma$ of pointwise convergence in $\mathscr{D}$ and the strong dual topology $\beta$ of uniform convergence on every bounded subset of $\mathscr{D}$.

Definition 2.7 The dual space $\mathscr{S}^{\prime}$ of the space $\mathscr{S}$ is the topological vector space of all continuous, linear, complex valued functionals, $\varphi^{\prime}: \mathscr{S} \rightarrow \boldsymbol{C}^{1}$, defined on $\mathscr{S}$. This is the space of tempered distributions on $\mathscr{S}$. The topologies on $\mathscr{S}^{\prime}$ are the weak dual topology $\sigma$ of pointwise convergence in $\mathscr{S}$ and the strong dual topology $\beta$ of uniform convergence on every bounded subset of $\mathscr{S}$.

If $\Omega$ is an open subset of $\boldsymbol{R}^{1}$ and $d x$ is the Lebesgue measure then $\mathscr{L}^{p}(\Omega)$ with $p \in \boldsymbol{R}^{1}, 1 \leqq p<\infty$, denotes the set of all measurable, complex valued functions on $\boldsymbol{R}^{1}, f: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, where $\int_{\Omega}|f(x)|^{p} d x<\infty$. In particular $\mathscr{L}^{1}(\Omega)$ is the space of all functions which are locally integrable in $\Omega$.

From this the topological vector space $L^{p}$ is defined as the quotient space $L^{p}(\Omega)=\mathscr{L}^{p}(\Omega) /\left\{\left.f \in \mathscr{L}^{p}(\Omega)\left|\int_{\Omega}\right| f(x)\right|^{p} d x=0\right\}$ of equivalence classes of functions which are equivalent modulo the relation " $f=g$ except on a set of measure zero". The topology on $L^{p}$ is determined by defining the norm $\|f\|_{L} p=\left(\int_{\Omega}|f(x)|^{p} d x\right)^{1 / p}$.

The set of all continuous, linear mappings $\varphi^{\prime}$ of $L^{p}(\Omega)$ into $\boldsymbol{C}^{1}$, $\varphi^{\prime}: L^{p}(\Omega) \rightarrow \boldsymbol{C}^{1}\left(p \in \boldsymbol{R}^{1}, \quad 1 \leqq p<\infty\right)$, constitutes the topological vector space $\left(L^{p}(\Omega)\right)^{\prime}(1 \leqq p<\infty)$ dual to $L^{p}(\Omega)$. The topologies on $\left(L^{p}\right)^{\prime}$ are the weak dual topology $\sigma$ of pointwise convergence in $L^{p}$ and the strong dual topology $\beta$ of uniform convergence on every bounded subset of the space $L^{p}(\Omega)$.

If $E$ and $F$ are two topological vector spaces, a natural injection of $E$ into $F$ with a dense image is a continuous, linear mapping, $j: E \rightarrow F$, such that $j(E)$ is dense in $F$. In diagram 2.1

(diagram 2.1)
the arrows indicate possible natural injections with dense images.
From all the images being dense it follows by application of the HahnBanach theorem that all the transpose mappings, $j^{\prime}: F^{\prime} \rightarrow E^{\prime}$, in diagram 2.2 are injective,

(diagram 2.2)

Furthermore, if the two dual spaces $E^{\prime}$ and $F^{\prime}$ both carry the weak dual topology $\sigma$, or both carry the strong dual topology $\beta$, then the transpose mapping, $j^{\prime}: F^{\prime} \rightarrow E^{\prime}$, is continuous. This result may be applied to diagram 2.2. Accordingly, all of the spaces in the diagram may be considered as subspaces of the space of distributions $\mathscr{D}^{\prime}(\Omega)$, i.e. all are spaces of distributions. The spaces are all dense in $\mathscr{D}^{\prime}(\Omega)$.

Again, let $\Omega$ be an open subset of $\boldsymbol{R}^{1}$ and let $p \in \boldsymbol{R}^{1}, 1 \leqq p<\infty$. Define $p^{\prime}=\frac{p}{p-1}$ for $p>1$, and $p^{\prime}=\infty$ for $p=1$. Let the space $L^{p^{\prime}}(\Omega)$ carry the norm topology defined above, and let the space $\left(L^{p}(\Omega)\right)^{\prime}$ carry the weak dual topology $\sigma$ or the strong dual topology $\beta$. If a bilinear form on $L^{p}(\Omega) \times$ $L^{p^{\prime}}(\Omega)$ is defined by

$$
\begin{equation*}
(f, g) \rightarrow\langle f, g\rangle=\int_{\Omega} \overline{f(x)} g(x) d x, \tag{2.1}
\end{equation*}
$$

where the bar denotes complex conjugation, then it is an important result from the theory of duality between topological vector spaces that an isomorphism exists between the spaces $L^{p^{\prime}}(\Omega)$ and $\left(L^{p}(\Omega)\right)^{\prime}$, i.e. then a linear mapping exists, $i: L^{p^{\prime}}(\Omega) \rightarrow\left(L^{p}(\Omega)\right)^{\prime}$, which is bicontinuous and bijective. From this it follows that the spaces $\mathscr{D}(\Omega), \mathscr{S}(\Omega), \mathscr{C}(\Omega)$, and $L^{p}(\Omega)(1<$ $p<\infty$ ) may all be considered as subspaces of the space of distributions $\mathscr{D}^{\prime}(\Omega)$, i.e. their elements may be considered as distributions. The spaces of diagram 2.1 are all dense in the space $\mathscr{D}^{\prime}(\Omega)$.

Furthermore, the restriction of the continuous, linear form, $L^{1}(\Omega) \rightarrow \boldsymbol{C}^{1}$, defined by

$$
\begin{equation*}
\varphi \rightarrow \int_{\Omega} \overline{f(x)} \varphi(x) d x, \quad f \in L^{1}(\Omega) \tag{2.2}
\end{equation*}
$$

to the space $\mathscr{D}(\Omega)$ defines $f$ as a distribution in $\mathscr{D}^{\prime}(\Omega)$. As finally $\mathscr{D}(\Omega)$ is dense in $L^{1}(\Omega)$ it follows that if $f_{1}$ and $f_{2}$ are different as elements of $L^{1}(\Omega)$ then they will also be different when considered as elements of $\mathscr{D}^{\prime}(\Omega)$, i.e. as distributions.

Theorem 2.3 Let $\Omega$ be an open, non-void subset of $\boldsymbol{R}^{1}, \Omega \subseteq \boldsymbol{R}^{1}$. Let $p, p^{\prime} \in \boldsymbol{R}^{1}$ such that $\frac{1}{p}+\frac{1}{p^{\prime}}=1$ and $1 \leqq p, p^{\prime} \leqq \infty$. Let $f \in L^{p^{\prime}}(\Omega)$ and $\varphi \in L^{p}(\Omega)$. Define a mapping by

$$
f \rightarrow\left(\varphi \rightarrow\langle f, \varphi\rangle=\int_{\Omega} \overline{f(x)} \varphi(x) d x\right) .
$$

Then, (i) for $1 \leqq p<\infty$ and $1<p^{\prime} \leqq \infty$ the mapping is a bijective isometry of $L^{p^{\prime}}(\Omega)$ onto $\left(L^{p}(\Omega)\right)^{\prime}$,
and (ii) for $p=\infty$ and $p^{\prime}=1$ the mapping is an injective isometry of $L^{1}(\Omega)$ into $\left(L^{\infty}(\Omega)\right)^{\prime}$.

If a function $f$ in $L^{1}(\Omega)$ exists, $f \in L^{1}(\Omega)$, such that the continuous, linear form (2.2) defines a distribution $T_{f}$ in $\mathscr{D}^{\prime}(\Omega), T_{f} \in \mathscr{D}^{\prime}(\Omega)$, which by theorem 2.3 may be identified with the function, $f=T_{f}$, then the distribution $T_{f}$ is called regular. If a distribution $T, T \in \mathscr{D}^{\prime}(\Omega)$, is not regular, it is called singular.

The space $\mathscr{D}^{\prime}(\Omega)$ possesses a linear vector space structure, such that addition of two distributions $f_{1}$ and $f_{2}$ in $\mathscr{D}^{\prime}(\Omega)$ is defined by

$$
\begin{equation*}
\left\langle f_{1}+f_{2}, \varphi\right\rangle=\left\langle f_{1}, \varphi\right\rangle+\left\langle f_{2}, \varphi\right\rangle, \quad \varphi \in \mathscr{D}(\Omega), \tag{2.3}
\end{equation*}
$$

and multiplication of a distribution $f$ in $\mathscr{D}^{\prime}(\Omega)$ by a complex number $\lambda$ is defined by

$$
\begin{equation*}
\langle f \lambda, \varphi\rangle=\bar{\lambda}\langle f, \varphi\rangle, \quad \varphi \in \mathscr{D}(\Omega), \tag{2.4}
\end{equation*}
$$

where the bar denotes complex conjugation.
Multiplication as a bilinear, associative operation on two distributions $f_{1}$ and $f_{2}$ from a distribution space and coinciding with the multiplication of two elements of $L^{1}(\Omega)$ (i.e. two locally integrable functions) in the case of $f_{1}$ and $f_{2}$ being regular distributions cannot be defined for arbitrary $f_{1}$ and $f_{2} .{ }^{3}$

However, the multiplication defined by

$$
\begin{equation*}
\varphi \rightarrow \alpha \varphi, \quad \alpha \in \mathscr{C}^{\infty}(\Omega), \tag{2.5}
\end{equation*}
$$

where $\Omega$ is an open subset of $\boldsymbol{R}^{1}$, is a continuous, linear mapping of $\mathscr{D}(\Omega)$ into itself, $\mathscr{D}(\Omega) \rightarrow \mathscr{D}(\Omega)$. Hence the transpose mapping is a continuous, linear mapping of $\mathscr{D}^{\prime}(\Omega)$ into itself, $\mathscr{D}^{\prime}(\Omega) \rightarrow \mathscr{D}^{\prime}(\Omega)$, and this transpose mapping is adopted as the definition of multiplication of a distribution in $\mathscr{D}^{\prime}(\Omega)$ by the function $\alpha, \alpha \in \mathscr{C}^{\infty}(\Omega)$.

Definition 2.6 If $\Omega$ is an open subset of $\boldsymbol{R}^{1}, \alpha$ is a function in $\mathscr{C}^{\infty}(\Omega)$, $\alpha \in \mathscr{C}^{\infty}(\Omega)$, and $T$ is a distribution in $\mathscr{D}^{\prime}(\Omega)$, then multiplication of the distribution $T$ with the multiplier $\alpha$ gives the distribution $\alpha T$ defined by $\langle\alpha T, \varphi\rangle=$ $\langle T, \bar{\alpha} \varphi\rangle$.
${ }^{3}$ ) This is a result due to Schwartz. See ref. (14).

The sets of multipliers in the test function spaces possess linear vector space structures.

Theorem 2.4 Multipliers in the space $\mathscr{D}(\Omega)$ are all infinitely differentiable functions of arbitrary support. Multipliers in the space $\mathscr{S}(\Omega)$ are all infinitely differentiable functions $s$ of slow increase, i.e. for which $\left|s^{(k)}(x)\right|=O\left(|x|^{l}\right)$, where $k$ and $l$ are integers, $k, l \geqq 0$.

The operation of differentiation of distributions may be defined in an analogous way.

Let $f$ be a function, $f: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, which is differentiable $n$ times, $n=$ $0,1,2,3, \ldots$, with continuous derivatives in the open subset $\Omega$ of $\boldsymbol{R}^{1}$, $f \in \mathscr{C}^{n}(\Omega)$. Hence $f$ is also locally integrable, $f \in L^{1}(\Omega)$, and, as has been expounded above, if $\varphi$ is a test function in $\mathscr{D}(\Omega)$ then the continuous, linear mapping

$$
\begin{equation*}
\varphi \rightarrow \int_{\Omega} \overline{f(x)} \varphi(x) d x, \quad x \in \boldsymbol{R}^{1}, \tag{2.6}
\end{equation*}
$$

defines in $\mathscr{D}^{\prime}(\Omega)$ a distribution which may be identified with the function $f$.
Suppose a homeomorphic mapping of $\mathscr{D}^{\prime}(\Omega)$ into $\mathscr{D}^{\prime}(\Omega)$ is defined by the formula

$$
\begin{equation*}
D^{n}: f \rightarrow D^{n} f, \quad n=0,1,2,3, \ldots, \tag{2.7}
\end{equation*}
$$

$D^{n}$ denoting the $n^{\prime}$ th order derivative of $f$ in the function sense. Then, as $\int_{\Omega} f^{(n)}(x) \varphi(x) d x=(-1)^{n} \int_{\Omega} f(x) \varphi^{(n)}(x) d x$, it is seen that $\left\langle D^{n} f, \varphi\right\rangle=$ $(-1)^{n}\left\langle f, D^{n} \varphi\right\rangle$. This leads to the following definition.

Definition 2.8 If $\Omega$ is an open subset of $\boldsymbol{R}^{1}, n$ is an integer, $n=0,1,2,3$, $\ldots$... and $T$ is a distribution in $\mathscr{D}^{\prime}(\Omega)$, then the distribution $D^{n} T$ is defined $b y\left\langle D^{n} T, \varphi\right\rangle=(-1)^{n}\left\langle T, D^{n} \varphi\right\rangle$.

Notice that $D^{n}$ is the transpose of $(-1)^{n} D^{n}$.
Subsequently the concept of the support of a distribution $T, \operatorname{supp} T$, will be of importance.

Again, $\Omega$ is an open subset of $\boldsymbol{R}^{1}$.
Definition 2.9 A distribution $T$ in the space $\mathscr{D}^{\prime}(\Omega)$ is said to vanish in an open subset $U$ of $\Omega$ if $\langle T, \varphi\rangle=0$ for all test functions $\varphi \in \mathscr{D}(\Omega)$ with $\operatorname{supp} \varphi \subseteq U$.

Definition 2.10 The support of a distribution $T$ in $\mathscr{D}^{\prime}(\Omega)$ is denoted by supp $T$ and defined as the complement of the largest open subset of $\Omega$ in which $T$ vanishes.

The subspace of $\mathscr{D}^{\prime}(\Omega)$ which consists of all distributions with support on the non-negative real axis $\boldsymbol{R}_{+}^{1}=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0 \leqq \sigma<\infty\right\}$ is denoted by $\mathscr{D}_{+}^{\prime} \subset \mathscr{D}^{\prime}(\Omega)$.

If $\lambda$ is a complex number, $\lambda \in \boldsymbol{C}^{1}$, such that $\operatorname{Re} \lambda>-1$, if $x$ is real, $x \in \boldsymbol{R}^{1}$, and if $\varphi$ is a test function in $\mathscr{D}(\Omega), \varphi \in \mathscr{D}(\Omega)$, then the product function $x^{\lambda} \varphi$ is locally integrable, $x^{\lambda} \varphi \in L^{1}$, and the continuous, linear mapping

$$
\begin{equation*}
\varphi \rightarrow\left\langle x_{+}^{\lambda}, \varphi\right\rangle=\int_{0}^{\infty} \overline{x^{\lambda}} \varphi(x) d x \tag{2.8}
\end{equation*}
$$

defines the regular distribution $x_{+}^{\lambda} \in \mathscr{D}_{+}$.
For $\operatorname{Re} \lambda \leqq-1$ the limit $\lim \int_{\varepsilon}^{\infty} x^{\lambda} \varphi(x) d x$ does not exist, i.e. $x^{\lambda} \varphi \notin L^{1}$, and therefore the integral may not be used to define a distribution $x_{+}^{\lambda}$. If, however, a sufficient number of terms are subtracted from the MacLaurin expansion of the test function the integral is rendered convergent. Thus, if $-n<\operatorname{Re} \lambda<-(n-1)$, where $n$ is a positive integer, $n=1,2,3, \ldots$, then the integral

$$
\begin{equation*}
\left\langle P f x_{+}^{\lambda}, \varphi\right\rangle=\int_{0}^{\infty} \overline{x^{\lambda}}\left[\varphi(x)-\sum_{\mu=0}^{n-2} \frac{x^{\mu} \varphi^{(\mu)}(0)}{\mu!}\right] d x \tag{2.9}
\end{equation*}
$$

converges and is used to define the singular distribution Pf $x_{+}^{\lambda} \in \mathscr{D}_{+}^{\prime} \subset \mathscr{D}^{\prime}(\Omega)$. Distributions of this type are termed pseudofunctions and are characterised by the prefix $P f$. This procedure of extracting a finite part from a divergent integral by subtracting the terms which cause the integral to diverge was first introduced by $\mathrm{Hadamard}^{4}$, and the result is called the finite part, Fin. P., of the integral.

For $-n<\operatorname{Re} \lambda<-(n-1)$, where $n$ is a positive integer, $n=1,2,3, \ldots$, the singular distribution $\operatorname{Pf} x_{+}^{\lambda}$ is defined by

$$
\begin{align*}
\left\langle P f x_{+}^{\lambda}, \varphi\right\rangle & =\text { Fin. } P \cdot \int_{0}^{\infty} \overline{x^{\lambda}} \varphi(x) d x \\
& \left.=\int_{0}^{\infty} \overline{x^{\lambda}} \left\lvert\, \varphi(x)-\sum_{\mu=0}^{n-2} \frac{x^{\mu} \varphi^{(\mu)}(0)}{\mu!}\right.\right] d x  \tag{2.10}\\
& =\lim _{\varepsilon \rightarrow 0+}\left\{\int_{\varepsilon}^{\infty} \overline{x^{\lambda}} \varphi(x) d x+\sum_{\mu=0}^{n-2} \frac{\varepsilon^{\lambda+\mu+1} \varphi^{(\mu)}(0)}{\mu!(\lambda+\mu+1)}\right\}
\end{align*}
$$

where $\varphi \in \mathscr{D}(\Omega)$.
For $-1<\operatorname{Re} \lambda$ the continuous, linear mapping
${ }^{4}$ ) See ref. (7).

$$
\begin{equation*}
\varphi \rightarrow\left\langle P f x_{+}^{\lambda}, \varphi\right\rangle=\text { Fin. P. } \int_{0}^{\infty} \overline{x^{\lambda}} \varphi(x) d x \tag{2.11}
\end{equation*}
$$

may still be used for defining the pseudofunction Pf $x_{+}^{\lambda}$, but no subtraction in the MacLaurin series is required, so that the distribution defined becomes regular and the notions of Fin. $P$. and $P f$ superfluous,

$$
\begin{equation*}
\left\langle x_{+}^{\lambda}, \varphi\right\rangle=\int_{0}^{\infty} \overline{x^{\lambda}} \varphi(x) d x . \tag{2.12}
\end{equation*}
$$

For $\operatorname{Re} \lambda=-n$ and $\lambda \neq n$, where $n$ is a positive integer, $n=1,2,3, \ldots$, the singular distribution $P f x_{+}^{\lambda}$ is defined by analytic continuation in the complex $\lambda$-plane from $-n<\operatorname{Re} \lambda<-(n-1)$. As for $\operatorname{Re} \lambda=-n$ the integral $\int_{\varepsilon}^{\infty} x^{\lambda} x^{n-1} \varphi(x) d x$ diverges as $\varepsilon \rightarrow 0+$, one more term must be included in the series to be subtracted in the integrand in order to obtain the finite part of the integral, Fin. P. $\int_{0}^{\infty} \overline{x^{\lambda}} \varphi(x) d x$.

Thus, for $\operatorname{Re} \lambda=-n$ and $\lambda \neq-n$, where $n$ is a positive integer, $n=$ $1,2,3, \ldots$, the singular distribution $P f x_{+}^{\lambda}$ is defined by

$$
\begin{align*}
& \left\langle P f x_{+}^{\lambda}, \varphi\right\rangle=\text { Fin. P. } \int_{0}^{\infty} \overline{x^{\lambda}} \varphi(x) d x \\
& \quad=\int_{0}^{\infty} \overline{x^{\lambda}}\left[\varphi(x)-\sum_{\mu=0}^{n-2} \frac{x^{\mu} \varphi^{(\mu)}(0)}{\mu!}-\frac{x^{n-1} \varphi^{(n-1)}(0)}{(n-1)!}\right] d x  \tag{2.13}\\
& \quad=\lim _{\varepsilon \rightarrow 0+}\left\{\int_{\varepsilon}^{\infty} \overline{x^{\lambda}} \varphi(x) d x+\sum_{\mu=0}^{n-2} \frac{\varepsilon^{\mu+\lambda+1} \varphi^{(\mu)}(0)}{\mu!(\mu+\lambda+1)}+\frac{\varepsilon^{n+\lambda} \varphi^{(n-1)}(0)}{(n-1)!(n+\lambda)}\right\},
\end{align*}
$$

where $\varphi \in \mathscr{D}(\Omega)$.
For $\lambda=-1,-2,-3, \ldots$ the above definitions of $P f x_{+}^{\lambda \mid}$ do not apply, essentially because in these cases the defining integrals diverge. Considered as functions of $\lambda \in \boldsymbol{C}^{1}$ the integrals have poles at $\lambda=-1,-2,-3, \ldots$. As $\varphi$ is in $\mathscr{D}(\Omega), \varphi \in \mathscr{D}(\Omega)$, an integration by parts shows that whereas the integral

$$
\begin{equation*}
\int_{\varepsilon}^{\infty} \frac{1}{x} \varphi(x) d x=-\ln \varepsilon \varphi(0)-\int_{\varepsilon}^{\infty} \ln x \varphi^{\prime}(x) d x-o(1) \tag{2.14}
\end{equation*}
$$

diverges as $\varepsilon \rightarrow 0+$ because of the term $-\ln \varepsilon \varphi(0)$, the integral
converges as $\varepsilon \rightarrow 0+$.

This leads to defining the singular distribution $\operatorname{Pf}\left(\frac{1}{x}\right)_{+}$corresponding to the case $\lambda=-1$ by

$$
\begin{align*}
\left\langle P f\left(\frac{1}{x}\right)_{+}, \varphi\right\rangle & =\int_{0}^{\infty} \frac{1}{x}\left[\varphi(x)-\varphi(0) u_{0}(1-x)\right] d x \\
& =\lim _{\varepsilon \rightarrow 0+}\left\{\int_{\varepsilon}^{\infty} \frac{1}{x} \varphi(x) d x+\ln \varepsilon \varphi(0)\right\} . \tag{2.16}
\end{align*}
$$

It is of importance to consider such effects on a distribution which stem from a change of independent variable in a test function.

Let $f$ be a function, $f: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, which is locally integrable in an open subset $\Omega$ of $\boldsymbol{R}^{1}, f \in L^{1}(\Omega)$. As has been expounded above, if $\varphi$ is a test function in $\mathscr{D}(\Omega)$ then the continuous, linear mapping

$$
\begin{equation*}
\varphi \rightarrow \int_{\Omega} \overline{f(x)} \varphi(x) d x, \quad x \in \boldsymbol{R}^{1}, \tag{2.17}
\end{equation*}
$$

defines in $\mathscr{D}^{\prime}(\Omega)$ a distribution which may be identified with the function $f$.
Suppose a homeomorphic mapping of $\mathscr{D}^{\prime}(\Omega)$ into $\mathscr{D}^{\prime}(\Omega)$ is defined by the formula

$$
\begin{equation*}
\tau_{a}: f(x) \rightarrow \tau_{a} f(x)=f(x-a), \quad a, x \in \boldsymbol{R}^{1} \tag{2.18}
\end{equation*}
$$

Then, as $\int_{\Omega} \overline{f(x-a)} \varphi(x) d x=\int_{\Omega} \overline{f(x)} \varphi(x+a) d x$, it is seen that $\left\langle\tau_{a} f, \varphi\right\rangle=$ $\left\langle f, \tau_{-a} \varphi\right\rangle$. This leads to the following definition.

Definition 2.11 If $\Omega$ is an open subset of $\boldsymbol{R}^{1}$, a is a real number, $a \in \boldsymbol{R}^{1}$, and $T$ is a distribution in $\mathscr{D}^{\prime}(\Omega)$, then the distribution $\tau_{a} T$ is defined by $\left\langle\tau_{a} T, \varphi\right\rangle=\left\langle T, \tau_{-a} \varphi\right\rangle$.

Notice that $\tau_{a}$ is the transpose of $\tau_{-a}$.
Likewise, let a homeomorphic mapping of $\mathscr{D}^{\prime}(\Omega)$ into $\mathscr{D}^{\prime}(\Omega)$ be defined by the formula

$$
\begin{equation*}
\chi_{a}: f(x) \rightarrow \chi_{a} f(x)=f(a x), \quad a, x \in \boldsymbol{R}^{1} \tag{2.19}
\end{equation*}
$$

Then, as $\int_{\Omega} \overline{f(a x)} \varphi(x) d x=\frac{1}{|a|} \int_{\Omega} \overline{f(x)} \varphi\left(\frac{x}{a}\right) d x$, it is seen that $\left\langle\chi_{a} f, \varphi\right\rangle=$ $\frac{1}{|a|}\left\langle f, \chi_{a^{-1}} \varphi\right\rangle$. This motivates the following definition.

Definition 2.12 If $\Omega$ is an open subset of $\boldsymbol{R}^{1}$, a is a real number, $a \in \boldsymbol{R}^{1}$, and $T$ is a distribution in $\mathscr{D}^{\prime}(\Omega)$, then the distribution $\chi_{a} T$ is defined by $\left\langle\chi_{a} T, \varphi\right\rangle=\frac{1}{|a|}\left\langle T, \chi_{a}-1 \varphi\right\rangle$.

Notice that $\chi_{a}$ is the transpose of $\frac{1}{|a|} \chi_{a^{-1}}$.
A linear change of scale, $x \rightarrow \alpha x, \alpha, x \in \boldsymbol{R}^{1}$, in the distribution $\operatorname{Pf}\left(\frac{1}{x}\right)_{+}$ defined in (2.16) shows that

$$
\begin{align*}
\left\langle P f\left(\frac{\alpha}{x}\right)_{+}, \varphi\right\rangle & =\int_{0}^{\infty} \frac{\alpha}{x}\left[\varphi(x)-\varphi(0) u_{0}\left(1-\frac{x}{\alpha}\right)\right] d x  \tag{2.20}\\
& =\lim _{\varepsilon \rightarrow 0+}\left\{\alpha \int_{\varepsilon}^{\infty} \frac{1}{x} \varphi(x) d x+\alpha \varphi(0) \ln \left(\frac{\varepsilon}{\alpha}\right)\right\},
\end{align*}
$$

i.e. that

$$
\begin{equation*}
\left\langle P f\left(\frac{\alpha}{x}\right)_{+}, \varphi\right\rangle=\left\langle\alpha P f\left(\frac{1}{x}\right)_{+}-\alpha \ln \alpha \delta, \varphi\right\rangle \tag{2.21}
\end{equation*}
$$

In the light of this property it is now possible to define ${ }^{5)}$ the distribution $\operatorname{Pf} x_{+}^{\lambda}$ also in the case when $\lambda$ is a negative integer.

Definition 2.13 Let $n$ be a positive integer, $n=1,2,3, \ldots,{ }^{6}$ ) let $\lambda$ be a complex number, $\lambda \in \boldsymbol{C}^{1}$, and let $\varphi$ be a test function in $\mathscr{D}, \varphi \in \mathscr{D}$.

For $-n<\operatorname{Re} \lambda<-(n-1)$ the distribution Pf $x_{+}^{\lambda} \in \mathscr{D}_{+}^{\prime}$ is defined by
$\left\langle P f X_{+}^{\lambda}, \varphi\right\rangle$
$=$ Fin. $P \cdot \int_{0}^{\infty} \overline{x^{\lambda}} \varphi(x) d x$

$$
\begin{aligned}
& =\int_{0}^{\infty} \overline{x^{\lambda}}\left[\varphi(x)-\sum_{\mu=0}^{n-2} \frac{x^{\mu} \varphi^{(\mu)}(0)}{\mu!}\right] d x \\
& =\lim _{\varepsilon \rightarrow 0+}\left\{\int_{\varepsilon}^{\infty} \overline{x^{\lambda}} \varphi(x) d x+\sum_{\mu=0}^{n-2} \frac{\varepsilon^{\lambda+\mu+1} \varphi^{(\mu)}(0)}{\mu!(\lambda+\mu+1)}\right\} .
\end{aligned}
$$

For $\operatorname{Re} \lambda=-n, \lambda \neq-n$, the distribution $\operatorname{Pf} x_{+}^{\lambda} \in \mathscr{D}_{+}^{\prime}$ is defined by

$$
\begin{aligned}
& \left\langle P f x_{+}^{\lambda}, \varphi\right\rangle \\
& =\text { Fin. P. } \int_{0}^{\infty} \overline{x^{\lambda}} \varphi(x) d x \\
& =\int_{0}^{\infty} \overline{x^{\lambda}}\left[\varphi(x)-\sum_{\mu=0}^{n-2} \frac{x^{\mu} \varphi^{(\mu)}(0)}{\mu!}-\frac{x^{n-1} \varphi^{(n-1)}(0)}{(n-1)!}\right] d x \\
& =\lim _{\varepsilon \rightarrow 0+}\left\{\int_{0}^{\infty} \overline{x^{\lambda}} \varphi(x) d x+\sum_{\mu=0}^{n-2} \frac{\varepsilon^{\mu+\lambda+1} \varphi^{(\mu)}(0)}{\mu!(\mu+\lambda+1)}+\frac{\varepsilon^{n+\lambda} \varphi^{(n-1)}(0)}{(n-1)!(n+\lambda)}\right\} .
\end{aligned}
$$

${ }^{5}$ ) The last part of the definition is due to Güttinger. See ref. (6).
${ }^{6}$ ) For $n=1$ see eq.s (2.11) and (2.12) and accompanying text.

For $\lambda=-n$ the distribution Pf $x_{+}^{\lambda} \in \mathscr{D}_{+}^{\prime}$ is defined by

$$
\begin{aligned}
& \left\langle P f x_{+}^{\lambda}, \varphi\right\rangle \\
& =\text { Fin. P. } \int_{0}^{\infty} x^{-n} \varphi(x) d x \\
& =\int_{0}^{\infty} x^{-n}\left[\varphi(x)-\sum_{\mu=0}^{n-2} \frac{x^{\mu} \varphi^{(\mu)}(0)}{\mu!}-u_{0}\left(1-\frac{x}{\alpha}\right) \frac{x^{n-1} \varphi^{(n-1)}(0)}{(n-1)!}\right] d x \\
& =\lim _{\varepsilon \rightarrow 0+}\left\{\int_{\varepsilon}^{\infty} x^{-n} \varphi(x) d x+\sum_{\mu=0}^{n-2} \frac{\varepsilon^{\mu-n+1} \varphi^{(\mu)}(0)}{\mu!(\mu-n+1)}+\frac{\ln (\varepsilon / \alpha) \varphi^{(n-1)}(0)}{(n-1)!}\right\},
\end{aligned}
$$

where $\alpha \in \boldsymbol{R}^{1}$.
Considered as a function of the complex variable $\lambda, \lambda \in \boldsymbol{C}^{1}$, the integral $F(\lambda)=\left\langle P f x_{+}^{\lambda}, \varphi\right\rangle$ is a complex valued function which is holomorphic everywhere in the finite $\lambda$-plane except at the isolated points $\lambda=-1,-2$, $-3, \ldots$ which constitute a set of simple poles. The function $F$ thus is meromorphic.

The residue at $\lambda=-n$, where $n$ is a positive integer, $n=1,2,3, \ldots$, is found to be

$$
\begin{align*}
& \operatorname{Res} F(\lambda) \\
&= \lim _{\lambda \rightarrow-n+}(\lambda+n) \int_{0}^{\infty} \overline{x^{\lambda}}\left[\varphi(x)-\sum_{\mu=0}^{n-2} \frac{x^{\mu} \varphi^{(\mu)}(0)}{\mu!}\right] d x \\
&= \lim _{\lambda \rightarrow-n+}(\lambda+n)\left\{\left[\frac{x^{\lambda+1}}{\lambda+1}\left(\varphi(x)-\sum_{\mu=0}^{n-2} \frac{x^{\mu} \varphi^{(\mu)}(0)}{\mu!}\right)\right]_{0}^{\infty}\right. \\
& \quad-\left[\frac{x^{\lambda+2}}{(\lambda+1)(\lambda+2)}\left(\varphi^{\prime}(x)-\sum_{\mu=0}^{n-3} \frac{x^{\mu} \varphi^{(\mu+1)}(0)}{\mu!}\right)\right]_{0}^{\infty} \\
&+\cdots \\
&+(-1)^{n-2}\left[\frac{x^{\lambda+n-1}}{(\lambda+1)(\lambda+2) \cdots(\lambda+n-1)}\left(\varphi^{(n-2)}(x)-\varphi^{(n-2)}(0)\right)\right]_{0}^{\infty}  \tag{2.22}\\
&+(-1)^{n-1}\left[\frac{x^{\lambda+n}}{(\lambda+1)(\lambda+2) \cdots(\lambda+n)} \varphi^{(n-1)}(x)\right]_{0}^{\infty} \\
&\left.+(-1)^{n} \int_{0}^{\infty} \frac{x^{\lambda+n}}{(\lambda+1)(\lambda+2) \cdots(\lambda+n)} \varphi^{(n)}(x) d x\right\}
\end{align*}
$$

$$
\begin{align*}
& =\frac{-1}{(n-1)!} \int_{0}^{\infty} \varphi^{(n)}(x) d x  \tag{2.22}\\
& =\frac{1}{(n-1)!} \varphi^{(n-1)}(0) \\
& =\frac{(-1)^{n-1}}{(n-1)!}\langle\delta(n-1), \varphi\rangle .
\end{align*}
$$

The $\Gamma$-function as a function of the complex variable $\lambda+1, \lambda+1 \in \boldsymbol{C}^{1}$, is meromorphic with isolated, simple poles on the negative, real axis just like the function $F: \lambda \rightarrow\left\langle P f x_{+}^{\lambda}, \varphi\right\rangle$ studied above. For the $\Gamma$-function the poles of $\Gamma(\lambda+1)$ are situated at $\lambda=-n$, where $n$ is a positive integer, $n=1,2,3, \ldots$, and the residues are

$$
\begin{equation*}
\operatorname{Res}_{\lambda=-n} \Gamma(\lambda+1)=\frac{(-1)^{n-1}}{(n-1)!} \tag{2.23}
\end{equation*}
$$

For every $\lambda \in \boldsymbol{C}^{1}, \Gamma(\lambda+1) \neq 0$.
The Riesz distributions, ${ }^{7}$ ) first introduced by M. Riesz, are defined from the distributions $\operatorname{Pf} x_{+}^{\lambda}$.

Definition 2.14 Let $x \in \boldsymbol{R}^{1}, \lambda \in \boldsymbol{C}^{1}$, and let $\Gamma$ denote the $\Gamma$-function. The Riesz distribution $R_{+}^{\lambda} \in \mathscr{D}_{+}^{\prime}$ is defined as the distribution $R_{+}^{\lambda}=\operatorname{Pf} \frac{x_{+}^{\lambda}}{\Gamma(\lambda+1)}$.

Because of the properties of the functions $F(\lambda)=\left\langle P f x_{+}^{\lambda}, \varphi\right\rangle$ and $\Gamma(\lambda+1)$, the integral of the Riesz distribution $\left\langle P f \frac{x_{+}^{\lambda}}{\Gamma(\lambda+1)}, \varphi\right\rangle=\frac{F(\lambda)}{\Gamma(\lambda+1)}$ considered as a function of $\lambda \in \boldsymbol{C}^{1}$ is holomorphic in the finite $\lambda$-plane, i.e. $\frac{F(\lambda)}{\Gamma(\lambda+1)}$ is an entire function of $\lambda \in \boldsymbol{C}^{1}$. In particular, the value of the function $\frac{F(\lambda)}{\Gamma(\lambda+1)}$ at the points where $F(\lambda)$ and $\Gamma(\lambda+1)$ both have poles may be determined as the quotient of the residues. Therefore

$$
\begin{align*}
\left\langle R_{+}^{-n}, \varphi\right\rangle & =\lim _{\lambda \rightarrow-n}\left\langle P f \frac{x_{+}^{\lambda}}{\Gamma(\lambda+1)}, \varphi\right\rangle \\
& =\lim _{\lambda \rightarrow-n} \frac{F(\lambda)}{\Gamma(\lambda+1)} \tag{2.24}
\end{align*}
$$

${ }^{7}$ ) See ref.s (5), (6), (12), and (14).

$$
\begin{align*}
& \operatorname{Res}_{\lambda=-n} F(\lambda)  \tag{2.24}\\
= & \frac{(-1)^{n-1}}{\lambda=-n} \Gamma(\lambda+1) \\
= & \frac{(-1)^{n-1}}{(n-1)!} \varphi^{(n-1)}(0) \\
= & \varphi^{(n-1)}(0) \\
= & \left\langle(-1)^{n-1} \delta^{(n-1)}, \varphi\right\rangle .
\end{align*}
$$

Hence the following result.
Theorem 2.5 For $\lambda=-n$, where $\lambda \in \boldsymbol{C}^{1}$, and $n$ is a positive integer, $n=1,2,3, \ldots$, the Riesz distribution $R_{+}^{\lambda}$ is

$$
R_{+}^{-n}=\lim _{\lambda \rightarrow-n} \operatorname{Pf} \frac{x_{+}^{\lambda}}{\Gamma(\lambda+1)}=(-1)^{n-1} \delta^{(n-1)}, \quad x \in \boldsymbol{R}^{1}
$$

In the particular case of $\lambda=-1$ the Riesz distribution is the delta distribution, $R_{+}^{-1}=\delta$.

## 3. Properties of the Transformation $T$

In the following a physical system will be characterised by describing the way it responds to some physical stimulus, i.e. by describing it as a transformation $T$ of an excitation $f$ from the domain of $T, f \in D(T)$, to a response $r$ in the range of $T, r \in R(T)$. As to the physical nature of $f$ and $r$ no description in more precise terms will be required. The test functions will be defined on $\boldsymbol{R}^{1}, \varphi: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, and though no physical interpretation of the independent variable will be needed the notation and terminology will agree with the case of the variable being real time. It will be assumed subsequently that $T$ is single valued, and therefore the transformation may be written as the mapping $T: f \rightarrow r$. In general both $D(T)$ and $R(T)$ will be considered as subsets of the space $\mathscr{D}^{\prime}(\Omega)$, where $\Omega$ is an open subset of $\boldsymbol{R}^{1}$, i.e. both $f$ and $r$ will be assumed to be distributions.

The transformation $T$ will be proposed to have the following six properties.
3. (i) Single valuedness. To each excitation, $f \in D(T)$, the transformation associates exactly one response, $r \in R(T)$,

$$
\begin{equation*}
T(f)=r \tag{3.1}
\end{equation*}
$$

3. (ii) Linearity. If $\alpha$ and $\beta$ are complex numbers, $\alpha, \beta \in \boldsymbol{C}^{1}$, and $f_{1}$ and $f_{2}$ are two excitations, $f_{1}, f_{2} \in D(T)$, then

$$
\begin{equation*}
T\left(\alpha f_{1}+\beta f_{2}\right)=\alpha T\left(f_{1}\right)+\beta T\left(f_{2}\right) \tag{3.2}
\end{equation*}
$$

3. (iii) Stationaryness. If $f$ is an excitation, $f \in D(T)$, and $\tau_{a}$ is the operator defined by definition 2.11 then the property of stationaryness of $T$ may be stated as $T\left(\tau_{a}(f)\right)=\tau_{a}(T(f))$, i.e. as the commutative property

$$
\begin{equation*}
T \circ \tau_{a}=\tau_{a} \circ T, \quad a \in \boldsymbol{R}^{1} \tag{3.3}
\end{equation*}
$$

3. (iv) Continuity. The topologies on $D(T)$ and on $R(T)$ are the topologies induced by the topology on $\mathscr{D}^{\prime}(\Omega)$. The transformation $T$ is continuous if and only if to each neighbourhood $V$ of $T(0)$ in $R(T)$ there corresponds a neighbourhood $U$ of 0 in $D(T)$ such that $T(U) \subseteq V$.

There is an important connection between the class of transformations which possess the four properties 3 . (i)-3. (iv) above and the class of transformations which may be represented by a convolution in $\mathscr{D}^{\prime}(\Omega)$.

If $t \in \boldsymbol{R}^{1}, \tau \in \boldsymbol{R}^{1}$, and $(t, \tau) \in \boldsymbol{R}^{2}$, let $\mathscr{D}_{t}, \mathscr{D}_{\tau}$, and $\mathscr{D}_{t, \tau}$ be the test function spaces $\mathscr{D}$ of all infinitely differentiable functions with compact support defined on $\boldsymbol{R}^{1}, \boldsymbol{R}^{1}$, and $\boldsymbol{R}^{2}$, respectively. Denote the corresponding dual spaces by $\mathscr{D}_{t}^{\prime}, \mathscr{D}_{\tau}^{\prime}$, and $\mathscr{D}_{t, \tau}^{\prime}$, respectively, and let the distributions in the dual spaces be marked by the corresponding indices, e.g. $U_{t}, U_{\tau}$, and $U_{t, \tau}$, respectively.

Suppose $\varphi: \boldsymbol{R}^{1} \times \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$ is a test function in the space $\mathscr{D}_{t, \tau}$ defined on $\boldsymbol{R}^{2}$. Then, evidently, the restriction of $\varphi$ to $\varphi: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$ is a test function defined on $\boldsymbol{R}^{1}$, e.g. $\varphi \in \mathscr{D}_{t}$.

The tensor product of two distributions is a distribution defined as follows.

Definition 3.1 If $t \in \boldsymbol{R}^{1}$ and $\tau \in \boldsymbol{R}^{1}, U_{t}$ and $V_{\tau}$ are two distributions in $\mathscr{D}^{\prime}$, $U_{t} \in \mathscr{D}_{t}^{\prime}$, and $V_{\tau} \in \mathscr{D}_{\tau}^{\prime}$, and $\varphi$ is a test function in $\mathscr{D}_{t, \tau}$, then the tensor product $U_{t} \otimes V_{\tau}$ of the two distributions $U_{t}$ and $V_{\tau}$ is a distribution in $\mathscr{D}_{t, \tau}^{\prime}$, $U_{t} \otimes V_{\tau} \in \mathscr{D}_{t, \tau}^{\prime}$, defined by

$$
\left\langle U_{t} \otimes V_{\tau}, \varphi(t, \tau)\right\rangle=\left\langle U_{t},\left\langle V_{\tau}, \varphi(t, \tau)\right\rangle\right\rangle .
$$

The following two properties of the tensor product are of importance.
Theorem 3.1 The commutative rule holds for the tensor product $U_{t} \otimes V_{\tau} \in$ $\mathscr{D}_{t, \tau}^{\prime}$ of $U_{t} \in \mathscr{D}_{t}^{\prime}$ and $V_{\tau} \in \mathscr{D}_{\tau}^{\prime}$, i.e.

$$
\begin{aligned}
& \left\langle U_{t} \otimes V_{\tau}, \varphi(t, \tau)\right\rangle=\left\langle U_{t},\left\langle V_{\tau}, \varphi(t, \tau)\right\rangle\right\rangle, \\
& \left\langle V_{\tau} \otimes U_{t}, \varphi(t, \tau)\right\rangle=\left\langle V_{\tau},\left\langle U_{t}, \varphi(t, \tau)\right\rangle\right\rangle,
\end{aligned}
$$

and

$$
\left\langle U_{t} \otimes V_{\tau}, \varphi(t, \tau)\right\rangle=\left\langle V_{\tau} \otimes U_{t}, \varphi(t, \tau)\right\rangle .
$$

Theorem 3.1 is Fubini's theorem in distribution theory.
Theorem 3.2 The support of the tensor product of two distributions $U_{t}$ and $V_{\tau}$ equals the product of the individual supports of the factors, i.e.

$$
\operatorname{supp}\left(U_{t} \otimes V_{\tau}\right)=\left(\operatorname{supp} U_{t}\right) \times\left(\operatorname{supp} V_{\tau}\right) .
$$

Suppose that $t \in \boldsymbol{R}^{1}$ and $\tau \in \boldsymbol{R}^{1}$, and that $\varphi \in \mathscr{D}, \varphi: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, is a test function defined on $\boldsymbol{R}^{1}$. From the fact that, for $\varphi$ defined on $\boldsymbol{R}^{1}, \varphi$ is a test function in $\mathscr{D}_{t}, \varphi \in \mathscr{D}_{t}$, i.e. $\varphi$ is infinitely differentiable and has compact support on $\boldsymbol{R}^{1}$, it cannot be implied that $\varphi$ extended to $\boldsymbol{R}^{2}, \varphi: \boldsymbol{R}^{2} \rightarrow \boldsymbol{C}^{1}$, by $\varphi(t, \tau)=\varphi(t+\tau)$ is a test function in $\mathscr{D}_{t, \tau}$, because even though $\varphi(t, \tau)=$ $\varphi(t+\tau)$ is infinitely differentiable, it does not have compact support on $\boldsymbol{R}^{2}$. However, if $I$ is a compact subset of $\boldsymbol{R}^{2}, I \subset \boldsymbol{R}^{2}$, and the function $\alpha \in \mathscr{C}^{\infty}$, $\alpha: \boldsymbol{R}^{2} \rightarrow \boldsymbol{R}^{1}$, is the characteristic function of $I$, i.e. equals one on a neighbourhood of $I$ and equals zero elsewhere, then the product function $\alpha \varphi: \boldsymbol{R}^{2} \rightarrow \boldsymbol{C}^{1}$ is a test function, $\alpha \varphi \in \mathscr{D}$, defined on $\boldsymbol{R}^{2}$.

It is now possible to define the convolution of two distributions in the following cases.

Definition 3.2 Let $t \in \boldsymbol{R}^{1}$ and $\tau \in \boldsymbol{R}^{1}$, let $U_{t} \in \mathscr{D}_{t}^{\prime}$ and $V_{\tau} \in \mathscr{D}_{\tau}^{\prime}$ be two distributions, and let $\varphi \in \mathscr{D}, \varphi: \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, be a test function defined on $\boldsymbol{R}^{1}$. Let I be the intersection $I=\left(\operatorname{supp} U_{t}\right) \cap\left(\operatorname{supp} V_{\tau}\right) \cap(\operatorname{supp} \varphi(t+\tau)) \subset \boldsymbol{R}^{2}$, and let $\alpha \in \mathscr{C}^{\infty}, \alpha: \boldsymbol{R}^{2} \rightarrow \boldsymbol{R}^{1}$, be the characteristic function of the set $I$.

If I is compact then the convolution product $U_{t} * V_{\tau}$ of the distributions $U_{t}$ and $V_{\tau}$ is a distribution in $\mathscr{D}_{t+\tau}^{\prime}$ and is defined by

$$
\left\langle U_{t} * V_{\tau}, \varphi(t, \tau)\right\rangle=\left\langle U_{t} \otimes V_{\tau}, \alpha(t, \tau) \varphi(t+\tau)\right\rangle .
$$

Let the sum of sets $\left(\operatorname{supp} U_{t}\right)+\left(\operatorname{supp} V_{\tau}\right)$ be understood to be the set of points which may be written as the sum of a point $t \operatorname{in} \operatorname{supp} U_{t}, t \in \operatorname{supp} U_{t}$, and a point $\tau$ in $\operatorname{supp} V_{\tau}, \tau \in \operatorname{supp} V_{\tau}$. The following statement holds about the support of a convolution product.

Theorem 3.3 Let the convolution product $U_{t} * V_{\tau} \in \mathscr{D}_{t+\tau}^{\prime}$ of $U_{t} \in \mathscr{D}_{t}^{\prime}$ and $V_{\tau} \in \mathscr{D}_{\tau}^{\prime}$ be defined. Then $\left(\operatorname{supp}\left(U_{t} * V_{\tau}\right)\right) \subseteq\left(\operatorname{supp} U_{t}\right)+\left(\operatorname{supp} V_{\tau}\right)$.

The following theorem is a corollary of theorem 3.1.

Theorem 3.4 The commutative rule holds for the convolution product $U_{t} * V_{\tau} \in \mathscr{D}_{t+\tau}^{\prime}$ of $U_{t} \in \mathscr{D}_{t}^{\prime}$ and $V_{\tau} \in \mathscr{D}_{\tau}^{\prime}$, i.e. $U_{t} * V_{\tau}=V_{\tau} * U_{t}$.

It is of importance to establish sufficient conditions under which the convolution product of two distributions may be defined as above. Only the following two cases will be needed.

Theorem 3.5 Let $t \in \boldsymbol{R}^{1}$ and $\tau \in \boldsymbol{R}^{1}$. (i) If at least one of he two distributions $U_{t} \in \mathscr{D}_{t}^{\prime}$ and $V_{\tau} \in \mathscr{D}_{\tau}^{\prime}$ has compact support then the convolution product $U_{t} * V_{\tau} \in \mathscr{D}_{t+\tau}^{\prime}$ may be defined. (ii) If both distributions $U_{t} \in \mathscr{D}_{t}^{\prime}$ and $V_{\tau} \in \mathscr{D}_{\tau}^{\prime}$ have their supports bounded and closed to the left then the convolution product $U_{t} * V_{\tau} \in \mathscr{D}_{t+\tau}^{\prime}$ may be defined.

In both cases the intersection $I=\left(\operatorname{supp} U_{t}\right) \cap\left(\operatorname{supp} V_{\tau}\right) \cap(\operatorname{supp} \varphi(t+\tau))$ is compact and hence the convolution product well defined by $\left\langle U_{t} * V_{\tau}, \varphi(t, \tau)\right\rangle=$ $=\left\langle U_{t} \otimes V_{\tau}, \alpha(t, \tau) \varphi(t+\tau)\right\rangle$.

Such distributions as were encountered in the case (ii) above, i.e. which have their supports on $\boldsymbol{R}^{1}$ bounded and closed to the left, are termed rightsided distributions. The set of all right-sided distributions in $\mathscr{D}^{\prime}$ is denoted by $\mathscr{D}_{R}^{\prime}$.

Definition $3.3 \mathscr{D}_{R}^{\prime} \subset \mathscr{D}^{\prime}$ is the topological vector space of all right-sided distributions. The topology on $\mathscr{D}_{R}^{\prime}$ is the inductive limit topology of compact convergence inherited from the space $\mathscr{D}^{\prime}$.

The space $\mathscr{D}_{R}^{\prime}$ possesses the following important property.
Theorem 3.6 The space $\mathscr{D}_{R}^{\prime}$ is a commutative algebra with convolution as rule of composition and with the delta distribution as unit element.

Notice that the space $\mathscr{D}_{+}^{\prime}$ is a particular instance of a space $\mathscr{D}_{R}^{\prime}$. Thus, from theorem 3.3 and theorem 3.6 it follows that the convolution product of two distributions in $\mathscr{D}_{+}^{\prime}$ is again a distribution in $\mathscr{D}_{+}^{\prime}$.

The transformations $T$ which may be written as convolutions are of particular interest. Suppose that only distributions in $\mathscr{D}_{R}^{\prime}$ are considered as excitations, $f \in \mathscr{D}_{R}^{\prime}$, and suppose there exists in $\mathscr{D}_{R}^{\prime}$ a distribution $B, B \in \mathscr{D}_{R}^{\prime}$, such that the response $r$ produced by the excitation $f$ may be written as the convolution

$$
\begin{equation*}
r=T(f)=B * f, \quad f \in \mathscr{D}_{R}^{\prime}, B \in \mathscr{D}_{R}^{\prime} \tag{3.4}
\end{equation*}
$$

The domain of $T$ is $\mathscr{D}_{R}^{\prime}, D(T)=\mathscr{D}_{R}^{\prime}$, and as the excitation $f$ traverses $D(T)=\mathscr{D}_{R}^{\prime}$ the response $r$ also traverses $\mathscr{D}_{R}^{\prime}$, i.e. the range of $T$ is likewise $\mathscr{D}_{R}^{\prime}, R(T)_{-}=\mathscr{D}_{R}^{\prime}$.

It is readily established that if a transformation $T$ is defined by the convolution (3.4) then it possesses the four properties 3. (i)-3. (iv) of single valuedness, linearity, stationarynes, and continuity. The validity of the converse assertion has been demonstrated by Schwartz. For the special case of the excitation being right-sided, $f \in \mathscr{D}_{R}^{\prime}$, the proposition states that if a transformation $T$ has the whole subspace $\mathscr{D}_{R}^{\prime}$ as its domain, $D(T)=\mathscr{D}_{R}^{\prime}$, and possesses the four properties 3.(i)-3. (iv), then it is a convolution transformation over $\mathscr{D}_{R}^{\prime}$, i.e. then there exists a unique distribution $B \in \mathscr{D}_{R}^{\prime}$ such that (3.4) is fulfilled. It was seen above that also the range of $T$ will be $\mathscr{D}_{R}^{\prime}, R(T)=\mathscr{D}_{R}^{\prime}$.

The two propositions for right-sided distributions may be stated as a necessary and sufficient condition for the transformation $T$ to be a convolution transformation over $\mathscr{D}_{R}^{\prime}$ as follows.

Theorem 3.7 A unique, right-sided distribution $B, B \in \mathscr{D}_{R}^{\prime}$, exists such that transformation $T$ may be defined as the convolution $r=T(f)=B * f$ for $f \in \mathscr{D}_{R}^{\prime}$ if and only if $T$ has $\mathscr{D}_{R}^{\prime}$ as its domain, $D(T)=\mathscr{D}_{R}^{\prime}$, and the transformation possesses the four properties of single valuedness, linearity, stationaryness, and continuity.

The transformation $T$ will be proposed to possess the two further properties of passivity and causality. In this connection the following operations on distributions will be required.

Definition 3.4 Let $U \in \mathscr{D}^{\prime}$ and $\varphi \in \mathscr{D}$. Then
(i) $\bar{U} \in \mathscr{D}^{\prime}$ is defined by $\langle\bar{U}, \varphi\rangle=\overline{\langle U, \bar{\varphi}\rangle}$, where the bar denotes complex conjugation,
(ii) $\check{U} \in \mathscr{D}^{\prime}$ is defined by $\langle\check{U}, \varphi\rangle=\langle U, \check{\varphi}\rangle$, where $\check{\varphi}(t)=\varphi(-t)$, and (iii) $\hat{U} \in \mathscr{D}^{\prime}$ is defined by $\langle\hat{U}, \varphi\rangle=\langle U, \hat{\varphi}\rangle$, where $\hat{\varphi}(t)=\overline{\varphi(-t)}$.

Also the next theorem, which essentially informs that the transpose of convolution in $\mathscr{D}$ with the distribution $\hat{V}$ is a convolution in $\mathscr{D}^{\prime}$ with the distribution $V$, is called for.

Theorem 3.8 Let $U \in \mathscr{D}_{R}^{\prime}, V \in \mathscr{D}_{R}^{\prime}$, and $\varphi \in \mathscr{D}$. Then the convolution product $U * V$ is defined, $U * V \in \mathscr{D}_{R}^{\prime}$, and $\langle U * V, \varphi\rangle=\langle U, \hat{V} * \varphi\rangle$.

Suppose that both the excitation $f$ and the response $r$ are elements in $\mathscr{D}, f, r \in \mathscr{D}(\Omega)$, where $\Omega$ is an open set in $\boldsymbol{R}^{1}$. Then the transformation

$$
\begin{equation*}
T: f \rightarrow r, \quad f, r \in \mathscr{D}(\Omega), \tag{3.5}
\end{equation*}
$$

is said to be passive if

$$
\begin{equation*}
\int_{\Omega}[f(t) \overline{f(t)}-r(t) \overline{r(t)}] d t=\int_{\Omega}\left[|f(t)|^{2}-|r(t)|^{2}\right] d t \geqq 0 \tag{3.6}
\end{equation*}
$$

Using distribution notation together with definition 3.4 equation (3.6) becomes

$$
\begin{equation*}
\langle f, f\rangle-\langle r, r\rangle \geqq 0, \quad f, r \in \mathscr{D}(\Omega) \tag{3.7}
\end{equation*}
$$

Hence, in the case of $f, r \in \mathscr{D}(\Omega)$ the transformation $T$ is said to be passive if equation (3.7) holds. If only right-sided distributions are admitted as excitations, $D(T)=\mathscr{D}_{R}^{\prime}$, and if the transformation $T$ is supposed to have the properties 3. (i)-3. (iv) of single valuedness, linearity, stationaryness, and continuity, then according to theorem 3.7 a unique right-sided distribution $B$ exists, $B \in \mathscr{D}_{R}^{\prime}$, such that the transformation may be written as

$$
\begin{equation*}
r=T(f)=B * f, \quad f, r, B \in \mathscr{D}_{R}^{\prime} \tag{3.8}
\end{equation*}
$$

As $f \in \mathscr{D}$ and $r \in \mathscr{D}$ implies that $f \in \mathscr{D}_{R}^{\prime}$ and $r \in \mathscr{D}_{R}^{\prime}$, respectively, equation (3.7) with $f, r \in \mathscr{D}$ may be restated as

$$
\begin{align*}
\langle f, f\rangle-\langle r, r\rangle & =\langle\delta * f, f\rangle-\langle B * f, B * f\rangle \\
& =\langle\delta, f * \hat{f}\rangle-\langle B * \hat{B}, f * \hat{f}\rangle \\
& =\langle\delta-B * \hat{B}, f * \hat{f}\rangle  \tag{3.9}\\
& \geqq 0, \quad f, r \in \mathscr{D}
\end{align*}
$$

Here $f \in \mathscr{D}$, and it follows that $\hat{f} \in \mathscr{D}$ and that $f * \hat{f} \in \mathscr{D}$. Distributions with the property of (3.9) carry a special name.

Definition 3.5 Let $\Omega$ be an open subset of $\boldsymbol{R}^{1}$, let $U \in \mathscr{D}^{\prime}(\Omega)$, and let $\varphi \in \mathscr{D}(\Omega)$. If $\langle U, \varphi * \hat{\varphi}\rangle \geqq 0$ then the distribution $U$ is called positive semidefinite.

For transformations $T$ which have $D(T)=\mathscr{D}_{R}^{\prime}$ and which may be defined as convolutions by equation (3.8) and which therefore according to theorem 3.7 possess the properties 3 .(i)-3. (iv) the property of passivity is stated as follows.
3. (v) Passivity. The transformation $T$, which by equation (3.8) is characterised by the distribution $B \in \mathscr{D}_{R}^{\prime}$, possesses the property that

$$
\begin{equation*}
\langle\delta-B * \hat{B}, \varphi * \hat{\varphi}\rangle \geqq 0, \quad \varphi \in \mathscr{D}, \tag{3.10}
\end{equation*}
$$

i.e. the distribution $\delta-B * \hat{B}$ is positive semi-definite.
3. (vi) Causality. Let $\Omega$ be an open set in $\boldsymbol{R}^{1}$, and let $t_{0} \in \boldsymbol{R}^{1}$. The property of causality is expressed by stating that if $f_{1}$ and $f_{2}$ are two excitations in $\mathscr{D}^{\prime}(\Omega), f_{1}, f_{2} \in \mathscr{D}^{\prime}(\Omega)$, such that their difference $f_{1}-f_{2}$ vanishes for $t<t_{0}$ then this shall imply that $T\left(f_{1}-f_{2}\right)$ likewise vanishes for $t<t_{0}$, i.e.

$$
\begin{align*}
& \operatorname{supp}\left(f_{1}-f_{2}\right)=\left\{t \in \boldsymbol{R}^{1} \mid t_{0} \leqq t\right\} \\
& \text { implies that }  \tag{3.11}\\
& \operatorname{supp} T\left(f_{1}-f_{2}\right) \subsetneq\left\{t \in \boldsymbol{R}^{1} \mid t_{0} \leqq t\right\} .
\end{align*}
$$

For the particular cases when $T$ may be described as a convolution the following theorem is of importance.

Theorem 3.9 Let $T$ be a convolution transformation with $D(T)=\mathscr{D}_{R}^{\prime}$, such that $r=T(f)=B * f$, where $f, r, B \in \mathscr{D}_{R}^{\prime}$. The transformation $T$ is causal if and only if $\operatorname{supp} B \leqq\left\{t \in \boldsymbol{R}^{1} \mid 0 \leqq t\right\}$.

It may be shown that if the transformation $T$ possesses the first five properties 3.(i)-3.(v) of single valuedness, linearity, stationaryness, continuity, and passivity, then it also possesses the sixth property 3. (vi) of causality. In view of theorem 3.7 this assertion may be stated as the following sufficient condition for causality.

Theorem 3.10 Let $T$ be a convolution transformation with $D(T)=\mathscr{D}_{R}^{\prime}$, such that $r=T(f)=B * f$, where $f, r, B \in \mathscr{D}_{R}^{\prime}$, and let $T$ be passive, then it is also causal.

## 4. Laplace Transformation of the Transformation Equation

By reference to theorem 3.7 a transformation $T$ for which $D(T)=\mathscr{D}_{R}^{\prime}$ and which possesses the four properties 3 .(i)-3.(iv) may be completely described as a convolution transformation by

$$
\begin{equation*}
r=T(f)=B * f, \quad f, r, B \in \mathscr{D}_{R}^{\prime} \tag{4.1}
\end{equation*}
$$

This means that if only excitations $f$ which are elements in the space $\mathscr{D}_{R}^{\prime}$ considered as a convolution algebra (cfr. theorem 3.6) are admitted, $f \in \mathscr{D}_{R}^{\prime}$, then $T$ is completely characterised by the element $B \in \mathscr{D}_{R}^{\prime}$, i.e. by giving the $t$-representation of the transformation $T$. If the distributions $f, r$, and $B$ of (4.1) all possess Laplace transforms then the transformation $T$ and the corresponding physical system are completely characterised by the

Laplace transform of $B, \mathscr{L} B=S(p)$, i.e. by giving the $p$-representation of the transformation $T$. The function $S: \boldsymbol{C}^{1} \supseteqq D(S) \rightarrow R(S) \subseteq \boldsymbol{C}^{1}$ is a complex valued function of a complex variable, $p \in \boldsymbol{C}^{1}$. It is called the system function ${ }^{8)}$. The distribution $B$ in (4.1) is called the $t$-representation of the system function.

Definition 4.1 Let $\Gamma$ be a subset of $\boldsymbol{R}^{1}$, and let $x \in \boldsymbol{R}^{1}$ and $\sigma \in \boldsymbol{R}^{1}$. The topological vector space $\mathscr{S}_{x}^{\prime}(\Gamma)$ is the space of all distributions $U_{x} \in \mathscr{D}_{x}^{\prime}$ such that $e^{-\sigma x} U_{x} \in \mathscr{S}_{x}^{\prime}$ for $\sigma \in \Gamma$. A sequence $\left\{U_{\nu}\right\}, v=1,2,3, \ldots$ is defined to converge to the limit $U$ in the topology on $\mathscr{S}_{x}^{\prime}(\Gamma)$ if and only if for every $\sigma \in \Gamma$ the sequence $\left\{e^{-\sigma x} U_{\nu}\right\}, v=1,2,3, \ldots$ converges to the limit $e^{-\sigma x} U$ in the weak dual topology $\sigma$ on $\mathscr{S}_{x}^{\prime}$.

It may be shown that $\Gamma$ is convex and hence in the present case of $\Gamma \subseteq \boldsymbol{R}^{1}$, if $\Gamma$ is not empty, $\Gamma$ is an interval on the real axis, finite, semiinfinite, or infinite.

A sufficient condition for the Laplace transform of a distribution to exist is that the distribution is an element of the space $\mathscr{S}^{\prime}(\Gamma)$.

Definition 4.2 Let $\Gamma$ be a convex subset of $\boldsymbol{R}^{1}$, let $x, \sigma, \omega \in \boldsymbol{R}^{1}$, let $B_{x} \in \mathscr{D}_{x}^{\prime}$, and let $\alpha \in \mathscr{C}^{\infty}, \alpha: \boldsymbol{R}^{1} \rightarrow \boldsymbol{R}^{1}$, be the characteristic function of supp $B_{x}$. If $B_{x} \in \mathscr{S}_{x}^{\prime}(\Gamma)$ then the Laplace transform of $B, \mathscr{L} B$, is defined as

$$
\mathscr{L} B=\left\langle B_{x}, \alpha(x) e^{-\sigma x} e^{-i \omega x}\right\rangle=\left\langle B_{x}, \alpha(x) e^{-p x}\right\rangle=S(p),
$$

where $\quad p \in \Gamma+i \boldsymbol{R}^{1} \subset \boldsymbol{R}^{1}+i \boldsymbol{R}^{1}=\boldsymbol{C}^{1}$.
The following theorem establishes a very important connection between the properties of a distribution $B$ and the properties of its Laplace transform. In the theorem the same notation is used as in the definition 4.2 above.

Theorem 4.1 Let $\Gamma$ be an open, convex subset of $\boldsymbol{R}^{1}$. If $S: \boldsymbol{C}^{1} \supset \Gamma+i \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$ is a function which is holomorphic in the open strip $\Gamma+i \boldsymbol{R}^{1}$, and if $|S(p)|$, where $p=\sigma+i \omega \in \Gamma+i \boldsymbol{R}^{1} \subset \boldsymbol{R}^{1}+i \boldsymbol{R}^{1}=\boldsymbol{C}^{1}$, on each compact subset $K$ of $\Gamma, K \subset \Gamma$, is majorised by a polynomial in $|\omega|$ depending on $K,|S(p)| \leqq \mathscr{P}_{K}(|\omega|)$, then a unique distribution $B$ in $\mathscr{S}^{\prime}(\Gamma)$ exists, $B \in \mathscr{S}^{\prime}(\Gamma)$, such that $\mathscr{L} B=S(p)$. Conversely, if $B$ is a distribution in $\mathscr{S}^{\prime}(\Gamma), B \in \mathscr{S}^{\prime}(\Gamma)$, then a unique function exists, $S: \boldsymbol{C}^{1} \supset \Gamma+i \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, which is holomorphic in the open strip $\Gamma+i \boldsymbol{R}^{1}$, which on each compact subset $K$ of $\Gamma, K \subset \Gamma$, is majorised by a polynomial in $|\omega|,|S(p)| \leqq \mathscr{P}_{K}(|\omega|)$, and which is the Laplace transform of $B, S(p)=\mathscr{L} B$.

[^3]If a complex valued function is known to be the Laplace transform of a distribution then information about the support of the distribution may be obtained from the following theorem.

Theorem 4.2. Let $x_{0} \in \boldsymbol{R}^{1}$, and let $\Gamma$ be the open, convex half line $\Gamma=$ $\left\{\sigma \in \boldsymbol{R}^{1} \mid x_{0}<\sigma\right\} \subset \boldsymbol{R}^{1}$. If $S: \boldsymbol{C}^{1} \supset \Gamma+i \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$ is a function which is holomorphic in the open half plane $\Gamma+i \boldsymbol{R}^{1}$, and if $|S(p)|$, where $p=\sigma+i \omega \in$ $\Gamma+i \boldsymbol{R}^{1} \subset \boldsymbol{R}^{1}+i \boldsymbol{R}^{1}=\boldsymbol{C}^{1}$, on each 'compact subset $K$ of $\Gamma, K \subset \Gamma$, is majorised by the product of a function $e^{-x_{0} \sigma}$ and a polynomial in $|\omega|^{\prime}$ depending on $K,|S(p)| \leqq e^{-x_{0} \sigma} \mathscr{P}_{K}(|\omega|)$, then a unique, right-sided distribution $B$ in $\mathscr{S}^{\prime}(\Gamma) \cap \mathscr{D}_{R}^{\prime}$ exists, $B \in \mathscr{S}^{\prime}(\Gamma) \cap \mathscr{D}_{R}^{\prime}$, such that its support is bounded to the left by $x_{0}$, $\operatorname{supp} B_{x} \subseteq\left\{\sigma \in \boldsymbol{R}^{1} \mid x_{0} \leqq \sigma\right\}=\bar{\Gamma}$, and such that $\mathscr{L} B=S(p)$. Conversely, if $B$ is a right-sided distribution in $\mathscr{S}^{\prime}(\Gamma) \cap \mathscr{D}_{R}^{\prime}, B \in \mathscr{S}^{\prime}(\Gamma) \cap \mathscr{D}_{R}^{\prime}$, such that its support is bounded to the left by $x_{0}, \operatorname{supp} B_{x} \subseteq\left\{\sigma \in \boldsymbol{R}^{1} \mid x_{0} \leqq \sigma\right\}$ $=\bar{\Gamma}$, then a unique function exists, $S: \boldsymbol{C}^{1} \supset \Gamma+i \boldsymbol{R}^{1} \rightarrow \boldsymbol{C}^{1}$, which is holomorphic in the open half plane $\Gamma+i \boldsymbol{R}^{1}$, which on each compact subset $K$ of $\Gamma, K$ $\subset \Gamma$, is bounded by the product of a function $e^{-x_{0} \sigma}$ and a polynomial in $|\omega|$ depending on $K,|S(p)| \leqq e^{-x_{0} \sigma} \mathscr{P}_{K}(|\omega|)$, and which is the Laplace transform of $B, S(p)=\mathscr{L} B$.

For transformations $T$ which may be written as convolution transformations according to theorem 3.7 the following theorem is important.

Theorem 4.3 Let $\Gamma$ be an open, convex subset of $\boldsymbol{R}^{1}$, and let $f, r, B \in \mathscr{S}^{\prime}(\Gamma)$. The Laplace transforms $\mathscr{L}_{f}=\mathscr{F}(p), \mathscr{L} B=S(p)$, and $\mathscr{L}_{r}=\mathscr{R}(p)$, where $p \in \Gamma+i \boldsymbol{R}^{1} \subset \boldsymbol{R}^{1}+i \boldsymbol{R}^{1}=\boldsymbol{C}^{1}$, are holomorphic functions in the open strip $\Gamma+i \boldsymbol{R}^{1}$. If $r=B * f$ then also $\mathscr{R}(p)=S(p) \mathscr{F}(p)$.

The particular instances of Laplace transforms given in the next two theorems will be required.

Theorem 4.4 The Laplace transform of the $\delta$-functional is one, $\mathscr{L} \delta=1$.
Theorem 4.5 Let $\lambda, p \in \boldsymbol{C}^{1}$. The Laplace transform of the Riesz distribution $\operatorname{Pf} \frac{x_{+}^{\lambda-1}}{\Gamma(\lambda)} \in \mathscr{S}^{\prime} \cap \mathscr{D}_{R}^{\prime}$ is $\mathscr{L} P f \frac{x_{+}^{\lambda-1}}{\Gamma(\lambda)}=\frac{1}{p^{\lambda}}$.

Certain symmetry properties in the distribution $B$ are reflected in the properties of its Laplace transform $\mathscr{L} B$.

Theorem 4.6 Let $\Gamma$ be an open, convex subset of $\boldsymbol{R}^{1}$, let $B \in \mathscr{S}^{\prime}(\Gamma)$, and let $\mathscr{L} B=S(p)$, where $p \in \Gamma+i \boldsymbol{R}^{1} \subset \boldsymbol{R}^{1}+i \boldsymbol{R}^{1}=\boldsymbol{C}^{1}$.

Then (i) $\quad \mathscr{L} \bar{B}=\overline{S(\bar{p})}$,
$\begin{aligned} \text { (ii) } \mathscr{L} \breve{B} & =S(-p) \\ \text { and (iii) } \mathscr{L} \hat{B} & =\overline{S(-\bar{p})}\end{aligned}$
The distribution $B$ which characterises a convolution transformation $T$ in (4.1) will be supposed to be real. Compare with the definition 3.4 of the complex conjugate of a distribution.

Definition 4.3 Let $\Omega$ be an open subset of $\boldsymbol{R}^{1}$, and let $B$ be a distribution in $\mathscr{D}^{\prime}(\Omega), B \in \mathscr{D}^{\prime}(\Omega) . B$ is defined to be a real distribution if and only if $B=\bar{B}$ on $\Omega$.

The Laplace transforms of distributions which are real possess the following property.

Theorem 4.7 Let $\Gamma$ be an open, convex subset of $\boldsymbol{R}^{1}$, let $B \in \mathscr{S}^{\prime}(\Gamma)$, and let $\mathscr{L} B=S(p)$, where $p \in \Gamma+i \boldsymbol{R}^{1} \subset \boldsymbol{R}^{1}+i \boldsymbol{R}^{1}=\boldsymbol{C}^{1}$. The distribution $B$ is real, $B=\bar{B}$, if and only if $S(p)=\overline{S(\bar{p})}$.

The following result is a consequence of the theorems 4.4, 4.5, and 4.6.
Theorem 4.8 Let $B$ be as in theorems 4.5 and 4.6. Then $\mathscr{L}(\delta-B * \hat{B})=$ $1-S(p) \overline{S(-\bar{p})}$. If furthermore $B$ is real, $B=\bar{B}$, then $\mathscr{L}(\delta-B * \hat{B})=$ $1-S(p) S(-p)$.

Finally, in order to state the theorem of Bochner and Schwartz ${ }^{9}$ which will be needed subsequently the concept of a positive, tempered measure must be introduced.

Definition 4.4 Let $\Omega$ be an open subset of $\boldsymbol{R}^{1}$, and let $\varphi$ be a test function in the space $\mathscr{C}(\Omega)$, such that $\varphi(x) \in \boldsymbol{R}^{1}$ and $\varphi(x) \geqq 0$ for all $x \in \Omega$. Let $\mu$ be a measure in the dual space, $\mu \in \mathscr{C}^{\prime}(\Omega)$. The measure $\mu$ is defined to be positive if and only if $\langle\mu, \varphi\rangle \geqq 0$ for all such $\varphi$.

Definition 4.5 Let $r, A \in \boldsymbol{R}^{1}$, let $\Omega$ be an open subset of $\boldsymbol{R}^{1}$, and let the measure $\mu \in \mathscr{C}^{\prime}(\Omega)$ be positive. The positive measure $\mu$ is defined to be a positive, tempered measure if and only if an integer l exists, $l \geqq 0$, such that $\int_{r \leqq}|d \mu|=$ $O\left(A^{l}\right)$ as $A \rightarrow \infty$.

As indicated in $3 .(v)$, if the transformation $T$ is a convolution, so that $r=T(f)=B * f$, then $T$ is defined to be passive if the distribution $\delta-B * \hat{B}$

[^4]is positive semi-definite. In this connection the following theorem due to Bochner and Schwartz is of importance as it presents a criterion to establish if a distribution is positive semi-definite.

Theorem 4.9 Let $\Gamma$ be an open, convex subset of $\boldsymbol{R}^{1}, \Gamma \subset \boldsymbol{R}^{1}$, let $B \in \mathscr{S}^{\prime}(\Gamma)$, and let $\mathscr{L} B=S(p)$, where $p=\sigma+i \omega \in \Gamma+i \boldsymbol{R}^{1} \subset \boldsymbol{R}^{1}+i \boldsymbol{R}^{1}=\boldsymbol{C}^{1}$. The distribution $B$ is positive semi-definite if and only if the restriction of the Laplace transform to the imaginary axis $i \boldsymbol{R}^{1},\left.\mathscr{L} B\right|_{\sigma=0}=S(i \omega)$, is a positive, tempered measure.

## 5. The General Debye Function as System Function

When measurement of dielectric relaxation of physical systems is carried out the $p$-representation of the transformation $T$, which maps the excitation $E$, the electric field in the dielectric, into the response $D$, the displacement field in the dielectric, is determined as the system function

$$
\begin{equation*}
S(p)=\frac{\varepsilon(p)-\varepsilon_{\infty}}{\varepsilon_{s}-\varepsilon_{\infty}}, \quad p \in \boldsymbol{C}^{1} \tag{5.1}
\end{equation*}
$$

where $p$ is the complex frequency, $p=\sigma+i \omega, \varepsilon(p)$ is the complex dielectric constant, and where $\varepsilon_{s}$ and $\varepsilon_{\infty}$ are the limit values $\varepsilon_{s}=\lim _{\omega \rightarrow 0+} \varepsilon(\sigma+i \omega)$ and $\varepsilon_{\infty}=\lim _{\omega \rightarrow \infty} \varepsilon(\sigma+i \omega)$, both of which are real.

The assumption that the response of the dielectric, the displacement field $D$, displays exponential decay to a delta functional excitation in the electric field $E$ is equivalent to the assumption that the system function $S$ is of the form

$$
\begin{equation*}
S(p)=\frac{\varepsilon(p)-\varepsilon_{\infty}}{\varepsilon_{s}-\varepsilon_{\infty}}=\frac{1}{1+p \tau_{0}}, \quad p \in \boldsymbol{C}^{1}, \quad \tau_{0} \in \boldsymbol{R}^{1} \tag{5.2}
\end{equation*}
$$

Here $\tau_{0}$ is a positive number, $\tau_{0}>0$, the relaxation time.
The function

$$
\begin{equation*}
S(p)=\frac{1}{1+p \tau_{0}} \tag{5.3}
\end{equation*}
$$

is called the Debye function. It is holomorphic in the open half plane $\Gamma+i \boldsymbol{R}^{1}$, where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid-1 / \tau_{0}<\sigma\right\}$, and it maps the half line $L_{\sigma_{0}}$ in the $p$-plane

$$
\begin{equation*}
L_{\sigma_{0}}=\left\{\sigma_{0}+i \omega \in \boldsymbol{R}^{1}+i \boldsymbol{R}^{1} \mid 0 \leqq \omega\right\}, \quad \sigma_{0}>\frac{-1}{\tau_{0}}, \tag{5.4}
\end{equation*}
$$

into the semi circle in the $S(p)$-plane

$$
\left.\begin{array}{r}
A_{\sigma_{0}}=\left\{\left.S(p) \in \boldsymbol{C}^{1}| | S(p)-\frac{1}{2\left(1+\sigma_{0} \tau_{0}\right)} \right\rvert\,=\frac{1}{2\left(1+\sigma_{0} \tau_{0}\right)},\right.  \tag{5.5}\\
\operatorname{Im} S(p) \leqq 0\}, \quad \sigma_{0}>\frac{-1}{\tau_{0}},
\end{array}\right\}
$$

the Cole-Cole semi circle. A special instance is the case of $\sigma_{0}=0$, when

$$
\begin{equation*}
S(i \omega)=\frac{\varepsilon(i \omega)-\varepsilon_{\infty}}{\varepsilon_{s}-\varepsilon_{\infty}}=\frac{1}{1+i \omega \tau_{0}}, \tag{5.6}
\end{equation*}
$$

and the half line $L_{0}$ is mapped into the semi circle $A_{0}$,

$$
\begin{equation*}
A_{0}=\left\{\left.S(p) \in \boldsymbol{C}^{1}| | S(i \omega)-\frac{1}{2} \right\rvert\,=\frac{1}{2}, \quad \operatorname{Im} S(p) \leqq 0\right\} . \tag{5.7}
\end{equation*}
$$

In many cases, however, e.g. of dielectric systems, there has been reported experimental evidence that the half line $L_{0}$ in the $p$-plane is not mapped into a semi circle $A_{0}$ in the $S(p)$-plane, but rather into various forms of continuous arcs, circular arcs, skew symmetric arcs, etc. All of this evidence indicates that the primary assumption of the response of the dielectric system displaying an exponential decay characterised by the sole parameter $\tau_{0}$, the relaxation time, to a delta functional excitation, cannot hold in general.

This has led to attempts to alter the system function $S$ to a form justified by its compatibility with experimental observations, i.e. a phenomenological form.

The functions

$$
\begin{equation*}
\left.S(p)=\frac{1}{1+\left(p \tau_{0}\right)^{1-\alpha}}, p \in \boldsymbol{C}^{1}, \alpha, \tau_{0} \in \boldsymbol{R}^{1}(\text { Cole-Cole }),{ }^{10}\right) \tag{5.8}
\end{equation*}
$$

and

$$
\begin{equation*}
S(p)=\frac{1}{\left[1+p \tau_{0}\right]^{\beta}}, p \in \boldsymbol{C}^{1}, \beta, \tau_{0} \in \boldsymbol{R}^{1}(\text { Davidson-CoLe }),{ }^{11)} \tag{5.9}
\end{equation*}
$$

where $0 \leqq \alpha, \beta \leqq 1$, both have been used to characterise dielectric systems. A few years ago the still more general function

[^5]\[

$$
\begin{equation*}
S(p)=\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}, p \in \boldsymbol{C}^{1}, \alpha, \beta, \tau_{0} \in \boldsymbol{R}^{1}\left(\text { Havriliak-NeGami), }{ }^{12}\right) \tag{5.10}
\end{equation*}
$$

\]

where again $0 \leqq \alpha, \beta \leqq 1$, was proposed as system function to characterise certain polymer dielectric systems, the proposal being justifiable by the ensuing agreement with the experimental observations.

The function (5.10) is called the general Debye function. It is a complex valued function of a complex variable, $S: \boldsymbol{C}^{1} \supseteq D(S) \rightarrow R(S) \subseteq \boldsymbol{C}^{1}$. In_contrast to the Debye function (5.3), $S(p)=\frac{1}{1+p \tau_{0}}$, which as its sole singularity has a first order pole at $p=-1 / \tau_{0}$, the general Debye function (5.10), $S(p)=\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}$, possesses singularities which may be essential.

$$
\text { 5.(i) } \alpha, \beta, \tau_{0} \in \boldsymbol{R}^{1}, \quad \alpha=1, \quad 0 \leqq \beta \leqq 1, \quad \tau_{0}>0
$$

In this case the function (5.10) becomes

$$
\begin{equation*}
S(p)=\frac{1}{2^{\beta}} \tag{5.11}
\end{equation*}
$$

which is a holomorphic function in the entire $p$-plane, and $|S(p)|$ is bounded by

$$
\begin{equation*}
\frac{1}{2} \leqq|S(p)|=\frac{1}{2^{\beta}} \leqq 1 \tag{5.12}
\end{equation*}
$$

The domain of holomorphy includes the open half plane $\Gamma+i \boldsymbol{R}^{1}$, where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0<\sigma\right\}$, and it follows from theorem 4.2 that a unique rightsided distribution $B_{t}$ exists, $B_{t} \in \mathscr{S}^{\prime}(\Gamma) \cap \mathscr{D}_{R}^{\prime}$, such that $\mathscr{L} B=\frac{1}{2^{\beta}}$, and which has its support bounded to the left at $t=0$, $\operatorname{supp} B_{t} \subseteq\left\{t \in \boldsymbol{R}^{1} \mid 0 \leqq t\right\}$. An application of theorem 4.7 shows that $B_{t}$ is real. It is seen immediately that $B=\frac{1}{2^{\beta}} \delta$.

$$
\text { 5.(ii) } \alpha, \beta, \tau_{0} \in \boldsymbol{R}^{1}, \quad 0 \leqq \alpha<1, \quad 0 \leqq \beta \leqq 1, \quad \tau_{0}>0 \text {. }
$$

In this case the function $(5.10)$ is many valued and has discrete branch points $p_{k}$, which may be dense on the circle $|p|=\frac{1}{\tau_{0}}$, and which are situated at
$\left.{ }^{12}\right)$ See ref.s (8) and (9).


Fig. 5.1.

$$
\begin{equation*}
p_{k}=\frac{1}{\tau_{0}} \exp \left[i \pi \frac{1+2 k}{1-\alpha}\right], k=0, \pm 1, \pm 2, \pm 3, \ldots \tag{5.13}
\end{equation*}
$$

In addition, a branch point is situated at $p=0$.
Each of the branch points $p_{k}$ is of infinitely high order if and only if $\beta$ is irrational. The branch points $p_{k}$ are dense on the circle $|p|=\frac{1}{\tau_{0}}$, and the branch point $p=0$ is of infinitely high order if and only if $\alpha$ is irrational. However, the branch points $p_{k}$ are situated on different sheets of the Riemann surface. In fig. 5.1 the sheet of the Riemann surface corresponding to the principal branch of the function (5.10), i.e. corresponding to the branch which contains the set $\left\{S(p) \in \boldsymbol{C}^{1} \mid \operatorname{Arg} S(p)=0\right\}$, is indicated. The sheet contains the open half plane $\left\{p \in \boldsymbol{C}^{1}|0<|p| \wedge| \operatorname{Arg} p \mid<\pi / 2\right\}$, which may be continued to the sector $\left\{p \in \boldsymbol{C}^{1}|0<|p| \wedge| \operatorname{Arg} p \mid<\pi /(1-\alpha)\right\}$ and even further, compare fig. 5.1. The mapping

$$
\begin{equation*}
S: p \rightarrow \frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}} \quad \text { (principal branch) } \tag{5.14}
\end{equation*}
$$

from this sheet of the Riemann surface to the principal branch of (5.10) is holomorphic.

Let a branch cut in the $p$-plane be introduced along the negative, real axis from $p=0$ to the point at infinity. Then the mapping (5.14) is holomorphic in the entire $p$-plane except on the negative, real axis, the set $\left\{\sigma \in \boldsymbol{R}^{1} \mid \sigma \leqq 0\right\}$. As this domain of holomorphy includes the open half plane $\Gamma+i \boldsymbol{R}^{1}$, where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0<\sigma\right\}$ and as

$$
\begin{equation*}
|S(p)| \leqq 1, \tag{5.15}
\end{equation*}
$$

it follows again from the theorem 4.2 that a unique, right-sided distribution $B_{t}$ exists, $B_{t} \in \mathscr{S}^{\prime}(\Gamma) \cap \mathscr{D}_{R}^{\prime}$, such that $\mathscr{L} B=S(p)$, where $S(p)$ is understood to be the principal branch of the function (5.14), and which distribution has its support bounded to the left at $t=0, \operatorname{supp} B_{t} \subseteq\left\{t \in \boldsymbol{R}^{1} \mid 0 \leqq t\right\}$. As $S(\bar{p})=\overline{S(p)}$, it follows from theorem 4.7 that $B_{t}$ is real.

Analogous considerations may be applied to the function $S \circ n$, where $n$ is the mapping

$$
\begin{equation*}
n: p \rightarrow-p, \quad p \in \boldsymbol{C}^{1} . \tag{5.16}
\end{equation*}
$$

If a branch cut in the $p$-plane is introduced along the positive, real axis from $p=0$ to the point at infinity then the function $S \circ n$ is holomorphic in the entire $p$-plane except on the positive, real axis, the set $\left\{\sigma \in \boldsymbol{R}^{1} \mid 0 \leqq \sigma\right\}$. Consequently the function $1-S(p) S(-p)$ is holomorphic in the two open half planes $\boldsymbol{R}^{1}+i \Gamma$ and $\boldsymbol{R}^{1}-i \Gamma$, where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0<\sigma\right\}$. In particular, the function $1-S(p) S(-p)$ is holomorphic on the imaginary axis with the point $p=0$ excluded, $i \boldsymbol{R}^{1} \backslash\{0\}$. At the point $p=0$ the function $1-S(p) S(-p)$ is continuous.

The restriction of the function $1-S(p) S(-p)$ to the imaginary axis $i \boldsymbol{R}^{1}$ is

$$
\begin{equation*}
1-S(i \omega) S(-i \omega)=1-|S(i \omega)|^{2} \in \boldsymbol{R}^{1} \tag{5.17}
\end{equation*}
$$

for which

$$
\begin{equation*}
0 \leqq 1-|S(i \omega)|^{2} \leqq 1, \quad 0 \leqq \alpha, \beta \leqq 1, \quad 0<\tau_{0} \tag{5.18}
\end{equation*}
$$

From theorem 4.9 (Bochner-Schwartz) it follows that the distribution $\delta-B * \hat{B}$, where $\mathscr{L} B=\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}$ (principal branch), is positive
semi-definite.

The situation is summarised in the following theorem.

Theorem 5.1 Let $T$ be a convolution transformation with $D(T)=\mathscr{D}_{R}^{\prime}$, such that $r=T(f)=B * f$, where $f, r, B \in \mathscr{D}_{R}^{\prime}$. Let $\alpha, \beta, \tau_{0} \in \boldsymbol{R}^{1}$, with $0 \leqq \alpha, \beta \leqq 1$, and $0<\tau_{0}$, and let $\mathscr{L} B=S(p)$, where $S(p)$ is the principal branch of the function $S(p)=\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}$.

Then the transformation $T: f \rightarrow r$ possesses the six properties of (i) single valuedness, (ii) linearity, (iii) stationaryness, (iv) continuity, (v) passivity, and (vi) causality.

## 6. The $\boldsymbol{t}$-Representation of the General Debye Function

According to the results in sections 5. (i) and 5. (ii) the function

$$
\begin{equation*}
S(p)=\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}} \quad(\text { principal branch }) \tag{6.1}
\end{equation*}
$$

where $p \in \boldsymbol{C}^{1}$, and $\alpha, \beta, \tau_{0} \in \boldsymbol{R}^{1}$ with $0 \leqq \alpha, \beta \leqq 1,0<\tau_{0}$, is holomorphic in the open half plane $\Gamma+i \boldsymbol{R}^{1}$ where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0<\sigma\right\}$. In the rest of section 6 when referring to the function (6.1) only the principal branch is considered.

If $\frac{1}{\tau_{0}}<|p|$ and hence also if $p$ is in the open half plane $\Gamma_{1}+i \boldsymbol{R}^{1}, p \in \Gamma_{1}+$ $i \boldsymbol{R}^{1}$, where $\Gamma_{1}=\left\{\sigma \in \boldsymbol{R}^{1} \left\lvert\, \frac{1}{\tau_{0}}<\sigma\right.\right\}$, the function (6.1) may be expanded in an infinite binomial series. For $\alpha, \beta, \tau_{0} \in \boldsymbol{R}^{1}$, with $0 \leqq \alpha, \beta \leqq 1$, and $0<\tau_{0}$, the expansion is

$$
\begin{align*}
S(p) & =\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}} \\
& =\sum_{n=0}^{\infty} \frac{\Gamma(1-\beta)}{n!\Gamma(1-\beta-n)} \cdot \frac{1}{\left(p \tau_{0}\right)^{(1-\alpha)(\beta+n)}}  \tag{6.2}\\
& =\sum_{n=0}^{\infty} \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} \cdot \frac{1}{\left(p \tau_{0}\right)^{(1-\alpha)(\beta+n)}}
\end{align*}
$$

where $\Gamma$ denotes the $\Gamma$-function and where the identity

$$
\begin{equation*}
\Gamma(\beta) \Gamma(1-\beta)=(-1)^{n} \Gamma(\beta+n) \Gamma[1-(\beta+n)], n=0, \pm 1, \pm 2, \ldots \tag{6.3}
\end{equation*}
$$

has been used. If $p$ is in the intersection of $\frac{1}{\tau_{0}}<|p|$ and the open half plane $\Gamma+i \boldsymbol{R}^{1}$, i.e. for $p \in\left\{z \in \boldsymbol{C}^{1}\left|\frac{1}{\tau_{0}}<|z| \wedge z \in \Gamma+i \boldsymbol{R}^{1}\right\}\right.$ where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0<\sigma\right\}$, the series (6.2) is (C, 1) summable on the set $\left\{(\alpha, \beta) \in \boldsymbol{R}^{2} \mid 0 \leqq \alpha \leqq 1 \wedge 0 \leqq\right.$ $\beta \leqq 1\}$ and uniformly convergent on the subset $\left\{(\alpha, \beta) \in \boldsymbol{R}^{2} \mid 0 \leqq \alpha<1\right.$ ^ $0 \leqq \beta<1\}$.

The function (6.1) $S(p)=\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}$ (principal branch) is the analytic continuation to the open half plane $\Gamma+i \boldsymbol{R}^{1}$, where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid\right.$ $0<\sigma\}$, of the function which for $p \in\left\{z \in \boldsymbol{C}^{1}\left|\frac{1}{\tau_{0}}<|z| \wedge z \in \Gamma+i \boldsymbol{R}^{1}\right\}\right.$ is
represented by the infinite series (6.2).

From theorem 4.5 it follows that the $n$ 'th term of the series (6.2) is the Laplace transform of the Riesz distribution $\left(B_{t}\right)_{n}=\frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)}$. $\operatorname{Pf} \frac{\left(t / \tau_{0}\right)_{+}^{(1-\alpha)(\beta+n)-1}}{\Gamma[(1-\alpha)(\beta+n)]}$, i.e.

$$
\begin{align*}
\mathscr{L}\left(B_{t}\right)_{n} & =\mathscr{L} \frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} P f \frac{\left(t / \tau_{0}\right)_{+}^{(1-\alpha)(\beta+n)-1}}{\Gamma[(1-\alpha)(\beta+n)]}  \tag{6.4}\\
& =\frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} \cdot \frac{1}{\left(p \tau_{0}\right)^{(1-\alpha)(\beta+n)}} .
\end{align*}
$$

For $p \in\left\{z \in \boldsymbol{C}^{1}\left|\frac{1}{\tau_{0}}<|z| \wedge z \in \Gamma+i \boldsymbol{R}^{1}\right\}\right.$, where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0<\sigma\right\}$, termvise application of the result (6.4) to the series (6.2) yields the infinite series of Riesz distributions

$$
\begin{align*}
B_{t} & =\sum_{n=0}^{\infty}\left(B_{t}\right)_{n}  \tag{6.5}\\
& =\sum_{n=0}^{\infty} \frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} P f \frac{\left(t / \tau_{0}\right)_{+}^{(1-\alpha)(\beta+n)-1}}{\Gamma[(1-\alpha)(\beta+n)]} .
\end{align*}
$$

According to theorem 4.2 the function (6.1) $S(p)=\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}$ (principal branch) determines a unique distribution $B_{t}$, which is rightsided and is an element of $\mathscr{S}_{t}^{\prime}(\Gamma)$ where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0<\sigma\right\}, B_{t} \in \mathscr{D}_{R}^{\prime} \cap$
$\mathscr{S}_{t}^{\prime}(\Gamma)$, which has its support bounded to the left at $t=0, \operatorname{supp} B_{t} \subseteq$ $\left\{t \in \boldsymbol{R}^{1} \mid 0 \leqq t\right\}$, and which is such that $\mathscr{L} B_{t}=S(p)$, where $S(p)$ is the function (6.1). The series (6.5) does not converge in the topology on $\mathscr{S}_{t}^{\prime}(\Gamma)$, but in the coarser topology on $\mathscr{S}_{t}^{\prime}\left(\Gamma_{1}\right)$, where $\Gamma_{1}=\left\{\sigma \in \boldsymbol{R}^{1} \left\lvert\, \frac{1}{\tau_{0}}<\sigma\right.\right\}$, the series $(6.5)$ is $(\mathrm{C}, 1)$ summable on the set $\left\{(\alpha, \beta) \in \boldsymbol{R}^{2} \mid 0 \leqq \alpha \leqq 1 \wedge 0 \leqq \beta \leqq 1\right\}$ and convergent on the subset $\left\{(\alpha, \beta) \in \boldsymbol{R}^{2} \mid 0 \leqq \alpha<1 \wedge 0 \leqq \beta<1\right\}$.

It is of interest to indicate the series for $B_{t}$ and for $S(p)$ in the four special cases of $(\alpha, \beta)=(1,1),(1,0),(0,1)$, and $(0,0)$. In all four cases $p \in\left\{z \in \boldsymbol{C}^{1}\left|\frac{1}{\tau_{0}}<|z| \wedge z \in \Gamma+i \boldsymbol{R}^{1}\right\}\right.$, where $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0<\sigma\right\}$, and $0<\tau_{0}$.
6.(i) $\alpha=1, \beta=1$.

$$
\begin{align*}
B_{t} & =\left.\sum_{n=0}^{\infty} \frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} P f \frac{\left(t / \tau_{0}\right)_{+}^{(1-\alpha)(\beta+n)-1}}{\Gamma[(1-\alpha)(\beta+n)]}\right|_{\substack{\alpha=1 \\
\beta=1}} \\
& =\sum_{n=0}^{\infty} \frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \delta_{t / \tau_{0}}  \tag{6.6}\\
& =\sum_{n=0}^{\infty}(-1)^{n} \delta_{t} \\
& =\frac{1}{2} \delta_{t}
\end{align*}
$$

$$
\begin{equation*}
S(p)=\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}=\frac{1}{2} . \tag{6.7}
\end{equation*}
$$

6. (ii) $\alpha=1, \beta=0$.

$$
\begin{align*}
B_{t} & =\left.\sum_{n=0}^{\infty} \frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} P f \frac{\left(t / \tau_{0}\right)_{+}^{(1-\alpha)(\beta+n)-1}}{\Gamma[(1-\alpha)(\beta+n)]}\right|_{\substack{\alpha=1 \\
\beta=1}} \\
& =\frac{1}{\tau_{0}} \delta_{t / \tau_{0}}  \tag{6.8}\\
& =\delta_{t}
\end{align*}
$$

6.(iii) $\alpha=0, \beta=1$.

$$
\begin{align*}
B_{t} & =\left.\sum_{n=0}^{\infty} \frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} P f \frac{\left(t / \tau_{0}\right)_{+}^{(1-\alpha)(\beta+n)-1}}{\Gamma[(1-\alpha)(\beta+n)]}\right|_{\substack{\alpha=0 \\
\beta=1}} \\
& =\sum_{n=0}^{\infty} \frac{1}{\tau_{0}}(-1)^{n} P f \frac{\left(t / \tau_{0}\right)_{+}^{n}}{\Gamma(n+1)}  \tag{6.10}\\
& =u_{0}\left(\frac{t}{\tau_{0}}\right) \frac{1}{\tau_{0}} \exp \left(-\frac{t}{\tau_{0}}\right) .
\end{align*}
$$

$$
\begin{equation*}
S(p)=\left.\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}\right|_{\substack{\alpha=0 \\ \beta=1}}=\frac{1}{1+p \tau_{0}} . \tag{6.11}
\end{equation*}
$$

6.(iv) $\alpha=0, \beta=0$.

$$
\begin{align*}
B_{t} & =\left.\sum_{n=0}^{\infty} \frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} P f \frac{\left(t / \tau_{0}\right)_{+}^{(1-\alpha)(\beta+n)-1}}{\Gamma[(1-\alpha)(\beta+n)]}\right|_{\beta=0} ^{\alpha=0} \\
& =\frac{1}{\tau_{0}} \delta_{t / \tau_{0}}  \tag{6.12}\\
& =\delta_{t} .
\end{align*}
$$

$$
\begin{equation*}
S(p)=\left.\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}\right|_{\substack{\alpha=0 \\ \beta=0}}=1 . \tag{6.13}
\end{equation*}
$$

The whole situation may be summarised in the following theorem.
Theorem 6.1 Let $p \in \boldsymbol{C}^{1}$, and $\alpha, \beta, \tau_{0} \in \boldsymbol{R}^{1}$ with $0 \leqq \alpha, \beta \leqq 1$, and $0<\tau_{0}$. Let $\Gamma=\left\{\sigma \in \boldsymbol{R}^{1} \mid 0<\sigma\right\}$ and $\Gamma_{1}=\left\{\sigma \in \boldsymbol{R}^{1} \left\lvert\, \frac{1}{\tau_{0}}<\sigma\right.\right\}$. Let $B_{t} \in \mathscr{S}_{t}^{\prime}(\Gamma) \cap \mathscr{D}_{R}^{\prime}$ be the unique distribution such that $\mathscr{L} B_{t}=S(p)$, where $S(p)$ is the principal branch of the function $S(p)=\frac{1}{\left[1+\left(p \tau_{0}\right)^{1-\alpha}\right]^{\beta}}$.

Then, (i) the distribution $B_{t}$ has its support bounded to the left at $t=0$, $\operatorname{supp} B_{t} \subseteq\left\{t \in \boldsymbol{R}^{1} \mid 0 \leqq t\right\}$,
and (ii) the distribution $B_{t}$ is determined by the infinite series of Riesz distributions

$$
B_{t}=\sum_{n=0}^{\infty} \frac{1}{\tau_{0}} \cdot \frac{(-1)^{n}}{n!} \cdot \frac{\Gamma(\beta+n)}{\Gamma(\beta)} P f \frac{\left(t / \tau_{0}\right)_{+}^{(1-\alpha)(\beta+n)-1}}{\Gamma[(1-\alpha)(\beta+n)]}
$$

In the topology on $\mathscr{S}_{t}^{\prime}\left(\Gamma_{1}\right)$ the series is $(\mathrm{C}, 1)$ summable on the set $\left\{(\alpha, \beta) \in \boldsymbol{R}^{2} \mid 0 \leqq \alpha \leqq 1 \wedge 0 \leqq \beta \leqq 1\right\}$ and convergent on the subset $\left\{(\alpha, \beta) \in \boldsymbol{R}^{2} \mid 0 \leqq \alpha<1 \wedge 0 \leqq \beta<1\right\}$.

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# PRECISION ENERGY LOSS MEASUREMENTS FOR NATURAL ALPHA PARTICLES IN ARGON 

Det Kongelige Danske Videnskabernes Selskab Matematisk-fysiske Meddelelser 38, 3



Kommissionær: Munksgaard
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## Synopsis

Energy losses of natural alpha particles from $\mathrm{Bi}^{212}$ and $\mathrm{Po}^{212}$ have been determined in argon gas with an accuracy of about $0.2 \%$. The Lewis correction and the multiple scattering correction are briefly discussed. The data are compared with the Bethe theory, formulated with two different shell correction functions. $I$-values of 182 eV and 167 eV are obtained, respectively. Northcliffe's measurements at higher energies favor $I=182 \mathrm{eV}$. Comparison with hydrogen ion stopping power data confirms the recently discovered dependence on the particle charge.

## 1. Introduction

While the Bethe theory of stopping power ${ }^{1,2,3}$ is generally accepted, there are many details at low particle velocities which are not well established. In particular it is not clear how valid the Born approximation is. Accurate experiments are a necessity for the clarification of these questions. Furthermore, accurate measurements are needed for applications in nuclear physics, health physics, radiobiologi, industrial radiation uses and related fields.

Energy loss and range measurements for natural alpha particles in many materials have been performed for over half a century ${ }^{4,5,6,7,8}$. The development of solid state ionization detectors has permitted a more accurate measurement of particle energies and allows fairly simple experiments ${ }^{9}, 10$, 11, 12 .

Data for precision measurements in gases are scarce ${ }^{13,14}$. Consideration of the details in the detector operation permit an accuracy of close to $0.1 \%$ in the energy loss measurements (section 2).

With the parameters obtained in this work we present a range energy table for $\alpha$-particles. Recently ${ }^{15,16}$ it has been confirmed, that stopping powers and ranges of particles with different charges $z$ are not exactly proportional to $z^{2}$, as the Bethe-formula predicts. A comparison with available proton and triton measurements will be shown.

## 2. Energy Loss Measurements

Bethe's theory furnishes the mean energy loss of initially monoenergetic particles in absorbers of a given thickness, and therefore will be applicable to the present experiment. While it is possible to determine energy losses directly, if the absorber can be used as a detector (ref. 17; an interesting variation is described by Andersen, et al. ${ }^{18}$ ), in most substances it will be necessary to measure an incident energy $T$ and a residual energy $T_{1}$ with mean values $\langle T\rangle$ and $\left\langle T_{1}\right\rangle$ respectively. The mean energy loss will be determined by

$$
\bar{\Delta}=\langle T\rangle-\left\langle T_{1}\right\rangle .
$$

In the measurements presented here, absorber thicknesses will be expressed in mass per unit area. For gases, the distance $d$ between the particle source and the surface of a silicon detector will have to be measured as well as the pressure of the gas.

## 2 A. Measurements of Energies

The radioactive decay of Th C and $\mathrm{Th} \mathrm{C}^{\prime}$ nuclei is used as a source of alpha particles of well-known energies for the experiment. For the preparation of a source, a stainless steel pin with a diameter of 2 mm and a flat and polished end surface was connected to the negative pole of a 300 volt battery, and was exposed in the thorium emanation $\left(\mathrm{Rn}^{220}\right)$ of a $10 \mathrm{mc} \mathrm{Th}^{228}$ source for 60 minutes.
a) Determination of Energy $<T>$ of Incident Alpha Particle.

Since the thoron atoms attached to the source undergo two shortlived alpha decays (to $\mathrm{Po}^{216}$ and $\mathrm{Pb}^{212}$, which has a half life for beta decay of 11 hours), it is to be expected that recoil nuclei will penetrate a small distance into the source. The alpha particles from $\mathrm{Bi}^{212}$ (Th C) and $\mathrm{Po}^{212}$ (Th C') used in the experiment therefore will often come from inside the stainless steel source pin. No direct evidence is available for Th sources, but Rytz ${ }^{19}$ found for $\mathrm{Bi}^{211}$ sources a mean energy which was about 3 keV lower than the energy of the "line head" (estimated by us from Fig. 7 of ref. 19). It will therefore be assumed that the energies given by Rytz have to be reduced by 3 keV and 4 keV for $\mathrm{Po}^{212}$ and $\mathrm{Bi}^{212}$, respectively. The values adopted for this paper are listed in Table I.

Measurements of the shape and the pulseheight of the $\mathrm{Po}^{212}$ line in the silicon detector showed no change as a function of the time used to prepare the source. The exposure of the source to argon gas for 12 hours also did not change the mean pulseheight.

Table I

| Nucleus | $\begin{gathered} T(\mathrm{keV}) \\ \text { Rytz } \end{gathered}$ | Self <br> Absorption | $T(\mathrm{keV})$ <br> Adopted | Relative Abundance |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Po}^{212}$ | $8785.4 \pm 0.8$ | $3 \pm 2 \mathrm{keV}$ | $8782 \pm 2$ | $100 \%$ |
| $\mathrm{Bi}^{212}{ }_{1}$ | $6089.8 \pm 0.7$ | $4 \pm 3 \mathrm{keV}$ | $6086 \pm 3$ | $27.1{ }^{\circ}$ |
| , | $6050.6 \pm 0.7$ | $4 \pm 3 \mathrm{keV}$ | $6047 \pm 3$ | 69.7 \% |

The separation of 39 keV for the two energies found for $\mathrm{Bi}^{212}$ can only be observed for zero energy loss. For finite energy losses, straggling amounts to considerably more than 39 keV , and it is necessary to use a weighted mean energy for the two energies. Using the branching ratio given by Perlman and $\mathrm{Asaro}^{20}$ (see Table I), a mean energy $T=6058 \mathrm{keV}$, corrected for source thickness, is obtained.

## b) Determination of Residual Energies $T_{1}$.

The reduced energies $T_{1}$ are determined in a detection system consisting of a surface barrier silicon detector, test pulser, preamplifier, amplifier and a 100 channel analyzer. Since it was found that amplification changes of the system amounted to more than $1 \%$ per day, all measurements were based on a comparison of alpha pulseheights to test pulseheights. The quantity observed in the silicon detector is a charge pulse caused by the collection of the electrons and holes produced by the particle. The detailed detector performance will be discussed in connection with the energy calibration of the detector system.

Testpulses with a rise time comparable to the rise time of alpha-pulses (less than $0.1 \mu \mathrm{sec}$ ) are fed into the preamplifier in parallel with the alphas through a 1 pF capacitor. It has been assumed that testpulses and alphapulses of the same magnitude will experience exactly the same amplification in the system. No complete check of this assumption has been performed, but some tests on the same system are described by Tschalär ${ }^{21}$. Problems within the accuracy desired here ( $\sim 0.1^{\%} / 0$ ) occur for pulse rise times exceeding $0.1 \mu \mathrm{sec}$.

It is not practical to superimpose a testpulse group on the alpha group. Therefore, in each measurement, the group of alphapulses is bracketed by two groups of testpulses. Since the analyzing system is somewhat nonlinear, a third group of testpulses is also recorded. The testpulses are recorded during the period of the alpha measurement (Fig. 1). The magnitude of the testpulses is proportional to the dial setting of a helipot. Its linearity has been measured with a Wheatstone bridge and is better than $0.05 \%$. The voltage for the testpulses is supplied from a Zener reference diode, its random drifts were slow during a day and amounted to less than $0.05 \%$.

The following evaluation procedure is used for the determination of the mean alpha-pulseheight for each spectrum.
i) Calculate the mean channel number for the alphas and the three testpulse groups.


Fig. 1. Typical spectrum of alpha particles reduced in energy from $<T>=8.782 \mathrm{MeV}$ to $<\mathrm{T}_{1}>\sim 7.0 \mathrm{MeV}$. Thus, the average energy loss is about 1.8 MeV . With the indicated cut-off points for the spectrum, the location of the mean channel is calculated to be 72.01. The "peak location" obtained by visually drawing tangent lines to the sides of the spectrum is located at 72.3 channels. The full width at half maximum obtained from the figure is 109 keV , while the calculated standard deviation for the spectrum is $\varrho=48.4 \mathrm{keV}$. The ratio of these two numbers is 2.26 . For a gaussian, this ratio is 2.36 . Two testpulses with dial readings of 68 and 72 are also shown.
ii) Calculate a quadratic calibration curve for the conversion of channel number into dial setting of testpulses.
iii) Express mean alpha channel number as the dial setting of a testpulse that would give the same mean channel number.

For all the spectra recorded in a particular run (typically about 30 spectra, measured during 8 hours), an absolute energy calibration was obtained in the following manner.

The stopping of the $\alpha$-particles in the detector material is mainly due to inelastic collisions with silicon electrons, which result in the charge pulse collected at the detector surfaces. Lindhard et al. ${ }^{22}$ calculated the energy loss due to nuclear collisions which can not be detected by this method. The theoretical values have been confirmed at lower energies ${ }^{23}$. In our energy range this "ionization defect" is $9-13 \mathrm{keV}$, increasing with energy. The incident energies of table I have to be reduced respectively, because we must find the linear relationship between the $\alpha$-pulseheights on the multichannel analyzer and the electronic energy loss in the detector.

The calibration energies were also corrected for the undetected energy losses in the gold surface layer and the adjoining deadlayer in the detector
material ${ }^{24}$. They were determined experimentally by observing the line shift of alphas incident at different angles. The total thickness corresponds to about $100 \mu \mathrm{gcm}^{-2}$ gold, and gold stopping power ${ }^{25}$ was used to find the energy loss for other alpha energies.

A linear least squares fit was calculated for the pulseheights (expressed in equivalent dial readings) versus the corrected calibration energies. An energy calibration factor $f$ is thus obtained. Zero energy was assigned to a testpulse dial setting of zero.

Occasionally, during a day's observation, a drift of the energy calibration factor amounting to a few kilovolts at 9 MeV could be seen. This was corrected for by interpolating the energy calibration with respect to the time of the day, so that every run effectively had its own calibration. If the drift amounted to more than 10 keV , the measurements would be rejected. The average standard deviation of the energy calibration runs is between 2 and 5 keV . Second order fits did not improve the standard deviations.

On one occasion, calibrations with a commercial Th ${ }^{228}$ source were performed, using the $\alpha$-lines at 5.338 MeV and 5.421 MeV (Ref. 20). Their pulseheights agreed with the usual calibration within 2 keV .

For the alpha particles travelling through the gas, the mean energy $<T_{1}>$ is calculated from the equivalent dial reading of the mean alpha pulseheight, adding the calculated energy loss in the detector surface layer and deadlayer, and the ionization defect.

In addition to the uncertainty due to the energy calibration, a systematic error is introduced due to the choice of cutoffs of the distribution functions $f\left(T_{1}\right)$ of the reduced energies $T_{1}$ at finite values $T^{\prime}$ and $T^{\prime \prime} . f\left(T^{\prime}\right)=f\left(T^{\prime \prime}\right)$ are usually between $5 \%$ and $10 \%$ of the peak value of $f\left(T_{1}\right)$; thus $<T_{1}>$ is determined by

$$
\int_{T^{\prime}}^{T^{\prime \prime}} f\left(T_{1}\right) T_{1} d T_{1} / \int_{T^{\prime}}^{T^{\prime \prime}} f\left(T_{1}\right) d T_{1}
$$

Chetham-Strode et al. ${ }^{26}$ investigated low energy tails of various $\alpha$-spectra from silicon detectors, and found, that the mean energy of a $6 \mathrm{MeV} \alpha$-source decreased $0.07 \%$ relative to the mean energy derived from the symmetric part of the spectrum. If we assume the same relative decrease for all energies, this correction is negligible, when we do not take the tails into account in the energy calibration.

The most probable energy $T_{1}$, mode for the energy spectra was determined by the limit of the mean energy, when the distance between the cut-off energies $T^{\prime}$ and $T^{\prime \prime}$ was narrowed, so that the values of the distribution functions at these energies, $f\left(T^{\prime}\right)=f\left(T^{\prime \prime}\right)$, increased from $10^{\%}$ to $100 \%$ of
the peakvalues. We compared $T_{1}$, mode $-<T_{1}>$ with Tschalär's ${ }^{27}$ calculations, based on the classical collision spectrum with free absorber electrons. The deviations were less than 2 keV for higher $<T_{1}>$, increasing to 5 keV for the lowest $<T_{1}>$. They are probably caused by the neglect of the resonance contribution to the straggling in Tschalär's theory. ${ }^{65}$

Uncertainties caused by the statistical nature of the number of counts in each channel are estimated to be less than 1 keV .

## 2 B. Absorber Measurements

a) Apparatus.

A stainless steel vacuum chamber about 9 cm in diameter and 32 cm in lenght was used for the measurements. The silicon detector is mounted on one of the end plates. The source is installed in a holder attached to a lead screw with a pitch of approximately 1 mm . The lead screw was connected to a counter, indicating tenths of revolutions. The screw was calibrated every measuring day using a stainless steel tube as a gauge block between the scource holder and the detector mount. The length of the gauge tube was measured with a micrometer screw within 0.03 mm .

The distance from the detector mount to the gold layer of the detector surface was measured with a microscope, whose focus system was attached to a dial indicator. The distance was found, by focussing on the detector mount and on the gold layer, respectively, to be $1.54 \pm .02 \mathrm{~mm}$.

Distances $d$ between 8 and 25 cm were used. No discrepancies connected with $d$ were observed within the experimental accuracy. The over-all accuracy is estimated to be 0.04 mm . Since the detector used had a diameter of about 5 mm , the distance from source to detector varies slightly over the detector surface. The maximum correction in $d$ would amount to $0.05 \%$ for the edge of the detector surface. No correction for this effect has been made.

## b) Gas Density.

Commercial compressed argon gas with a stated purity of $99.995 \%$ was used for the measurements. Impurities should falsify the data by less than $0.01 \%$. The vacuum system was evacuated to better than $5 \cdot 10^{-5} \mathrm{~atm}$ before filling with argon. Also, it was flushed three times before the final filling was introduced. Leakage of the system, including outgassing, amounted to less than $5 \cdot 10^{-6}$ atm per hour.

The argon gas pressure $p$ was measured with a mercury manometer, which consisted of two vertical glass tubes (inside diameter about $1.87 \pm$ 0.02 cm ) filled with doubly distilled mercury. The height of each mercury
column was measured by observing through a cathetometer telescope, simultaneously, the top of the meniscus and a stainless steel meterstick mounted next to the glass tubes. The accuracy of the measurement is about $\pm 0.01 \mathrm{~cm}$. Capillary corrections are estimated to be less than 0.003 cm , and the density of mercury was temperature corrected.

The temperature $t$ of the gas was measured with a mercury-in-glass thermometer to within $0.1^{\circ} \mathrm{C}$. Thermocouples were used to monitor the temperature at different places on the vacuum system. No gradients greater than $0.1^{\circ} \mathrm{C}$ were observed. For the calculation of the gas density $\varrho$, the Van der Waals equation is used in the following approximate form:

$$
\begin{equation*}
\varrho=\varrho_{0}\left(1+\varrho_{0}^{2} a / p A^{2}\right)\left(1-b \varrho_{0} / A\right) \tag{1}
\end{equation*}
$$

where $A=$ atomic weight of argon $=39.948 \mathrm{~g} / \mathrm{mole}, \varrho_{0}=A p / R T, p=$ gas pressure in atm, $R=0.08206 \mathrm{l} \mathrm{atm} /$ mole ${ }^{0} K, T=$ gas temperature in absolute scale, $a=$ first Van der Waals coeff. $=1.345 \mathrm{l}^{2} \mathrm{~atm} / \mathrm{mole}^{2}$, and $b=$ second Van der Waals coeff. $=0.03219 \mathrm{l} / \mathrm{mole}$. The difference between the liter l and the cubic decimeter $\mathrm{dm}^{3}$ has been neglected. Since at 1 atm , the Van der Waals correction amounts to only $0.123 \%$, the first approximation to the density given by eq. (1) is sufficient.

The final absorber thickness $s$ is derived by the product of the corrected distance $d$ and the density $\varrho: s=d \cdot \varrho$.

The experimental errors of the measured energies and absorber thicknesses are summarized in Table II.

Table II
Errors Associated with Energy Loss Measurements.

|  | Errors |  |
| :---: | :---: | :---: |
|  | Absolute | Relative |
| Pressure Measurement |  |  |
| Height of Columns. | $\pm 0.1 \mathrm{~mm}$ | 0.01 to $0.1{ }^{\circ} \%$ |
| Density of Mercury | $\pm 0.002 \mathrm{~cm}^{-3}$ | $0.01 \%$ |
| Temperature Measurement | $\pm 0.1^{\circ} \mathrm{K}$ | 0.03 \% |
| Distance Measurement | $\pm 0.04 \mathrm{~mm}$ | 0.02 to $0.04{ }^{\circ} / 0$ |
| Energy Measurement |  |  |
| $5 \mathrm{MeV}<T_{1}<9 \mathrm{MeV}$ | $\pm 2 \mathrm{keV}$ | $0.04 \%$ |
| $1 \mathrm{MeV}<T_{1}<5 \mathrm{MeV}$ | $\pm 5 \mathrm{keV}$ | 0.1 to $0.5 \%$ |

## 3. Corrections to the Experiment

Since the Bethe theory provides the integrated energy loss along the path of particles, corrections have to be estimated for the experimental data: for multiple scattering and for discrete energy loss (Lewis correction).

## 3 A. Multiple Scattering Correction

During their passage through the gas, the particles experience many small changes in the direction of their velocity, caused by Coulomb scattering by the nuclei. This results in pathlengths longer than the thickness of material traversed. The $\alpha$-particles are not all emitted in the direction of the detector, and the multiple scattering distribution functions have to be integrated over the incident angles as well as the exit angles. This case has been treated by $\emptyset_{v e r i ̊ s}{ }^{28}$, not taking energy loss into account. The method has been extended including the energy loss, as shown in the Appendix. The difference between mean pathlength and perpendicular absorberthickness $s$ amounts to $8 \mu \mathrm{gcm}^{-2}$ for $<T>=8.78 \mathrm{MeV}$ and $<T_{1}>=1 \mathrm{MeV}$. The correction decreases rapidly for increasing $<T_{1}>$ and is negligible for $<T_{1}>\gtrsim 3 \mathrm{MeV}$.

## 3 B. Lewis Correction

The Bethe theory provides the mean energy loss of particles in a thin absorber; for thick absorbers we have to integrate the inverse stopping power function, as if there was a continuous slowing down of the particles ("csda approximation'"). The increasing energy spread of the initially monoenergetic particles will in a finite absorber cause a difference between the mean csda energy loss and the actual energy loss. Lewis ${ }^{29}$ has given a derivation of this effect, using the classical single collision law:

$$
P(Q, T)=k /\left(2 T \cdot Q^{2}\right)
$$

where $Q$ is the energy transferred to an electron and $k=2 \pi N Z z^{2} e^{4} M / m$ [see eq. (3)]. For small energy losses (less than 800 keV for our problem), $T$ is approximately constant, and $P(Q, T)$ will be constant. Then the experimental spectrum $\varphi(Q, T)$ will give the same average energy loss as the csda calculation.

For larger energy losses the $T$-dependence of $P(Q, T)$ makes the distribution broader, and a tail appears at the low energy end of the spectrum. $<T_{1}>$ thus becomes lower than the theoretical csda energy, which is used for the further evaluation of the experimental data.

Table IIl
Corrected energy loss data for $\alpha$-particles in Argon. $\langle T\rangle$ is the incident $\alpha$-energy corrected for selfabsorbtion and $\left.<T_{1}\right\rangle$ is the average energy at the detector surface after passing through the gas. Corrections for the detector surface layer and the ionization defect are included in $\left\langle T_{1}\right\rangle . s$ is the gas thickness corrected for multiple scattering to give the mean pathlength. Two sets of measurements are presented.

| $<T>=6.058 \mathrm{MeV}$ |  | $<T>=8.782 \mathrm{MeV}$ |  |
| :---: | :---: | :---: | :---: |
| $\begin{gathered} s \\ \mathrm{mgcm}^{-2} \end{gathered}$ | $\begin{gathered} <T_{1}> \\ \mathrm{MeV} \end{gathered}$ | $\begin{gathered} s \\ \mathrm{mgcm}^{-2} \end{gathered}$ | $\begin{gathered} <T_{1}> \\ \mathrm{MeV} \end{gathered}$ |
| 7.617 | 1.044 | 13.948 | 1.358 |
| 7.576 | 1.095 | 13.748 | 1.589 |
| 7.192 | 1.526 | 13.202 | 2.074 |
| 6.608 | 2.071 | 12.718 | 2.465 |
| 6.559 | 2.104 | 11.976 | 3.040 |
| 5.995 | 2.573 | 11.168 | 3.588 |
| 5.297 | 3.089 | 10.446 | 4.038 |
| 4.625 | 3.545 | 9.590 | 4.533 |
| 3.810 | 4.054 | 8.733 | 4.997 |
| 3.016 | 4.515 | 7.779 | 5.490 |
| 1.995 | 5.072 | 6.660 | 6.029 |
| 1.070 | 5.542 | 5.661 | 6.490 |
|  |  | 4.442 | 7.028 |
|  |  | 3.207 | 7.539 |
|  |  | 1.973 | 8.041 |
|  |  | 0.659 | 8.539 |
| 7.768 | 0.864 | 14.014 | 1.310 |
| 7.254 | 1.477 | 13.167 | 2.124 |
| 6.698 | 2.006 | 10.630 | 3.936 |
| 6.144 | 2.468 | 10.470 | 4.022 |
| 5.513 | 2.943 | 9.942 | 4.341 |
| 4.808 | 3.422 | 8.969 | 4.879 |
| 4.006 | 3.935 | 7.887 | 5.445 |
| 3.140 | 4.450 | 6.871 | 5.938 |
| 2.217 | 4.960 | 6.797 | 5.972 |
| 1.258 | 5.448 | 5.784 | 6.440 |
|  |  | 4.696 | 6.920 |
|  |  | 3.698 | 7.339 |
|  |  | 2.348 | 7.888 |
|  |  | 1.014 | 8.401 |

The positive correction to $\left.<T_{1}\right\rangle$ gives a negative correction to the energy loss and to the stopping power used for computation of the theoretical mean range

$$
\begin{equation*}
R=\int_{0}^{<T>}\left[1 / S\left(T^{\prime}\right)\right] d T^{\prime} \tag{2}
\end{equation*}
$$

Therefore the integrand in (2) will increase due to the correction, and $R$ will be slightly larger. This effect was discussed by Lewis ${ }^{29}$ for the total range of a charged particle. Tschalär ${ }^{27}$ calculated the correction to $<T_{1}>$ by a similar method. According to his results, the increase of $<T_{1}>$ is less than 0.5 keV for $<T_{1}>\sim 1 \mathrm{MeV}$, and smaller at higher values. No correction therefore is applied for this effect.

## 3 C. Corrected Experimental Results

An experimental data point consists of three numbers: a) initial alpha particle energy $<T>$, b) corrected mean energy $<T_{1}>$ of alpha particles after the absorber, c) corrected mean pathlength $s$. A list of the data points is given in Table III. No empirical range energy relation is presented; instead a comparison with Bethe's theory will be presented in Section 5. No independent data are available for a direct comparison. A comparison with other data, using the theory, will be given in Section 6. The results deviate slightly from those reported in ref. 30 due to previous errors in the data treatment.

## 4. Theoretical Interpretation

## 4A. Bethe Stopping Power Theory

Bethe's theory is used for the interpretation of the data. The basic formulation for the stopping power $S=-d T / d s$ follows from the Born approximation :

$$
\begin{equation*}
S=4 \pi e^{4}\left(z^{2} / m v^{2}\right) \cdot N \cdot B \tag{2}
\end{equation*}
$$

where $e$ and $m$ are electron charge and mass, $z$ and $v$ charge number and velocity of the particle, $N$ the number of stopping atoms per $\mathrm{cm}^{3}$ and $B$ the stopping number. In the quantum mechanical theory (see e.g. ref. 2) $B$ is defined as ${ }^{31}$

$$
\begin{equation*}
B=Z \ln \left(2 m v^{2} / I\right)-\sum_{i} C_{i} \tag{3}
\end{equation*}
$$

where $Z$ is the atomic number of the absorber, $I$ the average ionization potential, and $C_{i}$ the so-called shell corrections, one term for each electronic shell of the absorber atom. For argon, the following expression is obtained:

$$
\begin{equation*}
S=\left(0.30706 z^{2} / A \beta^{2}\right) \cdot\left\{Z[f(\beta)-\ln 1]-C_{K}-C_{L}-C_{M}\right\} \tag{4}
\end{equation*}
$$

where $A$ is the atomic mass of argon, $\beta$ is $v$ relative to the velocity of light in vacuum, and $f(\beta)=\ln 2 m c^{2} \beta^{2} /\left(1-\beta^{2}\right)-\beta^{2}$.

For $C_{K}$ and $C_{L}$, Walske's values ${ }^{32,33}$ can be used approximately. No reliable theoretical determination of $I$ and $C_{M}$ are available. Since Khandelwal's calculation ${ }^{34}$ of $C_{M}$ is based on hydrogenic wave functions, it cannot be considered to be applicable to argon. Even the $L$-shell correction is not strictly applicable, but it will be practical as a first approximation.

## 4 B. Particle Charge Dependence

According to the Bethe formula (2) the stopping power is proportional to the square of the particle charge $z$, since $B$ as defined in (3) only depends on the particle velocity. Recently Heckman and Lindstrom ${ }^{15}$ discovered differences in the stopping powers of positive and negative pions at the same velocity, and Andersen et al. ${ }^{16}$ also detected deviations from the theoretical charge dependence for hydrogen and helium ions. The latter authors indicate, that the discrepancy is present in previous data, although the errors are of the same order of magnitude as the deviations.

This effect is not taken into account in the present data treatment, since no satisfactory theoretical approach is available. The following presentation of stopping powers and ranges is thus strictly confined to $\alpha$-particles. In section 6 a comparison with available hydrogen ion data will be presented.

## 4C. Charge Exchange Correction

When the $\alpha$-particles slow down below 2 MeV , they begin to capture electrons from the gas atoms, and subsequently lose electrons also. By this process the $\alpha$-particles suffer energy losses in addition to the normal electronic stopping, and Bethe's formula cannot be used, even if the average charge of the He-ions is known. However, it is practical to apply the total correction to $z^{2}$ in eq. (2), and Whaling's table ${ }^{35}$ for determination of $S$ for $\alpha$-particles from proton stopping powers is used. Whaling's table is an average over a collection of experimental data, and the charge corrections are estimated to be within $20 \%$ of the tabulated values. Intermediate values were determined from the table by linear interpolation.

## 4D. Fitting Procedure

For the comparison with the experimental data, two methods of approximation for shell corrections will be used. In both cases, $I$ is a parameter to be determined from experiment, and Walske's $C_{K}$ is assumed to be correct.

Method 1 It will be assumed that the shell corrections for the $L$ and $M$ electrons can be combined into one function:

$$
\begin{equation*}
C_{L+M}=V_{L} \cdot C_{L}\left(H_{L} \cdot \beta^{2}\right) \tag{5}
\end{equation*}
$$

where $C_{L}$ is Walske's $L$-shell function and $V_{L}$ and $H_{L}$ are parameters determined from experiment.

Method 2 Walske's $C_{L}$ is assumed to be correct and an $M$-shell correction is determined with two parameters $V_{M}$ and $H_{M}$ :

$$
\begin{equation*}
C_{M}=V_{M} \cdot C_{L}\left(H_{M} \cdot \beta^{2}\right) \tag{6}
\end{equation*}
$$

where again $H_{M}$ and $V_{M}$ are determined from the experiment.

A Fortran program similar to the one described in ref. 36 was used for the evaluation of the experimental data and the comparison with theory. The theoretical range difference $r$, obtained by integrating over the stopping power $S$ (eq. (2)), using the experimental energies $<T>$ and $<T_{1}>$ :

$$
\begin{equation*}
r=\int_{<T_{1}>}^{\langle T\rangle} S^{-1} d T \tag{7}
\end{equation*}
$$

was compared with $s$, the experimental pathlength.
A least squares fit was obtained for the three parameters $I$, and $H_{L}, V_{L}$ of eq. (5), or $H_{M}, V_{M}$ of eq. (6), using $\chi^{2}=\sum(r-s)^{2}$ to find the minimum. The weighting factor is approximately constant, and assumed to be 1 . Furthermore the program computed the sum of the estimated shell-corrections, divided by $Z$, plotted in Fig. 6. Due to the large errors in the charge exchange corrections, the experimental measurements for $<T_{1}>\lesssim 2 \mathrm{MeV}$ should have a weighting factor less than 1 , but this was omitted.


Fig. 2. Least squares fit of range difference measurements in argon. $r$ is the calculated range difference [from eq. (7)]. The horizontal line at $0.00 \mathrm{mgcm}^{-2}$ represents the fit, where the $L$ and $M$-shell corrections are combined into one function, $C_{L+M}$ (method 1 ). The other curve appears, when Walske's $C_{L}$ is assumed to be correct, and the $M$-shell correction is fitted seperately (method 2). Method 1 and method 2 have rms errors 8.7 and $9.1 \mu \mathrm{gcm}^{-2}$, respectively. $\Delta\left(<T_{1}>\right)$ indicates the estimated error in ( $r-s$ ) due to the total error in the energy measurements. The slope zero of the horizontal line represents the inverse of the stopping power $S$ in Table IV, and the tangent of the angle $\gamma$ indicates an $0.3 \%$ change of $S$ at the energies 1 and 9 MeV , respectively. : incident $\alpha$-energy $\langle T\rangle=6.058 \mathrm{MeV} ; \bigcirc:<T\rangle=8.782 \mathrm{MeV}$.

## 5. Results

The evaluation of the experimental data according to Method 1, using Walske's $C_{K}$ and scaling $C_{L}$ with two parameters to obtain a best fit, yields $I=182 \mathrm{eV}, H_{L}=1.6, V_{L}=1.2$. The rms deviation is $\xi= \pm 8.7 \mu \mathrm{gcm}^{-2}$. Values of $q=r-s$ are plotted versus residual mean energy $<T_{1}>$ in Fig. 2. $r$ is computed according to eq. (7). Total ranges

$$
\begin{equation*}
r_{t}=\int_{1}^{T} S^{-1} d T+R(1 \mathrm{MeV}) \tag{8}
\end{equation*}
$$

with $R(1 \mathrm{MeV})=0.85 \mathrm{mgcm}^{-2}$ and the stopping power $S$ obtained in the course of the calculation are given in Table IV.

It can be shown mathematically ${ }^{37}$, that experimental rms deviations $\Delta S$ of $S$ are those in Table IV, and they agree with the estimated errors obtained empirically by drawing curves of different shapes through the experimental points of Fig. 2.

It is quite obvious from eq. (4), that small changes in $I$ can be compensated for by corresponding changes in the shell corrections over a limited

## Table IV

Stopping power and range as a function of energy for $\alpha$-particles in argon. $S$ are the theoretical values using eq. (11) (Method 1), and $\Delta S$ are the estimated rms deviations of $S$. The range is defined by eq. (8). The value $0.846 \mathrm{mgcm}^{-2}$ for 1 MeV is adopted from a comparison with total mean ranges from ref. 38 (see section 6)

| $\begin{gathered} \alpha \text {-energy } \\ \text { MeV } \end{gathered}$ | $\begin{gathered} S \\ \mathrm{keV} / \mathrm{mgcm}^{-2} \end{gathered}$ | $\begin{aligned} & \Delta S \\ & \% / 0 \end{aligned}$ | Range $\mathrm{mgcm}^{-2}$ |
| :---: | :---: | :---: | :---: |
| 1.0 | 1169 | $\ldots$ | 0.846 |
| 1.25 | 1103 | 1.5 | 1.067 |
| 1.5 | 1039 | 0.8 | 1.299 |
| 2.0 | 901 | 0.3 | 1.820 |
| 2.5 | 793 | " | 2.413 |
| 3.0 | 715 | " | 3.078 |
| 3.5 | 654 | " | 3.810 |
| 4.0 | 605 | " | 4.606 |
| 4.5 | 564 | " | 5.462 |
| 5.0 | 529 | " | 6.379 |
| 5.5 | 498.7 | " | 7.353 |
| 6.0 | 472.2 | " | 8.384 |
| 6.5 | 448.9 | " | 9.470 |
| 7.0 | 428.0 | " | 10.62 |
| 7.5 | 409.3 | " | 11.81 |
| 7.75 | 402.6 | " | 12.47 |
| 8.0 | 392.3 | 0.8 | 13.06 |
| 8.5 | 369.7 | $\ldots$ | 15.03 |
| 8.75 | 376.9 | 1.5 | 14.36 |

energy range. Thus, e.g., for this method, a local minimum is also found at $I=179 \mathrm{eV}, H_{L}=1.6$, and $V_{L}=1.3$ with $\xi= \pm 8.8 \mu \mathrm{gcm}^{-2}$. Therefore it is not possible to assign unambiguous errors to the experimentally determined parameters.

The second method (using Walske's $C_{K}$ and $C_{L}$, and $C_{M}$ scaled from $C_{L}$ ) yields an $I$-value of 167 eV with $H_{M}=3.6$ and $V_{M}=1.1$. The rms deviation $\xi$ is $\pm 9.1 \mu \mathrm{gcm}^{-2}$.

The analysis of Martin and Northcliffe's $\alpha$-particle data ${ }^{39}$ using Walske's unmodified $C_{K}$ and $C_{L}$ gave an $I$-value of $184 \mathrm{eV}^{40}$. This indicates that Method 2 overestimates the shell corrections, and the not unexpected conclusion is that $C_{L}$ cannot be used for $Z=18$ without modification.

Table V
Stopping power $S$ in $\mathrm{keV} / \mathrm{mgcm}^{-2}$ and ranges in $\mathrm{mgcm}^{-2}$ for $\alpha$-particles in argon computed using the program of ref. 36 with $I=182 \mathrm{eV}$, Walske's K-shell correction and the $L$-shell correction fitted to the present experimental data.

| Energy <br> MeV | $S$ | Range | Energy <br> MeV | $S$ | Range | Energy <br> MeV | $S$ | Range |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1.0 | 1169 | 0.85 | 10 | 337.8 | 18.57 | 100 | 60.3 | 937.6 |
| 1.1 | 1137 | 0.93 | 11 | 316.4 | 21.63 | 110 | 60.0 | 1110 |
| 1.2 | 1111 | 1.02 | 12 | 297.9 | 24.89 | 120 | 52.3 | 1295 |
| 1.3 | 1092 | 1.11 | 13 | 281.7 | 28.34 | 130 | 49.11 | 1492 |
| 1.4 | 1074 | 1.21 | 14 | 267.3 | 31.99 | 140 | 46.35 | 1702 |
| 1.5 | 1039 | 1.30 | 15 | 254.5 | 35.82 | 150 | 43.92 | 1924 |
| 1.6 | 1005 | 1.40 | 16 | 243.0 | 39.84 | 160 | 41.77 | 2157 |
| 1.7 | 974 | 1.50 | 17 | 232.6 | 44.05 | 170 | 39.84 | 2403 |
| 1.8 | 944 | 1.60 | 18 | 223.1 | 48.44 | 180 | 38.11 | 2659 |
| 1.9 | 922 | 1.71 | 19 | 214.5 | 53.01 | 190 | 36.55 | 2927 |
| 2.0 | 901 | 1.82 | 20 | 206.6 | 57.77 | 200 | 35.13 | 3206 |
| 2.2 | 854 | 2.05 | 22 | 192.6 | 67.80 |  |  |  |
| 2.4 | 811 | 2.29 | 24 | 180.6 | 78.53 |  |  |  |
| 2.6 | 776 | 2.54 | 26 | 170.1 | 89.95 |  |  |  |
| 2.8 | 744 | 2.80 | 28 | 160.9 | 102.0 |  |  |  |
| 3.0 | 715 | 3.08 | 30 | 152.8 | 114.8 |  |  |  |
| 3.2 | 689 | 3.36 | 32 | 145.5 | 128.2 |  |  |  |
| 3.4 | 665 | 3.66 | 34 | 139.0 | 142.3 |  |  |  |
| 3.6 | 643 | 3.96 | 36 | 133.1 | 157.0 |  |  |  |
| 3.8 | 623 | 4.28 | 38 | 127.7 | 172.3 |  |  |  |
| 4.0 | 605 | 4.61 | 40 | 122.8 | 188.3 |  |  |  |
| 4.2 | 588 | 4.94 | 42 | 118.3 | 204.9 |  |  |  |
| 4.4 | 571 | 5.29 | 44 | 114.1 | 222.1 |  |  |  |
| 4.6 | 556 | 5.64 | 46 | 110.3 | 240.0 |  |  |  |
| 4.8 | 542 | 6.01 | 48 | 106.8 | 258.4 |  |  |  |
| 5.0 | 529 | 6.38 | 50 | 103.4 | 277.4 |  |  |  |
| 5.5 | 498.7 | 7.35 | 55 | 96.1 | 327.6 |  |  |  |
| 6.0 | 472.2 | 8.38 | 60 | 89.8 | 381.5 |  |  |  |
| 6.5 | 448.8 | 9.47 | 65 | 84.4 | 438.9 |  |  |  |
| 7.0 | 428.0 | 10.61 | 70 | 79.7 | 499.9 |  |  |  |
| 7.5 | 409.3 | 11.81 | 75 | 75.5 | 564.4 |  |  |  |
| 8.0 | 392.3 | 13.06 | 80 | 71.8 | 632.3 |  |  |  |
| 8.5 | 376.9 | 14.36 | 85 | 68.5 | 703.7 |  |  |  |
| 9.0 | 362.7 | 15.71 | 90 | 65.5 | 778.3 |  |  |  |
| 9.5 | 349.8 | 17.11 | 95 | 62.8 | 856.3 |  |  |  |

Thus for argon, the three parameters to be used for a calculation of stopping power for $\alpha$-particles are

$$
\begin{aligned}
I & =182 \mathrm{eV} \\
H_{L} & =1.6 \\
V_{L} & =1.2
\end{aligned}
$$

Table V gives the stopping powers and ranges for $0.5-200 \mathrm{MeV} \alpha$-particles computed with the above values for the parameters according to Method 1. In ref. 30 tables for hydrogen ions are calculated with the same parameters, not taking into account the charge dependence of the particles.

## 6. Discussion

## 6 A . Range Measurements

Experimental measurements of extrapolated ranges by Harper and Salaman ${ }^{4}$ for $\mathrm{Po}^{210}, \mathrm{Bi}^{212}$ and $\mathrm{Po}^{212}$ alphas in argon were modified to yield mean ranges by Bogaardt and Koudiss ${ }^{38}$. Since the present data are range difference measurements, the range for 1 MeV alphas was estimated by adjusting Bogaardt's values to our data. This value is $0.846 \mathrm{mgcm}^{-2}$, and the resulting range energy curve agrees within $0.03 \mathrm{mgcm}^{-2}$ with Bogaardt's ranges. The error estimated by Bogaardt is $0.07 \mathrm{mgcm}^{-2}$. An earlier evaluation of Bogaardt's data using Walske's $C_{K}$ and $C_{L}$ gave a value $I=183 \mathrm{eV}^{40}$. Fig. 3 presents a comparison with other range data $R$ on this basis. Our results $r_{t}$ correspond to the horizontal line at $0.00 \mathrm{mgcm}^{-2}$ framed by dotted lines at a distance of rms $=0.009 \mathrm{mgcm}^{-2}$.

Mano ${ }^{41}$ measured range differences for several $\alpha$-sources, and Bogatrdt ${ }^{38}$ fitted the results to Harper and Salaman's mean ranges. The good agreement with our range-energy relation at 10.538 MeV indicates, that the errors of the stopping powers at the upper limit of our energy range is considerably lower than estimated in table IV.

Several extrapolated range measurements for $\mathrm{Po}^{210}{ }^{42,43,44,45}$ reduced to mean ranges fluctuate with errors around $0.05-0.10 \mathrm{mgcm}^{-2}$, giving an error of the same order of magnitude to the above determined, initial 1 MeV -range. The $\alpha$-energy value was taken from Rytz ${ }^{19}$ and corrected for selfabsorption as described in section 2 A .a).

Bertolini and Bettoni46 measured ranges up to 3.5 MeV within $3 \%$, in reasonable agreement with our results.


Fig. 3. Range measurements for $\alpha$-particles in argon. Other data $R$ are compared with present results $r_{t}$ from Table V. $R-r_{t}$ is plotted versus the $\alpha$-energy $E$. The dotted lines indicate the $r m s=0.009 \mathrm{mgcm}^{-2}$ of the present results. $+:$ Harper and Salaman ${ }^{4} ; \triangle:$ Mano ${ }^{41}$; ○: Naidu ${ }^{42}$; Colby and Hatfield ${ }^{43}$; : Schmieder ${ }^{44}$; A: Eichholz and Harrick ${ }^{45}$; 똠: Chang ${ }^{14}$. The fully drawn curve below 3.5 MeV represent the ranges measured by Bertolini and Bettoni ${ }^{46}$.

Chang ${ }^{14}$ measured range differences $s_{\mathrm{Ch}}$ with the same $\alpha$-source energies and the results can be plotted in Fig. 3 directly, without introducing any initial alpha range. The deviations are so large, that some of the points could not be plotted on the scale. The fractional difference $\left(r-s_{\mathrm{Ch}}\right) / r$ (eq.(7)) is approximately constant $(1-2 \%)$, indicating a systematic error due to the measurements of $R$.

## 6B. Stopping Power Measurements

Figure 4 shows available stopping power data in our energy range. Curve 1 are the results of Bertolini and $\mathrm{Bettoni}^{46}$; from the error of their range measurements an overall error of about $5 \%$ can be estimated ${ }^{37}$ for the stopping powers. They are in reasonable agreement with curve 2, a plot of table $V$, where the dotted curves indicate the estimated standard deviations. Curve 3 are values from Ramirez et al. ${ }^{47}$; no errors are reported.


Fig. 4. Experimental stopping powers $S$ of $\alpha$-particles in argon versus $\alpha$-energy. Curve 1: Bertolini and Bettoni ${ }^{46}$, curve 2: present results (errors indicated with dotted curves), and 3: Ramirez et al. ${ }^{47}$.

## 6 C. Hydrogen Ion Stopping Powers

Recently ${ }^{15,16}$ it has been confirmed, that stopping powers of ions with different charges but the same velocity do not exactly follow the simple charge dependence of the Bethe formula (2). For a comparison we make use of the following procedure adopted from ref. 16.

We define the quantity $L$ as

$$
L=B / Z=f(\beta)-\ln I-C / Z
$$

where $B$ is the stopping number in eq. (3), and $C=\sum_{i} C_{i}$, the sum of the shell-corrections. $L$ can be determined from eq. (2), when the experimental stopping power $S$ is known. Andersen et al. ${ }^{16}$ have shown, that the difference between $L$ for helium ions $L_{H e}$ and $L$ for hydrogen ions $L_{H}$ at the same particle velocity is almost independent of the absorber material. A plot of $L$-differences is shown in Fig. 5. Curve 1 is an average over Andersen's aluminium and tantalum measurements, and the open circles indicate the data of ref. 15 giving the $L$-difference for negative and positive pions, $L_{\pi-}-L_{\pi+}$, in nuclear emulsion. If we assume, that the particle charge correction is a linear function of $z$, we can from Andersen's and Heckman's measurements estimate $L_{o}-L_{H}$, the correction of $L$ for some artificial particles with zero charge.

Several hydrogen ion stopping power data for argon were compared with the present results by derivation of $L_{H e}-L_{H}$. Wolke et al. ${ }^{48}$ measured triton


Fig. 5. Comparison of stopping powers in various materials for particles with different charges and identical velocities. The difference $L_{H e}-L_{H}$ and $L_{\pi-}-L_{\pi}+$ as defined in section 6 is plotted versus equivalent proton energy $E_{p}=\left(M_{p} / M\right) \cdot E$ ( $M$ and $E$ mass and charge of appropriate ion). Curve 1: Andersen et al. ${ }^{16}$; curve 2: Wolke et al. ${ }^{48} /$ present; curve 3: Janni ${ }^{53} /$ present; - - $1 / Z(C(H e)-C(B))$ as defined in section $6 \mathrm{D} ; \bigcirc$ : Heckman and Lindstrom ${ }^{15} ;+: \mathrm{Cu}$ and $0: \mathrm{Au}$ from Ehrhardt et al. ${ }^{25} /$ Green et al. ${ }^{52}$; $\times$ : Reynolds et al. ${ }^{49} /$ present; $\square$ : Chilton et al. ${ }^{50} /$ present: $\boldsymbol{\Delta}$ : Brolley and $\mathrm{Ribe}^{51} /$ present. The errorbar indicates the effect of a $1 \%$ change in the stopping power of one particle.
ranges* and evaluated the stopping powers in the range $0.5-0.8 \mathrm{MeV}$ equivalent proton energies. Stopping powers of protons are reported by Reynolds et al. ${ }^{49}$ at $0.5-0.6 \mathrm{MeV}$, by Chilton et al. ${ }^{50}$ at $0.5-1 \mathrm{MeV}$, and by Brolley and Ribe ${ }^{51}$ at 4.43 MeV . Brolley and Ribe's data have to be compared with the $\alpha$-stopping power value of table V at 17.7 MeV , i.e. outside our experimental energy range.

For all argon data the errors of the proton measurements are of the same order of magnitude as the difference $L_{H e}-L_{H}$, but from figure 5 is seen, that the effect is systematic and significant. At $E_{p}=0.5 \mathrm{MeV}$ we have included the differences for some $\alpha$-particle and proton measurements in Cu and $\mathrm{Au}^{52,25}$, indicating the week dependence of the stopping material.

Janni's table of proton stopping powers in argon ${ }^{53}$ is also compared with the present measurements (curve 3 of fig. 5). They are semiempirical results from scaling and interpolating the shell-corrections for $E_{p} \gtrsim 1 \mathrm{MeV}$. At $E_{p}=$

[^6]

Fig. 6. Sum of shell-corrections $C$ to the stopping power formula (5), divided by $Z$, versus reduced energy $E_{p}=\left(M_{p} / M\right) E$, as defined in figure 5. Curve 1 : Bonderup ${ }^{57}$; curve 2 : present, derived from the fitting procedure described in section 4 D .

1 MeV a discontinuity appears, because the scaling method could not be applied in this region.

Recently Swint et. al. ${ }^{66}$ measured proton stopping powers for argon in the energy range $0.6-3.4 \mathrm{MeV}$. Their data are several percent higher than the measurements by other authors, and this would give $L$-differences far below zero on fig. 5 .

## 6D. Theory

Although no theoretical treatment of the particle charge dependence is available, a selection of theoretical computations of $I$-values and shellcorrections is presented.

Dalton and Turner ${ }^{54}$ reanalyzed a series of high and medium-energy proton data for argon, and made use of Fano's ${ }^{3}$ asymptotic shell corrections for the entire atom. Their $I$-value for argon is 189 eV , but no measurements were used for the computation, where the protons were in the same velocity range as our $\alpha$-particles.

A theoretical calculation of $I$ has been done by BELL ${ }^{55}$, using a procedure suggested by Dalgarno ${ }^{56}$ for interpolation of $I$ from known oscillator strength sums in Bethe's theory. Bell reports $I=196 \pm 23 \mathrm{eV}$.

Bonderup ${ }^{57}$ performed calculations of electronic stopping powers for heavy charged particles to quite low energies, by refining the procedure suggested by Lindhard and Scharff ${ }^{58}$, which makes extensive use of statis-
tical models of the atom. He presented his results as the shell corrections $C^{(B)}$ to the original Bethe formula, and used the $I$-value as a parameter*. They are plotted in Figure 6 versus equivalent proton energy $E_{p}$ together with the present shell corrections from the fitting procedure described in section 4 D , divided by $Z$. Since Bonderup's shell corrections are the same for different charged particles at the same velocity, it might be valuable to assign the calculations to particles with zero charge correction.

Andersen et al. ${ }^{16}$ indicated, that stopping powers for low charged particles were identical at the same velocities for $E_{p} \gtrsim 50 \mathrm{MeV}$, and we conclude, that the $L$-differences in Figure 5 are negligible for high energies. Also the shell-corrections are smaller than the experimental errors for high $E_{p}$ (ref. 3), and according to the definition of $L$-differences it is then reasonable to assign identical $I$-values for different charged particles. The $L$-differences, e.g. $L_{H e}-L_{H}$, are thus actually the differences in the shell-corrections $\left(C^{(H)}\right.$ - $\left.C^{(H e)}\right)$, divided by $Z$. By this interpretation we have in Figure 5 plotted the difference $(1 / Z) \cdot\left(C^{(H e)}-C^{(B)}\right)$ (dotted) with curve 1 as zero line; it is seen, that the resulting curve coincides with that zero charge correction, one could obtain from interpolation of Andersen's and Heckman's $L$-differences - in agrecment with the assignment of Bonderup's shell corrections $C^{(B)}$ to zero charged particles.

## 7. Conclusion

Energy losses up to 7.5 MeV of 6.058 MeV and $8.782 \mathrm{MeV} \alpha$-particles in argon have been measured within $2-5 \mathrm{keV}$. After correction of the data for multiple scattering, a fitting procedure using the Bethe theory for stopping powers gave the mean excitation potential $I=182 \mathrm{eV}$, and the shell-corrections. The derived stopping powers are within $0.3 \%$ for $2-8 \mathrm{MeV} \alpha$-particles. The comparison with other proton stopping power data is in agreement with the newly confirmed differences in stopping powers of different charged particles with identical velocities.

## 8. Acknowledgement

C.C.H. wants to thank dr. H. H. Andersen for our valuable discussions and private communications.

[^7]
## APPENDIX

## Correction to the Pathlength due to Multiple Scattering

Several authors have treated multiple scattering corrections to the pathlength of a beam of charged particles incident at right angles to a planeparallel slab of material $59,60,61,62$. In our case, however, it is a reasonable approximation, that the $\alpha$-particle source is isotropic over the plane facing the detector, and we cannot directly use the calculated corrections for a monodirectional beam.

Øveras ${ }^{28}$ has treated multiple scattering also for an "isotropic" beam, corresponding to the integration over all incident angles. Example 1) p. 64


Fig. 7. Exaggerated view of charged particle track suffering multiple scattering in plane layer of material. Symbols are defined in the text.
of ref. 28 fits to our geometry, except that the energy loss of the particles during their passage is neglected. Overas included the energy loss in several other cases, and it is the aim to present the derivation of the correction for example 1) with energy loss.

The definition of a series of formulas used in Overas's treatment will be necessary. For further details it is suggested to consult his report.

Formulation of problem: Consider a plane parallel layer of the material with a particle at angular incidence $\bar{\theta}_{0}=\left\{\Phi_{0}^{(2)}, \Phi_{0}^{(3)}\right\}$ as shown in Figure 7. The particle undergoes $N$ small angle scatterings $\bar{\theta}_{j}$ and emerges at the coordinate $\bar{r}=\left\{y^{(2)}, y^{(3)}\right\}$ relative to the line A. $\bar{\theta}=\left\{\Phi^{(2)}, \Phi^{(3)}\right\}$ is the angle of emergence.

The pathlength $s$ is then

$$
s=x+\varepsilon=\Lambda \sum_{j=0}^{N-1}\left(1+\bar{\theta}_{j}^{2}\right)^{1 / 2} \approx N \Delta+\frac{\Delta}{2} \sum_{j=0}^{N} \bar{\theta}_{j}^{2},
$$

where $x$ is the thickness of the layer, $\varepsilon$ the correction, and $\Delta=x / N$. The problem is to find $\varepsilon$ averaged over all possible paths $s$.

Probability Distribution: The probability for a single scattering event is approximated by the Gaussian

$$
\begin{equation*}
P\left(\bar{\theta}_{j}, \bar{\theta}_{j-1}\right)=\frac{\alpha_{j}}{\pi \Delta} \exp \left(-\frac{\alpha_{j}}{\Delta}\left(\bar{\theta}_{j}-\bar{\theta}_{j-1}\right)^{2}\right) \tag{9}
\end{equation*}
$$

where $\alpha_{j}$ is the mean square space angle per unit length, which gives the best Gaussian fit to Moliére's theory ${ }^{63,64}$.

Distribution of Projected Angle: It is more convenient to express $\varepsilon$ in the projected angle $\bar{\chi}_{j}=\left\{\xi_{j}^{(2)}, \xi_{j}^{(3)}\right\}$, where $\bar{\chi}_{j}=\bar{\theta}_{j}-\bar{\theta}_{j-1}$ for $j \geq 1$, and $\bar{\chi}_{0}=$ $\bar{\theta}_{0}$. Then the mean value $\bar{\varepsilon}$ of $\varepsilon$ for all incident angles $\bar{\theta}_{0}$ can be written

$$
\begin{equation*}
\bar{\varepsilon}=\frac{\Delta}{2} \sum_{k, l=0}^{N} D_{k l}\left[\overline{\xi_{k}^{(2)} \xi_{l}^{(2)}}+\overline{\xi_{k}^{(3)} \xi_{l}^{(3)}}\right]=\bar{\varepsilon}_{2}+\bar{\varepsilon}_{3}, \tag{10}
\end{equation*}
$$

where $D_{k l}=(N-k)$ for $k \geq l,(N-1)$ for $l \geq k$, and

$$
\overline{\xi_{k}^{(2)} \xi_{l}^{(2)}}=\overline{\xi_{k}^{(3)} \xi_{l}^{(3)}}=\overline{\xi_{k} \xi_{l}}=\int_{-\infty}^{\infty} \xi_{k} \xi_{l} p\left(\xi_{j} \mid v_{v}\right) d \xi_{0} \ldots d \xi_{N} .
$$

$p\left(\xi_{j} \mid v_{v}\right)$ is the distribution function of the projected angle, in close relation to the probability distribution in eq. (9). $p$ also depends on the experimental geometry - some specific conditions $v_{v}$, usually standing for $\Phi_{0}, \Phi$ and $y$. Average values of quantities projected in the directions (2) and (3) will be the same, because our geometry is symmetric along line A in figure 7.

Energy Loss: $\alpha_{j}$ in eq. (9) is not constant, but depends on the energy of the decelerated particle. Øveras used the approximate range-energy relation $R=C \cdot E^{1.8}$ to find $\alpha_{j}$ from $\alpha_{0}$, the mean square spaceangle at the particles entrance into the material.

Fourier Representation: In Øveras's treatment the distribution function $p\left(\xi_{j} \mid v_{\nu}\right)$ is transformed to the Fourier representation, and the geometrical conditions take form as Dirac $\delta$-functions

$$
\delta\left(\sum_{j=0}^{N} U_{\nu j} \xi_{j}-v_{v}\right),
$$

where $U_{v j}$ is defined in table VI.
The distribution function $p\left(\xi_{j} / v_{v}\right)$ has to be normalized by integration over all $\xi_{j}$. The resultant constant $w\left(v_{v}\right)$ takes the form

$$
\begin{equation*}
w\left(v_{\nu}\right)=\left(\frac{1}{4 \pi}\right)^{n / 2}\left(\frac{\pi}{a}\right)^{1 / 2} \frac{1}{\left\|\sigma_{v v^{\prime}}\right\|^{1 / 2}} \exp \left(b^{2} / 4 a-c\right) \tag{11}
\end{equation*}
$$

Tabel VI

| $v_{v}$ | $U_{v j}$ |
| :--- | :---: |
| $\Phi_{o}$ | $\delta_{j 0}$ |
| $\Phi$ | 1 |
| $y$ | $\Delta(N-j)$ |

where $n$ is the number of conditions $v_{v}$ defined by the geometry, and

$$
\left.\begin{array}{rlrl}
\sigma_{v v^{\prime}} & =(\Delta / 4) \sum_{j=1}^{N} U_{v j} U_{\nu^{\prime} j} / \alpha_{j} & & a=1 / 4 \sum_{\nu v^{\prime}=1}^{n} U_{v 0} U_{\nu^{\prime} 0} / \sigma_{\nu v^{\prime}} \\
b & =1 / 2 \sum_{\nu v^{\prime}=1}^{n} U_{\nu 0} v_{\nu^{\prime}} / \sigma_{\nu v^{\prime}} & & c=1 / 4 \sum_{\nu v^{\prime}=1}^{n} v_{\nu} v_{\nu^{\prime}} / \sigma_{\nu v^{\prime}} \tag{12}
\end{array}\right\}
$$

In this formalism it is possible to give an operative expression for the mean value $\bar{\xi}_{k} \xi_{l}$ :

$$
\begin{equation*}
\overline{\xi_{k} \xi_{1}}=\frac{1}{w}\left\{\frac{\Delta}{2 \alpha_{k}} \delta_{k l}+\frac{\Lambda^{2}}{4 \alpha_{k} \alpha_{l}} b_{k} b_{l}+\left(\frac{\Delta}{2 \alpha_{k}} \delta_{l 0} b_{k}+\frac{\Delta}{2 \alpha_{l}} \delta_{k 0} b_{l}\right) \xi_{0}+\xi_{0}^{2} \delta_{k 0} \delta_{l 0}\right\} w \tag{13}
\end{equation*}
$$

$b_{k}, b_{l}$, and $\xi_{0}$ are operators depending on the geometrical conditions:

$$
\begin{equation*}
b_{k}^{\chi} b_{1}^{\lambda} \zeta_{0}^{\omega}=\left(-\sum_{v=1}^{n} U_{v k} \frac{\partial}{\partial v_{v}}\right)^{\chi}\left(-\sum_{v^{\prime}=1}^{n} U_{v^{\prime} l} \frac{\partial}{\partial v_{v^{\prime}}}\right)^{\lambda} \frac{\partial^{\omega}}{\partial b^{\omega}} \tag{14}
\end{equation*}
$$

where $\kappa, \lambda, \omega$ are arbitrary positive integers.
When inserting (13) into (10), $\bar{\varepsilon}$ can be determined.
$\Phi_{0}$ and $\Phi$ integrated, $y$ specified: This situation corresponds to our special geometry, which is treated in expl 1) of Øveras's report ${ }^{28}$ p. 64 without energy loss. Since only one geometrical condition is present, $n=1$, and $v_{1}=y$. From table VI we get $U_{1 k}=\Delta(N-k)$, and we obtain from (11) and (12)

$$
\begin{aligned}
\sigma_{\nu v^{\prime}} & =\sigma_{11}=\frac{\Delta^{3}}{4} \cdot \sum_{k=1}^{N}(N-k)^{2} / \alpha_{k}, \quad a=\left(N^{2} / \Delta\right) / \sigma_{11} \\
b & =(\Delta N y / 2) \sigma_{11}, c=\left(y^{2} / 4\right) / \sigma_{11}, \quad \text { and } w=1 /(N \Lambda)
\end{aligned}
$$

For the operators defined in eq. (14) we get

$$
b_{k}=-\Delta(N-k) \partial / \partial y, \quad \text { and } \quad b_{j}=-\Delta(N-j) \partial / \partial y
$$

The operations on $w$, defined in eq. (11) reduce to

$$
\partial w / \partial y=0, \quad \text { and } \quad \partial w / \partial b=(w \cdot b) / 2 a
$$

We are now able to derive $\overline{\xi_{k} \xi_{l}}$ in eq. (13) and insert the result in (10) to find $\bar{\varepsilon}$ :

$$
\begin{equation*}
\bar{\varepsilon}(y)=\left(\Delta^{2} / 2\right) \sum_{k=0}^{N}(N-k) / \alpha_{k}-\left(\Lambda^{2} / 2 N\right) \sum_{k=0}^{N}(N-k)^{2} / \alpha_{k}+y^{2} / \Delta N \tag{15}
\end{equation*}
$$

Energy Loss: The summations in eq. (15) can be expressed as integrals defined by Øveras:

$$
\begin{aligned}
& A(m)=\left(6 \alpha_{0} / x^{3}\right) \int_{0}^{x}(x-\xi)^{2} / \alpha(\xi) d \xi \\
& B(m)=\left(2 \alpha_{0} / x^{2}\right) \int_{0}^{x}(x-\xi) / \alpha(\xi) d \xi
\end{aligned}
$$

where $m=Q x / R_{0}, Q=$ density of absorber, and $R_{0}=$ total range of incident particle. The final result for $y=0$ is

$$
\bar{\varepsilon}=\left(x^{2} / 12 a_{0}\right)(3 B(m)-A(m)),
$$

and table VII shows $\bar{\varepsilon}$ in $\mu \mathrm{gcm}^{-2}$ for some typical energy losses.

## Table VII

Average increase $\bar{\varepsilon}$ in pathlength of $\alpha$-particles due to multiple scattering. $<T>=$ incident energy, $\left\langle T_{1}\right\rangle=$ mean exit energy.

| $<T>=6.06 \mathrm{MeV}$ |  | $<T>=8.78 \mathrm{MeV}$ |  |
| :---: | :---: | :---: | :---: |
| 1 | 4.0 | 1 | 8.0 |
| 2 | 2.4 | 2 | 5.8 |
| 3 | 1.3 | 3 | 4.0 |
| 4 | 0.5 | 4 | 2.4 |
| 5 | 0.1 | 5 | 1.6 |
|  |  | 6 | 0.8 |
|  |  | 7 | 0.3 |

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## ENERGY LOSS AND STRAGGLING OF $100-500 \mathrm{keV}$ ATOMS WITH $2 \leq Z_{1} \leq 12$ IN VARIOUS GASES

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## Synopsis

The stopping cross section $S=\Delta E / N \Delta R$ and the reduced straggling $\Omega^{2} / N \Delta R$ for ions with $2 \leq Z_{1} \leq 12$ in the $100-500 \mathrm{keV}$ energy range was measured in helium, air, and neon. For $Z_{1}=2$ and $Z_{1}=8$, the stopping cross section was also measured in hydrogen and oxygen. The energy-loss distribution of the ions in the forward direction after penetration of a thin layer of gas contained in a differentially pumped gas cell was determined by means of a magnetic analyzer.

The previously found oscillatory dependence of the stopping cross section on the atomic number of the incident atom was also observed for the present target gases. Further, it was found that the stopping cross section for atoms with $Z_{1} \leq 10$ is smaller in neon than in air. By including data of other investigators, the $Z_{2}$ dependence of the stopping cross sections for $100-\mathrm{keV}$ $\mathrm{He}^{4}$ and $200-\mathrm{keV} \mathrm{O}{ }^{16}$ was investigated, and an oscillatory dependence with some similarity to the $Z_{1}$ oscillations was found.

At constant velocity, the energy straggling was found to be a monotonic function of $Z_{1}$. The straggling is compared with a theoretical prediction based on Firsov's equation for inelastic energy transfer in a single collision, and qualitative agreement is obtained.

## Introduction

TThe stopping cross section of heavy, charged particles of a few hundred keV has recently become a subject of renewed interest, see e.g. Ref. ${ }^{1)}$. In spite of this, only a few investigations of energy-loss straggling have been reported ${ }^{2,3)}$, so it was decided to make a rather broad investigation of energy-loss distributions of heavy, charged particles at keV energies penetrating thin layers of gas.

The present paper, which is only a part of a larger experimental study, deals with the energy loss and energy straggling suffered by light ions $\left(2 \leq Z_{1}\right.$ $\leq 12$ ) penetrating a layer of helium, air, and neon gas with energies from 100 to 500 keV , i.e. the energy region, where inelastic collisions are dominant in the slowing-down process. The remainder of the work will be published in two forthcoming papers, one of which will deal with energy-loss distributions in the velocity range, where the dominant mode of energy loss is elastic encounters between the projectile and the target atoms, and the other will deal with the energy-loss distribution of protons in the $100-500-\mathrm{keV}$ energy range, where slowing-down is due to inelastic collisions and may be treated by quantum-mechanical perturbation methods.

The main reason for the renewed interest in stopping cross-section measurements in the region, where the electronic stopping cross section $S_{e}$ is velocity-proportional, is the experimentally found oscillatory dependence of $S_{e}$ versus the atomic number $Z_{1}{ }^{4}$ ).

The nature of these oscillations have been subjected to various experimental tests both in random ${ }^{3,5-9)}$ and in crystalline materials ${ }^{10-12)}$. So far, the most pronounced oscillations have been found in single crystals for the well-channeled part of the transmitted beam.

The fact that the ratio between maxima and minima in stopping cross sections in an oriented single crystal is much larger that that of an amorphous target indicates that the oscillations are influenced by the selection of impact parameters in the collisions contributing to the stopping power. In order to
gain further insight in the slowing-down process, especially in the $Z_{1}$ oscillations, it was decided to investigate the energy straggling as a function of $Z_{1}$. Straggling in a random material is more strongly influenced by the close collisions than is the stopping power. Therefore, straggling measurements are well suited for systematic investigations of the extent to which the close collisions contribute to e.g. the $Z_{1}$ oscillations in stopping power. In the present paper, straggling is reported for projectiles with $2 \leq Z_{1} \leq 12$ in helium, air, and neon.

Stopping power can, of course, be obtained simultaneously from the experimetal data, and therefore also atomic stopping cross sections for the same combinations of projectile and target gas are reported.

As the present measurements include stopping cross sections in neon, where no previous measurements exist for projectiles heavier than protons, and also because of the growing interest in the $Z_{2}$ dependence of the stopping cross sections ${ }^{1,13)}$, it was decided to investigate this dependence in further detail. Therefore, stopping cross-section measurements of $\mathrm{He}^{4}$ and $\mathrm{O}^{16}$ have been extended to other gases (hydrogen, helium, air, oxygen, and neon). A discussion of the $Z_{2}$ dependence of the stopping cross sections is given on the basis of the existing data for $100-\mathrm{keV} \mathrm{He}{ }^{4}$ and $200-\mathrm{keV} \mathrm{O}^{16}$, together with the values reported in this paper.

## II. Theory

The penetration of charged particles through matter is normally treated by dividing the collisions into electronic and nuclear collisions (Ref. 14). The scattering of a particle is always dominated by nuclear collisions, whereas its energy loss in the present velocity range is mostly due to electronic collisions. Energy straggling is a more complicated problem to treat theoretically because the electronic and nuclear collisions cannot be considered to be independent. The energy straggling measured in the present experiment is, however, (as shown in section IV E), mainly determined by electronic collisions.

## A. Energy Loss.

A theoretical treatment of electronic stopping at low velocities has been given by Lindhard and Scharff ${ }^{15)}$. On the basis of the Thomas-Fermi statistical model, they calculated the electronic stopping cross section valid for ion velocities lower than $v_{0} Z_{1}^{2 / 3}$

$$
\begin{align*}
S_{e} & =\xi_{e} 8 \pi e^{2} a_{0}\left(Z_{1} Z_{2} / Z\right) \frac{v}{v_{0}}  \tag{1}\\
\left(Z^{2 / 3}\right. & \left.=Z_{1}^{2 / 3}+Z_{2}^{2 / 3}\right),
\end{align*}
$$

where $a_{0}$ and $v_{0}$ are the Bohr radius and the Bohr velocity, respectively, $Z_{1}$ and $Z_{2}$ the atomic numbers of projectile and target, $e$ the electron charge, and $\xi_{e}$ a constant of the order of $1-2$, which may vary approximately as $Z_{1}^{1 / 6}$.

At veloties around $v_{0}$, Lindhard et al. ${ }^{16)}$ have shown that the nuclear collisions also contribute to the slowing-down of atoms, and the total stopping cross sections may then be written

$$
\begin{equation*}
S=S_{e}+S_{n} \tag{2}
\end{equation*}
$$

where $S_{n}$ is the stopping cross section for nuclear collisions.
From a semiclassical Thomas-Fermi treatment, Firsov ${ }^{17)}$ calculated the inelastic energy transfer as a function of impact parameter:

$$
\begin{equation*}
T(p)=\frac{\left(Z_{1}+Z_{2}\right)^{5 / 3} 4.310^{-8} v}{\left[1+3.1\left(Z_{1}+Z_{2}\right)^{1 / 3} 10^{7} p\right]^{5}}[e V] \tag{3}
\end{equation*}
$$

valid when the atomic numbers of the colliding particles differ by no more than a factor of $4 . p$ is the impact parameter in cm and $v$ the velocity in $\mathrm{cm} / \mathrm{sec}$. From this formula, the electronic stopping cross section can be calculated as shown by Teplova et al. ${ }^{18)}$ :

$$
\begin{equation*}
S_{e}=\int_{0}^{\infty} T(p) 2 \pi p d p=5.15\left(Z_{1}+Z_{2}\right) 10^{-15}\left(\frac{v}{v_{0}}\right) e V \mathrm{~cm}^{2} / \text { atom } \tag{4}
\end{equation*}
$$

## B. Energy Straggling

When an initially monoenergetic beam passes through matter, the statistical nature of collision processes will cause an energy spread in the beam. The mean square deviation $\Omega^{2}$ of the energy distribution, commonly called the energy straggling, is, as shown by Bohr ${ }^{14)}$, given by

$$
\begin{equation*}
\Omega^{2}=N \Delta R \int T^{2} d \sigma, \tag{5}
\end{equation*}
$$

where $N \Delta R$ is the number of atoms per $\mathrm{cm}^{2}$, $T$ the energy transfer in a single collision, and $d \sigma$ the cross section for the energy transfer $T$. Here it is assumed that the energy is changed only little when passing the stopping layer. Under the further assumption that the energy transfer is a function of the impact parameter only, the straggling can be calculated as

$$
\begin{equation*}
\Omega^{2}=N \Delta R \int_{0}^{\infty} T^{2}(p) 2 \pi p d p . \tag{6}
\end{equation*}
$$

When Firsov's value for the inelastic energy transfer (Eq. (3)) is inserted, the electronic straggling is

$$
\begin{equation*}
\Omega^{2}=N \Delta R 8\left(Z_{1}+Z_{2}\right)^{8 / 3} 10^{-15}\left(\frac{v}{v_{0}}\right)^{2} \mathrm{eV}^{2} \mathrm{~cm}^{2} / \text { atom } . \tag{7}
\end{equation*}
$$

## III. Experimental

The ion beams used in this experiment were produced by the Aarhus $600-\mathrm{keV}$ heavy-ion accelerator. After acceleration and deflection in a $75^{\circ}$ double-focusing sector magnet, the beam entered the differentially pumped target region through small apertures. Having passed the target area, the beam was energy-analyzed by means of an analyzing magnet and detected by an open electron multiplier (see Fig. 1).

## A. Stopping Cell and Gas Equipment

The stopping cell consists of a differentially pumped gas cell, 828 mm $\pm 1 \mathrm{~mm}$ long and 100 mm in diameter. The gas cell has $1-\mathrm{mm}$ apertures (A) in both ends, and $2-\mathrm{mm}$ apertures (B) separating the differentially pumped region from the high vacuum (Fig. 1). Aperture C in Fig. 1 defines the beam divergence to within one third of a degree.

Helium, air, and neon were used as target gases. Dried atmospheric air was let in through a needle valve, while helium and neon were taken from steel flasks, where the pressure was held a little above 1 atm . These flasks were connected to the gas cell through a servo-controlled magnet valve. The control signal to the valve was supplied by an oil manometer ${ }^{19)}$, measuring the pressure in the gas cell. By this arrangement, the pressure could be kept constant to within 0.1 percent for sufficient time for the recording of the energy distribution. By the commercial supplier, the purities of the gases used were stated to be as follows: helium $99.9992 \%$ and neon $99.99 \%$.

The target pressure, normally around 0.1 torr, was measured with a McLeod manometer (Consolidated Vacuum Corporation, type GM-100A) with a systematic error smaller than $2 \%$. The outside pressure (regions AB, Fig. 1) was found to be $0.1 \%$ of the target pressure, and since the total distance $\mathrm{AB}+\mathrm{BA}$ is only one third of the distance BB , no correction for this effect was made. The target temperature was measured with a thermometer in close contact with the gas cell.


Figure 1. General diagram of the apparatus.

## B. Analyzing Magnet, Detectors, and Electronic Equipment

The analyzing magnet is a double-focusing sector magnet. The magnetic field was measured with a Hall probe, which, in turn, was calibrated against a resonance probe. The field measured with the Hall probe (to within $\pm 0.4 \%$ ) was fed to the $x$ axis of an $x y$ recorder. The deflected ions were detected with an open multiplier E (Fig. 1), and the undeflected neutral atoms were counted with a second open multiplier D (Fig. 1) for beam normalization during the period of measurement. The sensitive length of detector $E$ was $\sim 1 \mathrm{~mm}$, perpendicular to the magnetic field, giving an energy resolution of $\sim 0.1 \%$. The electronic equipment is shown in Fig. 1. The intensity of the deflected beam was plotted as a function of magnetic field by means of an $y x$ curve plotter.

## C. Determination of Energy Loss and Straggling

At each energy, a momentum spectrum was obtained with and without gas in the target chamber, cf. Fig. 2. The energy loss $\Delta E_{0}$ was calculated under the assumption that the energy $E$ of the transmitted beam is related to the magnetic field $B$ by the equation $E=k B^{2}$, where $k$ is a constant. On the basis of this equation, the most probable energy loss can be calculated as follows:


Figure 2. Momentum distributions of an incident 200 keV carbon beam and the same beam emerging from a $3.910^{17}$ atoms $/ \mathrm{cm}^{2}$ neon layer. $\Delta B$ is the reduction in the magnetic field corresponding to the two peak values. The latter distribution is transformed into a straight line on probability paper, and twice the standard deviation $\Delta B^{*}$ can be read directly.

$$
\begin{equation*}
\Delta E_{0}=E_{i} \frac{\Delta B}{B_{i}}\left(2-\frac{\Delta B}{B_{i}}\right), \tag{8}
\end{equation*}
$$

where $B_{i}$ is the analyzer magnetic field corresponding to the peak in the momentum distribution without gas in the target chamber, and $\Delta B / B_{i}$ the corresponding relative reduction in magnetic field for the peak of the momentum distribution with gas in the target chamber. $E_{i}$ is the energy of the incident beam.

For small values of $\Delta B / B$, the approximate relation

$$
\begin{equation*}
\Delta E=2 E \frac{\Delta B}{B}, \tag{9}
\end{equation*}
$$

where $E$ and $B$ are corresponding values, can be used. This means that over a short distance, the $B$ axis can be considered an energy axis. This approximation is used in the calculation of the standard deviations of the distributions, where normally $\Delta B / B<0.01$. The energy-distribution curve is expected to
be Gaussian in shape, and therefore the integral distribution was plotted on probability paper (Fig. 2). From the straight line, the standard deviation $\Omega_{2}$ was easily obtained as

$$
\begin{equation*}
\Omega_{2}=E \frac{\Delta B^{*}}{B} \tag{10}
\end{equation*}
$$

The standard deviation of the primary energy distribution $\Omega_{1}$ is experimentally found to be

$$
\begin{equation*}
\Omega_{1}=\frac{E}{2300} \tag{11}
\end{equation*}
$$

The straggling is given by

$$
\begin{equation*}
\Omega^{2}=\Omega_{2}^{2}-\Omega_{1}^{2} \tag{12}
\end{equation*}
$$

since the standard deviations add up geometrically.
In all cases reported here, $\Omega_{1}$ is small compared to $\Omega_{2}$, i.e. the exact magnitude of $\Omega_{1}$ is not important.

The number of molecules per $\mathrm{cm}^{2}$ is

$$
\begin{equation*}
N \Delta R=A L \frac{273}{(T+273)} \frac{P}{760} \tag{13}
\end{equation*}
$$

where $A=2.68710^{19}$ molecules/atm $\mathrm{cm}^{3}$ is Loschmidt's constant, $L$ the length of the gas cell, $T$ the temperature in ${ }^{\circ} \mathrm{C}$, and $P$ the pressure in mmHg .

The observed stopping cross section $S_{0}$ is defined as

$$
\begin{equation*}
S_{0}=\frac{\Delta E_{0}}{N \Delta R} \tag{14}
\end{equation*}
$$

at the energy $E=E_{i}-\Delta E_{0} / 2$, and the reduced straggling is defined as $\Omega^{2} / N \Delta R$ at the same energy.

The non-systematic errors are as follows:
(i) uncertainties in the determination of $\Delta E$ and $\Omega$ (mainly uncertainties in $\triangle B): 3 \%$,
(ii) uncertainty in gas pressure: $3 \%$, and,
(iii) uncertainty in the temperature measurements : $10 / 0$.

The uncertainty of $E_{i}$ is $\sim 0.1 \%$.

## IV. Results and Discussion

## A. Values of Stopping Cross Sections

The measured stopping cross section $S_{0}$ is corrected for nuclear stopping in the way shown by Fastrup et al. ${ }^{7}$. Here, the measured stopping cross section is assumed to be the sum of the electronic stopping cross section $S_{e}$ and the partial nuclear stopping cross section $S_{n}^{*}$, corresponding to the most probable energy loss in nuclear collisions, i.e.

$$
\begin{equation*}
S_{0}=S_{e}+S_{n}^{*} \tag{15}
\end{equation*}
$$

For details, see ref. 7). In the measurements reported here, the corrections for nuclear collisions are smaller than $10^{\circ} / 0$ and in most cases can be neglected.

Figure 3 shows the electronic stopping cross section of $\mathrm{Li}^{7}$ in neon as a function of energy. It is observed that the experimental values over the energy interval investigated are well described by a straight line on a $\log$ - $\log$ plot. This is valid for all the target-projectile combinations investigated, except for $\mathrm{He}^{4}$ in hydrogen.

The results for the electron stopping cross sections are listed in Table I in the convenient form of

$$
\begin{equation*}
S_{e}=k E^{P}, \tag{16}
\end{equation*}
$$

where $k$ and $P$ are constants.
It is estimated that the correct stopping cross section lies within $\pm 5 \%$ of the best straight line through the experimental points.

## B. Comparison with Other Experiments

$W_{E Y L}{ }^{20}$ has measured the stopping cross sections for $\mathrm{He}^{4}, \mathrm{~N}^{14}$, and $\mathrm{Ne}^{20}$ projectiles in helium and air in the $150-$ to $400-\mathrm{keV}$ energy interval. In the cases where helium is used as target gas, the agreement with the present results is better than $2 \%$. On the other hand, Weyl's results lie approximately $10 \%$ higher than the present values for $\mathrm{He}^{4}$ and $\mathrm{N}^{14}$ in air, and $20 \%$ higher for Ne in air. The fact that Weyl did not correct for nuclear stopping partly explains this discrepancy. Allison and Littlejohn ${ }^{21}$ have measured the stopping cross section for Li ions in helium and air in the $100-$ to $500-\mathrm{keV}$ energy interval. In helium, the agreement is within $2 \%$, but their results in air lie $10 \%$ below the present results.

For $6 \leq Z_{1} \leq 12$ and with air as target gas, the present data may be compared with the data reported by Fastrup et al. ${ }^{9}$, where the same experimental setup was used. The older data lie from $10 \%$ to $16 \%$ above the present results.


Figure 3. Electronic stopping cross section $S_{e}$ versus energy for $\mathrm{Li}^{7}$ in neon.

This discrepancy is difficult to understand, but it should be mentioned that in the present experiment, a McLeod gauge was connected to the experimental setup so that the actual pressure could be read directly. In the older experiment, the pressure was measured with a membrane manometer, which afterwards was calibrated against a McLeod gauge, and most likely a change in the membrane manometer may have taken place between the time of the measurements and the calibration.

Since the stopping power is the same (within experimental error) in air and oxygen, it should be possible also to compare the present stopping cross sections in air with Ormrod's values ${ }^{6}$ for stopping cross sections in nitrogen. At $\sim 200 \mathrm{keV}$, his data lie from $0 \%$ to $6 \%$ above the data obtained in this experiment.

With neon as target gas, no other experimental data are available for comparison.

The conclusion is that all available stopping-power data with helium as target gas agree to within $2 \%$, whereas the experimental data with air as target gas scatter much more than the quoted experimental errors.

Table I.
Experimental values of exponent $P$ and coefficient $k$ in $S_{e}=k E^{P}, S_{e}$ in $\left(\mathrm{eV} \mathrm{cm}^{2} /\right.$ atom) and $E$ in (keV).

| $\qquad$ | Air |  | He |  | Ne |  | Energy <br> Interval (keV) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $k \cdot 10^{15}$ | $P$ | $k \cdot 10^{15}$ | $P$ | $k \cdot 10^{15}$ | $P$ |  |
| $\mathrm{He}^{4}$ | 5.14 | 0.33 | 0.802 | 0.51 | 3.48 | 0.38 | 100-500 |
| Li ${ }^{7}$. | 1.15 | 0.60 | 0.136 | 0.77 | 1.29 | 0.55 | 100-500 |
| $\mathrm{Be}^{9}$ | 1.95 | 0.53 | . . | . . . | 3.00 | 0.43 | 200-500 |
| $\mathrm{B}^{11}$. | 2.12 | 0.55 | 0.50 | 0.59 | 1.74 | 0.55 | 200-500 |
| $\mathrm{C}^{12}$ | 3.93 | 0.46 | 1.30 | 0.50 | 1.88 | 0.56 | 200-500 |
| $\mathrm{N}^{14}$. | 4.13 | 0.47 | 1.20 | 0.51 | 2.35 | 0.53 | 200-500 |
| $\mathrm{O}^{16}$ | 3.97 | 0.46 | 1.77 | 0.44 | 3.29 | 0.48 | 200-500 |
| $\mathrm{F}^{19}$ | 2.75 | 0.49 | 1.48 | 0.43 | 4.00 | 0.43 | 200-500 |
| $\mathrm{Ne}^{20}$. | 1.96 | 0.53 | 0.74 | 0.53 | 1.79 | 0.56 | 200-500 |
| $\mathrm{Na}^{23}$. | 1.08 | 0.61 | 0.286 | 0.63 | 1.86 | 0.53 | 200-500 |
| $\mathrm{Mg}^{24}$. | 0.663 | 0.67 | 0.133 | 0.70 | 0.93 | 0.63 | 200-500 |


| Gas <br> Projectile | $\mathrm{O}_{2}$ |  | $\mathrm{H}_{2}$ |  | Energy <br> Interval <br> $(\mathrm{keV})$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  | $k \cdot 10^{15}$ | $P$ | $k \cdot 10^{15}$ | $P$ |  |
|  | 5.08 | 0.34 |  |  | $100-300$ |
| $\mathrm{O}^{16} \ldots \ldots \ldots \ldots$ | 3.35 | 0.49 | 0.446 | 0.61 | $100-300$ |

$\mathrm{He}^{4}$ in $\mathrm{H}_{2}$

| $E$ <br> $(\mathrm{keV})$ | $S_{e} \times 10^{14}$ <br> eV cm |
| :---: | :---: |
| 100 | 0.62 |
| 150 | 0.80 |
| 200 | 0.93 |
| 300 | 1.08 |

## C. $Z_{1}$ Dependence of Stopping Cross Section

Figures 4 and 5 show $S_{e}$ versus $Z_{1}$ in different target gases at a constant velocity $0.9 v_{0}$ of the projectile, together with the theoretical curves by Lindhard and Scharff ${ }^{15}$. It is observed that in all cases, the experimental curves are below theoretical estimates, as was found earlier by Ormbod ${ }^{6)}$ and Fastrup et al. ${ }^{9)}$ in gaseous targets. Further, it is seen that the experimental curves


Figure 4. Electronic stopping cross section and straggling values at constant velocity ( $0.9 v_{0}$ ) for a helium target, as a function of $Z_{1}$.


Figure 5. Electronic stopping cross section values at constant velocity ( $0.9 v_{0}$ ) for an air target and a neon target, as a function of $Z_{1}$. Theoretical curve from equation (1).
exhibit oscillations similar to those found in single crystals and in other solid and gaseous targets. The positions of maxima and minima are roughly the same as those found by others in various target materials.

## D. $Z_{2}$ Dependence of Stopping Cross Section

Figure 5 shows that for a given projectile and energy, the stopping power is smaller in neon than in atmospheric air for $Z \leq 9$. Also in cases where


Figure 6. Electronic stopping cross section versus $Z_{2}$. The experimental values are partly from this paper and partly measured or interpolated values from Refs. 1, 3, 4-6 and 22. Theoretical curves from equation (1).
there is an energy overlap with Ormbod's ${ }^{6}$ ) measurements of stopping power in nitrogen, the same decrease in stopping power is observed when going from nitrogen to neon.

Based on the stopping cross sections measured by others ${ }^{1,3,4-6,22)}$ and on present results, Fig. 6 shows the variation in stopping cross section for $200-\mathrm{keV}$ $\mathrm{O}^{16}$ ions and $100-\mathrm{keV} \mathrm{He}{ }^{4}$ ions. The velocity of the ions is well below $v_{0} Z_{1}^{2 / 3}$, and the stopping cross sections may be compared with the theoretical values given by Eq. (1). It should be mentioned here that the relative uncertainty in a plot of $S_{e}$ versus $Z_{2}$ is larger compared with a plot of $S_{e}$ versus $Z_{1}$, due to the difficulty of measuring the absolute thickness of the targets. In spite of this, at a given energy $S_{e}$ clearly demonstrates an "oscillatory" dependence on $Z_{2}$. It is observed that the theoretical curves represent good mean values of the experimental points and that the $Z_{2}$ "oscillations" have some similarity to the $Z_{1}$ oscillations.

Recently, various groups have investigated the stopping power for a given projectile as a function of target material. White and Mueller ${ }^{1)}$ measured
the stopping power of $\mathrm{H}^{1}$ and $\mathrm{He}^{4}$ in $\mathrm{Cr}, \mathrm{Mn}, \mathrm{Fe}, \mathrm{Ca}, \mathrm{Ni}$, and Cu at 100 keV and found, by collecting all stopping-power data for $100-\mathrm{keV}$ protons, that the stopping power exhibits an oscillatory dependence on $Z_{2}$ with minima at $Z_{2}=10$ and $Z_{2} \simeq 30$.

Bernhard et al. ${ }^{13)}$ have measured stopping cross sections for Li ions in $\mathrm{C}, \mathrm{Al}, \mathrm{Ti}$, and Cu , and in comparison with the data of others, they obtain a characteristic $Z_{2}$ dependence for the stopping power. They conclude that the dependence of the electronic stopping cross section on the atomic number of the target atom may be influenced by the structure of the target, i.e. by the target being in the gas phase or in the solid phase. This statement is not strongly supported by Fig. 6, but this is possibly due to the higher velocities compared with the velocity used by Bernhard et al. ${ }^{13}$ ) , $v \sim 0.4 v_{0}$ ). The abrupt change in $S_{e}$ from carbon to nitrogen, which Bernhard et al. took as a support of the dependence of $S_{e}$ on the target density, decreases when the energy is increased (see Refs. ${ }^{4)}$ and ${ }^{6)}$ ).

## E. Energy Straggling

Like the stopping cross section, the measured energy straggling also depends on both the elastic and the inelastic energy transfer to the target atoms, but in a more complex way. In the present velocity range, range straggling is normally attributed to nuclear collisions only ${ }^{23)}$. In the present experiment, however, particles which have experienced violent nuclear collisions with target atoms, are scattered out of the small acceptance angle of the analyzing magnet and do not contribute to the observed energy-loss distribution.

In order to illustrate what is measured in this experiment, an example will be calculated. Figure 7 shows the energy transfer in a collision as a function of the impact parameter. The inelastic energy loss is calculated from Eq. (3), and the elastic energy transfer is calculated from a power potential $V(r) \propto r^{-2}$ (see Ref. 16). Also shown is the total energy transfer.

The angular distribution of the particles emerging from the target gas may be divided into a Gaussian peak and a tail. Collisions involving individual deflection angles smaller than $\varphi^{*}$ produce the Gaussian distribution, and collisions with deflection angles larger than $\varphi^{*}$ produce the tail distribution.

A good first-order estimate of $\varphi^{*}$ is, as shown by Bohr ${ }^{14)}$, the standard deviation of the Gaussian distribution, i. e.

$$
\begin{equation*}
\left(\varphi^{*}\right)^{2} \approx N \Delta R \int_{0}^{\varphi^{*}} \varphi^{2} d \sigma \tag{17}
\end{equation*}
$$



Figure 7. Energy transfer in a single collision as a function of the impact parameter. Inelastic energy transfer from equation (3). The elastic energy transfer is calculated from a power potential $V(r) \propto r^{-2}{ }^{16)} . T_{n}^{*}$ and $p_{\min }$ refer to the maximum elastic energy transfer, and the corresponding impact parameter for atoms still belonging to the forward-directed beam as defined in text. $\left(N \Delta R=5 \cdot 10^{17}\right.$ atoms $\left./ \mathrm{cm}^{2}\right)$.
where $d \sigma$ is the differential scattering cross section for an angular deflection $\varphi$. For $\varphi^{*} \ll 1$, which is normally the case,

$$
\begin{equation*}
\left(\varphi^{*}\right)^{2} \sim \frac{M_{2} T_{n}^{*}}{M_{1} E}, \tag{18}
\end{equation*}
$$

where $T_{n}^{*}$ is the nuclear energy transfer from the projectile with mass $M_{1}$ to the target atom with mass $M_{2}$.

Now, since the acceptance angle is small compared to $\varphi^{*}$ (i.e. $\sim 0.1 \varphi^{*}$ ), the particles accepted by the analyzer will be those experiencing collisions in the energy interval $0<T<T_{n}^{*}$.

In Fig. 7, $T_{n}^{*}$ is shown for the actual case. If the straggling is now calculated as

$$
\begin{equation*}
\Omega^{2}=N \Delta R \int_{p_{\min }}^{\infty} 2 \pi p\left(T_{n}+T_{e}\right)^{2} d p, \tag{19}
\end{equation*}
$$

where $p_{\min }$ is defined as the impact parameter corresponding to the nuclear energy transfer $T_{n}^{*}$, then in the actual case, 100 keV Li in $\mathrm{Ne}\left(N \Delta R=5 \times 10^{17}\right.$ atoms $/ \mathrm{cm}^{2}$ ),

$$
\begin{equation*}
\Omega>T_{n}^{*}+T_{e}\left(p_{\min }\right) \tag{20}
\end{equation*}
$$

This means that one would expect a Gaussian energy distribution for the forward-directed beam. If the foundation of these calculations is accepted, the elastic part of the collisions will contribute with less than $10 \%$ to the measured straggling $\Omega^{2}$. On the other hand, the straggling resulting from inelastic collisions with impact parameters smaller than $p_{\text {min }}$ is excluded. In the present example, this also amounts to $\sim 10 \%$, so the straggling in the forward-directed beam is, as described above, a rather well-defined quantity, mainly determined by inelastic collisions.

As the elastic and inelastic part of a collision cannot be treated as two independent collisions, it is difficult to separate the straggling into an electronic and a nuclear part as is done for the stopping cross section. Therefore no corrections for nuclear straggling have been applied for the straggling measurements.

Figure 8 shows the experimental values of $\Omega^{2} / N \Delta R$ for different projectiles in helium and air together with the theoretical curve as calculated from Eq. 7. It should be mentioned that the energy distribution curves for low energy and large $Z_{1}$ are slightly asymmetric. This is attributed to the fact that $\Omega<T_{n}^{*}+T_{e}\left(p_{\min }\right)$ which, according to $\mathrm{BoHR}^{14}$, should give rise to an asymmetric energy distribution. Each of the experimental points is an average of at least two experimental measurements. The values of $\Omega^{2} / N \Delta R$, read from a smooth curve through the experimental points, are given in Table II.

It is estimated that apart from probable mixing from nuclear collisions, the correct straggling values lie within $\pm 10 \%$ of the values given by the smooth curves through the data of Fig. 8.

Due to the linear dependence of $\frac{\Omega^{2}}{N \Delta R}$ on $E$ in a log-log plot found in most cases (Fig. 8), it seems justified to assume the following equation for the energy dependence of the straggling for a fixed target-projectile combination:

$$
\begin{equation*}
\frac{\Omega^{2}}{N \Delta R}=k_{1} E^{P_{1}} \tag{21}
\end{equation*}
$$

Equation (7) indicates that the theoretical value of $P_{1}$ is unity. Table III shows the experimental $P_{1}$ values for the four low- $Z$ projectiles, since here

Table II. Relative straggling $\Omega^{2} / N \Delta R$ in units of $10^{-12} \mathrm{eV}^{2} \mathrm{~cm}^{2} /$ atom.

| Projectile | Energy (keV) | He | $\begin{aligned} & \text { Gas } \\ & \text { Air } \end{aligned}$ | Ne |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{He}^{4}$ | 100 | 0.54 | 2.4 | 1.85 |
|  | 200 | 0.94 | 4.4 | 3.6 |
|  | 300 | 1.40 | 5.6 | 4.9 |
|  | 400 | 1.80 | 6.4 | 5.7 |
|  | 500 | . | 6.9 | 6.4 |
| $\mathrm{Li}^{7}$. | 100 | 0.38 | 2.1 | . |
|  | 200 | 0.77 | 4.4 | . |
|  | 300 | 1.13 | 6.9 | . |
|  | 400 | 1.55 | 9.2 | . |
|  | 500 | 1.93 | 11.0 | . |
| $\mathrm{B}^{11}$. | 200 | 0.65 | 5.8 | 3.6 |
|  | 300 | 0.94 | 8.0 | 5.2 |
|  | 400 | 1.42 | 9.7 | 6.9 |
|  | 500 | 1.80 | . | . |
| $\mathrm{C}^{12}$. | 200 | 0.86 | 7.6 | 4.7 |
|  | 300 | 1.16 | 12.0 | 7.4 |
|  | 400 | 1.45 | 16.0 | 9.6 |
|  | 500 | 1.70 | 20.0 | 11.8 |
| $\mathrm{N}^{14}$. | 200 | 1.20 | 9.8 | 6.0 |
|  | 300 | 1.63 | 12.6 | 8.8 |
|  | 400 | 2.05 | 16.0 | 11.0 |
|  | 500 | 2.40 | 19.5 | 13.9 |
| $\mathrm{O}^{16}$. | 200 | 1.25 | 10.6 | 8.1 |
|  | 300 | 1.75 | 13.6 | 10.2 |
|  | 400 | 2.20 | 17.8 | 13.0 |
|  | 500 | 2.80 | 22.4 | 16.8 |
| $\mathrm{Ne}^{20} \ldots . .$. | 200 | 1.28 | 11.5 | 12.2 |
|  | 300 | 1.65 | 14.0 | 13.8 |
|  | 400 | 2.10 | 18.3 | 16.1 |
|  | 500 | 2.65 | 22.0 | 19.2 |
| Mg ${ }^{24} \ldots . .$. | 200 | -• | 10.0 | 12.0 |
|  | 300 | - | 13.0 | 12.9 |
|  | 400 | . | 15.5 | 16.2 |
|  | 500 | . | 18.8 | 19.5 |



8 a .


Fig. 8 c .


Fig. 8 b.


Fig. 8 d .
Figure 8. Relative straggling $\Omega_{2} / N \triangle R$ versus energy. Theoretical curves from equation (7).

Table III. Experimental values of exponent $P_{1}$ in $\Omega^{2} / N \Delta R=k_{1} E^{P_{1}}$.

|  | Gas | He | Air |
| :--- | ---: | ---: | ---: |
| Projectile |  | Ne |  |
| $\mathrm{He}^{4} \ldots \ldots \ldots \ldots$ | $\sim 0.87$ | 0.86 | 0.95 |
| $\mathrm{Li}^{7} \ldots \ldots \ldots \ldots$ | 1.00 | 1.02 | - |
| $\mathrm{B}^{11} \ldots \ldots \ldots \ldots$ | 1.25 | 0.74 | 0.92 |
| $\mathrm{C}^{12} \ldots \ldots \ldots \ldots$ | 0.74 | 1.04 | 0.95 |

the contribution from nuclear collisions is expected to be negligible. It is seen that the experimental values are fairly close to the theoretical value $P_{1}=1$. With $\mathrm{He}^{4}$ as projectile, only the experimental values at 100 and 200 keV are used for the determination of $P_{1}$ because the points at higher energies fall outside the region of the validity of Eq. (7). The upward bend of the experimental curves at low energies for $Z_{1}>6$ is believed to be caused by an increasing mixture from nuclear collisions with decreasing energy.

On Figure $4,\left(\Omega^{2} / N \Delta R\right)^{1 / 2}$ is plotted together with the stopping cross section $S_{e}$ at a constant velocity $v=0.9 v_{0}$ as a function of $Z_{1}$. It is noticed that the straggling (contrary to the stopping power) is a monotonic function of $Z_{1}$. Further it is observed that the $Z_{1}$ oscillations in straggling, if any, are much less pronounced compared with the $Z_{1}$ oscillations found for $S_{e}$. This may indicate that a statistical model of the atom is well suited for describing straggling, with its enhanced dependence on collisions with small impact parameters compared with the stopping power.

Figure 9 shows the straggling $\Omega^{2} / N \Delta R$ at a constant velocity $v=0.9 v_{0}$ plotted for different target-projectile combination as a function of ( $Z_{1}+Z_{2}$ ). It is observed that the straggling for a fixed energy and projectile is smaller in neon than in air. The deviation is larger for $Z_{1} \sim 7$, just as was the case for the stopping cross section. Although large deviations exist between theory and experiment, Fig. 9 shows that the theoretical curve represents a good mean curve to the present experimental points.

## V. Conclusions

Stopping power measurements in single crystals and in amorphous targets, together with this investigation of energy straggling, demonstrate that the $Z_{1}$ oscillations depend strongly on the relative importance of collisions with various impact parameters. The most pronounced oscillations have been found


Figure 9. Relative straggling $\Omega^{2} / N \Delta R$ at constant velocity $\left(0.9 v_{0}\right)$ as a function of $\left(Z_{1}+Z_{2}\right)$. Also shown is the theoretical curve (eq. (7)).
in the stopping power in aligned single crystals, and no clear indication of $Z_{1}$ oscillations of the same kind have been found in the straggling in a random material.

The present measurements show that the functional dependence of straggling on $Z_{1}, Z_{2}$, and energy, is rather well accounted for by Eq. (7). Further,
the absolute values of straggling agree with the theory within a factor of two. It means that Eq. (7) is well suited for first-order estimates of the straggling in the forward-directed beam.

Some evidence of $Z_{2}$ oscillations in stopping power have been found, but further experimental investigations are needed. At present, it is not clear whether these oscillations are of the same nature as the $Z_{1}$ oscillations or whether to some extent they depend also on other mechanisms, such as target density.

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# A. N. GORDEYEV <br> PLASMA SURFACE RADIATION 

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## Synopsis

A simple model for the radiation from a plasma surface layer is proposed. The intensity of the radiation, its frequency spectrum, and its pressure on the emitting surface are considered.

## 1. Introduction

TThere are three main mechanisms of electromagnetic radiation in a hightemperature plasma. These are: 1) bremsstrahlung due to Coulomb collisions of electrons with massive particles, 2) synchrotron radiation from electrons spiraling in a magnetic field, and 3) Cherenkov radiation. All these radiation processes take place inside a plasma volume.

However, in addition to these, electromagnetic radiation of another type must exist in a plasma. It is the bremsstrahlung from the electrons of a space charge near a plasma surface due to their deceleration in a selfconsistent electric field. In the following, we consider the simplest model for such a radiation, its intensity, frequency spectrum, and the pressure which acts on the emitting surface as a result of a radiative reaction.

With regard to the radiative pressure, it should be noticed that usually it is regarded as part of a total pressure, which causes the expansion of the system (e.g., inside stars). However, this is true only for a radiation inside a cavity which, while it reflects from the walls of the cavity, causes an outward pressure. In the case of an open system, the radiation emitted into the outer space acts on the radiating surface with a force of reaction directed inwards. Thus, the momentum carried out with the radiation from the unit area of the surface per unit time is equivalent to a pressure compressing the system.

If a plasma existed radiating like a black body at sufficiently high temperature, the radiative reaction would produce an effect of "walls" preventing the system from expanding. In that case, the radiative pressure would be equal to $\sigma T^{4} / C$ according to the Stefan-Boltzmann law.

Since the kinetic pressure in a plasma $p$ can be expressed by its temperature $k T$ from the equation of state for the perfect gas $p=n k T$, where $n$ is the numerical density of plasma particles, it is seen that, at $T=10^{5}{ }^{\circ} \mathrm{K}$, the radiative reaction would be able to compensate the pressure of a plasma with concentration $n=10^{16}$ particles $/ \mathrm{cm}^{3}$ (that is enough, for example, if the thermonuclear fusion took place in a deitherium plasma). At a temperature $10^{8}{ }^{\circ} \mathrm{K}$, the "confinement concentration" is equal to $10^{25}$ particles $/ \mathrm{cm}^{3}$.

Actually the radiation from a tenuous plasma is considerably less than that of a black body and therefore the contribution of its reaction to the confinement, though positive, is very small. At the same time, in the case of a more dense plasma of stars, the contribution can be rather essential. It is especially important in view of the well-known feature of gravitation that cannot provide the stable existence of a finite hot system in vacuo. There is also a chance that, in a future device for controlled thermonuclear fusion, the radiative reaction can help essentially to a main confinement mechanism if the process takes place in a dense plasma and the energy is utilized through the radiation.

## 2. Situation near a plasma surface

We consider a quasi-neutral plasma in which an electronic charge is compensated on the average by a positive ion background. Like any hot conductor, the plasma must be surrounded with a cloud of a space charge which consists of thermo-emission electrons crossing a plasma surface owing to their thermal motion. These electrons and the plasma surface itself produce an electric field.

To obtain an electrostatic potential of that self-consistent field, we have to solve the Poisson equation with the density of the thermo-electronic space charge in the right-hand side and the boundary condition corresponding to the equality between a surface charge density and the total space charge under unity area (neutrality condition). Since a layer of the space charge is very thin (its thickness has an order of the Debye length), one can restrict oneself to a one-dimensional solution of the Poisson equation that provides an expression for the electric field near the plasma surface independently of a configuration of the system.

With a usual assumption, the electron density of the space charge obeying the Boltzmann distribution law and taking the $z$-axis along an outward normal to a plasma surface, one has the following solution for the potential $\left.\Psi(z)^{1}\right)$ :

$$
\begin{equation*}
\Psi(z)=-\frac{2 k T}{e} \ln \left(\frac{z}{a}+1\right) \tag{1}
\end{equation*}
$$

where $k T$ is the temperature in energy units, $e$ is the electronic charge, $a=\sqrt{ } k T / 2 \pi e^{2} n_{0}$ is the Debye length, $n_{0}$ being an electron density at $z=0$ (at the plasma surface).

This gives the electric field $E$ :

$$
\begin{equation*}
E_{z}=-\partial \Psi / \partial z=2 k T / e(z+a), E_{x}=E_{y}=0, \tag{2}
\end{equation*}
$$

which acts on the electrons of the space charge and returns them backwards into a plasma.

Such a motion of electrons must be accompanied by an electromagnetic radiation. The power $d W_{n}(t)$ radiated by one charge into the solid angle $d \Omega=\sin \Theta d \Theta d \Phi$ in the direction of the unit vector $\boldsymbol{n}$ is $^{2}$ )

$$
\left.\begin{array}{rl}
d W_{\boldsymbol{n}}(t)= & \frac{e^{2}}{4 \pi c}\left\{\frac{2(\boldsymbol{n} \cdot \dot{\beta})(\beta \cdot \dot{\beta})}{(1-\boldsymbol{n} \cdot \beta)^{4}}+\frac{\dot{\beta}^{2}}{(1-\boldsymbol{n} \cdot \beta)^{3}}\right.  \tag{3}\\
& \left.-\frac{\left(1-\beta^{2}\right)(\boldsymbol{n} \cdot \dot{\beta})^{2}}{(1-\boldsymbol{n} \cdot \beta)^{5}}\right\} d \Omega,
\end{array}\right\}
$$

$\beta=\boldsymbol{V} / C, \nabla$ and $\dot{\nabla}$ being a velocity and an acceleration of the charge, respectively.

Expressing the acceleration $\dot{\boldsymbol{V}}$ by an electric field $\boldsymbol{E}$ from the relativistic equation of an electron motion and taking into account that the field (2) has a constant direction along the $z$-axis, we can rewrite (3) in the form

$$
\begin{equation*}
d W_{\boldsymbol{n}}(t)=\frac{e^{4} E^{2}}{4 \pi m^{2} c^{3}}\left\{\frac{\left(1-\beta^{2}\right)\left(1-\beta_{z}^{2}\right)}{(1-\boldsymbol{n} \cdot \beta)^{3}}-\frac{\left(1-\beta^{2}\right)^{2}\left(\cos \Theta-\beta_{z}\right)^{2}}{(1-\boldsymbol{n} \cdot \beta)^{5}}\right\} d \Omega . \tag{4}
\end{equation*}
$$

Here, $E$ is the $Z$-component of the field (2) and a polar axis has been taken along the $z$-axis (i.e., along the direction of the field $\boldsymbol{E}$ ). With such a choice for the polar axis, we get

$$
\begin{equation*}
1-\boldsymbol{n} \cdot \beta=1-\beta_{z} \cos \Theta-\left(\beta_{x} \cos \Phi+\beta_{y} \sin \Phi\right) \sin \Theta! \tag{5}
\end{equation*}
$$

Since we are interested in the total power radiated, we have to take a sum of expressions like (4) for all the charges crossing the unit area of the plasma surface. The electrons cross the surface with different initial velocities, but we consider for a while only the particles which pass through a plasma surface element $\Delta S$ having almost equal initial velocities $\boldsymbol{V}_{\mathbf{0}}$ in an interval $\boldsymbol{d} \boldsymbol{V}_{0}$. These particles are moving in the field (2) inside a narrow current tube, which would have a parabolic shape if the motion were a nonrelativistic one and the field $\boldsymbol{E}$ were uniform (projectile motion).

Since electrons in the space charge are supposed to have a stationary distribution, the same number of particles pass any cross section of the tube
per unit time. This is just the same number of particles that leaves the plasma and enters the field through $\Delta S$ per unit time and returns back in another place having the same magnitude but the opposite sign of the $Z$ component of the velocity $V_{z}$.

To obtain a radiation from the current tube, consider its element of length $d l$. A volume of the element equals $\Delta S_{n} d l$, and the number of particles inside is $n \Delta S_{n} d l$, where $n$ is the electron concentration in the tube and $\Delta S_{n}$ is its normal cross section (both values are varying along the tube). Then, the radiation of the particles is

$$
\begin{equation*}
\frac{d W_{n}^{\prime}}{d \Omega}=\int\left(\frac{d W_{n}}{d \Omega}\right)_{1} n \Delta S_{n} d l \tag{6}
\end{equation*}
$$

where the integrand is the radiation power for one particle (4) and the integral is to be taken along the current tube.

Using the time of the motion $t$ as a parameter and taking into account that $d \boldsymbol{l}=\boldsymbol{V} d t$, we can rewrite the expression (6) as an integral along the path of a particle:

$$
\begin{equation*}
\frac{d W_{n}^{\prime}}{d \Omega}=\int_{0}^{\tau}\left(d W_{n} / d \Omega\right)_{1} n \Delta S_{n} V d t \tag{7}
\end{equation*}
$$

where $\tau$ is the total time of the particle motion in the field $\boldsymbol{E}$.
It is evident that $n v=j$ is a current density in the tube and $j \Delta S_{n}$ is the total number of particles that cross any section of the tube in unit time. In view of the stationarity,

$$
\begin{equation*}
n \wedge S_{n} V=d N\left(\boldsymbol{V}_{0}\right) \Delta S \tag{8}
\end{equation*}
$$

where $d N\left(\boldsymbol{V}_{\mathbf{0}}\right)$ is the number of particles hitting $\Delta S$ from the plasma interior per unit time with the velocity $\boldsymbol{V}_{0}$.

The number $d N\left(\boldsymbol{V}_{\mathbf{0}}\right)$ can be expressed with a velocity distribution function of electrons $f_{e}\left(V_{0}\right)$, which is regarded as independent of a velocity vector direction. If $\Theta_{0}$ is an angle of incidence, we have

$$
\begin{equation*}
d N\left(V_{0}, \Theta_{0}\right)=n_{0} f_{e}\left(V_{0}\right) V_{0} \cos \Theta_{0} 2 \pi V_{0}^{2} \sin \Theta_{0} d \Theta_{0} d V_{0} \tag{9}
\end{equation*}
$$

where $2 \pi V_{0}^{2} \sin \Theta_{0} d \Theta_{0} d V_{0}=V_{0}^{2} d V_{0} d \Omega_{0}$ is a volume element of a velocity space, which has been integrated over an azimuthal angle $\Phi_{0}$.

After integration (7) over all possible $V_{0}$ and all directions $\Theta_{0}$ corresponding to outward motions of electrons from a plasma, we have the final ex-
pression for the total power emitted from the unit area of the plasma surface in the direction of $n$ :

$$
\begin{equation*}
\left(\frac{d W_{n}}{d \Omega}\right)_{\text {tot }}=2 \pi n_{0} \int_{0}^{\infty} V_{0}^{3} f\left(V_{0}\right) d V_{0} \int_{0}^{\pi / 2} \cos \Theta_{0} \sin \Theta_{0} d \Theta_{0} \int_{0}^{\tau}\left(\frac{d W_{n}}{d \Omega}\right)_{1} d t . \tag{10}
\end{equation*}
$$

## 3. Total power of the surface radiation

Since we are interested in a total energy emitted into the outer space, we have to integrate the expression (10) over all directions of $\boldsymbol{n}$, corresponding to the outer hemisphere. For the power $\left(d W_{n} / d \Omega\right)_{1}$ radiated by one particle, an integration of the expression (4) over the azimuthal angle $\Phi$ in $d \Omega$ leads to the integrals

$$
\begin{gather*}
\int_{0}^{2 \pi} \frac{d \Phi}{(p+q \cos \Phi+r \sin \Phi)^{3}}=\pi \frac{2 p^{2}+q^{2}+r^{2}}{\left(p^{2}-q^{2}-r^{2}\right)^{5 / 2}} \\
\int_{0}^{2 \pi} \frac{d \Phi}{(p+q \cos \Phi+r \sin \Phi)^{5}}=\pi \frac{8 p^{4}+24 p^{2}\left(q^{2}+r^{2}\right)+3\left(q^{2}+r^{2}\right)^{2}}{4\left(p^{2}-q^{2}-r^{2}\right)^{9 / 2}} \tag{11}
\end{gather*}
$$

where $p=1-\beta_{z} \cos \Theta, q=\beta_{x} \sin \Theta, r=\beta_{y} \sin \Theta$.
Inserting the notations $\beta_{\tau}=\sqrt{\beta_{x}^{2}+\beta_{y}^{2}}$ and $\cos \Theta=x$ (that is not the $\Theta_{0}$ !), we obtain the following expression for the power radiated from the current tube (7):

$$
\begin{equation*}
W^{\prime}=\frac{e^{4}}{4 m^{2} c^{3}} \int_{0}^{\tau} E^{2}\left(1-\beta^{2}\right)\left[\int_{0}^{1} I(x) d x\right] d t \tag{12}
\end{equation*}
$$

where

$$
\begin{gather*}
I(x)=\frac{2\left(1-\beta_{z}^{2}\right)}{R^{3}}+\frac{3 \beta_{\tau}^{2}\left(1-x^{2}\right)\left(1-\beta_{z}^{2}\right)}{R^{5}} \\
-\left(1-\beta^{2}\right)\left(x-\beta_{z}\right)^{2}\left[\frac{2}{R^{5}}+\frac{10 \beta_{\tau}^{2}\left(1-x^{2}\right)}{R^{7}}+\frac{35 \beta_{\tau}^{4}\left(1-x^{2}\right)^{2}}{4 R^{9}}\right] \tag{13}
\end{gather*}
$$

and

$$
R=\sqrt{p^{2}-q^{2}-r^{2}}=\sqrt{\beta^{2} x^{2}-2 \beta_{z} x+1-\beta_{\tau}^{2}}
$$

If we ignore the influence of the radiative reaction force on the motion of the particles, we can regard their total energy as a constant. This means that their motion during the first half of the total time of motion $\tau$ (while they are "raising") coincides with that during the second half (while they are "falling") if we change $V_{z \rightarrow-} V_{z}$. Thus,

$$
\begin{gather*}
W^{\prime}=\frac{e^{4}}{4 m^{2} c^{3}}\left[\int_{0}^{\tau / 2} E^{2}\left(1-\beta^{2}\right)\left\{\int_{0}^{1} I\left(x, V_{z}\right) d x\right\} d t\right. \\
+\int_{\tau / 2}^{\tau} E^{2}\left(1-\beta^{2}\right)\left\{\int_{0}^{1} I\left(x, V_{z}\right) d x\right\} d t  \tag{14}\\
\left.=\frac{e^{4}}{4 m^{2} c^{3}}\right] \int_{0}^{\tau / 2} E^{2}\left(1-\beta^{2}\right)\left\{\int_{0}^{1} I\left(x, V_{z}\right) d x+\int_{0}^{1} I\left(x,-V_{z}\right) d x\right\} d t
\end{gather*}
$$

From (13) it is seen that the integrand $I\left(x, V_{z}\right)$ has the following property:

$$
\begin{equation*}
I\left(x, V_{z}\right)=I\left(-x,-V_{z}\right), \tag{15}
\end{equation*}
$$

but from this it follows that

$$
\int_{0}^{1} I\left(x,-V_{z}\right) d x=\int_{-1}^{0} I\left(-x,-V_{z}\right) d x=\int_{-1}^{0} I\left(x, V_{z}\right) d x .
$$

Taking this into account, we have from (14):

$$
\begin{equation*}
W^{\prime}=\frac{e^{4}}{4 m^{2} c^{3}} \int_{0}^{\tau / 2} E^{2}\left(1-\beta^{2}\right)\left\{\int_{-1}^{1} I\left(x, V_{z}\right) d x\right\} d t . \tag{16}
\end{equation*}
$$

The integral over $x$ in (16) expresses the total intensity of the radiation over all directions and for this we may use the Larmor formula. ${ }^{2}$ ) In that case, we obtain

$$
\begin{equation*}
W^{\prime}=\frac{2 e^{4}}{3 m^{2} c^{3}} \int_{0}^{\tau / 2} \frac{E^{2}\left(1-\beta_{z}^{2}\right)}{1-\beta^{2}} d t . \tag{17}
\end{equation*}
$$

Thus, we have the following theorem:
the energy emitted by a charge in a "projectile" motion in a constant electric field into a hemisphere in the direction of the field during the
total time of its motion is equal to the total energy emitted during half of this time (ignoring the influence of the radiative reaction on the motion of the charge).

Substituting the expression (2) for the field $E$ into (17) and using the 4 -velocity $\boldsymbol{u}=\beta / \sqrt{1-\beta^{2}}$, we have

$$
\begin{equation*}
W^{\prime}=\frac{2 e^{2}(2 k T)^{2}}{3 m^{2} c^{3}} \int_{0}^{\tau / 2} \frac{1+u_{\tau}^{2}}{(z+a)^{2}} d t . \tag{18}
\end{equation*}
$$

With the aid of the equations of motion for a relativistic electron in the field (2):

$$
\begin{equation*}
\frac{d u_{\tau}}{d t}=0 ; \quad \frac{d u_{z}}{d t}=-\frac{2 k T}{m c(z+a)}, \tag{19}
\end{equation*}
$$

we can come in (18) from the integral over $d t$ to an integral over the $z$-component of the 4 -velocity $u_{z}$ :

$$
\begin{equation*}
W^{\prime}=\frac{4 e^{2}}{3} \frac{k T}{m c^{2}}\left(1+u_{\tau}^{2}\right) \int_{0}^{u_{0 z}} \frac{d u_{z}}{z+a} \tag{20}
\end{equation*}
$$

Here, we have taken into account that $u_{\tau}=$ const, in accordance with (19), and also that during the first half of the motion a particle reaches the maximum distance from the plasma surface where the $z$-component of its velocity $u_{z}$ becomes zero.

Expressing $(z+a)$ from an energy integral for equations (19),

$$
\begin{equation*}
m c^{2} \sqrt{1+u^{2}}=m c^{2} \sqrt{1+u_{0}^{2}}-2 k T \ln \left(\frac{z}{a}+1\right), \tag{21}
\end{equation*}
$$

and inserting it into the integrand of (20), we have

$$
\begin{equation*}
W^{\prime}=\frac{4 e^{2} k T}{3 a m c^{2}}\left(1+u_{\tau}^{2}\right) \int_{0}^{u_{0} z} \exp \left\{-\frac{m c^{2}}{2 k T}\left(\sqrt{1+u_{0}^{2}}-\sqrt{1+u^{2}}\right)\right\} d u_{z} . \tag{22}
\end{equation*}
$$

After the substitutions

$$
u_{z}=u_{0 z} \xi, \quad u_{0} z=u_{0} \cos \Theta_{0}, \quad u_{\tau}=u_{0 \tau}=u_{0} \sin \Theta_{0},
$$

the expression (22) becomes

$$
\begin{equation*}
W^{\prime}=\frac{4 e^{2} k T}{3 a m c^{2}}\left(1+u_{0}^{2} \sin ^{2} \Theta_{0}\right) u_{0} \cos \Theta_{0} \int_{0}^{1} e^{-\frac{m c^{2}}{2 k T}\left(\sqrt{1+u_{0}^{2}}-\sqrt{1+u^{2}}\right)} d \xi \tag{23}
\end{equation*}
$$

wherein the integrand $u^{2}=u_{0}^{2}\left(\sin ^{2} \Theta_{0}+\xi^{2} \cos ^{2} \Theta\right)$.
To obtain the final expression for the power radiated, we have to integrate (23) in accordance with (10) over all $u_{0}$ and $\Theta_{0}$. In the relativistic case, we ought to take for $f\left(u_{0}\right)$ the Jüttner-Synge distribution function ${ }^{3}$ )

$$
\begin{equation*}
f\left(u_{0}\right)=\frac{m c^{2}}{4 \pi k T K_{2}\left(m c^{2} / k T\right)} \exp \left\{-\frac{m c^{2} \sqrt{1+u_{0}^{2}}}{k T}\right\} \tag{24}
\end{equation*}
$$

with the modified Bessel function $K_{2}\left(\frac{m c^{2}}{k T}\right)$ of second order.
Then (10) and (23) give

$$
\left.\begin{array}{c}
W=\frac{2 e^{2} c n_{0}}{3 a K_{2}\left(\frac{m c^{2}}{k T}\right)} \int_{0}^{\infty} u_{0}^{4} d u_{0} \int_{0}^{1} d \xi  \tag{25}\\
\times \int_{0}^{1}\left[1+u_{0}^{2}\left(1-x_{0}^{2}\right)\right] x_{0}^{2} \exp \left\{-\frac{m c^{2}}{2 k T}\left(3 \downarrow \sqrt{1+u_{0}^{2}}-\sqrt{1+u^{2}}\right)\right\} d x_{0}
\end{array}\right\}
$$

where $x_{0}=\cos \Theta_{0}$.
Considering a weakly relativistic case $u_{0} \ll 1$, we have

$$
\begin{gather*}
\frac{m c^{2}}{2 k T}\left(3 \sqrt{1+u_{0}^{2}}-\sqrt{1+u^{2}}\right) \\
\simeq \frac{m c^{2}}{k T} \sqrt{1+u_{0}^{2}\left(1+\frac{1-\xi^{2}}{2} x_{0}^{2}\right)+\frac{3 m c^{2}\left(1-\xi^{2}\right)^{2} x_{0}^{4} u_{0}^{4}}{32 k T}} \tag{26}
\end{gather*}
$$

and

$$
\exp \left\{-\frac{\left.3 m c^{2} x_{0}^{4}\left(1-\xi^{2}\right)^{2} u_{0}^{4}\right\}}{32 k T}\right\} \sim 1-\frac{3 m c^{2} x_{0}^{4}\left(1-\xi^{2}\right)^{2} u_{0}^{4}}{32 k T}
$$

so that the expression (25) becomes

$$
\begin{gathered}
W=\frac{2 e^{2} c n_{0}}{3 a K_{2}\left(\frac{m c^{2}}{k T}\right)} \int_{0}^{1} d x_{0} \int_{0}^{1} d \xi \int_{0}^{\infty}\left[1+\left(1-x_{0}^{2}\right) u_{0}^{2}\right. \\
\left.-\frac{3 m c^{2} x_{0}^{4}\left(1-\xi^{2}\right)^{2}}{32 k T} u_{0}^{4}\right] u_{0}^{4} x_{0}^{2} e^{-\frac{m c^{2}}{k T}} \sqrt{1+u^{2}\left(1+\frac{1-\xi^{2}}{2} x^{2}\right)}
\end{gathered} u_{0} .
$$

Replacement of the variable

$$
u_{0} \sqrt{1+\frac{1-\xi^{2}}{2} x_{0}^{2}}=\eta
$$

leads to

$$
\begin{equation*}
W=\frac{2 e^{2} c n_{0}}{3 a K_{2}\left(m c^{2} / k T\right)}\left\{I_{1}+I_{2}-\frac{3 m c^{2}}{32 k T} I_{3}\right\}, \tag{27}
\end{equation*}
$$

where

$$
\begin{gather*}
I_{1}=\int_{0}^{1} d \xi \int_{0}^{1} \frac{x_{0}^{2} d x_{0}}{R^{5}} \int_{0}^{\infty} \eta^{4} \exp \left\{-\frac{m c^{2} \sqrt{1+\eta^{2}}}{k T}\right\} d \eta \\
I_{2}=\int_{0}^{1} d \xi \int_{0}^{1} \frac{\left(1-x_{0}^{2}\right) x_{0}^{2} d x_{0}}{R^{7}} \int_{0}^{\infty} \eta^{6} \exp \left\{-\frac{m c^{2} \sqrt{1+\eta^{2}}}{k T}\right\} d \eta  \tag{28}\\
I_{3}=\int_{0}^{1}\left(1-\xi^{2}\right)^{2} d \xi \int_{0}^{1} \frac{x_{0}^{6} d x_{0}}{R^{9}} \int_{0}^{\infty} \eta^{8} \exp \left\{-\frac{m c^{2} \sqrt{1+\eta^{2}}}{k T}\right\} d \eta \\
R=\sqrt{1+\frac{1-\xi^{2}}{2} x_{0}^{2}}
\end{gather*}
$$

The integrals over $x_{0}=\cos \Theta_{0}$ and $\xi=u_{z} / u_{0} z$ are rather simple and the integrals over $\eta$ can be expressed by the modified Bessel functions. Thus, we have

$$
W=\frac{4 e^{2} c n_{0} \alpha^{2}}{9 a K_{2}\left(\alpha^{-1}\right)}\left\{K_{3}\left(\alpha^{-1}\right)+2 \alpha\left[K_{4}\left(\frac{1}{\alpha}\right)-\frac{1}{6} K_{5}\left(\frac{1}{\alpha}\right)\right]\right\}
$$

where $\alpha=k T / m c^{2}$.
In accordance with our approximation (26), we have to take here the asymptotic expansions for $K_{v}$ corresponding $\alpha \ll 1$. Finally, we have

$$
\begin{equation*}
W=\frac{4 \sqrt{2 \pi} e^{3}\left(n_{0} k T\right)^{3 / 2}}{9 m^{2} c^{3}}\left[1+\frac{35}{3}\left(\frac{k T}{m c^{2}}\right)\right] \tag{29}
\end{equation*}
$$

for the total power radiated from the unity area of a plasma surface.

## 4. Radiative reaction

It has already been pointed out in the introduction that the radiative reaction is equivalent to a pressure compressing the system. The pressure is equal to a normal component of the momentum carried out with the radiation from unit area of the plasma surface per unit time.

In accordance with (7) and taking into account the connection $\boldsymbol{P}=(\varepsilon / c) \boldsymbol{n}$ between the energy $\varepsilon$ and the momentum $\boldsymbol{P}$ of an electromagnetic wave, we have for the radiation pressure of particles belonging to the current tube (6) by analogy with (12);

$$
\begin{equation*}
p^{\prime}=\frac{e^{4}}{4 m^{2} c^{4}} \int_{0}^{\tau} E^{2}\left(1-\beta^{2}\right)\left\{\int_{0}^{1} x I(x) d x\right\} d t \tag{30}
\end{equation*}
$$

where again $x=\cos \Theta$, and for $I(x)$ we have to take the expression (13). Here we also have taken into account that we need only the $z$-component of a wave's momentum which is equal to $\varepsilon \cos \Theta / c=\varepsilon x / c$.

Like the case of expression (14) we can write again, taking into account a reversibility of the motion:

$$
p^{\prime}=\frac{e^{4}}{4 m^{2} c^{4}}\left[\int_{0}^{\tau / 2} E^{2}\left(1-\beta^{2}\right)\left\{\int_{0}^{1} x I\left(x, v_{z}\right)+\int_{0}^{1} x I\left(x,-v_{z}\right) d x\right\}\right] d t
$$

However, now the integrand $x I\left(x, V_{z}\right)$ does not possess the property (15) and a theorem analogous to that of section 3 does not take place. This makes the calculation rather long, and at last we come to the expression

$$
\begin{align*}
& p^{\prime}=\frac{e^{4}}{3 m^{2} c^{4}} \int_{0}^{\tau / 2} E^{2}\left\{\frac{2\left(1-\beta_{z}^{2}\right) \sqrt{1-\beta_{\tau}^{2}}}{1-\beta^{2}}-\frac{1-\beta_{z}^{2}}{\sqrt{1-\beta_{\tau}^{2}}}\right.  \tag{31}\\
& \left.+\frac{\left(1-\beta_{z}^{2}\right)\left(1-\beta^{2}\right)}{8\left(1-\beta_{\tau}^{2}\right) \sqrt{1-\beta_{\tau}^{2}}}-\frac{3\left(1-\beta^{2}\right)^{2}}{8\left(1-\beta_{\tau}^{2}\right)^{2} \sqrt{1-\beta_{\tau}^{2}}}\right) d t
\end{align*}
$$

or, expressing this with the 4 -velocity $\boldsymbol{u}$,

$$
\begin{align*}
& p^{\prime}=\frac{e^{4}}{3 m^{2} c^{4}} \int_{0}^{\tau} E^{2} \sqrt{\frac{1+u_{z}^{2}}{1+u^{2}}}\left\{2\left(1+u_{\tau}^{2}\right)\right.  \tag{32}\\
& \left.-\frac{1+u_{\tau}^{2}}{1+u_{z}^{2}}+\frac{1}{8} \frac{1+u_{\tau}^{2}}{\left(1+u_{z}^{2}\right)^{2}}-\frac{3}{8} \frac{1+u^{2}}{\left(1+u_{z}^{2}\right)^{3}}\right\} d t
\end{align*}
$$

This expression has to be averaged over all the magnitudes of the initial parameters $\left(u_{0}, \cos \Theta_{0}\right)$ with a corresponding distribution function. We restrict ourselves only to a non-relativistic approximation. Ignoring in (32) all the $u_{i}$ in comparison with unity, we have

$$
\begin{equation*}
p^{\prime}=\frac{e^{4}}{4 m^{2} c^{4}} \int_{0}^{\tau / 2} E^{2} d t=\frac{3 W^{\prime}}{8 c} \tag{33}
\end{equation*}
$$

where $W^{\prime}$ is the power radiated, for which we have the expression (17) in which we have to ignore $\beta_{z}^{2}$ and $\beta^{2}$ in comparison with unity.

Equation (33) saves us from repeating the calculation with a distribution function. Using the first term of formula (29), we get the following final expression for the compression of a radiating system:

$$
\begin{equation*}
p=\frac{\sqrt{2 \pi}}{6} \frac{e^{3}}{m^{2} c^{4}}\left(n_{0} k T\right)^{3 / 2} \tag{34}
\end{equation*}
$$

From the expression (34) one can see that the pressure is proportional to the gas pressure $n k T$ in the power $3 / 2$. At the same time, the factor $e^{3} / m^{2} c^{4}$ is very small (of an order of $10^{-16}$ in $C G S$ units) and therefore the pressure is negligible in the laboratory. Nevertheless, in cosmic situations it can be essential, because with it the Boltzmann law in a gravitational field can give us the finite size for a radiating system (it is known that the Boltzmann law with gravitational force only leads to an infinite size for a hot system).

## 5. Surface radiation spectrum

To detect the surface radiation experimentally one has to know its frequency spectrum. For one particle the energy radiated per unit solid angle per unit frequency interval is ${ }^{2}$ )

$$
\begin{equation*}
\frac{d I^{\prime}(\omega)}{d \Omega}=\frac{e^{2}}{4 \pi^{2} c}\left|\int_{0}^{\tau} \frac{\boldsymbol{n} \times[(\boldsymbol{n}-\boldsymbol{\beta}) \times \dot{\boldsymbol{\beta}}]}{(1-\overrightarrow{\boldsymbol{n}} \cdot \overrightarrow{\boldsymbol{\beta}})^{2}} e^{i \omega[t-\boldsymbol{n} \boldsymbol{r}(t) / c]} d t\right|^{2} \tag{35}
\end{equation*}
$$

where the integral is spread over the trajectory $\boldsymbol{r}=\boldsymbol{r}(t)$ of the motion.
To find the spectrum of the total surface radiation, one has to multiply the expression (35) by the number of particles (9) that pass through the unit area of the plasma surface per unit time and integrate then over all the initial velocities $V_{0}$ and over all solid angles $d \Omega$ and $d \Omega_{0}$, corresponding to outward directions for the radiation and outgoing particles.

However, for the calculation of the integral (35), one needs a solution of the relativistic equations of motion (19) that is not expressible in a closed form. To simplify the problem, we can change the real field (2) in which the motion of electrons takes place with a uniform field $E^{*}$ independent of the coordinate $Z$. Then, we have to choose $E^{*}$ in such a way that the result for a total power radiated would be as close as possible to the correct expression (29).

If we calculate the power radiated, assuming the electrons to move in a uniform field $E^{*}$, we get

$$
\begin{equation*}
W=\frac{c e^{3} E^{*} n_{0} \alpha^{2}}{3 k T K_{2}\left(\alpha^{-1}\right)}\left\{K_{3}\left(\alpha^{-1}\right)+2 \alpha K_{4}\left(\alpha^{-1}\right)\right\} \tag{36}
\end{equation*}
$$

where again $\alpha=k T / m c^{2}$.
In contradistinction to the result (28), this expression is precise, because in yielding it we need not make any approximation like (26) or so on. Comparing (36) with (29), one concludes that, if we put

$$
\begin{equation*}
E^{*}=\frac{4 k T}{3 e \alpha}=\frac{2}{3} E_{\max } \tag{37}
\end{equation*}
$$

where $E_{\max }=E(0)$ in the formula (2), we will have almost the same result for $W$ with $E^{*}$ as with (2) (with an error within $3^{0} / 0$ ).

Although the calculation becomes simpler now, we are still not able to perform the Fourier analysis in a relativistic case in accordance with the expression (35). Therefore, we consider only the non-relativistic limit, when (35) becomes

$$
\begin{equation*}
\left.\frac{d I^{\prime}(\omega)}{d \Omega}=\frac{e^{2}}{4 \pi^{2} c^{3}} \right\rvert\, \int_{0}^{\tau} \boldsymbol{n} \times(\boldsymbol{n} \times \dot{\boldsymbol{V}}) e^{i \omega t} d t \tag{38}
\end{equation*}
$$

In the case of a uniform field $E^{*}$, we get for the radiation of one particle

$$
\begin{equation*}
I^{\prime}(\omega)=\frac{2 e^{2} E^{*}}{3 \pi c^{3} \omega^{2}}(1-\cos \omega \tau), \tag{39}
\end{equation*}
$$

where $\tau=2 \mathrm{~m} V_{0 z} / e E^{*}$ is the total time of electron motion in a field $E^{*}$ and an integration has been performed in (39) over solid angles, corresponding to the radiation leaving the system.

To obtain a spectrum of the total radiation, we have to average (39) with the aid of the Maxwell distribution function

$$
\begin{equation*}
I(\omega)=\frac{4\left(e E^{*}\right)^{2}}{3 \pi c^{3} \omega^{2}} \sqrt{\frac{m}{2 \pi k T}} \int_{0}^{\infty} V_{0 z} \sin ^{2}\left(\frac{m \omega V_{0 z}}{e E^{*}}\right) e^{-\frac{m V^{o_{0 z}}}{2 V_{0 z}}} . \tag{40}
\end{equation*}
$$

The integral in (40) can be expressed with a confluent hypergeometric function $F(\alpha, \gamma, z)$.

After substitution of the expression (37) for the effective field $E^{*}$ and using the Kummer transformation to transform $F(\alpha, \gamma,-z)$ into $F(\gamma-\alpha, \gamma, z)$, we have the following final expression for the spectrum:

$$
\begin{equation*}
I(\omega)=\frac{16 k T\left(n_{0} e\right)^{2}}{27 c^{3} \omega^{2}} \sqrt{\frac{8 k T}{\pi m}} \times\left\{1-e^{-\omega^{2} /\left(\omega_{0}^{2}\right.} F\left(-\frac{1}{2}, \frac{1}{2} ; \omega^{2} / \omega_{0}^{2}\right)\right\}, \tag{41}
\end{equation*}
$$

where $\omega_{0}=\sqrt{16 e^{2} \pi n_{0} / 9 m}$ has an order of a reciprocal time that a particle with the thermal velocity $\sqrt{k T / m}$ spends in travelling a distance equal to the Debye length $a=V^{\prime} k T / 2 \pi e^{2} n_{0}$.

The function $I(\omega)$ decreases steadily from its maximum value when $\omega=0$ :

$$
I_{\max }(\omega)=I(0)=\frac{32 k T\left(n_{0} e\right)^{2}}{27 c^{3}} \sqrt{\frac{8 k T}{\pi m}}
$$

to zero when $\omega \rightarrow \infty$, so as for large $\omega$ it tends to zero like $\left(1 / \omega^{2}\right)$.

## 6. Discussion

The mechanism of the generation of surface radiation is a rather general one. Such a radiation must take place not only in the case of a plasma but from any hot system, if only the system contains free electrons. The power of the radiation in any case will be of the same form as (29), though maybe with another factor.

A characteristic feature of the surface radiation is its dependence on the temperature $T$ and the electron density $n$ in the combination $n k T$. In contradistinction to the usual bremsstrahlung due to Coulomb collisions ${ }^{4}$ ), the surface radiation has a stronger dependence on the temperature (power $3 / 2$ instead of $1 / 2$ ).

Our expressions (29), (34), and (41) are valid independent of the plasma configuration and the confinement mechanism. This is so because only a very thin layer of a space charge is responsible for the surface radiation.

Since we have ignored the influence of the force of radiative reaction on the particle motion, all our theory is a zeroth approximation in $2 e^{2} / 3 m C^{3}$, the "noncausality" time. Nevertheless this does not prevent us from evaluating the radiative reaction pressure (34) in that approximation.

In obtaining the expressions (29), (34), and (41), we have assumed that only the radiation directed outwards leaves the plasma, and the part of the total radiation that falls backwards into the plasma has been absorbed. If the reflection coefficient for this radiation differs from zero, its intensity and pressure reaction would be larger than those given by the formulae (29) and (34). Thus, our expressions give the lower limit for the respective values. At the same time it must be pointed out that the radiation from the surface layer which is directed inwards cannot be considered macroscopically, and therefore neglecting its reflection is not equivalent to the assumption of the plasma being a black body.

Finally, we have to notice that our formulae are valid only if the energy emitted is compensated by its storage, e.g. as a result of some reactions, because our considerations imply an equilibrium. Moreover, the energy transfer in the plasma interior has to be fast enough, otherwise the radiation will cause a cooling of the surface layer.

## Acknowledgements

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ASGER AABOE

# LUNAR AND SOLAR VELOCITIES AND THE LENGTH OF LUNATION INTERVALS IN BABYLONIAN ASTRONOMY 

Det Kongelige Danske Videnskabernes Selskab
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## Synopsis

The fragments of late-Babylonian cuneiform texts published here extend our evidence of the elegant and consistent manner in which account was made of the influence of lunar and solar anomalies upon the variable time intervals between syzygies of the same kind of sun and moon.

Several new functions appear for the first time, most notably two associated with the lengths of six-month intervals.

ACT No. 55 is republished as an appendix. It turns out to be a lunar ephemeris in which the 223 months of the Saros are broken up into twenty intervals: eighteen 12-month intervals, one six-month, and one one-month interval.

The texts ${ }^{1}$ published here, all in the British Museum, and all deriving from unscientific excavations at Babylon some ninety years ago, amplify and extend our evidence for the treatment of the influence of lunar velocity on various interesting time intervals in Babylonian lunar theory according to System A, in the terminology of ACT. ${ }^{2}$

In the course of the last years, a series of texts has luckily come within our ken and control which, in conjunction with the ACT material, has made it possible to understand and appreciate the consistent and elegant manner in which account was made of the effect of lunar and solar anomaly upon the variable time intervals between syzygies of sun and moon. ${ }^{3}$

The problem is, in modern terms, the following: If the velocity of the sun is $v_{s}$, that of the moon $v_{m}$, and the time of a syzygy $t_{0}$, then the length of the subsequent month, $\Delta t$, is determined by

$$
\int_{t_{0}}^{t_{0}+\Delta t}\left(v_{m}-v_{s}\right) \mathrm{d} t=360^{\circ},
$$

and analogously, if more syzygies are involved.
The Babylonian approach is to separate the effect of the variable lunar velocity and that of the variable solar velocity into two independent, additive terms, for the interval between two consecutive syzygies of the same kind, that is, one true synodic month, is expressed thus:
${ }^{1}$ The texts are published through the courtesy of the Trustees of the British Museum. My visits to the British Museum, as well as part of my subsequent work, were supported by grants from the National Science Foundation. I wish to acknowledge, once again, my debt of gratitude to Dr. Richard Barnett, Keeper, and Dr. Edmond Sollberger, Deputy Keeper, of Western Asiatic Antiquities for their hospitality and helpfulness. Finally, I wish to thank Miss Janice Henderson for her great assistance in the preparation of the reconstructed tables. Moreover, a variety of auxiliary tables concerning $B, \Phi$, and related functions, executed by the Yale Computer according to her very ingenious programs, have greatly facilitated the work with these texts.
${ }^{2}$ For this and similar abbreviations see the Bibliography at the end. I shall adhere, wherever possible, to the terminology of this central work.
${ }^{3}$ See Neugebauer [1], Aaboe [1] and [2]. The present paper is, as it were, the fourth in this sequence of publications of texts, and I shall assume some familiarity with the previous three.

$$
\Delta t=29^{\mathrm{d}}+\mathrm{G}^{\mathrm{H}}+\mathrm{J}^{\mathrm{H}}, 4
$$

where G depends on lunar velocity, and $J$ on solar velocity, or rather the longitude of the latter syzygy involved. ${ }^{5}$ Similarly it was discovered recently that the length of twelve consecutive months is determined by

$$
\Delta t=354^{\mathrm{d}}+\Lambda^{\mathrm{H}}+\mathrm{Y}^{\mathrm{H}}
$$

where it is $\Lambda$ that depends on lunar velocity, and Y on longitude. ${ }^{6}$
It is the family of functions to which G and $A$ belong that is of primary concern. These functions are derived, not, as one might suspect, from the column representing lunar velocity, but from the related Column $\Phi$ through the application of a simple difference principle.

Column $\Phi$, we have learned, measures the length of one Saros, i.e., of 223 consecutive lunations, taking into account only the effect of a variable lunar velocity so that

$$
1 \text { Saros }=6585^{\mathrm{d}}+\Phi \text { Н }
$$

omitting, possibly, a term depending on solar anomaly, or longitude. ${ }^{7}$
The relations between $\Phi$ and lunar velocity F , as well as between $\Phi$ and G, and $\Phi$ and $\Lambda$, have been discussed in earlier publications. ${ }^{8}$ There is, however, a certain symmetry relation which will be important in the following, and which I should like to derive here, though the derivation is very obvious. First it must be noted that to a certain syzygy is assigned the $\Phi$-value associated with the Saros beginning at that syzygy, while a value of one of the other functions ( $G, \Lambda$, etc.) is assigned to the syzygy ending the relevant lunation interval.

Figure 1 shows in schematic form the structure of the table generating G from $\Phi$. Here $\Phi$ is to appear in its truncated version. ${ }^{9}$ The readily justified relation underlying this scheme is

$$
\mathrm{G}(n+224)=\mathrm{G}(n+1)+(\Phi(n+1)-\Phi(n))
$$

The symmetry rule in question may now be derived as follows. The value $\Phi(n)$ measures the Saros bounded by syzygies number $n$ and $n+223$; im-

[^8]

Fig. 1.
mediately preceding this Saros is the month measured by $G(n)$, and immediately following it is the month measured by $G(n+224)$ as shown in Figure 2.

If we now invert the time axis, the following two changes will take place:
(i) $\Phi(n)$ will now belong to a branch of the opposite kind (ascending or descending) of the zig-zag function, and
(ii) it will be associated with the value $\mathrm{G}(n+224)$ which measures the now immodiately preceding month.


Fig. 2.

Thus, if we take a $\Phi$-value in the first column of the table generating G from $\Phi$, and place it on a branch of the opposite kind, it is to be associated with the G-value in the next line. The same holds for other schemes of the same character.

Texts A and B below doubtless derive from the same tablet, though they do not join physically. Text A consists of ACT No. 207cd joined by three new fragments. My earlier conjecture that ACT No. 207cd once was part of a table generating $G$ from $\Phi$ is now confirmed. ${ }^{10}$ Further, Text A gives evidence of a hitherto unattested function - I call it Column G'- which, I believe, is $G$ transformed into days and augmented by a constant which I cannot justify to my satisfaction.

In Text C we find $\Phi$ related to another new column - I call it $\Lambda^{\prime}$ - which is simply $\Lambda$ increased by a constant for which, once again, I fail to find a satisfactory astronomical motivation.

10 Aaboe [1], p. 25.

Text D, though fragmentary and ill preserved, presents us with yet another new function - I call it W - belonging to the family of derivates from $\Phi$. I am quite certain that it is associated with a six-month interval, even as $\Lambda$ is with twelve lunations.

ACT No. 55 is republished and reconstructed as a natural appendix to these new texts. It was principally an awareness of the functions associated with various lunation intervals that made it possible to understand this text. It turns out to be a fragment of an "ephemeris" for conjunctions of sun and moon, probably covering an entire Exeligmos, or triple Saros, with each Saros of 223 months broken up into 18 twelve-month intervals, one one-month interval, and one six-month interval. These various intervals are represented by $A, G$, and a version of $W$, with their associated corrections for solar anomaly and for change in length of daylight. The agreement between the text and $W$ as reconstructed from Text $D$ is not quite what $I$ had hoped for, though the corresponding correction $Z$ is precisely what was predicted.

A remark about my transcriptions: I usually represent the Babylonian month names by Roman numerals ( $I=$ bar, etc.), the two-wedge separation sign, most often used as zero, by ".", and zodiacal signs by their standard sigla. All the texts employ the cursive form of 9 . Whenever possible, I outline the preserved surface of the text in the larger reconstructed tables. Photographs of Texts $A-D$ are presented on Plate I.

## Text A and B

Text A: B.M. $36699(80-6-17,431)+36846(80-6-17,586)+37079(80-6-17$, $825)+37886(80-6-17,1643)$
Text B: B.M. 36908 (80-6-17,649)
Provenance: Babylon (B.M. numbers).
Content: Auxiliary table for Columns $\Phi, G, G$ from lunar System A. Transcription: Tables 1 and 2.

Description of Text
The fragments which make up Text A form a piece of a tablet with part of the upper edge, but no other edges, preserved. Hand, size of writing, and content indicate that Text $B$ doubtless was part of the same original tablet, but too much clay is missing for a physical join. B. M. 36846 was previously published as ACT No. 207cd.

Horizontal alignment is strictly observed, but the scribe has the habit of occasionally spacing the digits of a short entry so as to fill the entire width of the column.

Identification of obverse and reverse is made on the basis of content and the presence of a horizontal ruling and a blank space near the bottom of the reverse; nothing remains of the expected colophon.

The text appears to be analogous to the one in which $\Lambda$ is derived from $\Phi$. Thus I expect that when unbroken it had some 60 lines to each side, as does my reconstruction, and four columns, of which only three are still in evidence. The missing column, also giving $\Phi$-values, would be the first of the four.

The preserved parts of Texts $A$ and $B$ are outlined in Tables 1 and 2.
In my transcription of Col. III, I have used " 0 " to indicate an empty sexagesimal place, though the text has nothing corresponding save, perhaps, a gap between 29 and the next non-zero digit.

## Commentary

Of the three preserved columns only two - those giving corresponding values of $\Phi$ and $G$ - are in evidence in the fragment published as ACT No. 207 cd . From the obverse, and the few traces then visible on the reverse, Neugebauer concluded that the text when unbroken gave a complete list of corresponding values of $\Phi$ and $G$ in agreement with the standard conversion table. This conclusion is confirmed by the new fragments, but two new features are now apparent.

First, the first ten lines of Obv. I have entries which are shorter than the normal 6 -place sexagesimals of the $\Phi$-values in this column. Whenever endings are preserved they are $\ldots, 20$. It is now clear - as it could not have been at the time of publication of ACT - that the entries all must be $2,13,20$, the effective maximum of $\Phi$. This strengthens my earlier suspicion that ACT No. 207cd was a text in which G was generated from $\Phi$ by a method analogous to that for deriving $\Lambda$ from $\Phi$; thus Texts A and B are largely reconstructed according to my earlier proposed scheme for computing G from $\Phi .{ }^{11}$ I expect that the first preserved column was preceded by another, also giving values of $\Phi$, but corresponding to moments one month earlier, as in the reconstructed table generating $G$ from $\Phi$.

Second, the rejoined fragments give evidence of a hitherto unattested column, Col. III, which I call G'. Col. III is poorly preserved, but since the entries on obverse and reverse are symmetrical, as for G in Col. II, quite a few may be restored with some confidence.
${ }^{11}$ Aaboe [1], p. 26.

Table 1.


Table 2.

|  | $I$ | II | III |
| :---: | :---: | :---: | :---: |
| Rev. - 42. | 1, 58,37, 2, 13,20 | 4.56 | 29,22,51,20 |
|  | 1,58,33,42, 3,20 | 4,56 | 29,22,51,20 |
|  | 1,58,31, 6,40 | 4,54, 48, 53,20 | 29,22,31,20 |
|  | 1,58,31, 6,40 | 4,53,14, 4, 26, 40 | 29,22,21,20 |
|  | 1, 58, 31, 6,40 | y, 51, 21, 28, 53,20 | 29,22, 0,20 |
|  | 1,58,31, 6, \%0 | $4,49,11,6,40$ | 29,21,36,20 |
|  | 1,58,31, 6,40 | $4,46,42,57,6,40$ | 29,21, 9, 20 |
| -3s. | 1,58,48, 53,20 | $4,43,57,2,13,20$ | 29,20,41, \%0 |
|  | 1,59, 6,40 | 4, 41, 11, 6,40 | 29,20,14 |
|  | 1,59,24,26,40 | 4,38,25,11,6,40 | 29,19,46,20 |
|  | 1,59,42,13,20 | 4,35,39,15,33,20 | 29, 19, 8 , 40 |
|  | 2 | 4,32,53,20 | 29, 18,51 |
| -30. | 2,0,17,46,40 | $4,30,7,24,26,40$ | 29, 18, 23, 20 |
|  | 2, 0,35,33,20 | 4,27,21,28, 53,20 | 29, 12,55,40 |
|  | 2, 0,53, 20 | 4,24,35,33,20 | 29,17,28 |
|  | 2,1,11,6,40 | $4,21,49,37,46,40$ | 29, 17, 0,20 |
|  | 2, 1, 28,53,20 | $4,19,3,42,13,20$ | 29, $16,32,40$ |
| -25. | $2,1,46,40$ | 4, 16, $17,46,40$ | 29,16,5 |
|  | 2,2,4,26,40 | 4,13,31,51,6,40 | 29, 15, 37,20 |
|  | 2, 2,22,13,20 | 4,10,45,55,33,20 | 29,15,9,40 |
|  | 2,2,40 | 4,8 | $29.14,42$ |
|  | 2, 2, 5i, \%6, 40 | 4, 5, 14, 4, 26,40 | 29.14,14,20 |
| -20. | 2, 3, 15,33,20 | 4, 2, 28, 8, 53, 20 | 29, $13,46,40$ |
|  | 2,3,33,20 | 3, 59, 42, 3,20 | 29,13,19 |
|  | 2,3,51,6,40 | 3,56,56, $17,46,40$ | 29,12,51,20 |
|  | $2,4,8,53,20$ | 3, $54,10,22,13,20$ | 29,12,23,40 |
|  | 2, 4,26,40 | 3, 51, $24,26,40^{\prime}$ | $29,11,56$ |
| -15. | $2,4,44,26,40$ | 3,48,38,31, 6,40 | 29,11,28,20 |
|  | 2,5,2,13,20 | 3,45,52,35,33,20 | 29,11,0,40 |
|  | 2,5,20 | 3,43, 6,40 | 29, 10,33 |
|  | 2, 5,37,46, 40 | 3,40,20,44, 26,40 | 29,10,5,20 |
|  | 2, 5,55,33,20 | 3,37,34, $38,53,20$ | $29,9,37,40$ |
| -10. | 2, 6, 13,20 | 3,34, 48, 33,20 | 29,9,10 |
|  | $2,6,31,6,40$ | 3,32, 2, 57, 46,40 | 29, 8, 42, 20 |
|  | 2, 6,48,53,20 | 3,29,17, 2, 13, 20 | 29, 8, 14, 40 |
|  | $2,7,6,40$ | $3,26,31,6,40$ | 29, 7,47 |
| -5. | 2, 7,24,26, \% | 3,23,45, $11,6,40$ | 29, 7,19,20 |
|  | 2, $2,42,13,20$ | 3,20,59, 15,33,20 | 29, 6, 51, \%0 |
|  | 2,8 | 3,18,13,20 | 29,6,24 |
|  | 2, 8, $17,46,40$ | 3,15,27,24,26,40 | 29, 5, 56,20 |
|  | 2, 8, 35,33,20 | 3, 12,41, 28,53,20 | 29, 5,28, 40 |
|  | 2, 8, 53,20 | 3, 9, 55, 33,20 | 29, 5,1 |
| 0. | 2,9,11,6,40 | 3, 7, 9,37, 46, 40 | $29,4,33,20$ |
|  | 2,9,28,53,20 | 3, 4, 23, , 12,1,3,20 | -29, 4, 5,40 |
|  | 2,9,46,40 | $3,1,37,4,40$ | 29, 3,38 |
|  | 2,10, 4,26,40 | 2,58,51,51,6,40 | 29,3,10, 20 |
|  | 2,10,22,13,20 | 2,56, 5,55,33,20 | 29, 2, 42, \%0 |
| $\bigcirc$. | 2,10,40 | 2, 53,20 | 29,2,15 |
|  | 2,10, 57, $46,40^{\circ}$ | 2, $2,0,40]$ | 29, 1.48 |
|  | 2, 11, 15,35,20 | $2,48,17.46,40 \quad 7$ | 29, 1.24 |
|  | 2,11,33,20 | 2,46, 3 [20] ${ }^{2}$ | 29, 1.4 |
|  | 2,11,51,6,40 | $2,44,26,4000$ | 29,0,45 |
| 10. | 2,12, 8, 53,20 | 2, 42, 57, 46, 20$]$ | -29.-0, 30 |
|  | 2,12,26,40, | 2, 41,46,40 | 29,0,18 |
|  | $2,12,44,26,40$ |  | 29,0, 9 |
|  | $2,13,2,13,20$ | $2,40,17,46,40,1$ |  |
|  | 2,13,20! |  | $29 \text { tab }$ |

Opposite the minimal value of $G$,

$$
\mathrm{G}=2 ; 40^{\mathrm{H}}
$$

securely restored in Obv. II, 1,2, we find in Col. III the entry " 29 tab", i.e., "add 29 ". The length of the month, disregarding the correction J for solar anomaly, is

$$
29^{\mathrm{d}}+\mathrm{G}^{\mathrm{H}}
$$

so the meaning of Obv. III, 1,2 is clear, and the units of the entries of Col. III must be days.

However, it is trivial that Col. III does not merely give what has to be added to $G$, for in that case it would be constant. Indeed, the preserved values all fit the conjecture that Col. III represents a new function, G', where

$$
\begin{equation*}
\mathrm{G}^{\prime}=29+\frac{\mathrm{G}-2 ; 40}{6} \tag{1}
\end{equation*}
$$

If this is correct, Col. G' gives the length of a lunation in days, taking into account only the effect of lunar anomaly, but so normed that the minimum of $G^{\prime}$ is precisely $29^{d}$. A justification of this norm escapes me.

A few further comments on G' are in order. First, though the text is broken at or near the end of Col. G', it looks as if the entries in the preserved stretch are limited to three sexagesimal digits. Thus either G' was computed according to (1), and abbreviated to three or four digits, or the parameters of $G^{\prime}$, as expected from (1), are abbreviated.

I believe the latter is the case. First, if G' itself were abbreviated, then there are instances where the text indicates that the last retained digit is raised even if the first discarded digit is too small according to Babylonian custom. Second, in the $\Phi-\Lambda$ text, ${ }^{12} \mathrm{Col} . X$ is a precedent for abbreviated parameters. Thus I have reconstructed Col. G', first with a constant second difference of

$$
\Delta \Delta \mathrm{G}^{\prime}=0 ; 0,3
$$

as an abbreviation of the precise value

$$
\Delta \Delta \mathrm{G}^{\prime}=\frac{1}{6} \cdot 0 ; 0,17,46,40=0 ; 0,2,57,46,40,
$$

then with constant first difference

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$$
\Delta \mathrm{G}^{\prime}=0 ; 0,27,40
$$

as an approximation to

$$
\Delta \mathrm{G}^{\prime}=\frac{1}{6} \cdot d_{\Phi}=0 ; 0,27,39,15,33,20,
$$

and finally with the second difference in part

$$
\Delta \Delta \mathrm{G}^{\prime}=0 ; 0,3
$$

and for the rest

$$
\Delta \Delta G^{\prime}=0 ; 0,6
$$

as required by the structure of $\mathrm{G}^{\prime}$.
My reconstruction of Col. G' is admittedly quite fanciful.

## Text C

Text C: B.M. 36793 (80-6-17,531)
Provenance: Babylon.
Content: Auxiliary table for Columns $\Phi$ and $\Lambda^{\prime}$ from lunar System A. Transcription: Table 3.

Description of Text
Text C is a small flake with only one side and part of "upper" edge preserved.

The hand is clear and looks much like that of Texts A and B. I do not believe that this fragment was part of the same tablet as Texts A and B , but it may well be that the tablet it came from belonged to the same series as the one from which Texts A and B were broken.

The preserved writing is in two columns, with horizontal alignment strictly observed.

## Commentary

The text gives corresponding values of $\Phi$ and of a hitherto unattested function which I call $\Lambda^{\prime}$. To a certain value of $\Phi$ corresponds a value of $\Lambda^{\prime}$ which obeys, as far as the fragment is preserved, the simple relation

$$
\Lambda^{\prime}=\Lambda+0 ; 3,24,7, \ldots \mathrm{H}
$$

Table 3.

|  | $I$ | II | [ $\wedge$ ] |
| :---: | :---: | :---: | :---: |
| 1. | $[2,2,42,35] 33,20$ | 2, [8, $6, \ldots$ lal $]$ | - 5,42,13,20 |
|  | $[2,3,0,3] 2,13,20$ | $1,53,[23, \cdots t a b]$ | 1,30,44, 26,40 |
|  | $[2,3,18] 8,53,20$ | $6,22,38, \ldots]$ | 2,58,31, 6,40 |
|  | $[2,3,35,45,33,20$ | 11, 9,40,[..] $]$ | 7,45,33,20 |
| 5. | $[2,3,53,42] 13,20$ | 16,14,29, [ $\ldots$ | 12, 50, $22,13,20$ |
|  | $[2,4,11,28853,20$ | 21,37, 4 [ $\ldots$ | 18,12,57,46,40 |
|  | $[2,4,29,15] 33,20$ | 26,59,4这, . $]$ | 23,35,33,20 |
|  | $[2,4,47,2,13,20]$ | $32,22,[15, \ldots]$ | 28,58, 8, 53, 20 |
|  | $[2,5,4,48,53,20]$ | $37,[44,5 l, \ldots]$ | 34,20,44, 26, 40 |

$$
\text { B.M. } 36793
$$

if the entry in Col.II, 1 is taken as negative, and the rest as positive. In the transcription I have listed the corresponding values of $\Lambda$.

I have no explanation to offer for the constant

$$
c=0 ; 3,24,7, \ldots \mathrm{H}
$$

of which no more digits may be reconstructed from the fragmentary Col. II. There is, to be sure, a parameter

$$
3,24[\ldots]
$$

in evidence in ACT No. 207ca. The fragmentary passage says:
[fro]m Pisces to Virgo $3,24[\ldots]$
which would indicate that the constant is a correction tied to the slow are of solar motion. However, the proper correction of $\Lambda$ on the slow are is

$$
Y=0 ; 21,2,59^{\mathrm{H}}
$$

as we learn from the text B.M. 40094. ${ }^{13}$
The only peculiarity of the $\Phi-\Lambda^{\prime}$ pair that is chosen to be in line 1 is that here the second difference of $\Lambda$ changes from

$$
\Delta \Delta \Lambda=2 \cdot 0 ; 0,17,46,40=0 ; 0,35,33,20
$$

to

$$
\Delta \Delta A=0 ; 0,17,46,40 .
$$

[^9]
## Text D

Text D: B.M. 45930 (SH 81-7-6,366)
Provenance: Babylon (B.M. number).
Content: Auxiliary table for Columns $\Phi$ and W from lunar System A. Transcription: Table 4.

Description of Text
B.M. 45930 is a fragment, $1^{1} / 2$ inches wide, $2^{1} / 2$ inches long, with no edges, and only one side, preserved. The surface of the lower half of the preserved side is crumbling badly so that only isolated wedges are visible. The writing is small and in two columns with horizontal alignment observed.

## Critical Apparatus

Col. II, l. 5: 1,39,27[...]; 39 might be 29, and 27 could be read 17.
Col. II, l. $10 \mathrm{f} .:$ the readings are very uncertain.

## Commentary

Text D appears to give corresponding values of $\Phi$ and a hitherto unattested function which I call W. The significance of W is that the length of the six months preceding a certain syzygy number $n$ is

$$
177^{\mathrm{d}}+\mathrm{W}(n)^{\mathrm{H}}
$$

where $W(n)$ is the $W$-value assigned to syzygy number $n$, and where account is taken only of the influence of a variable lunar velocity.

Table 4.
I II

| 0. | $[2,3,15,33,20 \mathrm{lall}]$ | $[56,1,51,6,40]$ |
| :---: | :---: | :---: |
|  | [2] $2^{2}, 57,46,40$ latid | $[1,6,34,4,26,40]$ |
|  | [2]2.40 lal | $[1,17,14,4,26,40]$ |
|  | [2, 3, 22,13,20 lal | 1,28, [1, 51, 6,40] |
|  | [2] 2, 4,26,40 lal | 1,39,27,[24,26,40] |
| 5. | [2] 1,46,40 Lal | $1,51, .4[4,26,40]$ |
|  | [2]1,28,53,20 lal | 2, 2, 51,5[1, 6,40] |
|  | [2] 1,11, 6,40 hal | 2, 15, $\cdot 4[4,26,40]$ |
|  | $[2,0] 53,20]$ lal | [2, 27, 27, $24,26,40]$ |
|  | $[3, \cdots 35,33,20$ lall | [2] 40,11, ई1, 6, 40] |
| 10. | $2,[0,17,46,40 \quad$ lall $]$ | $[2,53] 14,4,[26,40]$ |
|  | $2[\mathrm{lal}]$ | [3, 6, 34, ] $4,226,40]$ |
|  | $1,59,42,13,20 \mathrm{lal}]$ | 3,[20, ]1, 5L, 6, 40] |
|  | $[1,59,24,26, \% 0 \quad$ a 21$]$ | [3,34, 7, 24, 26, 40] |

$$
\text { B.M. } 45930
$$

In table 5 and its continuation, I present the derivation of W from $\Phi$. Using $\mathrm{I}(n)$ to denote the entry in Col. I, line $n$, and similarly, the structure of the table is as follows:
(i) I and II contain $\Phi$-values; $\mathrm{I}(1)=2 ; 13,20 \uparrow$.
(ii) to go from $\mathrm{I}(n)$ to $\mathrm{I}(n+1)$ corresponds to an advance of 223 months.
(iii) to go from $\mathrm{I}(n)$ to $\mathrm{II}(n)$ corresponds to an advance of 6 months.
(iv) $\operatorname{III}(n)=\mathrm{II}(n)-\mathrm{I}(n)$.
(v) $\operatorname{IV}(n+1)=\operatorname{IV}(n)+\operatorname{III}(n)$.

Column IV gives values of W so that IV $(n)$ is the value of W assigned to the same syzygy as the $\Phi$-value in $\mathrm{II}(n)$.

Columns I-III are determined by the rules (i)-(iv), so in addition to rule (v), only an initial value is wanted for the complete determination of Column IV.

I have provided the equivalent of an initial value by fitting plausible endings to the preserved beginnings of the W -values in Text D . The resulting extrema are

$$
\max \mathrm{W}=8 ; 35,48,53,20^{\mathrm{H}}
$$

and

$$
\min W=-0 ; 50,17,2,13,20^{\mathrm{H}} .
$$

By taking six monthly values of G symmetrically disposed about the appropriate extremum of G, I obtained the following extrema for the sum of six consecutive values of G :

$$
\max \sum_{i=1}^{6}\left(29^{\mathrm{d}}+\mathrm{G}(i)^{\mathrm{H}}\right)=177^{\mathrm{d}}+8 ; 35,42,57,46,40^{\mathrm{H}}
$$

and

$$
\min \sum_{i=1}^{6}\left(29^{\mathrm{d}}+\mathrm{G}(i)^{\mathrm{H}}\right)=177^{\mathrm{d}}-0 ; 50,16,50,22,13,20^{\mathrm{H}} .
$$

The agreement is very good, though not perfect. The endings of W, though plausible, cannot, of course, yet be guaranteed. Further, the adjustments of G near its maximum would, a priori, make even as close an agreement as this unlikely.

In this reconstructed table for generating W from $\Phi$, I have only given one half, as it were, of the $\Phi-\mathrm{W}$ scheme. The other half is derived by means of the already justified symmetry rule which we have learnt from the $\Phi-\Lambda$ and $\Phi-\mathrm{G}$ schemes. It is that if we take a $\Phi$-value in Col. I, line $n$, place it on the opposite branch, then it is to be assigned the $W$-value in line $n+1$.

Table 5.

| $I$ | $\frac{\pi}{(\Phi)}$ | $(\mathbb{I I}$ | $\frac{\pi}{(I)}$ |
| :--- | :---: | :---: | :---: |
| $(W)$ |  |  |  |

1. 

2，13，20 $\uparrow$
$2,1,20 \uparrow$
$2,13,2,13,20$
$2,12,44,26,40 \uparrow$
$2,12,26,40 \uparrow$
5
$2,12,8,53,20$
$2,11,51,6,40 \uparrow$
$2,11,33,20 \uparrow$
$2,11,15,33,20 \uparrow$
$2,10,57,46,40 \uparrow$
10.
$2,10,40 \uparrow$
$2,10,22,13,20^{1}$
$2,10,4,26,40 \uparrow$
$2,9,46,40 \uparrow$
$2,9,28,53,20 \uparrow$
$2,9,11,6,40 \uparrow$
$2,8,53,20 \uparrow$
$2,8,35,33,20 \uparrow$
$2,8,17,46,40 \uparrow$
$2,8 \uparrow$
20.
$2,7,42,13,20$
$2,7,24,26,40$
$2,7,6,40 \uparrow$
$2,6,48,53,20 \uparrow$
$2,6,31,6,40 \uparrow$
$2,6,13,20 \uparrow$
$2,5,55,33,20 \uparrow$
2，5，37，46，40 $\uparrow$
2，5，20个
$2 ; 5,2,13,20 \uparrow$
$2,4,44,26,40$
$2,4,26,40 \uparrow$
$2,4,8,53,20 \uparrow$
$2,3,51,6,40 \uparrow$
$2 ; 3,33,20$
$2,3,15,33,20 \uparrow$
$2,2,57,46,40 \uparrow$ 2，2，40个
2，2，22，3，20个
$2,2,4,26,40 \uparrow$
$2,1,46,40 \uparrow$
$2,1,28,53,20 \uparrow$
$2,1,11,6,40 \uparrow$
$2,0,53,20 \uparrow$
$2,0,35,33,20 \uparrow$
$2,0,17,46,40 \uparrow$ $2 \uparrow$
1．59，42．13，20个
$1,59,24,26,40 \uparrow$
$1,59,6,40 \uparrow$
$1,58,48,53,20 \uparrow$
$1,58,31,6,40 \uparrow$
$1,58,31,6,40 \quad(1,58,13,20) \uparrow$
$1,58,31,6,40 \quad(1,57,55,33,20) \uparrow$
$1,58,31,6,40$
$1,58,31,6,40 \quad(1,58,15,55,33,20) \downarrow$
55.


Table 5 （continued）．

|  | $I$ | II | III | N |
| :---: | :---: | :---: | :---: | :---: |
| 57. | 1，58，51，28，53，20廿 | 2，13，20 ${ }^{\text {a }}$ | $0 ; 14,28,31,6,40$ | $5 ; 31,42,35,33,20$ |
|  | 1，59，9，15，33，20 | 2，13，2，13，201 | $0 ; 13,52,57,46,40$ | $5 ; 46,11,6,40$ |
|  | 1，59，27，2，13，201 | 2，12，44，26，40ヶ | $0,13,17,24,26,40$ | 6：0，4，4，26，40 |
| 60. | 1，59，44，48，53，201 | 2，12，26，40 $\uparrow$ | $0: 12,41,51,6,40$ | $6 ; 13,21,28,53,20$ |
|  | 2， $0,2,35,33,206$ | 2，12，8，53， $20 \dagger$ | $0 ; 12,6,17,46,40$ | 6：26，3，20 |
|  | $2,0,20,22,13,20 \downarrow$ | $2,11,51,6,40 \uparrow$ | $0,11,30,44,26,40$ | $6,38,9,37,46,40$ |
|  | 2，0，38，8，53，20 $\downarrow$ | 2，11，33，20ヶ | 0；10，55，11，6，40 | $6 ; 49,40,22,13,20$ |
|  | 2，0，55，55，33，20】 | 2，11，15，33，20t | $0 ; 10,19,37,46,40$ | $7,0,35,33,20$ |
| 65. | $2,1,13,42,13,20 \downarrow$ | 2，10，57，46，401 | $0,9,44,4,26,40$ | $7,10,55,11,6,40$ |
|  | 2，1，31，28，53，20レ | 2， $10,40 \uparrow$ | 0，9，8，31，6，40 | $7,20,3915,33,20$ |
|  | 2，1，49，15，33，20】 | 2，10，22，13，201 | $0 ; 8,32,57,46,40$ | 7，29，47，46，40 |
|  | $2,2,7,2,13,20 \downarrow$ | 2，10，4，26，40t | $0 ; 7,57,24,26,40$ | 7，38，20，44，26，40 |
|  | 2，2，24，48，53，20ฟ | 2，9，46，40ヶ | 0：7，21，51，6，40 | $7,46,18,8,53,20$ |
| 70. | 2，2，42，35，33，20 | 2，9，28，53，20t | $0,6,46,17,46,40$ | 7；53，40 |
|  | $2,3,0,22,13,20 \downarrow$ | 2，9，11，6，401 | 0，6，10，44，26，40 | 8，0，26，17，46，40 |
|  | $2,3,18,8,53,20 \downarrow$ | 2，8，53，201 | 0；5，35，11，6，40 | 8，6，37，2，13，20 |
|  | $2,3,35,55,33,20 \downarrow$ | 2，8，35，33，20t | 0，4，59，37，46，40 | 8；12，12，13，20 |
|  | $2,3,53,42,13,20 \downarrow$ | 2，8，17，46，40＾ | $0,4,24,4,26,40$ | 8；17，11，51，6，40 |
| 75. | 2，4，11，28，53，20 $\downarrow$ | $2,8 \uparrow$ | $0,3,48,31,6,40$ | 8；21，35，55，33，20 |
|  | $2,4,29,15,33,20 \downarrow$ | 2，7，42，13，20t | 0，3，12，57，46，40 | 8，25，24，26，40 |
|  | $2,4,47,2,13,20 \downarrow$ | 2，7，24，26，40t | 0；2，37，24，26，40 | 8，28，37，24，26，40 |
|  | $2,5,4,48,53,20 \downarrow$ | $2,7,6,40 \uparrow$ | $0,2,1,51,6,40$ | 8，31，14，48，53，20 |
|  | 2，5，22，35，33，20ل | 2，6，48，53，20ヶ | $0 ; 1,26,17,46,40$ | $8,33,16,40$ |
| 80. | 2，5，40，22，13，20】 | $2,6,31,6,40 \uparrow$ | $0,0,50,44,26,40$ | 8，34，42，57，46，40 |
|  | $2,5,58,8,53,20 \downarrow$ | $2,6,13,20 \uparrow+$ | $0,0,15,11,6,40$ | $8,35,33,42,13,20$ |
|  | $2,6,15,55,33,20 \downarrow$ | $2,5,55,33,20 \uparrow$－ | －0，0，20，22，13，20 | 8，35，48，53，20 |

Text D contains a fragment of this part of the scheme．The $\Phi$－values are all designated＂lal，＂i．e．，they belong to a descending branch．The same $\Phi$－values，but on ascending branches，are found in Col．I，lines $35-48$ ，of Table 5，so the W －values of Text D ought to be the ones in Table 5 one line lower，which indeed they are．

Since it appears that，at least very nearly，

$$
W(n)=\sum_{i=n-5}^{n} G(i)
$$

we can expect that $W$ must receive a correction for solar anomaly which is simply

$$
\mathrm{Z}(n)=\sum_{i=n-5}^{n} \mathrm{~J}(i)
$$

where $J$ is the standard correction for solar anomaly to $G$ ．
It is not difficult to see that $Z(n)$ will become a continuous，piecewise


Fig. 3.
linear function of $\lambda(n)$, as is $J(n)$, where $\lambda(n)$ is the longitude of the sun at syzygy number $n$. Specifically it can be described thus:

Pisces $13^{\circ} \leqq \lambda(n) \leqq$ Pisces $27^{\circ}: Z(n)=0^{H}$
Pisces $27^{\circ} \leqq \lambda(n) \leqq$ Virgo $13^{\circ}: Z(n)$ decreases linearly to $-5 ; 36,47,44^{\mathrm{H}}$
Virgo $13^{\circ} \leqq \lambda(n) \leqq$ Virgo $15 ; 56^{\circ}: Z(n)=-5 ; 36,47,44^{\text {Н }}$
Virgo $15 ; 56^{\circ} \leqq \lambda(n) \leqq$ Pisces $13^{\circ} \quad: Z(n)$ increases linearly to $0^{H}$.
A comparison between this correction and the corresponding correction Y to $\Lambda$ is in order. ${ }^{14} \mathrm{Y}$ agrees with J only in its differences, as it should, but is subject to the entirely independent condition that it be 0 on the fast arc. This last condition decides the initial value of $\Lambda$. The stretches where Y is not constant are very short, so the desire to have $Y$ vanish on one of the constant arcs is very understandable.

The correction $Z$, however, has very short constant stretches, and with the above definition it is already 0 on one of them. The functions $\mathrm{J}, \mathrm{Y}$ and Z are compared graphically in Figure 3.

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Table 6.

|  | $I$ | $\frac{\pi}{(\Phi)}$ | $\mathbb{I I I}_{(I-I)}$ | $\frac{\sqrt{V}}{(V)}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1. | 2，13，20 $\dagger$ | 2， $7 \downarrow$ | －0，6，40 |  |
|  | 2，13，2，13，201 | 2，7，17，46，40ね | －0，5，44，26，40 |  |
|  | 2，12，44，26，40 1 | 2，7，35，33，20ね | －0；5，8，53，20 |  |
|  | $2,12,26,40 \uparrow$ | 2，7，53，20 ${ }^{2}$ | 0，4，33，20 |  |
| 5. | $2,12,8,53,20 \uparrow$ | 2，8，11，6， $90 \downarrow$ | －0，3，57，46，40 |  |
|  | 2，11，51，6，40 $\uparrow$ | 2，8，28，53，20ฟ | －0，3，22，13，20 |  |
|  | 2，11，33， $20 \uparrow$ | 2，8，46，401 | －0；2，46，40 |  |
|  | $2,11,15,33,20 \uparrow$ | 2，9，4，26，401 | －0；2，11，6，40 |  |
|  | $2,10,57,46,40 \uparrow$ | 2，9，22，3，20V | －0；1，35，33，20 |  |
| 10. | $2,10,40 \uparrow$ | 2，9，401 | －0， 11 |  |
|  | 2，10，22，13，20 $\dagger$ | 2，9，5，46，40V | －0，0，24，26，40 |  |
|  | 2，10，4，26，40 $\uparrow$ | 2，10，15，33，20 | ＋0，0，11，6，40 | 0 |
|  | 2，9，46，40 $\uparrow$ | 2， $10,33,20 \downarrow$ | 0；0，46，40 | 0；0，11，6，40 |
|  | 2，9，28，53，20 $\uparrow$ | 2，10，51，6，40 $\downarrow$ | 0；1，22，13，20 | 0；0，57，46，40 |
| 15. | $2,9,11,6,40 \uparrow$ | 2，11，8，53，20ね | 0；1，57，46，40 | $0 ; 2,20$ |
|  | 2，8，53，20 $\uparrow$ | 2，11， $26,40 \downarrow$ | 0；2，33，20 | 0，4，17，46，40 |
|  | 2，8，35，33，20 $\uparrow$ | 2，11，44，26，40ฟ | 0；3，8，53，20 | 0；6，51，6，40 |
|  | $2,8,17,46,40 \uparrow$ | 2，12，2，13，20V | 0；3，44， 26,40 | $0 ; 10$ |
|  | 2，8 1 | 2，12，201 | $0 ; 4,20$ | 0；13，44，26，40 |
| 20. | 2，7，42，13，20 ${ }^{2}$ | 2，12，37，96，401 | 0；4，55，33，20 | 0，18，4，26，40 |
|  | 2，7，24，26，40 $\uparrow$ | 2，12，55，33，20巾 | 0；5，31，6，40 | 0，23 |
|  | $2,7,6,40 \uparrow$ | 2，13， $3,20 \downarrow$ | $0,6,6,40$ | 0，28，31，6，40 |
|  | 2，6，48，53，20 $\dagger$ | 2，13，20（2，13，31，6，40V ） | 0，6，31，6，\％ | 0，34，37，46，40 |
|  | $2,6,31,6,40 \uparrow$ | 2，13，20（2，13，48，53，201） | 0．6，48，53，20 | 0，41，8，53，20 |
| 25. | $2,613,20 \uparrow$ $2,50 \times 3,20 \uparrow$ | $\begin{array}{ll}2,13,20 & (2,14,6,40 \downarrow) \\ 2,3,20 & (2,14,24,2640 \downarrow)\end{array}$ | 0；7，6，40 | 0，47，57，46，40 |
|  | 2，S，55，33，20 $\uparrow$ | 2，13，20（2，14，24，26，40У） | 0， $7,24,26,40$ | $0,55,4,26,40$ |
|  | $2,5,37,46,40 \uparrow$ | 2，13，20（2，14，42， 3,201$)$ | 0，7，42， 13,20 | 1，2，28，53，20 |
|  | 2，5，20 $\uparrow$ ， | 2，13，20 $(2,15 \downarrow)$ | 0， 8 | $1 ; 10,11,6,40$ |
|  | 2，5，2，13， $20 \uparrow$ | 2，13，20（2，15， $77,46,401)$ | 0，8， $17,46,40$ | 1，18，11，6，40 |
| 30. | $2,4,44,26,40 \uparrow$ $2,426,40 \uparrow$ | 2，3，20 $\quad(2,15,35,33,20 \downarrow)$ | 0；8， $35,33,20$ | 1，26，28，53，20 |
|  | 2，4，26， $40 \uparrow$ | 2，13，20（2，5，53，201） | 0，8，53，20 | 1，35，4，26，40 |
|  | $2,4,8,53,20 \uparrow$ | 2，13，20（2，16，11，6，40 V） | $0 ; 9,11,6,40$ | 1，43，57，46， $0_{0}$ |
|  | $2,3,51,6,40 \uparrow$ | 2，13，20（2，16，28，53，20V） | 0；9，28，53，20 | 1，53，8，53，20 |
|  | 2，3，33， $20 \uparrow$ | 2，13，20（2，16，46，40，V） | $0,9,46,40$ | 2，2，37，46，40 |
| 35. | 2，3， $15,33,20 \uparrow$ | 2，13，20 $\frac{(2,17,4,26,40 \downarrow)}{(2,472640}$ | $0^{\prime} 10,4,26,40$ | 2，12，24， 26,40 |
|  | 2， $2,57,46,40 \uparrow$ | 2，13，20 $\overline{(2,16,47,24,26,40 \uparrow)}$ | 0；10，22，13，20 | 2，22，28，53，20 |
|  | 2，2，40ヶ | 2， $3,20 \quad(2,16,29,37,46,40 \uparrow)$ | $0,10,40$ | 2，32，51，6，\％0 |
|  | $2,2,22,13,20 \uparrow$ | 2，13，20（2，16， $11,51,6,40 \uparrow)$ | $0,10,57,46,40$ | 2，43，31，6，40 |
|  | $2,2,4,26, \% 0 \uparrow$ | 2，13，20 $(2,15,54,4,26,40 \uparrow)$ | 0； $11.15,33,20$ | 2， $54,28,53,20$ |
| 40 | 2，1，46，40 $\uparrow$ | 2，13，20 $(2,15,36,17,46,40 \uparrow)$ | $0 ; 11,33,20$ | 3，5，44，26，40 |
|  | $2,1,28,53,20 \uparrow$ | 2，13，20（2，15，18，31，6，40 $)$ | 0； $11,51,6,40$ | 3，17，17，4，40 |
|  | $2,1,11,6,40 \uparrow$ | 2，13，20（2，15，0，44，，6，40 $)$ | 0，12，8，53，20 | 3，29，8，53，20 |
|  | 2，0，53，20 $\uparrow$ | 2，13，20 $\quad(2,14,42,57,46,40 \uparrow)$ | $0 ; 12,26,40$ | 3，41， $17.46,40$ |
|  | $2,0,35,33,20 \uparrow$ | 2，13，20 $\quad(2,14,25,11,6,40 \uparrow)$ | $0 ; 12,44,26,40$ | 3，53，44，26，40 |
| 45. | $2,0,17,46,40 \uparrow$ | 2，13，20 $\quad(2,14,7,24,26,40 \uparrow)$ | 0，13，2，13， 20 | 4．6，28，53， 20 |
|  | $2 \uparrow$ | 2，13，20（2，13，49，3，46，40 ¢） | 0； 13,20 | 4；1931，6，40 |
|  | 1，59，42，13，20 | 2，13，20（2，13，31，51，6，40ヶ） | 0，13，37，46，40 | 4，32，51，6，40 |
|  | 1，59，24，26，40 $\uparrow$ | 2，13，14，4，26，40¢ | $0,13,49,37,46,40$ | 4，46，28，53，20 |
|  | 1，59，6，40 $\uparrow$ | 2，12，56， $17,46,40 \uparrow$ | $0: 13,49,37,46,40$ | S： $0,18,31,6,40$ |
| 50. | 1，58，48，53，20 $\uparrow$ | $2,12,38,31,6,40 \uparrow$ | $0 ; 13,49,37,46,40$ | $5: 14,8,8,53,20$ |
|  | 1，58，31，6，40 1 ¢ | 2，12，20，44，26，401 | $0 ; 13,49,37,46,40$ | $5 ; 27,57,46,40$ |
|  | $\begin{array}{lll}1,58,31,6,40 & (1,58,13,20 \uparrow)\end{array}$ | $2,12,2,57,46,40 \uparrow$ | $0,13,31,51,6,40$ | $5,41,47,24,26,40$ |
|  | $1,58,31,6,40 \quad(1,57,55,33,20 \uparrow)$ | 2，11，45，11，6，40ヶ | $0,13,14,4,26,40$ | $5,15,19,15,33,20$ |
|  | $1,58,31,640 \quad(1,57,58,8,53,201)$ | $2,11,27,24,26,40 \uparrow$ | $0,12,56,17,46,40$ | $6: 8,33,20$ |
| 55. | $\begin{aligned} & 1,58,31,6,40 \quad(1,58,15,55,33,20 \downarrow) \\ & 1,58,33,42,13,20 \downarrow \end{aligned}$ | $\begin{aligned} & 2^{\prime}, 11,9,33,46,40 \uparrow \\ & 2,10, \operatorname{si}, 5,1,40 \uparrow \end{aligned}$ | $\begin{aligned} & 0.1,38,31,6,40 \\ & 0.1,18885320 \end{aligned}$ | $\begin{aligned} & 6,21,29,37,46,40 \\ & 6.34,8,8,53,20 \end{aligned}$ |
|  | $1,58,33,42,13,20 \downarrow$ | $2,10,51,51,6,40 \uparrow$ | $0_{i} 12,18,8,53,20 .$ | $6,34,8,8,53,20$ |

Table 6 (continued).

|  | $I$ | II | III | V |
| :---: | :---: | :---: | :---: | :---: |
| 57. | 1,58,51,28,53,20 | 2,10,34, 4, 26,401 | $+0,11,42,35,33,20$ | $6,46,26,17,46,40$ |
|  | 1,59, 9, 15, 33,201 | 2,10,16, 17,46,40 $\uparrow$ | $0 ; 11,7,2,13,20$ | $6 ; 57,8,53,20$ |
|  | 1,59,27, 2, 13,20ل | $2,9,58,31,6,401$ | $0 ; 10,31,28,53,20$ | $7,9,15,55,33,20$ |
| 60. | 1,59,44,48,53,20ل | $2,9,40,44,26,40 \uparrow$ | $0 ; 9,55,55,33,20$ | $7,19,47,24,26,40$ |
|  | $2,0,2,35,33,20 \downarrow$ | $2,9,22,57,46,40 \uparrow$ | $0,9,20,22,13,20$ | 7, 29,43,20 |
|  | $2,0,20,22,13,20 \downarrow$ | $2,9,5,11,6,40 \uparrow$ | $0 ; 8,44,48,53,20$ | 7, 39, 3, 42, 13, 20 |
|  | 2, 0,38, 8, 53,20 $\downarrow$ | $2,8,47,24,26,40 \uparrow$ | $0 ; 8,9,15,33,20$ | $7,47,48,31,6,40$ |
|  | 2, 0,55,55,33,201 | $2,8,29,37,46,40 \uparrow$ | $0 ; 7,33,42,13,20$ | 7,55,57,46,40 |
| 65. | $2,1,13,42,13,20 \downarrow$ | 2,8,11,51,6,40ヶ | $0,6,58,8,53,20$ | 8, 3, 31, 28, 53, 20 |
|  | 2, 1, 31,28, 33, 20 | $2,7,54,4,26,40 \uparrow$ | $0 ; 6,22,35,33,20$ | 8,10,29, 37, 46, 40 |
|  | 2, 1, 49, 15, 33, 20 $\downarrow$ | $2,7,36,17,46,40 \uparrow$ | 0, 5,47, 2,13,20 | $8 ; 16,52,13,20$ |
|  | $2,2,7,2,13,20 \downarrow$ | $2,7,18,31,6,40 \uparrow$ | 0, 5, 11, 28,53,20 | 8,22,39,15,33,20 |
|  | 2, 2, 24, 48, 53, 20 $\downarrow$ | $2,7,0,44,26,40 \uparrow$ | 0, 4, 35,55,33,20 | 8,27,50,44,26,40 |
| 70. | 2, 2, 42,35,33,20ل | $2,6,42,57,46,40 \uparrow$ | oi Y, 0, 22, 13,20 | 8,32,26,40 |
|  | $2,3,0,22,13,20 \downarrow$ | $2,6,25,11,6,40 \dagger$ | 0; 3,21,48,53,20 | 8,36,27, 2, 13,20 |
|  | $2,3,18,8,53,20 \downarrow$ | $2,6,7,24,26,40 \uparrow$ | 0; 2, 41, 15,33,20 | 8,39,51,51, 6,40 |
|  | $2,3,35,55,33,20 \downarrow$ | $2,5,49,37,46,40 \pm$ | $0,2,13,42,13,20$ | $8,42,41,6,40$ |
|  | $2,3,53,42,13,20 \downarrow$ | $2,5,31,51,6,40 \uparrow$ | $0 ; 1,38,8,53,20$ | 8,44,54, 48,53,20 |
| 75. | 2, 4, 11, 28,53,20 | $2,5,14,4,26,40 \uparrow$ | 0; 1, 2, 35,33,20 | 8,46,32,57,46,40 |
|  | $2,4,29,15,33,20 \downarrow$ | $2,4,56,17,46,40 \uparrow$ | $+0 ; 0,27,2,13,20$ | 8,47,35,33,20 |
|  | 2, 4, 47, 2,13,20\ | $2,4,38,31,6,40 \uparrow$ | -0; 0, 8,31,6,40 | 8,48, 2, 35,33,20 |

The propriety of basing as large reconstructions and conclusions as these on such fragile evidence as Text $D$ may well be questioned, yet I am quite confident of the results set forth above. First, the endings of $\Phi$-values in Col. I of Text $D$ of obvious constant difference $17,46,40$ forcibly suggest the canonical column of such values, descending from $2,13,20$, present in any scheme for deriving some useful time interval from $\Phi$. Second, the preserved beginnings in Col. II of Text D indicate a constant second difference of $17,46,40$. Now two possible interpretations of Col. II come to mind: as a measure of a six-month interval - as W above - or of a five-month interval. The latter possibility is displayed in Table 6 and its continuation. The rules for its construction are like the rules (i)-(v) for the construction of Table 5 except that " 6 months" in rule (iii) is replaced by " 5 months." Further, I have arbitrarily set the minimum of the fourth column - I call it Col. V - equal to zero. It will be observed that the differences of V in the crucial stretch corresponding to the preserved part of Text D happen to be identical with the differences in W.

Non etheless, the very excellent agreement between the extrema of W and of sums of six consecutive monthly G-values effectively excludes any other interpretation of Col. II of Text D. However, before Col. V is entirely dismissed I shall discuss certain of its features, for I suspect that such a function may well be found, which is also my excuse for including Table 6.

Indeed, in eclipse texts one proceeds usually in steps of six months, but occasionally in steps of five months. Since the obvious justification for a six-month function $W$ is its usefulness for eclipse computations, a fivemonth function can equally well be expected.

I find, as above, that the extrema of sums of five consecutive monthly values of G - including the 29 days - are

$$
\max \sum_{i=1}^{5}\left(29^{\mathrm{d}}+\mathrm{G}(i)^{\mathrm{H}}\right)=147^{\mathrm{d}}+10 ; 41,31,51,6,40^{\mathrm{H}}
$$

and

$$
\min \sum_{i=1}^{5}\left(29^{\mathrm{d}}+\mathrm{G}(i)^{\mathrm{H}}\right)=147^{\mathrm{d}}+1 ; 53,44,26,40^{\mathrm{H}} .
$$

The difference between the extrema is

$$
8 ; 47,47,24,26,40^{\text {н }}
$$

which agrees well with the amplitude of $V$ (which is also its maximum in Table 6, since its minimum is 0 )

$$
\max \mathrm{V}=8 ; 48,2,35,33,20^{\mathrm{H}} .
$$

If the function $V$ is found I expect its values to be those of Table 6 augmented by about $1 ; 53, \ldots$, the large hours of the minimal value of the sum of five consecutive G-values, for the correction for solar anomaly ought to be the sum of five consecutive J-values, in analogy with W.

## Appendix

ACT No. 55
ACT No. 55: B.M. 46015 (SH 81-7-6,461).
Provenance: Babylon.
Content: Data concerning selected conjunctions of sun and moon for, at least, Seleucid Era 180, IX to 202, III (132 B.C. ff.).
Transcription: Table 7.

## Critical Apparatus

For Obv. Col. I, see ACT p. 116 (it should be noted that since Obv. and Rev. are now joined, I continue the numbering of columns of the obverse to the corresponding columns of the reverse, so that Rev. IV in my termi-
nology is, in fact, the first preserved column of the reverse and identical with Neugebauer's Rev. I).

The few differences between Neugebauer's readings and my reconstruction can all readily be resolved by reference to a photograph of the ill preserved text, e.g., a damaged cursive 9 can be mistaken for a poorly preserved 10, and vice versa. Of particular interest is Rev. IV, 7 (Neugebauer's Rev. I, 7): Neugebauer reads 32,39 or 33,39 where the text should have $34,29,9$. The bottom of the 4 in 34 is damaged, so the number can be mistaken for a 3 , and the 9 in 29 can easily be read as a fuzzy 10 , hence NeuGEbaUER's 39 .

## Description of Text

The text is, as mentioned, poorly preserved with all edges destroyed. Of the surface of the reverse only little remains. When unbroken, the tablet probably had 30 lines to a side.

## Commentary

An unprecedented feature of this text - and so one that made its interpretation singularly difficult - is that its columns contain a mixture of different astronomical functions. Hitherto the identification of function and column has justifiably been taken for granted, and it is reflected in the standard terminology of the literature on Babylonian mathematical astronomy where the words column and function are freely interchanged.

It appears that the aim of the tablet is to compute the time of conjunction of sun and moon, not at consecutive syzygies, but at intervals of one, six, or twelve lunations - most frequently twelve.

The functions are separated into columns according to their kind. In Column II, the second preserved column, we find functions which take account of the influence of the variation of lunar velocity: $\Lambda$, most frequently, measuring a twelve-month interval, G measuring a one-month interval, and W measuring a six-month interval. These functions are all placed end to end, as it were, so that the value of $G$ in line 4 ' of the obverse refers to the preceding month, while that of $\Lambda$ in line 5 ' refers to the length of preceding 12 months and is derived from a $\Phi$-value belonging to a syzygy twelve lunations later than that in play in line 4', and similarly in all other cases. I have introduced in the leftmost column a tally of syzygies - akin to the Julian days - so normed that the syzygy where $\Phi_{1}$ assumes the minimal value of $\Phi$ is arbitrarily called 1 ; this is convenient for the tables of $\Phi$ and related functions which have come forth from the Yale computer.
Table 7.

|  |  |
| :---: | :---: |
|  |  <br>  <br>  のト <br>  |
| N |  |
| $\rightarrow \stackrel{\text { N．}}{\text { N }}$ |  |
| $\mathcal{J}$ |  <br>  <br>  <br>  |
| $\stackrel{?}{m}$ |  <br>  <br>  <br>  |
| "- |  |



Column III contains the corresponding functions registering the influence of solar anomaly (or longitude) on these intervals: J correcting G, Z correcting W , or Y correcting $\Lambda$.

Column IV gives the corrections due to changing length of daylight so that the entry in Column IV, line $n$, is

$$
\operatorname{IV}(n)=\frac{1}{2} \cdot(C(n-1)-C(n))
$$

where $\mathrm{C}(n)$ is the length of daylight, in large hours, corresponding to line $n$.
Column V, which is only partially preserved on the Reverse, gives the equivalent of Column $K$ for $G$, i.e., the sum of the values in Columns II, III, and IV for the line in question.

The moment of conjunction, in large hours before sunset (denoted šu in the texts), would then arise by continuous subtraction of the values in Column V from an initial value, as usual in lunar texts according to System A; no trace of this column - of the type of Column M-remains. The computation of the date of the conjunction - usually 28 or 29 - implies knowledge of the character (full or hollow) of the preceding month or months, which the prediction of the hour does not.

A few remarks are in order, and first about the columns which I have reconstructed. The $\Phi$-values were recaptured from recognisable values in the preserved Column II, particularly that of G in Obv. II, 4 and that of $\Lambda$ in Obv. II, 5. ${ }^{15}$ They turned out to be what in ACT are called $\Phi_{1}$-values, i.e., values of $\Phi$ associated with conjunction, rather than opposition, of sun and moon. Relying on the now well-established fact that the function $\Phi$ runs uninterruptedly through all the System A lunar texts, I determined the dates in Column T, of course only mod $\Pi_{\Phi}$, the period of $\Phi$ (6247 lunations or some 505 years), yet the ones given in T - the years in the Seleucid Era were historically the most likely. That these dates are not only likely, but certain, is established by Columns III and IV, both of which ultimately depend on the longitude of the conjunction, for they are in exact agreement with the longitudes derived from T , taking advantage of the continuability of $\mathrm{B}_{1}$, the longitude column.

A feature of greatest interest is the appearance in our text of the functions W and Z , the six-month functions, W for the first time in an ephemeris, and Z for the first time anywhere.

I had hopes that the value of W in Obv. II, 3 ' would serve to determine

[^10]the endings of W as reconstructed from the $\Phi-W$ scheme in Text D above, but I was disappointed. There can be no doubt that Neugebauer's reading
$$
\mathrm{W}=1 ; ., 6,55,48,20 \mathrm{tab}
$$
is the best possible from the photograph of the text in its present state, and it is confirmed by Dr. Sollberger who has kindly looked at the original tablet for me. However, my $\Phi-W$ scheme given above in the commentary to Text D would have
\[

$$
\begin{equation*}
W=+1 ; 0,15,4,51,40 \tag{i}
\end{equation*}
$$

\]

corresponding to

$$
\Phi=2 ; 0,37,35,33,20 \uparrow
$$

and the sum of the six $G$-values corresponding to this and the five preceding $\Phi$-values turn out to be (see Table 8)

$$
\begin{equation*}
\sum_{1}^{6} \mathrm{G}=1 ; 0,7,13,20^{\mathrm{H}}\left(\bmod 6^{\mathrm{H}}\right) . \tag{ii}
\end{equation*}
$$

Table 8.

I am not completely sure how this dilemma may be resolved. It is out of the question that the value in the text can be reconciled with what I reconstructed from Text $D$, for the first four digits of the $W$-values in this scheme are secure, and (i) is in excess by about 8 in the third significant place. Thus, if a scheme for deriving $W$ directly from $\Phi$ was employed, it must have been a variant of the one in evidence in Text $D$. It seems equally plausible, however, that the author of the text wished to present in this place the sum of six G-values, but did not give the value (ii) for one of two reasons, either that he employed a $\Phi-\mathrm{G}$ scheme at variance with the standard one, ${ }^{16}$
${ }^{16}$ ACT No. 207ca shows the existence of such variant $\Phi-\mathrm{G}$ schemes, but little more, though I have recently added a new fragment to it.
or - and this one should not admit unless under duress - that he committed an arithmetical error.

The value in the same line of the correction $Z$ due to solar anomaly, computed according to the rules I predicted above, agrees perfectly with what is preserved in the text.

The next time a six-month interval occurs is between Rev., line 6' and 7', as is clear from the preserved numbers in Col. IV. In Col. III, 7' I have entered the sum (modulo $6^{\mathrm{H}}$ ) of the relevant six G -values.

It, too, is followed immediately by a one-month interval, and then by twelve-month intervals, as is unambiguously clear from the C'-values in Col. IV. Indeed, it is upon these C'-values that a safe bridge can be built from the obverse to the reverse.

It is lucky that this part of the reverse is preserved, for based on it we can perceive yet another feature of the text's structure. It appears that the W-values (and the G-values) occur separated by an interval of 223 lunations, as is immediately seen from the tally numbers. Thus it appears reasonable that the pattern of the text is that the Saros is divided into one six-month interval, one one-month interval, and eighteen twelve-month intervals, so

$$
223 \mathrm{mo}=(1 \cdot 6+1 \cdot 1+18 \cdot 12) \mathrm{mo} .
$$

The bottom edge of the tablet must, for reasons of symmetry, have been two or three lines beyond what is preserved of the obverse; a reasonable guess of the size of the unbroken tablet is that it in all contained three Saroi, which would give 30 lines to a side, 20 lines to each Saros.

That this pattern is not an isolated instance is shown by ACT No. 76. The preserved columns of this text, which also concerns conjunctions of sun and moon, are $B_{1}$, the longitude column, $C_{1}$ which gives length of daylight, and $\mathrm{E}_{1}$ representing lunar latitude. The text's top and bottom edges are preserved, so we have representatives of all twenty lines of the complete tablet, corresponding to one Saros.

It so happens that ACT No. 55 and No. 76 are very close in time; indeed, if my guess that No. 55 contained three Saroi is correct, then they overlap. It is, however, not so that they contain the same sequence of conjunctions. If No. 55 is continued in the same pattern, only one conjunction in the continuation is also found in No. 76, that at the end of S.E. 208, month I, which happens to be at the end of the six-month interval in No. 76. ${ }^{17}$

17 ACT No. 75 may derive from a text of similar structure, though only twelve-month intervals are still in evidence in the preserved parts.

It is clear that texts of this sort cannot be intimately associated with solar eclipses, for in that case intervals of five and six months, and combinations thereof, would be relevant, but not, as we have here, a six-month followed by a one-month interval.

Finally a remark about Column I. Neugebauer assumed that it is a Col. F, giving lunar velocity; this still seems the best assumption, for though my attempts at reconstruction have failed we have already so many variants of Col. F that a new one would not be very surprising.

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## Added in Proof

Since my manuscript went to the printer I had occasion to examine the above texts, once again, in the British Museum. As a result, the following critical remarks should be added:

Text C
Col. II, l. 1: 2,1[8,6...lal]; traces check with 8.
Col. II, l. $6: 21,37,4[\ldots]$; contrary to my reconstruction, collation shows at least 7 , instead of 4 .

ACT No. 55
Obv. II, l. 5': 9,17,38, ...; 17 looks more like 27.
Rev. III, l. $1^{\prime}-8^{\prime}:$ the surface is preserved and is blank where is should be; there are traces of signs in 1. 7' and 8', precisely where the writing should begin again. Hints of tab and lal are just visible at the end of Col. II.

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## BENT FUGLEDE

## CAPACITY AS A SUBLINEAR FUNCTIONAL GENERALIZING AN INTEGRAL



Kommissionær: Munksgaard København 1971

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## Synopsis

With a view at certain applications in potential theory a general study is made of a capacity $c$ in the sense of a finite valued, increasing, and sublinear functional $>0$ defined on the cone of all finite valued, continuous functions $\geq 0$ of compact support on a locally compact space $X$.

It is shown that any such capacity $c$ is representable as the supremum of the family of all linear capacities ( $=$ positive Radon measures) majorized by $c$. Like in integration theory, $c$ may be extended to a lower capacity $c_{*}$ and an upper capacity $c^{*}$, both defined for arbitrary functions on $X$ to $[0,+\infty]$. The main object is the investigation of certain function classes, closed with respect to $c^{*}$.

## Introduction

TThe notion of capacity is usually that of a set function (having some of the properties of a measure). For the investigation of the capacities in potential theory I have found it advantageous to view a capacity $C$ primarily as a functional (with some of the properties of an integral) rather than a set function. Thus one avoids the separate consideration of several capacities with respect to different "weight functions" (usually hyperharmonic functions or potentials), cf. § 6.7.

In the present paper we treat a rather general notion of capacity as a sublinear functional. More precisely we begin (Chapter I) by considering a capacity as an increasing and countably sublinear mapping $C: \mathscr{F}+(X) \rightarrow$ $[0,+\infty]$. Here $\mathscr{F}^{+}(X)$ denotes the class of all functions on a set $X$ into $[0,+\infty]$. When $X$ is a topological space we call $C$ an upper capacity if, in addition, the value $C(f)$ for any $f \in \mathscr{F}+(X)$ is the infimum of $C(g)$ for $g \geqq f$ and $g$ belonging to the class $\mathscr{G}=\mathscr{G}(X)$ of all lower semicontinuous functions $g \in \mathscr{F}+(X)$.

Next we study (Chapter II), likewise under the name of capacity, an increasing sublinear functional $c: \mathscr{C}_{0}^{+}(X) \rightarrow\left[0,+\infty\left[\right.\right.$, where $\mathscr{C}_{0}^{+}(X)$ denotes the class of all continuous functions of compact support on a locally compact space $X$, and with finite values $\geqq 0$. As in the special (linear) case of a Radon measure (cf. Cartan [8], Bourbaki [2]) such a functional (capacity) $c$ has natural extensions to a lower capacity $c_{*}$ and an upper capacity $c^{*}$. The latter is also an upper capacity in the sense of Chapter I.

The main interest will be focussed upon the investigation of certain subclasses of $\mathscr{F}+(X)$. In addition to the above class $\mathscr{G}$ we have the class $\mathscr{H}_{0}$ of all upper semicontinuous functions of finite values $\geqq 0$ and of compact support. By a process of closure defined in terms of the (upper) capacity in question we arrive at the basic function classes $\mathscr{G}^{*}$ and $\mathscr{H}_{0}^{*}$. In the special case of a Radon measure on a locally compact space which is countable at infinity, $\mathscr{G}^{*}$ and $\mathscr{H}_{0}^{*}$ consist of those functions (in $\mathscr{F}+(X)$ ) which are $\mu$-measurable and $\mu$-integrable, respectively. In the general case the two classes are unrelated, $\mathscr{G}^{*}$ being the class of all quasi lower semicontinuous
functions in $\mathscr{F}+(X)$ whereas the particularly important class $\mathscr{H}_{0}^{*}$ consists of certain quasi upper semicontinuous functions in $\mathscr{F}+(X)$, cf. § 2.5 .

In $\S 5$ it is shown by a standard application of the Hahn-Banach theorem that any capacity $c: \mathscr{C}_{0}^{+}(X) \rightarrow[0,+\infty[$ (in the sense of Chapter II) is representable as the "upper envelope" (supremum) of a certain family $\mathscr{S}$ of positive Radon measures on the given locally compact space $X-a$ result announced earlier by Choquet [10]. This allows us (Theorem 6.2) to characterize $\mathscr{G} * \cap \mathscr{H}_{0}^{*}$ as the class of those functions $f \in \mathscr{G} * \cup \mathscr{H}_{0}^{*}$ for which $\int f d \mu$ is finite and continuous when considered as a function of $\mu \in \mathscr{S}$, using the vague topology. In the theory of the "energy capacity" with respect to a symmetric lower semicontinuous kernel $G: X \times X \rightarrow[0,+\infty]$-a principal domain of application for the present study-this result implies that $G$ is consistent (cf. [14], [15] in the case of a positive definite kernel) if and only if every potential $G \mu$ of finite energy $\int G \mu d \mu$ is of class $\mathscr{H}_{0}^{*}$ (with respect to the upper energy capacity). Brief indications of this and other potential theoretic applications of the present study are given in $\S \S 3.8,5.7$, and 6.7. A systematic account of such applications is in preparation.

## Notations

For any set $X$ we denote by $\mathscr{P}(X)$ the set of all subsets of $X$, and by $\mathscr{F}(X)$, resp. $\mathscr{F}+(X)$, the set of all functions on $X$ with values in $[-\infty$, $+\infty]$, resp. $[0,+\infty]$. The indicator function for a set $A$ is denoted by $1_{A}$. The symmetric difference between two sets $A, B$ is denoted by $A \triangle B$. Furthermore, $\boldsymbol{R}$ and $\boldsymbol{N}$ denote the real and the natural numbers, respectively.

The usual lattice operations (pointwise supremum and infimum) on $\mathscr{F}(X)$ or $\mathscr{F}+(X)$ are often designated by the symbols $\vee$ and $\wedge$, respectively, and we write $f^{+}=f \vee 0, f^{-}=(-f) \vee 0$. Moreover, we write $f_{n} \nmid f$ (resp. $\left.f_{n} \searrow f\right)$ to signify that the sequence $\left(f_{n}\right)_{n \in \boldsymbol{N}}$ of functions $f_{n} \in \mathscr{F}(X)$ is pointwise increasing (resp. decreasing) with the pointwise supremum (resp. infimum) $f$.

All the usual indeterminate expressions involving extended real numbers are interpreted as 0 . For example,

$$
0 \cdot( \pm \infty)=0,(+\infty)+(-\infty)=0 .
$$

Thus the elementary algebraic operations with extended real numbers are always well defined. Note that the triangle inequality

$$
|a-b| \leqq|a-c|+|c-b|
$$

holds for arbitrary $a, b, c, \in[-\infty,+\infty]$.

## Chapter I

## Capacity as a Countably Sublinear Functional on $\mathscr{F}+(\boldsymbol{X})$

## 1. Capacity on an Abstract Space

In the present section $X$ denotes a fixed set (without topology).
1.1. Definitions. By a capacity on $X$ we understand, in this chapter, an increasing, countably sublinear (= positive homogeneous and countably subadditive) mapping $C$ of $\mathscr{F}+(X)$ into $[0,+\infty]$.

Thus we should have, for $f, f_{1}, f_{2}, \ldots \in \mathscr{F}+(X)$,
$\left(\mathrm{C}_{1}\right) \quad\left[f_{1} \leqq f_{2}\right] \Rightarrow\left[C\left(f_{1}\right) \leqq C\left(f_{2}\right)\right]$,
$\left(\mathrm{C}_{2}\right) \quad C(a f)=a C(f)$ for $a \in[0,+\infty[$,
( $\left.\mathrm{C}_{3}\right) \quad C\left(\sum_{n \in \boldsymbol{N}} f_{n}\right) \leqq \sum_{n \in N} C\left(f_{n}\right)$.
Note that $C(0)=0$ on account of $\left(\mathrm{C}_{2}\right)$.
Given a capacity $C$ on $X$ we put, for any extended real valued function $f \in \mathscr{F}(X)$,

$$
\widetilde{C}(f):=C(|f|) .
$$

Taking into account our conventions regarding indeterminate expressions (see Notations above) we obtain for $f, f_{1}, f_{2} \in \mathscr{F}(X)$ and $\left.a \in\right]-\infty,+\infty[$

$$
\begin{gathered}
\widetilde{C}(a f)=|a| \widetilde{C}(f), \\
\widetilde{C}\left(f_{1}+f_{2}\right) \leqq \widetilde{C}\left(f_{1}\right)+\widetilde{C}\left(f_{2}\right) .
\end{gathered}
$$

It follows that $\widetilde{C}\left(f_{1}-f_{2}\right)=C\left(\left|f_{1}-f_{2}\right|\right)$ defines a pseudometric on $\mathscr{F}(X)$ (in particular on $\mathscr{F}+(X)$ ), to which we shall refer as the $C$-metric on $\mathscr{F}(X)$ (resp. $\mathscr{F}+(X)$ ). Two functions $f_{1}, f_{2} \in \mathscr{F}(X)$ are called $C$-equivalent (or just equivalent) if $C\left(\left|f_{1}-f_{2}\right|\right)=0$.
1.2. The associated set function. From the functional $C$ on $\mathscr{F}+(X)$ we derive a set function, likewise denoted by $C$, defined for all subsets of $X$ by

$$
C(A)=C\left(1_{A}\right) .
$$

Thus our capacity $C: \mathscr{F}+(X) \rightarrow[0,+\infty]$ induces an increasing and countably subadditive set function $C: \mathscr{P}(X) \rightarrow[0,+\infty]$ for which $C(\varnothing)=0$. Explicitly we have, for $A_{1}, A_{2}, \ldots \subset X$,

$$
\begin{gathered}
{\left[A_{1} \subset A_{2}\right] \Rightarrow\left[C\left(A_{1}\right) \leqq C\left(A_{2}\right)\right],} \\
C\left(\mathcal{U}_{n \in N} A_{n}\right) \leqq \sum_{n \in N} C\left(A_{n}\right), \\
C(\varnothing)=0 .
\end{gathered}
$$

A set function with these properties was studied in [17], likewise under the name of a capacity on $X$. Concepts and results from [17] will be carried over freely to the present case of the set function associated with a capacity in the sense of $\S 1.1$ above.

In particular, a property $P[x]$ is said to hold quasi everywhere (q. e.) in a set $A \subset X$ if $C(\{x \in A \mid$ non $P[x]\})=0$. If $A=X$ we may write simply q. e. (in place of q. e. in $X$ ).
1.3. Lemma: For functions $f, f_{1}, f_{2} \in \mathscr{F}+(X)$ we have:
(a) $[f(x)=0$ q.e. $] \Leftrightarrow[C(f)=0]$.
(b) $\left[f_{1}(x) \leqq f_{2}(x)\right.$ q. e. $] \Leftrightarrow\left[C\left(\left(f_{1}-f_{2}\right)^{+}\right)=0\right] \Rightarrow\left[C\left(f_{1}\right) \leqq C\left(f_{2}\right)\right]$.
(c) $[C(f)<+\infty] \Rightarrow[f(x)<+\infty$ q.e. $]$.

Proof. (a) Let $E:=\{x \in X \mid f(x)>0\}$. Then

$$
f \leqq 1_{E}+1_{E}+\ldots ; \quad 1_{E} \leqq f+f+\ldots,
$$

from which the assertion follows by use of $\left(\mathrm{C}_{3}\right)$. As to (b), write $f:=$ $\left(f_{1}-f_{2}\right)^{+}$, and apply (a). Next observe that $f_{1} \leqq f_{2}+f$, and hence by $\left(\mathrm{C}_{1}\right)$, $\left(\mathrm{C}_{3}\right): C\left(f_{1}\right) \leqq C\left(f_{2}+f\right) \leqq C\left(f_{2}\right)+C(f)=C\left(f_{2}\right)$ if $C(f)=C\left(\left(f_{1}-f_{2}\right)^{+}\right)=0$. To establish (c) let $E_{t}:=\{x \in X \mid f(x) \geqq t\}$ for any $\left.\left.t \in\right] 0,+\infty\right]$. Then $t 1_{E_{t}} \leqq f$ for every finite $t$, and hence by ( $\mathrm{C}_{1}$ ), ( $\mathrm{C}_{2}$ )

$$
C\left(E_{+\infty}\right) \leqq C\left(E_{t}\right)=t^{-1} C\left(t 1_{E_{t}}\right) \leqq t^{-1} C(f),
$$

from which the result follows for $t \rightarrow+\infty$. I
Corollary 1. Let $\left.f \in \mathscr{F}^{+}(X), t \in\right] 0,+\infty[, A \subset X$, and suppose that

$$
f(x) \geqq t \quad \text { q. e. in } A .
$$

Then $C(A) \leqq t^{-1} C(f)$.
(In fact, $1_{A} \leqq t^{-1} f$ quasi everywhere.)
Corollary 2. Two functions $f_{1}, f_{2} \in \mathscr{F}(X)$ are $C$-equivalent if and only if $f_{1}(x)=f_{2}(x)$ q.e.
(Apply Lemma 1.3. (a) to $f:=\left|f_{1}-f_{2}\right|$.)
1.4. Quasi uniform convergence. A sequence of functions $f_{n} \in \mathscr{F}(X)$ is said to converge quasi uniformly to a function $f \in \mathscr{F}(X)$ if there exists for every $\varepsilon>0$ a set $\omega \subset X$ with $C(\omega)<\varepsilon$ such that $f_{n}$ converges uniformly to $f$ on $\boldsymbol{\complement} \omega$ as $n \rightarrow \infty$. In the affirmative case we clearly have $f_{n}(x) \rightarrow f(x)$ pointwise q.e.

Theorem. If a sequence of functions $f_{n} \in \mathscr{F}(X)$ converges in the $C$-metric to a function $f \in \mathscr{F}(X)$, then there exists a subsequence of $\left(f_{n}\right)$ which converges quasi uniformly to $f$.

Proof. Passing to a suitable subsequence we may suppose that $C\left(\left|f_{n}-f\right|\right)<4^{-n}$ for $n=1,2, \ldots$ Writing

$$
\begin{aligned}
& M_{n}:=\left\{x \in X| | f_{n}(x)-f(x) \mid>2^{-n}\right\}, \\
& N_{p}:=\underset{n>p}{\cup} M_{n},
\end{aligned}
$$

we get, from Cor. 1 to Lemma 1.3, $C\left(M_{n}\right) \leqq 2^{n} C\left(\left|f_{n}-f\right|\right)<2^{-n}$, and hence $C\left(N_{p}\right) \leqq \sum_{n>p} 2^{-n}=2^{-p}$. Clearly $f_{n}(x) \rightarrow f(x)$ uniformly on $\complement N_{p}$ for each $p$, hence quasi-uniformly. I
1.5. The Banach space $L(C)$. Like in integration theory one might consider the subset $\mathscr{L} \subset \mathscr{F}(X)$ consisting of all $f \in \mathscr{F}(X)$ with $C(|f|)<+\infty$ (and hence $|f(x)|<+\infty$ q.e.). The quotient space $L=L(C)$ of $\mathscr{L}$ with respect to $C$-equivalence is a vector space (unlike $\mathscr{L}$ itself), and the mapping $f \mapsto C(|f|)$ of $\mathscr{L}$ into $[0,+\infty[$ induces a norm on $L(C)$. By the standard Riesz-Fischer technique it can be easily shown that $L(C)$ is complete in this norm, i.e. $L(C)$ is a Banach space. (This result, however, will not be used in the sequel.)
1.6. Souslin functions. Capacitability. Let $\mathscr{H}$ denote a subset of $\mathscr{F}+(X)$ containing 0 and stable under countable infimum. By an $\mathscr{H}$-Souslin function $f \in \mathscr{F}+(X)$ we understand a function which can be obtained from functions of class $\mathscr{H}$ by application of Souslin's operation (A) as described e.g. in Choquet [11] (with the obvious changes caused by our consideration of the function lattice $\mathscr{F}+(X)$ instead of the lattice $\mathscr{P}(X)$ of all subsets of $X$ ).

The class of all $\mathscr{H}$-Souslin functions is stable under countable supremum or infimum and contains $\mathscr{H}$.

Consider now a capacity $C$ on $X$, or equally well any increasing mapping

$$
C: \mathscr{F}+(X) \rightarrow[0,+\infty] .
$$

According to Choquet [12], a function $f \in \mathscr{F}+(X)$ is called ( $C, \mathscr{H}$ )-capacitable if

$$
C(f)=\sup \{C(h) \mid h \in \mathscr{H}, h \leqq f\} .
$$

We quote the main theorem of capacitability in the present abstract case:

Theorem (Choquet [12]). Suppose that the increasing functional C: $\mathscr{F}+(X) \rightarrow[0,+\infty]$ is sequentially order continuous from above on $\mathscr{H}$, and sequentially order continuous from below on all of $\mathscr{F}+(X)$ :

$$
\begin{aligned}
& {\left[h_{n} \searrow h, h_{n} \in \mathscr{H}\right] \Rightarrow\left[C\left(h_{n}\right) \rightarrow C(h)\right],} \\
& {\left[f_{n} \nsucc f, f_{n} \in \mathscr{F}+(X)\right] \Rightarrow\left[C\left(f_{n}\right) \rightarrow C(f)\right] .}
\end{aligned}
$$

Then every $\mathscr{H}$-Souslin function $f \in \mathscr{F}+(X)$ is $(C, \mathscr{H})$-capacitable.

## 2. Some Basic Classes of Functions

In the sequel $X$ denotes a Hausdorff ${ }^{1)}$ topological space. Writing l.s.c. and u.s.c. for lower and upper semicontinuous, respectively, we shall consider the following subclasses of the class $\mathscr{F}+(X)$ of all functions $f: X \rightarrow[0,+\infty]$ :
$\mathscr{G}(=\mathscr{G}(X))=\{f \in \mathscr{F}+(X) \mid f$ is l.s.c. $\}$,
$\mathscr{H}=\{f \in \mathscr{F}+(X) \mid f$ is u.s.c. and finite $\}$,
$\mathscr{H}_{0}=\{f \in \mathscr{H} \mid f$ has compact support $\}$,
$\mathscr{C}^{+}=\mathscr{G} \cap \mathscr{H}=\{f \in \mathscr{F}+(X) \mid f$ is continuous and finite $\}$,
$\mathscr{C}_{0}^{+}=\mathscr{G} \cap \mathscr{H}_{0}=\{f \in \mathscr{C}+\mid f$ has compact support $\}$.
2.1. The closed classes. $\mathscr{G}^{*}, \mathscr{H}^{*}, \mathscr{H}_{0}^{*}$. Let $C$ denote a given capacity on $X$ in the sense of $\S 1.1$. We denote by $\mathscr{G}^{*}, \mathscr{H}^{*}$, and $\mathscr{H}_{0}^{*}$ the closures of $\mathscr{G}, \mathscr{H}$, and $\mathscr{H}_{0}$, respectively, in the $C$-metric topology on $\mathscr{F}+(X)$. Thus we have, for $f \in \mathscr{F}+(X)$,

$$
\left[f \in \mathscr{G}^{*}\right] \Leftrightarrow[\inf \{C(|f-\varphi|) \mid \varphi \in \mathscr{G}\}=0],
$$

and similarly with $\mathscr{H}_{\text {or }} \mathscr{H}_{0}$ in place of $\mathscr{G}$ (and $\mathscr{H}^{*}$ or $\mathscr{H}_{0}^{*}$ in place of $\mathscr{G}^{*}$ ). Clearly $\mathscr{H}_{0}^{*} \subset \mathscr{H}^{*}$. Every function of class $\mathscr{H}^{*}$ is finite q.e. Each of the 3 classes is a convex cone which is saturated with respect to $C$-equivalence (§ 1.1.) within $\mathscr{F}^{+}(X)$.
2.2. Theorem. $\mathscr{G}^{*}$ is stable under countable supremum and finite infimum. $\mathscr{H}^{*}$ and $\mathscr{H}_{0}^{*}$ are stable under countable infimum and finite supremum.

Proof. Follows easily from the corresponding properties of $\mathscr{G}, \mathscr{H}, \mathscr{H}_{0}$ in view of the inequalities

$$
\left.\begin{array}{c}
\left|\sup _{n} f_{n}-\sup _{n} \varphi_{n}\right| \\
\left|\inf _{n} f_{n}-\inf _{n} \varphi_{n}\right|
\end{array}\right\} \leqq \sup _{n}\left|f_{n}-\varphi_{n}\right| \leqq \sum_{n}\left|f_{n}-\varphi_{n}\right|
$$

for finite or infinite families $\left(f_{n}\right)$ and $\left(\varphi_{n}\right)$ of functions of class $\mathscr{F}+(X)$. I
${ }^{1}$ ) The Hausdorff separation property is needed only in contexts involving compact subsets of $X$, e.g. in connection with functions of compact support, thus in particular for the classes $\mathscr{H}_{0}, \mathscr{C}_{0}^{+}$, and $\mathscr{H}_{0}^{*}$.
2.3. Lemma. If $g \in \mathscr{G}^{*}, h \in \mathscr{H}^{*}$, then

$$
(g-h)^{+} \in \mathscr{G}^{*}, \quad(h-g)^{+} \in \mathscr{H}^{*} .
$$

Similarly with $\mathscr{H}_{0}^{*}$ in place of $\mathscr{H}^{*}$.
Proof. Follows easily from the corresponding properties of $\mathscr{G}$ and $\mathscr{H}$ (resp. $\mathscr{H}_{0}$ ) in view of the inequality

$$
\left|(g-h)^{+}-(\varphi-\psi)^{+}\right| \leqq|g-\varphi|+|h-\psi|
$$

for functions $g, h, \varphi, \psi$ of class $\mathscr{F}+(X)$. I
2.4. Lemma, Let $A \subset X$. Then $A$ is quasi open (quasi closed) if and only if $1_{A} \in \mathscr{G}^{*}\left(1_{A} \in \mathscr{H}^{*}\right)$. Moreover, $A$ is quasi compact if and only if $1_{A} \in \mathscr{H}_{0}^{*}$.

Proof. As to the notions quasi open, etc., see [17, § 2], to be applied here to the set function $C(A)=C\left(1_{A}\right)$ associated with the given capacity functional $C: \mathscr{F}+(X) \rightarrow[0,+\infty]$ as described in $\S 1.2$. The "only if" part of the lemma is obvious since

$$
\begin{aligned}
{[A \text { open }(\text { closed })] } & \Leftrightarrow\left[1_{A} \in \mathscr{G}\left(1_{A} \in \mathscr{H}\right)\right], \\
{[A \text { compact }] } & \Leftrightarrow\left[1_{A} \in \mathscr{H}_{0}\right] .
\end{aligned}
$$

Conversely, let $1_{A} \in \mathscr{H}^{*}$ (resp. $\mathscr{H}_{0}^{*}$ ), and choose $\varphi \in \mathscr{H}^{(r e s p .} \mathscr{H}_{0}$ ) so that $C\left(\left|1_{A}-\varphi\right|\right)<\varepsilon$. The set $E:=\left\{x \in X \left\lvert\, \varphi(x) \geqq \frac{1}{2}\right.\right\}$ is closed (resp. compact), and $\left|1_{A}-\varphi\right| \geqq \frac{1}{2}$ on $A \Delta E$, that is,

$$
1_{A \Delta E} \leqq 2\left|1_{A}-\varphi\right| .
$$

Consequently, $C(A \Delta E) \leqq 2 C\left(\left|1_{A}-\varphi\right|\right)<2 \varepsilon$. The proof is quite similar in the case $1_{A} \in \mathscr{G}^{*}$. I
2.5. Theorem. Let $f \in \mathscr{F}+(X)$. Then
(a) $f \in \mathscr{G}^{*}$ if and only if $f$ is quasi l.s.c.
(b) The following propositions are equivalent:
(i) $f \in \mathscr{H}_{0}^{*}$.
(ii) $f$ is quasi u.s.c. and has a majorant of class $\mathscr{H}_{0}^{*}$.
(iii) $f$ is quasi u.s.c., and $\inf \left\{C\left((f-h)^{+}\right) \mid h \in \mathscr{H}_{0}\right\}=0$.

Proof. As to the notions of quasi continuity and quasi semicontinuity, see $[17, \S 3]$. Any function $f$ of class $\mathscr{G}^{*}$ (resp. $\mathscr{H}^{*}$ ) is by definition a limit in the $C$-metric topology (§ 1.1) of a sequence of functions of class $\mathscr{G}$ (resp. $\mathscr{H}$ ), and hence $f$ is quasi l.s.c. (resp. quasi u.s.c.) according to Theorem 1.4, because the quasi uniform limit of a sequence of quasi l.s.c. (resp. quasi u.s.c.) functions is a function of the same kind ([17, th. 3.2]). This
establishes the "only if" part of (a) and the implication (i) $\Rightarrow$ (ii) (even with $\mathscr{H}^{*}$ in place of $\mathscr{H}_{0}^{*}$ ).

Next suppose that $f$ is quasi l.s.c. For every $n \in \boldsymbol{N}$ the function $f_{n}:=$ $f \wedge n$ is quasi l.s.c. and bounded. We propose to show that $f_{n} \in \mathscr{G}^{*}$ for all $n \in \boldsymbol{N}$, and consequently that $f=\sup f_{n} \in \mathscr{G}^{*}$ according to Theorem 2.2. By definition there are sets $\omega$ of arbitrary small $C(\omega)$ such that $f_{n}$ is I.s.c. relatively to $\left\lceil\omega\right.$. Since $0 \leqq f_{n} \leqq n$ there is a l.s.c. function $\varphi_{n}$ such that $0 \leqq \varphi_{n} \leqq n$ which agrees with $f_{n}$ on $\boldsymbol{C} \omega{ }^{2}{ }^{2}$ Clearly $C\left(\left|f_{n}-\varphi_{n}\right|\right) \leqq n C(\omega)$ is as small as we please.

As to (b), the implication (ii) $\Rightarrow$ (iii) is obvious (even without quasi u.s.c.), since for any $g \in \mathscr{H}_{0}^{*}$ such that $g \geqq f$ and for any $h \in \mathscr{H}_{0}$

$$
(f-h)^{+} \leqq(g-h)^{+} \leqq|g-h| .
$$

Finally suppose that (iii) holds. Since $(f-h)^{+}=f-f \wedge h$, this implies that $f$ may be approximated in the $C$-metric topology by functions of the form $f \wedge h$ with $h \in \mathscr{H}_{0}$. Since $f \wedge h$ is quasi u.s.c. and $\leqq h \in \mathscr{H}_{0}$, it suffices to prove that any quasi u.s.c. function $f \in \mathscr{F}+(X)$ having a majorant $h \in \mathscr{H}_{0}$, is of class $\mathscr{H}_{0}^{*}$. By definition there are sets $\omega$ of arbitrary small $C(\omega)$ such that the restriction of $f$ to $\boldsymbol{C} \omega$ is u.s.c. The u.s.c. envelope $\varphi$ of $f \cdot 1_{\mathbf{C} \omega}$ is $\leqq h$, hence $\varphi \in \mathscr{H}_{0}$, and agrees with $f$ on $\lceil\omega$. Since $h$, and hence $f$, is bounded, say $\leqq a$, we find that $C(|f-\varphi|)=C\left(1_{\omega}|f-\varphi|\right) \leqq a C(\omega)$ is as small as we please. I

Definition. A function $f \in \mathscr{F}(X)$ is called semibounded if

$$
\inf _{t \geqq 0} C\left((|f|-t)^{+}\right)=0 .
$$

Corollary. A function $f \in \mathscr{F}+(X)$ is of class $\mathscr{H}_{0}^{*}$ if and only if $f$ is quasi u.s.c., semibounded, and has the further property

$$
\inf \left\{C\left(f \cdot 1_{\mathrm{c} K}\right) \mid K \text { compact }\right\}=0 .
$$

This follows by use of (iii) of the above theorem since any $h \in \mathscr{H}_{0}$ has a majorant of the form $t \cdot 1_{K}$ with $t \in[0,+\infty[, K$ compact; and since any such function $t \cdot 1_{K}$ is of class $\mathscr{H}_{0}$.

Note also that the above condition $\inf C\left(f \cdot 1_{\mathrm{c} K}\right)=0$ is (necessary and) sufficient for a function $f \in \mathscr{H}^{*}$ to belong to $\mathscr{H}_{0}^{*}$. This appears from the estimate
${ }^{2}$ ) For instance take for $\varphi_{n}$ the l.s.c. envelope of the function which equals $f_{n}$ in $\mathbf{C} \omega$, and $n$ in $\omega$.

$$
\left|f-h \cdot 1_{K}\right| \leqq f \cdot 1_{\mathbf{C} K}+|f-h|
$$

with $h \in \mathscr{H}, K$ compact, and hence $h \cdot 1_{K} \in \mathscr{H}_{0}$.
Remark. In the case of an upper capacity C ( $\$ 3.1$ below) on our Hausdorff space $X$, any function of class $\mathscr{H}_{0}^{*}$, and more generally any function $f \in \mathscr{F}(X)$ such that $\inf \left\{C\left(|f| \cdot 1_{\mathbf{c} K}\right) \mid K\right.$ compact $\}=0$, has in particular the quasi limit 0 at infinity, in the sense that there are open sets $\omega \subset X$ with $C(\omega)$ as small as we please such that the restriction of $f$ to $\boldsymbol{C} \omega$ vanishes at infinity in the closed, hence locally compact, subspace $\lceil\omega$. This follows from [17, § 3.6.] since any function $f$ as stated is the limit in the $C$-metric topology (hence also the quasi uniform limit) of a sequence of functions of compact support.

Similarly, any function $f \in \mathscr{H}_{0}^{*}$, and more generally any semibounded function $f \in \mathscr{F}(X)$, is in particular quasi bounded in the sense that there are sets $\omega \subset X$ with $C(\omega)$ as small as we please such that $f$ is bounded on〔 $\omega$. Note also that any function $f \in \mathscr{F}(X)$ such that $C(|f|)<+\infty$, is quasi bounded, and that any quasi bounded function is finite quasi everywhere. (This follows from the proof of Lemma 1.3 (c).)
2.6. Theorem. Let $f \in \mathscr{F}+(X)$, and consider the following statements:
(i) $f \in \mathscr{H}^{*}$.
(ii) $f$ is quasi u.s.c. and has a majorant of class $\mathscr{H}^{*}$.
(iii) $f$ is quasi u.s.c., and $\inf \left\{C\left((f-h)^{+}\right) \mid h \in \mathscr{H}\right\}=0$.
(iv) $\varphi f \in \mathscr{H}_{0}^{*}$ for every $\varphi \in \mathscr{H}_{0}$ (or just for every $\varphi \in \mathscr{C}_{0}^{+}$, or every $\varphi=1_{K}$ with $K$ compact).
Then (i) $\Rightarrow$ (ii) $\Rightarrow$ (iii) $\Rightarrow$ (iv). Conversely (iv) implies (i) if $X$ is locally compact and countable at infinity.

Proof. For the implications (i) $\Rightarrow$ (ii) $\Rightarrow$ (iii) see the corresponding parts of the proof of Theorem 2.5. For any $\varphi \in \mathscr{H}_{0}$, say with $\varphi \leqq a$, the estimate

$$
(\varphi f-\varphi h)^{+}=\varphi \cdot(f-h)^{+} \leqq a(f-h)^{+}
$$

allows us to conclude from (iii) that $\varphi f \in \mathscr{H}_{0}^{*}$ (by use of (iii) of Theorem 2.5.) because $\varphi h \in \mathscr{H}_{0}$ (when $\varphi \in \mathscr{H}_{0}$ and $h \in \mathscr{H}$ ), and $\varphi f$ is quasi u.s.c. along with $f$ (when $\varphi$ is u.s.c.). Finally, the validity of (iv) for all $\varphi=1_{K}$ with $K$ compact implies the same for any $\varphi \in \mathscr{H}_{0}$ (thus in particular for any $\varphi \in \mathscr{C}_{0}^{+}$) because the relation $\varphi f=\varphi \cdot\left(1_{K} f\right)$ (with $K=$ the compact support of $\varphi$ ) shows that $\varphi f$ is of class $\mathscr{H}_{0}^{*}$ as product of $\varphi \in \mathscr{H}_{0}$ and
$1_{K} f \in \mathscr{H}_{0}^{*}$. Thus it remains to prove that $f$ is of class $\mathscr{H} *$ whenever $\varphi f \in \mathscr{H}_{0}^{*}$ (or equivalently $\varphi f \in \mathscr{H}^{*}$ ) for all $\varphi \in \mathscr{C}_{0}^{+}$, assuming that $X$ is locally compact and countable at infinity. It is well known that there exists on such a space a partition of unity $\left(\varphi_{n}\right)_{n \in N}$ of class $\mathscr{C}_{0}^{+}$with the property that every compact subset of $X$ meets the support of at most finitely many $\varphi_{n}$. For given $\varepsilon>0$ choose functions $h_{n} \in \mathscr{H}$ so that $C\left(\left|\varphi_{n} f-h_{n}\right|\right)<$ $\varepsilon / 2^{n}$. Clearly we may assume that $h_{n}$ vanishes outside the support of $\varphi_{n}$. The function $h:=\sum_{n \in N} h_{n}$ is then likewise of class $\mathscr{H}$ because the sum is finite in any compact neighbourhood of a point of $X$. For $f-h=\sum_{n \in \boldsymbol{N}}\left(\varphi_{n} f-h_{n}\right)$
we find $C(|f-h|)<\varepsilon$. $\mid$

Corollary. On a locally compact space $X$ which is countable at infinity a function $f \in \mathscr{F}^{+}(X)$ is of class $\mathscr{H}^{*}$ if and only if $f$ is quasi u.s.c. and locally semibounded in the sense that $f \cdot 1_{K}$ is semibounded for every compact set $K$ (or equivalently for some neighbourhood $K$ of every point of $X$ ).

## 3. Upper Capacity

3.1. Definition. By an upper capacity on a topological space $X$ we understand a functional $C: \mathscr{F}+(X) \rightarrow[0,+\infty]$ which, in addition to $\left(\mathrm{C}_{1}\right),\left(\mathrm{C}_{2}\right)$, $\left(\mathrm{C}_{3}\right)$ of § 1.1, has the following property for every $f \in \mathscr{F}+(X)$ :

$$
\begin{equation*}
C(f)=\inf \{C(g) \mid g \in \mathscr{G}, g \geqq f\} . \tag{4}
\end{equation*}
$$

The associated set function $C: \mathscr{P}(X) \rightarrow[0,+\infty](\S 1.2)$ is then an outer capacity in the sense of $[17, \S 1.5]$ because

$$
C(A)=\inf \{C(G) \mid G \text { open, } G \supset A\}
$$

for every set $A \subset X$. In fact, let $g \in \mathscr{G}, g \geqq 1_{A}$, and let $0<t<1$. Then

$$
G:=\{x \in X \mid g(x)>t\}
$$

is open and contains $A$. According to Cor. 1 to Lemma 1.3 (or directly), $C(G) \leqq t^{-1} C(g)$, and here the right hand member may be taken as close as we please to $C\left(1_{A}\right)=C(A)$ by virtue of $\left(\mathrm{C}_{4}\right)$

In the sequel we always suppose that $C: \mathscr{F}+(X) \rightarrow[0,+\infty]$ denotes an upper capacity, and moreover that the topological space $X$ is a Hausdorff space (at least in contexts involving compactness).
3.2. Lemma. In the case of an upper capacity $C$ we have, for any $f \in \mathscr{F}+(X):$

$$
\begin{aligned}
& {\left[f \in \mathscr{G}^{*}\right] \Leftrightarrow[\inf \{C(\varphi-f) \mid \varphi \in \mathscr{G}, \quad \varphi \geqq f\}=0]} \\
& {\left[f \in \mathscr{H}^{*}\right] \Leftrightarrow[\inf \{C(f-\varphi) \mid \varphi \in \mathscr{H}, \quad \varphi \leqq f\}=0]} \\
& {\left[f \in \mathscr{H}_{0}^{*}\right] \Leftrightarrow\left[\inf \left\{C(f-\varphi) \mid \varphi \in \mathscr{H}_{0}, \varphi \leqq f\right\}=0\right] .}
\end{aligned}
$$

Proof. By definition (§ 2.1), the implication $\Leftarrow$ holds (for any capacity). Conversely, let $f \in \mathscr{G}^{*}$ and $\varepsilon>0$ be given. Choose $\psi \in \mathscr{G}$ so that $C(|f-\psi|)<$ $\varepsilon / 2$, and next $g \in \mathscr{G}$ with $g \geqq|f-\psi|$ so that $C(g)<\varepsilon / 2$. Then we may use $p=\psi+g(\in \mathscr{G})$ since $\varphi \geqq \psi+|f-\psi| \geqq f, \varphi-f=g+(\psi-f)$, and hence

$$
C(\varphi-f) \leqq C(g)+C(|\psi-f|)<\varepsilon .
$$

In the case $f \in \mathscr{H}^{*}$ (or $\mathscr{H}_{0}^{*}$ ), proceed similarly, now with $\psi \in \mathscr{H}^{(\text {or }} \mathscr{H}_{0}$ ), and take $\varphi=(\psi-g)^{+}$. I
3.3. Theorem. In the case of an upper capacity $C$ on a locally compact space $X, \mathscr{G}^{*} \cap \mathscr{H}_{0}^{*}$ is the closure of $\mathscr{G} \cap \mathscr{H}_{0}=\mathscr{C}_{0}^{+}$in the C-metric topology on $\mathscr{F}+(X)$.

Proof. We shall prove that any function $f \in \mathscr{G}^{*} \cap \mathscr{H}_{0}^{*}$ can be approximated in the $C$-metric (§1.1) by functions $\varphi \in \mathscr{C}_{0}^{+}$. For any $\varepsilon>0$ there exist, by the preceding lemma, functions $g \in \mathscr{G}$ and $h \in \mathscr{H}_{0}$ such that $h \leqq f \leqq g, C(g-f)<\varepsilon / 2, C(f-h)<\varepsilon / 2$, and hence $C(g-h)<\varepsilon$. According to Lemma 3.4 below there exists $\varphi \in \mathscr{C}_{0}^{+}$such that $h \leqq \varphi \leqq g$. It follows that $|f-\varphi| \leqq g-h$, and hence $C(|f-\varphi|)<\varepsilon$. I
3.4. Lemma. On a locally compact space $X$, let $g \in \mathscr{G}, h \in \mathscr{H}_{0}$, and suppose that $h \leqq g$. Then there exists $\varphi \in \mathscr{C}_{0}^{+}$such that $h \leqq \varphi \leqq g$.

Proof. This follows from the "between theorem", due to H. Hahn in the metrizable case (for a simple proof see Hausdorff [18]), and to H . Tong [20] in the most general case, viz. that of a normal space. The between theorem asserts that, if $h$ is u.s.c. and $g$ is l.s.c. on a normal space, and if $h \leqq g$, then there exists a continuous function $\varphi$ such that $h \leqq \varphi \leqq g$. In the special case of a compact space $X$ a simple direct proof can easily be given (cf. Bourbaki [1, 1. ed., exerc. 27, p. 72]), and this leads to the above lemma by compactification as follows (in the non-compact case):

Let $\hat{X}=X \cup\{\infty\}$ be the 1 point compactification of the locally compact space $X$, and define extensions $\hat{g}, \hat{h}$ of $g, h$ from $X$ to $\hat{X}$ by putting $\hat{g}(\infty)=$ $\hat{h}(\infty)=0$. Then $\hat{g}$ is l.s.c., and $\hat{h}$ is u.s.c. According to the between theorem for the compact space $\hat{X}$ there exists a continuous function $\hat{\varphi}$ on $\hat{X}$ such that $\hat{h} \leqq \hat{\varphi} \leqq \hat{g}$ (hence $\hat{\varphi} \geqq 0$ ). Let $\varphi$ denote the restriction of $\hat{\varphi}$ to $X$, and put $a=\sup _{x} h(x)(<+\infty)$. Replacing if necessary $\varphi$ by $\varphi \wedge a$ we may suppose $\varphi$ finite. Since $h \in \mathscr{H}_{0}$ we may achieve that $\varphi$ has compact support, hence $\varphi \in \mathscr{C}_{0}^{+}$, replacing if necessary $\varphi$ by $\varphi \psi$, where $\psi \in \mathscr{C}_{0}^{+}(X)$ is so chosen that $\psi=1$ on the support of $h$, and $\psi \leqq 1$ everywhere. I

Remark. The assumption that the space $X$ be locally compact is easily shown to be necessary in Lemma 3.4 as well as in Theorem 3.3.
3.5. Definition. An upper capacity $C: \mathscr{F}+(X) \rightarrow[0,+\infty]$ will be called locally finite if it has one of the following equivalent properties:
(i) $C(\{x\})<+\infty$ for every point $x \in X$.
(ii) Every point of $X$ has a neighbourhood of finite capacity.
(iii) $C(K)<+\infty$ for every compact (or quasi compact) set $K \subset X$.
(iv) $C(h)<+\infty$ for every $h \in \mathscr{H}_{0}$ (or $\mathscr{H}_{0}^{*}$ ).
3.6. Theorem. Suppose that $X$ is locally compact, and that the upper capacity $C$ is locally finite. Then
(a) For any downward directed family of functions $h_{\alpha} \in \mathscr{H}_{0}$

$$
C\left(\inf _{\alpha} h_{\alpha}\right)=\inf _{\alpha} C\left(h_{\alpha}\right) .
$$

(b) The same holds with $\mathscr{H}_{0}$ replaced by the larger class of all u.s.c. functions of class $\mathscr{H}_{0}^{*}$.
(c) For any decreasing sequence of functions $h_{n} \in \mathscr{H}_{0}^{*}$

$$
C\left(\inf _{n} h_{n}\right)=\inf _{n} C\left(h_{n}\right) .
$$

Proof. (a) Let $h=\inf h_{\alpha}$. For any $t>C(h)$ there exists by ( $\mathrm{C}_{4}$ ), $g \in \mathscr{G}$ such that $g \geqq h, C(g)<t$. For such a function $g$, the downward directed family of functions $\left(h_{\alpha}-g\right)^{+} \in \mathscr{H}_{0}$ converges pointwise to 0 . According to Dini's theorem the convergence is uniform. For every $\varepsilon>0$ there is, therefore, an index $\alpha$ such that $\left(h_{\alpha}-g\right)^{+}<\varepsilon$ everywhere. We may take $\alpha \geqslant \beta$ where $\beta$ denotes a fixed index. Denoting by $K$ the compact support of $h_{\beta}$, we obtain $h_{\alpha} \leqq g+\varepsilon \cdot 1_{K}$, and hence

$$
C\left(h_{\alpha}\right) \leqq C\left(g+\varepsilon \cdot 1_{K}\right) \leqq C(g)+\varepsilon C(K)<t
$$

by suitable choice of $\varepsilon$ and next of $\alpha \geqslant \beta$. This implies $\inf C\left(h_{\alpha}\right)<t$, and consequently $\inf C\left(h_{\alpha}\right) \leqq C(h)$. The converse inequality is obvious.
(b) In the slightly more general case where each $h_{\alpha}$ is u.s.c. and of class $\mathscr{H}_{0}^{*}$ we choose for some fixed index $\beta$ and for any $\varepsilon>0$ a function $\varphi \in \mathscr{H}_{0}$, $\varphi \leqq h_{\beta}$, so that $C\left(h_{\beta}-\varphi\right)<\varepsilon$. Since $h_{\alpha} \wedge \varphi \in \mathscr{H}_{0}$ decreases to $h \wedge \varphi$ (where again $h:=\inf _{\alpha} h_{\alpha}$ ), we obtain from (a)

$$
C(h \wedge \varphi)=\inf _{\alpha} C\left(h_{\alpha} \wedge \varphi\right),
$$

and hence there is an index $\alpha \geqslant \beta$ such that

$$
\begin{gathered}
C\left(h_{\alpha} \wedge \varphi\right)<C(h \wedge \varphi)+\varepsilon \leqq C(h)+\varepsilon, \\
C\left(h_{\alpha}\right) \leqq C\left(h_{\alpha} \wedge \varphi\right)+C\left(\left(h_{\alpha}-\varphi\right)^{+}\right)<C(h)+2 \varepsilon .
\end{gathered}
$$

(c) Given $\varepsilon>0$ choose $\varphi_{n} \in \mathscr{H}_{0}$ so that $\varphi_{n} \leqq h_{n}$ and $C\left(h_{n}-\varphi_{n}\right)<\varepsilon / 2^{n}$ (Lemma 3.2), and put

$$
f_{n}:=\varphi_{1} \wedge \ldots \wedge \varphi_{n}, \quad f:=\inf _{n} \varphi_{n}=\inf _{n} f_{n} .
$$

Then $\left(f_{n}\right)_{n \in \boldsymbol{N}}$ is a decreasing sequence of functions of class $\mathscr{H}_{0}$, and $f \leqq \inf _{n} h_{n}$. According to (a) above,

$$
C\left(f_{n}\right) \leqq C(f)+\varepsilon \leqq C\left(\inf _{n} h_{n}\right)+\varepsilon
$$

for all sufficiently large $n$. Since $\left(h_{n}\right)_{n \in N}$ is decreasing, we have for every $n \in \boldsymbol{N}$

$$
0 \leqq h_{n}-f_{n} \leqq \sup _{p \leqq n}\left(h_{p}-\varphi_{p}\right) \leqq \sum_{p \leqq n}\left(h_{p}-\varphi_{p}\right) .
$$

Consequently,

$$
C\left(h_{n}\right) \leqq C\left(f_{n}\right)+C\left(h_{n}-f_{n}\right) \leqq C\left(f_{n}\right)+\varepsilon \leqq C\left(\inf _{n} h_{n}\right)+2 \varepsilon
$$

for $n$ sufficiently large. I
3.7. Use of the quasi Lindelöf principle (cf. Doob [13], Fuglede [17]). Suppose now that the Hausdorff space $X$ has a countable base of open sets, and that the capacity $C$ is sequentially order continuous from below (on $\mathscr{F}+(X)$, cf. Theorem 1.6). Further let there be given on $X$ a new topology $\tau$, compatible with $C$ in the sense of $[17, \S 4.3]$ (more precisely: compatible with the quase topology determined by the set function $A \mapsto C(A):=C\left(1_{A}\right)$ associated with $A$ ).

Under these hypotheses we have established in [17, § 4.4] the validity of the "quasi Lindelöf principle" of Dоов [13]. Formulated for functions it states that any family $\left(f_{\alpha}\right)$ of $\tau$-l.s.c. (resp. $\tau$-u.s.c.) functions $f_{\alpha} \in \mathscr{F}(X)$ contains a countable subfamily $\left(f_{\alpha_{n}}\right)_{n \in N}$ whose pointwise supremum (resp. infimum) equals that of the given family quasi everywhere.-If $\left(f_{\alpha}\right)$ is upward (resp. downward) directed, we may of course achieve that the sequence ( $f_{\alpha_{n}}$ ) becomes increasing (resp. decreasing).

Theorem. Under the hypotheses specified above we have (a) $C\left(\sup f_{\alpha}\right)=$ $\sup C\left(f_{\alpha}\right)$ for any upward directed family of $\tau$-l.s.c. functions $f_{\alpha} \in \mathscr{F}+(X)$.
(b) If moreover $X$ is locally compact and $C$ a locally finite, upper capacity, then $C\left(\inf f_{\alpha}\right)=\inf C\left(f_{\alpha}\right)$ for any downward directed family of $\tau$-u.s.c. functions $f_{\alpha}$ having majorants of class $\mathscr{H}_{0}^{* *}$ (and hence being themselves of class $\mathscr{H}_{0}^{*}$ ).

Proof. The functions $f_{\alpha}$ are quasi l.s.c., respectively quasi u.s.c. (and hence of class $\mathscr{H}_{0}^{*}$ by Theorem 2.5), by virtue of the required compatibility between the new topology $\tau$ and the quasi topology determined by $C$, see [17, Lemma 4.3]. In view of the quasi Lindelöf principle stated above, statement (a) now follows from the assumed sequential order continuity of C from below, and (b) from Theorem 3.6 (c). I
3.8. Example. The first results of the type of Theorem 3.7 were established by Brelot [5], [6] in the framework of classical or axiomatic potential theory, the new topology $\tau$ being here the fine topology of Cartan [9], that is, the coarsest topology on $X$ such that every function in the cone $\mathscr{U}$ of all superharmonic functions $\geqq 0$ on $X$ becomes continuous. The space $X$ is now a "harmonic space", satisfying the group of axioms ( $\mathrm{A}_{1}$ ) in Brelot's axiomatic theory of harmonic functions [4]. It was proved by Brelot [5], [6] that ${ }^{3)}$

$$
\begin{aligned}
& \hat{R}_{\alpha \mathrm{inf} f_{\alpha}}=\inf _{\alpha}^{\hat{R}} \hat{R}_{f_{\alpha}}, \\
& \hat{R}_{\alpha}, \\
& \operatorname{supf}_{\alpha}
\end{aligned}=\sup _{\alpha} \hat{R}_{f_{\alpha}}, ~ l
$$

or in the equivalent integrated form

$$
\begin{aligned}
& \int \hat{R}_{\text {inf } f_{\alpha}} d m=\inf _{\alpha} \int \hat{R}_{f_{\alpha}} d m, \\
& \int \hat{R}_{{\sup f_{\alpha}}} d m=\sup _{\alpha} \int \hat{R}_{f_{\alpha}} d m .
\end{aligned}
$$

Here $\left(f_{\alpha}\right)$ denotes an upward (resp. downward) directed family of finely l.s.c. (resp. finely u.s.c.) functions $\geqq 0$ on the harmonic space $X$. In the second case the finely u.s.c. functions $f_{\alpha}$ should, moreover, be majorized by a semibounded potential $V . .^{4)}$ The measure $m$ may be any harmonic
${ }^{3}$ ) For any function $f \in \mathscr{F}^{+}(X), \hat{R}_{f}$ denotes the infimum of $\left\{u \in \mathscr{U}_{\infty} u \geqslant f\right\}$ in the complete lattice $\mathscr{U}_{\infty}=\mathscr{U} \cup\{+\infty\}$ of all hyperharmonic functions $\geq 0$ on $X$. Explicitly, the infimum $\widehat{\alpha} \underset{\alpha}{\hat{n} f} u_{\alpha}$ of any family of hyperharmonic functions $u \alpha \in \mathscr{U}_{\infty}$ in this lattice $\mathscr{U}_{\infty}$ is the 1.s.c. envelope of the pointwise infimum $\inf _{\alpha} u_{\alpha}$ (from which it differs only in some polar set, that is, a set contained in $\{x \in X \mid u(x) \stackrel{\alpha}{=}+\infty\}$ for some $u \in \mathscr{U})$. In particular, $\hat{R}_{f}$ is the 1.s.c. envelope of the pointwise infimum $R_{f}$ of $\left\{u \in \mathscr{U}_{\infty} \mid u \geq f\right\}$.
${ }^{4}$ ) It is known that any finite valued potential is semibounded. In the classical case of a Green space $X$ with the Green kernel $G$, a potential $V=G \lambda$ of a measure $\lambda \geqq 0$ on $X$ is semibounded if and only if $\lambda$ does not charge the polar sets and $G \lambda$. $\equiv+\infty$.
measure, or more generally any positive Radon measure ( $\neq 0$ ) such that $\int u d m<+\infty$ for every $u \in \mathscr{U}$.

These results of Brelot may be viewed as a particular case of Theorem 3.7, corresponding to the locally finite, upper capacity $C$ defined by

$$
C(f)=\int \hat{R}_{f} d m, \quad f \in \mathscr{F}+(X),
$$

with $m$ as specified above. This capacity $C$ is known to be sequentially order continuous from below (in case ( $\mathrm{A}_{1}$ ) of Brelot's axiomatic theory). According to Brelot [7] the fine topology on $X$ is compatible with the quasi topology determined by the set function $A \rightarrow \int \hat{R}_{1}^{A} d m$ associated with $C$ (see also [17, §5.6]). Hence it is easily shown by application of Theorem 2.5 that a finely (hence quasi) u.s.c. function $f \geqq 0$ on $X$ is of class $\mathscr{H}_{0}^{*}$ (with respect to the above capacity $C$ ) if and only if $f$ is majorized quasi everywhere by some hyperharmonic function $V$ of class $\mathscr{H}_{0}^{*}$ (the smallest such $V$ being $\hat{R}_{f}$ ). And in view of the corollary in $\S 2.5$, a hyperharmonic function $V \geqq 0$ is of class $\mathscr{H}_{0}^{*}$ if and only if $V$ is a potential which is semibounded in the sense of Brelot [6], or equivalently in the sense of Def. 2.5 above (with the capacity $f \rightarrow C(f)=\int \hat{R}_{f} d m$ ).
3.9. $\sigma$-finite sets. A set $A \subset X$ is called $\sigma$-finite with respect to a capacity $C: \mathscr{F}+(X) \rightarrow[0,+\infty]$ if $A$ can be covered by a sequence of sets $A_{n}$ such that $C\left(A_{n}\right)<+\infty$. When $C$ is an upper capacity the sets $A_{n}$ may of course be taken as open sets.

Lemma. $A$ set $A \subset X$ is $\sigma$-finite with respect to an upper capacity $C$ if and only if there exists a function $g \in \mathscr{G}$ such that $C(g)<+\infty$ and $g(x)>0$ for all $x \in A$.

Proof. If $g$ has these properties then $A$ is covered by the sets $A_{n}:=$ $\{x \in X \mid g(x)>1 / n\}$, and $C\left(A_{n}\right) \leqq n C(g)<+\infty$. Conversely, any covering $\left(A_{n}\right)$ as stated gives rise to a function $f:=\Sigma 2^{-n} C\left(A_{n}\right)^{-1} 1_{A_{n}} \in \mathscr{F}+(X)$ such that $C(f)<+\infty$ and $f>0$ in $A$. Since $C$ is an upper capacity there exists $g \in \mathscr{G}, g \geqq f(>0$ in $A)$ such that $C(g)<+\infty$. I
3.10. Use of a weight function. Let $C: \mathscr{F}+(X) \rightarrow[0,+\infty]$ denote a capacity in the sense of Def. 1.1, and let a function $f \in \mathscr{F}+(X)$ be given. The set function $C_{f}: \mathscr{P}(X) \rightarrow[0,+\infty]$ defined by

$$
C_{f}(A)=C\left(f \cdot 1_{A}\right)
$$

is then a capacity in the sense of [17] (cf. § 1.2 above for the particular case $f=1$ ).

Theorem. Suppose that the functional $C: \mathscr{F}+(X) \rightarrow[0,+\infty]$ is an upper capacity on a topological space $X$, that the weight function $f$ is of class $\mathscr{H}^{*}$, and that the set $X_{0}:=\{x \in X \mid f(x)=0\}$ is $\sigma$-finite. Then the above set function $C_{f}$ is an outer capacity:

$$
C_{f}(A)=\inf \left\{C_{f}(G) \mid G \text { open, } G \supset A\right\}
$$

for every set $A \subset X$.
In establishing this latter relation for a specified set $A$, it suffices to assume that $A \cap X_{0}$, rather than all of $X_{0}$, be $\sigma$-finite. Note that, for $f=1$, the theorem was obtained in $\S 3.1$. As to the notion of outer capacity in general see $[17, \S 1.5]$.

Proof. We may suppose that $C_{f}(A)<+\infty$. Consider functions $h \in \mathscr{H}$ and $g_{1}, g_{2} \in \mathscr{G}$ with $C\left(g_{2}\right)<+\infty$, such that

$$
\begin{gathered}
h \leqq f, \quad g_{1} \geqq f \cdot 1_{A}, \\
g_{2}>0 \text { on }\{x \in A \mid f(x)=0\}
\end{gathered}
$$

(cf. Lemma 3.9). Let $\varepsilon>0$, and write

$$
g:=(1+\varepsilon) g_{1}+\varepsilon g_{2} .
$$

Then $g \in \mathscr{G}, g>f$ on $A$, and hence the set

$$
G:=\{x \in X \mid g(x)>h(x)\}
$$

is open and contains $A$. Since $g>h \cdot 1_{G}$, we obtain

$$
\begin{gathered}
C_{f}(G)=C\left(f \cdot 1_{G}\right) \leqq C\left(h \cdot 1_{G}\right)+C(f-h) \\
\leqq C(g)+C(f-h) \\
\leqq(1+\varepsilon) C\left(g_{1}\right)+\varepsilon C\left(g_{2}\right)+C(f-h),
\end{gathered}
$$

which may be taken as close to $C\left(f \cdot 1_{A}\right)=C_{f}(A)$ as we please by appropriate choice of $h, g_{1}$, and $\varepsilon>0$. I

Remarks. 1) Note that $X_{0}$ is $\sigma$-finite if $f>0$, or if $C$ is locally finite and $X$ is of class $\mathscr{K}_{\sigma}$. Simple examples show that the $\sigma$-finiteness hypothesis in the above theorem cannot be dropped. Also the hypothesis $f \in \mathscr{H}^{*}$ cannot be replaced by $f$ quasi u.s.c. and quasi bounded (cf. § 2.5).
2) Under the same hypotheses as in the above theorem the functional $C_{f}$ defined by $C_{f}(\varphi)=C(f \varphi), \varphi \in \mathscr{F}+(X)$, is an upper capacity. (The proof is similar).

## Chapter II

## Capacity as a Sublinear Functional on $\mathscr{C}_{0}^{+}$

Throughout this chapter, $X$ denotes a locally compact (Hausdorff) space.

## 4. Extension to a Lower and an Upper Capacity

4.1. Definition. By a capacity on a locally compact space $X$ we understand, in this chapter, an increasing, sublinear functional c defined on $\mathscr{C}_{0}^{+}=\mathscr{C}_{0}^{+}(X)$ (the cone of continuous functions on $X$ to $[0,+\infty[$ of compact support) and with finite values $\geqq 0$.

Thus we should have, for $\varphi, \varphi_{1}, \varphi_{2} \in \mathscr{C}_{0}^{+}$and $a \in[0,+\infty[$, the following properties

$$
\begin{align*}
& {\left[\varphi_{1} \leqq \varphi_{2}\right] \Rightarrow\left[c\left(\varphi_{1}\right) \leqq c\left(\varphi_{2}\right)\right],}  \tag{1}\\
& c(a \varphi)=a c(\varphi),  \tag{2}\\
& c\left(\varphi_{1}+\varphi_{2}\right) \leqq c\left(\varphi_{1}\right)+c\left(\varphi_{2}\right), \tag{c3}
\end{align*}
$$

and furthermore $0 \leqq c(\varphi)<+\infty$. Note that $c(0)=0$ on account of $\left(c_{2}\right)$.
4.2. Extension to $\mathscr{H}_{0}$ and $\mathscr{G}$. Given a capacity $c$ on $X$, we define for $h \in \mathscr{H}_{0}$ and $g \in \mathscr{G}$

$$
\begin{aligned}
& c(h)=\inf \left\{c(\varphi) \mid \varphi \in \mathscr{C}_{0}^{+}, \varphi \geqq h\right\} \\
& c(g)=\sup \left\{c(\varphi) \mid \varphi \in \mathscr{C}_{0}^{+}, \varphi \leqq g\right\} .
\end{aligned}
$$

This is permissible and leads to a well-defined extension of $c$ to $\mathscr{G} \cup \mathscr{H}_{0}$ because $\mathscr{G} \cap \mathscr{H}_{0}=\mathscr{C}_{0}^{+}$, and $c$ is increasing on $\mathscr{C}_{0}^{+}$by $\left(c_{1}\right)$. Note that $c(h)<+\infty$ for every $h \in \mathscr{H}_{0}$. This extension of $c$ to $\mathscr{G} \cup \mathscr{H}_{0}$ is likewise increasing, the only non-trivial case being the implication

$$
\begin{equation*}
\left[h \in \mathscr{H}_{0}, g \in \mathscr{G}, h \leqq g\right] \Rightarrow[c(h) \leqq c(g)], \tag{1}
\end{equation*}
$$

which is an immediate consequence of the "between theorem" in the form given in Lemma 3.4.
4.3. Theorem. (a) For any upward directed family of functions $g_{\alpha} \in \mathscr{G}$

$$
c\left(\sup _{\alpha} g_{\alpha}\right)=\sup _{\alpha} c\left(g_{\alpha}\right) .
$$

(b) For any downward directed family of functions $h_{\alpha} \in \mathscr{H}_{0}$

$$
c\left(\inf _{\alpha} h_{\alpha}\right)=\inf _{\alpha} c\left(h_{\alpha}\right) .
$$

Proof. (a) Write $g:=\sup _{\alpha} g_{\alpha}$. Since $g \in \mathscr{G}$, there exists for any number $t<c(g)$ a function $\varphi \in \mathscr{C}_{0}^{+}$such that $\varphi \leqq g$ and $c(\varphi)>t$. Choose $\psi \in \mathscr{C}_{0}^{+}$ so that $\psi=1$ on the compact support of $\varphi$, and $\psi \leqq 1$ everywhere. Since the downward directed family of functions $\left(\varphi-g_{\alpha}\right)^{+} \in \mathscr{H}_{0}$ converges pointwise to 0 , the convergence is uniform by Dini's theorem. Denoting by $\beta$ a fixed index, there exists for any $\varepsilon>0$ an index $\alpha \geqslant \beta$ such that $\left(\varphi-g_{\alpha}\right)^{+}<\varepsilon$ everywhere. It follows by our choice of $\psi$ that $\varphi \leqq g_{a}+\varepsilon \psi$ everywhere. From this inequality we obtain ${ }^{5)}$

$$
c(\varphi) \leqq c\left(g_{\alpha}\right)+\varepsilon c(\psi) .
$$

Choosing $\varepsilon>0$ small enough so that $\varepsilon c(\psi) \leqq c(\varphi)-t$, we have now established the existence of an index $\alpha$ such that $c\left(g_{\alpha}\right) \geqq t$, and we have thus obtained the non-trivial inequality $c(g) \leqq \sup c\left(g_{\alpha}\right)$.

The case (b) is analogous and even simpler, cf. also the similar proof of Theorem 3.6 (a). Actually (b) follows from Theorems 3.6 (a) and 4.5. I
4.4. The lower capacity $c_{*}$ and the upper capacity $c^{*}$. These are defined for arbitrary $f \in \mathscr{F}+(X)$ by

$$
\begin{aligned}
& c_{*}(f)=\sup \left\{c(h) \mid h \in \mathscr{H}_{0}, h \leqq f\right\}, \\
& c_{*}(f)=\inf \{c(g) \mid g \in \mathscr{G}, g \geqq f\} .
\end{aligned}
$$

The functionals $c_{*}, c^{*}: \mathscr{F}+(X) \rightarrow[0,+\infty]$ are evidently increasing, and we get from (1), § 4.2 ,

$$
\begin{equation*}
c_{*}(f) \leqq c^{*}(f) \tag{2}
\end{equation*}
$$

for every $f \in \mathscr{F}^{+}(X)$. A function $f \in \mathscr{F}^{+}(X)$ such that $c_{*}(f)=c^{*}(f)$ is called capacitable (with respect to the capacity $c$ ), or $c$-capacitable. For any capacitable function $f$ we shall allow ourselves to write simply $c(f)$ in place of $c_{*}(f)$ or $c^{*}(f)$, and to call $c(f)$ the capacity of $f$. This is permissible (and leads to our ultimate extension of the original functional $c$ on $\mathscr{C}^{+}$) on account of the following lemma.

Lemma. Every function $f$ of class $\mathscr{G}$ or $\mathscr{H}_{0}$ is capacitable, and

$$
c_{*}(f)=c^{*}(f)=c(f) .
$$

Proof. If $f \in \mathscr{H}_{0}$ we have

$$
c^{*}(f) \leqq c(f)=c_{*}(f) .
$$

$\left.{ }^{5}\right)$ In fact, $(p-\varepsilon \psi)^{+} \in \mathscr{C}_{0}^{+},(\varphi-\varepsilon \psi)^{+} \leq g_{\alpha}$, and hence $c(p) \leq c\left((\varphi-\varepsilon \psi)^{+}\right)+c(\varepsilon \psi) \leq c\left(g_{\alpha}\right)$ $+\varepsilon c(\psi)$.

Here the inequality follows from the definitions of $c^{*}(f)$ and of $c(f)$ (for $f \in \mathscr{H}_{0}$ ) because $\mathscr{G} \supset \mathscr{C}_{0}^{+}$.-The case $f \in \mathscr{G}$ is quite analogous. I
4.5. Further properties of $c_{*}$ and $c^{*}$. It is immediately verified that $c_{*}$ and $c^{*}$ are positive homogeneous (just like $c$ itself on $\mathscr{C}_{0}^{+}$), that is,

$$
c_{*}(a f)=a c_{*}(f), c^{*}(a f)=a c^{*}(f)
$$

for $f \in \mathscr{F}^{+}(X), 0 \leqq a<+\infty$. Moreover, $c^{*}$ is countably subadditive:

$$
\begin{equation*}
c^{*}\left(\sum_{n \in \boldsymbol{N}} f_{n}\right) \leqq \sum_{n \in \boldsymbol{N}} c^{*}\left(f_{n}\right) \quad\left(f_{n} \in \mathscr{F}+(X)\right) . \tag{3}
\end{equation*}
$$

The proof of this is easily reduced to the case $f_{n} \in \mathscr{G}$, in which case Theorem 4.3 (a) allows us to reduce further to the case of a finite sum, or, by recurrence, to a sum of just 2 functions of class $\mathscr{G}$. Approximating each of these two functions by the upward directed family of all its minorants of class $\mathscr{C}_{0}^{+}$, and applying Theorem 4.3 (a) once again, we have finally reduced (3) to the subadditivity of $c$ on $\mathscr{C}_{0}^{+}$as stipulated in $\left(c_{3}\right)$ of Def. 4.1.

Next we propose to show that

$$
\begin{equation*}
c_{*}\left(f_{1}+f_{2}\right) \leqq c_{*}\left(f_{1}\right)+c^{*}\left(f_{2}\right) \tag{4}
\end{equation*}
$$

for all $f_{1}, f_{2} \in \mathscr{F}+(X)$. Let $h \in \mathscr{H}_{0}, h \leqq f_{1}+f_{2}, g \in \mathscr{G}, g \geqq f_{2}$. Then $(h-g)^{+} \in \mathscr{H}_{0}$, $(h-g)^{+} \leqq f_{1}$, and hence, by (3) and Lemma 4.4,

$$
c(h) \leqq c\left((h-g)^{+}\right)+c(g) \leqq c_{*}\left(f_{1}\right)+c(g) .
$$

This establishes (4) because $c(h)$ and $c(g)$ may be taken as close as we please to $c_{*}\left(f_{1}+f_{2}\right)$ and $c^{*}\left(f_{2}\right)$, respectively.

In view of (3) we have established, in particular, the following theorem serving to justify our use of the name upper capacity for $c^{*}$.

Theorem. For any capacity $c: \mathscr{C}_{0}^{+}(X) \rightarrow[0,+\infty[$ (in the sense of Def. 4.1) on a locally compact space $X$ the associated upper capacity $c^{*}: \mathscr{F}+(X) \rightarrow$ $[0,+\infty]$ is an upper capacity in the sense of Def. 3.1. Moreover, $c^{*}$ is locally finite (Def. 3.5). A function $f \in \mathscr{F}+(X)$ is c-capacitable $\left(c^{*}(f)=c_{*}(f)\right)$ if and only if $f$ is $\left(c^{*}, \mathscr{H}_{0}\right)$-capacitable in the sense of $\S 1.6$.

Remarks. 1) In order that a locally finite, upper capacity $C: \mathscr{F}^{+}(X) \rightarrow$ $[0,+\infty]$ (in the sense of Def. 3.1) on the locally compact space $X$ have the form $C=c^{*}$ for some $c$ as above, it is necessary and sufficient that

$$
\begin{equation*}
C(g)=\sup \left\{C(\varphi) \mid \varphi \in \mathscr{C}_{0}^{+}, \varphi \leqq g\right\} \tag{5}
\end{equation*}
$$

for every $g \in \mathscr{G}$. In the affirmative case $c$ is of course uniquely determined as the restriction of $C$ to $\mathscr{C}_{0}^{+}$. Note also that, according to the between theorem (in the form given in Lemma 3.4 above) it suffices to verify the apparently weaker condition derived from (5) by replacing $\mathscr{C}_{0}^{+}$by $\mathscr{H}_{0}$ (in other words the $\left(C, \mathscr{H}_{0}\right)$-capacitability of any $\left.g \in \mathscr{G}\right)$.

If $X$ has a countable base, and if $C$ is sequentially order continuous from below, then (5) holds because any $g \in \mathscr{G}$ is representable as the pointwise supremum of an increasing sequence of functions of class $\mathscr{C}_{0}^{+}$.
2) If $c^{*}$ is sequentially order continuous from below (on $\mathscr{F}+(X)$ ), it follows from Choquet's theory that every $\mathscr{H}_{0}$-Souslin function is $c$-capacitable in view of Theorem 1.6 above because $c^{*}$ is order continuous from above on $\mathscr{H}_{0}$ according to Theorem 3.6 (a) or Theorem 4.3 (b).
3) In view of the above theorem we may of course freely use the concepts and results from Chapter I, and also from [17], taking $C=c^{*}$, the upper capacity associated with a given capacity $c: \mathscr{C}_{0}^{+}(X) \rightarrow[0,+\infty[$. In particular, we have the closed classes $\mathscr{G}^{* *} \mathscr{H}^{*}, \mathscr{H}_{0}^{*}$, etc. The expression quasi everywhere (q.e.) means: everywhere except in some set $E$ such that $c^{*}(E)=0$. (We put $c^{*}(E)=c^{*}\left(1_{E}\right)$ for every set $E \subset X$, cf. § 4.7.)
4.6. Lemma. The capacitable functions $f \in \mathscr{F}+(X)$ form a closed subset of $\mathscr{F}+(X)$ in the $c^{*}$-metric topology. In particular, every function of class $\mathscr{G}^{*}$ or $\mathscr{H}_{0}^{*}$ is capacitable, in the latter case with finite capacity.

Proof. Let $f \in \mathscr{F}+(X)$, and suppose that there corresponds to any $\varepsilon>0$ a capacitable function $\varphi \in \mathscr{F}+(X)$ such that $c^{*}(|f-\varphi|)<\varepsilon$. Since $f \leqq \varphi+$ $(f-\varphi)^{+}$, and vice versa, we obtain from (3) and (4), § 4.5,

$$
\begin{aligned}
& c^{*}(f) \leqq c^{*}(\varphi)+c^{*}\left((f-\varphi)^{+}\right) \leqq c_{\circledast}(\varphi)+\varepsilon, \\
& c_{*}(\varphi) \leqq c_{*}(f)+c^{*}\left((\varphi-f)^{+}\right) \leqq c_{*}(f)+\varepsilon,
\end{aligned}
$$

and hence $c^{*}(f) \leqq c_{*}(f)+2 \varepsilon$. The last assertion follows now from the finiteness of $c$ on $\mathscr{H}_{0}$. I
4.7. Capacity with respect to a weight function. Let $c: \mathscr{C}_{0}^{+}(X) \rightarrow[0,+\infty[$ denote a capacity in the sense of Def. 4.1 on a locally compact space $X$. For any compact set $K \subset X$ we put

$$
c(K):=c\left(1_{K}\right) .
$$

More generally, let a function $f \in \mathscr{H}^{*}$ be given, and define for any compact set $K$

$$
c_{f}(K):=c\left(f \cdot 1_{K}\right)
$$

This makes sense because $f \cdot 1_{K} \in \mathscr{H}_{0}^{*}$ by virtue of Theorem 2.6 (iv), and hence is $c$-capacitable by the above lemma. Clearly $c_{f}$ is finite valued, increasing, and subadditive, and $c_{f}(\theta)=0$.

It will be shown in the theorem below that the set function $c_{f}$, defined on the class $\mathscr{K}=\mathscr{K}(X)$ of all compact subsets of $X$, is "continuous from the right", and hence is a capacity in the sense of Choquet [10, § 15]. We call this set function $c_{f}$ the set function, or capacity, with the weight function $f \in \mathscr{H}^{*}$ associated with $c$. In the case $f=1$, where we write $c_{1}(K)=$ $c(K)$, we simply speak of the associated set function.

From the finite and increasing set function $c_{f}: \mathscr{K}(X) \rightarrow[0,+\infty]$ (where $f \in \mathscr{H}^{*}$ ) we derive in the usual way inner and outer set functions $c_{f *}, c_{f}^{*}$ : $\mathscr{P}(X) \rightarrow[0,+\infty]:$

$$
\begin{aligned}
c_{f *}(A): & =\sup \left\{c_{f}(K) \mid K\right. \text { compact, } & K \subset A\}, \\
c_{f}^{*}(A): & =\inf \left\{c_{f *}(G) \mid G\right. \text { open, } & G \supset A\} .
\end{aligned}
$$

Clearly these set functions are increasing, and take the value 0 at the void set $\varnothing$. Moreover $c_{f *}(A) \leqq c_{f}^{*}(A)$ for any set $A \subset X$. We call a set $A$ capacitable with respect to $c_{f}$, or $c_{f}$-capacitable, if $c_{f *}(A)=c_{f}^{*}(A)$. In that case we may write simply $c_{f}(A)$ for the common value. This is justified because compact sets are $c_{f}$-capacitable in view of the following theorem. (It is trivial that open sets are $c_{f}$-capacitable.)

Theorem. For any $f \in \mathscr{H}^{*}$ and any set $A \subset X$ we have $c_{f * *}(A)=c_{*}\left(f \cdot 1_{A}\right)$. If moreover $\{x \in A \mid f(x)=0\}$ is $\sigma$-finite with respect to $c^{*}$ then $c_{f}^{*}(A) \leqq$ $c^{*}\left(f \cdot 1_{A}\right)$. The sign of equality subsists here if, in addition, $f \in \mathscr{G}^{*}$.

Proof. Ad $c_{f *}(A)$. For any compact set $K \subset A$ we have $f \cdot 1_{K} \in \mathscr{H}_{0}^{*}$, $f \cdot 1_{K} \leqq f \cdot 1_{A}$, and hence

$$
c_{f}(K):=c\left(f \cdot 1_{K}\right) \leqq c_{*}\left(f \cdot 1_{A}\right) .
$$

This shows that $c_{f *}(A) \leqq c_{*}\left(f \cdot 1_{A}\right)$. Conversely, let $h \in \mathscr{H}_{0}, h \leqq f \cdot 1_{A}$, and write

$$
K_{n}:=\{x \in X \mid h(x) \geqq 1 / n\}
$$

for $n \in \boldsymbol{N}$. Then $K_{n}$ is a compact subset of $A$, and so $c_{f}\left(K_{n}\right) \leqq c_{f *}(A)$. Denoting by $K$ the compact support of $h$, we have

$$
h \leqq n^{-1} 1_{K}+f \cdot 1_{K_{n}},
$$

and hence from the sublinearity of $c^{*}$

$$
c(h) \leqq n^{-1} c\left(1_{K}\right)+c_{f}\left(K_{n}\right) .
$$

Since $c\left(1_{K}\right)<+\infty$ and $c_{f}\left(K_{n}\right) \leqq c_{f *}(A)$, we conclude for $n \rightarrow+\infty$ that $c(h) \leqq c_{f *}(A)$, and consequently $c_{*}\left(f \cdot 1_{A}\right) \leqq c_{f *}(A)$.

Ad $c_{f}^{*}(A)$. According to Theorem 3.10,

$$
c^{*}\left(f \cdot 1_{A}\right)=\inf \left\{c^{*}\left(f \cdot 1_{G}\right) \mid G \text { open, } G \supset A\right\},
$$

and hence $c^{*}\left(f \cdot 1_{A}\right) \geqq c_{f}^{*}(A)$ because $c^{*}\left(f \cdot 1_{G}\right) \geqq c_{*}\left(f \cdot 1_{G}\right)=c_{f *}(G)$. This argument shows, moreover, that $c^{*}\left(f \cdot 1_{A}\right)=c_{f}^{*}(A)$ holds provided that $c^{*}\left(f \cdot 1_{G}\right)$ $=c_{*}\left(f \cdot 1_{G}\right)$, that is, if $f \cdot 1_{G}$ is $c$-capacitable for every open set $G$. And this is the case, in particular, if $g \in \mathscr{G}^{*}$, for then $g \cdot 1_{G} \in \mathscr{G}^{*}$ for every open set $G$. (For another case where $f \cdot 1_{G}$ is capacitable for all open sets $G$ see Remark 1 below.)

Corollary. Let $f \in \mathscr{H}^{*}$. The inner capacity $c_{f *}$ with the weight function $f$ is countably subadditive on universally measurable sets. The outer capacity $c_{f}^{*}$ is countably subadditive.

The former statement follows from Theorem 7.1 below in view of the identity $c_{f *}(A)=c_{*}\left(f \cdot 1_{A}\right)$. The latter statement follows easily from the former applied to open sets.

Remarks. 1) Suppose that the upper capacity $c^{*}$ is sequentially order continuous from below (on arbitrary functions $X \rightarrow[0,+\infty]$ ). Suppose further that either (i) $f \in \mathscr{G}^{*} \cap \mathscr{H}^{*}$, and $\{x \in X \mid f(x)=0\}$ is $\sigma$-finite; or (ii) $f \in \mathscr{H}^{*}$, and $X$ has a countable base. Then

$$
c_{f}^{*}(A)=c^{*}\left(f \cdot 1_{A}\right), \quad c_{f *}(A)=c_{*}\left(f \cdot 1_{A}\right)
$$

for arbitrary sets $A \subset X$. It follows that the outer capacity $c_{f}^{*}$ with respect to the weight function $f$ is sequentially order continuous from below on arbitrary sets, and hence, by Choquet's theory, that any $K$-analytic set $A \subset X$ is $c_{f}$-capacitable (Choquet [10, § 30], see also Sion [19]).

As to the proof of the equality $c_{f}^{*}(A)=c^{*}\left(f \cdot 1_{A}\right)$ in the remaining case (ii) we merely have to note (cf. the end of the proof of Theorem 4.7) that $f \cdot 1_{G}$ is $c$-capacitable for every open set $G$; and this is clear also in case (ii) since $f \cdot 1_{G}$ is then equivalent to a function of class $\left(\mathscr{H}_{0}\right)_{\sigma}$ and hence $c$ capacitable because $c^{*}$ is sequentially order continuous from below. (In fact, the open set $G$ is of class $\mathscr{K}_{\sigma}$ here, and $f \in \mathscr{H}^{*}$ is obviously equivalent to a function of class $\mathscr{H}_{\sigma}$.)
2) Consider a function $f \in \mathscr{G}^{*} \cap \mathscr{H}^{*}$ such that $\{x \in X \mid f(x)=0\}$ is $\sigma$ finite with respect to $c^{*}$. For any $\varphi \in \mathscr{C}_{0}^{+}$we have $f \varphi \in \mathscr{H}_{0}^{*}$ by Theorem 2.6. Hence a new capacity $c_{f}$ (in the sense of Def. 4.1) is defined by

$$
c_{f}(\varphi):=c(f \varphi) \quad\left(\varphi \in \mathscr{C}_{0}^{+}\right) .
$$

By the same method as in the proof of the above theorem it can be shown that the associated lower and upper capacities are given by

$$
c_{f *}(\varphi)=c_{*}(f \varphi), \quad c_{f}^{*}(\varphi)=c^{*}(f \varphi) \quad(\varphi \in \mathscr{F}+(X)) .
$$

4.8. Let us now return to the principal case of the weight function $f=1$ and the set function $c: \mathscr{K} \rightarrow[0,+\infty[$ associated with the given capacity functional $c: \mathscr{C}_{0}^{+} \rightarrow\left[0,+\infty\left[\right.\right.$ by the definition $c(K)=\mathrm{c}\left(1_{K}\right)$. This set function is finite valued, increasing, subadditive, continuous from the right (in the sense of Choquet [10, § 15], that is, $c^{*}(K)=c(K)$ for all $\left.K \in \mathscr{K}\right)$, and $c(\varnothing)=0$. Not every set function $c: \mathscr{K} \rightarrow[0,+\infty[$ with these properties is associated in this way with a capacity in the sense of Def. 4.1. As observed by Choquet [10, §53.7] a simple necessary condition on the set function $c$ is that

$$
2 c(A \cup B \cup C) \leqq c(A \cup B)+c(B \cup C)+c(C \cup A)
$$

for arbitrary compact sets $A, B, C$, and this condition is not always fulfilled. ${ }^{6}$ ) It seems difficult to obtain a simple necessary and sufficient condition. As shown by Choquet [10, §54.2] it is sufficient that $c$ be strongly subadditive in the sense that

$$
c(A \cup B)+c(A \cap B) \leqq c(A)+c(B)
$$

for arbitrary compact sets $A, B$. This condition, however, is not a necessary one, as it appears say from the usual capacity associated with a kernel (cf. e.g. [16]). And if $c$ is strongly subadditive (on compact sets) there may exist several extensions to a functional capacity in the sense of Def. 4.1.7)

## 5. Representation of a Capacity by a Set of Measures

We show (Theorem 5.3) that every capacity $c: \mathscr{C}_{0}^{+}(X) \rightarrow[0,+\infty[$ may be obtained as the supremum of a family $\mathscr{S}$ of linear capacities (that is, positive Radon measures) $\mu: \mathscr{C}_{0}^{+}(X) \rightarrow[0,+\infty[$,

$$
c(f)=\sup _{\mu \in \mathscr{S}} \mu(f), \quad f \in \mathscr{C}_{0}^{+} .
$$

The largest such family is the set $\mathscr{S}_{c}$ of all positive Radon measures $\mu$ such that $\mu \leqq c$ (that is, $\mu(f) \leqq c(f)$ for all $f \in \mathscr{C}_{0}^{+}$). Conversely, for any vaguely
${ }^{6}$ ) Example: Let $X$ consist of 3 points; let $c(K)=1$ for any set $K \subset X$ consisting of 1 or 2 points; and let $c(X)=2$ (and $c(\emptyset)=0$ ).
${ }^{7}$ ) Take for $c$ the newtonian capacity $c_{1}$ (as a functional on $\mathscr{C}_{0}^{+}$, see $\S 5.7$ below). The restriction of $c_{1}$ to (indicator functions for) compact sets is then strongly subadditive as shown by Choquet [10, ch. 2], but the extension of this latter set function constructed in Choquet [10, §54.2] is not equal to the functional $c_{1}$.
bounded set $\mathscr{S}$ of positive Radon measures the above supremum clearly defines a capacity $c$. We show (Theorem 5.4) that $\mathscr{S}_{c}$ is the hereditary convex closure of $\mathscr{S}$.
5.1. The strong topology on $\mathscr{C}_{0}$. The vector space $\mathscr{C}_{0}=\mathscr{C}_{0}(X)$ of all finite real valued continuous functions of compact support on the locally compact space $X$ has a well known locally convex separated topology called the strong topology. If $X$ is compact, the strong topology on $\mathscr{C}_{0}(X)=\mathscr{C}(X)$ is simply the uniform topology defined by means of the uniform norm $f \rightarrow \max _{x \in X}|f(x)|, f \in \mathscr{C}_{0}(X)$. If $X$ is locally compact, but not compact, the strong topology on $\mathscr{C}_{0}(X)$ is defined as the inductive limit of the uniform topologies on the subspaces $\mathscr{C}_{0}(X, K)$, where $K$ ranges over all compact subsets of $X$. Here $\mathscr{C}_{0}(X, K)$ denotes the set of all functions $f \in \mathscr{C}_{0}(X)$ vanishing outside $K$. The topology on $\mathscr{C}_{0}^{+}(X)$ induced by the strong topology on $\mathscr{C}_{0}(X)$ is called the strong topology on $\mathscr{C}_{0}^{+}(X)$. We refer to Bourbaki [3, ch. II, § 4, no. 4].

Theorem. Any capacity $c: \mathscr{C}_{0}^{+}(X) \rightarrow[0,+\infty[$ on a locally compact space $X$ is continuous in the strong topology on $\mathscr{C}_{0}^{+}(X)$.

Proof. We extend $c$ from $\mathscr{C}_{0}^{+}$to $\mathscr{C}_{0}$ by defining

$$
\begin{equation*}
\tilde{c}(f):=c(|f|) \quad\left(f \in \mathscr{C}_{0}\right) \tag{6}
\end{equation*}
$$

Clearly $\tilde{c}$ is homogeneous, that is,

$$
\begin{equation*}
\tilde{c}(a f)=|a| \tilde{c}(f) \tag{7}
\end{equation*}
$$

for any real number $a$ and any $f \in \mathscr{C}_{0}$. Since $c$ is subadditive and increasing on $\mathscr{C}_{0}^{+}$, we have

$$
\begin{align*}
& \tilde{c}\left(f_{1}+f_{2}\right) \leqq \tilde{c}\left(f_{1}\right)+\tilde{c}\left(f_{2}\right),  \tag{8}\\
& \left|f_{1}\right| \leqq\left|f_{2}\right| \Rightarrow \tilde{c}\left(f_{1}\right) \leqq \tilde{c}\left(f_{2}\right) \tag{9}
\end{align*}
$$

for all $f_{1}, f_{2} \in \mathscr{C}_{0}$. The properties (7), (8) together with the finiteness of $\tilde{c}$ amount to saying that $\tilde{c}$ is a seminorm on $\mathscr{C}_{0}$. In particular, for $f_{1}, f_{2} \in \mathscr{C}_{0}$,

$$
\begin{equation*}
\left|\widetilde{c}\left(f_{1}\right)-\widetilde{c}\left(f_{2}\right)\right| \leqq \widetilde{c}\left(f_{1}-f_{2}\right) . \tag{10}
\end{equation*}
$$

For functions $f \in \mathscr{C}_{0}(X, K)$ we have $|f| \leqq a \cdot 1_{K}$ with $a:=\max |f(x)|$, and hence

$$
\tilde{c}(f)=c(|f|) \leqq a \cdot c(K) .
$$

Applying this to $f=f_{1}-f_{2}$ with $f_{1}, f_{2} \in \mathscr{C}_{0}(X, K)$, we obtain from (10)

$$
\left|\widetilde{c}\left(f_{1}\right)-\widetilde{c}\left(f_{2}\right)\right| \leqq c(K) \max _{x \in K}\left|f_{1}(x)-f_{2}(x)\right| .
$$

This inequality shows that $c$ is indeed continuous relative to each $\mathscr{C}_{0}(X, K)$ with the uniform topology, and hence continuous on all of $\mathscr{C}_{0}(X)$ with the strong topology according to Bourbaki [3, ch. II, § 4, prop. 5] because $\bar{c}$ is a seminorm. I
5.2. Measures and integration. We give a brief exposition of the theory of Radon measures (integrals) on a locally compact space (cf. Bourbaki [2], Cartan [8]), noting that such a measure may be identified with an additive capacity.

By a (real valued Radon) measure $\mu$ on a locally compact space $X$ is understood a (strongly) continuous real linear form $\mu$ on $\mathscr{C}_{0}(X)$. The vector space $\mathscr{M}=\mathscr{M}(X)$ of all measures on $X$ is thus the dual space of $\mathscr{C}_{0}$. The value of a measure $\mu \in \mathscr{M}$ at a function $f \in \mathscr{C}_{0}$ is denoted by

$$
\mu(f)=\int f d \mu .
$$

The weak*-topology on the dual space $\mathscr{M}$ is called the vague topology on $\mathscr{M}$. A set $\mathscr{S} \subset \mathscr{M}$ is relatively compact (in the vague topology) if and only if $\mathscr{S}$ is vaguely bounded in the sense that the linear form $\mu \mapsto \mu(f)$ is bounded on $\mathscr{S}$ for every fixed $f \in \mathscr{C}_{0}$.

We shall mainly consider positive measures $\mu$, that is, measures such that $\mu(f) \geqq 0$ for every $f \in \mathscr{C}_{0}^{+}$. The set of all positive measures on $X$ is a convex cone denoted by $\mathscr{M}^{+}=\mathscr{M}^{+}(X)$. The restriction of a positive measure $\mu$ to $\mathscr{C}_{0}^{+}$is a capacity on $X$ in the sense of Def. 4.1, but with the further property of being additive (not just subadditive). Conversely, it is well known that any additive capacity $c$ on $X$ has a unique extension to a positive Radon measure $\mu$ on $X$, viz.

$$
\mu(f)=\mu\left(f^{+}\right)-\mu\left(f^{-}\right)
$$

Having thus identified a positive measure $\mu$ (or rather its restriction to $\mathscr{C}_{0}^{+}$) with an additive capacity, we note that the integral $\int h d \mu=\mu(h)$ of a function $h \in \mathscr{H}_{0}$ and the integral (Bourbaki: upper integral) $\int g d \mu=\mu(g)$ of a function $g \in \mathscr{G}{ }^{8}$ ) coincide by definition with the capacity of $h$ and $g$, respectively, as defined in $\S 4.2$.

Furthermore the lower and the upper integral of an arbitrary function $f \in \mathscr{F}+(X)$ with respect to $\mu$ are precisely the lower and the upper capacity of $f$, respectively, as defined in $\S 4.4$ :

$$
\begin{gathered}
\int_{*} f d \mu=\mu_{*}(f)=\sup \left\{\int h d \mu \mid h \in \mathscr{H}_{0}, h \leqq f\right\}, \\
\int^{*} f d \mu=\mu^{*}(f)=\inf \left\{\int g d \mu \mid g \in \mathscr{G}, g \geqq f\right\} .
\end{gathered}
$$

${ }^{8}$ ) See $\S 2$ for the classes $\mathscr{H}_{0}$ and $\mathscr{G}$.

Conforming with our general convention we shall allow ourselves to write simply $\int f d \mu=\mu(f)$ for these two integrals whenever they coincide, that is, when $f$ is capacitable with respect to the measure $\mu$.

It is well known that the upper integral $\mu^{*}$ is sequentially order continuous from below: ${ }^{9)}$

$$
\begin{equation*}
\left[f_{n} \not \subset f, f_{n} \in \mathscr{F}+(X)\right] \Rightarrow\left[\mu^{*}\left(f_{n}\right) \rightarrow \mu^{*}(f)\right] . \tag{11}
\end{equation*}
$$

Moreover $\mu^{*}$ is countably subadditive (special case of (3), § 4.5).
The lower integral $\mu_{*}$ is known to possess similar properties when considered only on $\mu$-measurable functions. Thus

$$
\begin{gather*}
{\left[f_{n} \nearrow f\right] \Rightarrow\left[\mu_{*}\left(f_{n}\right) \rightarrow \mu_{*}(f)\right],}  \tag{12}\\
\mu_{* *}\left(\sum_{n \in N} f_{n}\right) \leqq \sum_{n \in N} \mu_{*}\left(f_{n}\right), \tag{13}
\end{gather*}
$$

for any sequence of $\mu$-measurable functions $f_{n} \in \mathscr{F}+(X)$.
Recall also that a $\mu$-measurable function $f \in \mathscr{F}^{+}(X)$ is $\mu$-capacitable provided that $\{x \in X \mid f(x)>0\}$ is $\sigma$-finite with respect to $\mu$. Finally, a function $f \in \mathscr{F}+(X)$ is $\mu$-integrable if and only if $\mu^{*}(f)=\mu_{*}(f)<+\infty$.

The quasi topological notions discussed in [17], and the classes $\mathscr{G}^{*}, \mathscr{H}^{*}$, $\mathscr{H}_{0}^{*}$ introduced in $\S 2$ reduce to well known concepts in the present case of the upper capacity $\mu^{*}$ (the upper integral) associated with a positive measure $\mu$. Thus $\mathscr{H}_{0}^{*}$ consists of all non-negative $\mu$-integrable functions. If the space $X$ is countable at infinity, quasi continuity (or quasi semicontinuity) with respect to $\mu^{*}$ reduces to measurability with respect to $\mu$. In particular, $\mathscr{G}^{*}$ is then the class of all non-negative $\mu$-measurable functions, and $\mathscr{H}^{*}$ the class of all non-negative locally $\mu$-integrable functions (cf. Theorems 2.5 and 2.6).

The trace $\mu_{A}$ of a measure $\mu \in \mathscr{M}^{+}$on a $\mu$-measurable set $A \subset X$ is defined by

$$
\mu_{A}(\varphi)=\int \varphi \cdot 1_{A} d \mu \quad\left(\varphi \in \mathscr{C}_{0}^{+}\right) .
$$

(Observe that $\varphi \cdot 1_{A}$ is $\mu$-integrable.) The total mass of $\mu_{A}$ is

$$
\mu_{A}(X)=\mu_{*}(A)
$$

A measure $\mu \in \mathscr{M}^{+}$is said to be concentrated on (or carried by) a set $A$ if C $A$ is locally $\mu$-negligible, or equivalently if $A$ is $\mu$-measurable and $\mu_{A}=\mu$. It follows then that $\mu(X)=\mu_{*}(A)$. If $A$ is closed, or if e.g. $\mu_{*}(A)<+\infty$,

[^11]then $\mu^{*}(\complement A)=0$, that is, $\complement A$ is $\mu$-negligible. A measure $\mu$ is, therefore, concentrated on a closed set $A$ if and only if $\operatorname{supp} \mu \subset A$. Here $\operatorname{supp} \mu$ denotes the (closed) support of $\mu$ (the smallest closed set carrying $\mu$ ). Finally note that, for any measure $\mu \in \mathscr{M}^{+}$and any $\mu$-measurable set $A$, the trace $\mu_{A}$ is concentrated on $A$.

Definition. A set $\mathscr{S} \subset \mathscr{M}^{+}$of positive measures is called hereditary (from above) if

$$
\forall \mu \in \mathscr{S} \quad \forall v \in \mathscr{M}^{+}:[v \leqq \mu] \Rightarrow[v \in \mathscr{S}]
$$

5.3. The representation theorem. Returning now to the case of an arbitrary capacity $c$ on $X$ in the sense of Def. 4.1, we write

$$
\begin{equation*}
\mathscr{S}_{c}:=\left\{\mu \in \mathscr{M}^{+} \mid \mu \leqq c\right\}, \tag{14}
\end{equation*}
$$

where $\mu \leqq c$ means $\mu(f) \leqq c(f)$ for all $f \in \mathscr{C}_{0}^{+}$.
Theorem. ${ }^{10)}$ Every capacity $c: \mathscr{C}_{0}^{+}(X) \rightarrow[0,+\infty[$ is representable as the upper envelope $c=\sup \mu$ of the associated set $\mathscr{S}_{c}$ of all poitive measures $\mu \in \mathscr{S}_{c}$ $\mu \leqq c$. More precisely, we have for every $f \in \mathscr{C}_{0}^{+}$,

$$
c(f)=\max _{\mu \in \mathscr{S}_{c}} \mu(f)
$$

Proof. For every $f_{0} \in \mathscr{C}_{0}^{+}$we shall prove the existence of a measure $\mu \in \mathscr{S}_{c}$ such that $\mu\left(f_{0}\right)=c\left(f_{0}\right)$. According to the Hahn-Banach theorem, applied to the locally convex space $\mathscr{C}_{0}$ with the strong topology ( $\S 5.1$ ) and the continuous semi-norm $\tilde{c}$ defined in (6), there exists an extension of the linear form $t f_{0} \mapsto t \tilde{c}\left(f_{0}\right)$ (on the 1 -dimensional subspace generated by $f_{0}$ ) to a continuous linear form $\lambda$ on $\mathscr{C}_{0}$ such that $|\lambda(f)| \leqq \tilde{c}(f)$ for all $f \in \mathscr{C}_{0}$. Thus $\lambda$ is a (Radon) measure on $X$. The positive part $\mu:=\lambda^{+}$of $\lambda$ has the desired properties. In fact, $\mu \geqq \lambda$, and hence

$$
\mu\left(f_{0}\right) \geqq \lambda\left(f_{0}\right)=\tilde{c}\left(f_{0}\right)=c\left(f_{0}\right)
$$

because $f_{0} \geqq 0$. On the other hand, for every $f \in \mathscr{C}_{0}^{+}$,

$$
\mu(f)=\sup \left\{\lambda(h) \mid h \in \mathscr{C}_{0}^{+}, h \leqq f\right\} \leqq c(f)
$$

since $\lambda(h) \leqq \tilde{c}(h)=c(h) \leqq c(f)$. I
The set $\mathscr{S}_{c} \subset \mathscr{M}^{+}$defined in (14) is evidently hereditary (cf. end of $\S 5.2)$, convex, and vaguely compact.
${ }^{10}$ ) This result is mentioned in Choquet [10, § 53.7].
5.4. On the other hand, for any set $\mathscr{S}$ of positive measures, the functional c defined on $\mathscr{C}_{0}^{+}$as the upper envelope of $\mathscr{S}$,

$$
\begin{equation*}
c(f)=\sup _{\mu \in \mathscr{S}} \mu(f) \quad\left(f \in \mathscr{C}_{0}^{+}\right) \tag{15}
\end{equation*}
$$

is evidently increasing and sublinear. Thus $c$ is a capacity in the sense of Def. 4.1 if and only if $c$ is finite valued, or equivalently if $\mathscr{S}$ is vaguely bounded (that is, vaguely relatively compact).

Theorem. For any vaguely bounded set $\mathscr{S} \subset \mathscr{M}^{+}$the upper envelope $c=\sup \mu$ is a capacity. The associated set $\mathscr{S}_{c}$ of all positive measures $\mu \leqq c$ $\mu \in \mathscr{S}$
is the hereditary convex closure of $\mathscr{S} .{ }^{11)}$
Proof. It remains to establish that the hereditary convex closure $\mathscr{T}$ of $\mathscr{S}$ coincides with $\mathscr{S}_{c}$. Since $\mathscr{S}_{c}$ is hereditary, convex, and closed, and since $\mathscr{S}_{c} \supset \mathscr{S}$, we have $\mathscr{S}_{c} \supset \mathscr{T}$. To prove that $\mathscr{S}_{c} \subset \mathscr{T}$ we use the duality between $\mathscr{M}$ and $\mathscr{C}_{0}$ determined by the bilinear form $(\mu, f) \rightarrow \mu(f)=\int f d \mu$. The polar $\mathscr{T}^{0} \subset \mathscr{C}_{0}$ of $\mathscr{T}(\subset \mathscr{M})$ consists by definition of all $f \in \mathscr{C}_{0}$ such that

$$
\begin{equation*}
\mu(f) \leqq 1 \quad \text { for every } \mu \in \mathscr{T} \tag{16}
\end{equation*}
$$

Similarly, the bi-polar $\mathscr{T}^{00} \subset \mathscr{M}$ consists of all $\mu \in \mathscr{M}$ such that

$$
\begin{equation*}
\mu(f) \leqq 1 \text { for every } f \in \mathscr{T}^{0} \tag{17}
\end{equation*}
$$

Since $\mathscr{T}$ is convex, closed, and contains 0 (being hereditary), it is known that $\mathscr{T} 00=\mathscr{T}$ (Bourbaki [3, ch. II, § 6, th. 1]). In order to prove that $\mathscr{S}_{c} \subset \mathscr{T}^{00}$ we consider any measure $\mu_{0} \in \mathscr{S}_{c}$ and propose to verify (17) with $\mu=\mu_{0}$. It suffices to consider positive functions $f \in \mathscr{T} 0$ because $\mathscr{T}$ is hereditary. In fact, for any $f \in \mathscr{T}^{0}$ we have $f^{+} \in \mathscr{T}^{0},{ }^{12)}$ hence $\mu_{0}(f) \leqq$ $\mu_{0}\left(f^{+}\right) \leqq 1$ because $f \leqq f^{+}$and $\mu_{0} \geqq 0$. Consider, therefore, a function $f \geqq 0$ in $\mathscr{T}{ }^{0}$. Since $\mathscr{T} \supset \mathscr{S}$ we infer from (16) that $\mu(f) \leqq 1$ for every $\mu \in \mathscr{S}$, or equivalently that $c(f) \leqq 1$ according to $(15)$. When $\mu_{0} \in \mathscr{S}_{c}$ we conclude from $(14)$ that $\mu_{0}(f) \leqq c(f) \leqq 1$, and so $\mu_{0} \in \mathscr{T}{ }^{00}=\mathscr{T}$. I

Corollary. A vaguely bounded set of positive measures determines the same enveloping capacity as its hereditary convex closure.

[^12]5.5. Representation of the lower capacity. Let $\mathscr{S}$ denote a vaguely compact set of positive measures on the locally compact space $X$, and let $c$ denote the enveloping capacity as defined in (15).

Theorem. For any function $h \in \mathscr{H}$ we have

$$
\begin{equation*}
c(h)=\max _{\mu \in \mathscr{S}} \int h d \mu . \tag{18}
\end{equation*}
$$

For any function $f \in \mathscr{F}+(X)$

$$
\begin{align*}
& c_{*}(f)=\sup _{\mu \in \mathscr{S}} \int_{*} f d \mu,  \tag{19}\\
& c^{*}(f) \geqq \sup _{\mu \in \mathscr{S}} \int^{*} f d \mu . \tag{20}
\end{align*}
$$

Proof. When $h \in \mathscr{H}_{0}$, the mapping $\mu \rightarrow \int h d \mu$ of $\mathscr{M}^{+}$into $[0,+\infty[$ is u.s.c. in the vague topology, being the lower envelope of the family of vaguely continuous mappings $\mu \mapsto \int \varphi d \mu$ as $\varphi$ ranges over the downward directed family $\Phi$ of all functions $\varphi \in \mathscr{C}_{0}^{+}$with $\varphi \geqq h$. Hence this mapping has a greatest value $c^{\prime}(h)$ on the compact set $\mathscr{S} \subset \mathscr{M}^{+}$. For any $\mu \in \mathscr{S}$ we have $\int h d \mu \leqq \int \varphi d \mu \leqq c(\varphi)$ for all $\varphi \in \Phi$, and hence $\int h d \mu \leqq \inf c(\varphi)=c(h)$ by Def. 4.2. This shows that $c^{\prime}(h) \leqq c(h)$.

To prove the converse inequality $c^{\prime}(h) \geqq c(h)$ we denote for every $\varphi \in \Phi$ by $\mu_{\varphi}$ a measure in $\mathscr{S}$ such that $\mu_{\varphi}(\varphi)=c(\varphi)$. Since $\mathscr{S}$ is vaguely compact, there exists a cluster point $\mu \in \mathscr{S}$ for the net $\left(\mu_{\varphi}\right)_{\varphi \in \Phi}$. For any $\psi \in \Phi$ we obtain along $\Phi$

$$
c(h)=\lim c(\varphi)=\lim \mu_{\varphi}(\varphi) \leqq \lim \inf \mu_{\varphi}(\psi) \leqq \mu(\psi)
$$

because we may restrict the attention to functions $\varphi \leqq \psi$ in $\Phi$. It follows that

$$
c(h) \leqq \inf \{\mu(\psi) \mid \psi \in \Phi\}=\mu(h) \leqq c^{\prime}(h) .
$$

Next we obtain for any $f \in \mathscr{F}+$

$$
\begin{aligned}
c_{*}(f)= & \sup \left\{c(h) \mid h \in \mathscr{H}_{0}, h \leqq f\right\} \\
= & \sup _{h \leqq f} \sup _{\mu \in \mathscr{S}} h d \mu=\sup _{\mu \in \mathscr{S}} \sup _{h \leqq f} \int h d \mu \\
= & \sup \int_{*} f d \mu . \\
& \mu \in \mathscr{S} \\
c^{*}(f)= & \inf \left\{c_{* *}(g) \mid g \in \mathscr{G}, g \geqq f\right\} \\
= & \inf _{g \geqq f} \sup _{\mu \in \mathscr{S}} \int_{*} g d \mu \geqq \sup _{\mu \in \mathscr{S}} \inf _{g \geqq f} \int g d \mu \\
& =\sup _{\mu \in \mathscr{S}} \int * d \mu . \mathbf{I}
\end{aligned}
$$

Note that the sign of equality need not hold in (20), cf. §5.6.

Remark. If the vaguely compact set $\mathscr{S} \subset \mathscr{M}^{+}$is hereditary (Def. 5.2), the lower capacity $c_{*}(f)$ of $f \in \mathscr{F}+(X)$ is even the supremum of $\int_{*} f d \mu$ as $\mu$ ranges over the smaller set consisting of those measures $\mu \in \mathscr{S}$ whose support is compact and contained in

$$
A:=\{x \in X \mid f(x)>0\} .
$$

In fact, for any $t<c_{\circledast}(f)$ there exists $h \in \mathscr{H}_{0}$ such that $h \leqq f, c(h)>t$; and hence there exists $\mu \in \mathscr{S}$ such that $\int h d \mu>t$. The sets

$$
K_{n}:=\{x \in X \mid h(x) \geqq 1 / n\}
$$

are compact and contained in $A$. The trace $\mu_{n}$ of $\mu$ on $K_{n}$ belongs to $\mathscr{S}$ when $\mathscr{S}$ is hereditary. Clearly

$$
\int_{*} f d \mu_{n} \geqq \int h d \mu_{n}=\int_{K_{n}} h d \mu \rightarrow \int h d \mu>t
$$

as $n \rightarrow \infty$. Hence $\int_{*} f d \mu_{n}>t$ for $n$ sufficiently large.
5.6. Example. Let $X=\boldsymbol{R}^{2}=$ the $x y$-plane; $\mathscr{S}=\left\{m_{x} \mid x \in \boldsymbol{R}\right\}$, where $m_{x}$ denotes linear Lebesgue measure on the line $\{x\} \times \boldsymbol{R}$. The enveloping capacity $c$ is given by

$$
c(h)=\max _{x \in \boldsymbol{R}} \int h(x, y) d y, \quad h \in \mathscr{C}_{0}^{+}\left(\boldsymbol{R}^{2}\right)
$$

and similarly for the extension of $c$ to $\mathscr{H}_{0}$ in view of (18). Now put $f=1_{A}$, where $A$ denotes the union of the compact sets

$$
A_{0}=\{0\} \times[1,2], \quad A_{n}=\{1 / n\} \times[0,1]
$$

for $n=1,2, \ldots$. Then we obtain from (19) in view of Theorem 4.7 (with the weight function 1)

$$
c_{*}(A)=c_{*}(f)=\sup _{x \in R} \int_{*} f(x, y) d y=\sup _{n \geq 0} m\left(A_{n}\right)=1 .
$$

Any open set $G \supset A$ contains $A_{0}$ and hence also the segment $\{1 / n\} \times[1,2]$ for some $n \in \boldsymbol{N}$. Thus $G \supset\{1 / n\} \times[0,2]$ for some $n$, and so $c_{*}(G) \geqq m([0,2])$ $=2$. It follows that

$$
c^{*}(A)=c^{*}(f) \geqq 2 \geqq \sup _{x \in \boldsymbol{R}} \int^{*} f(x, y) d y(=1) .
$$

The set $A$ of class $\mathscr{K}_{\sigma}$ is, therefore, not capacitable with respect to $c$ (although $A$ is universally measurable). It follows that $c$ is not sequentially order continuous from below. This also appears directly since $A$ is the union
of the increasing sequence of compact sets $K_{n}=A_{0} \cup A_{1} \cup \ldots \cup A_{n}$ with $c\left(K_{n}\right)=1$, whereas $c^{*}(A) \geqq 2$ (actually, $c^{*}(A)=2$ ).
5.7. Example (Newtonian capacity). Let $X=\boldsymbol{R}^{3}$, and consider the newtonian kernel

$$
G(x, y)=\frac{1}{|x-y|}, \quad x, y \in X
$$

The potential $G \mu$ of a measure $\mu \in \mathscr{M}^{+}$is defined by

$$
G \mu(x)=\int G(x, y) d \mu(y), \quad x \in X .
$$

The energy of $\mu \in \mathscr{M}^{+}$is defined as $\int G \mu d \mu$. Let

$$
\begin{gathered}
\mathscr{S}=\left\{\mu \in \mathscr{M}^{+} \mid \int G \mu d \mu \leqq 1\right\} \\
\mathscr{S}_{1}=\left\{\mu \in \mathscr{M}^{+} \mid G \mu \leqq 1 \text { everywhere }\right\} .
\end{gathered}
$$

Then $\mathscr{S}$ and $\mathscr{S}_{1}$ are hereditary, convex, ${ }^{13)}$ and vaguely compact. The enveloping capacities

$$
c=\sup _{\mu \in \mathscr{S}} \mu, \quad c_{1}=\sup _{\mu \in \mathscr{S}_{1}}{ }^{\mu}
$$

are called the newtonian energy capacity, resp. the ordinary newtonian capacity. The associated upper capacities $c^{*}$ and $c_{1}^{*}$ are both sequentially order continuous from below (Choquet [10] in the typical case of sets). It is a well known consequence of the maximum principle for newtonian potentials that

$$
c(K)^{2}=c_{1}(K) \quad \text { for every compact set } K
$$

This quantity is the classical capacity of $K$. There is of course a similar relation between the inner, resp. outer, capacities (of arbitrary sets) associated with $c$ and $c_{1}$. For the potential $G \mu \in \mathscr{G}$ of a measure $\mu \in \mathscr{M}^{+}$we have

$$
c(G \mu)^{2}=\int G \mu d \mu, \quad c_{1}(G \mu)=\int d \mu .
$$

We refer to a forthcoming general discussion of these two types of capacity (energy capacity and usual capacity) for very general kernels $G$. (See also [14], [15], [16], and § 6.7 below.)

## 6. More about the Classes $\mathscr{G} *$ and $\mathscr{H}_{0}^{*}$

In this section $\mathscr{S}$ denotes a hereditary (see end of § 5.2) and vaguely compact set of positive measures, and $c=\sup \mu$ the enveloping capacity $\mu \in \mathscr{S}$

[^13]as defined in (15), §5.4. According to the representation theorem (§5.3) the results obtained are of course applicable to any capacity $c$ (in the sense of Def. 4.1), taking for $\mathscr{S}$ e.g. the set $\mathscr{S}_{c}$ of all measures $\mu \leqq c$. We shall continue the study of the classes $\mathscr{G}^{*}$ and $\mathscr{H}_{0}^{*}$ as defined in $\S 2.1$, now with $C=c^{*}$, the upper capacity associated with $c$. (See also Lemma 3.2.)
6.1. Lemma. For any measure $\mu \in \mathscr{S}$ the $\mu$-integrable (resp. $\mu$-measurable, or $\mu$-capacitable) functions $X \rightarrow[0,+\infty]$ form a closed subset of $\mathscr{F}+(X)$ in the $c^{*}$-metric topology.

Proof. It is well known that each of these 3 subsets of $\mathscr{F}+(X)$ is closed in the $\mu^{*}$-metric topology determined by the (pseudo)distance $\int{ }^{*}\left|f_{1}-f_{2}\right| d \mu$ between functions $f_{1}, f_{2} \in \mathscr{F}+(X)$. (In the case of the $\mu$-capacitable functions, that is, functions $f \in \mathscr{F}+(X)$ such that $\int_{*} f d \mu=\int^{*} f d \mu$, this fact is also a special case of Lemma 4.6.) Hence the present lemma follows from (20), $\S 5.5$, according to which the $\mu^{*}$-distance is majorized by the $c^{*}$-distance when $\mu \in \mathscr{S}$ :

$$
\int^{*}\left|f_{1}-f_{2}\right| d \mu \leqq c^{*}\left(\left|f_{1}-f_{2}\right|\right) . \mid
$$

Corollary. Any function of class $\mathscr{G}^{*}$ is $\mu$-measurable and $\mu$-capacitable for every $\mu \in \mathscr{S}$. Any function of class $\mathscr{H}_{0}^{*}$ is $\mu$-integrable for every $\mu \in \mathscr{S}$.

In fact, the functions of class $\mathscr{G}$ are l.s.c., hence universally capacitable and universally measurable, and the functions of class $\mathscr{H}_{0}$ are universally integrable, that is, integrable with respect to every (Radon) measure on $X$.
6.2. Theorem. If $f \in \mathscr{G}^{*}$ (resp. $f \in \mathscr{H}_{0}^{*}$ ) then the mapping $\mu \mapsto \int f d \mu$ of $\mathscr{S}$ into $[0,+\infty]$ is l.s.c. (resp. u.s.c. and finite valued). The converse implication is valid under the additional hypothesis that $f \in \mathscr{H}_{0}^{*}$ (resp. $f \in \mathscr{G}^{*}$ ).

Proof. For the applications of the converse implication in potential theory (cf. $\S 6.7$ below) the second case $f \in \mathscr{H}_{0}^{*}$ is of particular importance, and so we shall give the proof for this case, the case $f \in \mathscr{G} *$ being quite analogous.

First suppose that $f \in \mathscr{H}_{0}^{*}$, and choose for any $\varepsilon>0$ a function $h \in \mathscr{H}_{0}$ so that $h \leqq f$ and $c^{*}(f-h)<\varepsilon$ (Lemma 3.2). For every $\mu \in \mathscr{S}$ we obtain from (20), $\S 5.5$, since $f$ and $h$ are $\mu$-integrable (Cor. to Lemma 6.1):

$$
\begin{aligned}
\int h d \mu & \leqq \int f d \mu=\int h d \mu+\int(f-h) d \mu \\
& \leqq \int h d \mu+c^{*}(f-h)<\int h d \mu+\varepsilon .
\end{aligned}
$$

The mapping $\mu \mapsto \int f d \mu$ of $\mathscr{S}$ into $[0,+\infty[$ has thus been approximated uniformly on $\mathscr{S}$ by mappings $\mu \mapsto \int h d \mu$ with $h \in \mathscr{H}_{0}$, and these latter
mappings are finite and u.s.c. (on all of $\mathscr{M}^{+}$) as observed in the beginning of the proof of Theorem 5.5.

Conversely, suppose that $f \in \mathscr{G} *$ and that the (upper) integral $\int f d \mu$ is a finite valued u.s.c. function of $\mu \in \mathscr{S}$. (Note that $f \in \mathscr{G} *$ is indeed $\mu$ measurable and $\mu$-capacitable for every $\mu \in \mathscr{S}$, again according to Cor. to Lemma 6.1.) Given $\varepsilon>0$, there exists according to Lemma 3.2 a function $g \in \mathscr{G}$ such that $g \geqq f$ and $c^{*}(g-f)<\varepsilon$. Denote by $\Phi$ the upward directed family of all functions $\varphi \in \mathscr{C}_{0}^{+}$such that $\varphi \leqq g$. Considered as functions of $\mu \in \mathscr{S}$, the integrals $\int \varphi d \mu, \varphi \in \Phi$, form an upward directed family of finite valued continuous functions on the compact space $\mathscr{S}$. It follows e.g. from Theorem 4.3 (a) applied to $\mu$ that

$$
\sup _{\varphi \in \Phi} \int \varphi d \mu=\int g d \mu \geqq \int f d \mu
$$

for every $\mu \in \mathscr{S}$. By hypothesis the function $\mu \mapsto \int f d \mu$ on $\mathscr{S}$ is finite valued and u.s.c. It follows from Dini's theorem that there exists $\varphi \in \Phi$ such that $\int \varphi d \mu>\int f d \mu-\varepsilon$ for all $\mu \in \mathscr{S}$, and hence

$$
c_{*}\left((f-\varphi)^{+}\right)=\sup _{\mu \in \mathscr{S}} \int(f-\varphi)^{+} d \mu \leqq \varepsilon^{14)}
$$

in view of (19), §5.5. Now $f \in \mathscr{G}^{*}$, and $\varphi \in \mathscr{C}_{0}^{+} \subset \mathscr{H}_{0} \subset \mathscr{H}_{0}^{*}$. Thus it follows from Lemma 2.3 that $(f-\varphi)^{+}$is of class $\mathscr{G}^{*}$ and hence capacitable (Lemma 4.6). We conclude that $c^{*}\left((f-\varphi)^{+}\right) \leqq \varepsilon$ and hence $c^{*}(|f-\varphi|)<2 \varepsilon$ because

$$
|f-\varphi|=(f-\varphi)^{+}+(\varphi-f)^{+} \leqq(f-\varphi)^{+}+(g-f) .
$$

Consequently, $f$ belongs to the closure of $\mathscr{C}_{0}^{+}$in the $c^{*}$-metric topology on $\mathscr{F}+(X)$, in particular $f \in \mathscr{H}_{0}^{*}$ by definition (§ 2.1). I

Remark. Actually, the latter part of the proof shows that $\mathscr{G} * \cap \mathscr{H}_{0}^{*}$ is contained in the $c^{*}$-metric closure of $\mathscr{C}_{0}^{+}$, and this is the non-trivial part of Theorem 3.3 (for the case $C=c^{*}$ ).

Corollary. For any quasi closed set $H \subset X$ the set of all measures $\mu \in \mathscr{S}$ carried by $H$ is vaguely compact.

In fact, $f:=1_{\mathbf{c}_{H}} \in \mathscr{G}^{*}$ (Lemma 2.4), and so $\left\{\mu \in \mathscr{S} \mid \int f d \mu=0\right\}$ is vaguely closed, hence vaguely compact, on account of the first part of the theorem (for the case $f \in \mathscr{G} *$ ).
${ }^{14}$ ) This inequality follows from the fact that, for any $\mu \in \mathscr{S}$, the trace $v$ of $\mu$ on the $\mu$ measurable set $\{x \in X \mid f(x) \geqq \varphi(x)\}$ belongs to $\mathscr{S}$ because $\mathscr{S}$ is hereditary. Hence we obtain

$$
\int(f-\varphi)^{+} d \mu=\int(f-\varphi) d v<\varepsilon .
$$

6.3. Theorem. For any function $f \in \mathscr{H}_{0}^{*}$ we have

$$
c(f)=\max _{\mu \in \mathscr{S}} \int f d \mu<+\infty .
$$

The class $\mathscr{S}(f)$ of all measures $\mu \in \mathscr{S}$ such that $\int f d \mu=c(f)$, is vaguely compact. It is convex if $\mathscr{S}$ is convex.

Proof. The functions of class $\mathscr{H}_{0}^{*}$ are c-capacitable (Lemma 4.6) and $\mu$-integrable for every $\mu \in \mathscr{S}$ (Cor. to Lemma 6.1). Since $\mathscr{S}$ is compact it follows from the first part of Theorem 6.2 that the supremum $c(f)=c_{*}(f)$ in (19) of Theorem 5.5 is indeed attained and finite, and that $\mathscr{S}(f)$ is compact. If $\mathscr{S}$ is convex then any convex combination $\mu$ of measures $\mu_{1}, \mu_{2} \in \mathscr{S}(f)$ belongs to $\mathscr{S}$ and gives the maximal value $\int f d \mu=c(f)$. I
6.4. Lemma. Consider a decreasing sequence of functions $f_{n} \in \mathscr{H}_{0}^{*}$, and choose corresponding maximizing measures $\mu_{n} \in \mathscr{S}\left(f_{n}\right)$. Then every vague cluster point for the sequence $\left(\mu_{n}\right)$ belongs to $\mathscr{S}\left(\inf f_{n}\right)$.

Proof. Write $f=\inf _{n} f_{n}$, and let $\mu$ denote any vague cluster point for $\left(\mu_{n}\right)$. For any $m \in \boldsymbol{N}$ we have by Theorem 6.2

$$
\int f_{m} d \mu \geqq \liminf _{n} \int f_{m} d \mu_{n} \geqq \lim _{n} \int f_{n} d \mu_{n}=\lim _{n} c\left(f_{n}\right)=c(f) .
$$

It follows that $\mu \in \mathscr{S}(f)$ because $\mu \in \mathscr{S}$ and

$$
\int f d \mu=\inf _{m} \int f_{m} d \mu \geqq c(f) . \mathbf{I}
$$

Remark. There is a similar result for any downward directed family $\left(f_{\alpha}\right)_{\alpha \in I}$ of u.s.c. functions $f_{\alpha}$ of class $\mathscr{H}_{0}^{*}$ (cf. Theorem $\left.3.6(\mathrm{~b})\right)$. The proof is quite similar. In both cases the method of proof actually leads to a slightly stronger formulation. Thus, in the latter case, any vague cluster point $\mu$ for the filter on $\mathscr{S}$ generated by the "sections" $\cup \mathscr{S}\left(f_{\alpha}\right), \beta \in I$, belongs to $\mathscr{S}\left(\inf f_{\alpha}\right)$.
$\alpha$
6.5. We shall call the given hereditary (and vaguely compact) subset $\mathscr{S}$ of $\mathscr{M}^{+}$strictly hereditary if, for every $\mu \in \mathscr{S}$ and every $v \in \mathscr{M}^{+}$with $v \leqq \mu, v \neq \mu$, there exists a number $t>1$ such that $t v \in \mathscr{S}$.

Lemma. Let $f \in \mathscr{H}_{0}^{*}$. There always exist measures $\mu \in \mathscr{S}(f)$ concentrated on $\{x \in X \mid f(x)>0\}$. If $\mathscr{S}$ is strictly hereditary and if $c(f)>0$, then every measure $\mu \in \mathscr{S}(f)$ is concentrated on this set.

Proof. Let $\mu \in \mathscr{S}(f)$, and let $v$ denote the trace of $\mu$ on $A:=\{x \in X \mid f(x)$ $>0\}$. Then $v \in \mathscr{S}(f)$ because $\mathscr{S}$ is hereditary and $\int f d v=\int * f \cdot 1_{A} d \mu=\int f d \mu$. Suppose now that $\mathscr{S}$ is strictly hereditary and that $c(f)>0$. For every $t>1$ we then have

$$
\int f d(t v)=t \int f d v=t c(f)>c(f),
$$

and hence $t v \notin \mathscr{S}$. Consequently $\mu=v$, that is, $\mu$ is concentrated on $A$. I
6.6. The case of sets. We shall now specialize some of the results of the present section to the case of (indicator functions for) subsets of $X$. In that case the compactness of $\mathscr{S}$ can be weakened to closedness at the expense of a single precaution to be observed. This will appear from the following discussion which is largely independent of the preceding theory, but contained therein as a special case whenever $\mathscr{S}$ is compact.

Thus let $\mathscr{S}$ denote any hereditary and vaguely closed subset of $\mathscr{M}^{+}$. For any compact set $K \subset X$ define the capacity $c(K)$ by

$$
c(K)=\sup _{\mu \in \mathscr{S}} \mu(K)=\sup \{\mu(X) \mid \mu \in \mathscr{S}, \operatorname{supp} \mu \subset K\} .
$$

The identity between these two suprema follows from the assumption that $\mathscr{S}$ be hereditary (cf. remark to Theorem 5.5). Clearly each of the two suprema is attained provided that $c(K)<+\infty$ (this is the precaution alluded to above.) Note that $\mathscr{S}$ is compact if and only if $c(K)<+\infty$ for all compact sets $K \subset X$. In that case the above definition of $c(K)$ agrees with (18), § 5.5, applied to $h=1_{K} \in \mathscr{H}_{0}$.

We denote by $\mathscr{K}=\mathscr{K}(X)$ the class of all compact subsets of $X$. The mapping $c: \mathscr{K} \rightarrow[0,+\infty]$ defined above is increasing and order continuous from above. The latter assertion means that

$$
c\left(\bigcap_{\alpha} K_{\alpha}\right)=\inf c\left(K_{\alpha}\right)
$$

for every downward directed family of compact sets $K_{\alpha} .{ }^{15)}$ Since $X$ is locally compact it follows that $c$ is continuous from the right and hence is a capacity in the original sense of Choouet [ $10, \S 15$ ]. Moreover, this capacity $c: \mathscr{K} \rightarrow$ $[0,+\infty]$ is subadditive, and $c(\theta)=0$.
$\left.{ }^{15}\right)$ To prove this, let $t<\inf c\left(K_{\alpha}\right)$. For each $\alpha$ let $\mu_{\alpha} \in \mathscr{S}, \operatorname{supp} \mu_{\alpha} \subset K_{\alpha}$, and $\mu_{\alpha}(X) \geqq t$. Replacing, if necessary, $\mu_{\alpha}$ by $\left(t / \mu_{\alpha}(X)\right) \mu_{\alpha}$ (which belongs to $\mathscr{S}$ since $\mathscr{S}$ is hereditary) we may assume that $\mu_{\alpha}(X)=t$. Denoting by $\mu$ any vague cluster point for $\left(\mu_{\alpha}\right)$, we obtain $\operatorname{supp} \mu \subset K_{\beta}$. for each $\beta$, and hence supp $\mu \subset \cap K_{\alpha}$. Since $\mathscr{S}$ is closed, it follows that $\mu \in \mathscr{S}$, and we conclude (taking a fixed index $\beta$ ) that

$$
c\left(\cap K_{\alpha}\right) \geqq \mu(X)=\mu\left(K_{\beta}\right) \geqq \liminf _{\alpha} \mu_{\alpha}\left(K_{\beta}\right)=t
$$

because the mapping $v \mapsto v\left(K_{\beta}\right)$ is u.s.c., and $\mu_{\alpha}\left(K_{\beta}\right)=\mu_{\alpha}(X)$ for $\alpha \geqslant \beta$.

With the capacity $c$ we associate in the usual way the inner capacity $c_{*}$ and the outer capacity $c^{*}$ defined for arbitrary sets $A \subset X$ by

$$
\begin{aligned}
& c_{*}(A)=\sup \{c(K) \mid K \text { compact, } K \subset A\}, \\
& c^{*}(A)=\inf \left\{c_{*}(G) \mid G \text { open, } G \supset A\right\},
\end{aligned}
$$

and we may write $c(A)$ in place of $c_{*}(A)$ or $c^{*}(A)$ whenever $A$ is capacitable, that is, $c_{*}(A)=c^{*}(A)$. Compact sets and open sets are capacitable. As in the proof of (19), \& 5.5, we obtain the following representations of the inner capacity of a set $A \subset X$ :

$$
\begin{align*}
c_{*}(A) & =\sup \left\{\mu_{*}(A) \mid \mu \in \mathscr{S}\right\} \\
& =\sup \{\mu(X) \mid \mu \in \mathscr{S}, \operatorname{supp} \mu \text { compact and } \subset A\} . \tag{21}
\end{align*}
$$

Again the identity between these suprema follows from the assumption that $\mathscr{S}$ be hereditary. Using the former representation (21) we see that the inner capacity $c_{*}$ is countably subadditive on $\mathscr{S}$-measurable sets, and sequentially order continuous from below on such sets (cf. the analogous proof of Theorem 7.1 below). It follows that the outer capacity $c^{*}$ is countably subadditive. In particular the quasi topological notions and results of [17] are available.

Any quasi compact set $A$ is capacitable (cf. the proof of Lemma 4.6). If $c(A)<+\infty$ the former supremum in (21) is attained by some measure $\mu \in \mathscr{S}$ concentrated on the quasi compact set $A$. Thus

$$
c(A)=\max \{\mu(X) \mid \mu \in \mathscr{S}, \mu \text { conc. on } A\} .
$$

The set $\mathscr{S}(A)$ of all maximizing measures is vaguely compact (and convex if $\mathscr{S}$ is convex).

To prove this, note that the mapping $\mu \mapsto \mu(A)$ of $\mathscr{S}$ into $[0,+\infty]$ is finite valued and u.s.c. when $A$ is quasi compact. (This is easily reduced to the case of a compact set, cf. the proof of the first part of Theorem 6.2.) Similarly, the mapping $\mu \rightarrow \mu(B)$ of $\mathscr{S}$ into [ $0,+\infty$ ] is l.s.c. for any quasi open set $B$. When applied to $B=\complement A$ this latter observation implies that those measures $\mu \in \mathscr{S}$ which are concentrated on $A$ form a vaguely closed subset of $\mathscr{M}^{+}$when $A$ is quasi compact (or just quasi closed), cf. Cor. to Theorem 6.2. Finally, this vaguely closed set of measures is vaguely bounded, and hence vaguely compact, because

$$
\mu(X)=\mu(A) \leqq c(A)<\infty
$$

for every measure in the set.
6.7. An application. We return to the example in $\S 5.7$, the newtonian energy capacity $c$. Denote by $\mathscr{E}^{+}$the class of all measures $\lambda \in \mathscr{M}^{+}$such that $\int G \lambda d \lambda<+\infty$. It was proved by Cartan [9, p. 238] that, for each $\lambda \in \mathscr{E}^{+}$, the mapping $\mu \mid \rightarrow \int G \lambda d \mu$ of $\mathscr{S}=\left\{\mu \in \mathscr{M}^{+} \mid \int G \mu d \mu \leqq 1\right\}$ into $[0,+\infty]$ is vaguely continuous (and finite valued). Since $G \lambda \in \mathscr{G} \subset \mathscr{G}^{*}$, this result, by Theorem 6.2, is equivalent to stating that $G \lambda \in \mathscr{H}_{0}^{*}$ for every $\lambda \in \mathscr{E}^{+}$.

Consider now a function $f \in \mathscr{H}_{0}^{*}$. It follows from the energy principle (the strict positive definite character of the newtonian kernel $G$ ) that $\mathscr{S}(f)$ consists of precisely one measure $\mu$. By the Gauss variational method it is shown that the measure $\lambda:=c(f) \mu$ is characterized within $\mathscr{E}^{+}$by the following two properties
(a) $G \lambda \geqq f$ q. e.
(b) $G \lambda=f$ almost everywhere with respect to $\lambda$.

Moreover, $\lambda$ is concentrated on $\{x \in X \mid f(x)>0\}$ (Lemma 6.5), and $\int f d \lambda=$ $\int G \lambda d \lambda=c(f)^{2}$. This measure $\lambda=\lambda_{f}$ is called the capacitary measure for the function $f \in \mathscr{H}_{0}^{*}$.

Next it is shown that, for any function $f \in \mathscr{F}+(X)$, we have the following dual representation of the upper energy capacity:

$$
c^{*}(f)=\inf \left\{\left.\left(\int G \lambda d \lambda\right)^{\frac{1}{2}} \right\rvert\, \lambda \in \mathscr{E}^{+}, G \lambda \geqq f \text { q. e. }\right\} .
$$

This allows us to deduce that the quasi u.s.c. envelope $f^{*}$ of $f$ (which exists and is uniquely determined q.e. according to [17, Theorem 3.5]) is of class $\mathscr{H}_{0}^{*}$ if and only if $c^{*}(f)<+\infty$. In the affirmative case we have $c\left(f^{*}\right)=c^{*}(f)$, and the above infimum is attained by precisely one measure, viz. the capacitary measure $\lambda=\lambda_{f^{*}}$ for $f^{*}$. We call this measure the upper capacitary measure for $f$. (Its potential is also characterized as the smallest, $\hat{R}_{f}$, among all potentials majorizing $f$ quasi everywhere.)

Specializing to the case $f=1_{A}$, the indicator function of a set $A \subset X$ with $c^{*}(A)<+\infty$, we thus obtain the outer equilibrium measure $\lambda=\lambda_{A^{*}}$, characterized within $\mathscr{E}^{+}$by the properties that $\lambda$ is concentrated on the (quasi compact) quasi closure $A^{*}$ of $A$, and that
(a) $G \lambda=1$ q.e. in $A\left(\right.$ even in $\left.A^{*}\right)$,
(b) $G \lambda \leqq 1$ everywhere (by the maximum principle).

Moreover, $\lambda(X)=\int G \lambda d \lambda=c^{*}(A)^{2}\left(=c\left(A^{*}\right)^{2}\right)$.
A further important case is that of the outer balayage of a given measure $\mu \in \mathscr{M}^{+}$on a set $A \subset X$. Here we take $f=G \mu \cdot 1_{A}$ and assume again that $c^{*}(f)<+\infty$ (e.g. $\mu \in \mathscr{E}^{+}$). Since $G \mu$ is always quasi continuous, we have
again $f^{*}=G \mu \cdot 1_{A^{*}} \in \mathscr{H}_{0}^{*}$. We thus obtain the outer swept-out measure $\lambda=\lambda_{G \mu \cdot 1_{A^{*}}}$ of $\mu$ on $A$, characterized within $\mathscr{E}^{+}$by the properties that $\lambda$ is concentrated on the quasi closure $A^{*}$ of $A$, and that
(a) $G \lambda=G \mu$ q.e. in $A$ (even in $A^{*}$ ),
(b) $G \lambda \leqq G \mu$ everywhere (by the domination principle).

Moreover, $\int G \mu d \lambda=\int G \lambda d \lambda=c^{*}\left(G \mu \cdot 1_{A}\right)^{2}$.
In view of the compatibility between the "quasi topology" and the fine topology e.g. in the present newtonian case (cf. [17, §§ 4,5]), the results mentioned above for the two particular cases (outer equilibrium and outer balayage) coincide with those obtained by Cartan in his fundamental treatise [9] of the newtonian potential, except that our method is limited to the case $c^{*}(A)<+\infty$, resp. $c^{*}\left(G \mu \cdot 1_{A}\right)<+\infty$. On the other hand the present method is applicable to a very large class of kernels (consistent kernels), see [14], [15], and a comprehensive exposition to appear.

## 7. More about the Lower Capacity

We continue the study of a capacity $c$ represented as the upper envelope of a hereditary and vaguely compact set $\mathscr{S}$ of positive measures on the locally compact space $X$. According to Theorem 5.5 the associated lower capacity $c_{\text {* }}$ is given by

$$
\begin{equation*}
c_{*}(f)=\sup _{\mathbb{C}_{0}} \int_{*} f d \mu \tag{19}
\end{equation*}
$$

for every $f \in \mathscr{F}+(X)$. By the remark to this theorem it suffices here to let $\mu$ range over the set of all measures $\mu \in \mathscr{S}$ of compact support contained in $\{x \in X \mid f(x)>0\}$.

For brevity we shall say that a function $f$, or a set $A$, is $\mathscr{S}$-measurable if it is $\mu$-measurable for every $\mu \in \mathscr{S}$.

It is possible to develop a theory for the lower capacity $c_{*}$ analogous to that of Chapter I for the upper capacity $C=c^{*}$. In particular one may study the closed classes $\mathscr{G}_{*}, \mathscr{H}_{*}$, and $\mathscr{H}_{0 *}$, replacing the $c^{*}$-metric by the analogous $c_{*}$-metric on $\mathscr{S}$-measurable functions. We shall, however, limit our attention to those properties of the lower capacity which are relevant for the potential theoretic applications we have in mind.
7.1. Theorem. The lower capacity $c_{*}$ is countably subadditive and sequentially order continuous from below on $\mathscr{S}$-measurable functions, that is,

$$
\begin{gathered}
c_{*}\left(\sum_{n \in N} f_{n}\right) \leqq \sum_{n \in N} c_{*}\left(f_{n}\right), \\
{\left[f_{n} \not \subset f\right] \Rightarrow\left[c_{*}\left(f_{n}\right) \rightarrow c_{*}(f)\right]}
\end{gathered}
$$

for any sequence $\left(f_{n}\right)_{n \in N}$ of $\mathscr{S}$-measurable functions $f_{n} \in \mathscr{F}+(X)$.
Proof. By application of (19), the proof is easily reduced to the case $c=\mu$ of a single measure $\mu \in \mathscr{M}^{+}$, considered in (12), (13) of §5.2. I

Corollary. For any sequence of $\mathscr{S}$-measurable sets $A_{n}$,

$$
\begin{gathered}
c_{*}\left(\underset{n \in N}{\cup} A_{n}\right) \leqq \sum_{n \in N} c_{*}\left(A_{n}\right), \\
{\left[A_{n} \nmid A\right] \Rightarrow\left[c_{*}\left(A_{n}\right) \rightarrow c_{*}(A)\right] .}
\end{gathered}
$$

7.2. Exceptional sets determined by $c_{*}$. In addition to the sets $E \subset X$ with $c^{*}(E)=0$, the wider class of sets $E$ such that $c_{*}(E)=0$ plays a certain role in developing potential theory. According to the above corollary, the class of all $\mathscr{S}$-measurable sets $E$ with $c_{\circledast}(E)=0$ is stable under countable union. In view of (19) we have for any set $E \subset X$

$$
\left[c_{*}(E)=0\right] \Leftrightarrow\left[\mu_{*}(E)=0 \text { for all } \mu \in \mathscr{S}\right],
$$

(and similarly for a function $f \in \mathscr{F}^{+}(X)$ instead of the set $E$ ). If $E$ is $\mathscr{S}_{-}$ measurable, then $c_{*}(E)=0$ holds if and only if $E$ is locally $\mu$-negligible for every $\mu \in \mathscr{S}$.

Definition. A property $P[x]$ is said to hold nearly everywhere (French: à peu près partout) in a set $A \subset X$ (abbreviated: n.e. in $A)$ if $c_{*}(\{x \in A \mid$ non $P[x]\})=0$.

The following lemma is an immediate consequence of the preceding observations.

Lemma. If a property $P[x]$ holds locally almost everywhere with respect to every measure $\mu \in \mathscr{S}$, then it holds nearly everywhere. The converse implication is valid provided that the exceptional set $E:=\{x \in X \mid \operatorname{non} P[x]\}$ is $\mathscr{S}$-measurable.
7.3. Lemma. Let $f \in \mathscr{F}^{+}(X)$. In order that $f(x)=0$ n.e. it is necessary and sufficient that $c_{*}(f)=0$ and that moreover $f$ be $v$-measurable for every $v \in \mathscr{S}$ of compact support contained in $\{x \in X \mid f(x)>0\}$.

Proof. Writing $E:=\{x \in X \mid f(x)>0\}$, we have (as in the proof of Lemma 1.3 (a))

$$
\begin{equation*}
f \leqq 1_{E}+1_{E}+\ldots ; \quad 1_{E} \leqq f+f+\ldots \tag{22}
\end{equation*}
$$

If $f$, and hence $E$, is $\mathscr{S}$-measurable, these inequalities serve to establish that $f(x)=0$ n. e. is equivalent to $c_{*}(f)=0$ in view of Theorem 7.1.

For any $f \in \mathscr{F}^{+}(X)$ such that $f(x)=0$ n. e. let $h \in \mathscr{H}_{0}, h \leqq f$. Then $h(x)=0$ n. e., and so $c(h)=0$. It follows that $c_{*}(f)=0$. Moreover, the stated measurability condition is trivially fulfilled because the only measure $v$ in question is $v=0$ since $c_{*}(E)=0$, cf. (19) or (21).

Conversely, suppose that $c_{*}(f)=0$, and that $f$ is $v$-measurable for every $v \in \mathscr{S}$ of compact support contained in $E$. The second inequality (22) then shows that $\int_{*} 1_{E} d v=0$ for any such $v$ because $\int_{*} f d v=0$. Hence $c_{*}(E)=$ $c_{*}\left(1_{E}\right)=0$ according to (19) or (21). I
7.4. Theorem. Let $f_{1}, f_{2} \in \mathscr{F}+(X)$, and suppose that $f_{2}$ is $\mathscr{S}$-measurable. Consider the following statements:
(i) $\quad f_{1}(x) \leqq f_{2}(x)$ nearly everywhere,
(ii) $c_{*}\left(\left(f_{1}-f_{2}\right)^{+}\right)=0$,
(iii) $\int_{*} f_{1} d \mu \leqq \int_{*} f_{2} d \mu \quad$ for every $\mu \in \mathscr{S}$.

Then

$$
\text { (i) } \underset{(\Leftrightarrow)}{\Rightarrow} \text { (ii) } \Leftrightarrow \text { (iii) } \Rightarrow\left[c_{*}\left(f_{1}\right) \leqq c_{*}\left(f_{2}\right)\right] \text {, }
$$

the implication (ii) $\Rightarrow$ (i) being valid under the additional hypothesis that $f_{1}$ be $\mathscr{S}$-measurable, or just $v$-measurable for every $v \in \mathscr{S}$ of compact support contained in $\left\{x \in X \mid f_{1}(x)>0\right\}$.

Proof. The implication (i) $\Rightarrow$ (ii) holds without any assumption on $f_{1}, f_{2} \in \mathscr{F}+(X)$ and follows, like its conditional converse, from the preceding lemma applied to $f=\left(f_{1}-f_{2}\right)^{+}$.

To derive (iii) from (ii) let $h \in \mathscr{H}_{0}, h \leqq f_{1}$. Then

$$
c_{*}\left(\left(h-f_{2}\right)^{+}\right) \leqq c_{*}\left(\left(f_{1}-f_{2}\right)^{+}\right)=0,
$$

and hence $\int_{\approx}\left(h-f_{2}\right)^{+} d \mu=0$ for every $\mu \in \mathscr{S}$ according to (19). Since $\left(h-f_{2}\right)^{+}$is $\mu$-measurable and majorized by the $\mu$-integrable function $h$, it follows that $\int^{*}\left(h-f_{2}\right)^{+} d \mu=0$, and

$$
\int h d \mu \leqq \int_{*} f_{2} d \mu+\int^{*}\left(h-f_{2}\right) d \mu=\int_{*} f_{2} d \mu
$$

on account of (4), §4.5, applied to the measure $\mu$. Consequently, $\int_{\approx} f_{1} d \mu \leqq$ $\int_{:} f_{2} d \mu$.

Conversely, suppose that (iii) holds, and let $h \in \mathscr{H}_{0}, h \leqq\left(f_{1}-f_{2}\right)^{+}$. For any $\mu \in \mathscr{S}$ of compact support contained in $\left\{x \in X \mid f_{1}(x)>f_{2}(x)\right\}$ we have $h+f_{2} \leqq f_{1}$ almost everywhere with respect to $\mu$, and hence

$$
\int h d \mu+\int_{*} f_{2} d \mu=\int_{*}\left(h+f_{2}\right) d \mu \leqq \int_{*} f_{1} d \mu \leqq \int_{*} f_{2} d \mu
$$

by hypothesis. If $\int_{*} f_{2} d \mu<+\infty$, this shows that $\int h d \mu=0$. The same holds in general. In fact, the trace $\mu_{n}$ of $\mu$ on the $\mu$-measurable set $E_{n}:=$ $\left\{x \in X \mid f_{2}(x) \leqq n\right\}, n \in \boldsymbol{N}$, has the same properties as required above for $\mu$, and in addition $\int_{*} f_{2} d \mu_{n}<+\infty$. Hence $\int h d \mu_{n}=0$, and consequently $\int h d \mu=0$ because the sets $E_{n}, n \in \boldsymbol{N}$, cover $\{x \in X \mid h(x)>0\}$ (since $f_{2}(x)<+\infty$ for every $x$ with $\left.h(x)>0\right)$. Having thus proved that $\int h d \mu=0$ for every $h \in \mathscr{H}_{0}$ such that $h \leqq\left(f_{1}-f_{2}\right)^{+}$, we conclude that $\int_{*}\left(f_{1}-f_{2}\right)^{+} d \mu$ $=0$, and finally, by varying $\mu$, that $c_{*}\left(\left(f_{1}-f_{2}\right)^{+}\right)=0$.

Clearly (iii) implies that $c_{*}\left(f_{1}\right) \leqq c_{*}\left(f_{2}\right)$ without any hypotheses on $f_{1}, f_{2}$.I

Corollary 1. Let $f \in \mathscr{F}+(X)$ be $\mathscr{S}$-measurable, and let $0<t<+\infty$. If $f(x) \geqq t$ n.e. in some set $A \subset X$, then $c_{*}(A) \leqq t^{-1} c_{*}(f)$.

In fact, $t \cdot 1_{A} \leqq f$ n.e., hence $t c_{*}(A)=c_{*}\left(t \cdot 1_{A}\right) \leqq c_{*}(f)$.
Applying this result to $A=\{x \in X \mid f(x)=+\infty\}$, we obtain for $t \rightarrow+\infty$ :
Corollary 2. Let $f \in \mathscr{F}^{+}(X)$ be $\mathscr{S}$-measurable with $c_{\approx}(f)<+\infty$. Then $f(x)<+\infty$ n.e.

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# INELASTIC DEUTERON SCATTERING IN THE LEAD REGION 



Kommissionær: Munksgaard
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## Synopsis

Elastic and inelastic scattering of 13.1 MeV deuterons from the stable isotopes of $\mathrm{Bi}, \mathrm{Pb}$ and Tl have been studied. The scattered deuterons were observed at $120^{\circ}$, $125^{\circ}$, and $150^{\circ}$ with a high resolution magnetic spectrograph. Angular distributions of the elastically scattered deuterons were measured and fitted with a five-parameter optical model.

A number of multiplets in the odd-mass isotopes expected on the basis of a particlevibrational coupling model were located. Of these, the multiplets corresponding to the strong octupole states near 2.6 MeV were found in all four odd-mass nuclei and an acurate comparison of the relative population strengths was made. A large decrease in the cross section to the octupole states was observed in going from ${ }^{208} \mathrm{~Pb}$ to ${ }^{203} \mathrm{Tl}$.

## 1. Introduction

The nuclei in the region of ${ }_{82}^{208} \mathrm{~Pb}_{126}$ have been the subject of a large number of experimental ${ }^{1-13)}$ and theoretical studies ${ }^{14-17)}$ in the last few years. Of particular interest have been the low-lying levels in the nuclei which are one nucleon removed from the doubly-closed core and whose populations are found to be rather selectively dependent on the reaction used. Among these levels multiplets of states are expected on the particlevibration coupling model ${ }^{18)}$ due to the coupling of the rather pure one-particle configurations to the collective vibrations of the core, and inelastic scattering studies which are particularly suited for the population of such states have succeeded in locating a number of them. The multiplets based on the strongly collective octupole state at 2.615 MeV are found to be especially strongly populated in these reactions.

In addition to the nuclei which are one nucleon removed from the doubly-closed ${ }^{208} \mathrm{~Pb}$ core, those nuclei which are one nucleon removed from the closed proton-shell ${ }^{204} \mathrm{~Pb}$ and ${ }^{206} \mathrm{~Pb}$ cores are expected to exhibit similar multiplets. However, whereas the first level is at 2.615 MeV in ${ }^{208} \mathrm{~Pb}$, a number of collective levels are known in ${ }^{204} \mathrm{~Pb}$ and ${ }^{206} \mathrm{~Pb}$ below this energy, and the increase in level density can be expected to produce an appreciable mixing of the various configurations.

According to the particle-vibration ${ }^{18)}$ coupling model, the multiplet of states obtained by coupling a one-particle configuration (spin $J_{p}$ ) to a $2^{\lambda}$-pole oscillation of the core should be populated by transitions of multipolarity $\lambda$ in the inelastic scattering whose total intensity is equal to the intensity of the corresponding state $(\operatorname{spin} \lambda)$ in the core nucleus. Furthermore, this model predicts that the inelastic scattering cross section, $d \sigma$, to each member of the multiplet $(\operatorname{spin} J)$ is given by

$$
d \sigma(J)=d \sigma(c) \frac{2 J+1}{\left(2 J_{p}+1\right)(2 \lambda+1)},
$$

where $d \sigma(c)$ is the cross section to the state in the core nucleus. The "center-of-mass" energy should correspond to that of the core state. Mixing between
members of the multiplets and other states, however, is expected to exist and to cause energy shifts of the individual states and deviations from the cross section rules.

We present here results of the scattering of 13 MeV deuterons on the stable isotopes of $\mathrm{Bi}, \mathrm{Pb}$ and Tl . These results, in particular for the multiplets associated with the strongly collective octupole states near 2.6 MeV , will be discussed within the scope of the particle-vibration coupling model and compared with theoretical calculations and previous experimental results where possible.

## 2. Experimental Procedure

The 13 MeV deuteron beam used in these experiments was obtained from the tandem accelerator at the Niels Bohr Institute. Metallic targets with thicknesses of 30 to $150 \mu \mathrm{~g} / \mathrm{cm}^{2}$ were prepared by vacuum evaporation onto $\sim 40 \mu \mathrm{~g} / \mathrm{cm}^{2}$ carbon backings. The isotopic purities are listed in Table 1. During the bombardments, the targets were rotated in the plane of the target in order to reduce the deterioration found to be caused by the beam on these low-melting point metals. Particular care was taken to achieve a uniform target thickness over the enlarged area of bombardment.

The scattered beam was analyzed in a particle spectrograph whose operation has already been described ${ }^{19)}$. Detection was made with $25 \mu$ Ilford type K2 nuclear emulsion plates, which were covered with $27 \mathrm{mg} / \mathrm{cm}^{2}$ of aluminium absorber. The deuteron tracks could be distinguished from the triton tracks in the few cases where the latter interfered, and were counted in 0.125 or 0.25 mm strips by means of a microscope. The scattered particles were observed at $120^{\circ}, 125^{\circ}$, and $150^{\circ}$, and light element impurities were distinguished by their kinematic shifts.

The resolution obtained in these experiments was from 3 to 10 keV FWHM. The main contributions to this resolution were found to be due to straggling in the target and beam spot size. In the optimum cases, these two factors contributed about 2.0 keV (at $30 \mu \mathrm{~g} / \mathrm{cm}^{2}$ ) and 1.8 keV (beam spot size $0.15 \times 3 \mathrm{~mm}^{2}$ ), respectively.

Contributions from beam energy instability over bombardment periods of $\sim 15$ hours appear to be less than 1.5 keV in these cases. No aluminium absorbers in front of the photographic plates were used for the highest resolution exposures and the counting of tracks was done in 0.125 mm strips only over the central portion of the emulsion. Particular care was used in choosing wrinkle-free carbon backings and the bombardments where done with the targets in a reflective geometry.

Table 1. Isotopic Purities

| Mass <br> Number | ${ }^{203} \mathrm{Tl}$ | ${ }^{205} \mathrm{Tl}$ | ${ }^{204} \mathrm{~Pb}$ | ${ }^{206} \mathrm{~Pb}$ | ${ }^{207} \mathrm{~Pb}$ | ${ }^{208} \mathrm{~Pb}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |$|{ }^{209} \mathrm{Bi}$

The determination of absolute cross sections was made by normalizing all transitions to the elastic peaks whose cross sections were determined from elastic angular distribution measurements. The normalization procedure used is the same as has been earlier described ${ }^{20,21)}$.

The experimental arrangement used in the elastic angular distribution study has been described in detail elsewhere ${ }^{22)}$. After analysis in the particle spectrograph the scattered deuterons were detected in a pair of 2 mm thick Si(Li) detectors. No problems with light element impurities in the target were encountered down to a laboratory angle of $15^{\circ}$.

## 3. Results and Discussion

The results of elastic and inelastic deuteron scattering on the stable isotopes of $\mathrm{Bi}, \mathrm{Pb}$, and Tl are presented here. Typical spectra of the deuterons scattered from these nuclei are shown in Figs. 2-10. The level energies obtained as the average of the determinations at different angles are listed in Tables 4-10, which also contain the measured differential cross sections. The individual nuclei are discussed below together with the results of the elastic scattering measurement which are shown in Fig. 1.

### 3.1 Elastic Scattering Distributions

Angular distributions of the elastically scattered deuterons from the seven nuclei studied were measured from $15^{\circ}$ to $150^{\circ}$. Normalization of the cross sections was achieved on the assumption that the elastic scattering at $15^{\circ}$ is pure Rutherford. This assumption seems justified in view of the optical


Fig. 1. Angular distributions for 13 MeV deuterons elastically scattered from nuclei in the Pb region. The curves are the best five-parameter fits.
model calculations, which find the differential cross sections to agree with the Rutherford formula at $15^{\circ}$ within $2 \%$. The results of the measurements are listed in Table 2. Statistical errors were kept below $2 \%$ at all angles, and allowing for $\sim 0.1^{\circ}$ uncertainty in setting the scattering angle and for the small error in the normalization procedure, the accuracy of the absolute cross sections is estimated to be better than $4 \%$.
Table 2. Elastic Scattering Cross Sections for 13 MeV Deuterons

| $\theta_{\text {lab }}$ <br> degrees | ${ }^{209} \mathrm{Bi}$ |  | ${ }^{208} \mathrm{~Pb}$ |  | ${ }^{207} \mathrm{~Pb}$ |  | ${ }^{206} \mathrm{~Pb}$ |  | ${ }^{204} \mathrm{~Pb}$ |  | ${ }^{205} \mathrm{Tl}$ |  | ${ }^{203} \mathrm{Tl}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\Delta \theta$ | $\begin{gathered} \left(\frac{d \sigma}{d \Omega}\right) \\ (m b / s r) \end{gathered}$ | $\Delta \theta$ | $\begin{gathered} \left(\frac{d \sigma}{d \Omega}\right) \\ (m b / s r) \end{gathered}$ | $\Delta \theta$ | $\begin{gathered} \left(\frac{d \sigma}{d \Omega}\right) \\ (m b / s r) \end{gathered}$ | $\Delta \theta$ | $\begin{gathered} \left(\frac{d \sigma}{d \Omega}\right) \\ (m b / s r) \end{gathered}$ | $\Delta \theta$ | $\begin{gathered} \left(\frac{d \sigma}{d \Omega}\right) \\ (m b / s r) \end{gathered}$ | $\Delta \theta$ | $\begin{gathered} \left(\frac{d \sigma}{d \Omega}\right) \\ (m b / s r) \end{gathered}$ | $\Delta \theta$ | $\begin{aligned} & \left(\frac{d \sigma}{d \Omega}\right) \\ & (m b / s r) \end{aligned}$ |
| 15 | 0.14 | 1.76 (5) | 0.14 | 1.72 (5) | 0.14 | 1.72 (5) | 0.14 | 1.72 (5) | 0.15 | 1.72 (5) | 0.14 | 1.68 (5) | 0.15 | 1.67 (5) |
| 20 | 0.19 | 5.49 (4) | 0.19 | 5.37 (4) | 0.19 | 5.41 (4) | 0.19 | 5.50 (4) | 0.19 | 5.53 (4) | 0.19 | 5.23 (4) | 0.19 | 5.60 (4) |
| 25 | 0.23 | 2.32 (4) | 0.23 | 2.33 (4) | 0.23 | 2.33 (4) | 0.24 | 2.33 (4) | 0.24 | 2.34 (4) | 0.24 | 2.20 (4) | 0.24 | 2.37 (4) |
| 30 | 0.28 | 1.18 (4) | 0.28 | 1.18 (4) | 0.28 | 1.18 (4) | 0.28 | 1.19 (4) | 0.28 | 1.20 (4) | 0.28 | 1.15 (4) | 0.28 | 1.21 (4) |
| 35 | 0.32 | 6.30 (3) | 0.32 | 6.39 (3) | 0.32 | 6.37 (3) | 0.32 | 6.38 (3) | 0.33 | 6.44 (3) | 0.32 | 6.24 (3) | 0.33 | 6.47 (3) |
| 40 | 0.35 | 3.68 (3) | 0.35 | 3.69 (3) | 0.35 | 3.67 (3) | 0.36 | 3.78 (3) | 0.37 | 3.73 (3) | 0.36 | 3.56 (3) | 0.37 | 3.73 (3) |
| 45 | 0.39 | 2.41 (3) | 0.39 | 2.33 (3) | 0.39 | 2.27 (3) | 0.40 | 2.37 (3) | 0.40 | 2.29 (3) | 0.40 | 2.15 (3) | 0.40 | 2.30 (3) |
| 50 | 0.42 | 1.45 (3) | 0.42 | 1.42 (3) | 0.42 | 1.42 (3) | 0.43 | 1.49 (3) | 0.44 | 1.45 (3) | 0.43 | 1.39 (3) | 0.44 | 1.46 (3) |
| 55 | 0.45 | 9.06 (2) | 0.45 | 8.83 (2) | 0.45 | 8.88 (2) | 0.46 | 9.19 (2) | 0.47 | 9.32 (2) | 0.46 | 8.42 (2) | 0.47 | 9.23 (2) |
| 60 | 0.49 | 5.80 (2) | 0.49 | 5.53 (2) | 0.49 | 5.65 (2) | 0.49 | 5.82 (2) | 0.49 | 5.87 (2) | 0.49 | 5.46 (2) | 0.49 | 5.83 (2) |
| 65 | 0.50 | 3.93 (2) | 0.50 | 3.67 (2) | 0.50 | 3.85 (2) | 0.51 | 3.92 (2) | 0.52 | 3.96 (2) | 0.51 | 3.65 (2) | 0.52 | 3.86 (2) |
| 70 | 0.52 | 2.81 (2) | 0.52 | 2.79 (2) | 0.52 | 2.71 (2) | 0.53 | 2.82 (2) | 0.53 | 2.77 (2) | 0.53 | 2.60 (2) | 0.53 | 2.81 (2) |
| 75 | 0.53 | 2.05 (2) | 0.53 | 2.02 (2) | 0.53 | 2.10 (2) | 0.54 | 2.08 (2) | 0.55 | 2.07 (2) | 0.54 | 1.89 (2) | 0.55 | 2.10 (2) |
| 80 | 0.54 | 1.50 (2) | 0.54 | 1.43 (2) | 0.54 | 1.51 (2) | 0.55 | 1.54 (2) | 0.56 | 1.49 (2) | 0.55 | 1.37 (2) | 0.56 | 1.50 (2) |
| 85 | 0.55 | 1.06 (2) | 0.55 | 1.04 (2) | 0.55 | 1.07 (2) | 0.56 | 1.10 (2) | 0.57 | 1.10 (2) | 0.56 | 9.59 (1) | 0.57 | 1.10 (2) |
| 90 | 0.55 | 7.74 (1) | 0.55 | 7.44 (1) | 0.55 | 7.73 (1) | 0.56 | 7.97 (1) | 0.57 | 8.00 (1) | 0.56 | 7.07 (1) | 0.57 | 7.84 (1) |
| 95 | 0.55 | 5.89 (1) | 0.55 | 5.79 (1) | 0.55 | 5.95 (1) | 0.56 | 5.76 (1) | 0.57 | 6.20 (1) | 0.56 | 5.49 (1) | 0.57 | 6.03 (1) |
| 100 | 0.54 | 5.12 (1) | 0.54 | 4.75 (1) | 0.54 | 4.91 (1) | 0.55 | 5.04 (1) | 0.56 | 4.97 (1) | 0.55 | 4.60 (1) | 0.56 | 4.94 (1) |
| 110 | 0.52 | 3.48 (1) | 0.52 | 2.96 (1) | 0.52 | 3.45 (1) | 0.53 | 3.45 (1) | 0.53 | 3.48 (1) | 0.53 | 3.28 (1) | 0.53 | 3.33 (1) |
| 120 | 0.49 | 2.31 (1) | 0.49 | 2.22 (1) | 0.49 | 2.24 (1) | 0.49 | 2.31 (1) | 0.49 | 2.33 (1) | 0.49 | 2.10 (1) | 0.49 | 2.30 (1) |
| 12 | 0.45 | 1.90 (1) | 0.45 | 1.92 (1) | 0.45 | 1.90 (1) | 0.48 | 1.94 (1) | 0.47 | 1.99 (1) | 0.46 | 1.77 (1) | 0.47 | 1.95 (1) |
| 130 | 0.42 | 1.70 (1) | 0.42 | 1.68 (1) | 0.42 | 1.66 (1) | 0.43 | 1.70 (1) | 0.44 | 1.71 (1) | 0.43 | 1.61 (1) | 0.44 | 1.65 (1) |
| 140 | 0.35 | 1.45 (1) | 0.35 | 1.45 (1) | 0.35 | 1.41 (1) | 0.36 | 1.42 (1) | 0.37 | 1.40 (1) | 0.36 | 1.33 (1) | 0.37 | 1.37 (1) |
| 150. | 0.28 | 1.23 (1) | 0.28 | 1.24 (1) | 0.28 | 1.20 (1) | 0.28 | 1.21 (1) | 0.28 | 1.23 (1) | 0.28 | 1.12 (1) | 0.28 | 1.22 (1) |

Table 3. Five-Parameter Optical-Model Fits to the (d, d) Reaction at 13.0 MeV

| Nuclide | $V(\mathrm{MeV})$ | $a(\mathrm{fm})$ | $W(\mathrm{MeV})$ | $a^{\prime}(\mathrm{fm})$ | $r_{o}^{\prime}(\mathrm{fm})$ | $\chi^{2}$ |
| :---: | ---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{209} \mathrm{Bi} \ldots \ldots \ldots \ldots \ldots \ldots$ | 98.18 | 0.998 | 11.34 | 0.661 | 1.524 | 1.0 |
| ${ }^{208} \mathrm{~Pb} \ldots \ldots \ldots \ldots \ldots$ | 97.60 | 1.026 | 17.72 | 0.584 | 1.480 | 2.2 |
| ${ }^{207} \mathrm{~Pb} \ldots \ldots \ldots \ldots \ldots$ | 100.10 | 0.923 | 12.34 | 0.655 | 1.442 | 0.3 |
| ${ }^{206} \mathrm{~Pb} \ldots \ldots \ldots \ldots \ldots$ | 100.35 | 0.929 | 15.06 | 0.593 | 1.415 | 0.8 |
| ${ }^{204} \mathrm{~Pb} \ldots \ldots \ldots \ldots \ldots$ | 98.81 | 0.954 | 13.50 | 0.681 | 1.450 | 0.2 |
| ${ }^{205} \mathrm{Tl} \ldots \ldots \ldots \ldots \ldots$ | 99.10 | 0.983 | 12.91 | 0.652 | 1.492 | 0.5 |
| ${ }^{203} \mathrm{Tl} \ldots \ldots \ldots \ldots \ldots$ | 100.26 | 0.938 | 16.04 | 0.604 | 1.412 | 1.1 |

$r_{o}=1.15 \mathrm{fm}, r_{c}=1.25 \mathrm{fm}$.

The results have been analyzed in terms of the optical model with the parameters of best fit being obtained by using the optical-model search code JIB3 of F. C. Perey. Details of the code and of the five-parameter search procedure have been previously published ${ }^{23)}$. Figure 1 shows a comparison of the experimental results with the theoretical angular distributions calculated from the five-parameter fits. The parameters which are listed in Table 3 show very little change over the narrow mass range of study. The $Q$-value corrections required in order to make an accurate comparison of the relative vibrational strengths in the different nuclei have been calculated using the above parameters in the DWBA code JULIE. For the region near 2.6 MeV , this correction for $l=3$ excitations is $\sim 7 \%$ per 100 keV of excitation.

## 3.2. ${ }_{82}^{208} \mathrm{~Pb}_{126},{ }_{82}^{206} \mathrm{~Pb}_{124}$, and ${ }_{82}^{204} \mathrm{~Pb}_{122}$

The spectra of deuterons scattered from ${ }^{208} \mathrm{~Pb},{ }^{206} \mathrm{~Pb}$, and ${ }^{204} \mathrm{~Pb}$ are all dominated by a strong peak near 2.6 MeV of excitation. These levels, which have been previously identified as the first excited octupole states in these nuclei, are among the strongest octupole states observed. Previous inelastic scattering studies ${ }^{2)}$ report that, in addition to being at an almost constant excitation energy, these states have an essentially constant strength. The present inelastic deuteron scattering spectra, however, show an appreciable decrease in strength with decreasing neutron number.

Above the octupole state in ${ }^{208} \mathrm{~Pb}$ a second strongly populated level is observed. This is the 5 - level at 3.18 MeV . Several 5 - levels are reported in ${ }^{206} \mathrm{~Pb}$ in this energy region, but a strongly populated state of this spin and parity is not observed until 3.78 MeV . The lowest $5-$ level in ${ }^{208} \mathrm{~Pb}$ is dominated by the $\left(g_{9 / 2}, p_{1 / 2}\right)$ one-neutron particle-hole configuration ${ }^{14)}$ and a change from ${ }^{208} \mathrm{~Pb}$ to ${ }^{206} \mathrm{~Pb}$, which affects mainly the $p_{1 / 2}$ neutrons, causes a


Fig. 2. Spectrum of deuterons scattered from ${ }^{208} \mathrm{~Pb}$.

Table 4. Levels Populated in ${ }^{208} \mathrm{~Pb}$

| Energy | Previous <br> energy <br> $(\mathrm{MeV})$ | $(d \sigma / d \Omega) 125^{\circ}$ <br> $(\mu b / s r)$ | $(d \sigma / d \Omega) 150^{\circ}$ <br> $(\mu b / s r)$ | Assignment |
| :---: | :---: | :---: | :---: | :---: |

a) ref. 3).


Fig. 3. Spectrum of deuterons scattered from ${ }^{206} \mathrm{~Pb}$.
large increase in the energy of this configuration. However, as previously pointed out ${ }^{1)}$, it is not clear whether there exists a simple correspondence between these states in the two nuclei. In the present spectra, the 3.78 MeV state in ${ }^{206} \mathrm{~Pb}$ is populated with a cross section that is only about $40 \%$ of that to the 3.18 MeV state in ${ }^{208} \mathrm{~Pb}$. No dyotriacontapole vibration states have yet been identified in ${ }^{204} \mathrm{~Pb}$ in this energy region.

In contrast to ${ }^{208} \mathrm{~Pb}$ where the first excited state is found at 2.614 MeV , a number of relatively low-lying levels are observed in ${ }^{206} \mathrm{~Pb}$ and ${ }^{204} \mathrm{~Pb}$. The first excited state in both these nuclei is the $2+$ level at 0.803 and 0.900 MeV , respectively. These states which are predominantly two-neutron hole and four-neutron hole levels, respectively, do contain some collective strength and are appreciably populated in inelastic scattering. Of the remaining low-lying states presently observed, only the $4+$ levels at 1.69 MeV in ${ }^{206} \mathrm{~Pb}$ and 1.27 MeV in ${ }^{204} \mathrm{~Pb}$ are relatively strongly populated.

It is perhaps worth noting that the cross section for the unnatural parity 4 - state at 3.48 MeV in ${ }^{208} \mathrm{~Pb}$ is greater than that for the $5-$ level at 3.71 MeV

Table 5. Levels Populated in ${ }^{206} \mathrm{~Pb}$

| Energy <br> $(\mathrm{MeV})$ | Previous <br> energya) <br> $(\mathrm{MeV})$ | $(d \sigma / d \Omega) 125^{\circ}$ <br> $(\mu b / s r)$ | $(d \sigma / d \Omega) 150^{\circ}$ <br> $(\mu b / s r)$ | Assignment |
| :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 19400 | 12100 | $0+$ |
| 0.803 | 0.803 | 141 | 133 | $2+$ |
| 1.163 | 1.16 | 4 | 3 | $(0+)$ |
| 1.340 | 1.341 | 4 | 5 | $3+$ |
| 1.464 | 1.459 | 16 | 14 | $(2+)$ |
| 1.680 | 1.684 | 23 | 26 | $4+$ |
| 1.993 | 1.996 | 9 | 10 | $4+$ |
| 2.197 | 2.199 | 7 | 11 | $(7 \pm)$ |
| 2.649 | 2.648 | 291 | $3-$ |  |
| 2.782 | 2.787 | 8 | 11 | $(5-)$ |
| 2.925 | 2.931 | 10 | 12 | $(4+)$ |
| 3.014 | 3.020 | 2 | 3 | $(5-)$ |
| 3.256 | 3.267 | 2 | 3 |  |
| 3.276 |  | 3 | 4 |  |
| 3.400 | 3.403 | 4 | 6 | $5-$ |
| 3.450 | 3.453 | 4 | 5 |  |
| 3.559 | 3.560 | 70 | 9 | $(5-)$ |
| 3.719 | 3.721 | 29 | 9 |  |
| 3.774 | 3.776 |  | 31 | $5-$ |

a) ref. 3).
even though, at back angles, it is predominantly populated by a (deuteron) spin flip. The inelastic proton scattering ${ }^{3)}$, on the other hand, seems to yield less of the $4-$ state compared to the $5-$ at 3.71 MeV .

## 3.3. ${ }_{83}^{209} \mathrm{Bi}_{126}$

The low-lying levels in ${ }^{209} \mathrm{Bi}$ have been previously investigated by a number of one-particle transfer and inelastic scattering studies. The proton transferring $(\alpha, t)^{24)}$ and $\left({ }^{3} \mathrm{He}, d\right)^{4,25,26)}$ reactions on ${ }^{208} \mathrm{~Pb}$ targets are found to appreciably populate only the single-particle states at $0.0\left(h_{9 / 2}\right), 0.897\left(f_{7 / 2}\right), 1.608\left(i_{13 / 2}\right)$, $2.314\left(f_{5 / 2}\right)$, $3.108\left(p_{3 / 2}\right)$, and $3.624 \mathrm{MeV}\left(p_{1 / 2}\right)$ below 4.0 MeV of excitation. In striking contrast, the inelastic deuteron ${ }^{27)}$ and proton ${ }^{13)}$ spectra are dominated by strong groups near 2.62 and 3.18 MeV with very little population of the one-particle levels.

On the basis of the particle-vibration coupling model, the coupling of the $h_{9 / 2}$ ground-state proton in ${ }^{209} \mathrm{Bi}$ to the 3 - core vibration should produce a septuplet of positive parity levels near 2.62 MeV with spins ranging from

Table 6. Levels Populated in ${ }^{204} \mathrm{~Pb}$

| Energy <br> (MeV) | $\begin{gathered} \text { Previous } \\ \text { energy } \\ (\mathrm{MeV}) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) 125^{\circ} \\ (\mu b / s r) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) 150^{\circ} \\ (\mu b / s r) \end{gathered}$ | Assignment |
| :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 19900 | 12300 | $0+$ |
| 0.899 | 0.899 | 193 | 185 | $2+$ |
| 1.272 | 1.274 | 38 | 39 | $4+$ |
| 1.351 |  | 11 | 12 |  |
| 1.561 | 1.563 | 7 | 9 | $(4+)$ |
| 1.579 |  | 4 | 4 |  |
| 1.663 |  | 8 | 10 |  |
| 1.816 |  | 19 | 17 |  |
| 1.871 |  | 3 | 7 |  |
| 2.156 |  | 3 | 3 |  |
| 2.180 | 2.186 | 2 | 3 | $9-$ |
| 2.256 | $\begin{aligned} & 2.255 \\ & 2.258 \end{aligned}$ | 19 | 33 |  |
| 2.508 |  | 2 | 3 |  |
| 2.618 |  | 225 | 268 | $3-$ |
| 2.804 |  | 4 | 6 |  |
| 2.884 |  | 6 | 9 |  |
| 2.896 |  | 10 | 12 |  |
| 3.561 |  | 12 | 15 |  |
| 3.719 |  | 2 | 5 |  |
| 3.778 |  | 4 | 4 |  |
| 3.799 |  | 3 | 3 |  |
| 3.824 |  | 3 | 3 |  |
| 3.951 |  |  | 11 |  |
| 4.004 |  |  | 9 |  |

a) ref. 42).
$J=3 / 2$ to $15 / 2$ whose relative population cross sections should be proportional to $2 J+1$. Hafele and Woods ${ }^{13)}$ were able to locate six of the seven members and made the initial spin assignments for the multiplet, using this intensity rule and assuming that the strongest populated peak at 2.600 MeV (cf. Fig. 6) is a doublet containing the $11 / 2+$ and $13 / 2+$ states. Present attempts to resolve this doublet have been unable to distinguish any broadening of this peak relative to the other presumably single peaks even at a resolution of 3.5 keV , and an upper limit of 1.6 keV is placed on energy spacing of the two members. Recent Coulomb excitation experiments employing 70 MeV ${ }^{16} \mathrm{O}^{12)}$ and $19 \mathrm{MeV} \alpha$-beams ${ }^{11}{ }^{12)}$ report this spacing as $2.0 \pm 1.5 \mathrm{keV}$ on the basis of the energies of several highly Doppler-broadened gamma transitions.


Fig. 4. Spectrum of deuterons scattered from ${ }^{204} \mathrm{~Pb}$.

The spin assignments shown in Fig. 6 are the same as those first proposed by Hafele and Woods ${ }^{13)}$. In addition to the excellent adherence to the $2 J+1$ rule (cf. Table 14 ), the observed gamma decay of the Coulomb-excited septuplet ${ }^{11,12)}$ and the recent resonance fluoresence measurements of MetzGER $^{8)}$ offer strong evidence in support of this spin sequence.

A number of attempts have been made to calculate the shifts in energy of the multiplet members from the unperturbed position. The results of Hamamoto ${ }^{15)}$ using a perturbation theory approach and of Broglia et al. ${ }^{16)}$ using the Brown G-matrix method are shown in Fig. 11, together with the experimental results. Also shown are the recent results of Arita and Horie ${ }^{28)}$ who have used a shell-model approach without the assumption of weak particle-vibration coupling. The large number of small and cancelling contributions due to the many possible admixtures make the calculations somewhat sensitive to the individual components, and no good reproduction of the experimentally observed level order has yet been produced. Neither of the

Table 7. Levels Populated in ${ }^{209} \mathrm{Bi}$

| Energy <br> (MeV) | Previous energya) (MeV) | $\begin{gathered} (d \sigma / d \Omega) \\ 120^{\circ} \\ (\mu b / s r) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) \\ 125^{\circ} \\ (\mu b / s r) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) \\ 150^{\circ} \\ (\mu b / s r) \end{gathered}$ | Assignment |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 23100 | 19000 | 12300 | $9 / 2-$ |
| 0.900 | 0.897 | 1 | 1 | 1 | $7 / 2-$ |
| 1.608 | 1.609 | 14 | 14 | 13 | $13 / 2+$ |
| 2.494 | 2.493 | 12 | 13 | 13 | $3 / 2+$ |
| 2.565 | 2.563 | 47 | 45 | 48 | $9 / 2+$ |
| 2.585 | 2.584 | 36 | 40 | 42 | $7 / 2+$ |
| 2.600 | 2.600 | 119 | 116 | 121 | $11 / 2+, 13 / 2+$ |
|  | 2.602 |  |  |  |  |
| 2.618 | 2.617 | 28 | 30 | 34 | $5 / 2+$ |
| 2.744 | 2.741 | 69 | 65 | 72 | $15 / 2+$ |
| 2.768 |  | 3 | 2 | 3 | $5 / 2-$ |
| 2.828 |  | 4 | 4 | 5 |  |
| 2.958 |  | 2 | 3 | 4 |  |
| 2.988 |  | 9 | 8 | 10 | $(13 / 2+)$ |
| 3.041 |  | 3 | 3 | 4 | (3/2+) |
| 3.091 |  | 3 | 4 | 4 | ( $5 / 2+$ ) |
| 3.136 |  | 19 | 19 | 21 | $(11 / 2+, 19 / 2+)$ |
| 3.154 |  | 14 | 14 | 16 | $(17 / 2+, 7 / 2+)$ |
| 3.170 |  | 8 | 8 | 12 | $(15 / 2+)$ |
| 3.213 |  | 6 | 5 | 6 | (9/2+) |
| 3.308 |  | 2 |  | 4 |  |
| 3.379 |  | 1 |  | 1 |  |
| 3.407 |  | 2 |  | 2 |  |
| 3.466 |  | 4 |  | 5 |  |

a) ref. 12).
two particle-vibration approaches is able to account for the large depression of the $3 / 2+$ multiplet member. However, it may be noted that all three approaches do agree on the spin $15 / 2$ state being the one of highest energy as is in fact observed, and do predict the overall energy spread of the multiplet.

It is interesting to note that, although the $f_{7 / 2}$ state at 0.897 MeV , which may be populated from the $h_{9 / 2}$ ground state by an E2 transition, is not observed in the present spectra (cf. Fig. 5), a significant population of the $i_{13 / 2}$ level at 1.608 MeV , which is the only low-lying positive parity particle state, is observed. As previously noted ${ }^{27)}$, this is probably an indication of the mixing into this state of the $13 / 2+$ member of the octupole multiplet. Such a mixing has been used by Broglia, Damgaard and Molinari ${ }^{16)}$ in calculating the $B(\mathrm{E} 3)$ value to the $i_{13 / 2}$ level. Using an amplitude $\varepsilon=0.22$


Fig. 5. Spectrum of deuterons scattered from ${ }^{209} \mathrm{Bi}$.
of the $13 / 2+$ multiplet state into the single-particle level, they calculate $B$ (E3, $9 / 2 \rightarrow 13 / 2)=1.6 \times 10^{4} e^{2} \mathrm{fm}^{6}$. This is in good agreement with the value $(1.24 \pm$ $0.32) \times 10^{4} e^{2} \mathrm{fm}^{6}$ reported from Coulomb excitation ${ }^{11)}$ and with the value $1.4 \times 10^{4} e^{2} \mathrm{fm}^{6}$ deduced from the present results by use of the empirical relationship found to exist between $B(\mathrm{E} \lambda)$ values and inelastic deuteron cross sections ${ }^{29)}$. An upper limit for the mixing of these two states can be calculated by assuming that all the observed ( $d, d^{\prime}$ ) intensity at 1.608 MeV comes from the octupole component. The percent mixing is then just the cross section for excitation of this level divided by the sum of the cross sections for excitation of the $i_{13 / 2}$ and $13 / 2+$ multiplet states after correction for the difference in the yields due to the difference in $Q$-value for the two levels. Using $7 / 13$ of the cross section to the unresolved group at 2.600 MeV , as predicted by the $2 J+1$ rule, this comes out $13 \%$, but is only an upper limit as there is some excitation of the single-particle state directly. A rough estimate of this leads to a mixing probability $\varepsilon^{2} \sim 0.07$. It is also worth noting that a weak high-spin group has been observed at 2.61 MeV in both the $\left.{ }^{208} \mathrm{~Pb}(\alpha, t){ }^{209} \mathrm{Bi}^{24}\right)$ and ${ }^{208} \mathrm{~Pb}\left({ }^{3} \mathrm{He}, d\right){ }^{209} \mathrm{Bi}^{4,25,26)}$ transfer reaction spectra. Such a peak would be expected to arise from the admixture of the $i_{13 / 2}$ state into the $13 / 2+$ multiplet


Fig. 6. Spectrum of deuterons scattered from the octupole multiplet in ${ }^{209} \mathrm{Bi}$.
member. From its intensity relative to the strong group at 1.608 MeV , Lilley and $\mathrm{Stein}^{24)}$ were able to calculate the percent mixing as about $9 \%$ (in this case an actual number and not a limit, if, as expected, there is no core excitation). In a similar manner, Ellegaard and Vedelsby ${ }^{4)}$ extract a value of $6 \%$ from their $\left({ }^{3} \mathrm{He}, d\right)$ results.

Above the octupole multiplet, a number of weaker groups are observed in the present spectra. The weak transition at 2.828 MeV corresponds to the very strong transitions observed in $\left.{ }^{208} \mathrm{~Pb}(\alpha, t){ }^{209} \mathrm{Bi}^{24}\right)$ and ${ }^{208} \mathrm{~Pb}\left({ }^{3} \mathrm{He}, d\right)$ ${ }^{209} \mathrm{Bi}^{4,25,26)}$ studies and assigned to the $f_{5 / 2}$ proton state. The strong groups around 3.2 MeV (cf. Fig. 7) must correspond to the collective 5 - level in ${ }^{208} \mathrm{~Pb}$. In ${ }^{209} \mathrm{Bi}$, the coupling of an $h_{9 / 2}$ proton to the dyotriacontapole vibration should yield ten positive parity levels ranging from $1 / 2$ to $19 / 2$ in spin. The blocking of one $h_{9 / 2}$ orbital is not expected to damage the wave function ${ }^{14)}$ of this state any more than that of the first $3-$ state, and so the cross section for excitation of the multiplet should be almost as high as that of the corresponding state in ${ }^{208} \mathrm{~Pb}$. No published calculations exist at present on the expected energy spectrum of this multiplet. However, the admixtures are expected to be smaller than in the octupole case and so the energy spread


Fig. 7. Spectrum of deuterons scattered from the dyotriacontapole multiplet in ${ }^{209} \mathrm{Bi}$. This spectrum is the sum of several exposures at $120^{\circ}$.
is expected to be less (about 150 keV$)^{30}$ ) and the adherence to the $2 . J+1$ rule for population intensities should hold well.

The tentative assignments shown in Fig. 7 have been made on the basis of excitation cross sections. The agreement with prediction is shown in Table 11 for this and also a second possible choice. Of the ten peaks expected in the multiplet, the $1 / 2+$ member is expected to be low in intensity and has not been assigned in the spin sequence proposed. Seven peaks, whose total cross section is $(76 \pm 5) \%$ of the cross section to the corresponding 5 - peak in ${ }^{208} \mathrm{~Pb}$, are then used to account for the remaining levels. Higher resolution spectra than those presented on this multiplet, but with somewhat decreased statistics, have resolved the peak at 3.154 MeV into two components about 4 keV in separation. Two levels are assumed also to exist at 3.136 MeV because of the large population of the group at that position. However, these two states have not yet been resolved and only an upper limit of 3.0 keV can be placed on their separation. Further experimental studies including angular distributions which might determine the states definitely belonging to the multiplet are required before a conclusive identification can be made.

Table 8. Levels Populated in ${ }^{207} \mathrm{~Pb}$

| Energy <br> (MeV) | Previous energya) (MeV) | $\begin{gathered} (d \sigma / d \Omega) 125^{\circ} \\ (\mu b / s r) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) 150^{\circ} \\ (\mu b / s r) \end{gathered}$ | Assignment |
| :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 19000 | 12000 | $1 / 2-$ |
| 0.570 | 0.570 | 45 | 37 | $5 / 2-$ |
| 0.897 | 0.897 | 54 | 38 | 3/2- |
| 1.625 | 1.634 | 8 | 5 | 13/2+ |
| 2.333 | 2.332 | 9 | 14 | $7 / 2-$ |
| 2.616 | 2.610 | 136 | 153 | $5 / 2+$ |
| 2.656 | 2.655 | 169 | 193 | $7 / 2+$ |
| 2.721 | 2.725 | 18 | 17 | $9 / 2+$ |
| 3.188 |  | 3 | 4 |  |
| 3.205 | 3.200 | 2 | 3 |  |
| 3.377 | 3.380 | 8 | 10 |  |
| 3.402 | 3.405 | 1 | 2 |  |
| 3.415 |  | 1 | 1 |  |
| 3.426 | 3.430 | 1 | 2 |  |
| 3.469 |  | 2 | 3 |  |
| 3.503 | 3.505 | 7 | 6 |  |
| 3.578 | 3.575 | 7 | 7 |  |
| 3.611 | 3.615 | 6 | 8 |  |
| 3.625 |  | 5 | 5 |  |
| 3.644 | 3.640 | 7 | 7 |  |
| 3.898 | 3.890 | 4 | 5 |  |
| 4.094 | 4.090 | 7 | 8 | $3 / 2-$ |
| 4.133 | 4.125 | 8 | 8 | $5 / 2-$ |

a) Refs. 3) and 7).

## 3.4. ${ }_{82}^{207} \mathrm{~Pb}_{125}$

The spectrum of deuterons scattered from ${ }^{207} \mathrm{~Pb}$ (cf. Fig. 8) is dominated by the two states at $2.616 \mathrm{MeV}(5 / 2+)$ and $2.656 \mathrm{MeV}(7 / 2+)$ produced by the coupling of the ground-state $p_{1 / 2^{-1}}$ neutron configuration to the octupole core vibration. These states are expected to be quite pure ${ }^{31)}$ and have so far been observed only in scattering experiments. A similar doublet of states $(J \pi=9 / 2+, 11 / 2+)$ is expected at 3.2 MeV due to a coupling of the ground state to the 5 - state in ${ }^{208} \mathrm{~Pb}$. Angular distributions corresponding to $l=5$ angular momentum transfer have been measured for inelastic proton scattering ${ }^{3)}$ from the states at 3.205 and 3.377 MeV . The inelastic deuteron cross section presently observed to these two levels, however, is 4 to 6 times smaller than that to the corresponding $5-$ state in ${ }^{208} \mathrm{~Pb}$, indicating that if these two


Fig. 8. Spectrum of deuterons scattered from ${ }^{207} \mathrm{~Pb}$.
states do in fact form the 5 - doublet, then a substantial dilution of the collective strength exists. It should be noted that the one-particle $g_{9 / 2}$ and $i_{11 / 2}$ neutron configurations have been observed in this region of excitation. These configurations, which have the proper spin and parity to mix with the expected $9 / 2+$ and $11 / 2+$ doublet states, are found to be somewhat fragmented ${ }^{32)}$ and may contain a substantial portion of the collective strength. The state at 2.730 MeV which contains the major portion of the $g_{9 / 2}$ strength ${ }^{7,9,33)}$ is in fact populated with a cross section which is comparable to the combined cross section observed to the 3.205 and 3.377 MeV levels.

Spin-parity assignments of $3 / 2-$ and $5 / 2$ - have been previously made ${ }^{3)}$ for the states at 4.094 and 4.133 MeV , respectively. This doublet, interpreted as arising from the coupling of the ground state to the $2+{ }^{208} \mathrm{~Pb}$ core vibration at 4.078 MeV , is populated in the present experiment with a cross section essentially equal to the cross section to the $2+$ state .

In addition to the expected collective levels, the first two excited states are rather strongly excited in the present study. The measured spectroscopic factors for the excitation of these states in neutron ${ }^{7,32)}$ pick-up reactions are in agreement with pure one-hole configurations, and the relatively large cross sections observed in this study are therefore surprising. It is interesting to
note that a somewhat similar situation has been found in the scattering of 20 MeV protons from ${ }^{207} \mathrm{~Pb}$ by Glashausser et al. ${ }^{6}$. There it was found that appreciable polarization of the ${ }^{208} \mathrm{~Pb}$ core was required to account for the excitation of the observed hole states. It should also be noted that the ratio of the inelastic deuteron cross sections to the $B(\mathrm{E} 2)$ values which is found to be fairly constant in the rare-earth region ${ }^{29)}$ is a factor of three larger for these two states than for other levels in the present mass region.

It appears that this effect can be ascribed to the polarization of the lead core by the neutron hole. The deuteron excites the polarization charge together with the single-neutron transition whereas only the polarization contributes to the matrix element measured by Coulomb excitation. The effective charge of the neutron hole is known to be close to unity and is mostly of isoscalar type (equal participation of protons and neutrons). On this basis one estimates a value for the above-mentioned ratio of $(3 / 2)^{2}=2.25$ in approximate agreement with the observed value.

## 3.5. ${ }_{81}^{205} \mathrm{Tl}_{124}$

The levels of the odd-mass Tl isotopes have been investigated recently in a number of experimental ${ }^{5,34,35,43)}$ and theoretical ${ }^{17,36,37)}$ studies. The proton pick-up studies of Hinds et al. ${ }^{34)}$ indicate that the ground-state configurations in ${ }^{203} \mathrm{Tl}$ and ${ }^{205} \mathrm{Tl}$ have spectroscopic factors somewhat smaller than those expected for pure $3 s_{1 / 2^{-1}}$ shell-model states. This factor together with the relatively large number of low-spin positive parity states expected below 1.5 MeV of excitation make the description of these nuclei somewhat more complex than first proposed by de Shalit ${ }^{38)}$ who considered simply a coupling of the ground-state proton to the vibrations of the Hg core.

The coupling of the $s_{1 / 2}{ }^{-1}$ proton configuration of the ${ }^{205} \mathrm{Tl}$ ground state to the $2+$ vibration of the ${ }^{206} \mathrm{~Pb}$ core is expected to produce a low-lying doublet $(J \pi=3 / 2+, 5 / 2+)$ of levels which should be strongly populated in inelastic scattering. Two states which are known to have these spin and parity assignments are in fact strongly populated in the low excitation energy portion of the present spectra. However, it must be noted that the $d_{3 / 2^{-1}}$ shell-model configuration is expected to be found in these nuclei and should strongly mix with the $3 / 2+$ member of the doublet. The $(t, \alpha)$ spectra of Hinds et al. ${ }^{34)}$ show a strong population of the $3 / 2+$ state at 0.203 MeV , which the authors report to contain about $60 \%$ of the cross section predicted for a $2 d_{3 / 2}$ proton hole. They also observe a second $3 / 2+$ state at 1.14 MeV and suggest that this

Table 9. Levels Populated in ${ }^{205} \mathrm{Tl}$

| Energy <br> (MeV) | Previous energya) (MeV) | $\begin{gathered} (d \sigma / d \Omega) \\ 120^{\circ} \\ (\mu b / s r) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) \\ 125^{\circ} \\ (\mu b / s r) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) \\ 150^{\circ} \\ (\mu b / s r) \end{gathered}$ | Assignment |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 21000 | 17700 | 11200 | 1/2+ |
| 0.203 | 0.205 | 75 | 62 | 63 | $3 / 2+$ |
| 0.616 | 0.615 | 148 | 124 | 116 | $5 / 2+$ |
| 0.920 |  | 15 | 15 | 19 |  |
| 1.136 | 1.14 | 11 | 10 | 8 | $3 / 2+$ |
| 1.174 |  | 3 |  | 2 |  |
| 1.336 | 1.34 | 7 |  | 6 |  |
| 1.426 | 1.43 | 32 | 30 | 31 |  |
| 1.479 | 1.48 | 6 |  | 5 |  |
| 1.571 | 1.58 | 1 |  | 1 |  |
| 1.637 |  | 3 |  | 2 |  |
| 1.668 |  | 1 |  | 1 |  |
| 1.768 |  | 2 |  | 2 |  |
| 1.858 | 1.86 | 3 |  | 5 |  |
| 2.482 | 2.49 | 31 | 28 | 35 |  |
| 2.623 | $2.61{ }^{\text {b) }}$ | 75 | 76 | 85 | $5 / 2-$ |
| 2.717 | $2.69{ }^{\text {b) }}$ | 96 | 89 | 107 | $7 / 2$ - |
| 2.933 |  | 4 |  |  |  |
| 2.974 |  | 4 |  |  |  |
| 3.173 |  | 6 |  | 8 |  |
| 3.213 |  | 12 |  | 12 |  |
| 3.259 |  | 26 | 25 | 29 |  |
| 3.411 |  | 8 |  | 9 |  |
| 3.473 |  | 2 |  | 4 |  |
| 3.523 |  | 4 |  | 4 |  |
| 3.540 |  | 10 |  | 14 |  |

[^14]may be the major component of the $3 / 2+$ doublet member. Such an order of these two $3 / 2+$ levels is also in agreement with the calculations of Covello and his co-workers ${ }^{17}$ ) who also have calculated the reduced E2-transition probabilities to the low-lying states in ${ }^{205} \mathrm{Tl}$ and predict a value of 0.15 for the ratio of the $B(\mathrm{E} 2)$ to the upper $3 / 2+$ state to that to lower. The corresponding ratio of cross sections presently observed is 0.16 and this factor together with the $120^{\circ}$ to $150^{\circ}$ cross section ratio, which is in agreement with the transition being $l=2$, support such an assignment for the 1.137 MeV state. The strongly populated level at 0.615 MeV has been previously assigned as the major component of the $5 / 2+$ doublet member. A weak-coupling
prediction of this state would require that it contains $60 \%$ of the $2+$ inelastic cross section; the observed value is $80 \%$.

A low-lying quadruplet of levels $(J \pi=1 / 2+$ to $7 / 2+)$ whose wave functions contain large components of the $2 d_{3 / 2^{-1}}$ shell-model state coupled to the $2+$ core vibration is expected ${ }^{17)}$ in both ${ }^{203} \mathrm{Tl}$ and ${ }^{205} \mathrm{Tl}$. The lowest-lying member of this quadruplet is predicted to be the $7 / 2+$ which also contains a substantial portion of the ground state coupled to the $4+$ vibrational state in its calculated wave function ${ }^{17)}$. A level at 0.920 MeV is seen in the present spectra which has recently been reported to be populated by an $l=4$ transition in the ( $p, p^{\prime}$ ) studies of Glashausser et al. ${ }^{5}$. This level, which then is restricted to spin $7 / 2+$ or $9 / 2+$, is populated in the present spectra with a cross section ( $Q$-value corrected) which is $59 \%$ of the cross section observed to the $4+$ level at 1.684 MeV in ${ }^{206} \mathrm{~Pb}$. The ( $p, p^{\prime}$ ) experiment ${ }^{5)}$ reports this ratio to be $45 \%$. A $7 / 2+$ assignment for this state as suggested by comparison with the calculated spectra is consistent with the proton pick-up results of Hinds et al. These authors see no population of the 0.920 MeV level. Covello and coworkers ${ }^{17)}$ calculate that the strength of the $2 g_{7 / 2}{ }^{-1}$ component in the low-lying $7 / 2+$ state (predicted at 0.85 MeV ) is only $1.5 \%$.

A state at 1.21 MeV is reported by Hinds et al. ${ }^{34)}$, which they suggest may contain the major component of the $1 / 2+$ member of the quadruplet. No population of this state, which would be populated directly only via the admixture of the excited level into the ground state, is observed in the present spectra.

The two remaining quadruplet members, the $3 / 2+$ and $5 / 2+$, have spins appropriate to admix with the strongly populated doublet formed by coupling the ground state to the $2+$ core vibration and would be expected to contain some inelastic cross section. A number of yet unidentified states are seen below 1.7 MeV , which may correspond to these levels. Of these, the two most strongly populated, at 1.336 and 1.426 MeV , appear to be observed also in the $\left(\gamma, \gamma^{\prime}\right)$ reaction ${ }^{35,43)}$ where they are directly populated from a $1 / 2$ - resonance state and hence are restricted to spins $1 / 2,3 / 2$ or $5 / 2$. However, no conclusive assignments yet seem possible. The only other state identified below 2.0 MeV , the $h_{11 / 2}$ at 1.479 MeV , is only slightly populated.

The higher energy portion of the spectrum is dominated by a doublet of peaks near 2.65 MeV , which is undoubtedly the configuration produced by a coupling of the $1 / 2+$ ground state to the octupole vibration. These two states at 2.623 and 2.717 MeV were previously observed in inelastic proton studies ${ }^{37}$ ) and were given respective spin assignments of $5 / 2-$ and $7 / 2-$ on the basis of the $2 J+1$ cross section rule. Solf et al. ${ }^{39)}$ suggest that the doublet should


Fig. 9. Spectrum of deuterons scattered from ${ }^{205} \mathrm{Tl}$.
contain no more than about $70 \%$ of the ${ }^{206} \mathrm{~Pb}$ cross section to the octupole state. The present ratio observed is $62 \%$. Three additional levels which are populated by $l=3$ transitions have been recently ${ }^{5)}$ identified in ${ }^{205} \mathrm{Tl}$. These states, at $2.482,3.213$, and 3.259 MeV , are, except for the above-mentioned octupole doublet, the most strongly populated states above 2.0 MeV of excitation. The relative cross sections presently observed for the five octupole transitions are in good agreement with those reported by Glashausser et al. ${ }^{5}$. As pointed out by these authors, a quadruplet of levels ( $J \pi=3 / 2-$ to $9 / 2-$ ) is expected about 0.35 MeV above the previously identified octupole doublet due to a coupling of the $2 d_{3 / 2^{-1}}$ state to the 3 - level. Of these four levels the $5 / 2-$ and $7 / 2-$ might be expected to admix with the strongly populated 2.623 and 2.717 MeV state and to then be populated in inelastic scattering. The only other $5 / 2$ - or $7 / 2$ - levels expected in this region of excitation, which might be populated via admixtures with these states, would be due to a coupling of the $h_{11 / 2}$ configuration to the $2+$ state. However, the excitation of such a configuration is not expected to be very large.

The inelastic cross section observed to the octupole doublet in ${ }^{205} \mathrm{Tl}$ is somewhat less than observed to the 3 - levels near 2.65 MeV in both ${ }^{204} \mathrm{~Pb}$ and ${ }^{206} \mathrm{~Pb}$ (see Table 13) as well as in ${ }^{204} \mathrm{Hg}^{41)}$, indicating that there may, in fact, be some of the inelastic cross section carried to other levels. If all five octupole levels are considered, the total octupole cross section observed in ${ }^{205} \mathrm{Tl}$ is $91 \%$ of that observed to the 2.649 MeV state in ${ }^{206} \mathrm{~Pb}$. As a final comment, it may be noted that, while the ratio of 0.75 predicted by the weakcoupling model for the cross section to the $5 / 2$ - state to that to the $7 / 2-$ state would probably be disturbed by the substantial admixtures required to explain the appreciable population observed to the additional octupole states, a value of $0.73 \pm 0.03$ is presently observed.

## 3.6. ${ }_{81}^{203} \mathrm{Tl}_{122}$

The low excitation energy portion of the spectrum of deuterons scattered from ${ }^{203} \mathrm{Tl}$ is dominated by strong peaks corresponding to the first two excited states. As in the case of ${ }^{205} \mathrm{Tl}$, a low-lying $d_{3 / 2^{-1}}$ shell-model state is expected in this region of excitation together with the doublet of states due to a coupling of the $1 / 2+$ ground state to the $2+$ vibrational state at 0.900 MeV in ${ }^{204} \mathrm{~Pb}$. The first excited state in ${ }^{203} \mathrm{Tl}$ is the $3 / 2+$ level at 0.280 MeV . The strong population of this level in the inelastic deuteron spectrum (cf. Fig. 10) suggests that it may be the $3 / 2+$ member of the vibrational doublet. However, both the $(t, \alpha)$ results of Hinds et al. ${ }^{34)}$ which indicate that this level contains about $65 \%$ of the $2 d_{3 / 2^{-1}}$ proton configuration, and the gamma-decay results of Karlsson ${ }^{40)}$, which yield a magnetic moment for the level near the Schmidt limit, indicate that the major component of the vibrational state must be found elsewhere. No higher-lying $3 / 2+$ state has yet been identified in this nucleus. As in ${ }^{205} \mathrm{Tl}$, it is predicted ${ }^{17}$ ) that the $B$ (E2) and hence inelastic cross section to this second $3 / 2+$ level is only about $15 \%$ of that to the predominantly $d_{3 / 2^{-1}}$ state at 0.280 MeV . The states at 1.042 and 1.073 MeV both are populated with cross sections of this magnitude, and from their $120^{\circ}$ to $150^{\circ}$ cross section ratio are consistent with $l=2$ momentum transfers. However, a conclusive identification of the predominantly vibrational $3 / 2+$ level with either of these states is not yet possible.

The only other positively identified state in ${ }^{203} \mathrm{Tl}$ is the $5 / 2+$ level at 0.680 MeV . As previously pointed out ${ }^{34}$ ), this state probably contains the main component of the $5 / 2+$ quadrupole doublet member. It is interesting to note that, within experimental uncertainty, the cross section to this state alone is equal to that to the $2+$ state in ${ }^{204} \mathrm{~Pb}$.

Table 10. Levels Populated in ${ }^{203} \mathrm{Tl}$

| Energy <br> (MeV) | $\begin{gathered} \text { Previous } \\ \text { energya) } \\ (\mathrm{MeV}) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) \\ 120^{\circ} \\ (\mu b / s r) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) \\ 125^{\circ} \\ (\mu b / s r) \end{gathered}$ | $\begin{gathered} (d \sigma / d \Omega) \\ 150^{\circ} \\ (\mu b / s r) \end{gathered}$ | Assignment |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 23300 | 19500 | 12200 | $1 / 2+$ |
| 0.280 | 0.285 | 107 | 89 | 85 | $3 / 2+$ |
| 0.680 | 0.690 | 195 | 177 | 175 | $5 / 2+$ |
| 1.042 |  | 13 | 11 | 8 |  |
| 1.073 | 1.07 | 12 | 9 | 11 |  |
| 1.181 |  | 7 | 5 | 4 |  |
| 1.210 |  | 17 | 17 | 23 |  |
| 1.228 | 1.24 | 9 | 11 | 6 |  |
| 1.262 |  | 10 | 8 | 9 |  |
| 1.386 |  | 5 |  | 4 |  |
| 1.446 |  | 13 | 13 | 16 |  |
| 1.481 | 1.47 | 16 | 16 | 20 |  |
| 1.861 |  |  | 12 | 10 |  |
| 2.430 |  | 3 |  | 4 |  |
| 2.483 |  | 29 | 33 | 39 | 5/2- |
| 2.539 |  | 53 | 51 | 62 | 7/2- |
| 2.683 |  |  |  | 16 |  |
| 2.828 |  | 11 |  | 17 |  |
| 2.893 |  | 27 |  | 37 |  |
| 2.954 |  | 16 | 16 | 19 |  |
| 3.081 |  | 18 |  | 23 |  |
| 3.110 |  | 8 |  | 10 |  |

a) ref. 34).

A number of relatively weakly populated states are found between 1.0 and 2.0 MeV of excitation and then at 2.483 and 2.539 MeV comes a strongly populated doublet of levels. The energy of this doublet and the magnitude of the cross sections observed make these immediate candidates for the octupole doublet expected in this region. On the basis of the $2 J+1$ cross section rule, spin assignments of $5 / 2-$ for the 2.483 MeV state and $7 / 2$ - for the 2.539 MeV state are proposed. This rule predicts a ratio of 0.75 for the cross section of the $5 / 2-$ state to the $7 / 2$ - state. The observed ratio which is $0.60 \pm 0.03$ indicates that there is appreciably more mixing into the octupole doublet in ${ }^{203} \mathrm{Tl}$ than in ${ }^{207} \mathrm{~Pb}$ and ${ }^{205} \mathrm{Tl}$.

A substantial population of the states between 2.4 and 3.5 MeV is observed in the present study. As in ${ }^{205} \mathrm{Tl}$, the quadruplet expected by coupling the $d_{3 / 2^{-1}}$ configuration to the 3 - state may correspond to these states which are observed in the inelastic scattering via the admixed components. The ratio


Fig. 10. Spectrum of deuterons scattered from ${ }^{203} \mathrm{Tl}$. Peaks marked by the letter A are due to ${ }^{205} \mathrm{Tl}$.
of the $120^{\circ}$ to $150^{\circ}$ cross sections indicates that the transitions to the stronger of these states are of multipolarity greater than two, but no definite identification is possible. Excluding the two strongest states at 2.483 and 2.539 MeV in ${ }^{205} \mathrm{Tl}$ and the octupole state at 2.618 MeV , the total inelastic cross section

Table 11. Relative Cross Sections of 5 - Multiplet in ${ }^{209} \mathrm{Bi}$

| Energy <br> (MeV) | Assignment A |  | Assignment B |  | Exp. ( $\left.{ }^{0} 0\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $J$ | $2 J+1(0 / 0)$ | $J$ | $2 J+1(\%)$ |  |
| 2.988 | 13/2 | 12.7 | $13 / 2$ | 12.7 | $12.5 \pm 1.0$ |
| 3.041 | $3 / 2$ | 3.6 | $3 / 2$ | 3.6 | $4.1 \pm 0.5$ |
| 3.091 | $5 / 2$ | 5.5 | $5 / 2$ | 5.5 | $5.4 \pm 0.5$ |
| 3.136 | $11 / 2+19 / 2$ | 29.1 | $11 / 2+19 / 2$ | 29.1 | $30.8 \pm 1.2$ |
| 3.154 | $17 / 2+7 / 2$ | 23.7 | $17 / 2+9 / 2$ | 25.5 | $23.6 \pm 1.1$ |
| 3.170 | 15/2 | 14.5 | $15 / 2$ | 14.5 | $14.5 \pm 1.0$ |
| 3.213 | $9 / 2$ | 9.1 | $1 / 2+7 / 2$ | 9.1 | $9.2 \pm 0.8$ |



Fig. 11. Comparison of the experimental and calculated energy spectrum of the octupole septuplet in ${ }^{209} \mathrm{Bi}$. Spectrum a) is the experimental spectrum while b) and c) are the results of particlevibrational model calculations of HAMAMOTO ${ }^{15}$ ) and Broglia et al. ${ }^{16)}$, respectively. Spectra d) and e) are the results of a shell-model calculation by Arita and Horie ${ }^{28}$ ).
in this energy region is about three times larger in ${ }^{203} \mathrm{Tl}$ than in ${ }^{204} \mathrm{~Pb}$. Including the octupole states, the cross sections are the same to within $25 \%$. The most strongly populated peak above 2.6 MeV (at 2.899 MeV ) is appreciably broader than adjacent groups and is probably a doublet.

A comment should be made about the states around 1.5 MeV of excitation. Hinds et al. ${ }^{34)}$ observe a level at 1.48 MeV , which they suggest may be the major component of the $h_{11 / 2^{-1}}$ shell-model configuration. In the present spectra, a level is observed at 1.48 MeV which may correspond to this state. It may be noted, however, that the corresponding state at 1.479 MeV in ${ }^{207} \mathrm{Tl}$ is populated with a cross section that is a factor of four smaller.

The states at 1.446 and 1.481 MeV have a ratio of $120^{\circ}$ to $150^{\circ}$ cross sections, which is essentially the same as that observed for the octupole states
near 2.5 MeV , and it is interesting to consider the existence of a component in the ground-state wave function of ${ }^{203} \mathrm{Tl}$ which corresponds to a proton coupled to the ${ }^{202} \mathrm{Hg}$ core. Recent inelastic deuteron scattering studies ${ }^{41)}$ report the existence of a low-lying collective state in the even Hg isotopes, and the doublet of states formed by considering the coupling of the $s_{1 / 2}$ proton to this state could then be populated via this component of the ground state. However, it must be noted that the structure of this low-lying state in ${ }^{202} \mathrm{Hg}$ is unknown and, since such a state is not observed in the Pb isotopes studied, it would appear that the two proton holes acquired in a change from Pb to Hg play a major role in its wave function. It is not immediately clear that the addition of a proton to the Hg core would not then block the major component of the core vibration.

## 4. Conclusions

The results of the present study are schematically summarized in Fig. 12 which shows the inelastic cross sections observed for the levels below 3.5 MeV of excitation. The increase in number of levels populated with decreasing mass number is immediately evident. Also notable is the decrease in size of the strong groups near 2.6 MeV of excitation. The total inelastic cross sections observed below 3.5 MeV of excitation in each nuclide at a scattering angle of $150^{\circ}$ are listed in table 12. It is interesting to note that this total does not vary greatly over the mass region studied. Of more particular interest is the comparison of the cross sections in the odd-mass isotopes to that in the even-mass cores. For ${ }^{205} \mathrm{Tl}$ and ${ }^{203} \mathrm{Tl}$, the total is identical to that observed in the respective ${ }^{206} \mathrm{~Pb}$ and ${ }^{204} \mathrm{~Pb}$ cores considered in the coupling schemes. Considering ${ }^{209} \mathrm{Bi},{ }^{208} \mathrm{~Pb}$, and ${ }^{207} \mathrm{~Pb}$, where the weak-coupling description appears to be more valid, the agreement is not as marked, but the sums still do agree within $20 \%$.

The states corresponding to the highly collective octupole vibration at 2.615 MeV in ${ }^{208} \mathrm{~Pb}$ dominate the high energy portion of each spectrum. Except for ${ }^{203} \mathrm{Tl}$, these states have been previously identified. The small energy spread of these states and the large cross sections observed for them make possible an accurate comparison of the relative population strengths. These results, corrected for the small $Q$-value dependence and normalized to ${ }^{208} \mathrm{~Pb}$, are summarized in Fig. 13 and Table 13. Also listed in the table are the results of several other inelastic scattering studies and the octupole strength calculations of Hamamoto ${ }^{30)}$. The present results show a larger decrease in strength away from ${ }^{208} \mathrm{~Pb}$ than observed by other methods, but the large experimental


Fig. 12. Comparison of the level spectra below 3.5 MeV excitation populated at $120^{\circ}$ in the present study.
${ }_{81}^{203} \mathrm{Tl}_{122} \quad{ }_{82}^{204} \mathrm{~Pb}_{122} \quad{ }_{81}^{205} \mathrm{Tl}_{124} \quad{ }_{82}^{206} \mathrm{~Pb}_{124} \quad{ }_{82}^{207} \mathrm{~Pb}_{125} \quad{ }_{82}^{208} \mathrm{~Pb}_{126} \quad{ }_{83}^{209} \mathrm{Bi}_{126}$


$\frac{7}{2}^{-}-2.539$
$\frac{5}{2}^{-}-2.483$

Fig. 13. Positions and relative strengths of the octupole states corresponding to the 2.614 MeV state in ${ }^{208} \mathrm{~Pb}$. The ${ }^{208} \mathrm{~Pb}$ strength is normalized to 100 .
errors which exist in earlier data do not yet allow any definite conclusions as to whether a genuine difference exists. As previously indicated, the cross sections observed with both ${ }^{203} \mathrm{Tl}$ and ${ }^{205} \mathrm{Tl}$ are substantially smaller than for the Pb and Hg isotopes ${ }^{41)}$ of corresponding neutron number. This may indicate that some of the octupole strength expected in the doublets is transferred to other levels, but no conclusion is possible before the structure of these additional levels is further investigated.

The $2 . J+1$ intensity rule has been used to assign the level spins of several of the particle-vibrational multiplets observed in the ${ }^{208} \mathrm{~Pb}$ region. This rule which is obtained on the assumption of a very weak particle-vibrational coupling can be used as an indicator of the amount of mixing between multiplet

Table 12. Total $150^{\circ}$ Inelastic Cross Section Below 3.5 MeV of Excitation

| Nuclide | ${ }^{209} \mathrm{Bi}$ | ${ }^{208} \mathrm{~Pb}$ | ${ }^{207} \mathrm{~Pb}$ | ${ }^{206} \mathrm{~Pb}$ | ${ }^{205} \mathrm{Tl}$ | ${ }^{204} \mathrm{~Pb}$ | ${ }^{203} \mathrm{Tl}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Cross section <br> $\mu b / s r \ldots \ldots .$. | 430 | 490 | 580 | 570 | 560 | 620 | 620 |

Table 13. Relative Strengths Observed in Octupole Multiplets

|  | ${ }^{203} \mathrm{Tl}$ | ${ }^{204} \mathrm{~Pb}$ | ${ }^{205} \mathrm{Tl}$ | ${ }^{206} \mathrm{~Pb}$ | ${ }^{207} \mathrm{~Pb}$ | ${ }^{208} \mathrm{~Pb}$ | ${ }^{209} \mathrm{Bi}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ( $d, d^{\prime}$ ) | $24.8 \pm 2.5$ | $62.1 \pm 3.0$ | $51.5 \pm 3.0$ | $83.4 \pm 3.5$ | $86.8 \pm 3.5$ | 100 | $86.9 \pm 3.5$ |
| $\begin{aligned} & 13 \mathrm{MeV} \\ & \left.\left(\alpha, \alpha^{\prime}\right)^{b}\right) \end{aligned}$ |  | $87 \pm 13$ |  | $100 \pm 12$ | $100 \pm 10$ |  | $\begin{aligned} & 89.7 \pm 4.0^{\text {a })} \\ & 100 \pm 10 \end{aligned}$ |
| $\begin{aligned} & 42 \mathrm{MeV} \\ & \left(e, e^{\prime}\right)^{\mathrm{c})} \end{aligned}$ |  |  |  | $89 \pm 6$ | $93 \pm 6$ |  | $93 \pm 7$ |
| $\begin{aligned} & 28-73 \mathrm{MeV} \\ & \left(p, p^{\prime}\right)^{\mathrm{d})} \end{aligned}$ |  |  |  | 93 | 91 |  |  |
| 24.5 MeV <br> Predictede) |  | 87 |  | 96 | 94 | 100 | 100 |

a) Including $i_{13 / 2}$ population at 1.608 MeV .
b) Ref. 2).
c) Ref. 10).
d) Ref. 3).
e) Ref. 30).

Table 14. Adherence to $2 J+1$ Cross Section Rule for Octupole Multiplets

| Nuclide | Energy <br> (MeV) | $J$ | $2 J+1(\%)$ | Experiment$(\% / 0)$ | Ratio of Experiment$\text { to } 2 J+1$ |  | Predicted ratio ${ }^{\text {b }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | Present study | $\left(p, p^{\prime}\right)^{\mathbf{a}}$ |  |
| ${ }^{209} \mathrm{Bi}$ | 2.494 | 3/2 | 5.7 | $4.2 \pm 0.3$ | $0.74 \pm 0.06$ | 0.72 | 0.93 |
|  | 2.566 | $9 / 2$ | 14.3 | $13.8 \pm 0.6$ | $0.97 \pm 0.05$ | 1.06 | 1.07 |
|  | 2.585 | 7/2 | 11.4 | $12.3 \pm 0.5$ | $1.08 \pm 0.04$ | 1.11 | 0.99 |
|  | 2.600 | $11 / 2+13 / 2$ | 37.2 | $37.4 \pm 0.0$ | $1.00 \pm 0.02$ | 1.01 | 1.04 |
|  | 2.618 | $5 / 2$ | 8.6 | $9.1 \pm 0.5$ | $1.06 \pm 0.06$ | 1.01 | 1.00 |
|  | 2.744 | 15/2 | 22.8 | $23.7 \pm 0.7$ | $1.02 \pm 0.04$ | 0.95 | 0.97 |
| ${ }^{207} \mathrm{~Pb}$ | 2.616 | 7/2 | 57.1 | $58.3 \pm 0.6$ | $1.02 \pm 0.02$ | 1.00 | 1.00 |
|  | 2.565 | $5 / 2$ | 42.9 | $41.7 \pm 0.6$ | $0.97 \pm 0.02$ | 1.00 | 1.00 |
| ${ }^{205} \mathrm{Tl}$ | 2.717 | 7/2 | 57.1 | $57.7 \pm 0.8$ | $1.01 \pm 0.02$ |  |  |
|  | 2.623 | $5 / 2$ | 42.9 | $42.3 \pm 0.8$ | $0.99 \pm 0.02$ |  |  |
| ${ }^{203} \mathrm{Tl}$ | 2.539 | 7/2 | 57.1 | $62.4 \pm 1.0$ | $1.09 \pm 0.02$ |  |  |
|  | 2.483 | 5/2 | 42.9 | $37.6 \pm 1.0$ | $0.88 \pm 0.03$ |  |  |

a) Ref. 3). b) Ref. 15).
members and other configurations. Of the multiplets observed, only those corresponding to the octupole states near 2.6 MeV have been identified in all four odd-mass nuclei studied and the adherence to this rule is summarized in Table 14 . Except for the weak $3 / 2+$ state in ${ }^{209} \mathrm{Bi}$, the agreement with the rule is quite good. As previously noted, the admixtures into the doublet in ${ }^{203} \mathrm{Tl}$ appear to be somewhat larger than in ${ }^{209} \mathrm{Bi},{ }^{207} \mathrm{~Pb}$, and ${ }^{205} \mathrm{Tl}$.

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# STUDIES IN STATISTICAL DYNAMICS 

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Kommissionær: Munksgaard

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## Synopsis

It is attempted to give a comprehensive theoretical account of the dynamics of statistical phenomena in physics. On the basis of merely a few simple constraints one arrives at equations of motion for a field, which field may be of type of a probability density. The basic equations of motion are linear integro-differential equations. In § 3 we discuss the formal properties of solutions of the equations of motion. Next, in $\S 4$ we derive the family of degradation functionsentropy being one example-which account for common properties of systems and for the approach towards equilibrium. In § 5 we treat the question of differential equations of motion. We find a remarkable limitation of differential equations. Finally, § 6 contains a number of exact solutions of simple integral equations with divergent kernels.

## § 1. Introduction

In the following we shall study the general theoretical framework for dynamical phenomena in statistical physics. We aim to discuss, on an abstract basis, the behaviour in time of physical systems. If a system is described by a time-dependent field within a generalized space, one can single out a few properties which must be common to many, or to all, phenomena in statistical physics. These properties can be reformulated as a framework for equations of motion of the field, in terms of integral equations or integrodifferential equations. Within this framework we derive a number of consequences as to the possible behaviour of the field, which results are obtained even before definite equations of motion are stipulated.

During our studies, the topic gradually separated into four distinct, though not unconnected, parts. One part is the question of linear equations of motion, and their formal properties. Another concerns actual analytic solutions of simple cases. A third question is that of common properties of systems, accounted for by a family of degradation functions, of which entropy is merely one example. The fourth part concerns differential equations, both as approximations and on their own. They turn out to have a surprising limitation. As it will appear, our account of each subject is incomplete, but we hope that it is carried far enough to elucidate the main questions in each instance.

As indicated, we enter on questions familiar from widely different fields of research. It may well be that many of the results at which we arrive are discussed with greater precision and in more detail in texts dealing with mathematical probability theory, with statistical mechanics, or with wave mechanics. Our aim is merely to build up a simple, consistent framework. We try' in particular to avoid concepts and structures, however admirable, that are unnecessary for our purpose. The reader is therefore asked to take much the same detached attitude as Gibbs in his discussion of statistical
mechanics, and to consider primarily whether there is agreement between the elementary premises and the conclusions.

Though abstract, these studies were in part prompted by a practical necessity. It arose in our previous investigations of a minor subgroup of phenomena, i.e. the integral equations occurring in atomic collisions where a penetrating particle dissipates energy and exchanges momentum in a substance ${ }^{12,13)}$. Characteristic cases are here, firstly, the multiple scattering in angle of the incoming particle by a randomly distributed substance ${ }^{3,18)}$; secondly, the distribution in energy of an incoming particle, as a function of time, this being a one-way process with only decrease of energy; thirdly, the quite complicated phenomena of changes of transverse energy in directional effects for fast charged particles moving through crystals ${ }^{14)}$. We have worked out a number of analytic solutions of the first two cases, with divergent total cross sections (cf. §6). For directional effects there is a particular need of establishing the rules to be followed when introducing approximation procedures - like differential equations or perturbation theory - in attempts to solve the equations of motion.

Another group of phenomena may be exemplified by the dynamics of a degenerate free electron gas where, by means of the dielectric description, one can study linear dynamic properties in considerable detail and follow the trend towards equilibrium.

It can be useful for the reader to take cases of the above kind as possible illustrations in the following. We might mention that although the problem of the behaviour in time and in phase space of an ensemble is within the scope of the present discussion, the reader should hardly, in the beginning at least, consider the phase space ensemble as a representative example (cf. §5).

## § 2. Basic Properties of Systems

This chapter should serve two purposes. As a secondary purpose we introduce the terminology and concepts to be used in the following. Primarily, however, we want to specify basic physical properties which characterize various types of systems. The properties are introduced as six constraints, of which four are common to those systems that are of main interest in this paper. Other constraints specify systems we wish to study first, because of their simple basic properties or because they are of interest in applications. The results derived in the following chapters rely on a varying number of constraints, to be specified in each case.

## The Basic Constraints

We suppose that phenomena in statistical physics, e.g. of the kind mentioned above, can be described by a function, $a(x, t)$, depending on a spatial variable $x$, within a generalized space, and on a time variable, $t$. The state of a system is completely specified at a time $t$ if $a(x, t)$ is given for all $x$. The physical quantities that can be calculated within such systems will be discussed later.

The space variable $x$ is usually considered as a continuum variable in a space of one or several dimensions. When necessary, we write the space variable explicitly as a vector, $\vec{x}$. It may also be a discrete variable $k=1,2$, $3, \ldots N$, with $N$ finite or infinite. The discussion is usually formulated for continuum variables and is meant to include the discrete case.

We now introduce a number of constraints, specifying properties of the systems in question. The first constraint, supposed to be valid for all systems, is that the state of a system at a given time uniquely determines its state at any later time, or

$$
\begin{equation*}
a(x, t) \text { given for all } x \rightarrow a\left(x^{\prime}, t^{\prime}\right) \text { for all } x^{\prime} \text { and all } t^{\prime}>t \tag{2.1}
\end{equation*}
$$

We have introduced the variable $t$ as a familiar time concept. The variable $t$ may, however, also represent other quantities with similar one-way properties, e.g. in atomic collisions the path length moved by a particle, or even the energy of a particle during slowing-down.

The second constraint corresponds to conservation of probability in simple phenomena. We demand that

$$
\begin{equation*}
\int \dot{a}(x, t) d x=0 \tag{2.2}
\end{equation*}
$$

where $\dot{a}(x, t) \equiv \frac{\partial}{\partial t} a(x, t)$. According to (2.2) we may usually suppose that $\int a(x, t) d x=$ const. and can be normalized to unity, which will be a standard convention. Still, it occasionally becomes convenient to treat functions which can not be normalized, even though (2.2) applies.

The third constraint indicates that the field $a(x, t)$ is not unlike a probability density. We assume that $a(x, t)$ is real and non-negative,

$$
\begin{equation*}
a(x, t) \text { real, } \quad a(x, t) \geq 0 \tag{2.3}
\end{equation*}
$$

This constraint turns out to have remarkable consequences.
The fourth constraint imposes superposition, thereby confining the phenomena to a linear behaviour. We demand that if $a_{1}(x, t)$ and $a_{2}(x, t)$ are
solutions of the equations of motion, then also $\lambda_{1} a_{1}(x, t)+\lambda_{2} a_{2}(x, t)$ will be a solution, or

$$
\begin{equation*}
a_{1}(x, t) \text { and } a_{2}(x, t) \rightarrow \lambda_{1} a_{1}(x, t)+\lambda_{2} a_{2}(x, t) . \tag{2.4}
\end{equation*}
$$

To be more precise, and in view of the other constraints, the content of eq. (2.4) is: If $a_{1}$ and $a_{2}$ are solutions for $t \geq t_{0}$, and if $\lambda_{1} a_{1}\left(x, t_{0}\right)+\lambda_{2} a_{2}\left(x, t_{0}\right)$ is an allowed function, then $\lambda_{1} a_{1}(x, t)+\lambda_{2} a_{2}(x, t), t \geq t_{0}$, is a solution.

The constraint (2.4) might seem to be a serious limitation of the scope of the treatment. It does, however, correspond to the basic cases one must necessarily treat at first. Moreover, it should be remembered that in the quite general cases of quantum theory or of dynamics of ensembles one is in fact concerned with linear equations of motion.

We next come to a useful limitation in many initial studies. In mechanics, for instance, it is often profitable to study first the case of a time-independent Hamiltonian. One may then later, at least to some extent, study a timedependent Hamiltonian, e.g. in order to initiate and terminate the phenomenon in question. The fifth constraint limits the treatment to time-independent dynamics, or invariance of solutions towards displacement in time,

$$
\begin{equation*}
a(x, t) \rightarrow a(x, t+\tau) \text {, any fixed real } \tau . \tag{2.5}
\end{equation*}
$$

For practical purposes one further simplification is often valid. The sixth constraint concerns invariance of solutions towards displacement in space, or

$$
\begin{equation*}
a(x, t) \rightarrow a(x+\xi, t), \text { for any real } \xi . \tag{2.6}
\end{equation*}
$$

The displacement may be within a multi-dimensional space $\vec{x}$.

## Equations of Motion

We construct next the equations of motion, as they emerge by successive introduction of the constraints. We always assume validity of the first constraint, (2.1). Although it is possible to consider non-linear cases, we shall for the present disregard them, and apply the fourth constraint, (2.4). From the first and fourth constraints we therefore conclude that if the field $a\left(x^{\prime}, t^{\prime}\right)$ is known at time $t^{\prime}$ then

$$
\begin{equation*}
a(x, t)=\int d x^{\prime} T\left(x, t ; x^{\prime}, t^{\prime}\right) a\left(x^{\prime}, t^{\prime}\right), \quad t>t^{\prime}, \tag{2.7}
\end{equation*}
$$

or

$$
a_{k}(t)=\sum_{j} T_{k j}\left(t, t^{\prime}\right) a_{j}\left(t^{\prime}\right), \quad \bar{a}(t)=\overline{\bar{T}}\left(t, t^{\prime}\right) \bar{a}\left(t^{\prime}\right)
$$

The quantity $T$ will be called the propagator, having the property

$$
\begin{equation*}
T\left(x, t ; x^{\prime}, t\right)=\delta\left(x-x^{\prime}\right) . \tag{2.8}
\end{equation*}
$$

This way of stating the constraint is, however, somewhat indefinite at first, although it will be useful later. When we ask for the equations of motion, it is more profitable to summarize the first and fourth constraints as an expression for the time derivative of $a(x, t)$, which must receive a contribution from the point $y$, of type of $\Gamma(x, y, t) a(y, t)$, so that

$$
\begin{equation*}
\dot{a}(x, t)=\int d y \Gamma(x, y, t) a(y, t) \tag{2.9}
\end{equation*}
$$

where the unspecified integral, as always, extends over the total system and may be multi-dimensional. Next, we apply the second constraint, (2.2), demanding conservation. It implies that, in (2.9), we must have

$$
\int d x \Gamma(x, y, t)=0, \text { for all } y
$$

for if (2.10) did not hold, one could choose such functions $a(y, t)$ in (2.9), e.g. $\delta$-functions, as would violate eq. (2.2).

We may make a preliminary reformulation of (2.10). Outside the diagonal, i. e. for $x \neq y$, we alternatively denote $\Gamma(x, y, t)$ as $G(x, y, t)$. The equation (2.10) is then formally fulfilled for any $G(x, y, t)$ if $\Gamma$ in (2.9) is given by

$$
\Gamma(x, y, t)=G(x, y, t)-\delta(x-y) \int d x^{\prime} G\left(x^{\prime}, x, t\right)
$$

The third constraint, (2.3), demands that $a(x, t)$ remains real and nonnegative. Suppose that, in some point $x_{0}, a\left(x_{0}, t\right)=0$, whereas in other points $a(x, t)$ is arbitrary but non-negative. In the equation of motion, (2.9), we must then demand $\dot{a}\left(x_{0}, t\right) \geq 0$. But this requires that $\Gamma(x, y, t)$ is nonnegative for $x \neq y$, or

$$
\begin{equation*}
G(x, y, t) \text { real, } \quad G(x, y, t) \geq 0 . \tag{2.12}
\end{equation*}
$$

The total result of the four constraints can now be written as a basic integral equation, superseding the preliminary equations (2.11) and (2.12)

$$
\begin{equation*}
\dot{a}(x, t)=\int d y\{G(x, y, t) a(y, t)-G(y, x, t) a(x, t)\}, \quad G(x, y, t) \geq 0 . \tag{2.13}
\end{equation*}
$$

This equation is the starting-point of most of our further studies.
As to the behaviour of $G(x, y)$, we generally consider it as a continuous function, but it may diverge for $y \rightarrow x$. In fact, we allow that $\int_{|x-y|>\varepsilon} d y G(y, x) \rightarrow \infty$ for $\varepsilon \rightarrow 0$. The permitted degree of divergence de-
pends on the symmetry of the system, as mentioned in $\S 6$. The limit of $G(x, y)$, or part of it, becoming infinitely narrow is discussed in connection with differential equation approximations in $\S 5$.

In the majority of the cases to be studied here, we add the fifth constraint, (2.5), so that solutions are invariant towards time displacements. It follows from eq. (2.13) that then $G(x, y, t+\tau)=G(x, y, t)$, for all $\tau$, and eq. (2.13) reduces to

$$
\begin{equation*}
\dot{a}(x, t)=\int d y\{G(x, y) a(y, t)-G(y, x) a(x, t)\}, \quad G(x, y) \geq 0 \tag{2.14}
\end{equation*}
$$

Finally, we occasionally invoke the special constraint (2.6), concerning displacement in space, according to which, apparently, in e.g. (2.14)

$$
\begin{equation*}
G(x, y)=G(x-y) \tag{2.15}
\end{equation*}
$$

## Classification of Systems

Consider time-independent systems, so that eq. (2.14) is valid. We have shown that $G(x, y) \geq 0$, but in regions of considerable size one can then have that $G(x, y)=0$. This may result in complete lack of connection, both directly and indirectly, between some regions of $x$-space. Such systems must be regarded as divisible into subsystems. We therefore define an elementary unit, the indivisible system. To this end, consider two points, $x_{1}$ and $x_{2}$, within a system. Let first $a\left(x, t_{0}\right)=\delta\left(x-x_{1}\right)$, and if then the integral equation implies that $a\left(x_{2}, t\right) \neq 0$ at some later time $t>t_{0}$, then $x_{1}$ is said to communicate with $x_{2}$. This communication is called direct if it occurs in one step, i. e. if $G\left(x_{2}, x_{1}\right) \neq 0$.

A system is now called indivisible if, for any set of points $\left(x_{1}, x_{2}\right)$ within it, both $x_{1}$ communicates with $x_{2}$, and $x_{2}$ with $x_{1}$. The system is indivisible, with direct communication, if $G\left(x_{1}, x_{2}\right) \neq 0$ for all $x_{1}, x_{2}$ within it. In the following, we are mainly concerned with indivisible systems. Some characteristic examples are discussed in the beginning of $\S 3$.

An opposite extreme to an indivisible system is, as indicated above, a system which can be divided into completely unconnected subsystems. This will be called a separable system.

In between these two extremes there is a considerable range of systems with partial communication of varying type. Of these systems we shall only be interested in one-way systems. They are essentially one-dimensional systems, and may for instance be characterized by the condition that $x_{1}$ communicates with $x_{2}$ if and only if $x_{1}<x_{2}$.

## Projections

The state of the system at the time $t$ is given by the distribution in space, $a(x, t)$, the integral of which is conserved in time. One may then calculate projections (or averages) of various functions. There are two types of projections.

Firstly, for a function $f(x)$, depending on the spatial variable $x$, the projection is

$$
\begin{equation*}
\langle f(x)\rangle=\int f(x) a(x, t) d x \tag{2.16}
\end{equation*}
$$

and will in general be a function of time. Note that for discrete variables, $f(x) \rightarrow f_{k}, a(x, t) \rightarrow a_{k}(t)$, this formula becomes the scalar product of two vectors, $\langle f\rangle=\sum_{k} f_{k} \cdot a_{k}(t)=\overline{f \cdot} \cdot \bar{a}(t)$. It is thus the projection of a fixed vector $\bar{f}$ on a time-dependent vector $\bar{a}(t)$. Obviously, the function $f$ may also be allowed to depend explicitly on time, $f=f(x, t)$.

Secondly, instead of (2.16), one may consider projections of another kind of functions, i.e. functions depending on $a$,

$$
\begin{equation*}
\langle q(a)\rangle=\int q(a(x, t)) a(x, t) d x \tag{2.17}
\end{equation*}
$$

or $\sum_{k} q\left(a_{k}(t)\right) a_{k}(t)$ for discrete variables. The functions $q(a)$ may be denoted as spectral functions. It is possible, but less common, to have projections of functions depending on both $x$ and $a$.

## Transformation of Spatial Variables

Suppose that the one-dimensional spatial variable $x$ is replaced by $z=z(x)$, and that $z(x)$ changes monotonically with $x$, the latter in order to have simple uniqueness of transformation. Since then

$$
a(x, t) d x=a(x, t) \frac{d x}{d z} d z
$$

the distribution $a_{1}(z, t)$ on the $z$-axis is

$$
\begin{equation*}
a_{1}(z, t)=a(x, t)\left|\frac{d x}{d z}\right| \tag{2.18}
\end{equation*}
$$

where $|d x / d z|$ becomes the Jacobian in the general multi-dimensional case. In all transformations the quantity

$$
\begin{equation*}
d P=a(x, t) d x=a_{1}(z, t) d z \tag{2.19}
\end{equation*}
$$

remains invariant, as does its integral over space.

## Conjugate Field

When the integral equation of motion (2.9) or (2.13) is given for the field $a(x, t)$, there exists immediately one other equation of motion, valid for a different field. In fact, introduce a field $b(x, t)$, obeying the equation*

$$
\begin{equation*}
\dot{b}(x, t)=-\int d y b(y, t) \Gamma(y, x, t)=-\int d y\{b(y, t)-b(x, t)\} G(y, x, t), \tag{2.20}
\end{equation*}
$$

or in matrix form $\dot{\bar{b}}=-\bar{b} \overline{\bar{\Gamma}}$. This equation of motion, which we call conjugate to (2.9) and (2.13), is governed by the transposed $\Gamma$-matrix. We describe the field $b(x, t)$ as conjugate to $a(x, t)$. Note that we introduce a minus sign in the time derivative in (2.20). This is so far a convention. Of the conjugate field we know immediately that it has an equilibrium solution

$$
\begin{equation*}
b^{0}(x)=\text { const. }, \quad \bar{b}^{0}=C \overline{1}, \tag{2.21}
\end{equation*}
$$

as is obvious from (2.20). We can evidently also conclude that, if $b(x, t)$ is non-negative, the function $b\left(x^{\prime}, t^{\prime}\right)$ is non-negative at all previous times $t^{\prime}<t$. In this backward sense, the conjugate field therefore fulfills the third constraint, (2.3). We do not, however, know beforehand whether the conjugate field obeys a conservation law.

It turns out that, in the discussion of solutions of the equation of motion for $a(x, t)$, the conjugate field is often a useful auxiliary quantity.

## The Gurrent

For a quantity with conservation in space one can introduce a current when the equation of motion is known. In one dimension this is straightforward. From knowledge of the transition rate $G\left(x^{\prime}, y\right)$ between any two points one finds immediately that the total flow per unit time in the positive direction past a point $x$ will be

$$
\begin{equation*}
j(x, t)=-\int^{x} d x^{\prime} \int_{x} d y\left\{G\left(x^{\prime}, y\right) a(y, t)-G\left(y, x^{\prime}\right) a\left(x^{\prime}, t\right)\right\}, \tag{2.22}
\end{equation*}
$$

where the integration over $y$ alternatively might be allowed to be between the system boundaries. The current then fulfills the equation

$$
\begin{equation*}
\dot{a}(x, t)=-\frac{\partial}{\partial x} j(x, t) \tag{2.23}
\end{equation*}
$$

[^15]
## Boundary Conditions and Sources

In the following we always discuss the behaviour of systems which are isolated. There is then no current away from the system or into it. For discrete systems with finite $N$ this condition is obviously fulfilled by the equations of motion (2.13). For a continuum system defined in a finite closed region, i.e. including its boundaries, the demand of an isolated system is also straightforward. When the system is infinite, however, the boundary conditions are less simple. For practical reasons, we usually consider a finite but arbitrarily large interval, $L$. The system is then supposed either to have zero current at the boundaries, or to be periodic. The two conditions are quite different, the former imposing a rest system and the latter allowing transformations to moving coordinate systems. These questions are elucidated by an example in $\S 6$.

Note that when we introduce the conjugate field, as well as eigenfunctions of the fields, the prescribed boundary conditions must be obeyed in each instance.

An alternative way of analysing the dynamics of systems is to introduce sources of the field, depending arbitrarily on space and time. One then adds a term $S(x, t)$ on the right-hand side of e.g. (2.14), and finds the forced motion. This procedure is familiar from, for instance, the dielectric description of an electron gas. The method can be advantageous, but we shall not employ it.

## § 3. Properties of Solutions

In this chapter we derive a number of general properties of the solutions of the integral equation. We first obtain the basic result that, for indivisible systems, there is exactly one equilibrium solution, and it is everywhere positive. Next, the equations of motion are transformed to normal coordinates, and the field is found to tend towards the equilibrium. Third, we treat summarily the general question of eigenvalues and eigenfunctions of the field and of the conjugate field. The formalism embraces features known from wave mechanics. Fourth, the field propagators are discussed, and are used to study reversibility in space.

## Equilibrium Solution

By equilibrium we mean that $\dot{a}(x, t)$ in (2.14) is zero everywhere, with the condition that the system is isolated in the sense mentioned above. An
equilibrium solution, $a^{0}(x)$, therefore satisfies, for any $x$, and with zero current through all boundaries,

$$
\begin{equation*}
\int d y \Gamma(x, y) a^{0}(y) \equiv \int d y\left\{G(x, y) a^{0}(y)-G(y, x) a^{0}(x)\right\}=0, \tag{3.1}
\end{equation*}
$$

or $\overline{\bar{\Gamma}} \cdot \bar{a}^{0}=0$, in matrix notation. As indicated, we suppose that $G$ is real and non-negative. The integration in (3.1) is the definite integral over the total system.

The original time-dependent function $a(x, t)$ was assumed to remain non-negative. If it tends towards an equilibrium function*, the latter must also be a non-negative function. In the present connection, however, we ask for all possible solutions $a^{0}(x)$ of (3.1). Equilibrium solutions $a^{0}(x)$ are real functions of $x$, because $G$ is real.

We must verify at first that there is at least one solution of (3.1). We refrain from proving this for the widest possible groups of systems. The proof would, at this stage, be more cumbersome than rewarding. We need only demonstrate, by examples, that systems of interest have the required property. The general reason for this is seen easily for the group of finite discrete systems, i.e. for a finite discrete matrix $\overline{\bar{\Gamma}}$. In fact, conservation, (2.10), implies that $\overline{1} \cdot \overline{\bar{T}}=0$, so that the determinant $|\overline{\bar{T}}|=0$, and then eq. (3.1) must have at least one solution, irrespective of the symmetry properties of $\overline{\bar{G}}$.

The systems of the second major group are the following ones, with explicit solutions of (3.1). Suppose that the kernel in (3.1) is symmetric, $G(x, y)=G(y, x)$, or may be made symmetric by transformation of the space variables. The symmetric kernel $G(x, y)$ may then be taken outside the brackets in (3.1), and an equilibrium solution is $a^{0}(x)=$ const., or $\bar{a}^{0}=$ $C \cdot \overline{1}$. This solution is valid for all symmetric discrete or continuum cases, irrespective of the interval within which the system is defined. The symmetric case is analogous to a situation often met with in quantal or classical scattering. More precisely, the case of symmetric kernel $G(x, y)$ will be referred to as microscopic reversibility in space. It may be noted that equilibrium solutions can persist also in time dependent systems. If $G=G(x, y, t)$, and is symmetric, then $a^{0}(x)=$ const. is always an equilibrium.

A third simple group of systems consists of those with displacement invariance in space, $G(x, y)=G(x-y)$, cf. eq. (2.6). As to boundary conditions, one possibility is that a system is periodic (like e.g. angular vari-

[^16]ables), with repetition after a fixed, but arbitrarily long period. It is then obvious that $a^{0}(x)=$ const. is a solution of (3.1) for the system in question.

Beside the above group of systems one has a quite different group, consisting of communicating systems. Of these, a well-defined subgroup is the set of one-way systems, where for a discrete variable (e.g. $k=1,2, \ldots, N$, and $G_{k j}=C_{k} \cdot \delta_{k, j-1}$ ) a typical equilibrium solution is $a_{1}^{0}=1, a_{2}^{0}=\ldots=$ $a_{N}^{0}=0$.

## Uniqueness of Equilibrium

Having ascertained that there is at least one equilibrium for the systems of interest, we propose to show the following result, valid for indivisible systems. Any solution of (3.1), if positive in one point, must be positive everywhere in $x$-space,

$$
\begin{equation*}
\text { indivisible systems: } a^{0}(x)>0 \text { for all } x \tag{3.2}
\end{equation*}
$$

Accept then that (3.2) holds and suppose that there are two or more equilibrium solutions. Any linear combination of these is also a solution of (3.1). But a linear combination can always be arranged to have both positive and negative values. This is in contradiction to (3.2). We have thus shown that (3.2) implies that there is exactly one equilibrium solution.

Let us now complete the proof by showing the validity of (3.2). We consider a system which is indivisible and isolated. Suppose that (3.2) is not fulfilled by $a^{0}(x)$, a solution of (3.1). Divide the space into region I where $a^{0}(x)>0$, and region II where $a^{0}(x) \leq 0$. Integrate (3.1) over $x$ within the whole region II. This integral is called $Q$, and must be zero according to (3.1). Now,

$$
\begin{align*}
Q & =\int_{\text {II }} d x \int d y\left\{G(x, y) a^{0}(y)-G(y, x) a^{0}(x)\right\} \\
& =\int_{\text {II }} d x \int_{\mathrm{I}} d y\left\{G(x, y) a^{0}(y)-G(y, x) a^{0}(x)\right\} \tag{3.3}
\end{align*}
$$

because the symmetric part, where both $y$ and $x$ belong to II, is identically zero. Since $a^{0}(I I) \leq 0$ we find by omitting the second term in (3.3)

$$
\begin{equation*}
Q \geqq \int_{\mathrm{II}} d x \int_{\mathrm{I}} d y G(x, y) a^{0}(y)>0 \tag{3.4}
\end{equation*}
$$

The latter inequality follows because $a^{0}(y)$ is positive everywhere, and $G$ (II,I) must be different from zero for some set $(x, y)$ in an indivisible
system. The resulting contradiction between eqs. (3.4) and (3.1) implies that (3.2) holds.

In the following we repeatedly use the result that, for indivisible systems, $a^{0}(x)$ is positive and equilibrium is unique. As to the properties of other systems, the communicating systems have not in general a unique equilibrium. In the special case of one-way systems there is uniqueness of equilibrium, but $a^{0}(x)=0$ except in one point, so that (3.2) is not fulfilled.

## Transformation to Normal Coordinates

For indivisible systems, with a unique, positive equilibrium solution $a^{0}(x)$, the quantity $a^{0}(x) d x=d z$ is a basic measure of a priori distribution, corresponding to phase space volume in statistical mechanics. It may then be worth while to indicate how the equation of motion can be transformed to suitable variables, i.e. normal coordinates, where the basic density measure is explicit. Still, it is not always necessary or convenient to make this transformation.

When transforming to the normal coordinates we find

$$
\begin{equation*}
a(x, t) d x=\frac{a(x, t)}{a^{0}(x)} a^{0}(x) d x=\alpha(z, t) d z . \tag{3.5}
\end{equation*}
$$

Hereby we have obtained an invariant measure of the field,

$$
\begin{equation*}
\alpha(z, t)=\frac{a(x, t)}{a^{0}(x)}, \tag{3.6}
\end{equation*}
$$

which function is well-defined, because $a^{0}(x)$ is positive. Usually, we consider $\alpha$ as a function in the $z$-space, but we may as well regard it as a function of $x$. The equilibrium solution $a^{0}(x)$ contains an arbitrary factor. If $a^{0}(x)$ is introduced as in eqs. (3.5) and (3.6), then $\alpha$ is normalized to unity because $a$ is normalized.

The field equation for $\alpha$ is easily obtained. Define $\gamma$ and $g$ by

$$
\begin{align*}
& \Gamma(x, y)=a^{0}(x) \gamma\left(z, z^{\prime}\right) \\
& G(x, y)=a^{0}(x) g\left(z, z^{\prime}\right) \tag{3.7}
\end{align*}
$$

where $z$ and $z^{\prime}$ are the normal coordinates corresponding to $x$ and $y$, respectively. Again, we may sometimes consider $\gamma$ and $g$ as explicit functions of $x$ and $y$.

According to (2.9), (2.14), (3.5) and (3.7)

$$
\begin{equation*}
\dot{\alpha}(z, t)=\int d z^{\prime} \gamma\left(z, z^{\prime}\right) \alpha\left(z^{\prime}, t\right)=\int d z^{\prime}\left\{g\left(z, z^{\prime}\right) \alpha\left(z^{\prime}, t\right)-g\left(z^{\prime}, z\right) \alpha(z, t)\right\}, \tag{3.8}
\end{equation*}
$$

where then, from conservation (2.10),

$$
\begin{equation*}
\int d z \gamma\left(z, z^{\prime}\right)=0, \tag{3.9}
\end{equation*}
$$

and from (3.1)

$$
\begin{equation*}
\int d z^{\prime} \gamma\left(z, z^{\prime}\right)=\int d z^{\prime}\left\{g\left(z, z^{\prime}\right)-g\left(z^{\prime}, z\right)\right\}=0, \tag{3.10}
\end{equation*}
$$

corresponding to equilibrium being the uniform distribution.
As to the field conjugate to $\alpha(z, t)$, we denote it as $\beta(z, t)$ and can simply introduce

$$
\begin{equation*}
\beta(z, t)=b(x, t), \tag{3.11}
\end{equation*}
$$

i. e. $\beta(z, t) d z=b(x, t) a^{0}(x) d x$, so that from (2.20)

$$
\begin{equation*}
\dot{\beta}(z, t)=-\int d z^{\prime} \beta\left(z^{\prime}, t\right) \gamma\left(z^{\prime}, z\right)=-\int d z^{\prime}\left\{\beta\left(z^{\prime}, t\right)-\beta(z, t)\right\} g\left(z^{\prime}, z\right) . \tag{3.12}
\end{equation*}
$$

Eqs. (3.12) and (3.8) show that $\beta(z, t)$ (or $b(x, t))$ is in fact the field conjugate to $\alpha(z, t)$, in the same way as (2.20) is conjugate to (2.13).

It is apparent that, because $a(x, t)$ has an equilibrium, the conjugate field has conservation. In fact, according to eqs. (3.12) and (3.10)

$$
\begin{equation*}
\int a^{0}(x) \dot{b}(x, t) d x=\int d z \dot{\beta}(z, t)=0 . \tag{3.13}
\end{equation*}
$$

## Trend towards Equilibrium

The trend towards equilibrium is easily found if, by means of (3.10) the equation of motion (3.8) is written in an alternative way,

$$
\dot{\alpha}(z, t)=\int d z^{\prime} g\left(z, z^{\prime}\right)\left\{\alpha\left(z^{\prime}, t\right)-\alpha(z, t)\right\} .
$$

Eq. (3.8') is seen to be quite similar to (3.12). It follows from (3.8') that the largest value of $\alpha(x, t)$ must always decrease, whereas the smallest value, if any, must increase. This indicates a tendency towards equilibrium, cf. also $\S 4$. The result remains valid if the function $\alpha$ in (3.8') is allowed to be negative.

For the conjugate field already the original equation of motion (2.20) implies that the largest value of $b(x, t)$ decreases, and the smallest increases, as one goes backwards in time.

## Eigenvalues and Eigenfunctions

The equilibrium solution $a^{0}(x)$ in (3.1) is merely one of the stationary solutions of (2.14), albeit the most important one. Consider now stationary solutions in general, for isolated, indivisible systems. Make the ansatz that a solution of $(2.14)$ is of the type $a_{\nu}(x) \cdot \exp \left(-\lambda_{\nu} t\right)$, i.e. the equation becomes

$$
\begin{equation*}
\lambda_{\nu} a_{v}(x)=-\int d y \Gamma(x, y) a_{\nu}(y) \quad \text { or } \quad \lambda_{\nu} \overline{a_{v}}=-\overline{\bar{I}} \cdot \overline{a_{\nu}} \tag{3.14}
\end{equation*}
$$

The equilibrium solution corresponds to $\lambda_{0}=0$. In parallel to (3.14) we may directly consider the invariant field $\alpha$, where

$$
\begin{equation*}
\lambda_{\nu} \alpha_{\nu}(z)=-\int d z^{\prime} \gamma\left(z, z^{\prime}\right) \alpha_{v}\left(z^{\prime}\right)=-\int d z^{\prime} g\left(z, z^{\prime}\right)\left(\alpha_{v}\left(z^{\prime}\right)-\alpha_{\nu}(z)\right) \tag{3.15}
\end{equation*}
$$

or

$$
\lambda_{v} \bar{\alpha}_{v}=-\overline{\bar{\gamma}} \cdot \bar{\alpha}_{v}
$$

The result obtained from (3.8') proves, firstly, that for the non-equilibrium stationary solutions it must hold that

$$
\begin{equation*}
\operatorname{Re}\left(\lambda_{v}\right)>0, \tag{3.16}
\end{equation*}
$$

because for no function $\alpha(z, t)$ is there a tendency away from equilibrium. Secondly, since $a(x, t)$ is conserved, these eigensolutions obey the equation, for $v \neq 0$,

$$
\begin{equation*}
\int a_{v}(x) d x \equiv \int \alpha_{v}(z) d z \equiv \bar{\alpha}_{v} \cdot \overline{1}=0 \tag{3.17}
\end{equation*}
$$

The result (3.17) is part of a more general orthogonality theorem. We prove the theorem in two steps. First, we consider the limited, but common, case of symmetric kernels (microscopic reversibility in space, cf. p. 19). Next, we give the proof in the general case.

Suppose then that $\overline{\bar{\gamma}}$ is symmetric, $\gamma\left(z, z^{\prime}\right)=\gamma\left(z^{\prime}, z\right)$, and use matrix notation for brevity. Prove first that the $\lambda_{\nu}$ are real. The complex conjugate of eq. (3.15) is $\lambda_{v}^{*} \bar{\alpha}_{v}^{*}=-\overline{\bar{\gamma}} \cdot \bar{\alpha}_{v}^{*}$. Multiply (3.15) by $\bar{\alpha}_{v}^{*}$ on the left

$$
\begin{equation*}
\lambda_{v} \bar{\alpha}_{v}^{*} \cdot \bar{\alpha}_{v}=-\bar{\alpha}_{v}^{*} \cdot \overline{\bar{\gamma}} \cdot \bar{\alpha}_{v}=-\bar{\alpha}_{v} \cdot \overline{\bar{\gamma}}^{T} \cdot \bar{\alpha}_{v}^{*}=-\bar{\alpha}_{v} \cdot \overline{\bar{\gamma}} \cdot \bar{\alpha}_{v}^{*}=\lambda_{v}^{*} \bar{\alpha}_{v}^{*} \cdot \bar{\alpha}_{v} \tag{3.18}
\end{equation*}
$$

so that $\lambda_{\nu}^{*}=\lambda_{\nu}$, and therefore the eigenfunctions $\bar{\alpha}_{v}=\alpha_{\nu}(z)$ may be chosen to be real.

Prove next, also for symmetric $\overline{\bar{\gamma}}$, that eigensolutions belonging to different $\lambda_{\nu}$ are orthogonal. Introduce two eigenfunctions, $\bar{\alpha}_{\nu}$ and $\bar{\alpha}_{\mu}$. Multiply (3.15) by $\bar{\alpha}_{\mu}$,

$$
\begin{equation*}
\lambda_{v} \bar{\alpha}_{\mu} \cdot \bar{\alpha}_{v}=-\bar{\alpha}_{\mu} \cdot \overline{\bar{\gamma}} \cdot \bar{\alpha}_{v}=-\bar{\alpha}_{v} \cdot \bar{\gamma}^{T} \cdot \bar{\alpha}_{\mu}=\lambda_{\mu} \bar{\alpha}_{\mu} \cdot \bar{\alpha}_{\nu} \tag{3.19}
\end{equation*}
$$

$\overline{\bar{\gamma}}^{T}$ being the transposed matrix. It follows that

$$
\begin{equation*}
\bar{\alpha}_{\mu} \cdot \bar{\alpha}_{v}=0 \quad \text { for } \quad \lambda_{\mu} \neq \lambda_{v}, \quad \text { if } \quad \overline{\bar{\gamma}}^{T}=\overline{\bar{\gamma}} . \tag{3.20}
\end{equation*}
$$

In the symmetric case, the $\bar{\alpha}_{\nu}$ may therefore form an orthonormal set.
For the purpose of studying the general orthogonality theorem we introduce the conjugate field. We define its eigenfunctions as $b_{\nu}(x) \cdot \exp \left(\lambda_{\nu} t\right)$, so that, corresponding to (3.14),

$$
\begin{equation*}
\bar{b}_{v} \lambda_{v}=-\bar{b}_{v} \cdot \overline{\bar{I}} . \tag{3.21}
\end{equation*}
$$

We multiply (3.14) by $\bar{b}_{\mu}$ and obtain

$$
\begin{equation*}
\lambda_{v} \bar{b}_{\mu} \cdot \bar{a}_{v}=-\bar{b}_{\mu} \cdot \overline{\bar{\Gamma}} \cdot \bar{a}_{v}=\lambda_{\mu} \bar{b}_{\mu} \cdot \bar{a}_{v} . \tag{3.22}
\end{equation*}
$$

It follows that

$$
\begin{equation*}
\bar{b}_{\mu} \cdot \bar{a}_{\nu}=0 \quad \text { if } \quad \lambda_{\mu} \neq \lambda_{\nu} . \tag{3.23}
\end{equation*}
$$

This result is quite general. It is independent of the previous results in this chapter, such as $a^{0}(x)>0$. It is valid not only for the original equations of motion (2.14) and (2.20), but even when $G(x, y)$ is allowed not to be real and positive. In fact, (3.23) is a consequence of merely the first, fourth, and fifth constraints, i.e. (2.9) with $\Gamma=\Gamma(x, y)$.

According to eq. (3.23) the eigenfunctions $a_{\nu}(x)$ do not in general form an orthonormal set. They do it when, as in eq. (3.20), $\bar{a}_{v}=\bar{b}_{v}$.

If we can normalize and may assume non-degeneracy, we obtain from (3.23)

$$
\begin{equation*}
\int b_{\mu}(x) a_{\nu}(x) d x=\delta_{\mu \nu} \tag{3.24}
\end{equation*}
$$

For a function $f(x)$ the coefficients of an expansion

$$
\begin{equation*}
f(x)=\sum_{v} c_{v} a_{\nu}(x), \tag{3.25}
\end{equation*}
$$

are according to (3.24)

$$
\begin{equation*}
c_{v}=\int b_{\nu}(x) f(x) d x \tag{3.26}
\end{equation*}
$$

Although it would be easy, we shall at this point not enter into further details of the formulation by eigenfunctions, as based only on eqs. (2.1), (2.4) and (2.5). It is apparent that the present formalism is quite as in quantum mechanics, the latter being in fact embraced by the former. As an example one might consider stationary perturbation theory. Perturbation theory is useful when one knows exact solutions of many cases of equations of motion, the neighbouring cases being then easily approximated. The examples of analytic solutions discussed in $\S 6$ can in this respect serve as a basis, both for indivisible systems and for, e.g., one-way systems.

## Propagators

We introduced in (2.7) the propagator $T\left(x, t ; x^{\prime}, t^{\prime}\right)$ as an expression for the integrated equation of motion, such that

$$
\begin{equation*}
a(x, t)=\int d x^{\prime} T\left(x, t ; x^{\prime}, t^{\prime}\right) a\left(x^{\prime}, t^{\prime}\right) \tag{3.27}
\end{equation*}
$$

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where, for $t=t^{\prime}, T=\delta\left(x-x^{\prime}\right)$. The propagator is defined for $t \geq t^{\prime}$, but not necessarily for $t<t^{\prime}$.

The equations of motion for the propagator are obtained from (3.27) by differentiation with respect to the time variables. Differentiate first (3.27) with respect to $t$, and find from (2.9), since $a\left(x^{\prime}, t^{\prime}\right)$ may be chosen arbitrarily,

$$
\begin{equation*}
\frac{\partial}{\partial t} T\left(x, t ; x^{\prime}, t^{\prime}\right)=\int d y \Gamma(x, y, t) T\left(y, t ; x^{\prime}, t^{\prime}\right) \tag{3.28}
\end{equation*}
$$

or $\frac{\partial}{\partial t} \overline{\bar{T}}\left(t, t^{\prime}\right)=\overline{\bar{T}}(t) \cdot \overline{\bar{T}}\left(t, t^{\prime}\right)$, i. e. again the equation of motion (2.9). Similarly, we differentiate (3.27) with respect to $t^{\prime}$ and obtain

$$
\begin{equation*}
\frac{\partial}{\partial t^{\prime}} T\left(x, t ; x^{\prime}, t^{\prime}\right)=-\int d y T\left(x, t ; y, t^{\prime}\right) \Gamma\left(y, x^{\prime}, t^{\prime}\right) \tag{3.29}
\end{equation*}
$$

We have hereby seen the significance of the equation of motion for the conjugate field, (2.20), the latter being identical to (3.29).

The above concerned the propagation of a field, cf. (3.27). The propagation of the conjugate field is evidently determined by

$$
\begin{equation*}
b\left(x^{\prime}, t^{\prime}\right)=\int d x b(x, t) T\left(x, t ; x^{\prime}, t^{\prime}\right) \tag{3.30}
\end{equation*}
$$

or $\bar{b}\left(t^{\prime}\right)=\bar{b}(t) \cdot \overline{\bar{T}}\left(t, t^{\prime}\right)$.
If we specialize to the case of time-independent equations of motion, i.e. the fifth constraint, or (2.14), we get from (3.27)

$$
\begin{equation*}
T=T\left(x, x^{\prime}, t-t^{\prime}\right)=T\left(x, x^{\prime}, \tau\right) \tag{3.31}
\end{equation*}
$$

the propagator being dependent on only the time difference $\tau=t-t^{\prime}$, and defined at least for $\tau \geq 0$. It follows that then

$$
\begin{equation*}
\frac{\partial}{\partial \tau} \overline{\bar{T}}(\tau)=\overline{\bar{T}}(\tau) \cdot \overline{\bar{T}}=\overline{\bar{\Gamma}} \cdot \overline{\bar{T}}(\tau)=\frac{1}{2}[\overline{\bar{T}}(\tau) \cdot \overline{\bar{\Gamma}}+\overline{\bar{I}} \cdot \overline{\bar{T}}(\tau)] \tag{3.32}
\end{equation*}
$$

the change of $T$ being determined by its anticommutator with $\Gamma$.
The equation of motion of the transposed $T$-matrix is

$$
\begin{equation*}
\frac{\partial}{\partial \tau} \overline{\bar{T}}^{T}(\tau)=\frac{1}{2}\left[\overline{\bar{\Gamma}}^{T} \cdot \overline{\bar{T}}^{T}(\tau)+\overline{\bar{T}}^{T}(\tau) \cdot \overline{\bar{\Gamma}}^{T}\right] \tag{3.33}
\end{equation*}
$$

being thus governed by the transposed $\Gamma$-matrix.

## Reversibility in Space

Let us consider transitions in space during finite times. For definiteness, suppose that at time $t_{1}$ the field is $a\left(x, t_{1}\right)=\delta\left(x-x_{1}\right)$. Ask for the field at time $t_{2}$ in the point $x_{2}, a\left(x_{2}, t_{2}\right)$, and call this field the transition rate $P_{a}\left(x_{1} \rightarrow x_{2}, t_{1} \rightarrow t_{2}\right)$. According to (3.27) the transition rate is given by the propagator

$$
P_{a}\left(x_{1} \rightarrow x_{2}, t_{1} \rightarrow t_{2}\right)=T\left(x_{2}, t_{2} ; x_{1}, t_{1}\right),
$$

and analogously for the conjugate field, cf. (3.30),

$$
P_{b}\left(x_{1} \rightarrow x_{2}, t_{1} \rightarrow t_{2}\right)=T\left(x_{1}, t_{1} ; x_{2}, t_{2}\right) .
$$

It follows that

$$
\begin{equation*}
P_{a}\left(x_{1} \rightarrow x_{2}, t_{1} \rightarrow t_{2}\right)=P_{b}\left(x_{2} \rightarrow x_{1}, t_{2} \rightarrow t_{1}\right) . \tag{3.34}
\end{equation*}
$$

The formula (3.34) is in fact of quite general validity, in that it states: If $P_{a}$ is defined for a transition, then $P_{b}$ of the opposite transition is also defined and equal to it.

Consider next time-independent equations of motion. According to (3.31), eq. (3.34) becomes

$$
\begin{equation*}
P_{a}\left(x_{1} \rightarrow x_{2}, \tau\right)=P_{b}\left(x_{2} \rightarrow x_{1},-\tau\right)=T\left(x_{2}, x_{1}, \tau\right), \tag{3.35}
\end{equation*}
$$

where $\tau=t_{2}-t_{1}$.
Finally, we suppose that there is microscopic reversibility in space, i.e. we are concerned with $z$-space, where $\gamma\left(z_{1}, z_{2}\right)=\gamma\left(z_{2}, z_{1}\right)$. The $a$ - and $b$ fields in $z$-space are called $\alpha$ and $\beta$. It is now observed that since $\overline{\bar{\gamma}}^{T}=\overline{\bar{\gamma}}$, the equations of motion (3.32) and (3.33) for $\overline{\bar{T}}(\tau)$ and $\overline{\bar{T}}^{T}(\tau)$ are identical. Since the initial value is symmetrical, $\overline{\bar{T}}(0)=\overline{\bar{T}}^{T}(0)=\delta\left(z_{2}-z_{1}\right)$, it follows that $\overline{\bar{T}}(\tau)=\overline{\bar{T}}^{T}(\tau)$, or from (3.35)

$$
\begin{equation*}
P_{\alpha}\left(z_{1} \rightarrow z_{2}, \tau\right)=P_{\alpha}\left(z_{2} \rightarrow z_{1}, \tau\right) \tag{3.36}
\end{equation*}
$$

and this again is equal to $P_{\beta}\left(z_{2} \rightarrow z_{1},-\tau\right)=P_{\beta}\left(z_{1} \rightarrow z_{2},-\tau\right)$. Eq. (3.36) states that if there is microscopic reversibility in space, then macroscopic reversibility in space follows. The result is valid in the same strong sense as (3.34). A transformation of (3.36) to arbitrary coordinates yields

$$
\frac{P_{a}\left(x_{1} \rightarrow x_{2}, \tau\right)}{a^{0}\left(x_{2}\right)}=\frac{P_{a}\left(x_{2} \rightarrow x_{1}, \tau\right)}{a^{0}\left(x_{1}\right)},
$$

so that transition rates are weighted by the equilibrium distribution.

## §4. Degradation Functions

The concept of entropy and the properties of entropy are familiar from statistical mechanics and from thermodynamics. The present integral equations contain main features of statistical mechanics. One might therefore be tempted to introduce entropy as a recipe, without further ado, thus obtaining a measure of the degradation of the field within a system. This is in fact a possible procedure. It appears the more plausible since entropy also plays a central role in the mathematical theory of information ${ }^{9}, 19$.

But in the present discussion we need not rely on concepts derived from applications. It seems therefore worth while to attempt independently a general formulation of the concept in question. We shall do this in the beginning of the present chapter. We arrive at the noteworthy result that entropy represents merely one choice within a family of degradation functions. Next, we briefly discuss the use of degradation functions as describing the trend towards equilibrium. It appears that entropy often is not the most convenient choice of degradation function.

## Basic Requirements

We ask for a universal quantity characterizing the state of a system. A quantity of this kind we call a degradation function. We make the following two demands, to be explained presently in more detail:

1. A degradation function must be unique, invariant, and common to indivisible systems.
2. A degradation function must have a well-defined rule of composition for a system consisting of two completely independent systems.

Consider the first demand. The stipulation of uniqueness has a straightforward meaning. As to invariance, this means that a degradation function remains unchanged, whatever transformation is made of the spatial coordinates of a system. Thirdly, we express the desired universality of the degradation function by requiring explicitly that it is common to indivisible systems. Indivisible systems form an exceedingly wide group, with the property of unique and positive equilibrium distribution. It may turn out that degradation functions apply for a still wider group of systems, but we need not mince matters by going beyond indivisible systems.

A degradation function must be of type of the projections introduced in § 2. They are of two kinds: projections of spatial functions, $\langle f(x)\rangle$ in (2.16), and projections of functions of the field, $\langle q(a)\rangle$ in (2.17). In these
integrals the differential $d P=a(x, t) d x$ is invariant, and thus $f(x)$ and $q(a)$ must be invariant too.

It is not particularly difficult to ascertain that projections of spatial functions do not fulfill the above demands. Without going into detail, we may briefly indicate some of the main aspects. One would expect that $f(x)$ is a function given beforehand, independently of the equations of motion of the system in question. Now, since $f(x)$ is invariant, it may be expressed by the invariant $b$-field, i.e. in terms of its complete set of eigenfunctions $b_{v}(x)$. But if $f(x)$ is to be independent of the equations of motion, there remains only the uninteresting choice $f(x)=b_{0}(x)=$ const. On the other hand, if $f$ were allowed to depend on the equations of motion, it could not be unique and common to all systems within discrete or continuum spaces.

Let us turn to functions of the field. In order to secure invariance we must introduce the invariant field $\alpha=a(x, t) / a^{0}(x)$, defined in (3.5). It exists for any indivisible system. The only quantities fulfilling the first demand are therefore, expressed in normal coordinates,

$$
\begin{equation*}
D(t)=\langle q(\alpha)\rangle=\int d z \alpha(z, t) q(\alpha(z, t)), \tag{4.1}
\end{equation*}
$$

where $q(\alpha)$ is arbitrary, so far.
Introduce now the second demand. Suppose that the physical quantity in question is $D_{1}$ and $D_{2}$ for two independent systems, and that it is $D_{12}$ for the two taken together. The demand is then that there is a well-defined rule of composition,

$$
\begin{equation*}
D_{12}=G\left(D_{1}, D_{2}\right) . \tag{4.2}
\end{equation*}
$$

This demand is often implicitly made by introduction of physical variables, sometimes as a more incautious statement of additivity or superposition.

Before applying (4.2) we consider the notion of independent systems. Let there be two systems, described in normal coordinates by the fields $\alpha_{1}\left(z_{1}, t\right)$ and $\alpha_{2}\left(z_{2}, t\right)$. The systems are independent if $\alpha_{1}\left(z_{1}, t\right)$ and $\alpha_{2}\left(z_{2}, t\right)$ separately account for their future behaviour. The two systems can also be considered as one system with a field $\alpha\left(z_{1}, z_{2}, t\right)$, if

$$
\begin{equation*}
\alpha\left(z_{1}, z_{2}, t\right)=\alpha_{1}\left(z_{1}, t\right) \alpha_{2}\left(z_{2}, t\right), \tag{4.3}
\end{equation*}
$$

where the fields are normalized to unity.
The second demand, (4.2), can now be formulated by means of (4.1) and (4.3). For the total system one has

$$
\begin{equation*}
D_{12}=\left\langle q\left(\alpha\left(z_{1}, z_{2}, t\right)\right)\right\rangle=\int d z_{1} \int d z_{2} \alpha\left(z_{1}, z_{2}, t\right) q\left(\alpha\left(z_{1}, z_{2}, t\right)\right), \tag{4.4}
\end{equation*}
$$

and for the individual systems

$$
\begin{align*}
D_{1} & =\left\langle q\left(\alpha_{1}\left(z_{1}, t\right)\right)\right\rangle_{1}=\int d z_{1} \alpha_{1}\left(z_{1}, t\right) q\left(\alpha_{1}\left(z_{1}, t\right)\right)  \tag{4.5}\\
D_{2} & =\left\langle q\left(\alpha_{2}\left(z_{2}, t\right)\right)\right\rangle_{2}=\int d z_{2} \alpha_{2}\left(z_{2}, t\right) q\left(\alpha_{2}\left(z_{2}, t\right)\right)
\end{align*}
$$

The solutions of eqs. (4.2), (4.3), (4.4) and (4.5) may be readily guessed. Let us indicate a more systematic procedure. Put $\alpha_{2}\left(z_{2}, t\right)=\xi=$ const. in one region of $z_{2}$-space, and $\alpha_{2}=0$ outside this region. Eq. (4.2) then becomes, according to eqs. (4.3), (4.4), and (4.5),

$$
\begin{equation*}
\left\langle q\left(\xi \alpha_{1}\right)\right\rangle_{1}=G\left(\left\langle q\left(\alpha_{1}\right)\right\rangle_{1}, q(\xi)\right) \tag{4.6}
\end{equation*}
$$

In eq. (4.6) we next vary $\alpha_{1}\left(z_{1}\right)$, retaining normalization of $\alpha_{1}$ and keeping $\left\langle q\left(\alpha_{1}\right)\right\rangle_{1}$ constant. Since $G$ is then unchanged, also $\left\langle q\left(\xi \alpha_{1}\right)\right\rangle_{1}$ must remain unchanged. Introducing $Q(\alpha)=\partial(\alpha q(\alpha)) / \partial \alpha$, one obtains, by variation of $\alpha_{1}$, the functional equation $Q\left(\xi \alpha_{1}\right)=C_{1}(\xi) Q\left(\alpha_{1}\right)+C_{2}(\xi)$, which may be solved $\left(Q(\alpha) \propto c+\alpha^{n}\right.$ or $\left.c+\log \alpha\right)$. A precise discussion of the functional equation is given in ref. 2.

The solutions for $q$ are then

$$
\begin{equation*}
q(\alpha)=C \alpha^{n} \quad \text { and } \quad q(\alpha)=-C \log \alpha, \tag{4.7}
\end{equation*}
$$

the latter solution being due to the normalization condition for $\alpha$, i.e. to conservation of the field. We have in (4.7) omitted a spurious solution, $q(\alpha)=C \alpha^{-1} \log \alpha$, for which the projection often diverges, in particular within an infinite system.

We have thus arrived at the family of functions satisfying the two demands. We call them degradation functions, writing

$$
\begin{equation*}
D^{(n)}(t)=\int d z \alpha(z, t)[\alpha(z, t)]^{n} \tag{4.8}
\end{equation*}
$$

and denoting by $S$ the familiar entropy,

$$
\begin{equation*}
S(t)=-\int d z \alpha(z, t) \log \alpha(z, t) \tag{4.9}
\end{equation*}
$$

where the arbitrary constants in eq. (4.7) are omitted. The number $n$ in eq. (4.8) is the order of the $D$-function. If one limits the order to be $n \geq 0$, convergence is always secured.

The value $n=0$ in (4.8) is the trivial normalization. Note here that the entropy, (4.9), which arose from conservation of the field, is the derivative of a $D$-function,

$$
\begin{equation*}
S=-\left.\frac{\partial}{\partial n} D^{(n)}\right|_{n=0}=-\left.\frac{1}{n} \log D^{(n)}\right|_{n \rightarrow 0}=-\left.\frac{D^{(n)}-1}{n}\right|_{n \rightarrow 0} \tag{4.10}
\end{equation*}
$$

Entropy is thus a degradation function of order zero.

It follows from eqs. (4.9) and (4.8) that when a system is composed of independent systems, then the entropy is additive, as is also the logarithm of the $D$-functions,

$$
\begin{gather*}
\log D_{12}^{(n)}=\log D_{1}^{(n)}+\log D_{2}^{(n)}  \tag{4.11}\\
S_{12}=S_{1}+S_{2}
\end{gather*}
$$

Strictly speaking, only the changes of the quantities in (4.11) are welldefined. This is because they contain an arbitrary additive constant in a continuum description, arising from an arbitrary factor in the definition of $z$, whereas $\alpha d z$ is invariant. The arbitrary constant is removed in the case of a discrete variable with finite $N$. This contrast is well-known for entropy in classical statistical mechanics as compared with quantal statistical mechanics.

The likeness between entropy and the $D$-functions, as contained in eqs. (4.11) and (4.10), may be further elucidated by introducing a set of functions $S^{(n)}$,

$$
\begin{equation*}
S^{(n)}=-\frac{1}{n} \log D^{(n)} \tag{4.12}
\end{equation*}
$$

According to eq. (4.10), $S^{(0)}=S$. Moreover, consider the example of a discrete variable, $k=1,2, \ldots, N$, with equilibrium $\alpha_{1}^{0}=\alpha_{2}^{0}=\ldots=\alpha_{N}^{0}=$ $1 / N$. In an initial state, where one $\alpha_{k}$ is unity, the others zero, we find that all functions in (4.12) are $S^{(n)}=0$. In the final equilibrium they are all $S^{(n)}=\log N$. Between the two extremes the different functions attain quite different values. The equality of the functions at the extremes is only due to the freedom in selection of origin and in unit of degradation. The likeness may, however, be one reason why attempts at deducing degradation functions from general principles have led only to the entropy, omitting the $D$-functions.

## Monotonic Change in Time of Degradation Functions

We now apply the linear integral equations of motion, in order to find the time behaviour of the degradation functions. It will be shown that for indivisible systems the $D$-functions always decrease, when the field deviates from the equilibrium solution. According to (3.8) and (3.10) we can write the equation of motion as

$$
\begin{equation*}
\dot{\alpha}(z, t)=\int d z^{\prime}\left\{g\left(z, z^{\prime}\right) \alpha\left(z^{\prime}, t\right)-\alpha(z, t)\left(C g\left(z^{\prime}, z\right)+(1-C) g\left(z, z^{\prime}\right)\right)\right\} \tag{4.13}
\end{equation*}
$$

where $C$ is an arbitrary constant.

The time derivative of the function $D^{(n)}(t)$ is therefore, according to (4.8),

$$
\left.\begin{array}{rl}
\frac{\partial}{\partial t} D^{(n)}(t) & =(n+1) \int d z \int d z^{\prime} g\left(z, z^{\prime}\right)\left\{\alpha\left(z^{\prime}, t\right) \alpha^{n}(z, t)-\right.  \tag{4.14}\\
& \left.-C \alpha^{n+1}\left(z^{\prime}, t\right)-(1-C) \alpha^{n+1}(z, t)\right\}
\end{array}\right\}
$$

In this equation we can choose the constant to be $C=(n+1)^{-1}$. Next we introduce an auxiliary function

$$
\begin{equation*}
f_{n}(\xi)=(n+1)(\xi-1)+1-\xi^{n+1}, \quad 0 \leq \xi<\infty \tag{4.15}
\end{equation*}
$$

with the property $f_{n}(1)=0$, while $f_{n}(\xi)<0$ for $\xi \neq 1$ and $n>0$.
In eq. (4.14) the function $\alpha^{n+1}(z, t)$ is taken outside the brackets, so that

$$
\begin{equation*}
\frac{\partial}{\partial t} D^{(n)}(t)=\int d z \int d z^{\prime} g\left(z, z^{\prime}\right) \alpha^{n+1}(z, t) f_{n}\left(\frac{\alpha\left(z^{\prime}, t\right)}{\alpha(z, t)}\right) \tag{4.16}
\end{equation*}
$$

Within the family of degradation functions, the time behaviour of the first order $D$-function is particularly simple for linear equations of motion. We specify (4.16) in this case

$$
\frac{\partial}{\partial t} D^{(1)}(t)=-\int d z \int d z^{\prime} g\left(z, z^{\prime}\right)\left\{\alpha(z, t)-\alpha\left(z^{\prime}, t\right)\right\}^{2}
$$

where we can replace $g\left(z, z^{\prime}\right)$ by $g^{s}\left(z, z^{\prime}\right)=\left(g\left(z, z^{\prime}\right)+g\left(z^{\prime}, z\right)\right) / 2$. Moreover, $D^{(1)}$ itself has a simple geometric interpretation, $D^{(1)}=\bar{\alpha} \cdot \bar{\alpha}$, being thus the square of the vector $\bar{\alpha}$, for which $\overline{1} \cdot \bar{\alpha}=1$.

It can be readily concluded from eq. (4.16), because of the properties of $f_{n}(\xi)$, that for indivisible systems, and for $n>0$,

$$
\begin{equation*}
\frac{\partial}{\partial t} D^{(n)}(t)<0, \text { unless } \frac{\alpha\left(z^{\prime}, t\right)}{\alpha(z, t)}=1 \text { for all } z, z^{\prime} \tag{4.17}
\end{equation*}
$$

In fact, suppose that $\dot{D}^{(n)}(t)=0$. Consider an arbitrary point $z_{a}$, where $\alpha=\alpha\left(z_{a}, t\right)$. According to eq. (4.16), all points $z_{1}$ for which $g^{s}\left(z_{a}, z_{1}\right) \neq 0$ must have $\alpha\left(z_{1}, t\right)=\alpha\left(z_{a}, t\right)$. The points $z_{1}$ communicate directly with other points $z_{2}$ which must have the same value of $\alpha$. Since the system is indivisible, the arbitrary point $z_{a}$ must communicate in this way with any other point $z_{b}$, such that $\alpha\left(z_{a}, t\right)=\alpha\left(z_{b}, t\right)$, from which follows eq. (4.17).

We have thus proved that all $D$-functions decrease monotonically towards their equilibrium value. The monotonic behaviour of entropy is also a consequence of (4.17). To be precise, the time derivative of entropy is
according to (4.10) obtained from (4.16) by division with $n$, letting $n \rightarrow 0$, whereby, in the integrand, $f_{n} / n \rightarrow f=\xi-1-\xi \log \xi$, i.e. one obtains the auxiliary function of Gibbs ${ }^{7}$ ).

Several conclusions may be drawn from (4.17). It follows, for instance, that any non-uniform function in $z$-space, normalized to unity, has a higher value of $D^{(n)}$ than the normalized uniform distribution, for any $n>0$. Further, we have proved previously that there is only one equilibrium of the linear equations of motion. It does, however, also follow from (4.17) that there could be no equilibrium solution other than the uniform distribution, because $\partial D^{(n)} / \partial t \neq 0$ for all other distributions.

## § 5. Connection to Differential Equations

We consider differential equations of first order in time and of first or higher order in space. Such differential equations have merits on their own, and can be considered as possible equations of motion obeying the constraints. Apart from this, they are often useful approximations to integral equations, and in diffusion phenomena they even lead to quite accurate solutions. The familiar approximation involved in a differential equation is that $G(x, y)$ is negligible unless $|x-y|$ is small. By expansion one may then obtain a differential equation in $x$, usually of second order.

We briefly discuss the limitations put on a differential equation by the constraints in $\S 2$. It turns out that differential equations can be of, at most, second order in space. The differential equations imply a trend towards equilibrium, with the notable exception of first order equations. We finally study the symmetry properties of the diffusion equation, and its use as an approximation to the integral equation.

## Basic Structure

When trying to find the possible structure of differential equations, one might start from the basic integral equation, (2.13). We prefer to use the equivalent procedure of introducing the initial four constraints of $\S 2$. In order to have simplicity of notation we consider the one-dimensional case. According to the first and fourth constraints, (2.1) and (2.4), we demand that, if the derivatives $\partial^{n} a(x, t) / \partial x^{n}$ are given, then the time derivative $\dot{a}(x, t)$ is known, being linear in the spatial derivatives. To finite order, $N$, we therefore find

$$
\begin{equation*}
\dot{a}(x, t)=\sum_{n=0}^{N} \lambda_{n}(x, t) \frac{\partial^{n}}{\partial x^{n}} a(x, t) \tag{5.1}
\end{equation*}
$$

In order to retain conservation explicitly, i.e. the second constraint, (2.2), we introduce $\dot{a}(x, t)$ as minus the divergence of the current density, (2.23),

$$
\begin{equation*}
\dot{a}(x, t)=-\frac{\partial}{\partial x} j(x, t) \tag{5.2}
\end{equation*}
$$

expanding the current in spatial derivatives of $a(x, t)$,

$$
\begin{equation*}
j(x, t)=-\sum_{n=0}^{N-1} \Lambda_{n}(x, t) \frac{\partial^{n}}{\partial x^{n}} a(x, t) \tag{5.3}
\end{equation*}
$$

The number of independent functions in (5.2), (5.3) is one less than in (5.1), giving the condition on the $\lambda_{n}$ 's,

$$
\begin{equation*}
\lambda_{n}(x, t)=\frac{\partial}{\partial x} \Lambda_{n}(x, t)+\Lambda_{n-1}(x, t) \tag{5.4}
\end{equation*}
$$

with $\Lambda_{N}=0$.
The freedom in the above scheme is strongly reduced by the third constraint, (2.3), demanding that a non-negative $a(x, t)$ remains non-negative at all later times. Suppose therefore that $a(x, t)=0$, and accordingly $a^{\prime}(x, t)=0, a^{\prime \prime}(x, t) \geq 0$. It should then follow that $\dot{a}(x, t) \geq 0$. This places no restrictions on $\lambda_{0}(x, t)$ or $\lambda_{1}(x, t)$, but $\lambda_{2}(x, t)$ must remain non-negative, $\lambda_{2}(x, t) \geq 0$.

Consider next the possibility of a differential equation of finite order $N$, i.e. (5.1), with $N>2$. We may suppose that, at a given time $t=0$,

$$
\begin{equation*}
a(x, t=0)=\frac{\left(x+C_{N} x^{N-1}\right)^{2}+x^{2 N-2}}{1+c^{2} x^{2 N}} \tag{5.5}
\end{equation*}
$$

This function is normalizable and it is positive everywhere, except at the origin, where $a(0,0)=0, a^{(N)}(0,0)=2 C_{N} \cdot N$ !, all lower spatial derivatives, except $a^{\prime \prime}(0,0)=2$, being zero. Therefore $\dot{a}(x=0, t=0)=\lambda_{2} \cdot 2+\lambda_{N} \cdot 2 C_{N} N$ !, and since $C_{N}$ may be chosen arbitrarily, the coefficient $\lambda_{N}$ in (5.1) must be $\lambda_{N}=0$, in order to fulfill always $\dot{a}(0,0) \geq 0$. The differential equation (5.1) therefore cannot be of higher than second order, if it obeys merely the first and third constraints. If we assume conservation, (5.2), we can only be concerned with the diffusion equation, or Fokker-Planck equation,

$$
\begin{equation*}
\dot{a}(x, t)=\frac{\partial}{\partial x} D(x, t) \frac{\partial}{\partial x} a(x, t)-\frac{\partial}{\partial x} w(x, t) a(x, t), \tag{5.6}
\end{equation*}
$$

with the current $j(x, t)=-D(x, t) a^{\prime}(x, t)+w(x, t) a(x, t)$, and where $D(x, t) \geq 0$.

In the case of multi-dimensional space the proof is completely analogous to the above one. The result is that one can only permit the following equation

$$
\begin{equation*}
\dot{a}(\vec{x}, t)=\sum_{i, k} \frac{\partial}{\partial x_{i}} D_{i k}(\vec{x}, t) \frac{\partial}{\partial x_{k}} a(\vec{x}, t)-\sum_{i} \frac{\partial}{\partial x_{i}} w_{i}(\vec{x}, t) a(\vec{x}, t) \tag{5.7}
\end{equation*}
$$

where the matrix $D_{i k}$ at any space-time point has non-negative eigenvalues, like $D$ in (5.6), because $\dot{a}$ must be non-negative when $a=0$. Note that we can always choose the matrix to be symmetric, $D_{i k}(\vec{x}, t)=D_{k i}(\vec{x}, t)$. With this choice there is a unique separation between the two terms in (5.7).

The impossibility of spatial derivatives of higher than second order is rather remarkable. It does not seem to be explicitly noted in connection with derivations of diffusion approximations. On the contrary, it is sometimes stated that higher order terms in an expansion are small and can be disregarded ${ }^{5)}$, or it is attempted to introduce explicitly a term of higher order $^{10)}$ (cf. also ref. 18, p. 238).

The above result shows that differential equations are not very flexible, and can hardly be expected to represent even the main general features of the basic integral equation. Quite apart from this conclusion, the actual kernels $G(x, y)$ with which we shall be concerned (cf. § 6) will often decrease comparatively slowly for $|x-y| \rightarrow \infty$, leading to e.g. a divergent moment $\left\langle x^{2}\right\rangle$ of the distribution. This does not fit in with a diffusion equation.

The equation for the conjugate field corresponding to (5.7) is easily obtained from (3.27)—by differentiation with respect to $t^{\prime}$ -

$$
\begin{equation*}
\dot{b}(\vec{x}, t)=-\sum_{i, k} \frac{\partial}{\partial x_{i}} D_{k i}(\vec{x}, t) \frac{\partial}{\partial x_{k}} b(\vec{x}, t)-\sum_{i} w_{i}(\vec{x}, t) \frac{\partial}{\partial x_{i}} b(\vec{x}, t) \tag{5.8}
\end{equation*}
$$

The first operator in (5.8) is equal to minus the first operator in (5.7) if $D_{i k}$ is symmetric. The second operator in (5.8) is equal to the second one in (5.7), provided $\operatorname{div} \vec{w}=0$.

Let us finally note that the diffusion equation may be considered as a singular operator to be added to the integral equation, because it only results from an integral equation by a limiting process. The integral equation (2.13), with a continuous $G(x, y, t)$, we denote as $\dot{a}=o_{i}(t)$. Similarly, the diffusion equation (5.7) is $\dot{a}=$ $o_{d}(t) a$. Within the present context the most general equation of motion, obeying the first four constraints, is $\dot{a}=o_{i}(t) \alpha+o_{d}(t) a$.

## Trend towards Equilibrium; Reversibility

We have previously shown, in $\S \S 3$ and 4 , that all systems with one equilibrium $a^{0}(x)>0$ tend towards this equilibrium if, in the integral equation, $G(x, y)$ does not vanish for all $y \neq x$. The diffusion equations constitute a somewhat singular limiting case. Let us consider the trend towards equilibrium by means of the degradation functions.

We may suppose, without essential loss of generality, that in (5.7) the equilibrium function $a^{0}(\vec{x})$ is a constant, corresponding to normal coordinates,

$$
\begin{equation*}
a^{0}(\vec{x})=\text { const., i. e. } \operatorname{div} \vec{w}(\vec{x})=0 \text {. } \tag{5.9}
\end{equation*}
$$

The latter equation shows that $a(\vec{x}, t)$ corresponds to the density of an incompressible liquid.

From (5.7) and (4.8) we find directly in a space of $m$ dimensions,

$$
\begin{align*}
& \frac{\partial}{\partial t} D^{(n)}(t)=\frac{\partial}{\partial t} \int_{e}^{(m)} d x(a(\vec{x}, t))^{n+1} \\
& \left.=(n+1) \int \begin{array}{c}
\bullet(m) \\
d x
\end{array} a^{n}(\vec{x}, t)\left\{\sum_{i, k} \frac{\partial}{\partial x_{i}} D_{i k}(\vec{x}, t) \frac{\partial}{\partial x_{k}} a(\vec{x}, t)-\sum_{i} \frac{\partial}{\partial x_{i}} w_{i}(\vec{x}, t) a(\vec{x}, t)\right\}\right\}  \tag{5.10}\\
& =-\sum_{i, k}(n+1) n \int_{\cdot}^{\bullet}{ }_{d}^{(m)} a^{n-1}(\vec{x}, t) D_{i k}(\vec{x}, t) \frac{\partial a(\vec{x}, t)}{\partial x_{i}} \frac{\partial a(\vec{x}, t)}{\partial x_{k}} \leq 0,
\end{align*}
$$

where we use that the current vanishes at the boundaries, or that the system is periodic. The equality sign in (5.10) holds only in equilibrium for an indivisible system, for positive eigenvalues of $D_{i k}$.

The proper diffusion equation is thus irreversible, like the integral equation. Still, there remains one singular exception since, if $D_{i k}=0$ everywhere, all degradation functions remain constant. The remaining reversible first order equations, fulfilling (5.9) for indivisible systems, are

$$
\begin{equation*}
\dot{a}(\vec{x}, t)=-\operatorname{div}[\vec{w}(\vec{x}, t) a(\vec{x}, t)], \operatorname{div} \vec{w}(\vec{x}, t)=0 \tag{5.11}
\end{equation*}
$$

It follows from (5.8) that the conjugate field also obeys (5.11). The eigenvalues $\lambda_{n}$ of (5.11) are purely imaginary and, as mentioned, all degradation functions are constant in time.

Eq. (5.11) is just of the kind with which one is concerned in a Hamiltonian description of the motion of an ensemble in classical phase space, with $\vec{x}=\left(x_{1}, \ldots, x_{2 N}\right)=\left(q_{1}, \ldots, q_{N}, p_{1}, \ldots, p_{N}\right)$. The' Hamiltonian equations of motion are inconveniently singular, in the sense that the least deviation from (5.11) brings about irreversibility.

It may be noted that the first order equation of motion (5.11) is the only possible one, if the first constraint is tightened. In fact, when the first four constraints are valid, the general equations (2.13) follow. Suppose here that the first constraint (2.1) is modified by the demand that $a\left(x^{\prime}, t^{\prime}\right)$ is determined by $a(x, t)$ not only for $t^{\prime}>t$, but also for $t^{\prime}<t$. It follows that for $x \neq y$ the kernel $G(x, y, t)$ is both nonnegative (from $t^{\prime}>t$ ) and non-positive (from $t^{\prime}<t$ ). We are then left with the singular case of infinitely narrow $G$, i.e. the differential equation (5.7). But here, again, the eigenvalues of $D_{i k}$ must be both non-negative and non-positive. There only remains first order equations, i.e. (5.11) if, e.g., the system is indivisible.

## One-dimensional Diffusion Equation

Let us study the one-dimensional diffusion equation, (5.6). It is worth while to consider this case in detail, although it lacks some of the features belonging to multi-dimensional spaces.

We assume that $D$ and $w$ are independent of time, and that $D>0$ everywhere within the system. Suppose that the boundary conditions demand zero current at the boundaries. The equilibrium then corresponds to zero current throughout, or $D(x) a^{0^{\prime}}(x)=w(x) a^{0}(x)$. We transform to normal coordinates and obtain, with $d z=a^{0}(x) d x$,

$$
\begin{equation*}
\dot{\alpha}(z, t)=\frac{\partial}{\partial z} \mathscr{D}(z) \frac{\partial}{\partial z} \alpha(z, t) \tag{5.12}
\end{equation*}
$$

where

$$
\mathscr{D}(z)=D(x)\left(a^{0}(x)\right)^{2}, \quad a^{0}(x)=\exp \left\{\int^{x} d x^{\prime} w\left(x^{\prime}\right) / D\left(x^{\prime}\right)\right\}
$$

The term containing $w$ has thus disappeared, and the equation of motion for $\beta(z, t)$ is according to (5.8) given by (5.12), with opposite sign. One may easily verify that the eigenvalues $\lambda_{v}$ are real. Moreover, we have found, in (5.10), that (5.12) tends towards equilibrium.

Show next that (5.12) leads to reversibility in space, in the sense stated in (3.36). The propagator $T$ defined in (3.27) is $T\left(z_{1}, t_{1} ; z_{2}, t_{2}\right)=$ $=T\left(z_{1}, z_{2}, t_{1}-t_{2}\right)$. Therefore the equation of motion

$$
\frac{\partial}{\partial \tau} T\left(z_{1}, z_{2}, \tau\right)=\frac{1}{2}\left(\frac{\partial}{\partial z_{1}} \mathscr{D}\left(z_{1}\right) \frac{\partial}{\partial z_{1}}+\frac{\partial}{\partial z_{2}} \mathscr{D}\left(z_{2}\right) \frac{\partial}{\partial z_{2}}\right) T\left(z_{1}, z_{2}, \tau\right)
$$

is symmetric in $z_{1}$ and $z_{2}$. Since $T\left(z_{1}, z_{2}, 0\right)=\delta\left(z_{1}-z_{2}\right)$, one finds macroscopic reversibility in space

$$
\begin{equation*}
P_{\alpha}\left(z_{1} \rightarrow z_{2}, \tau\right)=T\left(z_{2}, z_{1}, \tau\right)=T\left(z_{1}, z_{2}, \tau\right)=P_{\alpha}\left(z_{2} \rightarrow z_{1}, \tau\right) \tag{5.13}
\end{equation*}
$$

Note that (5.13) and the previous conclusions drawn from (5.12) are valid also in the multi-dimensional case if $\vec{w}=0$ and $D_{i k}=D_{k i}$ in (5.7).

The equation (5.12) is therefore so far in accord with an integral equation with microscopic reversibility in space, $g\left(z, z^{\prime}\right)=g\left(z^{\prime}, z\right)$. If $g\left(z, z^{\prime}\right)$ is asymmetric, eq. (5.12) becomes a less appropriate approximation.

In (5.12) we considered a system with closed boundaries, and therefore the $w$-term disappeared. If the system instead has periodic boundary conditions, the $w$-term in (5.6) does remain and is connected with the antisymmetric part of $g\left(z, z^{\prime}\right)$. A diffusion approximation to a one-way integral equation is mentioned in § 6, cf. (6.19) and Fig. 3.

## Diffusion Approximation

The diffusion approximation is not completely well-defined. Let us indicate one way of deriving its coefficients. We suppose that $G\left(\vec{x}, \vec{x}^{\prime}\right)$ is given in eq. (2.14), but that the equilibrium need not be known. The assumption belonging to a diffusion approximation is that the kernel $G$ must decrease rapidly when $\left|\vec{x}-\vec{x}^{\prime}\right|$ increases, whereas $G$ varies slowly with change of $\left|\vec{x}+\vec{x}^{\prime}\right|$. We therefore introduce new variables, $\vec{\xi}=\left(\vec{x}+\vec{x}^{\prime}\right) / 2$ and $\vec{\eta}=\vec{x}-\vec{x}^{\prime}$, writting $G\left(\vec{x}, \vec{x}^{\prime}\right) \equiv Q(\vec{\xi}, \vec{\eta})$. Since $Q=Q(\vec{x}-\vec{\eta} / 2, \vec{\eta})$, we may expand in powers of $\vec{\eta}$ in the former coordinate which varies slowly with $\vec{\xi}=\vec{x}-\vec{\eta} / 2$. In the integral equation

$$
\dot{a}(\vec{x}, t)=\int d^{(m)} \eta\{Q(\vec{x}-\vec{\eta} / 2, \vec{\eta}) a(\vec{x}-\vec{\eta}, t)-Q(\vec{x}-\vec{\eta} / 2,-\vec{\eta}) a(\vec{x}, t)\}
$$

we then expand, to second order in $\eta$. The result is eq. (5.7) with

$$
\left.\begin{array}{c}
D_{i k}(\vec{x})=\frac{1}{2} \int d^{(m)} \eta G\left(\vec{x}+\frac{\vec{\eta}}{2}, \vec{x}-\frac{\vec{\eta}}{2}\right) \eta_{i} \eta_{k} \\
\vec{w}(\vec{x})=\int d^{(m)} \eta G\left(\vec{x}+\frac{\vec{\eta}}{2}, \vec{x}-\frac{\vec{\eta}}{2}\right) \vec{\eta}, \text { where } G(\vec{x}+\vec{\eta} / 2, \vec{x}-\vec{\eta} / 2)=Q(\vec{x}, \vec{\eta}) . \tag{5.14}
\end{array}\right\}
$$

The approximation (5.14) appears acceptable, but it usually does not lead to the exact equilibrium distribution, $a^{0}(\vec{x})$. Thus, consider a one-dimensional integral equation and suppose that $a^{0}(x)=$ const. with zero current at the boundaries. If $G$ is symmetric, one does obtain (5.12) from (5.14), but if $G$ is not symmetric there appears a $w$-term, as implying a non-uniform equilibrium distribution in the diffusion approximation.

## § 6. Examples of Analytic Solutions

This chapter is devoted to exact solutions of the simplest integral equation for continuum variables. The advantages of these examples are threefold. They correspond to typical cases within atomic collisions. They allow solutions of neighbouring equations by perturbation methods. But, foremost, they give a direct insight in the integral equations, showing for instance the similarities and dissimilarities to differential equations.

We consider mainly two extremes. One is symmetric kernels of indivisible systems, as exemplified by multiple scattering at small angles. The other concerns one-way systems, connected with energy loss distributions of energetic particles. Finally, we solve an example of multiple scattering with inclusion of large angles.

## Elementary Basic Systems

The simplest kind of continuum systems is the one with displacement invariance in space, cf. eq. (2.6), corresponding to validity of all of the six constraints in $\S 2$. It follows that $g(x, y)=g(x-y)$, and the equilibrium solution is in fact $\alpha^{0}=$ const. for $g=g(|x-y|)$. Note here that we consider primarily the one-dimensional case and, in order to secure simplicity of the analysis, we impose the mild condition of periodicity with an arbitrary long period $L$. The integral equation is, with $g(\eta)$ real and non-negative

$$
\begin{equation*}
\dot{\alpha}(x, t)=\int d \eta g(\eta)\{\alpha(x-\eta, t)-\alpha(x, t)\} \tag{6.1}
\end{equation*}
$$

and that of the conjugate field

$$
\begin{equation*}
\dot{\beta}(x, t)=-\int d \eta g(-\eta)\{\beta(x-\eta, t)-\beta(x, t)\} . \tag{6.2}
\end{equation*}
$$

Because of displacement invariance the eigenfunctions of the field are plane waves

$$
\begin{equation*}
\alpha_{k}(x)=\exp (+i k x), \quad \beta_{k}(x)=\exp (-i k x), \tag{6.3}
\end{equation*}
$$

where $k=2 \pi n / L$. The eigenfunctions obey $\int d x \beta_{k}(x) \alpha_{l}(x)=L \cdot \delta_{k, l}$, and $\beta_{k}=\alpha_{-k}$.

The eigenvalues are, according to (3.15),

$$
\begin{equation*}
\lambda(k)=\int d \eta g(\eta)\left(1-e^{-i k \eta}\right) . \tag{6.4}
\end{equation*}
$$

Apparently, if $g(\eta)$ is symmetric, i.e. $g(\eta)=g(-\eta)$, the eigenvalues are real and $\lambda(k)=\lambda(-k)$. If there is asymmetry, the eigenvalues are complex
numbers, and $\lambda(k)=\lambda^{*}(-k)$. The case $k=0$ corresponds to equilibrium, with $\lambda(0)=0$. The other eigenvalues have a real part greater than zero.

As to asymptotic behaviour, it is apparent that $g(\eta)$ must decrease faster than $|\eta|^{-1}$ for $|\eta| \rightarrow \infty$, in order that the $\lambda_{k}$ converge. Similarly, for $|\eta| \rightarrow 0$, the symmetric part of $g(\eta)$ must diverge less than $|\eta|^{-3}$, whereas the asymmetric part must diverge slower than $|\eta|^{-2}$. The fundamental solution of (6.1) is the propagator, $T(x, t)$, which for $t=0$ is $T(x, 0)=\delta(x)$. According to (6.1), (6.3) and (6.4) we find for $t \geq 0$,

$$
\begin{equation*}
T(x, t)=\frac{1}{L} \sum_{k} e^{i k x} e^{-\lambda(k) t} \tag{6.5}
\end{equation*}
$$

In the solutions in the following we consider $L$ as infinitely large in (6.4) and (6.5). We replace the summation (6.5) by an integration,

$$
T(x, t)=\frac{1}{2 \pi} \int_{-\infty}^{\infty} d k e^{i k x} e^{-\lambda(k) t}
$$

The seemingly innocent transition from (6.5) to (6.5') is not without consequences for the properties of some systems, because the properties depend on the boundary conditions. When (6.5) is applied exactly, the field will return through the periodic boundary, and there will always be an equilibrium $\alpha^{0}=1 / L$. If $g$ is asymmetric, the equilibrium has an internal current in the system, and even a one-way system becomes indivisible. If we use (6.5'), however, the field does not return, and the system is an open one. In this case there is uniform equilibrium for a symmetric $g$, but not for one-way systems. This feature, together with a Galilei transformation of one-way systems, is discussed on p. 39, cf. (6.20). Although one thus finds noteworthy differences between (6.5) and (6.5'), it should be remembered that in practice the solutions of $(6.5)$ and $\left(6.5^{\prime}\right)$ do not differ for finite times $t$ and large $L$.

The simplest choice of $g$ is the power law

$$
\begin{equation*}
g_{n}(\eta)=\frac{C_{n}}{|\eta|^{1+n}} \tag{6.6}
\end{equation*}
$$

We distinguish between the symmetric case

$$
\begin{equation*}
g_{n}^{s}(\eta)=g_{n}^{s}(-\eta)=g_{n}(\eta), \quad 0<n<2 \tag{6.7}
\end{equation*}
$$

the possible range of $n$ being indicated, and the asymmetric one-way case

$$
g_{n}^{a}(\eta)=\left\{\begin{array}{cl}
g_{n}(\eta), & \eta>0  \tag{6.8}\\
0, & \eta<0
\end{array} \quad 0<n<1\right.
$$

We can now derive $\lambda(k)$, so that it only remains to integrate (6.5'). In the symmetric case we obtain from eqs. (6.6), (6.7) and (6.4) ${ }^{8)}$

$$
\begin{equation*}
\lambda_{n}^{s}(k)=|k|^{n} \cdot A_{n}^{s}, \quad A_{n}^{s}=2 C_{n} \frac{\Gamma(1-n)}{n} \cos \frac{\pi}{2} n=C_{n} \frac{\pi}{\Gamma(n+1) \sin \frac{\pi}{2} n}, \tag{6.9}
\end{equation*}
$$

where $0<n<2$. Correspondingly, in the asymmetric case, from eqs. (6.6), (6.8) and (6.4), for $k>0$,

$$
\begin{equation*}
\lambda_{n}^{a}(k)=|k|^{n} A_{n}^{a}, \quad A_{n}^{a}=C_{n} \frac{\Gamma(1-n)}{n} \cdot \exp \left(\frac{i \pi}{2} n\right), \tag{6.10}
\end{equation*}
$$

where $0<n<1$, and $\lambda_{n}^{a}(-k)=\left(\lambda_{n}^{a}(k)\right)^{*}$.
The simple structure of solutions for power law kernels may be obtained directly from dimensional arguments. In fact, note that since $C_{n}$ in eq. (6.6) has the dimensions $x^{n} t^{-1}$, the corresponding propagators must be of type of $T(x, t)=f_{n}\left(x^{n} / C_{n} t\right) x^{-1}$. The semi-group formed by such propagators is thus a stable one ${ }^{6)}$. Stable semi-groups are familiar in the mathematical literature, and among the examples to be presented below at least several are well-known in e.g. probability theory ${ }^{6)}$.

At this point we may illustrate the formulae by an example. Suppose that an energetic ion moves a small distance through a substance, losing a relatively small amount of energy by successive collisions. The distance, or the time elapsed, may represent $t$ in the above equations. The differential cross section times the density of atoms is equivalent to $g(\eta) d \eta$. In the case of multiple scattering $g$ is symmetric, cf. also p . 39. The $x$-component of the scattering angle in a single collision is $\vartheta_{x} \propto \eta$, the $x$-component of the total angle being $\psi_{x} \propto x$. It is assumed that $\psi_{x}\langle<1$ and $\vartheta_{x}$ << 1. A particle with initial angle 0 has therefore, at time $t$, the distribution (6.5'). The formulae (6.6) and (6.7) are then power law scattering ${ }^{15)}$, where Rutherford scattering is the limiting disallowed case at small angles, $n=2$. In fact, eq. (6.6) corresponds approximately to classical scattering in repulsive power law potentials $\propto R^{-s}$, with $n=2 / s$, so that $1<s<\infty$ is equivalent to the condition (6.7).

Next, consider the energy loss distribution of the ion. The individual energy loss, $\eta$, has a one-sided distribution given by (6.8). The total energy loss, $x$, is then distributed according to ( $6.5^{\prime}$ ). The above power law angular distribution corresponds to $n=1 / s$, so that, again, Rutherford scattering is the upper limit $n=1$ in (6.8), and $1<s<\infty$ is the allowed region in (6.8).

Thus, at low angles and for small relative energy losses the power law formula (6.6) serves as a useful basis. In practice, the above formalism without (6.6) has been used in numerical studies of the more complicated case of multiple scattering by Thomas-Fermi type screened Coulomb potentials by Molière ${ }^{17) \text {, cf. also }}$

Scott ${ }^{18)}$ and Meyer ${ }^{16)}$. An energy loss distribution was studied by Landau ${ }^{11)}$, in the important but again more complicated case of Rutherford scattering ( $n=1$ in (6.8)) with a cut-off at low energy losses.

## Symmetric Distribution, $n=1$

It is evident that the simplest distributions $T(x, t)$ will result if, in eq. (6.6), $n$ is an integer or a fraction of low order. The symmetric case with $n=2$, i.e. Rutherford scattering, is divergent, but would have led to a Gaussian distribution in $\left(x / t^{1 / 2}\right)$, according to eqs. (6.5 ) and (6.9). It is replaced by the second order diffusion equation in $\S 5$. Similarly, the asymmetric case with $n=1$ is again Rutherford scattering and divergent. In its place appears the first order differential equation in $\S 5$.

For integer $n$ we are left with the symmetric case and $n=1$. This is apparently multiple scattering with $s=2$, i. e. closely corresponding to scattering by a repulsive $R^{-2}$-potential. From eq. (6.9) we get $\lambda_{1}^{s}(k)=|k| C_{1} \pi$, and by integration of eq. $\left(6.5^{\prime}\right)$, for $t>0$,

$$
\begin{equation*}
T_{1}^{s}(x, t)=\frac{C_{1} t}{x^{2}+\pi^{2} C_{1}^{2} t^{2}} \tag{6.11}
\end{equation*}
$$

This distribution occurs in numerous connections. It is known as the Cauchy distribution ${ }^{6)}$. In physical problems it is particularly familiar as a BreitWigner formula. The width of the distribution (6.11) increases proportionally to time. If $x \gg \pi C_{1} t$, the propagator is $\sim C_{1} t x^{-2}$, i. e. determined by a single scattering process from the origin. The system is indivisible with uniform equilibrium, according to eq. (6.1). Correspondingly, we find that, for arbitrary $x_{1}$ and $x_{2}, T\left(x_{1}, t\right) / T\left(x_{2}, t\right) \rightarrow 1$ for $t \rightarrow \infty$.

We find that eq. (6.11) obeys a second order differential equation of Laplacian type

$$
\begin{equation*}
\left(\frac{\partial^{2}}{\partial x^{2}}+\frac{1}{\pi^{2} C_{1}^{2}} \frac{\partial^{2}}{\partial t^{2}}\right) T_{1}^{s}(x, t)=0, \quad t>0 \tag{6.12}
\end{equation*}
$$

The integral equation in the present case thus picks out one solution of a second order differential equation in time.

It may finally be noted that the propagator corresponding to (6.11) is readily found in a space of dimension $v>1$. The propagator is in fact proportional to $C_{1} t \cdot\left(r^{2}+\pi^{2} C_{1}^{2} t^{2}\right)^{-\frac{v+1}{2}}$.


Fig. 1. Symmetric stable distributions for $n=1$, (6.11), and $n=1 / 2$, (6.15), normalized to unity. The abscissa is chosen as $y=x /\left(C_{1} t \pi\right)$ for $n=1$, and $y=x /\left(4 C_{\frac{1}{2}}^{2} t^{2}\right)$ for $n=1 / 2$.

One-way Distribution, $n=1 / 2$
In the asymmetric one-way case, where $0<n<1$, the simplest case must be $n=1 / 2$. According to eq. (6.10) one obtains $\lambda_{\frac{1}{2}}^{a}=|k|^{\frac{1}{2}} C_{\frac{1}{2}}(2 \pi)^{\frac{1}{2}}(1+i)$, $k>0$. By integration of eq. (6.5'),

$$
\begin{equation*}
T_{\frac{1}{2}}^{a}(x, t)=\frac{C_{\frac{1}{2}} t}{x^{\frac{3}{2}}} \exp \left(-\frac{\pi C_{\frac{1}{2}}^{2} t^{2}}{x}\right), \quad x \geq 0 \tag{6.13}
\end{equation*}
$$

For large $x$, the distribution is $\sim C_{\frac{1}{2}} t x^{-\frac{3}{2}}$, and therefore already the first moment, $\langle x\rangle$, diverges. The distribution has a maximum at $x_{p}=2 \pi C_{\frac{1}{2}}^{2} t^{2} / 3$, moving with an acceleration $g=4 \pi C_{\frac{1}{2}}^{2} / 3$. The distribution (6.13) is shown in Fig. 2 together with (6.16).

The propagator (6.13), when considered as an energy loss distribution, as described previously, corresponds to $s=2$. It thus represents an energy loss distribution associated with the multiple scattering distribution (6.11).


Fig. 2. Stable one-way distributions for $n=1 / 2$, (6.13), and $n=1 / 3$, (6.16), normalized to unity. The abscissa is chosen as $y=x /\left(\pi C_{\frac{1}{2}}^{2} t^{2}\right)$ for $n=1 / 2$, and $y=$ const $\cdot x /(C t)^{3}$ for $n=1 / 3$. The scaling for $n=1 / 3$ is arbitrarily chosen to give equal heights of the two curves.

## Symmetric Distribution, $n=1 / 2$

The symmetric distributions are, as it seems, less simple than the asymmetric ones with the same index $n$. For $n=1 / 2$, the symmetric propagator becomes of type of Fresnel's integrals (cf. ref. 1). In fact, the Fresnel $g$ function is defined as

$$
\left.\begin{array}{c}
g(z)=\left[\frac{1}{2}-C(z)\right] \cos \left(\frac{\pi z^{2}}{2}\right)+\left[\frac{1}{2}-S(z)\right] \sin \left(\frac{\pi}{2} z^{2}\right), \\
C(z)=\int_{0}^{\alpha} \cos \left(\frac{\pi}{2} y^{2}\right) d y, \quad S(z)=\int_{0}^{z} \sin \left(\frac{\pi}{2} y^{2}\right) d y . \tag{6.14}
\end{array}\right\}
$$

The $g$-function is a smoothly decreasing function. It is tabulated in ref. 1; a crude estimate is $g(z) \approx\left(2+4 z+\pi^{2} z^{3}\right)^{-1}$.

The symmetric propagator for $n=1 / 2$ becomes, in terms of the Fresnel $g$-function,

$$
T_{\frac{1}{2}}^{s}(x, t)=\frac{2 C_{\frac{1}{2}} t}{|x|^{\frac{3}{2}}} g\left\{\begin{array}{l}
2 C_{\frac{1}{2}} t  \tag{6.15}\\
\left.|x|^{\frac{1}{2}}\right\}
\end{array}\right\} .
$$

This function is shown together with eq. (6.11) in Fig. 1. Like eq. (6.11), it tends towards a uniform distribution for $t \rightarrow \infty$, and the tails of $T_{\frac{1}{2}}^{\delta}$ correspond to single scattering.

## One-way Distribution, $n=1 / 3$

The index $n=1 / 3$ for the asymmetric distribution implies $\lambda_{\frac{1}{3}}^{a}=|k|^{\frac{1}{3}} \cdot C_{\frac{1}{3}} \Gamma(2 / 3)\left(3^{\frac{1}{2}}+i\right) 3 / 2$. The one-third power of $|k|$ indicates connection with Airy functions, and a somewhat lengthy calculation yields in fact, for $x \geq 0$,

$$
\begin{gather*}
T_{\frac{1}{3}}^{a}(x, t)=\frac{C t}{x^{4}} A i\left(\frac{C t}{x^{\frac{1}{3}}}\right),  \tag{6.16}\\
C=C_{\frac{1}{3}} 3^{\frac{2}{3}} \Gamma(2 / 3)=C_{\frac{1}{3}} / A i(0),
\end{gather*}
$$

$\operatorname{Ai}(z)$ being the Airy function ${ }^{1)}$. The distribution is shown in Fig. 2. Its general behaviour is somewhat similar to eq. (6.13), but the $x$-coordinates expand as $t^{3}$.

Apart from the above examples a comparatively simple further case is $T_{\frac{3}{2}}^{s}(x, t)$, which must decrease as $|x|^{-5 / 2}$ at large $|x|$. It is intimately connected with the so-called Holtsmark distribution ${ }^{4)}$, but we shall not study it here.

## One-way Distribution, $\mathrm{n}=1 / 2$, with Screening

The power law scattering (6.6) is a quite special example of displacement invariance. For one, the moments, such as $\left\langle x^{2}\right\rangle$, are divergent. It is then not easy to compare with a diffusion equation approximation. Next, one-way distributions with finite $\langle x\rangle$ have a constant average velocity, and the corresponding transformation to moving coordinates is of interest. In many practical cases, like energy loss distribution, there will in fact be an upper limit beyond which $g(\eta)=0$.

Let us therefore briefly study a simple example of screened power law distribution, where $g(\eta)$ in (6.1) is the one-way distribution

$$
\begin{equation*}
g(\eta)=\frac{C}{\eta^{\frac{3}{2}}} e^{-\alpha \eta}, \quad \eta>0 . \tag{6.17}
\end{equation*}
$$

This corresponds to the case (6.8) with $n=1 / 2$, as studied above, but now with screening given by the constant $\alpha$. Transform to dimensionless variables $\xi$ and $\tau$ in place of $x$ and $t$,


Fig. 3. Screened one-way distribution, (6.18), and its diffusion approximation (6.19), as functions of space, $\xi$, and time, $\tau$. The asymmetric curves are the exact screened distributions; the symmetric curves represent the diffusion approximation. The two full-drawn curves correspond to time $\tau=1 / 2$, and the dashed curves correspond to time $\tau=3 / 2$. The exact distribution always intersects the diffusion distribution at its maximum.

$$
\xi=x \alpha, \quad \tau=C t \cdot(\pi \alpha)^{\frac{1}{2}} .
$$

By integration of (6.4) and (6.5') we get from (6.17)

$$
\begin{equation*}
T(\xi, \tau)=\frac{\tau}{\pi^{\frac{1}{2} \xi^{\frac{3}{2}}}} \exp \left\{-\frac{(\tau-\xi)^{2}}{\xi}\right\} . \tag{6.18}
\end{equation*}
$$

The distribution (6.18) is shown in Fig. 3 for two values of the time variable, $\tau=1 / 2$ and $\tau=3 / 2$. The average velocity of the distribution is constant, and in fact $\langle\xi\rangle=\tau$. The average square deviation increases with time as $\left\langle\xi^{2}\right\rangle-\langle\xi\rangle^{2}=\tau / 2$. The most probable point at a given time is $\xi_{p}(\tau)=$ $=-3 / 4+\left(9 / 16+\tau^{2}\right)^{1 / 2}$, and is initially accelerated but tends towards having constant velocity, $\xi_{p}(\tau) \rightarrow \tau-3 / 4$.

The diffusion approximation (5.14) to the integral equation is determined by the above two moments. The solution of the diffusion equation is a travelling Gaussian distribution,

$$
\begin{equation*}
T_{\mathrm{diff}}(\xi, \tau)=\frac{1}{\pi^{\frac{1}{2}} \tau^{\frac{1}{2}}} \exp \left(\frac{-(\xi-\tau)^{2}}{\tau}\right) \tag{6.19}
\end{equation*}
$$

The diffusion approximation (6.19) is shown together with (6.18) in Fig. 3, for the same values of $\tau$. The deficiencies of $T_{\text {diff }}$ are not merely that, for small $\tau$, a substantial part of the function is in the disallowed region $\xi<0$, but it does not show the skewness of (6.18), for which the maximum $\xi_{p}$ remains a distance $3 / 4$ behind the maximum of $T_{\text {diff }}$, asymptotically.

Although there is displacement invariance, and $\alpha(x, t)=$ const. is a solution of eq. (6.1), this is not an equilibrium solution. That is because (6.7) is a one-way system, and $\alpha=$ const. corresponds to a constant current through the system, which therefore is not isolated. In fact, the ratio $T\left(\xi_{1}, \tau\right) / T\left(\xi_{2}, \tau\right)$ at any two fixed points, $\xi_{1}<\xi_{2}$, tends to zero for $\tau \rightarrow \infty$. It is, however, natural to transform to a coordinate system moving with the above constant velocity, i.e. $\xi^{\prime}=\xi-\tau$. In the $\xi^{\prime}$-coordinates the solution $\alpha=$ const. has no current. We have in fact an isolated indivisible system. In these coordinates both (6.18) and (6.19) tend towards the equilibrium.

The general equation (6.1) can thus be transformed to an isolated rest system

$$
\begin{equation*}
\dot{\alpha}\left(x^{\prime}, t\right)=\int d \eta g(\eta)\left\{\alpha\left(x^{\prime}-\eta, t\right)-\alpha\left(x^{\prime}, t\right)+\eta \frac{\partial}{\partial x^{\prime}} \alpha\left(x^{\prime}, t\right)\right\}, \tag{6.20}
\end{equation*}
$$

provided the velocity $w=\int d \eta g(\eta) \eta$ is convergent. Note that the transformation (6.20) is applicable both for a periodic system and for an open infinite one.

## Angular Distribution, $n=1$

The previous examples of symmetric systems, if applied to multiple scattering, are limited to small angles. Let us show, by means of an example, how the treatment may be extended to large angles. We still suppose that the energy loss of the particle is small within the distances in question. This means that cross sections are time-independent. If $v, N$ and $d \sigma$ are velocity, density of atoms and differential cross section, we can write

$$
\begin{equation*}
v N d \sigma=d \Omega S(\vartheta) \tag{6.21}
\end{equation*}
$$

Here the differential solid angle is $d \Omega=d \varphi d \cos \vartheta$, and $\vartheta$ the angle of deflection, while $\varphi$ is the azimuthal angle. The angular distribution of current is $S(\vartheta)$, depending only on the angle of deflection.

We ask for the propagator $T(\psi, t)$, i.e. the angular distribution at time $t$, if the angle is $\psi=0$ at $t=0$. It obeys the integral equation

$$
\begin{equation*}
\frac{\partial}{\partial t} T(\psi, t)=\int_{0}^{2 \pi} d \varphi \int_{-1}^{+1} d(\cos \vartheta) S(\vartheta)\left\{T\left(\psi^{\prime}, t\right)-T(\psi, t)\right\} \tag{6.22}
\end{equation*}
$$

where $\psi^{\prime}$ is given by

$$
\cos \psi^{\prime}=\cos \psi \cos \vartheta+\sin \psi \sin \vartheta \sin \varphi .
$$

We expand $T$ in Legendre polynomials, which are the eigenfunctions of the problem. Hereby the integration over $\varphi$ leads to a factorization, and we obtain finally

$$
\begin{equation*}
2 \pi T(\psi, t)=\sum_{\nu=0}^{\infty}\left(\nu+\frac{1}{\underline{2}}\right) P_{\nu}(\cos \psi) \exp \left(-t \lambda_{v}\right), \tag{6.23}
\end{equation*}
$$

where the eigenvalues $\lambda_{v}$ are

$$
\begin{equation*}
\lambda_{v}=2 \pi \int_{-1}^{+1} d(\cos \vartheta) S(\vartheta)\left\{1-P_{\nu}(\cos \vartheta)\right\} . \tag{6.24}
\end{equation*}
$$

As to $S(\vartheta)$, we ask for an extrapolation of power law distributions (6.6). Let us consider merely the simplest case, corresponding to $n=1$, and put

$$
\begin{equation*}
S(\vartheta)=\frac{C_{1} 2^{-\frac{5}{2}}}{(1-\cos \vartheta)^{\frac{3}{2}}} . \tag{6.25}
\end{equation*}
$$

In fact, for $\vartheta \ll 1$, this becomes $S(\vartheta) \rightarrow\left(C_{1} / 2\right) \cdot \vartheta^{3}$, where $\vartheta=\left(\vartheta_{x}^{2}+\vartheta_{y}^{2}\right)^{1 / 2}$; integrating over $\vartheta_{y}$ we obtain exactly the one-dimensional scattering (6.6) with $n=1$.

From eqs. (6.25) and (6.24) one gets easily $\lambda_{\nu}=\pi \nu C_{1}$ and, finally performing the sum (6.23)

$$
\begin{equation*}
T(\psi, t)=\frac{1-e^{-2 \pi C_{1} t}}{4 \pi\left[\left(1-e^{-\pi C_{1} t}\right)^{2}+2 e^{-\pi C_{1} t}(1-\cos \psi)\right]^{3 / 2}} . \tag{6.26}
\end{equation*}
$$

When $C_{1} t \ll 1$, the main part of $T(\psi, t)$ is within small angles, and $T \approx\left(C_{1} t / 2\right)\left(\pi^{2} C_{1}^{2} t^{2}+\psi^{2}\right)^{-3 / 2}$, i.e. it becomes the two-dimensional version of eq. (6.11). For large values of $t$, the distribution (6.26) tends to the uniform distribution, in agreement with eq. (6.22) being an indivisible system, with equilibrium $T=(4 \pi)^{-1}$.

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# ELSE HØYRUP <br> ON TORUS MAPS AND ALMOST PERIODIC MOVEMENTS 

Det Kongelige Danske Videnskabernes Selskab Matematisk-fysiske Meddelelser 38, 10



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## Notations

$S^{n}$ : the $n$-sphere.
$E^{n}$ : the $n$-cell.
$T^{n}=S^{1} \times \ldots \times S^{1}$ ( $n$ factors) : the $n$-dimensional torus.
$\sim$ homeomorphic.
$\simeq$ homotopic, bijective equivalent, isomorphic.
$f_{\#}, f \#$ maps induced by $f$ in homology, cohomology.
$f_{*}, f^{*}$ maps induced by $f$ in homotopy, cohomotopy.

## Synopsis

In this paper I show that the cohomotopy groups of the $n$-dimensional torus $T n$ usually are direct sums of homotopy groups of spheres. Further, I investigate homotopy classification problems of continuous maps from $T n$ into other topological spaces - especially spaces with "nice" homotopy groups in the lower dimensions. The results are applied to some "reducibility problems" for torus maps and almost periodic movements - in particular I find conditions for almost periodic movements being almost periodically homotopic to periodic movements.

## Introduction

In 1954 H . Tornehave [4] investigated the following problem: In which topological spaces $X$ is every almost periodic movement $x=f(t)$ $(t \in \boldsymbol{R}=]-\infty, \infty[, x \in X)$ almost periodically homotopic to a periodic movement?

A(lmost) p (eriodic) homotopy between two a.p. movements $f_{0}(t)$ and $f_{1}(t)$ means that there exists a uniformly continuous family $f(t, v), v \in[0,1]$, of almost periodic movements starting with $f_{0}(t)$ and ending with $f_{1}(t)$.

Let $\mathscr{C}$ denote the class of metric spaces $X$ which are "continuously locally arewise connected" (see p. 21). Because every $C W$ complex is "continuously locally arcwise connected", $\mathscr{C}$ includes the class $\mathscr{C}$ ' of metrizable $C W$ complexes. $\mathscr{C}^{\prime}$ includes the class $\mathscr{C}^{\prime \prime}$ of locally compact polyhedrons. Remark: In this paper I only look at continuous maps between topological spaces, though I do not explicitely write continuous everywhere. Nor do I everywhere write that I assume my spaces different from the empty set.

A theorem ([4] p. 28) states that every a.p. movement $\tilde{f}(t)$ in a space $X \in \mathscr{C}$ corresponds to some rationally independent real numbers ( $\beta_{1}, \ldots, \beta_{n}$ ) and a continuous torus map $f: \boldsymbol{R}^{n} \rightarrow X$ ( $f$ is periodic in all the variables with the period $2 \pi$ ) in such a way that $\tilde{f}(t)$ is almost periodically homotopic to the almost periodic movement $f\left(\beta_{1} t, \ldots, \beta_{n} t\right)$.

A small correction and generalization of Theorem 13 in [4] gives:
Every almost periodic movement in $X \in \mathscr{C}$ is almost periodically homotopic to a periodic movement if and only if for every continuous torus map $f$ (of any dimension) into $X$ there exists a number $N \in \boldsymbol{N}$ so that $f \circ(\times N)$ is homotopic to a torus map into a closed curve in $X$, where $(\times N)\left(u_{1}, \ldots, u_{n}\right)=\left(N u_{1}, \ldots\right.$, $N u_{n}$ ).

Because of this theorem it is natural to look at the following problem: For which $X$ is every torus map (of any dimension) into $X$ homotopic to a torus map into a closed curve in $X$ ? H. Tornehave had some intuitive ideas
of how to solve the new problem: he thought it was a necessary (and if all the homotopy groups $\pi_{i}\left(X, x_{0}\right)$ are trivial for $i>1$, sufficient) condition that for all $x_{0} \in X$ every abelian subgroup of the fundamental group $\pi_{1}\left(X, x_{0}\right)$ is cyclic. (This is not quite correct). In this paper I shall find a partial solution of a more general problem.

Definition 1. Let $X$ be a topological space. An $n$-dimensional torus map $f: T^{n} \rightarrow X$ is called m-reducible iff it is homotopic to a continuous map $g$ through $T^{m}$, i.e. $T^{n} \rightarrow T^{m} \rightarrow X$, where $1 \leq m<n$ are the only interesting cases.

Definition 2. The space $X$ is called n-dimensionally m-reducible iff every n-dimensional torus map into $X$ is m-reducible.

Definition 3. The space $X$ is called m-reducible iff every torus map into $X$ (of any dimension) is m-reducible.

Definition 4. An a.p. movement $x=\tilde{f}(t)$ in $X$ is said to be of dimension $\leqq n$ iff it is a.p. homotopic to some $x=f\left(\beta_{1} t, \ldots, \beta_{n} t\right)$, where $\left(\beta_{1}, \ldots, \beta_{n}\right)$ are rationally independent real numbers and $f: T^{n} \rightarrow X$ is an n-dimensional torus map.

Definition 5. The a.p. movement $x=\tilde{f}(t)$ in $X$ of dimension $\leqq n$ is called a.p. m-reducible iff it is a.p. homotopic to an a.p. movement of dimension $\leq m$.

Definition 6. The space $X$ is called a.p. n-dimensionally m-reducible iff every a.p. movement in $X$ of dimension $\leq n$ is a.p. m-reducible.

Definition 7. The space $X$ is called a.p. m-reducible iff every a.p. movement in $X$ is a.p. m-reducible.

We have the following theorem:
Theorem 16. Let the almost periodic movement $x=\tilde{f}(t)$ in $X \in \mathscr{C}$ be a.p. homotopic to $f\left(\beta_{1} t, \ldots, \beta_{n} t\right)$, where $f: T^{n} \rightarrow X,\left(\beta_{1}, \ldots, \beta_{n}\right)$ rationally independent. Then
$\tilde{f}(t)$ is a.p. m-reducible iff $f \circ(\times N)$ for some $N$ is m-reducible.
I shall further study the following problems:

1) When is a given $n$-dimensional torus map $m$-reducible?

1a) When is a given a.p. movement $\tilde{f}(t)$ of dimension $\leq n$, a.p. m-reducible?
2) Which spaces $X$ are $n$-dimensionally $m$-reducible?

2a) Which spaces $X$ are a.p. $n$-dimensionally $m$-reducible?
3) Which spaces $X$ are $m$-reducible?

3a) Which spaces $X$ are a.p. m-reducible?
The case $m=1$ is of course of special interest.
My way through the problems is the following:
First I use obstruction theory in dealing ,with extension problems and homotopy classification problems of continuous functions from subspaces of $T^{n}$ into topological spaces. I shall not go beyond the primary obstruction because otherwise the problems get too complicated to be of use for my original problems.

Next I look at the special case $X=S^{p}$, the $p$-dimensional sphere. The set of homotopy classes of torus maps $T^{n} \rightarrow S^{p}, \pi^{p}\left(T^{n}\right)$, is called the $p$ dimensional cohomotopy set. For some $p$ and $n$ the set $\pi^{p}\left(T^{n}\right)$ is an abelian group which is called the $p$-dimensional cohomotopy group of $T^{n}$. I compute the cohomotopy groups by means of the homotopy groups of the spheres $\pi_{i}\left(S^{m}, s_{0}\right)$. Unfortunately, most of these homotopy groups are not yet known.

The homotopy groups of $T^{n}$, on the other hand, are very simple: the fundamental group is free abelian of rank $n: \pi_{1}\left(T^{n}, t_{0}\right) \simeq \boldsymbol{Z}^{n}$, and all the higher homotopy groups $\pi_{i}\left(T^{n}, t_{0}\right)(i>1)$ are zero. - In general we know that $\pi_{i}\left(X, x_{0}\right)(i>1)$ is an abelian group, while $\pi_{1}\left(X, x_{0}\right)$ is a group, but not always abelian.

The results obtained on the homotopy classification of torus maps into $X$, are applied to the torus reducibility problems and this leads to results on the a.p. reducibility problems. For some special topological spaces $X$ this gives simple results, but for further work on almost periodic movements my method does not seem fruitful because the homotopy classification problems soon become extremely complicated and the torus reducibility problems turn out to be more complicated than the a.p. reducibility problems.

I shall state the principal results in a form independent of the choice of basis point. The corresponding theorems in the paper will be stated only for a fixed basis point.

Theorem 18'. Let $x=\tilde{f}(t)$ be an almost periodic movement in $X \in \mathscr{C}$ corresponding to the torus map $f: T^{n} \rightarrow X$. If $\pi_{2}\left(X, x_{0}\right)=\ldots=\pi_{n}\left(X, x_{0}\right)=0$ for all $x_{0} \in X$, then a necessary and sufficient condition for $\tilde{f}$ to be a.p. m-reducible $(1 \leq m<n)$ is that $f_{*} \pi_{1}\left(T^{n}, t_{0}\right)$, which is a finitely generated abelian subgroup of $\pi_{1}\left(X, f\left(t_{0}\right)\right)$, has rank $\leqq m$.

Theorem 19'. Let $X \in \mathscr{C}$ and let $\pi_{i}\left(X, x_{0}\right)=0$ for all $x_{0} \in X, i>1$. Then a necessary and sufficient condition for $X$ to be a.p. m-reducible $(m \geq 1)$ is that for all $x_{0} \in X$ every abelian subgroup of $\pi_{1}\left(X, x_{0}\right)$ has rank $\leqq m$.

Remark: If $\pi_{1}\left(X, x_{0}\right)$ is itself abelian, the above condition on $\pi_{1}\left(X, x_{0}\right)$ is equivalent to: rank $\pi_{1}\left(X, x_{0}\right) \leq m$.

Theorem 20'. A necessary and sufficient condition for $X$ to be a.p. 1-reducible is that, for all $x_{0} \in X$, every abelian subgroup $G$ of $\pi_{1}\left(X, x_{0}\right)$ has rank $\leqq 1$ and that, for all $n>1$, the condition that $f_{*}, g_{*}: \pi_{1}\left(T^{n}, t_{0}\right) \rightarrow \pi_{1}\left(X, x_{0}\right)$ are conjugate implies that for some natural number $N$ the maps $f \circ(\times N), g \circ(\times N)$ are homotopic.

Theorem 21'. Let $X \in \mathscr{C}$ be an H-space (for instance a topological group) with $\pi_{1}\left(X, x_{0}\right)=\ldots=\pi_{p-1}\left(X, x_{0}\right)=0$ for all $x_{0} \in X$. Then a necessary condition for $X$ to be a.p. m-reducible is that for all $x_{0} \in X$ the rank of $\pi_{p}\left(X, x_{0}\right)$ is $\leqq\binom{ m}{p}$.

Theorem 22'. Let $X \in \mathscr{C}$ and let for all $x_{0} \in X$

$$
\pi_{1}\left(X, x_{0}\right)=\ldots=\pi_{p-1}\left(X, x_{0}\right)=\pi_{p+1}\left(X, x_{0}\right)=\ldots=\pi_{m}\left(X, x_{0}\right)=0 ;
$$

then a necessary condition for $X$ to be a.p. m-reducible is that for all $x_{0} \in X$ the rank of $\pi_{p}\left(X, x_{0}\right)$ is $\leqq\binom{ m}{p}$ if $p>1$, and that every abelian subgroup of $\pi_{1}\left(X, x_{0}\right)$ has rank $\leqq m$, if $p=1$.

## Chapter 1

## The Functions $\boldsymbol{F}, \boldsymbol{G}$, and $\boldsymbol{G}$ '

Definition. Let $X$ be a topological space with $x_{0} \in X$. Let $n \in \boldsymbol{N}$ and let $\pi$ be a group $($ abelian for $n>1)$. I call $X$ an m-space of type $(\pi, n)(m \in \boldsymbol{N} \cup$ $\{+\infty\}, m \geq n)$ when $X$ is path-connected and its homotopy groups in dimensions $\leq m$, except $\pi_{n}\left(X, x_{0}\right)$, are zero, while $\pi_{n}\left(X, x_{0}\right)$ is isomorphic to $\pi$.

A usual $(\pi, n)$ space is then the same as my $\infty$-space of type $(\pi, n)$.
Examples: $\quad T^{n}$ is an $\infty$-space of type $\left(\boldsymbol{Z}^{n}, 1\right)$, $S^{n}$ is an $n$-space of type $(\boldsymbol{Z}, n)$.

For all $n \in \boldsymbol{N}$ and all groups $\pi$ (abelian if $n>1$ ) there exists a topological space $X$ of type $(\pi, n)$ ([3] p. 426).

We shall now look at maps $T^{n} \xrightarrow{f} X$ where $X$ is path-connected and $x_{0} \in X$. We know that $f$ is homotopic to a map $f^{\prime}:\left(T^{n}, t_{0}\right) \rightarrow\left(X, x_{0}\right)$. Because we are interested only in the homotopy classes of maps $T^{n} \rightarrow X$ we shall always choose representatives $g$ of the homotopy classes for which $g\left(t_{0}\right)=x_{0}$, but we do not write this explicitely everywhere.

If we denote the homotopy classes of maps equivalent to $f: T^{n} \rightarrow X$ by $[f]$ and the set of these classes by $\left[T^{n}, X\right]$, then we know that a function

$$
F_{n}:\left[T^{n}, X\right] \rightarrow \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right) / \sim,
$$

where $\sim$ means conjugate, (if $\pi_{1}\left(X, x_{0}\right)$ is abelian, then this group is isomorphic to $\left.\pi_{1}\left(X, x_{0}\right)^{n}\right)$ is defined by:

$$
F_{n}[f]=\left\{f_{*}\right\} \text { (the conjugacy class of } f_{*} \text { ). }
$$

If we denote the homotopy class relative to $t_{0}$ of maps $\left(T^{n}, t_{0}\right) \rightarrow\left(X, x_{0}\right)$ equivalent to $f$ by $[f]_{t_{0}}$ and the set of these maps by $\left[T^{n}, t_{0} ; X, x_{0}\right]_{t_{0}}$, then we know that $F_{n}^{\prime}[f]_{t_{0}}=f_{*}$ defines a map

$$
F_{n}^{\prime}:\left[T^{n}, t_{0} ; X, x_{0}\right]_{t_{0}} \rightarrow \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right) .
$$

If $X$ is an $H$-space, we know that $\left[T^{n}, X\right]$ and $\left[T^{n}, t_{0} ; X, x_{0}\right]_{t_{0}}$ are groups and that $\pi_{1}\left(X, x_{0}\right)$ is abelian. In this case it is easy to see that $F_{n}$ and $F_{n}{ }^{\prime}$ are homomorphisms.

As a cell complex $T^{n}=S_{1}^{1} \times \ldots \times S_{n}^{1}$ consists of
1 0-dimensional cell $t_{0}$,
n 1-dimensional cells $S_{i}^{1}$ (circles), ... ,
$\binom{n}{p} \quad p$-dimensional cells $T_{i}^{p}=S_{i_{1}}^{1} \times \ldots \times S_{i_{p}}^{1}, \ldots$,
and $1 \quad n$-dimensional cell $T^{n}$.
Let $L$ be a subcomplex of $T^{n}$, and let $i_{*}: \pi_{1}\left(L, t_{0}\right) \rightarrow \pi_{1}\left(T^{n}, t_{0}\right)$ be induced by the inclusion map $i: L \rightarrow T^{n}$. Because $\pi_{1}\left(T^{n}, t_{0}\right) \simeq \pi_{1}\left(S_{1}^{1}, t_{0}\right) \oplus \ldots \oplus$ $\pi_{1}\left(S_{n}^{1}, t_{0}\right) \simeq \boldsymbol{Z}^{n}$ we have that $i_{*} \pi_{1}\left(L, t_{0}\right)$ is a direct summand in $\pi_{1}\left(T^{n}, t_{0}\right)$ with rank equal to the number $r$ of 1 -cells in $L$. We also have $\pi_{1}\left(L, t_{0}\right) \sim$ $\boldsymbol{Z} a_{1} * \ldots * \boldsymbol{Z} a_{r} / \sim$, where * denotes free product and $\sim$ means that two generators $a_{i}$ and $a_{j}$ commute when the corresponding 1 -cells in $L$ are sides of a 2-cell in $L$.


A homomorphism $\mathrm{h} \in \operatorname{Hom}\left(\pi_{1}\left(L, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right)$ is said to be extensible over $T^{n}$ iff there exists an $\tilde{h} \in \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right)$ with $\tilde{h} i_{*}=h$.

The statements in the following theorem are proved in [2], VI.
Theorem 1. Let $X$ be an m-space of type $(\pi, 1)$. Then $F_{n}$ and $F_{n}{ }^{\prime}$ are surjective if $m \geqq n-1$, and bijective if $m \geqq n$. Let $L \neq \varnothing$ be a subcomplex of $T^{n}$ and let $g: L \rightarrow X$ be a given map. Then the following 3 statements are equivalent for $m \geq n-1$ :
(i) $g$ is continuously extensible over $T^{n}$;
(ii) $g_{*} \in \operatorname{Hom}\left(\pi_{1}\left(L, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right)$ is extensible over $T^{n}$;
(iii) $g_{*}\left(\pi_{1}\left(L, t_{0}\right)\right)$ abelian.

If $g_{*}$ is extensible to $h \in \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right)$, then we can find an extension $f$ of $g$ with $f_{*}=h$.

Examples. Let $P^{m}$ denote the $m$-dimensional real projective space. Because $\pi_{1}\left(P^{m}, p_{0}\right) \simeq \boldsymbol{Z}_{2}$ for $m \geqq 2$ and $\pi_{i}\left(P^{m}, p_{0}\right)=0$ for $1<i<m$, while $\pi_{m}\left(P^{m}, p_{0}\right) \simeq \boldsymbol{Z}$, we have the bijections

$$
\left[T^{n}, P^{m}\right] \simeq \boldsymbol{Z}_{2}^{n} \simeq\left[T^{n}, t_{0} ; P^{m}, p_{0}\right]_{t_{0}} \text { for } n<m \text {. }
$$

We also have

$$
\left[T^{n}, S^{m}\right] \simeq 0 \simeq\left[T^{n}, t_{0} ; S^{m}, s_{0}\right]_{t_{0}} \text { for } n<m,
$$

and

$$
\left[T^{n}, T^{m}\right] \simeq \boldsymbol{Z}^{m \cdot n} \simeq\left[T^{n}, t_{0} ; T^{n}, t_{0}\right]_{t_{0}},
$$

where the two last bijections are group isomorphisms.
Remark. It is easy to see that $F_{n}$ surjective (injective) implies $F_{m}$ surjective (injective) if $m \leqq n$.

Let $\left(T^{n}\right)^{m}$ denote the $m$-dimensional skeleton of $T^{n}$ as a cell-complex. The absolute and relative (with respect to subcomplexes) homology- and cohomology groups of $T^{n}$ and $\left(T^{n}\right)^{m}$ are easily computed: With coefficients in an abelian group $G$ we have

$$
\begin{gathered}
H_{p}\left(T^{n} ; G\right) \simeq G^{\left({ }_{p}^{n}\right)} \simeq H^{p}\left(T^{n} ; G\right), \\
H_{p}\left(T^{n}, L ; G\right) \simeq G^{\left({ }_{p}^{n}\right)-i(p)} \simeq H^{p}\left(T^{n}, L ; G\right), \\
H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime} ; G\right) \simeq G^{\left({ }_{p}^{n}\right)-i^{\prime}(p)} \simeq H^{p}\left(\left(T^{n}\right)^{m}, L^{\prime} ; G\right),
\end{gathered}
$$

where $i(p)$ and $i^{\prime}(p)$ denote the number of $p$-cells in $L$ and $L^{\prime}$. As generators for the homology groups we can take the elements $\left\{\sigma_{i} \otimes g\right\}, g \in G$, where
$\sigma_{i}$ is a $p$-cell of $T^{n}, T^{n} \backslash L,\left(T^{n}\right)^{m} \backslash L^{\prime}$ respectively corresponding to a p-dimensional torus $T_{i}^{p}$ in $T^{n}$. As generators for the cohomology groups we can take the elements $\left\{f_{i}^{g}\right\}$, where $f_{i}^{g}$ is the homomorphism determined by $f_{i}^{g}\left(\sigma_{i}\right)=g$ and $f_{i}^{g}\left(\sigma_{j}\right)=0, j \neq i$.

Further, it is easy to see that $H^{p}\left(T^{n}, \boldsymbol{Z}\right)$ as an algebra is the exterior algebra over $\mathbb{Z}$ with $n$ generators in dimension 1 corresponding to the generators of $H^{1}\left(S_{i}^{1}\right)$.

The homomorphism

$$
h: H^{p}\left(\left(T^{n}\right)^{m}, L^{\prime} ; G\right) \rightarrow \operatorname{Hom}\left(H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime}\right) ; G\right)
$$

defined by $h\{f\}\{c\}=f(c)$ is an isomorphism. Generators in $\operatorname{Hom}\left(H_{p}\left(\left(T^{n}\right)^{m}\right.\right.$, $\left.\left.L^{\prime}\right) ; G\right)$ corresponding to the $\left\{f_{i}^{g}\right\}$ are the $f_{i}^{g}$ themselves.

Dividing the $p$-cells $\sigma_{i}$ into those in $\left(T^{n}\right)^{m} \backslash \mathrm{~L}$ and those in $L$ I find that

$$
\begin{aligned}
& H_{p}\left(\left(T^{n}\right)^{m} ; G\right) \simeq H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime} ; G\right) \oplus H_{p}\left(L^{\prime}, G\right) \\
& H^{p}\left(\left(T^{n}\right)^{m} ; G\right) \simeq H^{p}\left(\left(T^{n}\right)^{m}, L^{\prime} ; G\right) \oplus H^{p}\left(L^{\prime}, G\right)
\end{aligned}
$$

Thus the homomorphisms
$i^{\#} \in \operatorname{Hom}\left(H^{p}\left(\left(T^{n}\right)^{m} ; G\right) ; H^{p}\left(L^{\prime}, G\right)\right)$ and $j^{\#} \in \operatorname{Hom}\left(H^{p}\left(\left(T^{n}\right)^{m}, L^{\prime} ; G\right)\right.$,

$$
\left.H^{p}\left(\left(T^{n}\right)^{m} ; G\right)\right)
$$

induced by the inclusion maps $i: L^{\prime} \rightarrow\left(T^{n}\right)^{m}, j:\left(T^{n}\right)^{m} \rightarrow\left(\left(T^{n}\right)^{m}, L^{\prime}\right)$ are injective, and so are the corresponding homomorphisms between the homology groups $i_{\#}$ and $j_{\#}$.

Now, let $g: L^{\prime} \rightarrow X$ be a given map. Suppose $f:\left(T^{n}\right)^{m} \rightarrow X$ is an extension of $g$ and denote by $[f]_{L^{\prime}}$ the homotopy class relative to $L^{\prime}$ of maps $\left(T^{n}\right)^{m} \rightarrow X$ equivalent to $f$. By $\left[\left(T^{n}\right)^{m}, L^{\prime}, g ; X\right]_{L^{\prime}}$ we denote the set of these maps. Then there is a well-defined function

$$
G_{n, m, p}^{\prime}:\left[\left(T^{n}\right)^{m}, L^{\prime}, g ; X\right]_{L^{\prime}} \rightarrow \operatorname{Hom}\left(H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime}\right) ; H_{p}(X)\right)
$$

defined by $G_{n, m, p}^{\prime}[f]_{L^{\prime}}=f_{\# p} \mid H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime}\right)$. We observe that

$$
\operatorname{Hom}\left(H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime}\right) ; H_{p}(X)\right) \simeq\left\{\begin{array}{c}
\left(H_{p}(X)\right)^{\binom{n}{p}-i^{\prime}(p)} \text { if } p \leqq m \\
0
\end{array} \quad \text { if } p>m\right.
$$

Even if $X$ is an $H$-space, $G^{\prime}$ is not in general a homomorphism.
If $X$ is a $p$-space of type $\left(\pi_{p}, p\right)\left(\pi_{p}\right.$ abelian), we have the Hurewicz isomorphism $x: \pi_{p} \rightarrow H_{p}(X)$ and $G_{n, m, p}^{\prime}$ corresponds to

$$
G_{n, m, p}:\left[T^{n}, L^{\prime}, g ; X\right]_{L^{\prime}} \rightarrow \operatorname{Hom}\left(H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime}\right), \pi_{p}\right)
$$

where $G_{n, m}, p[f]_{L^{\prime}}=\varkappa^{-1} \circ f_{\# p} \mid H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime}\right)$. We know from the theory of obstruction that $\pi_{1}\left(X, x_{0}\right)=\ldots=\pi_{p-1}\left(X, x_{0}\right)=0 \Rightarrow f \mid\left(T^{n}\right)^{p-1} \simeq 0$, hence we can choose a map $f^{\prime}:\left(T^{n}\right)^{m} \rightarrow X$ with $f^{\prime} \simeq f$ and $f^{\prime} \mid\left(T^{n}\right)^{p-1}=x_{0}$. If $\sigma$ denotes a $p$-cell in $\left(T^{n}\right)^{m} \backslash L^{\prime}$, then $f^{\prime}(\partial \sigma)=x_{0}$ and $f^{\prime} \mid \sigma$ represents an element of $\pi_{p} \simeq\left[S^{p}, X\right]$. Because $\chi\left(\left[f^{\prime} \mid \sigma\right]\right)=f_{\# p}^{\prime}(\sigma)=f_{\# p}(\sigma)$ we have:

$$
G_{n, m, p}[f]_{L^{\prime}}(\sigma)=\left[f^{\prime} \mid \sigma\right] .
$$

If $X \neq O$ is also an $H$-space, we know that $\tau_{1}\left(X, x_{0}\right)$ is abelian and that the group structure in $\pi_{p}\left(X, x_{0}\right)$ is defined by the multiplication map in $X$, so that in this case the functions $G$ and $G^{\prime}$ are homomorphisms.

Remark. $\quad G_{n}^{\prime}: \quad\left[T^{n}, X\right] \rightarrow \operatorname{Hom}\left(H_{p}\left(T^{n}\right), \quad H_{p}(X)\right)$ surjective (injective) implies that $G_{m}^{\prime}:\left[T^{m}, X\right] \rightarrow \operatorname{Hom}\left(H_{p}\left(T^{m}\right), H_{p}(X)\right)$ is surjective (injective) for $m \leqq n$.

From the above remarks and the results in [2], VI we get:
Theorem 2. Let $X$ be an (m-1)-space of type $\left(\pi_{p}, p\right)\left(\pi_{p}\right.$ abelian). Then we have $\left[\left(T^{n}\right)^{m}, L^{\prime}, g ; X\right]_{L^{\prime}} \neq \varnothing$ and the functions $G_{n, m, p}$ and $G_{n, m, p}^{\prime}$ are surjective. Let $X$ be an $m$-space of type $\left(\pi_{p}, p\right)\left(\pi_{p}\right.$ abelian $)$. Then we have $\left[\left(T^{n}\right)^{m}\right.$, $\left.L^{\prime}, g ; X\right]_{L^{\prime}} \neq \varnothing$ and $G_{n, m, p}$ and $G_{n, m, p}^{\prime}$ are bijective.

Thus

$$
\left[\left(T^{n}\right)^{m}, L^{\prime}, g ; X\right]_{L^{\prime}} \simeq \pi_{p}\binom{n}{p}-i^{\prime}(p),
$$

and, in particular

$$
\begin{gathered}
{\left[T^{n}, L, g ; X\right]_{L} \simeq \pi_{p}^{\binom{n}{p}-i(p)},} \\
{\left[T^{n}, X\right] \simeq\left[T^{n}, t_{0} ; X, x_{0}\right]_{t_{0}} \simeq \pi_{p}^{\binom{n}{p}} .}
\end{gathered}
$$

Remark. Let $\left[\left(T^{n}\right)^{m}, L^{\prime}, g ; X\right]$ denote the set of homotopy classes of maps $f:\left(T^{n}\right)^{m} \rightarrow X$ for which $\left.f\right|_{L^{\prime}}=g$. Then $I[f]_{L^{\prime}}=[f]$ defines a map $\left[\left(T^{n}\right)^{m}, L^{\prime}, g ; X\right]_{L^{\prime}} \rightarrow\left[\left(T^{n}\right)^{m}, L^{\prime}, g ; X\right]$, which is surjective. The map

$$
\tilde{G}_{n, m, p}^{\prime}:\left[\left(T^{n}\right)^{m}, L^{\prime}, g ; X\right] \rightarrow \operatorname{Hom}\left(H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime}\right), H_{p}(X)\right),
$$

where $\tilde{G}_{n, m, p}^{\prime}[f]=f_{\# p} \mid H_{p}\left(\left(T^{n}\right)^{m}, L^{\prime}\right)$ is also well defined. From this we get $\left(G_{n, m, p}^{\prime}=\tilde{G}_{n, m, p}^{\prime} \circ I\right):$

$$
G_{n, m, p}^{\prime} \text { surjective (injective) } \Rightarrow \widetilde{G}_{n, m, p}^{\prime} \text { surjective (injective). }
$$

Examples. $\left[\left(T^{n}\right)^{m}, S^{m}\right] \simeq \boldsymbol{Z}^{\binom{n}{m}},\left[T^{n}, S^{n}\right] \simeq \boldsymbol{Z}$. (Here $\simeq$ denotes bijection).

Now, let $X$ be an $H$-space and a $p$-space of type $\left(\pi_{p}, p\right)$ (then $\pi_{1}$ is automatically abelian). That $X$ is an $H$-space means that we have a fixed point $x_{0} \in X$, a continuous multiplication $\mu:\left(X \times X, x_{0} \times x_{0}\right) \rightarrow\left(X, x_{0}\right)$ for which the constant map $X \xrightarrow{c} x_{0}$ is a homotopy identity, i.e. $\mu \circ\left(c, 1_{x}\right) \simeq$ $\mu \circ\left(1_{x}, c\right) \simeq 1_{x}$ relative to $x_{0}$. From the above theorem we know that for $n \geq p$
$\left[\left(T^{n}\right)^{p-1}, X\right]=0$ and $\left[\left(T^{n}\right)^{p}, X\right] \simeq \operatorname{Hom}\left(H_{p}\left(\left(T^{n}\right)^{p}\right), \pi_{p}\right) \simeq \operatorname{Hom}\left(H_{p}\left(T^{n}\right), \pi_{p}\right)$.
Hence every $h \in \operatorname{Hom}\left(H_{p}\left(T^{n}\right), \pi_{p}\right)$ corresponds to a continuous map $\left(T^{n}\right)^{p} \xrightarrow{f} X$ with $f\left(\left(T^{n}\right)^{p-1}\right)=x_{0}$ and $f_{\# p}=x h$. Let $f_{i}$ denote the map

$$
T^{n} \xrightarrow{\text { proj }} T_{i}^{p} \xrightarrow{f \mid T_{i}^{p}} X
$$

Let $\tilde{f}$ denote "one of the products of the $f_{i}$ 's", for instance

$$
\mu \circ\left(1_{x} \times \mu\right) \circ \ldots \circ\left(1_{x} \times \ldots \times 1_{x} \times \mu\right) \circ\left(f_{\binom{n}{p}}, \ldots, f_{1}\right) .
$$

Then it is easy to see that $\tilde{f}$ is a continuous map $T^{n} \rightarrow X$ with $\tilde{f} \mid\left(T^{n}\right)^{p}\left(T^{n}\right)^{p-1} f$, i.e. $\tilde{f}_{\# p}=f_{\# p}=x h$. Thus we have $(n<p$ trivial $)$ :

Theorem 3. Let $X$ be an H-space and a p-space of type $\left(\pi_{p}, p\right)$. Then for all $n \in \boldsymbol{N}, G$ and $G^{\prime}$ are surjective homomorphisms; $G:\left[T^{n}, X\right] \rightarrow$ $\operatorname{Hom}\left(H_{p}\left(T^{n}\right), \pi_{p}\right) \simeq \pi_{p}{ }^{\binom{n}{p}}$, where $G([f])=\varkappa^{-1} f_{\# p}, \quad G^{\prime}: \quad\left[T^{n}, X\right] \rightarrow$ $\operatorname{Hom}\left(H_{p}\left(T^{n}\right), H_{p}(X)\right) \simeq \pi_{p}^{\binom{n}{p}}$, where $G^{\prime}([f])=f_{\# p}$.

For $p=1$ we have the Hurewicz isomorphism $\chi_{T^{n}}: \pi_{1}\left(T^{n}, t_{0}\right) \rightarrow H_{1}\left(T^{n}\right)$ and $G([f])=f_{*} \circ \varkappa_{T^{n}}^{-1}$ so that $F_{n}^{\prime}$ and $F_{n}$ are surjective.

## Chapter 2

## The Cohomotopy Groups of $\boldsymbol{T}^{\boldsymbol{n}}$

Definition. Let $X$ be a topological space and $A$ a subspace of $X$. The m'th (relative) cohomotopy set $\pi^{m}(X, A)$ of $(X, A)(m \in \boldsymbol{N})$ is defined to be $\left[X, A ; S^{m}, s_{0}\right]_{A}$ and the m'th (absolute) cohomotopy set $\pi^{m}(X)$ of $X$ is defined to be $\left[X, S^{m}\right]$.

A pair $(X, A)$ is called $n$-coconnected if it satisfies the condition $H^{q}(X, A ; G)=0$ for every $q \geqq n$ and every coefficient group $G$.

A cellular pair $(X, A)$ is a pair of a finite cell complex $X$ and a subcomplex $A$.

We need the following theorem ([2], VII, Theorem 5.2).
Theorem 4. If $(X, A)$ is a (2m-1) coconnected cellular pair, we can define a certain abelian group structure + in $\pi^{m}(X, A)$ with the class of the constant map as the neutral element. In this case $\pi^{m}(X, A)$ is called the m'th cohomotopy group of ( $X, A$ ).

Remarks. 1) Every map $f:(X, A) \rightarrow(Y, B)$ induces a transformation $f^{\infty}: \pi^{m}(Y, B) \rightarrow \pi^{m}(X, A)$. If both $(X, A)$ and $(Y, B)$ are (2m-1)-coconnected cellular pairs, then $f^{*}$ is a homomorphism ([2], VII, prop. 5.4).
2) When the cohomotopy group structure is defined in $\pi^{m}\left(S^{n}, s_{0}\right)$ (thus $n \leq 2 m-2)$, then the bijection $\pi^{m}\left(S^{n}, s_{0}\right) \simeq \pi_{n}\left(S^{m}, s_{0}\right)$ is an isomorphism ([2], VII, prop. 12.1).

We now try to compute the cohomotopy groups of $T^{n}$ by means of some exact sequences for the pairs $\left[\left(T^{n}\right)^{m},\left(T^{n}\right)^{m-1}\right]$.

If $i \geq)_{2}^{m}(+1$, where for $\alpha$ real $) \alpha\left(=\min _{p \in \boldsymbol{Z}}\{p \mid p \geq \alpha\}\right.$, then $\pi^{i}\left(\left(T^{n}\right)^{m}\right)$ and $\pi^{i}\left(\left(T^{n}\right)^{m},\left(T^{n}\right)^{m-1}\right)$ have the cohomotopy group structure.

From Theorem 2 we have the bijections ( $p \geq m$ )

$$
\pi^{p}\left(\left(T^{n}\right)^{m},\left(T^{n}\right)^{m-1}\right) \xrightarrow[i^{*}]{\simeq} \rightarrow \pi^{p}\left(\left(T^{n}\right)^{m}\right) \simeq \begin{cases}0 & p>m \\
\boldsymbol{Z}^{\left(\begin{array}{c}
n
\end{array}\right)} & p=m,\end{cases}
$$

where $i^{*}$ is a homomorphism for $\left.p \geq\right)^{\frac{m}{2}}(+1$, i.e. $p>1$.
If $X, Y$ are spaces with basis point, $X \vee Y$ denotes their one point union. If $p$ denotes the map

$$
\left(T^{n}\right)^{m} \rightarrow\left(T^{n}\right)^{m} /\left(T^{n}\right)^{m-1} \sim S_{1}^{m} \vee \ldots \vee S_{\binom{n}{m}}^{m}
$$

then

$$
p^{*}: \pi^{i}\left(S_{1}^{m} \vee \ldots \vee S_{\binom{n}{m}}^{m}, s_{0}\right) \rightarrow \pi^{i}\left(\left(T^{n}\right)^{m},\left(T^{n}\right)^{m-1}\right)
$$

is a bijection and for $i \geq) \frac{m}{2}(+1$ an isomorphism. It is easy to see that there is a bijection

$$
\pi^{i}\left(S_{1}^{m} \vee \ldots \vee S_{\binom{n}{m}}^{m}, s_{0}\right) \simeq \pi^{i}\left(S^{m}, s_{0}\right){ }^{\binom{n}{m}}
$$

Let $i^{\prime}$ denote the inclusion $S_{1}^{m} \vee \ldots \vee S_{r}^{m} \rightarrow S_{1}^{m} \vee \ldots \vee S_{r}^{m} \vee \ldots \vee S_{q}^{m}$ and
$p^{\prime}$ the projection $S_{1}^{m} \vee \ldots \vee S_{q}^{m} \rightarrow S_{1}^{m} \vee \ldots \vee S_{r}^{m}$. When $\left.i \geq\right) \frac{m}{2}(+1$ we get the following split exact sequences of abelian groups and homomorphisms because $\pi^{i}$ is a functor:

$$
0 \rightarrow \pi^{i}\left(S_{1}^{m} \vee \ldots \vee S_{q-1}^{m}, s_{0}\right) \underset{i^{\prime *}}{\stackrel{p^{\prime *}}{\rightleftarrows}} \pi^{i}\left(S_{1}^{m} \vee \ldots \vee S_{q}^{m}, s_{0}\right) \underset{p^{\prime *}}{\stackrel{i^{\prime *}}{\rightleftarrows}} \pi^{i}\left(S_{q}^{m}, s_{0}\right) \rightarrow 0 .
$$

An induction thus gives us the isomorphism

$$
\pi^{i}\left(S_{1}^{m} \vee \ldots \vee S_{q}^{m}, s_{0}\right) \simeq \pi^{i}\left(S_{1}^{m}, s_{0}\right) \oplus \ldots \oplus \pi^{i}\left(S_{q}^{m}, s_{0}\right)
$$

Because of the isomorphism $\pi^{i}\left(S^{m}, s_{0}\right) \simeq \pi_{m}\left(S^{i}, s_{0}\right)$ we have that the bijection

$$
\pi^{i}\left(\left(T^{n}\right)^{m},\left(T^{n}\right)^{m-1}\right) \simeq \pi_{m}\left(S^{i}, s_{0}\right)\binom{n}{m}
$$

is an isomorphism for $i \geq) \frac{m}{2}(+1$.
We have the following long exact cohomotopy sequences ([2], VII, 6.-9.) of abelian groups and homomorphisms except the first set and the first map in the first sequence and the two first sets and the two first maps in the second sequence.

1) $m=2 q \geqq 2$.

$$
\begin{aligned}
& \pi^{q}\left(\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{\delta_{q}^{2 q}} \\
\rightarrow & \pi^{q+1}\left(\left(T^{n}\right)^{2 q},\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{j_{q+1}^{2 q}} \pi^{q+1}\left(\left(T^{n}\right)^{2 q}\right) \xrightarrow{i_{q+1}^{2 q}} \pi^{q+1}\left(\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{\delta_{q+1}^{2 q}} \ldots \\
\rightarrow & \pi^{2 q-1}\left(\left(T^{n}\right)^{2 q},\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{j_{2 q-1}^{2 q}} \pi^{2 q-1}\left(\left(T^{n}\right)^{2 q}\right) \xrightarrow{i_{2 q-1}^{2 q}} \pi^{2 q-1}\left(\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{\delta_{2 q-1}^{2 q}} \\
\rightarrow & \pi^{2 q}\left(\left(T^{n}\right)^{2 q},\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{j_{2 q}^{2 q}} \pi^{2 q}\left(\left(T^{n}\right)^{2 q}\right) \xrightarrow{i_{2 q}^{2 q}} 0 .
\end{aligned}
$$

2) $m=2 q-1 \geqq 3$.

$$
\begin{aligned}
& \pi^{q}\left(\left(T^{n}\right)^{2 q-1},\left(T^{n}\right)^{2 q-2}\right) \xrightarrow{j^{2 q-1}} \pi^{q}\left(\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{i^{2 q-1}} \pi^{q}\left(\left(T^{n}\right)^{2 q-2}\right) \xrightarrow{\delta^{2 q-1}} \\
\rightarrow & \pi^{q+1}\left(\left(T^{n}\right)^{2 q-1},\left(T^{n}\right)^{2 q-2}\right) \xrightarrow{j_{q+1}^{2 q-1}} \pi^{q+1}\left(\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{i_{q+1}^{2 q-1}} \pi^{q+1}\left(\left(T^{n}\right)^{2 q-2}\right) \xrightarrow{\delta_{q+1}^{2 q-1}} \ldots \\
\rightarrow & \pi^{2 q-2}\left(\left(T^{n}\right)^{2 q-1},\left(T^{n}\right)^{2 q-2}\right) \xrightarrow{j_{2 q-2}^{2 q-1}} \pi^{2 q-2}\left(\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{i_{2 q-2}^{2 q-1}} \pi^{2 q-2}\left(\left(T^{n}\right)^{2 q-2}\right) \xrightarrow{\delta_{2 q-2}^{2 q-1}} \\
\rightarrow & \pi^{2 q-1}\left(\left(T^{n}\right)^{2 q-1},\left(T^{n}\right)^{2 q-2}\right) \xrightarrow{j_{2 q-1}^{2 q-1}} \pi^{2 q-1}\left(\left(T^{n}\right)^{2 q-1}\right) \xrightarrow{i_{2 q-1}^{2 q-1}} 0 .
\end{aligned}
$$

All maps $i, j$ are induced by inclusions, and the $\delta$ 's are connecting "homomorphisms".

We know that every finitely generated abelian group $G$ is isomorphic to a direct sum of cyclic groups. If $\left(b_{1}, \ldots, b_{n}\right)$ are generators of the cyclic groups in such a decomposition, then they are weakly linearly independent in the sense that $p_{1} b_{1}+\ldots+p_{n} b_{n}=0$ implies $p_{1} b_{1}=\ldots=p_{n} b_{n}=0$. We shall call $\left(b_{1}, \ldots, b_{n}\right)$ a basis of $G$.

We now choose basis elements for the finitely generated abelian groups $\pi_{j}\left(S^{i}, s_{0}\right)$ represented by $g_{j, i}^{\alpha}$. A generator of $\pi^{j}\left(T^{j}\right)$ is represented by the projection $p_{j}: T^{j} \rightarrow T^{j} /\left(T^{j}\right)^{j-1} \sim S^{j}$. We then look at the elements of $\pi^{i}\left(\left(T^{n}\right)^{m}\right)$ represented by

$$
\left(T^{n}\right)^{m} \xrightarrow{\operatorname{proj}^{\beta}}{ }_{m, j}^{\beta} T_{j}^{j} \xrightarrow{p_{j}} S^{j} \xrightarrow{g_{j, i}^{\alpha}} S^{i} ; \quad j \leqq m, \beta \in\left\{1, \ldots,\binom{n}{j}\right\} .
$$

By means of induction on $m$ we prove:
For all $i, n, m$ in $\boldsymbol{N}$ with $n \geq m$ such that $\pi^{i}\left(\left(T^{n}\right)^{m}\right)$ is a cohomotopy group, i.e. $i \geq) \frac{m}{2}(+1$, the following short exact sequence is split exact,
$0 \rightarrow j \not \pi^{i}\left(\left(T^{n}\right)^{m},\left(T^{n}\right)^{m-1}\right) \rightarrow \pi^{i}\left(\left(T^{n}\right)^{m}\right) \xrightarrow{i^{*}} \pi^{i}\left(\left(T^{n}\right)^{m-1}\right) \rightarrow 0$, and a basis for $\pi^{i}\left(\left(T^{n}\right)^{m}\right) \simeq \pi^{i}\left(\left(T^{n}\right)^{m-1}\right) \oplus j^{*} \pi^{i}\left(\left(T^{n}\right)^{m}\right.$, $\left.\left(T^{n}\right)^{m-1}\right)$ is represented by the elements $g_{j, i}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m, j}^{\beta}$ except that the long exact sequences are not long enough to the left to allow us to decide whether $g_{2 i-2, i}^{\alpha} \circ p_{2 i-2} \circ \operatorname{proj}^{\beta}{ }_{2 i-2,2 i-2}$ is homotopic to 0 or not.

The start of the induction is trivial by the long exact sequences.
Let the above be true for $m-1$. We see that all the elements $g_{j, i}^{\alpha} \circ p_{j}$ 。 $\operatorname{proj}_{m-1, j}^{\beta^{\prime}}$ of $\pi^{i}\left(\left(T^{n}\right)^{m-1}\right)$ where $\beta^{\prime} \in\left\{1, \ldots,\binom{n}{j}\right\}$ and $j \leq m-1$, have trivial extensions to $\left(T^{n}\right)^{m}: g_{j, i}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m, j}^{\beta^{\prime}}$, which proves that $i^{*}=i_{i}^{m}$ is surjective. Further,

$$
g_{j, i}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m-1, j}^{\beta^{\prime}} \operatorname{non} \simeq 0 \Leftrightarrow g_{j, i}^{\alpha} \circ p_{j} \operatorname{non} \simeq 0 \Leftrightarrow g_{j, i}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m, j}^{\beta^{\prime}} \operatorname{non} \simeq 0
$$

From the isomorphisms $\pi^{i}\left(S^{j}\right) \simeq \pi^{i}\left(S^{j}, s_{0}\right) \simeq \pi_{j}\left(S^{i}, s_{0}\right), j \leq 2 i-2$, we see for $p \in \boldsymbol{Z}$ that $p\left(g_{j, i}^{\alpha} \circ f\right)=\left(p g_{j, i}^{\alpha}\right) \circ f: X \rightarrow S^{j} \rightarrow S^{i}$ when $\pi^{i}(X)$ and $\pi^{i}\left(S^{j}\right)$ are cohomotopy groups ( $f^{*}$ is a homomorphism $\pi^{i}\left(S^{j}\right) \rightarrow \pi^{i}(X)$ ). From this we see that $p g_{j, i}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m-1, j}^{\beta^{\prime}}$ and its extension to $\left(T^{n}\right)^{m}: p g_{j, i}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m, j}^{\beta^{\prime}}$ are zero homotopic at the same time. This and the fact that the elements $g_{j, i}^{\alpha}$ 。 $p_{j} \circ \operatorname{proj}_{m-1, j}^{\beta^{\prime}}$ (when not zero homotopic) represent a basis for $\pi^{i}\left(\left(T^{n}\right)^{m-1}\right)$ gives us a well defined homomorphism $h: \pi^{i}\left(\left(T^{n}\right)^{m-1}\right) \rightarrow \pi^{i}\left(\left(T^{n}\right)^{m}\right)$ such that $i * h=1 \pi^{i}\left(\left(T^{n}\right)^{m-1}\right)$. This and the exactness of the long cohomotopy sequence proves that the sequence above is split exact. Thus

$$
\pi^{i}\left(\left(T^{n}\right)^{m}\right) \simeq \pi^{i}\left(\left(T^{n}\right)^{m-1}\right) \oplus j^{*} \pi^{i}\left(\left(T^{n}\right)^{m},\left(T^{n}\right)^{m-1}\right),
$$

where $\left.j^{*} \pi^{i}\left(\left(T^{n}\right)^{m}\right),\left(T^{n}\right)^{m-1}\right)$ is generated by

$$
g_{m, i}^{\alpha} \circ p_{m} \circ \operatorname{proj}_{m, m}^{\beta^{\prime \prime}}:\left(T^{n}\right)^{m} \rightarrow T_{\beta^{\prime \prime}}^{m} \rightarrow S^{m} \rightarrow S^{i},\left(\beta^{\prime \prime} \in\left\{1, \ldots,\binom{m}{n}\right\}\right)
$$

If $m=2 i-2$ we do not know whether $g_{m, i}^{\alpha} \circ p_{m} \circ \operatorname{proj}_{m, m}^{\beta^{\prime \prime}} \simeq 0$ or not.
If $m<2 i-3$, we get from the above that $j_{i}^{m}$ is injective, because $i_{i-1}^{m}$ is surjective and the sequence exact. The following proof is valid also if $m=$ $2 i-3$. Because all the generators $g_{j, i-1}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m-1, j}^{\beta^{\prime \prime}}:\left(T^{n}\right)^{m-1} \rightarrow S^{i-1}$ of $\pi^{i-1}$ $\left(\left(T^{n}\right)^{m-1}\right)$ have extensions to $\left(T^{n}\right)^{m}: g_{j, i-1}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m, j}^{\beta^{\prime \prime}}:\left(T^{n}\right)^{m} \rightarrow S^{i-1}$, the exactness gives us:
$\delta_{i-1}^{m}\left(\left[g_{j, i-1}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m-1, j}^{\beta^{\prime \prime}}\right]\right)=0 \Rightarrow \delta_{i-1}^{m}=0 \Rightarrow j_{i}^{m}$ injective, i.e. for $m<2 i-2$ we have $\pi^{i}\left(\left(T^{n}\right)^{m}\right) \simeq \pi^{i}\left(\left(T^{n}\right)^{m-1}\right) \oplus \pi^{i}\left(\left(T^{n}\right)^{m},\left(T^{n}\right)^{m-1}\right)$, and a basis for $\pi^{i}\left(\left(T^{n}\right)^{m}\right)$ is represented by all the

$$
g_{j, i}^{\alpha} \circ p_{j} \circ \operatorname{proj}_{m, j}^{\beta} \quad\left(\beta \in\left\{1, \ldots,\binom{n}{j}\right\} ; j \leq m\right) .
$$

Theorem 5. The cohomotopy groups $\pi^{i}\left(\left(T^{n}\right)^{m}\right)$ are finitely generated and for $2 i \geq m+3$ we have
$\pi^{i}\left(\left(T^{n}\right)^{m}\right) \simeq\left\{\begin{array}{l}0 \text { if } i>m \\ \pi_{i}\left(S^{i}, s_{0}\right)^{\binom{n}{i}} \oplus \pi_{i+1}\left(S^{i}, s_{0}\right)^{\left(\begin{array}{c}n+1\end{array}\right)} \oplus \ldots \oplus \pi_{m}\left(S^{i}, s_{0}\right)^{\binom{n}{m}} \text { if } i \leqq m\end{array}\right.$
and the last expression is valid for $m=2 i-2$, if the last factor is replaced by a suitable factor group.

For $m=n$ we get:
Theorem 6. For $2 i \geqq n+3$ we have

$$
\pi^{i}\left(T^{n}\right) \simeq\left\{\begin{array}{l}
0 \text { if } i>n \\
\pi_{i}\left(S^{i}, s_{0}\right)^{\binom{n}{i}} \oplus \pi_{i+1}\left(S^{i}, s_{0}\right)^{\binom{n}{i+1}} \oplus \ldots \oplus \pi_{n}\left(S^{i}, s_{0}\right) \text { if } i \leqq n
\end{array}\right.
$$

and the last expression is valid for $n=2 i-2$ if the last factor is replaced by a suitable factor group.

It is known that $\pi_{m}\left(S^{n}, s_{0}\right)$ is zero for $m<n, \boldsymbol{Z}$ for $m=n$ and a finite abelian group for $m>n$, except $\pi_{4 i-1}\left(S^{2 i}, s_{0}\right)$ which is the direct sum of $\boldsymbol{Z}$ and a finite group. This group is not a cohomotopy group and so it has no influence on the cohomotopy groups of $\left(T^{n}\right)^{m}$. Hence:

Corollary. $\pi^{i}\left(T^{n}\right)$ is the direct sum of $\boldsymbol{Z}^{\binom{n}{i}}$ and a finite abelian group, when $i \geq) \frac{1}{2} n\left(+1\right.$ (i.e. rank $\left.\pi^{i}\left(T^{n}\right)=\binom{n}{i}\right)$.

## Chapter 3

## Elementary Properties of Tori

Before I discuss the problems of reducibility mentioned in the introduction, I deduce a few elementary results:

Lemma 1. The homotopy classes of homeomorphisms $\left(T^{n}, t_{0}\right) \rightarrow\left(T^{n}, t_{0}\right)$ are in one to one correspondence with the unimodular $n \times n$ matrices.

Proof. [A unimodular $n \times n$ matrix $\boldsymbol{A}$ has elements in the integers $\boldsymbol{Z}$ and determinant $\pm 1]$. The lemma follows easily from the isomorphism $F_{n}$ : $\left[T^{n}, T^{n}\right] \rightarrow \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(T^{n}, t_{0}\right)\right) \simeq \operatorname{Hom}\left(\boldsymbol{Z}^{n}, \boldsymbol{Z}^{n}\right) \simeq \boldsymbol{Z}^{n^{2}}$ defined by $F_{n}\left[f^{\prime}\right]=f_{*}$.

Lemma 2. The homotopy classes in $T^{n}$ of $T^{m}$ 's imbedded in $T^{n}$ for which $T^{n}=T^{m} \times X$ are in one to one correspondence with the direct summands of $\pi_{1}\left(T^{n}, t_{0}\right)$ of rank $m$.

This follows easily from Lemma 1.
Theorem 7. $f: T^{n} \rightarrow X$ is m-reducible iff $f$ is homotopic to the projection of $T^{n}$ onto a $T^{m}$ imbedded in $T^{n}=T^{m} \times Y$ (possibly after a shift of coordinates in $T^{n}$ ), followed by a map $T^{m} \rightarrow X$.

Proof. Obviously, "if" is trivial. We shall prove "only if". It is enough to show that every map $f:\left(T^{n}, t_{0}\right) \rightarrow\left(T^{m}, t_{0}\right)$ can be projected through a $T_{1}^{m}$ imbedded in $T^{n}$. Because $\pi_{1}\left(T^{m}, t_{0}\right)$ is free, $f_{*}\left(\pi_{1}\left(T^{n}, t_{0}\right)\right)$ is also free and so $f_{*}\left(\pi_{1}\left(T^{n}, t_{0}\right)\right)$ is a direct summand in $\pi_{1}\left(T^{n}, t_{0}\right)$ of rank $m^{\prime} \leq m$. Let $G \subseteq \pi_{1}$ ( $\left.T^{n}, t_{0}\right)$ be a direct summand in $\pi_{1}\left(T^{n}, t_{0}\right)$ of rank $m$ including the isomorphic image of $f_{*}\left(\pi_{1}\left(T^{n}, t_{0}\right)\right)$. From Lemma $2 G$ corresponds to a $T_{1}^{m}$ imbedded in $T^{n}=T_{1}^{m} \times Y\left(\right.$ possibly after a shift of coordinates of $\left.T^{n}\right)$. Thus $f$ is homotopic to the projection in new coordinates of $T^{n}$ onto $T_{1}^{m}$ followed by the map $f \mid T_{1}^{m}: T_{1}^{m} \rightarrow T^{m}$.

## Chapter 4

## Remarks about Finitely Generated Abelian Groups

We know that there is an isomorphically unique decomposition of a finitely generated abelian group $G$ as a direct sum of cyclic groups $\boldsymbol{Z}^{n} \oplus \boldsymbol{Z}_{n_{1}}$ $\oplus \ldots \boldsymbol{Z}_{n}$, where $n_{i}$ divides $n_{i-1}$.

The number $n$ is the rank of $G$ and the $n_{i}$ 's are called the torsion coefficients of $G$.

We know that every subgroup of a free abelian group $F \cong \boldsymbol{Z}^{m}$ of rank $m$ is a free abelian group of rank $m^{\prime} \leq m$. A finite abelian group $G^{\prime}$ has in general many decompositions as a direct sum of cyclic groups, but we can define a dimension of a finitely generated abelian group $G$ as

$$
\operatorname{dim} G=\text { the smallest number of generators of } G .
$$

The usual proof of the theorem above starts with $m$ generators $g_{1}, \ldots$, $g_{m}$ of $G$ and then shows that there exists an $r \leq m$ and $\varepsilon_{1}, \ldots, \varepsilon_{r}$ with $\varepsilon_{i} \mid \varepsilon_{i-1}$ so that $G$ is isomorphic to $\boldsymbol{Z}^{m-r} \oplus \boldsymbol{Z} \varepsilon_{1} \oplus \ldots \oplus \boldsymbol{Z} \varepsilon_{r}$, where $\boldsymbol{Z}_{1}=0$. This gives us that
$\operatorname{dim} G=$ rank $G+$ the number of torsion coefficients of $G$.
The dimension of $G$ has the following properties:

1) $\operatorname{dim} G=m \Rightarrow \forall q \leq m \exists G^{\prime} \subseteq G: \operatorname{dim} G^{\prime}=q$.
2) If $f \in \operatorname{Hom}\left(\boldsymbol{Z}^{n}, \widetilde{G}\right), \tilde{G}$ a group, then $f\left(\boldsymbol{Z}^{n}\right)$ is a finitely generated abelian group with $\operatorname{dim} f\left(\boldsymbol{Z}^{n}\right) \leq n$.
3) $G^{\prime} \subseteq G \Rightarrow \operatorname{dim} G^{\prime} \leq \operatorname{dim} G$.

## Chapter 5

## Torus Reducibility Problems

Let $X \neq \varnothing$ be a topological space, $x_{0} \in X$ a fixed point of $X$. Looking at torus maps $T_{n} \rightarrow X$, we always assume them, as already mentioned, continuous, and if $X$ is path connected, we assume that $t_{0}$ is mapped into $x_{0}$. We are interested only in the homotopy classes of maps $T^{n} \rightarrow X$. We know that $\tau_{0}\left(X, x_{0}\right)$ is the set of path components of $X$ with the path component including $x_{0}$ as 0 -element, that, for all $i \geq 1$ and all $x_{0}, x_{1} \in X$ in the same path component, $\pi_{i}\left(X, x_{0}\right)$ is isomorphic to $\pi_{i}\left(X, x_{1}\right)$ and that $T^{n}$ itself is path connected. Hence a theorem about torus mappings into path connected spaces under some conditions on the $\pi_{i}\left(X, x_{0}\right)$ 's for fixed $x_{0}$ can be translated to a theorem about torus mappings into spaces not necessarily path connected, under the same conditions on the $\pi_{i}\left(X, x_{1}\right)$ 's for all $x_{1} \in X$. In the following I therefore assume the spaces $X$ path connected even if this is not written explicitely.

We start with some trivial remarks concerning the definitions 1-3 in the introduction:

For $f:\left(T^{n}, t_{0}\right) \rightarrow\left(X, x_{0}\right)$ we have: If $f$ is m-reducible, then $\operatorname{dim}$ $f_{*}\left(\pi_{1}\left(T^{n}, t_{0}\right)\right) \leq m$ and $\operatorname{dim} f_{\# p}\left(H_{p}\left(T^{n}\right)\right) \leq\binom{ m}{p}$ for every $p \in \boldsymbol{N}$, where

$$
f_{*} \in \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right), f_{\# p} \in \operatorname{Hom}\left(H_{p}\left(T^{n}\right), H_{p}(X)\right)
$$

and

$$
\pi_{1}\left(T^{n}, t_{0}\right) \simeq \boldsymbol{Z}^{n}, H_{p}\left(T^{n}\right) \simeq \boldsymbol{Z}^{\binom{n}{p}}
$$

The map $F_{m+1}:\left[T^{m+1}, X\right] \rightarrow \operatorname{Hom}\left(\pi_{1}\left(T^{m+1}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right) / \sim$ defined by $F_{m+1}[f]=\left\{f_{*}\right\}$ is surjective iff every homomorphism $h: \pi_{1}\left(T^{m+1}, t_{0}\right) \rightarrow \pi_{1}$ $\left(X, x_{0}\right)$ is induced by some map $f:\left(T^{m+1}, t_{0}\right) \rightarrow\left(X, x_{0}\right)$. From Theorems 1 and 3 it follows that this happens when $X$ is an $m$-space of type $(\pi, 1)$ and when $X$ is an $H$-space.

Theorem 8. If $F_{m+1}$ is surjective, and $X$ is [ $n$ dimensionally $(n>m)$ ] m-reducible, then every finitely generated abelian subgroup of $\pi_{1}\left(X, x_{0}\right)$ has dimension $\leqq m$.

Remark. If $\pi_{1}\left(X, x_{0}\right)$ is itself a finitely generated abelian group, then the above condition is equivalent to $\operatorname{dim} \pi_{1}\left(X, x_{0}\right) \leq m$.

Proof of Theorem 8. Suppose $\pi_{1}\left(X, x_{0}\right)$ has a finitely generated abelian subgroup of dimension greater than $m$, then $\pi_{1}\left(X, x_{0}\right)$ also has a subgroup $G$ of dimension $m+1$. Because $\pi_{1}\left(T^{m+1}, t_{0}\right) \simeq \boldsymbol{Z}^{m+1}$, we have a surjective $h \in \operatorname{Hom}\left(\pi_{1}\left(T^{m+1}, t_{0}\right), G\right)$, which because of the assumption corresponds to an $f: T^{m+1} \rightarrow X$ with $f_{*}=h$. If we define $f^{\prime}$ as $T^{n} \xrightarrow{\text { proj }} T^{m+1} \xrightarrow{f} X$, then dim $f_{*}^{\prime} \pi_{1}\left(T^{n}, t_{0}\right)=\operatorname{dim} h\left(\pi_{1}\left(T^{m+1}, t_{0}\right)\right)=m+1$. Thus $f^{\prime}$ is not m-reducible.

Theorem 9. Suppose $F_{n}:\left[T^{n}, X\right] \rightarrow \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right) / \sim$ defined by $F_{n}[f]=\left\{f_{*}\right\}$ is bijective. (From Theorem 1 we know that this is the case when $X$ is an $n$-space of type $\left.\left(\pi_{1}, 1\right)\right)$. Then

$$
f:\left(T^{n}, t_{0}\right) \rightarrow\left(X, x_{0}\right) \text { is m-reducible iff } f_{*}\left(\pi_{1}\left(T^{n}, t_{0}\right)\right)
$$

(an abelian group of dimension $\leqq n$ ) is of dimension $\leqq m$.
Proof. We have already proved "only if". If $\operatorname{dim} f_{*} \pi_{1}\left(T^{n}, t_{0}\right) \leq m$, then $f_{*}$ can be factorized through $\pi_{1}\left(T^{m}, t_{0}\right) \simeq \boldsymbol{Z}^{m}$ so that we can choose $\tilde{h} \in$ $\operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(T^{m}, t_{0}\right)\right)$ and $\tilde{g} \in \operatorname{Hom}\left(\pi_{1}\left(T^{m}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right)$ such that $f_{*}=\tilde{g} \circ \tilde{h}$. Because $F_{n}$ surjective implies that $F_{m}$ is surjective for $m \leqq n$ there exists a $g: T^{m} \rightarrow X$ with $g_{*}=\tilde{g}$, We also have an $h: T^{n} \rightarrow T^{m}$ with $h_{*}=\tilde{h}$. Thus $g_{*} \circ h_{*}=f_{*}$ or $g \circ h \simeq f$, i.e. $f$ is $m$-reducible.

This gives us the following theorems:
Theorem 10. Let $F_{n}$ be bijective. (This is the case when $X$ is an $n$-space of type $\left.\left(\pi_{1}, 1\right)\right)$. Then $X$ is $n$-dimensionally m-reducible $(1 \leq m<n)$ iff the dimension of any finitely generated abelian subgroup of $\pi_{1}\left(X, x_{0}\right)$ is $\leqq \mathrm{m}$.

Remark. Instead of " $F_{n}$ bijective" we could write " $F_{n}$ injective and $F_{m+1}$ surjective" ${ }^{\prime}$.

Theorem 11. Let $F_{n}$ be bijective for all $n>m$. (This is the case when $X$ is a space of type $\left(\pi_{1}, 1\right)$ ). Then $X$ is m-reducible iff the dimension of any finitely generated abelian subgroup of $\pi_{1}\left(X, x_{0}\right)$ is $\leqq m$.

We now show
Theorem 12. $X$ is $n$-dimensionally 1 -reducible $(n>1)$ iff every finitely generated abelian group of $\pi_{1}\left(X, x_{0}\right)$ is cyclic and $F_{n}$ is injective.

Corollary. Let $\pi_{1}\left(X, x_{0}\right)=0$. Then $X$ is $n$-dimensionally 1-reducible $(n>1)$ iff $\left[T^{n}, X\right]=0$.

Proof of Theorem 12. Because $F_{2}$ is always surjective, it follows from the remark above that it only remains to show that $F_{n}$ injective is a necessary condition.

Let $f, g: T^{n} \rightarrow X$ be given such that $f_{*} \sim g_{*}$ (i.e. $\left.f\left|\left(T^{n}\right)^{1} \simeq g\right|\left(T^{n}\right)^{1}\right)$. We suppose that $X$ is $n$-dimensionally 1 -reducible and then want to show that $f \simeq g$. Because $f$ and $g$ are 1 -reducible and

$$
\begin{aligned}
& {\left[T^{n}, S^{1}\right] \simeq \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(S^{1}, s_{0}\right)\right)} \\
& {\left[S^{1}, X\right] \simeq \operatorname{Hom}\left(\pi_{1}\left(S^{1}, s_{0}\right), \pi_{1}\left(X, x_{0}\right)\right) / \sim,}
\end{aligned}
$$

we can choose the factorizations $T^{n} \xrightarrow{h_{1}} S^{1} \xrightarrow{g_{1}} X$ and $T^{n} \xrightarrow{h_{2}} S^{1} \xrightarrow{g_{2}} X$ of $f$ and $g$ such that $g_{1_{*}} \pi_{1}\left(S^{1}, s_{0}\right)=f_{*} \pi_{1}\left(T^{n}, t_{0}\right)$ and $g_{2 *}\left(\pi_{1}\left(S^{1}, s_{0}\right)\right)=g_{*} \pi_{1}\left(T^{n}, t_{0}\right)$ and $h_{1 *}=h_{2 *}$. Then $h_{1} \simeq h_{2}$ and $g_{1} \simeq g_{2}$. Thus

$$
f \simeq g_{1} \circ h_{1} \simeq g_{2} \circ h_{2} \simeq g
$$

This gives us
Theorem 13. $X$ is 1-reducible iff every finitely generated abelian subgroup of $\pi_{1}\left(X, x_{0}\right)$ is cyclic and every $F_{n}$ is injective.

Theorem 14. Let $X$ be a p-space of type $\left(\pi_{p}, p\right)$ with $\pi_{p}$ abelian. Then we have:

1) If $m \leq n<p$, we have $\left[T^{n}, X\right] \simeq\left[T^{m}, X\right] \simeq 0$ so $X$ is trivially $n$ dimensionally m-reducible.
2) If $m<p \leqq n$, we have $\left[T^{m}, X\right]=0$, but $\left[T_{n}, X\right]$ is non trivial if $\pi_{p}$ is non trivial, so a necessary condition for $X$ to be $n$-dimensionally m-reducible is that $\pi_{p}=0$.
3) If $p \leqq m<n$ and $G_{m+1}:\left[T^{m+1}, X\right] \rightarrow \operatorname{Hom}\left(H_{p}\left(T^{m+1}\right)\right.$, $\left.\tau_{p}\right)$ defined by $G_{m+1}[f]=\varkappa^{-1} f_{\# p}$ is surjective (which is the case when $X$ is an $m$-space of type $\left(\pi_{p}, p\right)$ or when $X$ is an $H$-space of $p$-type $\left(\pi_{p}, p\right)$ ), then a necessary condition for $X$ to be $n$-dimensionally m-reducible is that the dimension of any finitely generated subgroup of $\pi_{p}$ is $\leqq\binom{ m}{p^{\prime}}=\operatorname{dim} H_{p}\left(T^{m}\right)$.

The proof of 3 ) is analogous to the proof of Theorem 8 because of the remark p. 17.

Corollary. Let $X$ be a p-space of type $\left(\tau_{p}, p\right)$ with $\pi_{p}$ abelian. Then we have:

1) For $m<p$ a necessary condition for $X$ being m-reducible is $\pi_{p}=0$.
2) For $m \geq p$ and $G_{m+1}$ surjective a necessary condition for $X$ being m-reducible is that the dimension of any finitely generated subgroup of $\pi_{p}$ is $\leqq\binom{ m}{p}$.

Examples. 1) Because the fundamental groups of the complex and quaternionic projective spaces are zero but not all the homotopy groups are zero, these spaces are not 1 -reducible.
2) $S^{n}(n>1)$ is not $m$-reducible for $m<n$.
3) $P^{n}(n>1)$ is not $m$-reducible for $m<n$ :

We have the covering projection $p: S^{n} \rightarrow P^{n}$ and a map $p_{n}: T^{n} \rightarrow S^{n}$ which is not 0 -homotopic. $p_{n}$ is not $m$-reducible, nor is $p_{n} \circ(\times N)_{n}: T^{n} \rightarrow$ $T^{n} \rightarrow S^{n}$ m-reducible. We now look back at $p \circ p_{n}: T^{n} \rightarrow S^{n} \rightarrow P^{n}$. The map $p \circ p_{n} \circ(\times N)_{n}$ is not 0 -homotopic since $p$ is a covering projection. If $p \circ p_{n}$ were $m$-reducible for some $m<n$, i. e. $p \circ p_{n} \cong g \circ h: T^{n} \xrightarrow{h} T^{m} \xrightarrow{g} P^{n}$, then, since $\left[T^{m}, P^{n}\right] \simeq \operatorname{Hom}\left(\boldsymbol{Z}^{m}, \boldsymbol{Z}_{2}\right)$, we would obtain

$$
p \circ p_{n} \circ(\times 2)_{n} \simeq g \circ h \circ(\times 2)_{n}=\left[g \circ(\times 2)_{m}\right] \circ h \simeq 0 \circ h=0
$$

(we assume $h$ linear because $\left[T^{n}, T^{m}\right] \simeq \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(T^{m}, t_{0}\right)\right.$ ), contradicting $p \circ p_{n} \circ(\times 2)_{n}$ non $\simeq 0$. Thus $p \circ p_{n}$ is not $m$-reducible.
4) From the computation of the cohomotopy groups of $T^{n}$ and the results in this chapter one can get further results about the reducibility of spheres; for instance:

If $2 i \geq n+3, i<n$ and $\pi_{n}\left(S^{i}, s_{0}\right) \neq 0$ then we get from Theorem 6 that the map $g_{n, i}^{\alpha} \circ p_{n}: T^{n} \rightarrow S^{n} \rightarrow S^{i}$ with $g_{n, i}^{\alpha}$ non $\simeq 0$ is not homotopic to zero. This map $f$ is algebraically trivial, i.e. its induced homomorphisms between the homology and cohomology groups are trivial. If $f$ were $i$-reducible, then

Theorem 7 would give that $f$ could be projected through a $T^{i}\left(T^{n}=T^{i} \times T^{n-i}\right.$, perhaps after a shift of coordinates). Thus $f$ would be homotopic to a composed map

$$
T^{n} \xrightarrow{h} T^{n} \xrightarrow{p r o j} T^{i} \xrightarrow{g} S^{i}
$$

where $g$ non $\simeq 0$, and $h$ is a change of basis. Because $\left[T^{i}, S^{i}\right] \simeq \operatorname{Hom}\left(H_{i}\left(T^{i}\right)\right.$, $\left.H_{i}\left(S^{i}\right)\right) \simeq \operatorname{Hom}(\boldsymbol{Z}, \boldsymbol{Z}), g_{\# i} \neq 0$ and so $g \circ \operatorname{proj} \circ h$ would not be algebraically trivial, contradicting $f \simeq g \circ \operatorname{proj} \circ h$. Thus if $2 n>2 i \geq n+3$ and $\pi_{n}\left(S^{i}, s_{0}\right) \neq 0$, then $S^{i}$ is not $i$-reducible.
5) In an analogous way we get:
$S^{2}$ is not 2 -reducible,
because the map $T^{3} \xrightarrow{p_{3}} S^{3} \xrightarrow{p} S^{2}$, where $p$ is the Hopf fibration, is known to be non $\simeq 0$ when $p_{3}$ non $\simeq 0$.

## Chapter 6

## Almost Periodic Movements

Definition. A topological space $X$ is called continuously locally arcwise connected when to every compact subspace $K$ of $X$ there exists a neighbourhood $O \subseteq K \times K$ of the diagonal $\triangle_{K}$ in $K \times K$ and a continuous map $\Phi: O \times I \rightarrow X$ so that $\Phi(x, x, t)=x, \Phi(x, y, 0)=x, \Phi(x, y, 1)=y$.

For metric spaces this is equivalent to the definition (for metric spaces only) used in [4].

Remarks. 1) When $X$ is a metric space for which any two points $x$ and $y$ whose distance remains below a certain number can be connected by a geodetic are which depends continuously on $x$ and $y$, then $X$ is continuously locally arcwise connected. 2) Any $C W$-complex is continuously locally arcwise connected. Indeed it satisfies the following:

There exists a covering $\left(U_{j} \mid j \in J\right)$ of $X$ with open sets and a continuous function $\Phi: O \times I \rightarrow X$, where $O=\bigcup_{J} U_{j} \times U_{j}$, such that $\Phi(x, x, t)=x, \Phi(x, y, 0)=$ $x, \Phi(x, y, 1)=y$. This can be shown by induction: Assuming $\left(U_{j}\right)$ chosen and $\Phi$ constructed on the $n-1$ skeleton $X^{n-1}$ of $X$, it can be shown that the definitions can be extended to $X^{n}$, which is obtained from $X^{n-1}$ by adjoining $n$-cells and which has the topology coherent with $X^{n-1}$ and the $n$-cells.

Definition. A continuous movement in a metric space $X$ is a continuous function $x=f(t), t \in \boldsymbol{R}, x \in X$. A number $\tau=\tau_{f}(\varepsilon)$ is called a translation
number of $f(t)$ corresponding to $\varepsilon>0$ if the condition dist $(f(t), f(t+\tau)) \leq \varepsilon$ is satisfied for all $t \in \boldsymbol{R}$. The movement $x=f(t)$ is called almost periodic if the range of $f(t)$ lies in a compact subset of $X$ and the set $\left\{\tau_{f}(\varepsilon)\right\}$ is relatively dense for every $\varepsilon>0$ (i.e. there exists an $l>0$ so that every interval of length I contains at least one of the $\tau_{f}(\varepsilon)$ 's).

Definition. A function $x=f(t, v) ; t \in \boldsymbol{R}, v \in[0,1], x \in X$; is called $a$ uniformly continuous family of almost periodic movements when 1) the range of $f(t, v)$ lies in a compact subset of $X, 2)$ for all $v_{0} \in[0,1] f\left(t, v_{0}\right)$ is almost periodic, 3) to all $\varepsilon>0$ and all $v_{0} \in[0,1]$ corresponds a neighbourhood $U_{\varepsilon}\left(v_{0}\right)$ of $v_{0}$ such that for all $t \in \boldsymbol{R}$, all $v \in U_{\varepsilon}\left(v_{0}\right)$ : $\operatorname{dist}\left(f\left(t, v_{0}\right), f(t, v)\right) \leq \varepsilon$.

Remark. Tornehave's definitions are the same except that he does not demand that the ranges lie in compact subsets. Instead he is mainly interested in complete metric spaces and he shows that the closure of the range of an almost periodic movement $f(t)$ in a complete metric space $X$ is a compact subspace. In the same way it can be shown that the closure of the range of a uniformly continuous family of a.p. movements in a complete metric space is a compact subspace. This gives us that the definitions coincide for complete metric spaces, and this is all I need. With the new definitions Tornehave's results about complete metric spaces can easily be extended to arbitrary metric spaces. The new definition can be extended further to arbitrary topological spaces because it is possible to introduce one and only one uniformity structure on compact spaces.

Let $\mathscr{C}$ denote the class of metric spaces which are continuously locally arcwise connected. Then $\mathscr{C}$ includes the class $\mathscr{C}$ ' of metrizable $C W$ complexes, which again includes the class $\mathscr{C}^{\prime \prime}$ of locally compact polyhedrons.

Definition. Two almost periodic movements $x_{1}=f_{1}(t)$ and $x_{2}=f_{2}(t)$ are called a(lmost) p(eriodically) homotopic iff there exists a uniformly continuous family $x=f(t, v)$ with $f(t, 0)=f_{1}(t)$ and $f(t, 1)=f_{2}(t)$.

This relation is obviously an equivalence relation in the set of a.p. movements in $X$ and it leads to a subdivision of this set into a.p. homotopy classes.

Remark. A continuous function $\tilde{f}: \boldsymbol{R}^{n} \rightarrow X$ which is periodic in all the variables with the same period $r \in \boldsymbol{R}$ (called a torus map by Tornehave) corresponds to torus maps $T^{n} \rightarrow X$ (we can look at $T^{n}$ as $\left.\boldsymbol{R}^{n} /(q r \boldsymbol{Z})^{n}, q \in \boldsymbol{Z}\right)$. The function $g: \boldsymbol{R}^{n} \rightarrow X: g(t)=\tilde{f}(p t), p \in \boldsymbol{R}$ has period $\frac{r}{p}$ and corresponds to the same torus maps as $\tilde{f}$ (we can look at $T^{n}$ as $\left.\boldsymbol{R}^{n} /\left(\frac{q r}{p} \boldsymbol{Z}\right)^{n}, q \in \boldsymbol{Z}\right)$. Usually

I think of $T^{n}$ as $\boldsymbol{R}^{n} / \boldsymbol{Z}^{n}$ and I call the variables $\left(u_{1}, \ldots, u_{n}\right)$ with $u_{i} \in[0,1]$. If $\left(\beta_{1}, \ldots, \beta_{n}\right)$ are real numbers and $t$ is also real, and $f: T^{n} \rightarrow X$ is a map, I write $f\left(\beta_{1} t, \ldots, \beta_{n} t\right)$ for $f\left(\left\{\beta_{1} t\right\}, \ldots,\left\{\beta_{n} t\right\}\right)$, where $\{\beta t\}$ is the (one of the) $u \in[0,1]$ for which $\beta t \equiv u(\bmod 1)$. It is well known that $x=f\left(\beta_{1} t, \ldots, \beta_{n} t\right)$ is an almost periodic movement in $X$. In the opposite direction we get from [4], p. 28:

Theorem. Every almost periodic movement $x_{1}=f(t)$ in $X \in \mathscr{C}$ is a.p. homotopic to a certain $x_{2}=g\left(\beta_{1} t, \ldots, \beta_{n} t\right)$ with $g: T^{n} \rightarrow X$ and $\left(\beta_{1}, \ldots, \beta_{n}\right)$ rationally independent real numbers (i.e. independent as vectors in a $\boldsymbol{Q}$-vector space).

The following theorem is [4] lemma 22 with a correction ${ }^{1}$ ).
Theorem 15. Let $\tilde{f}(t)$ and $\tilde{g}(t)$ be two almost periodic movements in $X \in \mathscr{C}$. In order to investigate whether $\tilde{f}$ and $\tilde{g}$ are a.p. homotopic we choose a common set of $n$ rationally independent real numbers $\left(\beta_{1}^{\prime}, \ldots, \beta_{p}^{\prime}\right)$ and torus maps $f^{\prime}, g^{\prime}: T^{p} \rightarrow X$ such that $\tilde{f}(t)$ is a.p. homotopic to $f^{\prime}\left(\beta_{1}^{\prime} t, \ldots, \beta_{p}^{\prime} t\right)$ and $\tilde{g}(t)$ is a.p. homotopic to $g^{\prime}\left(\beta_{1}^{\prime} t, \ldots, \beta_{p}^{\prime} t\right)$. Then $\tilde{f} \underset{\text { a.p. }}{\sim} \tilde{g}$ iff there exists a natural number $N$, such that $f^{\prime} \circ(\times N) \simeq g^{\prime} \circ(\times N)$, where $\times N: T^{p} \rightarrow T^{p}$ is defined by $(\times N)\left(u_{1}, \ldots, u_{p}\right)=\left(N u_{1}, \ldots, N u_{p}\right)$.

I shall now discuss the notions introduced in definitions 4-7 in the introduction.

Theorem 16. Let $X=\tilde{f}(t)$ be an a.p. movement in $X \in \mathscr{C}$. Let $f: T^{n} \rightarrow X$ be one of its corresponding torus maps (i.e. $f\left(\beta_{1} t, \ldots, \beta_{n} t\right) \underset{\text { a.p. }}{\sim} \tilde{f}(t)$ and $\left(\beta_{1}, \ldots, \beta_{n}\right)$ are rationally independent). Then $\tilde{f}$ is a.p. m-reducibel iff $f \circ(\times N)$ is m-reducible for some natural number $N$.

Proof. We may assume $m<n$. We shall first prove "only if". Let $\tilde{f}$ be a.p. m-reducible. We choose $g: T^{m} \rightarrow X$ and rationally independent numbers $\left(\gamma_{1}, \ldots, \gamma_{m}\right)$ such that

$$
g\left(\gamma_{1} t, \ldots, \gamma_{m} t\right) \underset{\mathrm{a} \cdot \mathrm{p} .}{\simeq} \tilde{f}(t) \underset{\mathrm{a} \cdot \mathrm{p} .}{\simeq} f\left(\beta_{1} t, \ldots, \beta_{n} t\right)
$$

We now look at the vector space $V$ over $\boldsymbol{Q}$ spanned by $\left(\beta_{1}, \ldots, \beta_{n}, \gamma_{1}, \ldots, \gamma_{m}\right)$. Then $p=\operatorname{dim} V \geq \max \{m, n\}$. We supplement $\left(\beta_{1}, \ldots, \beta_{n}\right)$ to a basis $\left(\beta_{1}^{\prime}, \ldots, \beta_{n}^{\prime}, \beta_{n+1}^{\prime}, \ldots, \beta_{p}^{\prime}\right)$ with $\beta_{v}^{\prime}=\beta_{v}, v=1, \ldots, n$. Then the $\gamma_{i}$ 's are rational linear combinations of $\left(\beta_{j}^{\prime}\right)$. Thus there exists a natural number $M$
${ }^{1}$ ) Tornehave told me about this mistake. He overlooked the possibility of the factor $(\times N)$ such that his condition is too strong. The examples proving the existence of non-trivial a.p. movements are never the less correct, because the relevant obstructions belong to infinite cyclic groups.
so that the $M \gamma_{i}$ 's are integral linear combinations $\Lambda_{i}, i=1, \ldots, m$ of $\left(\beta_{j}^{\prime}\right)$. We now define a map $f_{1}: T^{p} \rightarrow T^{n} \rightarrow X$ by $f_{1}\left(u_{1}, \ldots, u_{n}, u_{n+1}, \ldots, u_{p}\right)=$ $f\left(M u_{1}, \ldots, M u_{n}\right)$ and a map $g_{1}: T^{p} \rightarrow T^{m} \rightarrow X$ by $g_{1}\left(u_{1}, \ldots, u_{p}\right)=$ $g\left(\Lambda_{1}(\boldsymbol{u}), \ldots, \Lambda_{m}(\boldsymbol{u})\right)$.

Because $f\left(\beta_{1} t, \ldots, \beta_{n} t\right) \underset{\text { a.p. }}{\simeq} g\left(\gamma_{1} t, \ldots, \gamma_{m} t\right)$ we have $f\left(M \beta_{1} t, \ldots, M \beta_{n} t\right)=f_{1}\left(\beta_{1}^{\prime} t, \ldots, \beta_{p}^{\prime} t\right) \underset{\text { a.p. }}{\sim} g\left(M \gamma_{1} t, \ldots, M \gamma_{m} t\right)=g_{1}\left(\beta_{1}^{\prime} t, \ldots, \beta_{p}^{\prime} t\right)$ (and $\left(\beta_{1}^{\prime}, \ldots, \beta_{p}^{\prime}\right)$ are rationally independent). Theorem 15 tells us that there exists a natural number $N_{1}$ such that $f_{1} \circ\left(\times N_{1}\right) \simeq g_{1} \circ\left(\times N_{1}\right)$. Then the restrictions to the $T^{n} \subseteq T^{p}$ corresponding to $u_{n+1}=\ldots=u_{p}=0$ are homotopic, i.e.

$$
\begin{align*}
& f_{1}\left(N_{1} u_{1}, \ldots, N_{1} u_{n}, 0, \ldots, 0\right)=f\left(M N_{1} u_{1}, \ldots, M N_{1} u_{n}\right) \simeq g_{1}\left(N_{1} u_{1}, \ldots, N_{1} u_{n}, 0, \ldots, 0\right)  \tag{0}\\
& \quad=g\left(N_{1} \Lambda_{1}\left(u_{1}, \ldots, u_{n}, 0, \ldots, 0\right), \ldots, N_{1} \Lambda_{m}\left(u_{1}, \ldots, u_{n}, 0, \ldots, 0\right)\right)
\end{align*}
$$

Denoting by $h: T^{n} \rightarrow T^{m}$ the map defined by
$\left(u_{1}, \ldots, u_{n}\right) \rightarrow\left(N_{1} \Lambda_{1}\left(u_{1}, \ldots, u_{n}, 0, \ldots, 0\right), \ldots, N_{1} \Lambda_{m}\left(u_{1}, \ldots, u_{n}, 0, \ldots, 0\right)\right)$
we have $f \circ\left(\times N_{1} M\right) \simeq g \circ h$, where $h: T^{n} \rightarrow T^{m}$ and $g: T^{m} \rightarrow X$, so that $f \circ\left(\times N_{1} M\right)$ is m-reducible.

Next, we shall prove "if". Suppose $f^{\prime}=f \circ(\times N)$ is $m$-reducible. We have $f^{\prime}\left(\beta_{1}^{\prime} t, \ldots, \beta_{n}^{\prime} t\right) \underset{\text { a.p. }}{\sim} \tilde{f}(t)$, where $\left(\beta_{1}^{\prime}=\beta_{1} / N, \ldots, \beta_{n}^{\prime}=\beta_{n} / N\right)$ are rationally independent. Because $\left[T^{n}, T^{m}\right] \simeq \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(T^{m}, t_{0}\right)\right)$ we can choose $h: T^{n} \rightarrow T^{m}$ linear (corresponding to $\boldsymbol{A}_{m, n}$ ) and $g: T^{m} \rightarrow X$ so that $f^{\prime} \simeq g \circ h$. If we put

$$
\left(\begin{array}{c}
\tilde{\beta}_{1} \\
\vdots \\
\vdots \\
\tilde{\beta}_{m}
\end{array}\right)=\boldsymbol{A}_{m, n}\left(\begin{array}{l}
\beta_{1}^{\prime} \\
\vdots \\
\beta_{n}^{\prime}
\end{array}\right)
$$

then

$$
\tilde{f}(t) \underset{\mathrm{a} \cdot \mathrm{p} .}{\simeq} f^{\prime}\left(\beta_{1}^{\prime} t, \ldots, \beta_{n}^{\prime} t\right) \underset{\mathrm{a} \cdot \mathrm{p} .}{\simeq} g \circ h\left(\beta_{1}^{\prime} t, \ldots, \beta_{n}^{\prime} t\right)=g\left(\widetilde{\beta}_{1} t, \ldots, \tilde{\beta}_{m} t\right)
$$

so that $\tilde{f}$ is a.p. m-reducible.
Remarks. 1) $(f \circ(\times N))_{*}=N f_{*}$, so rank $f_{*} \pi_{1}\left(T^{n}, t_{0}\right)=r$ iff there exists a natural number $N$ such that $(f \circ(\times N))_{*} \pi_{1}\left(T^{n}, t_{0}\right) \simeq \boldsymbol{Z}^{r}$.
2) $(f \circ(\times N))_{\# p}=N^{p} f_{\# p}$, so rank $f_{\# p} H_{p}\left(T^{n}\right)=r$ iff there exists a natural number $N$ such that $(f \circ(\times N))_{\# p} H_{p}\left(T^{n}\right) \simeq \boldsymbol{Z}^{r}$.

Statement 2) follows immediately from the expression of elements of $H_{p}\left(T^{n}\right)$ as cross products of elements from $H_{1}\left(S^{1}\right)$. The remarks and Theorem 16 gives us that the theorems from chapter $V$ can be changed to theorems about almost periodic movements in $X \in \mathscr{C}$, by translating "dim" to "rank". Let $\mathscr{C}_{0}$ denote the class of path connected spaces in $\mathscr{C}$.

Remark. Let $x=\tilde{f}(t)$ be an a.p.-movement in $X \in \mathscr{C}_{0}$ corresponding (for some $\left(\beta_{1}, \ldots, \beta_{n}\right)$ ) to $f: T^{n} \rightarrow X$. If $\tilde{f}(t)$ is a.p. m-reducible, then rank $f_{*} \pi_{1}\left(T^{n}, t_{0}\right) \leq m$ and rank $f_{\# p} H_{p}\left(T^{n}\right) \leq\binom{ m}{p}$ for every $p$.

Theorem 17. Suppose that $F_{m+1}:\left[T^{m+1}, X\right] \rightarrow \operatorname{Hom}\left(\pi_{1}\left(T^{m+1}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right) / \sim$ is surjective and that $X \in \mathscr{C}_{0}$ (e.g. $X$ is an m-space of type $\left(\pi_{1}, 1\right)$ or an $H$-space). If, further, $X$ is a.p. m-reducible, then the rank of any abelian subgroup of $\pi_{1}\left(X, x_{0}\right)$ is $\leqq m$.

Theorem 18. Suppose that $F_{n}:\left[T^{n}, X\right] \rightarrow \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right) / \sim$ is bijective and that $X \in \mathscr{C}_{0}$ (e.g. $X$ is an $n$-space of type $\left(\pi_{1}, 1\right)$ ). Then an almost periodic movement corresponding to $f: T^{n} \rightarrow X$ is a.p. m-reducible iff $\operatorname{rank} f_{*}\left(\pi_{1}\left(T^{n}, t_{0}\right)\right) \leqq m$.

Theorem 19. Let $F_{n}:\left[T^{n}, X\right] \rightarrow \operatorname{Hom}\left(\pi_{1}\left(T^{n}, t_{0}\right), \pi_{1}\left(X, x_{0}\right)\right) / \sim$ be bijective for every $n>m$ (e.g. $X$ is a space of type $\left(\pi_{1}, 1\right)$ ), and let $X \in \mathscr{C} 0$. Then $X$ is a.p. m-reducible iff the rank of every abelian subgroup of $\pi_{1}\left(X, x_{0}\right)$ is $\leqq m$.

Theorem 20. A space $X \in \mathscr{C}_{0}$ is a.p. 1-reducible (i.e. every a.p. movement in $X$ is a.p. homotopic to a periodic movement) iff the rank of every abelian subgroup of $\pi_{1}\left(X, x_{0}\right)$ is $\leqq 1$ and for every natural number $n$ every pair of maps $f, g: T^{n} \rightarrow X$ satisfying $F_{n}[f]=F_{n}[g]$ also satisfies the condition $f \circ(\times N)$ $\simeq g \circ(\times N)$ for some natural number $N$.

Theorem 21, 22. Let $X \in \mathscr{C}_{0}$ be a p-space of type $\left(\pi_{p}, p\right)$ with $\pi_{p}$ abelian. Then

1) if $X$ is a.p. m-reducible for some $m<p$, then rank $\pi_{p}=0$.
2) if $p \leqq m$ and $G_{m+1}:\left[T^{m+1}, X\right] \rightarrow \operatorname{Hom}\left(H_{p}\left(T^{m+1}\right)\right.$, $\left.\pi_{p}\right)$ defined by $G_{m+1}[f]=\chi^{-1} f_{\# p}$ is surjective (e.g. $X$ is an m-space of type $\left(\pi_{p}, p\right)$ or $X$ is an $H$-space of $p$-type $\left(\pi_{p}, p\right)$ ) and $X$ is a.p. m-reducible, then rank $\pi_{p} \leqq\binom{ m}{p}$.

Examples. 1) Because the fundamental groups of the complex and quaternionic projective spaces are zero and the first nontrivial homotopy groups are isomorphic to $\boldsymbol{Z}$, these spaces are not a.p. 1-reducible.
2) $S^{n}(n>1)$ is not a.p. $m$-reducible for $m<n\left(\pi_{n}\left(S^{n}, s_{0}\right) \simeq \boldsymbol{Z}\right)$.
3) $P^{n}(n>1)$ is not a.p. $m$-reducible for $m<n$ (proof analogous to the proof p. 20).
4) $S^{2}$ is not a.p. 2 -reducible $\left(\left[T^{3}, S^{3}\right] \simeq \boldsymbol{Z}\right)$.

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# THE INTERPRETATION OF ULTRASONIC RELAXATION SPECTRA WITHIN THE THEORY OF IRREVERSIBLE THERMODYNAMICS 

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## Synopsis

Explicit expressions are given for the ultrasonic absorbtion spectrum caused by several coupled chemical reactions. The expressions are exact within the theory of irreversible thermodynamics and are given in a form which makes it easy to calculate the relaxation spectrum for a given kinetic model from knowledge of the rate constants and normally used thermodynamic parameters. The article also suggests approximations in terms of one or a few relaxation times of the relaxation spectrum caused by several reactions.

## I. Introduction

The interpretation of relaxation experiments within the theory of irreversible thermodynamics in the case of a single chemical degree of freedom has been treated very thoroughly in several places (see e.g. ref 1). When one wants to treat the possibility of more than a single chemical reaction, one normally makes at least one of the following approximations. Either one treats the coupling between the chemical reactions correctly but supposes that the concentrations are small so that the coupling between the chemical degrees of freedom and the physical degrees of freedom ( $p$ and $T$ ) cand be neglected (2). Or one supposes that the relaxation times for the different chemical reactions are separated so much that the coupling between the different chemical reactions can be neglected.

Only in one article (3) does it seem possible to find the correct treatment without other assumptions than the general assumptions of irreversible thermodynamics. This article, however, still leaves several questions open for the experimentalist, who wants to interpret his results in terms of a multistep mechanism. The most important of these questions are:

1) How are the functions $\varepsilon$ and $A$ in the general rate equation of irreversible thermody namics

$$
\begin{equation*}
\frac{d \xi}{d t}=\varepsilon(p, T, \xi) A(p, T, \xi) \tag{1}
\end{equation*}
$$

transformed into normal kinetic parameters?
2) What is the connection between the kinetic and thermodynamic parameters and the weight-factors of the different relaxation times? e.g. the $A$ 's in the expression for the attenuation factor as a function of the frequency $\omega$ :

$$
\begin{equation*}
\frac{\alpha}{\omega^{2}}=\sum_{j=1}^{n} \frac{A_{j}}{1+\left(\omega \tau_{j}\right)^{2}} \tag{2}
\end{equation*}
$$

where the $\tau$ 's are the relaxation times
3) If one makes one of the above-mentioned approximations, how large is then the error-term?
4) Is it possible to describe the results from measurements on multistepmechanisms with one or two relaxation times and how will these parameters then be connected with the kinetic and thermodynamic parameters?

It is the purpose of this article to try to answer these questions. Expressions will be given explicitly for the frequency dependence of the attenuation factor in the case of ultrasonic absorption, but the general approach should equally well applicable to other types of relaxation measurements. The treatment given here is closely related to that of the Groot and Mazur (1) for a single chemical reaction to which one should refer for a more detailed explanation of the problems of irreversible thermodynamics.

## II. The rate equations

The general reaction scheme for $n$ different chemical reactions involving altogether $m$ different chemical species, $A_{1}, A_{2}, \ldots A_{m}$, may be written:

$$
\left.\begin{array}{l}
v_{11}^{+} A_{1}+v_{12}^{+} A_{2}+\ldots+v_{1 m}^{+} A_{m} \rightleftarrows v_{11}^{-} A_{1}+v_{12}^{-} A_{2}+\ldots+v_{1 m}^{-} A_{m} \\
v_{21}^{+} A_{1}+v_{22}^{+} A_{2}+\ldots+v_{2 m}^{+} A_{m} \rightleftarrows v_{21}^{-} A_{1}+v_{22}^{-} A_{2}+\ldots+v_{2 m}^{-} A_{m}  \tag{3}\\
\cdot \\
\cdot \\
v_{n 1}^{+} A_{1}+v_{n 2}^{+} A_{2}+\ldots+v_{n m}^{+} A_{m} \rightleftarrows v_{n 1}^{-} A_{1}+v_{n 2}^{-} A_{2}+\ldots+v_{n m}^{-} A_{m}
\end{array}\right\}
$$

where many of the coefficients, $v^{+}$and $v^{-}$, of course, may be zero, since chemical reactions are normally either unimolecular of bimolecular.

The rate equations for the system (3) are most easily stated by first introducing a reaction parameter $\xi_{i}$ for each of the $n$ reactions $(i=, 2, \ldots, N)$. $\xi_{i}$ measures the change in chemical composition from the time $t_{0}$ until the time $t$ caused by the $i$ 'th reaction, such that the change in the number of moles of $A_{1}$ from time $t_{0}$ to time $t$ caused by the first reaction will be $\left(v_{11}^{-}-v_{11}^{+}\right) \xi_{1}$, owing to the second reaction the change will be $\left(v_{21}^{-}-v_{21}^{+}\right) \xi_{2}$, and so on. Altogether the change in the number of moles of $A_{1}$ from time $t_{0}$ to time $t_{1}$ will be equal to

$$
\begin{equation*}
x_{1}=\sum_{i=1}^{n}\left(v_{i 1}^{-}-v_{i 1}^{+}\right) \xi_{i} . \tag{4a}
\end{equation*}
$$

Similar for the change in the number of moles of $A_{2}$ :

$$
\begin{equation*}
x_{2}=\sum_{i=1}^{n}\left(v_{i 2}^{-}-v_{i 2}^{+}\right) \xi_{i} \tag{4b}
\end{equation*}
$$

etc. for $A_{3}, A_{4}, \ldots A_{m}$. These and the following equations can be brought into a more convenient form by introducing a matrix notation:

$$
\begin{equation*}
\xi^{T}=\left\{\xi_{1}, \xi_{2}, \ldots, \xi_{n}\right\} . \tag{5}
\end{equation*}
$$

(All vectors are supposed to be column vectors. Superscript $T$ stands for transposing and consequently $\xi^{T}$ is a row vector)

$$
\begin{gather*}
\boldsymbol{x}^{T}=\left\{\begin{array}{l}
\left\{x_{1}, x_{2}, \ldots, x_{n}\right\} \\
\boldsymbol{N}=\left\{\begin{array}{l}
v_{11}, v_{12}, \ldots \\
v_{21}, v_{22}, \ldots \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
v_{n 1}, \\
\cdot
\end{array}\right) \cdot \\
v_{n 2}, \\
\cdot \\
v_{i j}=v_{n m}^{-}-v_{i j}^{+}
\end{array}\right\} \tag{6}
\end{gather*}
$$

With this notation the equations (4) read:

$$
\begin{equation*}
\boldsymbol{x}=\boldsymbol{N}^{T} \xi \tag{9}
\end{equation*}
$$

Note that knowledge of a given chemical composition at time $t_{0}$ and a given chemical composition at time $t$ are not always sufficient information to determine the $\xi_{i}$ 's uniquely. The composition at time $t_{0}$ together with the rate equations given below, however are always sufficient to determine the $\xi_{i}$ 's uniquely.

Using $k_{i}$ for the forward and $k_{-i}$ for the backward rate constant for the $i$ 'th reaction $(i=1,2 \ldots, n)$, the normal rate equations for the system of chemical reactions (3) are:

$$
\begin{align*}
& \frac{1}{V} \frac{d \xi_{1}}{d t}=k_{1} \prod_{j=1}^{m} c_{j}^{v_{1 j}^{+}}-k_{-1} \prod_{j=1}^{m} c_{j}^{v_{1 j}^{-}} \\
& \frac{1}{V} \frac{d \xi_{2}}{d t}=k_{2} \prod_{j=1}^{m} c_{j}^{v_{2 j}^{+}}-k_{-2} \prod_{j=1}^{m} c_{j}^{v_{1 j}^{-}}  \tag{10}\\
& \quad \cdot \\
& \quad \cdot \\
& \frac{1}{V} \frac{d \xi_{n}}{d t}=k_{n} \prod_{j=1}^{m} c_{j}^{v_{n j}^{+}}-k_{-n} \prod_{j=1}^{m} c_{j} v_{n j}^{-}
\end{align*}
$$

where $V$ is the volume and $c_{j}$ is the concentration in moles/liter of $A_{j}(j=1$, $2, \ldots, m)$. As defined by equation (10) the rate constants $k_{i}$ and $k_{-i}$ will in general depend not only on $p$ and $T$ but also on the concentrations. In order to get through with the calculations one will need some specific assumption about the dependence of the rate constants on the concentrations. It is common to just take the simplest way out and assume that the rate constants are independent of the concentrations. This approximation, however, has some less satisfactory consequences.

Equations (10) implies the equilibrium conditions:

$$
\begin{equation*}
0=\frac{d \xi_{i} / V}{d t}=k_{i} \prod_{j=1}^{m} c_{j}^{v_{i j}^{+}}-k_{i} \prod_{j=1}^{m} c_{j}{ }^{v_{i j}^{-}} \tag{11}
\end{equation*}
$$

or :

$$
\begin{equation*}
\prod_{j=1}^{m} c_{j}^{v_{i j}}=\frac{k_{i}}{k_{-i}}=K_{i} \tag{12}
\end{equation*}
$$

where $K_{i}$ is the equilibrium constant for the $i$ 'th reaction. Writing $\mu_{j}$ for the chemical potential of the $j$ 'th component and $g_{i}$ for the molar change in chemical potential due to the $i$ th reaction:

$$
\begin{equation*}
g_{i}=\sum_{j=1}^{m} v_{i j} \mu_{j} \tag{13}
\end{equation*}
$$

eqn (12) implies

$$
\begin{gather*}
g_{i}=g_{i}^{0}+R T \ln \prod_{j=1}^{m} c_{j}^{v_{i j}}  \tag{14}\\
g_{i}^{0}=-R T \ln K_{i} \tag{15}
\end{gather*}
$$

Since the number of moles can only change by the chemical reactions, the differential of the Gibbs' free energy:

$$
\begin{equation*}
d G=-S d T+V d p+\sum_{j=1}^{m} \mu_{j} d x_{j} \tag{16}
\end{equation*}
$$

can be written:

$$
\begin{equation*}
d G=-S d T+V d p+\sum_{i=1}^{n} g_{i} d \xi_{i} \tag{17}
\end{equation*}
$$

and one consequently has the following Maxwell relation

$$
\begin{equation*}
\left(\frac{\delta g_{i}}{\delta \xi_{k}}\right)_{p, T, \xi^{-}}=\left(\frac{\delta g_{k}}{\delta \xi_{i}}\right)_{p, T, \xi^{-}} \tag{18}
\end{equation*}
$$

where the index $\xi^{-}$means that all other $\xi$ 's are kept constant. Using eqn. (14) and the assumption that $g_{i}^{0}$ depends only on $p$ and $T$, eqn. (18) gives

$$
\begin{equation*}
\frac{R T}{V} \Delta v_{i}\left(\frac{\delta V}{\delta \xi_{k}}\right)_{p, T, \xi^{-}}=\frac{R T}{V} \Delta v_{k}\left(\frac{\delta V}{\delta \xi_{i}}\right)_{p, T, \xi^{-}} \tag{19}
\end{equation*}
$$

with

$$
\begin{equation*}
\Delta v_{i}=\sum_{j=1}^{m} v_{i j} \tag{20}
\end{equation*}
$$

The implication of (19), namely that change in volume by the $i$ 'th reaction is proportional to the change in moles $\left(\Delta v_{i}\right)$ by the $i$ 'th reaction with a proportionality factor, which does not depend on $i$, is of course fulfilled for the ideal gases, but seems less satisfactory for solutions. (Note that the problem only arises in case of more than one chemical reaction). In many cases it will of course be a reasonable approximation for solutions to put $\left(\frac{\delta V}{\delta \xi_{i}}\right)_{p, T, \xi^{-}}$equal to zero, which solves the problem.

Here, however, we will prefer the more general solution which is obtained by using molar fractions in place of concentrations, and then in the end merely state the results for $g_{i}^{0}$ only depending on $p$ and $T$. With $z_{j}$ for the molar fraction of the $j$ 'th component, $v$ for the total number of moles and tildes on new parameters we get the following equations in place of equations (10), (12), (14) and (15):

$$
\begin{align*}
& \frac{d \xi_{i}}{d t}=v\left(\tilde{k}_{i} \prod_{j=1}^{m} z_{j}^{v_{i j}^{+}}-\tilde{k}_{-i} \prod_{j=1}^{m} z_{j} v_{i j}^{-}\right)  \tag{21}\\
& \tilde{K}_{i}=\prod_{j=1}^{m} z_{j}{ }^{v_{i j}}  \tag{22}\\
& g_{i}=\tilde{g}_{i}^{0}+R T \ln \prod_{j=1}^{m} z_{j}{ }^{v}{ }^{0}  \tag{23}\\
& \tilde{g_{i}^{0}}=-R T \ln \tilde{K}_{i} \quad(i=1,2,3, \ldots, n) \tag{24}
\end{align*}
$$

where it now is supposed that $g_{i}^{0}$ and $k_{i}$ and $k_{-1}$ only depend on $p$ and $T$ but are independent of the molar fractions. The rate equation (21) (respectively (10)) is different from the rate equation (1), which is the one normally used in irreversible thermodynamics. If one writes (21) as

$$
\begin{gather*}
\frac{d \xi_{i}}{d t}=v \tilde{\gamma}_{i}^{2}\left(1-\exp \left(g_{i} \mid R T\right)\right)  \tag{25}\\
\tilde{\gamma}_{i}^{2}=\tilde{k}_{i} \prod_{j=1}^{m} z_{j}^{v_{i j}^{+}} \tag{26}
\end{gather*}
$$

it is easily seen that the two equations become identical when one only keeps terms that are linear in the deviation from equilibrium, which is the normal approximation of irreversible thermodynamics.

Making this approximation one gets the rate equations:

$$
\begin{align*}
& \frac{d \xi_{i}}{d t}=v \tilde{\gamma}_{i}^{2}\left[\frac{1}{R T^{2}}\left(\frac{\delta H}{\delta \xi_{i}}\right)_{p, T, \xi^{-}} \delta T-\frac{1}{R T}\left(\frac{\delta V}{\partial \xi_{i}}\right)_{p, T, \xi^{-}} \delta p\right. \\
&\left.+\frac{1}{v} \sum_{k=1}^{n}\left(\Delta v_{i} \Delta v_{k}-\sum_{j=1}^{m} v_{i j} v_{k j} z_{j}\right) \xi_{k}\right]  \tag{27}\\
&(i=1,2,3, \ldots, n) .
\end{align*}
$$

where we have chosen the reference time, $t_{0}$, to correspond to the equilibrium state at the pressure $p$ and the temperature $T$, so that $\boldsymbol{\xi}$ and $\boldsymbol{x}$ measure deviations from this equilibrium state, while the deviation on other variables from this reference state is designated by a $\delta$.

In matrix notation the equations (27) read:

$$
\begin{equation*}
\dot{\boldsymbol{\xi}}=\tilde{\boldsymbol{G}}^{2}\left[\frac{v}{R T^{2}} \delta T \boldsymbol{h}-\frac{v}{R T} \delta p \boldsymbol{v}+\left(\boldsymbol{\nu} \nu^{T}-\boldsymbol{N} \boldsymbol{Z}^{-1} \boldsymbol{N}^{T}\right) \xi\right] \tag{28}
\end{equation*}
$$

where we have introduced the following vectors and matrices:

$$
\begin{align*}
& \boldsymbol{h}^{T}=\left\{\left(\frac{\delta H}{\delta \xi_{1}}\right)_{p, T, \xi^{-}},\left(\frac{\delta H}{\delta \xi_{2}}\right)_{p, T, \xi^{-}}, \ldots,\left(\frac{\delta H}{\delta \xi_{n}}\right)_{p, T, \xi^{-}}\right\}  \tag{29}\\
& \boldsymbol{v}^{T}=\left\{\left(\frac{\delta V}{\delta \xi_{1}}\right)_{p, T, \xi^{-}},\left(\frac{\delta V}{\delta \xi_{2}}\right)_{p, T, \xi^{-}}, \ldots,\left(\frac{\delta V}{\delta \xi_{n}}\right)_{p, T, \xi^{-}}\right\}  \tag{30}\\
& \boldsymbol{v}^{T}=\left\{\Delta v_{1}, \Delta v_{2}, \ldots, \Delta v_{n}\right\}=\boldsymbol{e}^{T} \boldsymbol{N}^{T}  \tag{31}\\
& \boldsymbol{e}^{T}=\{1,1,1, \ldots, 1\} \tag{32}
\end{align*}
$$

$$
\begin{align*}
\tilde{\boldsymbol{G}} & =\left\{\begin{array}{ccccc}
\tilde{\gamma}_{1} & 0 & 0 & \ldots & 0 \\
0 & \tilde{\gamma}_{2} & 0 & \ldots & 0 \\
0 & 0 & \tilde{\gamma}_{3} & \ldots & 0 \\
\cdot & \cdot & \cdot & & \cdot \\
\cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & & \cdot \\
0 & 0 & 0 & \ldots & \tilde{\gamma}_{n}
\end{array}\right\}  \tag{33}\\
\boldsymbol{Z} & =\left\{\begin{array}{llllll}
z_{1} & 0 & 0 & \ldots & 0 \\
0 & z_{2} & 0 & \ldots & 0 \\
0 & 0 & z_{3} & \ldots & 0 \\
\cdot & \cdot & \cdot & & \cdot \\
\cdot & \cdot & \cdot & & \cdot \\
\cdot & \cdot & \cdot & & \cdot \\
0 & 0 & 0 & \ldots & z_{m}
\end{array}\right\} \tag{34}
\end{align*}
$$

In many cases it will be useful to reduce the number of chemical variables to a minimum. This is attained by reducing the number of rows in $\boldsymbol{N}$. In general the rows of $\boldsymbol{N}$ will not be linearly independent, but it can of course always be arranged that the first $n$ ' rows are independent and that the remaining $n-n$ ' rows can be written as linear combinations of the first $n$ ' rows. With $\boldsymbol{N}^{\prime}$ for the matrix consisting of the first $n$ ' row of $\boldsymbol{N}$, this means that

$$
\begin{equation*}
\boldsymbol{N}=\boldsymbol{B N} \tag{35}
\end{equation*}
$$

where $\boldsymbol{B}$ is $n \times n^{\prime}$ matrix, whose first $n^{\prime}$ rows are identical with the $n^{\prime} \times n^{\prime}$ identity matrix. According to the definition $n$ ' is equal to the rank of $\boldsymbol{N}$. Since it follows from the conservation of mass, that there exists at least one linear relation between the columns of $\boldsymbol{N}$ the following restriction on $n^{\prime}$ is evident

$$
\begin{equation*}
n^{\prime} \leq m-1 \tag{36}
\end{equation*}
$$

Using $\boldsymbol{y}$ for the $n$ '-dimensional vector, whose elements are the new, independent chemical variables (9) is changed to:

$$
\begin{align*}
\boldsymbol{x} & =\boldsymbol{N}^{\prime T} \boldsymbol{y}  \tag{37}\\
\boldsymbol{y} & =\boldsymbol{B}^{T} \boldsymbol{\xi} \tag{38}
\end{align*}
$$

Note that $\boldsymbol{y}$ is not just the first $n$ ' elements of $\boldsymbol{\xi}$. (It is of course possible
to choose other basic sets of variables than $\boldsymbol{y}$ by substituting $\boldsymbol{D}^{-1} \boldsymbol{y}$ for $\boldsymbol{y}$, $\boldsymbol{B D}$ for $\boldsymbol{B}$ and $\boldsymbol{D}^{-1} \boldsymbol{N}^{\prime}$ for $\boldsymbol{N}^{\prime}$ where $\boldsymbol{D}$ is any non-singular $n^{\prime} \times n^{\prime}$ matrix).

The physical interpretation of the reduction from the variables $\xi$ to the variables $\boldsymbol{y}$ is, that the first $n$ ' reactions in (3) are really independent while the remaining reactions can be written as linear combinations of the first $n^{\prime}$ reactions. This means that if $\boldsymbol{h}^{\prime}, \boldsymbol{v}^{\prime}$ and $\boldsymbol{v}^{\prime}$ are $n^{\prime}$ dimensional vectors whose components are the first $n$ 'components of $\boldsymbol{h}, \boldsymbol{v}$, and $\boldsymbol{v}$ respectively, then one has the relations

$$
\begin{align*}
\boldsymbol{h} & =\boldsymbol{B} \boldsymbol{h}^{\prime}  \tag{39}\\
\boldsymbol{v} & =\boldsymbol{B} \boldsymbol{v}^{\prime}  \tag{40}\\
\boldsymbol{v} & =\boldsymbol{B} \boldsymbol{v}^{\prime} \tag{41}
\end{align*}
$$

The similar equation for the $g_{i}^{\tilde{0}}$,s gives that chemical equilibrium is determined by the first $n$ ' equations of (22), and that the remaining $n-n$ ' equations automatically are fulfilled, if the first $n$ ' are fulfilled.

The final form of the rate equation then becomes:

$$
\begin{equation*}
\dot{\boldsymbol{y}}=\tilde{\boldsymbol{G}}^{\prime 2}\left[\frac{v}{R T^{2}} \delta T \boldsymbol{h}^{\prime}-\frac{v}{R T} \delta p \boldsymbol{v}^{\prime}-\left(\boldsymbol{N}^{\prime} \boldsymbol{Z}^{-1} \boldsymbol{N}^{\prime} T-v^{\prime} v^{\prime} T\right) \boldsymbol{y}\right] \tag{42}
\end{equation*}
$$

with

$$
\begin{equation*}
\tilde{\boldsymbol{G}}^{\prime 2}=\boldsymbol{B}^{T} \boldsymbol{G}^{2} \boldsymbol{B} \tag{43}
\end{equation*}
$$

## III. The attenuation factor

In order to find the attenuation factor at the frequency $\omega$ one has primarily to find $\frac{\delta p}{\delta V}$ at constant entropy under the assumption that the deviations of the variables vary harmonically with time with the frequency $\omega$. The condition of the entropy being constant is attained by introducing the additional equations

$$
\begin{equation*}
\delta S=\frac{\nu C_{p}}{T} \delta T-V l \delta p+\frac{1}{T} \boldsymbol{h}^{\prime} T \boldsymbol{y}=0 \tag{44}
\end{equation*}
$$

where we have used that at equilibrium $\left(g_{i}=0\right)$ :

$$
\begin{equation*}
\left(\frac{\delta S}{\xi_{i}}\right)_{p, T, \xi^{-}}=\frac{1}{T}\left(\frac{\delta H}{\xi_{i}}\right)_{p, T, \xi^{-}} \tag{45}
\end{equation*}
$$

Here $C_{p}$ an $l$ are the molar heat capacity and the coefficient of thermal expansion respectively:

$$
\begin{align*}
& C_{p}=\frac{1}{v}\left(\frac{\delta H}{\delta T}\right)_{p, \xi}  \tag{46}\\
& l=\frac{1}{V}\binom{\delta V}{\delta T}_{p, \xi} \tag{47}
\end{align*}
$$

The assumption of harmonic variation with time has only influence on the equations through the time derivatives:

$$
\begin{equation*}
\boldsymbol{y}=\boldsymbol{y}^{0} e^{i \omega t} \tag{48}
\end{equation*}
$$

gives

$$
\begin{equation*}
\dot{y}=i \omega y . \tag{49}
\end{equation*}
$$

Finally we shall need the equation of state, which we write as

$$
\begin{equation*}
\delta V=V l \delta T-V \beta_{T} \delta p+\boldsymbol{y}^{\prime} T \boldsymbol{y} \tag{50}
\end{equation*}
$$

where $\beta_{T}$ is the isothermal compressibility

$$
\begin{equation*}
\beta_{T}=-\frac{1}{V}\left(\frac{\delta V}{\delta p}\right)_{T, \xi} \tag{51}
\end{equation*}
$$

Using eqn. (49) the equations (42), (44) and (50) are now fairly easily solved for $\frac{\delta V}{\delta p}$ (which gives neater expressions than solving for $\frac{\delta p}{\delta V}$ )

$$
\begin{equation*}
\frac{\delta V}{\delta p}=-\frac{V \beta_{T} C_{V}}{C_{p}}-\frac{v}{R T} \boldsymbol{f}^{\prime} T \tilde{\boldsymbol{G}}^{\prime}\left(\tilde{\boldsymbol{A}}^{\prime}+i \omega \boldsymbol{E}\right)^{-1} \tilde{\boldsymbol{G}}^{\prime} \boldsymbol{f}^{\prime} \tag{52}
\end{equation*}
$$

where we have used

$$
\begin{equation*}
C_{V}=C_{p}-T \frac{l^{2}}{\beta_{T}} \frac{V}{v} \tag{53}
\end{equation*}
$$

and furthermore introduced the vector

$$
\begin{equation*}
\boldsymbol{f}^{\prime}=\boldsymbol{v}^{\prime}-\frac{V l}{v C_{p}} \boldsymbol{h}^{\prime} . \tag{54}
\end{equation*}
$$

$\boldsymbol{E}$ denotes the identity matrix and $\boldsymbol{A}^{\prime}$ the matrix

$$
\begin{equation*}
\tilde{\boldsymbol{A}}^{\prime}=\tilde{\boldsymbol{G}}^{\prime}\left(\boldsymbol{N}^{\prime} \boldsymbol{Z}^{-1} \boldsymbol{N}^{\prime} T-\boldsymbol{v}^{\prime} \boldsymbol{\nu}^{\prime} T+\frac{1}{C_{p} R T^{2}} \boldsymbol{h}^{\prime} \boldsymbol{h}^{\prime} T\right) \tilde{\boldsymbol{G}}^{\prime} \tag{5ّ5}
\end{equation*}
$$

The matrix $\tilde{\boldsymbol{G}}^{\prime}$ needs some comments, since in equation (43) we have only defined $\tilde{\boldsymbol{G}}^{\prime 2} . \boldsymbol{G}^{\prime 2}$ is obviously a symmetric, positive semidefinite matrix and from the definition of $\boldsymbol{B}$ it can be seen that $\boldsymbol{G}^{\prime 2}$ is even positive definite. Hence we have no difficulties in defining the square root as a matrix, which is also symmetric and positive definite.

Since $\tilde{\boldsymbol{A}}^{\prime}$ is positive definite, $\tilde{\boldsymbol{A}}^{\prime}$ has positive eigenvalues. Writing $\varkappa_{1}(\omega)$ for the real part and $\varkappa_{2}(\omega)$ for the imaginary part of $\frac{\delta V}{\delta p}$, we have

$$
\begin{gather*}
\varkappa_{1}(\omega)=-\frac{V \beta_{T} C_{V}}{C_{P}}-\frac{v}{R T} \sum_{j=1}^{n^{\prime}} \frac{\tilde{\varphi}_{j}^{\prime 2} \tilde{\lambda}_{j}}{\tilde{\lambda}_{j}^{2}+\omega^{2}}  \tag{56}\\
\varkappa_{2}(\omega)=\frac{v \omega}{R T} \sum_{j=1}^{n^{\prime}} \frac{\tilde{\varphi}_{j}^{\prime 2}}{\tilde{\lambda}_{j}^{2}+\omega^{2}} \tag{57}
\end{gather*}
$$

where $\tilde{\varphi}_{j}^{\prime}$ is the $j^{\prime}$ th component of the vector $\tilde{\varphi}^{\prime}$. With $\boldsymbol{M}^{\prime}$ as the matrix whose columns are the eigenvectors of $\boldsymbol{A}^{\prime}$ (in the same order as the eigenvalues), $\psi^{\prime}$ is given by

$$
\begin{equation*}
\varphi^{\prime}=\boldsymbol{M}^{\prime T} \boldsymbol{G} \boldsymbol{f}^{\prime} \tag{58}
\end{equation*}
$$

The general formula for the attenuation factor $\alpha$, now reads (see ref. 1, p. 325)

$$
\begin{equation*}
\alpha=\frac{\omega \cdot Q}{\sqrt{2}}\left[\varkappa_{1}(\omega)+\sqrt{\varkappa_{1}(\omega)^{2}+\varkappa_{2}(\omega)^{2}}\right]^{\frac{1}{2}} . \tag{59}
\end{equation*}
$$

This may be simplified, if

$$
\begin{equation*}
\sum_{j=1}^{n^{\prime}} \tilde{\varphi}_{j}^{\prime 2} / \tilde{\lambda}_{j} \ll \frac{V \beta_{T} C_{V} R T}{C_{P} v} \tag{60}
\end{equation*}
$$

since one then has

$$
\begin{equation*}
\left|\varkappa_{2}(\omega)\right| \ll\left|\varkappa_{1}(\omega)\right| \tag{61}
\end{equation*}
$$

for all values of $\omega$. Using this and the expression

$$
\begin{equation*}
c=1 /\left(\varrho \chi_{1}(\omega)\right) \tag{62}
\end{equation*}
$$

for the velocity of sound, which is valid in the same approximation (see ref. 1, p. 326), one gets

$$
\begin{equation*}
\alpha=\frac{1}{2} \frac{\omega^{2}}{c} \frac{C_{P} v}{V \beta_{T} C_{V} R T} \sum_{j=1}^{n^{\prime}} \frac{\tilde{\varphi}_{j}^{2}}{\tilde{\lambda}_{j}^{2}+\omega^{2}} \tag{63}
\end{equation*}
$$

The approximation (60) is equivalent to the assumption that the relative variation in the velocity of sound is small, as may be seen from (62). The problem of finding the attenuation factor as a function of frequency for a given kinetic model is now reduced to finding the square root of one matrix and diagonalizing another. These operations are easily carried on numerically, but in general case they are are hard to handle theoretically. For theoretical calculations it may therefore be advantageous to leave out the reduction of the number of chemical variables introduced in the equations (35) and (37)-(41). If this is done, one gets in place of $\tilde{\boldsymbol{A}}^{\prime}$ a matrix $\tilde{\boldsymbol{A}}$, which has the same eigenvalues as $\tilde{\boldsymbol{A}}^{\prime}$, and further $n-n$ ' eigenvalues equal to zero. It can, however, easily be proved that the weight factors, $\tilde{\varphi}_{j}{ }^{2}$, corresponding to these eigenvalues are zero.

## IV. Approximations

From the expressions given above (for example eq. (52) or (63)) it is in general not difficult to evaluate the implications of different types of approximations. This can normally be attained by application of relatively uncomplicated parts of the theory of matrices.

Neglecting the coupling between chemical and physical degrees of freedom corresponds to neglecting the term

$$
\frac{1}{C_{P} R T^{2}} \tilde{\boldsymbol{G}}^{\prime} \boldsymbol{h}^{\prime} \boldsymbol{h}^{\prime} T \tilde{\boldsymbol{G}}^{\prime}
$$

in eq. (55). If the new eigenvalues are related to the eigenvalues of $\tilde{\boldsymbol{A}}^{\prime}$ (given by eq. (55) ) by

$$
\begin{equation*}
\lambda_{j}^{\prime}=\tilde{\lambda}_{j}-\varepsilon_{j}, \quad j=1,2, \ldots, n^{\prime} \tag{64}
\end{equation*}
$$

then one has for the errors, $\varepsilon_{j}$ :

$$
\begin{gather*}
\varepsilon_{j} \geq 0 \quad, \quad j=1,2, \ldots, n^{\prime} \\
\sum_{j=1}^{n^{\prime}} \varepsilon_{j}=\frac{1}{C_{P} R T^{2}} \boldsymbol{h}^{\prime T} \tilde{\boldsymbol{G}}^{\prime 2} \boldsymbol{h} \tag{65}
\end{gather*}
$$

If the reactions can be separated in two groups, such that reaction rates are much larger in the first group than in the second, then it is generally possible to separate them by a perturbation expansion. One should, however, be aware of the possibility that a large number of coupled reactions with approximatively equal rates may give rise to relaxation in a much wider frequency range due to the coupling between the reactions as can be seen from example 2 below.

If one wants to approximate a multistep mechanism with a spectrum corresponding to a few relaxation times then one might think of several possible methods. In the appendix is outlined a method for approximating an $n$-step mechanism with $k$ relaxation times. This method has the adavantage that it only involves calculating moments of the matrix $\tilde{\boldsymbol{A}}$ with the vector $\boldsymbol{f}$ which makes it especially suited for calculations in closed form. As pointed out in the appendix it is, however, less suited for numerical calculations and one might ask whether one could not find approximations which would be more useful for numerical calculation. The answer to this is that the numerical work connected with diagonalization of the matrix $\tilde{\boldsymbol{A}}$ in general will be of the same order of magnitude as the work connected with calculation of the approximation and that consequently it would be rather akward to use such an approximation in place of calculation of the exact expression.

We shall state the formulas for one and two relaxation times explicitly in order to facilitate the use of the method. Since there is no need for the reduction of the number of chemical variables, we leave it out and introduce the matrix

$$
\begin{equation*}
\tilde{\boldsymbol{K}}=\left(\boldsymbol{N} \boldsymbol{Z}^{-1} \boldsymbol{N}^{T}-\nu \nu^{T}+\frac{1}{C_{P} R T^{2}} \boldsymbol{h} \boldsymbol{h}^{T}\right) \tag{66}
\end{equation*}
$$

With the notation of the appendix we now find:

$$
\begin{gather*}
\pi_{1}=\boldsymbol{f}^{T} \tilde{\boldsymbol{G}}^{2} \boldsymbol{f}  \tag{67}\\
\delta_{1}=\left(\boldsymbol{f}^{T} \hat{\boldsymbol{G}}^{2} \tilde{\boldsymbol{K}} \tilde{\boldsymbol{G}}^{2} \boldsymbol{f}\right) / \pi_{1} \\
=\left(\boldsymbol{f}^{T} \tilde{\boldsymbol{G}}^{2} \boldsymbol{N} \boldsymbol{Z}^{-1} \boldsymbol{N}^{T} \tilde{\boldsymbol{G}}^{2} \boldsymbol{f}-\left(\boldsymbol{f}^{T} \tilde{\boldsymbol{G}}^{2} \boldsymbol{v}\right)^{2}+\left(\boldsymbol{f}^{T} \tilde{\boldsymbol{G}}^{2} \boldsymbol{h}\right)^{2} /\left(C_{P} R T^{2}\right)\right) / \pi_{1}  \tag{68}\\
\pi_{2}=\boldsymbol{f}^{T} \tilde{\boldsymbol{G}}^{2} \tilde{\boldsymbol{K}} \tilde{\boldsymbol{G}}^{2} \tilde{\boldsymbol{K}} \tilde{\boldsymbol{G}}^{2} \boldsymbol{f}-\delta_{1}^{2} \pi_{1}  \tag{69}\\
\delta_{2}=\left(\boldsymbol{f}^{T}\left(\tilde{\boldsymbol{G}}^{2} \tilde{\boldsymbol{K}}\right)^{3} \tilde{\boldsymbol{G}}^{2} \boldsymbol{f}-2 \delta_{1} \boldsymbol{f}^{T}\left(\tilde{\boldsymbol{G}}^{2} \tilde{\boldsymbol{K}}\right)^{2} \tilde{\boldsymbol{G}}^{2} \boldsymbol{f}+\delta_{1}^{3} \pi_{1}\right) / \pi_{2} \tag{70}
\end{gather*}
$$

The first order approximation for the attenuation factor then becomes:

$$
\begin{equation*}
\alpha_{1}=\frac{1}{z} \frac{\omega^{2}}{c} \frac{C_{P} v}{V \beta_{T} C_{V} R T} \frac{\pi_{1}}{\delta_{1}^{2}+\omega^{2}} \tag{71}
\end{equation*}
$$

with the relative error:

$$
\begin{equation*}
\varepsilon_{1}=\pi_{2} /\left(\pi_{1} \delta_{1}^{2}\right) \tag{72}
\end{equation*}
$$

while the second order approximation may be written

$$
\begin{equation*}
\alpha_{2}=\alpha_{1}\left(1+\frac{\pi_{2}}{\pi_{1}} \cdot \frac{\delta_{1}\left(\delta_{1}+\delta_{2}\right)+\left(\delta_{1} \delta_{2}-\frac{\pi_{2}}{\pi_{1}}-\omega^{2}\right)}{\left(\delta_{1} \delta_{2}-\pi_{2} / \pi_{1}-\omega^{2}\right)^{2}+\left(\delta_{1}+\delta_{2}\right)^{2} \omega^{2}}\right) . \tag{73}
\end{equation*}
$$

## V. An alternative set of formulas

If one wants the formulas with concentrations in place of molar fractions, then one has the rate equations (10) and the equilibrium condition (12). We will write the condition (19) as

$$
\begin{equation*}
\frac{1}{V} \boldsymbol{v}=\eta \boldsymbol{v} \tag{74}
\end{equation*}
$$

Where $\eta$ is a function of $p, T, \xi$ (for ideal gases one has $\eta=1 / \nu$ ). The linearized rate equation then reads:

$$
\begin{equation*}
\dot{y}=\boldsymbol{G}^{\prime 2}\left[\frac{V}{R T^{2}} \delta T \boldsymbol{h}^{\prime}-\frac{V^{2} \eta}{R T} \delta p \boldsymbol{v}+\left(V \eta \boldsymbol{v}^{\prime} \boldsymbol{v}^{\prime} T-\boldsymbol{N}^{\prime} \boldsymbol{C}^{-1} \boldsymbol{N}^{T}\right) \boldsymbol{y}\right] \tag{75}
\end{equation*}
$$

with the following definitions

$$
\begin{array}{r}
\boldsymbol{C}=\left\{\begin{array}{ccccc}
c_{1} & 0 & 0 & \ldots & 0 \\
0 & c_{2} & 0 & \ldots & 0 \\
0 & 0 & c_{3} & \ldots & 0 \\
\cdot & \cdot & \cdot & & \cdot \\
\cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & & \cdot \\
0 & 0 & 0 & \ldots & c_{m}
\end{array}\right\} \\
\boldsymbol{G}^{\prime 2}=\boldsymbol{B}^{T} \boldsymbol{G}^{2} \boldsymbol{B} \tag{77}
\end{array}
$$

$$
\begin{gather*}
\boldsymbol{G}=\left\{\begin{array}{ccccc}
\gamma_{1} & 0 & 0 & \ldots & 0 \\
0 & \gamma_{2} & 0 & \ldots & 0 \\
0 & 0 & \gamma_{3} & \ldots & 0 \\
\cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & & \\
\cdot & \cdot & \cdot & & \\
0 & 0 & 0 & \ldots & \gamma_{n}
\end{array}\right\}  \tag{78}\\
\gamma_{j}^{2}=k_{j} \prod_{k=1}^{m} c_{k}^{v_{j k}^{+}} \tag{79}
\end{gather*}
$$

The only changes in the formulas for the attenuation factor are that $\tilde{\boldsymbol{G}}^{\prime}$ is replaced by $\boldsymbol{G}^{\prime}, \tilde{\boldsymbol{A}}^{\prime}$ is replaced by

$$
\begin{equation*}
\boldsymbol{A}^{\prime}=\boldsymbol{G}^{\prime}\left(\boldsymbol{N}^{\prime} \boldsymbol{C}^{-1} \boldsymbol{N}^{\prime} T-V \eta v^{\prime} \nu^{\prime} T+\frac{V}{v C_{P} R T^{2}} \boldsymbol{h}^{\prime} \boldsymbol{h}^{\prime T}\right) \boldsymbol{G}^{\prime} \tag{80}
\end{equation*}
$$

$v$ is replaced by $V$, and the formula for $f^{\prime}$ alternatively may be written:

$$
\begin{equation*}
\boldsymbol{f}^{\prime}=V \eta v^{\prime}-\frac{V l}{v C_{P}} \boldsymbol{h}^{\prime} \tag{81}
\end{equation*}
$$

Leaving out the tildes on the new $\lambda$ 's and $\varphi$ 's formula (63) reads:

$$
\begin{equation*}
\alpha=\frac{1}{2} \frac{\omega^{2}}{c} \frac{C_{P}}{\beta_{T} C_{V} R T} \sum_{j=1}^{n} \frac{\varphi_{j}^{2}}{\lambda_{j}^{2}+\omega^{2}} . \tag{82}
\end{equation*}
$$

Similar changes should of course be introduced in the approximation formulas (66)-(73).

## VI. Examples

Three examples will be given below to show the application of the formulas and to illustrate some important implications of the theory. In the examples the formulas with concentrations will be used (eqs. 74-82)). The parameter $\eta$ introduced in equation (74) will be put equal to zero.

## Example 1

Consider the two chemically independent reactions

$$
\begin{align*}
& A_{1} \rightleftarrows A_{2}  \tag{83}\\
& A_{3} \rightleftarrows A_{4} .
\end{align*}
$$

One then has for the vectors and matrices:

$$
\begin{gather*}
\boldsymbol{N}=\left\{\begin{array}{c}
-1,1, \quad 0,0 \\
0,0,-1,1
\end{array}\right\}  \tag{84}\\
\gamma_{1}^{2}=k_{1} c_{1} ; \gamma_{2}^{2}=k_{2} c_{3}  \tag{85}\\
\boldsymbol{A}=\left\{\begin{array}{c}
k_{1}+k_{-1}+\mathscr{H}_{1}^{2}, \quad \mathscr{H}_{1} \mathscr{H}_{2} \\
\left.\mathscr{H}_{1} \mathscr{H}_{2}, h_{2}\right\}
\end{array}\right\} \tag{86}
\end{gather*}
$$

with:

$$
\begin{align*}
\mathscr{H}_{1} & =\gamma_{1} h_{1} \sqrt{V /\left(\nu C_{P} R T^{2}\right)} \\
\mathscr{H}_{2} & =\gamma_{2} h_{2} \sqrt{V /\left(\nu C_{P} R T^{2}\right)} \tag{88}
\end{align*}
$$

The eigenvalues of $\boldsymbol{A}$ become:

$$
\left.\begin{array}{c}
\lambda_{1} \\
\lambda_{2}
\end{array}\right\}=\frac{1}{2}\left(\lambda_{1}{ }^{0}+\lambda_{2}{ }^{0} \pm \sqrt{\left.\left(\lambda_{1}{ }^{0}-\lambda_{2}{ }^{0}\right)^{2}-4 \mathscr{H}_{1}{ }^{2} \mathscr{H}_{2}{ }^{2}\right)}\right.
$$

It is seen that the eigenvalues corresponding to two reactions ( $\lambda_{1}^{0}$ and $\lambda_{2}^{0}$ ) are perturbed even though the two reactions are chemically independent. This effect is important if one uses a solvent with a relaxation time near the relaxation time of the solute one is investigating. It will normally not be correct merely to substract the background in that case.

The maximal effect is obtained with

$$
\begin{equation*}
\lambda_{1}^{0}=\lambda_{2}^{0}=\lambda^{0} \tag{91}
\end{equation*}
$$

In this case one gets:

$$
\begin{align*}
& \lambda_{1}=\lambda^{0}+\mathscr{H}_{1} \mathscr{H}_{2}  \tag{92}\\
& \lambda_{2}=\lambda^{0}-\mathscr{H}_{1} \mathscr{H}_{2}
\end{align*}
$$

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$$
\begin{gather*}
\boldsymbol{M}=\frac{1}{\sqrt{2}}\left\{\begin{array}{cc}
1, & 1 \\
1, & -1
\end{array}\right\}  \tag{93}\\
\varphi_{1}{ }^{2}=\frac{1}{2}\left(V l /\left(v C_{P}\right)\right)^{2}\left(\gamma_{1} h_{1}+\gamma_{2} h_{2}\right)^{2}  \tag{94}\\
\varphi_{2}{ }^{2}=\frac{1}{2}\left(V l /\left(v C_{P}\right)\right)^{2}\left(\gamma_{1} h_{1}-\gamma_{2} h_{2}\right)^{2} .
\end{gather*}
$$

The formula for $\varphi$ for a single reaction is

$$
\begin{equation*}
\varphi^{2}=\left(V l /\left(\nu C_{P}\right)\right)^{2}(\gamma h)^{2} . \tag{95}
\end{equation*}
$$

The value of $\alpha / \omega^{2}$ found if one substracts the background (only the first reaction) from the measured value with both reactions is then, aside from a constant factor, given by

$$
\begin{equation*}
\frac{\alpha}{\omega^{2}}=\frac{1}{2} \frac{\left(\mathscr{H}_{1}+\mathscr{H}_{2}\right)^{2}}{\lambda_{1}^{2}+\omega^{2}}+\frac{1}{2} \frac{\left(\mathscr{H}_{1}-\mathscr{H}_{2}\right)^{2}}{\lambda_{2}^{2}+\omega^{2}}-\frac{\mathscr{H}_{1}^{2}}{\left(\lambda^{0}\right)^{2}+\omega^{2}} \tag{96}
\end{equation*}
$$

while the correct value corresponding to the second reaction is

$$
\begin{equation*}
\frac{\alpha}{\omega^{2}}=\frac{\mathscr{H}_{2}^{2}}{\left(\lambda^{0}\right)^{2}+\omega^{2}} \tag{97}
\end{equation*}
$$

The two curves are shown in figure 1.


Figure 1 shows $\alpha / \omega^{2}$ as a function of $\log (\omega)$ corresponding to the eqs. (96) ( - ) and (97) (- - ) for $\mathscr{H}_{1}=\mathscr{H}_{2}=0.2$.

## Example 2

Consider the polymerization scheme:

$$
\begin{equation*}
A_{1}+A_{i} \rightleftharpoons A_{i+1} \quad i=1,2, \ldots \tag{98}
\end{equation*}
$$

If it is assumed that all reactions have the same equilibrium constant, $K$, the same rate constants, $k^{+}$and $k^{-}$, and the same change in enthalpy, $\Delta H$, then one has

$$
\begin{gather*}
\zeta=K c_{1}  \tag{99}\\
c_{i}=\zeta^{i-1} c_{1}  \tag{100}\\
\gamma_{i}{ }^{2}=k^{-} c_{1} \zeta^{i}  \tag{101}\\
\boldsymbol{h}=\Delta H \boldsymbol{e}  \tag{102}\\
\nu_{i j}=-\delta_{1, j}-\delta_{j, i}+\delta_{j, i+1}  \tag{103}\\
a_{i j}=\gamma_{i} \gamma_{j}\left[c_{1}{ }^{-1}\left(\delta_{j, 1}+\delta_{i, 1}+1+\mathscr{H}^{2}\right)\right. \\
\left.+\delta_{i, j}\left(c_{i}-1+c_{i+1}{ }^{-1}\right)-\delta_{i+1, j} c_{j}^{-1}-\delta_{i, j+1} c_{i}-1\right] \\
=k^{-}\left[\zeta^{\frac{1}{2}(i+j)}\left(\delta_{j, 1}+\delta_{i, 1}+1+\mathscr{H}^{2}\right)\right.  \tag{104}\\
\left.+\delta_{i, j}(\zeta+1)-\left(\delta_{i, j+1}+\delta_{i+1, j}\right) \zeta^{\frac{1}{2}}\right] \\
\mathscr{H}^{2}=c_{1} \cdot V \cdot \Delta H^{2} /\left(\nu C_{P} R T^{2}\right) \tag{105}
\end{gather*}
$$

where $\delta_{i, j}$ is the Kronecker delta.
Applying the approximation method of the appendix one finds:

$$
\begin{gather*}
\pi_{1}=k^{-} c_{1}\left(\Delta H \cdot V \cdot l /\left(v C_{P}\right)\right)^{2} \sum_{j=1}^{\infty} \zeta_{j}  \tag{106}\\
=k^{-} c_{1}\left(\Delta H \cdot V \cdot l /\left(v C_{P}\right)\right)^{2} \zeta /(l-\zeta) \\
\delta_{1}=\left(1+\zeta+\left(1+\mathscr{H}^{2}\right) \zeta /(1-\zeta)\right) \cdot k^{-}  \tag{107}\\
\pi_{2}=\pi_{1} \zeta /(1-\zeta)  \tag{108}\\
\delta_{2}=k^{-}(1+\zeta) . \tag{109}
\end{gather*}
$$

Fig. 2 and 3 show for two values of $\zeta$ the approximations with one and two relaxation times together with the exact curve (calculated by diagonalizing a sufficiently large submatrix of $\boldsymbol{A}$ ). The calculated eigenvalues are also shown. It is seen that the eigenvalue spectrum gets rather broad for $\zeta$ close to one and that the approximations at the same time get less satisfactory. The calculations for $\zeta$ close to one show an interesting consequence of the


Figure 2 shows $\alpha / \omega^{2}$ as a function of $\log (\omega)$ for the reaction scheme given in example 2 with $\zeta=0.01$ and $\mathscr{H}^{2}=0.001(-)$. Also shown is the approximation with a single relaxation time given by eqs. $(71,106,107)(---)$. The approximation with two relaxation times cannot be distinguished from the correct curve.


Figure 3 shows $\alpha / \omega^{2}$ as a function of $\log (\omega)$ for the reaction scheme given in example 2 with $\zeta=0.8$ and $\mathscr{H}^{2}=0.1$ (—). Also shown is the approximation with two relaxation times, given by eqs. $(73,106-109)(-\cdot-$. $)$. The approximation with one releaxation time cannot be distinguished from the abscisse axis.

Table 1.

| eigenvalue(s) | Contribution to |  |
| :---: | :---: | :---: |
|  | $\alpha_{\omega}=\infty$ | $\left(\alpha / \omega^{2}\right) \omega=0$ |
| 0.03 | 0.006 | 6.554 |
| 0.07 | 0.011 | 2.490 |
| 0.12 | 0.017 | 1.136 |
| 0.19 | 0.019 | 0.539 |
| $0.20-0.80$ | 0.121 | 0.675 |
| $0.80-2.00$ | 0.159 | 0.101 |
| $2.00-3.60$ | 0.115 | 0.017 |
| 6.99 | 2.749 | 0.056 |

Table I shows that the large contributions to $\left(\alpha / \omega^{2}\right) \omega=0$ come from small eigenvalues although the corresponding values of $\varphi_{j}{ }^{2}$ are small $(\alpha \omega=\infty)$. The numbers are taken from a $31 \times 31$ matrix corresponding to the model in example 2 with $\zeta=0.8$ and $\mathscr{H}^{2}=0.1$.
broad spectrum, which arises from the strong coupling between the single reactions. The value of $\alpha / \omega^{2}$ at $\omega=0$ is often used to characterize the relaxation curve. This is, however, not a very suitable parameter since small changes in the kinetic model may give rise to a large change in $\left(\alpha / \omega^{2}\right)_{\omega=0}$. The largest contributions to $\left(\alpha / \omega^{2}\right)_{\omega=0}$ will normally come from small eigenvalues even if the corresponding values of $\varphi_{j}{ }^{2}$ are small, but if $\boldsymbol{G} \boldsymbol{f}$ only has a small component after a given eigenvector then it is very likely that small changes in $\boldsymbol{A}$ or $\boldsymbol{G}$ or $\boldsymbol{f}$ may result in a large, relative change in the component.

That the largest contribution to $\left(\alpha / \omega^{2}\right)_{\omega=0}$ actually comes from small eigenvalues with small weights in the present case is clearly exhibited in Table I.

In view of the proceeding remarks it is not surprising that the effect of leaving out the term $\mathscr{H}^{2}$ in eq. (104) is large for $\zeta$ close to one as can be seen from Fig. 4.

## Example 3

Finally an example to illustrate the reduction in case of chemical reactions which are not all independent is given. For this purpose example 2 is expanded to include all possible combinations of two molecules to one large, but only reactions up to formation of 5 -mers are included in order to get a reasonable simple problem.


Figure 4 shows $\alpha / \omega^{2}$ as a function of $\log (\omega)$ for the reaction scheme given in example 2 with $\zeta=0.8$ and $\chi^{2}=0.1(\longrightarrow)$ and $\zeta=0.8$ and $\varkappa^{2}=0(---)$.

The reactions are:

$$
\begin{align*}
& A_{1}+A_{1} \rightleftharpoons A_{2} \\
& A_{1}+A_{2} \rightleftharpoons A_{3} \\
& A_{1}+A_{3} \rightleftharpoons A_{4} \\
& A_{1}+A_{4} \rightleftharpoons A_{5}  \tag{110}\\
& A_{2}+A_{2} \rightleftharpoons A_{4} \\
& A_{2}+A_{3} \rightleftharpoons A_{5} .
\end{align*}
$$

The matrix $\boldsymbol{N}$ becomes:

$$
N=\left\{\begin{array}{rrrrr}
-2, & 1, & 0, & 0, & 0  \tag{111}\\
-1, & -1, & 1, & 0, & 0 \\
-1, & 0, & -1, & 1, & 0 \\
-1, & 0, & 0, & -1, & 1 \\
0, & -2, & 0, & 1, & 0 \\
0, & -1, & -1, & 0, & 1
\end{array}\right\}
$$

and the vector $\boldsymbol{h}$ :

$$
\begin{equation*}
\boldsymbol{h}^{T}=\left\{\Delta H_{1}, \Delta H_{2}, \Delta H_{3}, \Delta H_{4}, \Delta H_{5}, \Delta H_{6}\right\} . \tag{112}
\end{equation*}
$$

The two last reactions in (110) can evidently be written as a combination of the first four reactions. The matrix $\boldsymbol{B}$ is

$$
B=\left\{\begin{array}{rrrr}
1 & 0 & 0 & 0  \tag{113}\\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
-1 & 1 & 1 & 0 \\
-1 & 0 & 1 & 1
\end{array}\right\}
$$

while the matrix $\boldsymbol{N}^{\prime}$ is identical with the first four rows of $\boldsymbol{N}$, and the vector $\boldsymbol{h}^{\prime}$ is identical with the first four elements of $\boldsymbol{h}$. One has the thermodynamic relations:

$$
\begin{gathered}
\Delta H_{5}=-\Delta H_{1}+\Delta H_{2}+\Delta H_{3} \\
\Delta H_{6}=-\Delta H_{1}+\Delta H_{3}+\Delta H_{4} \\
K_{5}=K_{2} K_{3} / K_{1} \\
K_{6}=K_{3} K_{4} / K_{1} .
\end{gathered}
$$

The matrix $\boldsymbol{G}^{\prime 2}$ becomes

$$
\boldsymbol{G}^{\prime 2}=\left\{\begin{array}{ccccc}
\gamma_{1}^{2}+\gamma_{5}^{2}+\gamma_{6}{ }^{2}, & -\gamma_{5}^{2} & , & -\gamma_{5}^{2}-\gamma_{6}^{2} & ,  \tag{114}\\
-\gamma_{5}^{2} & , & \gamma_{2}{ }^{2}+\gamma_{5}^{2}, & \gamma_{5}^{2} & , \\
-\gamma_{5}^{2}-\gamma_{6}^{2} & , & \gamma_{5}^{2} & , \gamma_{3}{ }^{2}+\gamma_{5}^{2}+\gamma_{6}{ }^{2}, & \gamma_{6}^{2} \\
-\gamma_{6}{ }^{2} & , & 0 & , & \gamma_{6}{ }^{2}
\end{array}\right\}
$$

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## Appendix

The problem is to find a series of approximations to an expression of the form

$$
\begin{equation*}
\psi^{H}(\boldsymbol{A}+i \omega \boldsymbol{E})^{-1} \psi \tag{A.1}
\end{equation*}
$$

where $\psi$ is an $n$-dimensional vector and $\boldsymbol{A}$ is an $n \times n$-matrix.

We shall start by transforming $\boldsymbol{A}$ into a traditional matrix by Lanczo's algorithm for tridiagonalization (see ref. 4, p. 19). We generate two sequences of vectors

$$
\begin{gather*}
\boldsymbol{b}_{1}, \boldsymbol{b}_{2}, \ldots, \boldsymbol{b}_{n}  \tag{A.2}\\
\boldsymbol{c}_{1}, \boldsymbol{c}_{2}, \ldots, \boldsymbol{c}_{n} \tag{A.3}
\end{gather*}
$$

which fulfils:

$$
\begin{equation*}
\boldsymbol{c}_{i}^{H} \boldsymbol{b}_{j}=\delta_{i},{ }_{j} \pi_{j} \quad \pi_{j} \neq 0 \tag{A.4}
\end{equation*}
$$

and where the first $v$ is determined by $\left(\gamma_{1}=0\right)$ :

$$
\begin{gather*}
\boldsymbol{c}_{1}=\boldsymbol{b}_{1}=\boldsymbol{\psi}  \tag{A.5}\\
\boldsymbol{b}_{j+1}=\boldsymbol{A} \boldsymbol{b}_{j}-\delta_{j} \boldsymbol{b}_{j}-\gamma_{j} \boldsymbol{b}_{j-1}  \tag{A.6}\\
\boldsymbol{c}_{j+1}=\boldsymbol{A}^{H} \boldsymbol{c}_{j}=\delta_{j}^{*} \boldsymbol{c}_{j}-\gamma_{j} \boldsymbol{c}_{j-1} \quad(j=1,2, \ldots, v-1) \tag{A.7}
\end{gather*}
$$

(*stands for complex conjugate). $v$ is determined as the lowest value for which it is possible to get at least one of the following equations fulfilled

$$
\begin{align*}
& \boldsymbol{A} \boldsymbol{b}_{v}=\delta_{v} \boldsymbol{b}_{v}+\gamma_{v} \boldsymbol{b}_{v-1}  \tag{A.8}\\
& \boldsymbol{A}^{H} \boldsymbol{c}_{v}=\delta_{v}^{*} \boldsymbol{c}_{v}+\gamma_{v} \boldsymbol{c}_{v-1} . \tag{A.9}
\end{align*}
$$

The remaining $n-v$ vectors $\boldsymbol{b}$ and $\boldsymbol{c}$ can be chosen to be any vectors such that (A. 4) is fullfilled for all $i$ and $j$.

$$
\begin{array}{ll}
\delta_{j}=\boldsymbol{c}_{j}^{H} \boldsymbol{A} \boldsymbol{b}_{j} / \pi_{j}, & j \geq 1 \\
\gamma_{j}=\pi_{j} / \pi_{j-1}, & j \geq 2 . \tag{A.11}
\end{array}
$$

With $\boldsymbol{B}$ and $\boldsymbol{C}$ as the matrices

$$
\begin{align*}
\boldsymbol{B} & =\left\{\boldsymbol{b}_{1}, \boldsymbol{b}_{2}, \ldots, \boldsymbol{b}_{n}\right\}  \tag{A.12}\\
\boldsymbol{C} & =\left\{\boldsymbol{c}_{1}, \boldsymbol{c}_{2}, \ldots, \boldsymbol{c}_{n}\right\} \tag{A.13}
\end{align*}
$$

and $\boldsymbol{P}$ as the diagonal matrix whose diagonal elements are the $\pi_{j}$ 's, (A. 4) may be written

$$
\begin{equation*}
\boldsymbol{B}^{-1}=\boldsymbol{P}^{-1} \boldsymbol{C}^{H} \tag{A.14}
\end{equation*}
$$

The similarity transformation:

$$
\begin{equation*}
\boldsymbol{P}^{-1} \boldsymbol{C}^{H} \boldsymbol{A} \boldsymbol{B}=\boldsymbol{A}^{\prime} \tag{A.15}
\end{equation*}
$$

will transform (1) into:

$$
\begin{gather*}
\boldsymbol{e}_{1}^{T}\left(\boldsymbol{A}^{\prime}+i \omega \boldsymbol{E}\right)^{-1} \boldsymbol{e}_{1} \cdot \pi_{1}  \tag{A.16}\\
\boldsymbol{e}_{1}^{T}=\{1,0,0, \ldots, 0\} . \tag{A.17}
\end{gather*}
$$

If $\boldsymbol{A}^{\boldsymbol{\prime}}$ is partitioned:

$$
\boldsymbol{A}^{\prime}=\left\{\begin{array}{ll}
A_{11} & A_{12}  \tag{A.18}\\
A_{21} & A_{22}
\end{array}\right\}
$$

Where $\boldsymbol{A}_{11}$ is $v \times v$, one has

$$
\boldsymbol{A}_{11}=\left\{\begin{array}{lllll}
\delta_{1} & \gamma_{2} & 0 & \ldots & 0  \tag{A.19}\\
1 & \delta_{2} & \gamma_{3} & & 0 \\
0 & 1 & \delta_{3} & & 0 \\
\cdot & & & & \cdot \\
\cdot & & & & \cdot \\
\cdot & & & & \cdot \\
0 & 0 & 0 & & \delta_{\nu}
\end{array}\right\}
$$

while either $\boldsymbol{A}_{12}$ or $\boldsymbol{A}_{21}$ is zero depending on whether (A.9) or (A. 8) is fulfilled. (A. 16) is consequently reduced to:

$$
\begin{equation*}
\boldsymbol{e}_{1}^{T}\left(\boldsymbol{A}_{11}+i \omega \boldsymbol{E}\right)^{-1} \boldsymbol{e}_{1} \cdot \pi_{1} \tag{A.20}
\end{equation*}
$$

We will now return to the original problem. This may be viewed as the problem of finding approximate solutions to the equation:

$$
\begin{equation*}
(\boldsymbol{A}+i \omega \boldsymbol{E}) \boldsymbol{x}=\psi . \tag{A.21}
\end{equation*}
$$

A series of successive approximations to $x$ can be obtain by using the residual of the preceding approximation to determine the next approximation. This gives the general recursion formula:

$$
\begin{equation*}
\boldsymbol{x}_{k}=\boldsymbol{x}_{k-1}+\boldsymbol{C}_{k}\left(\boldsymbol{\psi}-(\boldsymbol{A}+i \omega \boldsymbol{E}) \boldsymbol{x}_{k-1}\right) . \tag{A.22}
\end{equation*}
$$

(se ref. 4, p. 92 ff .), where the matrices $\boldsymbol{C}_{k}$ should be chosen so that the "error" is minimalized. The error on $\boldsymbol{x}_{k}$ is given by:

$$
\boldsymbol{x}-\boldsymbol{x}_{k}=\boldsymbol{s}_{k}=\left(\boldsymbol{E}-\boldsymbol{C}_{k}(\boldsymbol{A}+i \omega \boldsymbol{E})\right) \boldsymbol{s}_{k-1} .
$$

If one starts the sequence (A.22) with

$$
\begin{equation*}
x_{0}=0 \tag{A.24}
\end{equation*}
$$

One gets:

$$
\begin{equation*}
\boldsymbol{s}_{k}=\left[\prod_{j=1}^{k}\left(\boldsymbol{E}-\boldsymbol{C}_{j}(\boldsymbol{A}+i \omega \boldsymbol{E})\right)\right] \boldsymbol{x} . \tag{A.25}
\end{equation*}
$$

Since we want to find $\psi^{H} \boldsymbol{x}$, it will be reasonable to try to minimize $\psi^{H} \boldsymbol{s}_{k}$, or since $\boldsymbol{x}$ is not known

$$
\begin{equation*}
\left|\psi^{H} \prod_{j=1}^{k}\left(\boldsymbol{E}-\boldsymbol{C}_{j}(\boldsymbol{A}+i \omega \boldsymbol{E})\right) \boldsymbol{x}_{k}\right| . \tag{A.26}
\end{equation*}
$$

We now have to choose the form of our matrices, $\boldsymbol{C}_{j}(j=1,2 \ldots k)$, and we choose them as simple as possible:

$$
\begin{equation*}
\boldsymbol{C}_{j}=\frac{1}{\xi_{j}} \boldsymbol{E} . \tag{A.27}
\end{equation*}
$$

From the recursion formula (A. 22) and the initializing (A.24), it is easily seen that (A. 26) only depends on $\boldsymbol{A}+i \omega \boldsymbol{E}$ and $\psi$ through the moments

$$
\begin{equation*}
\mu_{j}=\psi^{H}(\boldsymbol{A}+i \omega \boldsymbol{E})^{j} \psi \quad(j=0,1, \ldots, 2 k-1) . \tag{A.28}
\end{equation*}
$$

Using now the expression (A. 20), one has from the special form (A. 19) of $\boldsymbol{A}_{11}$, that the moments

$$
\begin{equation*}
\mu_{j}^{\prime}=\boldsymbol{e}_{1}^{T}\left(\boldsymbol{A}_{11}+i \omega \boldsymbol{E}\right)^{j} \boldsymbol{e}_{1} \quad(j=0,1, \ldots, 2 k-1) \tag{A.29}
\end{equation*}
$$

are the same as they are for the matrix $\boldsymbol{A}_{11}^{(k)}+i \omega \boldsymbol{E}$, where we have only kept the first $k$ columns and rows of $\boldsymbol{A}_{11}+i \omega \boldsymbol{E}$.

The approximation $\boldsymbol{x}_{k}$ will be exact for the equation:

$$
\begin{equation*}
\left(\boldsymbol{A}_{11}^{(k)}+i \omega \boldsymbol{E}\right) \boldsymbol{x}=\boldsymbol{e}_{1} \tag{A.30}
\end{equation*}
$$

if we make the choice

$$
\begin{equation*}
\xi_{j}=\lambda_{j}^{(k)}+i \omega \tag{A.31}
\end{equation*}
$$

where $\lambda_{j}^{(k)}$ is the $j^{\prime}$ th eigenvalue of $\boldsymbol{A}_{11}^{(k)}$. And we consequently have that the same choice make the expression (A. 26) for the error equal to zero. The $k^{\prime}$ th order approximation to (A. 1) can now be written

$$
\begin{equation*}
\psi^{H}(\boldsymbol{A}+i \omega \boldsymbol{E})^{-1} \psi \simeq \pi_{1} \sum_{j=1}^{k} \frac{\alpha_{j}^{(k)}}{\lambda_{j}^{(k)}+i \omega} \tag{A.32}
\end{equation*}
$$

$\alpha_{j}^{(k)}$ is the product of the first component of the $j^{\prime}$ th eigenvector to $\boldsymbol{A}_{11}^{(k)}$ from the right with the first component of the $j^{\prime}$ th eigenvector to $\boldsymbol{A}_{11}^{(k)}$ from the left.

It is, however, possible to give (A. 32) a form which is more convenient
for many purposes. Writing $D_{j}$ for the determinant of $v-j$ last row and columns of $\boldsymbol{A}_{11}+i \omega \boldsymbol{E}$, one has

$$
\left.\begin{array}{rl}
\boldsymbol{e}_{1}^{T}\left(\boldsymbol{A}_{11}+i \omega \boldsymbol{E}\right)^{-1} \boldsymbol{e}_{1}=\frac{D_{1}}{D_{0}} & = \\
\frac{1}{\delta_{1}+i \omega-\gamma_{2} \frac{D_{2}}{D_{1}}}=\frac{1}{\delta_{1}+i \omega-\gamma_{2}} \delta_{2}+i-\frac{\gamma_{3}}{\gamma_{3}+i-} \cdots \tag{A.33}
\end{array}\right\}
$$

This continued fraction can be transformed into a sum of fractions (ref. 5 p. 5):

$$
\begin{equation*}
\psi^{H}(\boldsymbol{A}+i \omega \boldsymbol{E})^{-1} \psi=\frac{\pi_{1}}{Q_{0} Q_{1}}+\frac{\pi_{2}}{Q_{1} Q_{2}}+\ldots+\frac{\pi_{v}}{Q_{v-1} Q_{v}} \tag{A.34}
\end{equation*}
$$

with the Q's given by the recursion formula

$$
\begin{align*}
Q_{j} & =\left(\delta_{j}+i \omega\right) Q_{j-1}-\gamma_{j} Q_{j-2}  \tag{A.35}\\
Q_{-1} & =0, Q_{0}=1
\end{align*}
$$

The $k$ 'th order approximation (A. 32) will be identical with the first $k$ terms of (A. 35). In order to estimate the error on the $k$ 'th approximation one can of course not use (A. 26). If one supposes that the following terms drop off reasonable fast one may use the $k+1$ 'th term in (A. 34) for estimating the error. A rough estimate of $Q_{j}$ in the range of $\omega$ which is of interest may be found by assuming that all the $\delta$ 's are of the same order of magnitude as $\omega$ (and that the $\gamma$ 's do not blow up):

$$
\begin{equation*}
\left|Q_{j}\right| \approx \omega^{j} \approx \delta_{1}^{j} \tag{A.36}
\end{equation*}
$$

which gives for the relative error on the $k$ 'th approximation

$$
\begin{equation*}
\varepsilon_{k} \approx \frac{\pi_{k+1}}{\pi_{1} \delta_{1}^{2 k}} \tag{A.37}
\end{equation*}
$$

Applicability of the method: Obviously the method applies to any expression of the form

$$
\begin{equation*}
\psi^{H}(\boldsymbol{A}+f(\omega) \boldsymbol{E})^{-1} \psi \tag{A.38}
\end{equation*}
$$

where $f(\omega)$ is a complex function. This might be used to find other similar approximations to the expression (A.1), since one can rewrite (A. 1) as

$$
\begin{gather*}
\operatorname{Re}\left\{\boldsymbol{\psi}^{H}(\boldsymbol{A}+i \omega \boldsymbol{E})^{-1} \psi\right\}=  \tag{A.39}\\
\left(\boldsymbol{A}^{\frac{1}{2}} \boldsymbol{\psi}\right)^{H}\left(\boldsymbol{A}^{2}+\omega^{2} \boldsymbol{E}\right)^{-1}\left(\boldsymbol{A}^{\frac{1}{2}} \boldsymbol{\psi}\right)  \tag{A.40}\\
\operatorname{Im}\left\{\psi^{H}(\boldsymbol{A}+i \omega \boldsymbol{E})^{-1} \boldsymbol{\psi}\right\}= \\
-\omega \psi^{H}\left(\boldsymbol{A}^{2}+\omega^{2} \boldsymbol{E}\right)^{-1} \psi  \tag{A.41}\\
\boldsymbol{\psi}^{H}(\boldsymbol{A}+i \omega \boldsymbol{E})^{-1} \boldsymbol{\psi}= \\
\left(\boldsymbol{A}^{-\frac{1}{2}} \boldsymbol{\psi}\right)^{H}\left(\boldsymbol{A}^{-1}-(i / \omega) \boldsymbol{E}\right)^{-1}\left(\boldsymbol{A}^{-\frac{1}{2}} \boldsymbol{\psi}\right) .
\end{gather*}
$$

The method of tridiagonalization can easily be generalized to expressions of the form

$$
\begin{equation*}
\psi^{H}(\boldsymbol{A}+f(\omega) \boldsymbol{E})^{-1} \varphi \tag{A.42}
\end{equation*}
$$

where $\psi$ and $\varphi$ any two $n$-dimensional vectors which are not orthogonal, i.e.:

$$
\begin{equation*}
\psi^{H} \varphi \neq 0 \tag{A.43}
\end{equation*}
$$

However, one warning should be given: Lanczo's method of tridiagonalization is in general not numerically stable, and the method should consequently in connection with numerical calculations only be used for calculating approximations of low order $(k=1$ or 2$)$.

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## THE MACROSCOPIC LEVEL OF QUANTUM MECHANICS

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## Synopsis

A synthetic account is given of a general treatment of large quantal systems, allowing of a clear-cut characterization of the macroscopic level of description of such systems. The time-evolution of the density operator is given by a Liouville equation, which is written down in a superspace formed by the direct product of the Hilbert space with itself. It is shown how to construct a projector $\tilde{I}$ in this superspace such that the subspace it defines contains the asymptotic timeevolution of the density operator for time intervals very large compared with those typical for atomic processes: this asymptotic subdynamics shows the characteristic features of macroscopic behaviour.

A quantitative criterium is formulated in superspace for the existence of a well-defined and unique macroscopic level in the sense just outlined of a separate subdynamics governing the asymptotic behaviour of the system. This "condition of dissipativity" can be directly tested on the Hamiltonian of any given system.

In general, the subdynamics can only be formulated in superspace: it is not possible to return from the $\tilde{I}$ subspace to a Hilbert space description of the system in terms of state-vectors. Thus, the scope of the latter description is clearly limited, and a precise formulation is obtained of the complementarity between the dynamical account of the system on the atomic scale and its description at the level of macroscopic observation.

The epistemological problems of quantum mechanics receive from the present point of view an especially transparent treatment. In particular, the consistency of the use of classical concepts for the account of quantal phenomena is obvious, since the macroscopic description operates directly with probabilities, all quantal interference effects being eliminated from the $\tilde{I}$ subspace; thus, the rule of "reduction" of the state-vector following a measurement performed upon an atomic system appears as an immediate consequence of the macroscopic character of the measuring process.

## 1. Introduction

In a detailed discussion of the epistemological problems of atomic physics, where explicit reference to the conditions of macroscopic observation is essential, ${ }^{1,2)}$ a decisive part is played by the analysis of the asymptotic approach to equilibrium of material bodies consisting of a very large number of interacting atomic constituents (and possibly also of a field of electromagnetic radiation). In the first place, such an analysis serves in its own right to establish the consistency of the atomistic description of macroscopic phenomena, by clarifying the relation of complementarity between the irreversible character of the macroscopic behaviour of the large system and the time-reversal invariance of its dynamical description at the atomic level. ${ }^{3)}$ In the second place, applied to the process of observation of an individual atomic phenomenon by means of a macroscopic apparatus interacting with the atomic object, it throws light on the conceptual foundations of quantum mechanics. ${ }^{4,5)}$

Recent progress in the quantum theory of large systems allows us, as we intend to show in this paper, to treat these problems with more precision and more completely than was hitherto possible. The method we use was initiated by one of $\mathrm{us}^{6}$ ) and developed in numerous publications by the Brussels group during the last decade. This method may be applied to arbitrary systems but becomes especially interesting and fruitful in the limit of large systems, whose energy spectrum is (at least in part) continuous. It is then possible to follow directly the time-evolution of observables depending on a finite number of degrees of freedom through the time evolution of the density operator, and in particular to study the asymptotic behaviour of the system for times of macroscopic order of magnitude. It turns out that this behaviour can be given a remarkably simple formal expression under very general assumptions about the correlations between the constitutive elements of the system: in physical terms these correlations should be of limited range and their effects should only persist for times of atomic order of magnitude. The asymptotic density operator will then exhibit the expected
approach to equilibrium, provided that a further condition - playing here somewhat the same part as the condition of mixing in the theory of classical systems - is fulfilled by the interactions. In contrast with the ergodicity and mixing conditions for classical systems*) this condition of "dissipativity" can be explicitly tested for typical systems of actual physical interest. Of course, our method can also be applied to classical systems, for which it again leads, in the limit of large systems, to a condition of dissipativity.

This condition plays a fundamental role in our theory, inasmuch as its fulfilment guarantees the existence of a well defined macroscopic level of description of a large system, besides its dynamical description on the atomic level. This new mode of description contains the usual phenomenological account of the behaviour of the system in terms of thermodynamics, chemical kinetics and other macroscopic theories. Thus, the condition of dissipativity, when fulfilled, establishes the possibility of introducing in a well defined way two complementary levels of description of atomic systems.

To illustrate the significance of this remarkable result, let us consider the evolution of the temperature of a gas. We may proceed in two ways: either we use the statistical definition of temperature and solve the dynamical problem (which is possible, at least in principle, by means of an appropriate computer), or we use the Fourier equation of heat conduction. These two quite different procedures, so far as we know, give results in agreement with each other. This shows that the complete dynamical description contains elements which in fact are irrelevant for the evolution of such an observable as the temperature. Now, our method, in the form elaborated in recent papers of the Brussels group, ${ }^{9-18)}$ allows us to define with precision the part of the dynamical description that is relevant and to discard in an unambiguous fashion the remainder.

As shown by Prigogine, George and Henin, ${ }^{14)}$ the evolution of a mechanical system may be split into formally independent "subdynamics", characterized by certain projection operators, as explained in subsection 2.7 below. One of these subdynamics, belonging to the projector $\tilde{I}$ defined in subsection 2.7, contains all the information about equilibrium and linear transport properties, and the macroscopic level of description of a large quantal system is accordingly defined as that entirely expressed in terms of the variables corresponding to this $\tilde{\Pi}$-subdynamics. The consideration of the macroscopic level of a system thus entails an enormous reduction of its mode of description, since all the variables associated to the other subdynamics are excluded

[^17]from it. In relation to the macroscopic description so defined, the condition of dissipativity plays a fundamental part. For non-dissipative systems, such as quantal systems with a discrete, non-degenerate energy spectrum, there is no dynamical evolution in the $\tilde{I}$-space, and a macroscopic level of description cannot be defined. The consideration of large dissipative systems is therefore essential. There also exist large quantal systems, with continuous spectrum, which are not dissipative (an extreme example would be a superfluid system at zero temperature) : for such systems there is no macroscopic description, in the above sense, of their dynamical evolution.

In the next section, we present a synthetic account of the formal framework of our theory, leading to the concept of subdynamics and the definition of the macroscopic level of quantum mechanics. Section 3 is devoted to a discussion of the physical content of the theory, with special emphasis on the epistemological problems of the atomic theory of material bodies. In section 4 the theory is applied to the analysis of the observation of an individual atomic process and its bearing on the epistemological aspects of quantum mechanics. This still leaves out of consideration a number of important problems upon which our approach throws new light, such as those related to transformation theory, the introduction of collective modes or quasiparticles, or the definition of unstable particles. ${ }^{*)}$ We hope nevertheless that the aspects discussed here are sufficient to show that the theory of large quantal systems is an essential part of quantum mechanics, both by its physical applications and its contributions to the questions of principle concerning the foundations of atomic theory. Indeed, it makes possible an incorporation in quantum theory of deep-lying, general properties of matter, which could not be achieved by means of the usual Hilbert space formalism of quantum mechanics.

[^18]
## 2. Dynamics and asymptotic behaviour of very large systems

### 2.1. The Liouville equation in superspace

The study of the time evolution of a quantal system can be performed in either of two ways. One may represent the state of the system by a vector $|\psi(t)\rangle$ in a Hilbert space and describe the change of the system in time as a rotation of this state vector, the rate of which is governed by the Hamiltonian $H$ according to the Schrödinger equation. Alternatively, one may define the density operator

$$
\varrho(t)=|\psi(t)\rangle\langle\psi(t)|
$$

whose time derivative $\dot{\varrho}(t)$ is then given by the Liouville equation

$$
\dot{\varrho}(t)=\frac{1}{\hbar}[H, \varrho(t)],
$$

where the right-hand side denotes $\hbar^{-1}$ times the commutator of $H$ and $\varrho(t)$. With the help of the density operator, one can compute the expectation value at any time of any quantity represented by a Hilbert space operator $A$ as the trace of the operator $\varrho(t) A$. This mode of representation of the dynamics of the system exhibits most directly the correspondence, in the limit $\hbar \rightarrow 0$, with the classical formulation of the kinetic approach to statistical thermodynamics, and is accordingly generally adopted for the quantal treatment of the same problem.

Since the quantal density operator embodies both density distributions in given states of the system and correlations between pairs of states, it is natural to regard it as describing the evolution of the system in the product space $\mathscr{H} \times \mathscr{H}$, which we shall call "superspace" (using the prefix "super-", when necessary, to distinguish vectors and operators in it from those in Hilbert space). Operators in Hilbert space are thus "supervectors", and the scalar product of two supervectors $A, B$ is defined as the trace of the product $A^{+} B$, where $A^{+}$denotes the Hilbert space operator adjoint to the operator $A$. The expectation value of the operator $A$ in the state represented by the (self-adjoint) density operator $\varrho$ is then the scalar product tr ( $\varrho A$ ) of the two supervectors $\varrho, A$. We may now introduce linear superoperators $O$ acting
upon supervectors; the adjoint $O^{\dagger}$ of the superoperator $O$ is defined*) by the condition

$$
\operatorname{tr}\left[A^{+}(O B)\right]=\operatorname{tr}\left[\left(O^{\dagger} A\right)^{+} B\right] .
$$

The transposition of a superoperator, i.e. its operating "to the left", denoted as $A O$, is defined by requiring that $\operatorname{tr}\left[\left(A^{+} O\right) B\right]=\operatorname{tr}\left[A^{+}(O B)\right]$; therefore, $A O=\left(O^{\dagger} A^{+}\right)^{+}$, or

$$
(O A)^{+}=A^{+} O^{\dagger} .
$$

Since, moreover, one has for the product of two superoperators $O, Q$,

$$
(O Q)^{\dagger}=Q^{\dagger} O^{\dagger},
$$

the adjoint of any expression involving products of superoperators and supervectors is obtained by the uniform rule of taking the adjoint of every superoperator and supervector and inverting the order of factors in every product.

A frequently occurring type of superoperator, which we shall call factorizable, is defined by a pair of supervectors $M, N$ as follows:

$$
O A \equiv M A N ;
$$

we shall denote such a factorizable superoperator as $O \equiv M \times N$; its adjoint is $O^{\dagger}=M^{+} \times N^{+}$, its transpose is given by $A(M \times N) \equiv(N \times M) A$. The product of two factorizable superoperators $M \times N, P \times Q$ is again factorizable: $(M \times N)$ $(P \times Q)=M P \times Q N$. A unitary transformation $U$ in Hilbert space, $U^{+} U=U U^{+}$ $=1$, gives rise to a linear transformation in superspace, which is represented by the factorizable superoperator $\mathscr{U}=U \times U^{+}$and is accordingly also unitary in superspace, in the sense that $\mathscr{U}^{\dagger} \mathscr{U}=\mathscr{U} \mathscr{U}^{\dagger}=1 \times 1=1$. The invariance of the scalar product of supervectors for unitary transformations is immediately proved:

$$
\operatorname{tr}\left[(\mathscr{U} A)^{+} \mathscr{U} B\right]=\operatorname{tr}\left[\left(\mathscr{U}^{\dagger} \mathscr{U} A\right)^{+} B\right]=\operatorname{tr}\left[A^{+} B\right] .
$$

The Liouville equation may now be written in the form

$$
\begin{equation*}
i \varrho(t)=L \varrho(t) \tag{1}
\end{equation*}
$$

with the help of a Liouville superoperator, which is a sum of factorizable superoperators:

$$
L \equiv \frac{1}{\hbar}\{H \times 1-1 \times H\} .
$$

[^19]The solution of eq. (1) corresponding to an initial state $\varrho(0)$ is formally expressed as

$$
\varrho(t)=\mathrm{e}^{-i L t} \varrho(0) ;
$$

the time-evolution superoperator $T(t) \equiv \exp (-i L t)$ is readily shown to be factorizable:*)

$$
\begin{equation*}
T(t)=\mathrm{e}^{-i L t}=\mathrm{e}^{-i H t / \hbar} \times \mathrm{e}^{i H t / \hbar} \tag{2}
\end{equation*}
$$

The Liouville superoperator is self-adjoint, and the time-evolution superoperator unitary.

Projection operators in superspace will play a fundamental part in the following argument, and we shall be led to generalize their usual definition. Let us briefly explain what this generalization amounts to. Besides idempotency, the most essential property of a projection superoperator $P$ must be to make the projection of any density supervector $\varrho$ self-adjoint: $(P \varrho)^{+}$ $=P Q$, in order to ensure the physical interpretation of the projection as density supervector in the projected subspace, and above all the reality of the expectation value

$$
\langle A\rangle_{P}=\operatorname{tr}\left[(P \varrho)^{+} A\right]
$$

of the quantity represented by the self-adjoint supervector $A$. A superoperator $O$ satisfying the condition $(O A)^{+}=O A$ for any self-adjoint supervector $A$ will be said to be adjoint-symmetrical, or to have adjoint symmetry. (This terminology is suggested by the special form $M \times M^{+}$which a factorizable superoperator must have in order to satisfy the above condition.) If the superoperator $O$ is adjoint-symmetrical, its adjoint $O^{\dagger}$ has the same property; this may be seen by considering the scalar product $\operatorname{tr}[B(O A)]$, where $A$ and $B$ are two arbitrary self-adjoint supervectors and $O A=A O^{\dagger}$ : this product may in fact be written tr $A O^{\dagger} B$ as well as $\operatorname{tr}\left[A\left(O^{\dagger} B\right)^{+}\right]$. Now, in virtue of

[^20]\[

$$
\begin{aligned}
& \frac{1}{n!} L_{1} n=\frac{1}{n!}\left\{H_{1} \times 1+1 \times H_{1}+\right\}^{n}=\sum_{p=0}^{n} \frac{1}{n!}\binom{n}{p}\left(H_{1} \times 1\right) p\left(1 \times H_{1}+\right)^{n-p} \\
= & \sum_{p=0}^{n} \frac{1}{p!(n-p!)}\left(H_{1} p \times 1\right)\left(1 \times\left[H_{1}+\right]^{n-p}\right)=\sum_{p=0}^{n} \frac{1}{p!} H_{1} p \times \frac{1}{(n-p)!}\left[H_{1}+\right] n-p,
\end{aligned}
$$
\]

and since

$$
\sum_{n=0}^{\infty} \sum_{p=0}^{n} \ldots=\sum_{p=0}^{\infty} \sum_{n-p=0}^{\infty} \ldots,
$$

it follows that

$$
\mathrm{e}^{L_{1}}=\mathrm{e} H_{1} \times \mathrm{e}^{H_{1}+} .
$$

the idempotency of $P$ and $P^{\dagger}$, the expectation value $\langle A\rangle_{P}$ may also be written $\operatorname{tr}\left[(P \varrho)\left(P^{\dagger} A\right)\right]$ : this shows that if we want to interpret it as that of the projected supervector $P A$, we must impose upon the projector the further requirement of being self-adjoint. This is the case for the usual projectors constructed from (self-adjoint) projection operators in Hilbert space $P_{m}, P_{m}$ :

$$
P=\frac{1}{2}\left[P_{m} \times P_{m^{\prime}}+P_{m^{\prime}} \times P_{m}\right] \equiv \overline{P_{m} \times P_{m^{\prime}}},
$$

the symmetrization being necessary in order to satisfy the adjoint-symmetry requirement. However, this further specification of the expectation value will prove too restrictive for our purposes, and the physical meaning of the above definition of $\langle A\rangle_{P}$ is perfectly clear and precise without it, provided that the adjoint-symmetry condition is fulfilled. Hence, we shall give up the requirement of self-adjointness for projectors in superspace, and consider as such the wider class of idempotent superoperators satisfying the condition of adjoint symmetry.

Although the superspace representation is equivalent to the usual one might therefore appear as no more than a convenient formalism, it will turn out that it actually opens possibilities of description of fundamental physical properties, not adequately dealt with in the Hilbert space representation, because they essentially require the use of non-factorizable superoperators, in particular projection superoperators in the generalized sense just defined.

### 2.2. Energy spectrum and time-behaviour of large systems

The structure of the energy spectrum leads to a clearcut distinction between two types of large systems: systems of finite degree of freedom and finite extension, whose energy spectrum is discrete, and systems of infinite degree of freedom and infinite extension, but finite density of constitutive elements: the latter have essentially a continuous energy spectrum, possibly combined with a set of discrete states. The spectral decomposition of the Hamiltonian may be written as a Stieltjes integral

$$
H=h \int v_{k} \mathrm{~d} P(k),
$$

where the symbol $k$ represents a set of appropriate quantum numbers, and $h v_{k}$ the energy eigenvalue corresponding to definite values $\{k\}$ of this set. According to eq. (2), the corresponding decomposition of the time-evolution superoperator is

$$
\begin{equation*}
T(t)=\iint \mathrm{d} P(k) \times \mathrm{d} P\left(k^{\prime}\right) \mathrm{e}^{-2 \pi i\left(v_{k}-v_{k^{\prime}}\right) t} \tag{3}
\end{equation*}
$$

Any discrete sequence of states, with eigenvalues $h v_{n}$, will accordingly give a contribution to $T(t)$ almost periodic in time. This shows that finite quantal systems, with discrete spectrum, cannot be expected to exhibit any irreversibility in their asymptotic behaviour. Infinite systems, on the other hand, allow of a direct approach to their dynamical time-evolution.

Indeed, it follows from eq. (3) that the contribution to $\varrho(t)=T(t) \varrho(0)$, with $\varrho(0)=\left|\psi_{0}\right\rangle\left\langle\psi_{0}\right|$, of a continuous part of the energy spectrum, has matrix elements of the form

$$
\langle k| \varrho(t)\left|k^{\prime}\right\rangle=\left\langle k \mid \psi_{0}\right\rangle\left\langle\psi_{0} \mid k^{\prime}\right\rangle \mathrm{e}^{-2 \pi i\left(v_{k}-v_{k}\right) t} .
$$

Now, an amplitude like $\left\langle k \mid \psi_{0}\right\rangle$, when continued analytically in the plane of the complex variable $v_{k}$, is in general*) a multivalued function of this variable, with branch-points on the real axis at various thresholds of excitation, and its domain of uniformity of physical interest for $t>0$ (owing to the time-reversal invariance of the evolution, it suffices to consider positive times) consists of adjacent parts of Riemann sheets below the real axis limited by cuts issuing from the thresholds. The integrations occurring in the calculation of an average $\operatorname{tr} \varrho(t) A$ may be transformed so as to involve integrations over the energy variables $v_{k}$ and $v_{k^{\prime}}$. The contour of integration in the plane of each variable may then be closed by a parallel to the real axis at infinite distance in the lower half-plane, with indentations along the cuts. The "resonance" poles of the integrand inside this contour,

$$
2 \pi v_{r}=2 \pi \varepsilon_{r}-\frac{1}{2} i \gamma_{r} \quad\left(\gamma_{r}>0\right)
$$

will yield exponentially decaying terms to the integral, to which is added a "background" whose time variation is more complicated. The resonance contributions to $\operatorname{tr} \varrho(t) A$ have accordingly a time dependence of the form $\exp \left[-2 \pi i\left(v_{r}-v_{r^{\prime}}^{*}\right) t\right]$, corresponding to processes of frequencies $\varepsilon_{r}-\varepsilon_{r^{\prime}}$, decreasing exponentially with decay times $\left[\frac{1}{2}\left(\gamma_{r}+\gamma_{r^{\prime}}\right)\right]^{-1}$. These life-times vary over a very wide range, extending from the time-scale characteristic of individual atomic processes to that of macroscopic relaxation times. In the simplest case, in which only these two extreme time-scales appear, one may expect that it would be possible, at least approximately, to separate the direct effects of short-lived atomic processes from the slower evolution of the system on the macroscopic time-scale.

Before pursuing this line of argument, we must mention another essential difference between finite and infinite systems, which, as we shall see, is of relevance for their asymptotic behaviour: it concerns the invariants of the
*) Cf. on this point, e.g., refs. ${ }^{6}$ ) and ${ }^{19}$ ).
system, i.e. those Hilbert space operators $\Phi$ which commute with the Hamiltonian, and accordingly satisfy the equation $L \Phi=0$. Whereas the invariants of finite systems are regular operators within the Hilbert space of state vectors of finite norm, those of infinite systems are of two distinct types: besides "regular" ones, there is an infinity of invariant operators which do not have the regularity property just mentioned.*) We shall discuss this point in detail in subsection 2.8.

### 2.3. Independent modes of motion and correlations

In order to proceed further, we must introduce a more explicit characterization of the constitutive elements of the system and the interactions between them, which would allow us to account for the continual change of the system in the course of time as the result of transition processes brought about by such interactions. As usual, this is done by reference to an idealized "model system", susceptible of independent, non-interacting, modes of motion, defining a complete orthogonal basis of representation in Hilbert space. The interactions producing correlations between these modes are then defined as those which transform the model into the real system. The choice of the model system is dictated by physical considerations: for a dilute gas, the natural model will be a perfect gas, for a crystal, a perfect lattice susceptible of collective harmonic oscillations. The essential requirement is that the basic modes should have some operational meaning, in the sense that we can imagine situations conveniently represented by them. In any case, all physical results of the theory, expressed as expectation values of suitable operators, are of course independent of the choice of the model system, since a change of basis is effected by a unitary transformation.

The total Hamiltonian $H$ is thus decomposed into the Hamiltonian $H^{(0)}$ of the model system and a residual interaction Hamiltonian $H^{(1)}$. The spectrum of the model Hamiltonian

$$
H^{(0)}=h \int v_{m}^{(0)} \mathrm{d} P(m),
$$

will generally be a continuum, in which a set of discrete states may be embedded; the "Friedrichs model"'21) is of this type, with only one discrete state. The collective index $m$ stands, as the case may be, for a set of quantum

[^21]numbers of single-particle states (properly symmetrized or antisymmetrized) or for a set of occupation numbers. In superspace, a complete orthogonal basis consists of the Hilbert space projection operators*) $P_{m}=|m\rangle\langle m|$; the corresponding orthogonal projectors in superspace are the factorizable superoperators $\overline{P_{m} \times P_{m}}$, formed by all the pairs of supervectors $P_{m}, P_{m}$.

With a view to distinguishing the effects of the correlations from the behaviour of the model system, we now introduce a subdivision of the total basis in superspace into two orthogonal and complementary subsets, defined by two superprojectors $P_{o}, P_{c}$ with $P_{o}+P_{c}=1$. Thus, for the Friedrichs model, where we wish to study how the correlations $H^{(1)}$ couple the discrete state of the Hamiltonian $H^{(0)}$ with its continuum, we may take for the subspace $P_{o}$ that defined by the discrete state, and consequently $P_{c}$ by the continuum. ${ }^{16,17)}$ More generally, we shall include in $P_{o}$ all the projectors $P_{m} \times P_{m}$ formed of pairs of identical states; if the external conditions allow for a bulk flow of the system, we shall add to these the projectors $\overline{P_{m} \times P_{m}}$, for all the pairs $P_{m}, P_{m}$, representing the same internal physical state of the system; the subspace $P_{c}$ consists of all the remaining projectors $\overline{P_{m} \times P_{m}}$, corresponding to those pairs of states between which transition processes take place owing to the short-range, atomic correlations. Still other decompositions may prove useful for specific problems; ${ }^{18)}$ for our general argument, the precise mode of decomposition chosen is irrelevant, provided that it confines the short-range correlation effects to one of the two subsets.

The adopted decomposition effects a separation of the density supervector into two components :**)

$$
\varrho(t)=\varrho_{o}(t)+\varrho_{c}(t), \quad \varrho_{o}(t)=P_{o} \varrho(t), \quad \varrho_{c}(t)=P_{c} \varrho(t) .
$$

The density $\varrho_{o}(t)$ represents an average distribution referred to the states of the model system, whereas the supervector $\varrho_{c}(t)$ accounts for the effects of the fluctuating correlations among these states. Between $\varrho_{o}$ and $\varrho_{c}$ we derive from eq. (1) a set of coupled Liouville equations:
*) For a continuous spectrum, we define $P_{m}=\int_{\varepsilon(m)}^{0} \mathrm{~d} P(m)$, where $\mathrm{d} P_{m}=|m>\mathrm{d} m<m|$, and $\varepsilon(m)$ is an infinitesimal neighbourhood of $m$. We further interpret a summation over $m$ as $\int d m \ldots$ and the Hilbert space scalar product $\left\langle m \mid m^{\prime}\right\rangle$ as the distribution $\delta\left(m-m^{\prime}\right)$. Then, the idempotency, orthogonality and completeness relations $P_{m} P_{m}{ }^{\prime}=P_{m} \delta_{m m^{\prime}}$ and $\Sigma_{m} P_{m}=1$ hold for both the continuous and the discrete part of the spectrum.
**) From now on, we adopt the elegant formalism developed by M. Baus, ${ }^{10}$ ) of which we present a version improved in some important respects, and extended to take account of later progress. ${ }^{12-17}$ ) Some mathematical aspects are discussed by J. RaE. ${ }^{11}$ ) Another general exposition has lately been given by Balesce and Wallenborn. ${ }^{18}$ )

$$
\begin{align*}
& \ddot{i \varrho_{o}}=L_{o o \varrho} \varrho_{o}+L_{o c} \varrho_{c},  \tag{4}\\
& \ddot{i}_{c}=L_{c c} \varrho_{c}+L_{c o} \varrho_{o}, \tag{5}
\end{align*}
$$

where

$$
L_{o o}=P_{o} L P_{o}, L_{c c}=P_{c} L P_{c}, L_{o c}=P_{o} L P_{c}, L_{c o}=P_{c} L P_{o}
$$

We shall especially use the equivalent integrated form of eq. (5),

$$
\begin{equation*}
\varrho_{c}(t)=\mathrm{e}^{-i L_{c c} t}\left\{\varrho_{c}(0)-i \int_{0}^{t} \mathrm{~d} \tau \mathrm{e}^{i L_{c c} \tau} L_{c o} \varrho_{o}(\tau)\right\}, \tag{6}
\end{equation*}
$$

exhibiting the occurrence of the time-evolution superoperator

$$
\begin{equation*}
T_{c}(t) \equiv \mathrm{e}^{-i L_{c c} t}=\mathrm{e}^{-i P_{c} L t} P_{c}=P_{c} \mathrm{e}^{-i L P_{c} t} \tag{7}
\end{equation*}
$$

which is going to play an essential part in our analysis.
The superoperator $T_{c}(t)$ describes a time-evolution proceeding entirely by transitions between states of the correlation subspace; we have called such sequences of processes confined to the correlation subspace the "irreducible dynamics" of the system: its explicit consideration is one of the main points of our approach. ${ }^{6,10)}$ Indeed, in contrast with the total timeevolution superoperator $T(t)$, we may expect that the superoperator $T_{c}(t)$ may have a simple asymptotic behaviour:*) in view of its exclusive dependence on correlation effects, its time-variation may be dominated by decaying pole terms of atomic life-times. More precisely, we shall consider the possibility that the application of the superoperator $T_{c}(t)$ to any regular supervector which is not an invariant in the correlation subspace gives a result which, in the asymptotic limit of positive values of the time of macroscopic order of magnitude, becomes of negligible importance. This condition may be formally expressed as

$$
\begin{equation*}
\lim _{t \rightarrow+\infty} T_{c}(t) A=0 \quad\left(\text { if } L P_{c} A \neq 0\right) ; \tag{8}
\end{equation*}
$$

in terms of the Laplace transform

$$
\begin{equation*}
\mathscr{T}_{c}(z)=\int_{0}^{\infty} T_{c}(t) \mathrm{e}^{-z t} \mathrm{~d} t=-i P_{c} \frac{1}{L P_{c}-i z}=-i \frac{1}{P_{c} L-i z} P_{c} \tag{9}
\end{equation*}
$$

an equivalent expression for it is

[^22]\[

$$
\begin{equation*}
\lim _{z \rightarrow+0} z \mathscr{T}_{c}(z) A=0 \quad\left(\text { if } L P_{c} A \neq 0\right) \tag{10}
\end{equation*}
$$

\]

implying that $\mathscr{T}_{c}(z) A$ is a regular function of $z$ in the neighbourhood of $z=+0$. If $P_{c} A$ is an invariant, one has instead $z \mathscr{T}{ }_{c}(z) A=P_{c} A$.

This analyticity condition may be used in principle for a classification of dynamical systems. It has indeed been shown that it is satisfied in the thermodynamic limit for large systems with short-range interactions, when a perturbation expansion can be carried out with respect to a 'small" physical parameter, such as the coupling constant or the density. Moreover, it is seen to be exactly fulfilled (independently of any perturbative approach) for soluble systems such as the Friedrichs model. ${ }^{17)}$ It is not the aim of the present paper to investigate this question any further. We shall simply assume that we are dealing with systems that satisfy the condition (8) or (10): it is for this class of systems that we shall arrive at a unique definition of a macroscopic level of description, complementary to the dynamical one. The assumption (8) will indeed prove convenient for the derivation of simple asymptotic forms for the density supervectors $\varrho_{o}$ and $\varrho_{c}$. It must be stressed that the introduction of this assumption destroys the invariance of the description for time-reversal: for in retrodiction the operator $T_{c}(-t)$ describes the buildup of the resonance states of the system - an aspect of the evolution on the atomic scale which is all but negligible. An interesting type of system from the physical point of view is that in which the interactions between the constitutive elements are such as to determine two characteristic time-scales of very different orders of magnitude: on the one hand, any coherent processes involving states collected in the subspace $P_{o}$ have relaxation times belonging to the macroscopic time-scale; on the other, the individual processes due to the finite-range interactions between the basic modes of the model system, which occur between states of the subspace $P_{c}$, have decay times of atomic dimension. Systems for which no such separation of time-scales can be made may be discussed by more general methods.

### 2.4. Asymptotic density supervectors and evolution equations

By means of the assumption (8), we will now set up solutions of the Liouville equations (4), (5) valid for large positive values of $t$; these solutions, which we shall denote as $\tilde{\varrho}_{o}(t)$, $\tilde{\varrho}_{c}(t)$, will then be associated with the actual density supervectors $\varrho_{o}(t), \varrho_{c}(t)$ by an appropriate condition : this will allow us to interpret $\tilde{\varrho}_{o}(t), \tilde{\varrho}_{c}(t)$ as the respective asymptotic forms of $\varrho_{o}(t)$, $\varrho_{c}(t)$. Taking eq. (6) first, we neglect the first term on the right-hand side
(which means, physically, that we assume the effect of any initial correlations to be dissipated), and in the second term, re-written as

$$
-i \int_{0}^{t} \mathrm{~d} \tau \mathrm{e}^{-i L_{c c} \tau} L_{c o} \varrho_{o}(t-\tau)
$$

we replace $\varrho_{o}(t-\tau)$ by the asymptotic solution $\tilde{\varrho}_{o}(t-\tau)$, since the integrand is only important for small values of $\tau$; we thus obtain

$$
\begin{equation*}
\tilde{\varrho}_{c}(t)=-i \int_{0}^{t} \mathrm{~d} \tau \mathrm{e}^{-i L_{c c} \tau} L_{c o} \tilde{\varrho}_{o}(t-\tau) . \tag{11}
\end{equation*}
$$

Next, let us consider eq. (4); for large values of $t$, it becomes, on account of eq. (11), an integro-differential equation for $\varrho_{o}$ :

$$
i \dot{\tilde{\varrho}}_{o}=L_{o o} \tilde{\varrho}_{o}-i L_{o c} \int_{0}^{t} \mathrm{~d} \tau \mathrm{e}^{-i L_{c c} \tau} L_{c o} \tilde{\varrho}_{o}(t-\tau) .
$$

Let us introduce*) an asymptotic time-displacement superoperator $\theta$ in the $P_{o}$ subspace by the definition

$$
i \mathrm{~d} \tilde{\varrho}_{o}=\theta \tilde{\varrho}_{o} \mathrm{~d} t,
$$

or, alternatively,

$$
\begin{equation*}
\tilde{\varrho}_{o}(t)=\mathrm{e}^{-i \theta t} \tilde{\varrho}_{o}(0) \quad(\text { for } t>0) . \tag{12}
\end{equation*}
$$

Inserting this expression in eq. (11) yields the asymptotic relation

$$
\left\{\theta-L_{o o}+i L_{o c} \int_{0}^{t} \mathrm{~d} \tau \mathrm{e}^{-i L_{c c} \tau} L_{c o} \mathrm{e}^{i \theta \tau}\right\} \tilde{\varrho}_{o}(t)=0
$$

which can be further modified, according to our assumption (8), by extending the integration over $\tau$ to infinity. We thus obtain a functional equation for the superoperator $\theta$ :

$$
\theta=L_{o o}-i L_{o c} \int_{0}^{\infty} \mathrm{d} \tau \mathrm{e}^{-i L_{c c} \tau} L_{c o} \mathrm{e}^{i \theta \tau}
$$

which may be solved by iteration, ${ }^{9,}{ }^{18)}$ starting from the ansatz $\theta=0$ (which would correspond to a stationary asymptotic distribution). By defining a time-independent superoperator
*) The superoperator $\theta$ was first considered by P. Résibois and further studied by C. George. ${ }^{9}$ )

$$
\begin{equation*}
i C \equiv \int_{0}^{\infty} \mathrm{d} \tau T_{c}(\tau) L_{c o} \mathrm{e}^{i \theta \tau} \tag{13}
\end{equation*}
$$

we may re-write the equation for $\theta$ as

$$
\begin{equation*}
\theta=L_{o o}+L_{o c} C, \tag{14}
\end{equation*}
$$

and treat the equations (13), (14) as a set of coupled equations for the determination of $\theta$ and $C$. The role of the latter appears when, returning to eq. (11), we repeat on the right-hand side the preceding transformations; this gives the very simple result

$$
\begin{equation*}
\tilde{\varrho}_{c}(t)=C \tilde{\varrho}_{o}(t) . \tag{15}
\end{equation*}
$$

According to its definition (13), $C$ describes the effect of an infinite sequence of processes starting from a state in the subspace $P_{o}$ and leading to a state of the correlation subspace $P_{c}$ either directly or through intermediate states: in other words, $C$ describes the "building up" of the correlation component $\tilde{\varrho}_{c}$, as expressed by eq. (15). We therefore call $C$ the "creation superoperator", of correlations. It should be noted that one may derive from the definition (13) of $C$, by partial integration, the identity

$$
\begin{equation*}
C \theta=L_{c o}+L_{c c} C, \tag{16}
\end{equation*}
$$

use being made once more of the assumption (8). Combining this with eq. (14), one obtains a non-linear equation for the determination of $C$ :

$$
C L_{o o}+C L_{o c} C=L_{c o}+L_{c c} C
$$

So far, we have defined the asymptotic supervectors $\tilde{\varrho}_{o}(t)$, $\tilde{\varrho}_{c}(t)$ by eqs. (12), (15), as solutions of the "kinetic equations"

$$
i \dot{\tilde{\varrho}}_{o}=\theta \tilde{\varrho}_{o}, \quad i \dot{\tilde{\varrho}}_{c}=C \theta \tilde{\varrho}_{o} .
$$

If, in these equations, we substitute for $\theta$ and $C \theta$ their respective expressions (14) and (16), and take account again of eq. (15), we see that they become identical in form with the Liouville equations (4), (5): in other words, the asymptotic density supervectors are exact solutions of the Liouville equations. It remains to be seen how they are related to the solutions $\varrho_{o}(t), \varrho_{c}(t)$ which describe the behaviour of the system on the atomic scale.

### 2.5. Heisenberg representation and time-reversal

As a preparation to the elucidation of this point, it will be necessary to repeat the preceding considerations from the point of view of Heisenberg's
representation. In the latter, any (time dependent) operator $A(t)$ satisfies the Liouville equation

$$
i \dot{A}(t)=-L A(t)
$$

where the Liouville superoperator is, of course, time-independent. Let us now define the time-inversion of any supervector or superoperator as the transformation which consists in both changing the direction of time and taking the adjoint:

$$
\bar{A}(t)=A^{+}(-t), \quad \bar{O}(t)=O^{\dagger}(-t)
$$

Since the Liouville superoperator, which is self-adjoint, changes sign on transposition, the time-inverse supervector $\bar{A}(t)$ obeys the same Liouville equation

$$
i \dot{\bar{A}}(t)=L \bar{A}(t)
$$

as the density supervector. The projectors $P_{o}, P_{c}$ being invariant for timereversal, we may define components

$$
\bar{A}_{o}(t)=P_{o} \bar{A}(t), \quad \bar{A}_{c}(t)=P_{c} \bar{A}(t)
$$

and corresponding asymptotic components $\tilde{\bar{A}}_{o}(t), \tilde{\bar{A}}_{c}(t)$, with a time-evolution governed by the superoperators $\theta$ and $C$ :

$$
\tilde{\bar{A}}_{o}(t)=\mathrm{e}^{-i \theta t} \tilde{\bar{A}}_{o}(0), \quad \tilde{\bar{A}}_{c}(t)=C \tilde{\bar{A}}_{o}(t)
$$

In this context, these superoperators appear as the time-inverses of new superoperators

$$
\eta=\bar{\theta}, \quad D=\bar{C}
$$

determined by functional equations derived from eqs. (14), (16) and (13) by time-inversion:

$$
\begin{gather*}
\eta=L_{o o}+D L_{c o},  \tag{17}\\
\eta D=L_{o c}+D L_{c c} ;  \tag{18}\\
i D=\int_{0}^{\infty} \mathrm{d} \tau \mathrm{e}^{i \eta \tau} L_{o c} T_{c}(\tau), \tag{19}
\end{gather*}
$$

In contrast to $C$, the superoperator $D$, according to its definition (19), leads from a state of the correlation subspace $P_{c}$ to a state of the subspace $P_{o}$ : it describes the processes leading to a "destruction" of correlations, and is called, accordingly, the "destruction superoperator".

It is important to notice that in applying the time-inversion transformation to the right-hand side of eq. (13) in order to obtain eq. (19), one has to leave the integration variable $\tau$ unchanged, but change the interval of integration over $\tau$ to $(0,-\infty)$. This clearly shows that the change of the direction of time can affect seemingly time-independent superoperators like $C$ and $D$ which are defined through an asymptotic time-limiting procedure. A comparison of the expressions (13) and (19) for $C$ and $D$, together with eqs. (14) and (17), shows that the time-inversion transformation, for such superoperators, consists in taking the adjoint and inverting the sign of $L$. The time-inversion may obviously be performed in the same way for operators depending explicitly on the time variable, since this time dependence may always be expressed as a functional dependence on iLt; one may therefore consider the transformation just defined as equivalent to time-inversion.

According to this definition, it is clear that time-reversal invariance of a superoperator depending on $L$ does not in general imply its self-adjointness: this is only the case if its functional dependence on $L$ is not affected by a change of sign of $L$ - in particular (trivially), if the superoperator does not depend on $L$. Thus, time-inversion appears as a natural generalization of adjointness for superspace operators, and time-reversal invariance as a natural generalization of self-adjointness. The adequacy of this generalization with respect to the requirements of physical interpretation is guaranteed by the simple, but very important fact that the superoperator $i L$, and consequently any superoperator which is a functional of $i L$, is adjoint-symmetrical. The equality $(i L A)^{+}=i L A$ for any self-adjoint supervector $A$ follows indeed immediately from the self-adjointness of $L$ and its transposition property $L A=-A L$. The superoperators $C$, $i \theta$ as well as $D$, $i \eta$, as appears from eqs. (13), (14), (17), (19) which define them, offer examples of superoperators which are functionals of $i L$, and accordingly adjoint-symmetrical. It will soon turn out that the time-dependence (in the extended sense just introduced) of all density supervectors of physical interest (such as $\varrho(t)$ and $\varrho(t))$ can be expressed in the general form $\varrho_{0}(t) \equiv O[i L] \varrho$, where $\varrho$ is the initial density supervector and $O[i L]$ an appropriate superoperator which is always a functional of $i L$ : these time-dependent density supervectors are therefore self-adjoint, as well as their time-inverses, and the expectation value of any self-adjoint supervector $A$, which can accordingly be written
$\operatorname{tr} \varrho_{O}(t) A$, or equivalently*) tr $\overline{\varrho_{O}(-t)} A$, is always real - a property essential for its physical interpretation.

The functional equations for $\theta$ and $\eta$, given by the combination of eqs. (14), (13) and (17), (19), respectively, can be put into a more compact form:

$$
\begin{equation*}
\theta=L_{o o}-i \int_{0}^{\infty} \mathrm{d} \tau \Psi(\tau) \mathrm{e}^{i \theta \tau}, \quad \eta=L_{o o}-i \int_{0}^{\infty} \mathrm{d} \tau \mathrm{e}^{i \eta \tau} \Psi(\tau), \tag{20}
\end{equation*}
$$

with the help of the superoperator

$$
\begin{equation*}
\Psi(t)=L_{o c} T_{c}(t) L_{c o} . \tag{21}
\end{equation*}
$$

The superoperator $\Psi(t)$ represents a transition from the subspace $P_{o}$ to the same subspace exclusively through states of the correlation subspace; it is therefore called the "irreducible collision operator". The formulae (20) show how the asymptotic superoperators $\theta$ and $\eta$ essentially arise from sequences of interaction processes belonging to the "irreducible" dynamics of the system. The interaction superoperator $\Psi(t)$, or its Laplace transform

$$
\begin{equation*}
\Psi_{\mathscr{L}}(z)=L_{o c} \mathscr{T}_{c}(z) L_{c o}=z L_{o c} \frac{1}{P_{c} L-i z} P_{o} \tag{22}
\end{equation*}
$$

has an important function, as we shall soon see, in the formulation of a general characterization of the asymptotic behaviour of infinite systems.

An explicit relation between $\theta$ and $\eta$ is readily derived from eqs. (14), (16) and(17), (18):

$$
\begin{equation*}
N_{o} \theta=\eta N_{o}, \quad \text { with } N_{o}=1+D C ; \tag{23}
\end{equation*}
$$

according to eqs. (13), (19) and (21), one may write

$$
\begin{equation*}
N_{o}=1-\int_{0}^{\infty} \mathrm{d} \tau \int_{0}^{\infty} \mathrm{d} \tau^{\prime} \mathrm{e}^{i \eta \tau} \Psi\left(\tau+\tau^{\prime}\right) \mathrm{e}^{i \theta \tau^{\prime}} . \tag{24}
\end{equation*}
$$

*) Such time-dependent expectation values are conserved under a group of time-dependent transformations $U[i L]$, defined in such a way that the transforms $A^{\prime}, \varrho^{\prime}(t)$ of $A, \varrho(t)$ are, respectively,

$$
A^{\prime}=U[i L] A, \quad \varrho^{\prime}(t)=U[-i L] \varrho(t),
$$

and characterized by the condition

$$
\overline{U[i L]} U[i L]=U[i L] \overline{U[i L]}=1 .
$$

This condition indeed ensures that $\operatorname{tr} \overline{\varrho^{\prime}(-t)} A^{\prime}=\operatorname{tr} \overline{\varrho(-t)} A$. This is a generalization of the group of unitary transformations, in which adjointness is replaced by time-inversion. It has been considered under the name of "star-unitary" group in previous papers of the Brussels group; see especially the second paper of ref. ${ }^{15}$ ). In contrast to the unitary transformation superoperators, the star-unitary ones are not factorizable: they belong specifically to the superspace.

In general, $N_{o}$ will have an inverse, and the relation (23) between $\theta$ and $\eta$ will then take the form

$$
\begin{equation*}
\eta=N_{o} \theta N_{o}^{-1}, \quad \theta=N_{o}^{-1} \eta N_{o} . \tag{25}
\end{equation*}
$$

### 2.6. Relation between asymptotic and dynamical behaviour

Let us now return to the asymptotic density supervector $\tilde{\varrho}_{o}(t)$ and its time-evolution (12). From the relation (23) we see that this evolution can be expressed by means of the superoperator $\eta$ as follows:

$$
\begin{equation*}
N_{o} \tilde{\varrho}_{o}(t)=N_{o} \mathrm{e}^{-i \theta t} \tilde{\varrho}_{o}(0)=\mathrm{e}^{-i \eta t} N_{o} \tilde{\varrho}_{o}(0) ; \tag{26}
\end{equation*}
$$

in other words, the time-evolution of $N_{o} \tilde{\varrho}_{o}(t)$ is governed by the superoperator $\eta$. On the other hand, it follows from eqs. (17) and (18) that

$$
\begin{equation*}
\eta\left(P_{o}+D\right)=\left(P_{o}+D\right) L \tag{27}
\end{equation*}
$$

This remarkable commutation property implies that the time-evolution of the supervector $\left(P_{o}+D\right) \varrho(t)$ is also given by the superoperator $\eta$ :

$$
\begin{equation*}
i\left(P_{o}+D\right) \dot{\varrho}=\left(P_{o}+D\right) L \varrho=\eta\left(P_{o}+D\right) \varrho . \tag{28}
\end{equation*}
$$

Hence, if we choose at any "initial" time

$$
\tilde{\varrho}_{o}(0)=N_{o}-1\left[\varrho_{o}(0)+D \varrho_{c}(0)\right],
$$

this relation will subsist at any future time and thus ensure the interpretation of $\tilde{\varrho}_{o}(t)$ and $\tilde{\varrho}_{c}(t)$ as the asymptotic form of the dynamical density supervectors $\varrho_{o}(t), \varrho_{c}(t)$.

### 2.7. Projection onto orthogonal subspaces and "subdynamics"

The relationship just established is part of a set of similar ones, which it is interesting to present systematically. According to eq. (15), the asymptotic density supervector $\tilde{\varrho}=\tilde{\varrho}_{o}+\tilde{\varrho}_{c}$ is contained in a subspace defined by the idempotent superoperator $P_{a}=P_{o}+C$ :

$$
\widetilde{\varrho}(t)=P_{a} \tilde{\varrho}(t) .
$$

Being also adjoint-symmetrical, the superoperator $P_{a}$ is a (generalized) projector. Let us consider the subdivision of the superspace into the orthogonal subspaces determined by the projector $P_{a}$ and its orthogonal complement:

$$
\begin{equation*}
P_{a}=P_{o}+C, \quad P_{b}=P_{c}-C, \tag{30}
\end{equation*}
$$

as well as the similar subdivision by means of the time-inverse projectors

$$
\begin{equation*}
\bar{P}_{a}=P_{o}+D, \quad \bar{P}_{b}=P_{c}-D \tag{31}
\end{equation*}
$$

Besides the superoperator $N_{o}$ defined by eq. (23), we introduce another one, $N_{c}$ :

$$
\begin{equation*}
N_{o}=1+D C, \quad N_{c}=1+C D \tag{32}
\end{equation*}
$$

and we readily verify the relations

$$
\begin{equation*}
\bar{P}_{a} P_{a}=P_{o} N_{o}=N_{o} P_{o}, \quad P_{b} \bar{P}_{b}=P_{c} N_{c}=N_{c} P_{c} \tag{33}
\end{equation*}
$$

Further, we note that

$$
\begin{equation*}
P_{a} P_{o}=P_{a}, \quad P_{o} \bar{P}_{a}=\bar{P}_{a} ; \quad P_{c} P_{b}=P_{b}, \bar{P}_{b} P_{c}=\bar{P}_{b} \tag{34}
\end{equation*}
$$

We already know the mutually time-inverse superoperators

$$
\begin{equation*}
\theta=P_{o} L P_{a}, \quad \eta=\bar{P}_{a} L P_{o} \tag{35}
\end{equation*}
$$

they satisfy the relation (27) and its time-inverse, i.e.

$$
\begin{equation*}
P_{a} \theta=L P_{a}, \quad \eta \bar{P}_{a}=\bar{P}_{a} L \tag{36}
\end{equation*}
$$

from which eq. (23) follows at once. We may now introduce a further superoperator $\zeta$ and its time-inverse $\lambda$ :

$$
\begin{equation*}
\zeta=P_{c} L \bar{P}_{b}, \quad \lambda=P_{b} L P_{c} \tag{37}
\end{equation*}
$$

they satisfy the relations

$$
\begin{equation*}
\bar{P}_{b} \zeta=L \bar{P}_{b}, \quad \lambda P_{b}=P_{b} L \tag{38}
\end{equation*}
$$

Hence we have, together with eq. (23), an analogous relation involving $\zeta$, $\lambda$ and $N_{c}$ :

$$
\begin{equation*}
N_{o} \theta=\eta N_{o}, \quad N_{c} \zeta=\lambda N_{c} \tag{39}
\end{equation*}
$$

With this notation the results of the preceding subsection, expressed by eqs. (12), (15 and (29), take the compact form

$$
\begin{equation*}
\tilde{\varrho}(t)=\tilde{\Sigma}\left(t-t_{0}\right) \varrho\left(t_{0}\right) \tag{40}
\end{equation*}
$$

with

$$
\begin{equation*}
\tilde{\Sigma}(t)=P_{a} \mathrm{e}^{-i \theta t} N_{o}^{-1} \bar{P}_{a}=P_{a} N_{o}^{-1} \mathrm{e}^{-i \eta t} \bar{P}_{a} \tag{41}
\end{equation*}
$$

the last form for $\tilde{\Sigma}(t)$ following from the first on account of eq. (23); the equivalence of these two forms shows that the superoperator $\tilde{\Sigma}(t)$ is invariant
for time-reversal. Eq. (40) expresses the general correspondence between the asymptotic density supervector $\tilde{\varrho}(t)$ at any time $t$ and the dynamic supervector $\varrho\left(t_{0}\right)$ at any former time $t_{0}$. By using eqs. (33) and (34) one readily verifies that the superoperator $\tilde{\Sigma}(t)$ has the semi-group property

$$
\begin{equation*}
\tilde{\Sigma}\left(t_{1}\right) \tilde{\Sigma}\left(t_{2}\right)=\tilde{\Sigma}\left(t_{1}+t_{2}\right) \quad\left(t_{1}, t_{2}>0\right) \tag{42}
\end{equation*}
$$

Taking the limit $t_{0} \rightarrow t$ in eq. (40), we obtain from it a relation between the asymptotic and the dynamic density at the same time:

$$
\begin{equation*}
\tilde{\varrho}(t)=\tilde{\Pi} \varrho(t) \tag{43}
\end{equation*}
$$

where the superoperator

$$
\begin{equation*}
\tilde{\Pi} \equiv P_{a} N_{o}^{-1} \bar{P}_{a} \tag{44}
\end{equation*}
$$

is a projector in superspace, since it is adjoint-symmetrical and, according to eq. (42), idempotent. We have, moreover, in virtue of eq. (42),

$$
\begin{equation*}
\tilde{\Sigma}(t)=\tilde{\Sigma}(t) \tilde{\Pi}=\tilde{\Pi} \tilde{\Sigma}(t) \tag{45}
\end{equation*}
$$

and therefore also, by combining eqs. (40) and (43),

$$
\begin{equation*}
\tilde{\varrho}(t)=\tilde{\Sigma}\left(t-t_{o}\right) \tilde{\varrho}\left(t_{0}\right) \tag{46}
\end{equation*}
$$

Finally, eqs. (36), (39) and (44) allow us to write

$$
\begin{equation*}
P_{a} \theta N_{o}^{-1} \bar{P}_{a}=L \tilde{\Pi}=\tilde{\Pi} L=P_{a} N_{o}^{-1} \eta \bar{P}_{a} \tag{47}
\end{equation*}
$$

and consequently

$$
\begin{equation*}
\tilde{\Sigma}(t)=\mathrm{e}^{-i L t} \tilde{\Pi}=\tilde{\Pi} \mathrm{e}^{-i L t} \tag{48}
\end{equation*}
$$

We thus arrive at the remarkable conclusion*) that the asymptotic density supervector is a solution of the Liouville equation, characterized as the projection of the dynamical solution onto a subspace $\tilde{\Pi}$ of the Hilbert superspace, and that the asymptotic time-evolution is entirely contained in this "asymptotic subspace".

The orthogonal complement of the subspace $\tilde{\Pi}$ is susceptible of an equally simple characterization, by means of the superoperator

$$
\begin{equation*}
\hat{\Pi}=\bar{P}_{b} N_{c}^{-1} P_{b} \tag{49}
\end{equation*}
$$

Indeed the latter is immediately recognized to be a projector orthogonal to

[^23]$\tilde{\Pi}$; it is actually $=1-\tilde{\Pi}$, since the idempotent operator $1-(\tilde{\Pi}+\hat{\Pi})$ has zero trace, according to eqs. $(33)$, and is therefore $=0$. The time-evolution of the supervector
\[

$$
\begin{equation*}
\hat{\varrho}(t) \equiv \hat{\Pi} \varrho(t)=\varrho(t)-\varrho(t) \tag{50}
\end{equation*}
$$

\]

is given, according to eqs. (38) (39), by the superoperator

$$
\begin{equation*}
\hat{\Sigma}(t)=\bar{P}_{b} \mathrm{e}^{-i \zeta t} N_{c}^{-1} P_{b}=\bar{P}_{b} N_{c}^{-1} \mathrm{e}^{-i \lambda t} P_{b} \tag{51}
\end{equation*}
$$

which has the same semi-group property as $\tilde{\Sigma}(t)$ and satisfies the similar relations

$$
\begin{equation*}
\hat{\Sigma}(t)=\mathrm{e}^{-i L t} \hat{\Pi}=\hat{\Pi} \mathrm{e}^{-i L t} \tag{52}
\end{equation*}
$$

In other words, the time-evolution of the supervector $\hat{\varrho}(t)$, which describes the fluctuations of the system on the atomic scale,*) is entirely contained in the "fluctuation subspace" $\hat{\Pi}$, orthogonal to the asymptotic subspace $\tilde{\Pi}$. Both components $\tilde{\varrho}(t), \hat{\varrho}(t)$ of the dynamic density supervector $\varrho(t)$ are, like the latter, solutions of the Liouville equation: they receive their respective characteristics - asymptotic irreversibility, atomic-scale fluctuations - exclusively from the projection onto the corresponding subspaces. One may say that the asymptotic evolution results from a "subdynamics" of the system,**) unfolding itself on the macroscopic time scale in the subspace $\tilde{\Pi}$.

### 2.8. Invariants of the system

Let us finally examine the relation of the subdynamics with the invariants of the system; as already mentioned in subsection 2.2 , this relation is an important aspect of the theory of large systems. If we decompose the invariant $\Phi$ into its components $\Phi_{o}, \Phi_{c}$, the invariance conditions take the form

$$
\begin{equation*}
L_{o o} \Phi_{o}+L_{o c} \Phi_{c}=0, \tag{53}
\end{equation*}
$$

[^24]\[

$$
\begin{equation*}
L_{c o} \Phi_{o}+L_{c c} \Phi_{c}=0 \tag{54}
\end{equation*}
$$

\]

Multiplying eq. (54) on the left with $-i T_{c}(t)$ and integrating over $t$ yields

$$
\begin{equation*}
-i \int_{0}^{t} \mathrm{~d} t T_{c}(t) L_{c o} \Phi_{o}+\left[T_{c}(t)-1\right] \Phi_{c}=0 \tag{55}
\end{equation*}
$$

If $\Phi_{c}$ is a regular supervector, not itself an invariant, our fundamental asymptotic assumption, expressed by eq. (8), ensures that $\lim _{t \rightarrow \infty} T_{c}(t) \Phi_{c}=0$ and that the supervector $C(0) \Phi_{o}$, with

$$
\begin{equation*}
C(0) \equiv-i \int_{0}^{\infty} \mathrm{d} t T_{c}(t) L_{c o} \tag{56}
\end{equation*}
$$

exists. Eq. (55) thus becomes, in the limit $t \rightarrow \infty$,

$$
\begin{equation*}
\Phi_{c}=C(0) \Phi_{o} \tag{57}
\end{equation*}
$$

inserting this expression for $\Phi_{c}$ into eq. (53), we get

$$
\begin{equation*}
\left[L_{o o}+L_{o c} C(0)\right] \Phi_{o}=0 \tag{58}
\end{equation*}
$$

As a comparison with eqs. (13), (14) shows, this means

$$
\begin{equation*}
\theta \Phi=0 \tag{59}
\end{equation*}
$$

(and therefore also, by time-reversal, $\Phi_{\eta}=0$ ). Making use of the notation (30) for $P_{b}=P_{c}-C(0)$, we may re-write eq. (57) as $P_{b} \Phi=0$, and therefore, according to eq. (49),

$$
\begin{equation*}
\hat{\Pi} \Phi=0: \tag{60}
\end{equation*}
$$

the invariant $\Phi$ is contained in the asymptotic subspace $\tilde{\Pi}$.
The above argument could be formulated with the help of the Laplace transform $\mathscr{T}_{c}(z)$ of $T_{c}(t)$ and the related superoperator $\mathscr{C}(z)=-i \mathscr{T}{ }_{c}(z) L_{c o}$ : instead of eq. (55), one could start from

$$
\begin{equation*}
\mathscr{C}(z) \Phi_{o}+\left[z \mathscr{T}_{c}(z)-1\right] \Phi_{c}=0 \tag{61}
\end{equation*}
$$

The assumed properties of $\Phi_{c}$ imply, according to eq. (10), $\lim _{z \rightarrow+0} z \mathscr{T}_{c}(z) \Phi_{c}$ $=0$ as well as the existence of $\lim _{z \rightarrow+0} \mathscr{C}(z) \Phi_{o}=C(0) \Phi_{o}$. Eq. (58) may then be written, in terms of the Laplace transform (22) of the interaction superoperator,

$$
\begin{equation*}
\left[L_{o o}-i \Psi_{\mathscr{L}}(+0)\right] \Phi=0, \tag{62}
\end{equation*}
$$

- an equation equivalent to eq. (59), but of a more convenient form for concrete applications of the theory. This limiting process is not permissible if $\Phi_{c}$ does not have the two properties assumed in the preceding argument; but one may always combine eq. (61) directly with eq. (53) to obtain

$$
\begin{equation*}
\left[L_{o o-}-i \Psi_{\mathscr{L}}(z)\right] \Phi+i z \mathscr{D}(z) \Phi_{c}=0 \tag{63}
\end{equation*}
$$

where

$$
\begin{equation*}
\mathscr{D}(z)=-i L_{o c} \mathscr{T}_{c}(z) . \tag{64}
\end{equation*}
$$

If $\Phi_{c}$ is a regular invariant, one has (as pointed out in subsection 2.2 after eq. (10)) $\lim _{z \rightarrow+0} z \mathscr{T}_{c}(z) \Phi_{c}=\Phi_{c}$ and therefore $\lim _{z \rightarrow+0} z \mathscr{D}(z) \Phi_{c}=0$ : in this case, eq. (62) is still valid. If $\Phi_{c}$ is a singular supervector, the limit of $z \mathscr{D}(z) \Phi_{c}$ for $z \rightarrow+0$ exists, but does not vanish, and eq. (62) does not hold. This discussion shows, therefore, that eq. (62) and the equivalent equation (59) are characteristic for the regular invariants. Moreover, it is readily seen that any supervector obeying these equations is an invariant if it belongs to the asymptotic subspace. Indeed, it follows from eq. (36) that the relation $\theta F=0$ implies $L P_{a} F=0$, i.e. the invariance of the supervector $P_{a} F$, and consequently the invariance of $F$ if $F=P_{a} F$; but according to the definition (44) of $\tilde{\Pi}$ the equations $F=\tilde{\Pi} F$ and $F=P_{a} F$ are equivalent. We thus arrive at the remarkable conclusion that the asymptotic subspace $\tilde{I}$ contains all the regular invariants of the system and only those; the validity of eq. (62) is a criterium for deciding whether any supervector of the asymptotic subspace is a regular invariant.

A further simple result can be obtained if the projectors $P_{o}, P_{c}$ can be adequately chosen in such a way that $L_{o o}=0$, as is the case, in particular, for homogeneous systems. Then, those systems for which the superoperators $\Psi_{\mathscr{L}}(+0)$ and, equivalently, $\theta, \eta$, vanish identically are such that all supervectors contained in their asymptotic subspace are invariant. The behaviour of systems of this class is strictly dynamical: in the asymptotic subspace, the density supervector, as well as, in the Heisenberg representation, all supervectors contained in this subspace, are stationary; all processes occur in the subspace $\hat{\Pi}$, in an entirely reversible way. The systems exhibiting the normal thermodynamic irreversibility are therefore characterized by the existence of a superoperator $\theta$ or $\eta$ which does not vanish identically: we call ${ }^{13,14,15}$ ) such systems dissipative, and the condition just formulated "condition of dissipativity". Especially in the form

$$
\begin{equation*}
\Psi_{\mathscr{L}}(+0) \equiv 0, \tag{65}
\end{equation*}
$$

this condition offers a convenient criterium to decide whether a given system has the normal asymptotic behaviour. Thus, the Friedrichs model, for which explicit calculations can be carried out completely and rigorously, ${ }^{17}$ ) offers in this context a very precise picture: if the coupling between the discrete state and the continuum preserves the former (leading for instance to a bound state), the superoperator $\theta$ vanishes identically; if the coupling destroys the discrete state, the system is dissipative.

Among the regular invariants one distinguishes the important set of those which Khintchin has called "controllable", because their values can be fixed by the external conditions of observation. Besides the Hamiltonian, this set consists of the operators defining the infinitesimal transformations of the groups with respect to which the system is invariant: space translations and rotations, for instance, with which the components of the total momentum and the total angular momentum are respectively associated. In the theory of classical finite systems, the controllable invariants determine the manifold in phase space on which the ergodicity condition can be formulated: the other invariants do not lead to any reduction of the dimensionality of this manifold. In the case of infinite systems, as we just have seen, only the regular invariants are retained at the macroscopic level of description, whereas the singular ones play no part in the definition of this level or of the asymptotic time-evolution taking place in it; in simple examples, such as that of a gas of weakly coupled particles or the more general Friedrichs model, one finds that the regular invariants are just the controllable set. ${ }^{17)}$ This clear-cut discrimination of the set of invariants which enter into the description of the irreversible macroscopic behaviour of the system is paralleled in the account of phase transitions : here also it is in the limit of infinite systems that a sharp distinction becomes possible between the regular points of an isotherm and those singular points at which a phase transition occurs.

## 3. Epistemological problems of the atomic description of macroscopic phenomena

### 3.1. The historical background

The epistemological problems raised by the attempt to base the description of the directly observed phenomena on the atomic constitution of matter have forced themselves on the attention of physicists since the pioneering work of Maxwell and Boltzmann, but they could only be clearly formulated after the dynamical behaviour of the atomic constituents had found its definitive expression in quantum mechanics and the conceptual foundations of this theory had been elucidated. In the perspective of XIXth century physics it was natural enough to assume that the dynamics of the atoms was the same as that of large bodies, and accordingly to interpret the quantities characterizing the properties of these bodies as suitable averages over quantities pertaining to the constituent atoms. This averaging process seemed so far from being problematic that in the early papers of Clausius and Boltzmann it was not even mentioned explicitly.

However, the apparent contradiction between the irreversible evolution of macroscopic bodies and the time-reversal invariance of their description as atomic systems soon led Maxwell and his follower Boltzmann to their still fundamental analysis of the role of statistical causality in atomic physics. Of course, sharing the universal belief in determinism as the ultimate causal pattern of natural laws, they regarded any recourse to statistics as a pis-aller, but they correctly insisted on the fact that such a recourse was dictated by the very conditions of macroscopic observation. This point was variously elaborated both by Gibbs and by the Ehrenfests; the former forcibly pointed out that irreversibility at the macroscopic level results from the circumstances defining the corresponding mode of observation, while the latter introduced the notion of "coarse-grained" distribution as a mathematical expression for a mode of observation not reaching down to the dynamical determination of the atomic system. On the other hand, it was clear to Maxwell and Boltzmann that the equilibrium distribution had to arise naturally from the dynamics, and they had the correct intuition (albeit incorrectly formulated) of ergodicity as the dynamical property primarily
responsible for fixing the form of the asymptotic distribution. Gibbs wanted to express the same physical conception by his "mixing" simile, which, however, turned out to be a stronger dynamical requirement than ergodicity.*)

The development of quantum mechanics cannot affect the specific epistemological problems arising from the atomistic structure of matter, but it makes it easier to cope with them, by supplying us with adequate mathematical and logical tools for handling statistical averages of atomic quantities and probabilities of atomic processes. The statistical form of causality is now prevailing both in the account of individual atomic processes and of macroscopic phenomena; it is essential, however, to maintain a sharp distinction between these two forms of statistical causality, which are logically independent: the former has its origin in the existence of the quantum of action, the latter depends on the degree of freedom of the systems investigated, which may be characterized by some critical parameter, such as Avogadro's number, defining the order of magnitude we call "macroscopic". The formalism offers us uniform rules for dealing with both types of statistics and the relations of complementarity associated with each of them. In particular, as pointed out in the preceding section, the quantal density operator determines both the average distributions and the correlation coefficients of any system of interacting constituents, and accordingly yields a unified formal basis for the discussion of the two aspects of the asymptotic time-evolution - existence of the asymptotic distribution and "mixing" effect of the correlations.

The ergodic approach leaves unanswered the question as to which physical characteristics of a dynamical system are decisive for its exhibiting a thermodynamic behaviour on the macroscopic time-scale; for the conditions of ergodicity and mixing are mere mathematical formulations of properties characteristic of such behaviour, but not explicitly related to the physical structure of the system. One lacks here, for distinguishing systems which allow of a thermodynamical description from those that do not, a criterium linking this property more directly to the Hamiltonian.

### 3.2. Kinetic approach vs. ergodic theory

Even from the formal point of view, the extension of classical ergodic theory to quantal systems is far from straight-forward: the stumbling block is the difficulty of finding a representation of the conditions of macroscopic observation of comparable simplicity to the classical concept of coarsegraining. In classical theory, it is permissible to replace a coarse-grained
$\left.{ }^{*}\right)$ See, e.g., ref. ${ }^{7}$ ).
distribution, referred to some arbitrary subdivision of phase space into finite cells, by an idealized continuous distribution, and thus to make it independent of the mode of subdivision adopted. It is certainly possible, as the Italian school has shown, ${ }^{8)}$ to introduce a "cell" subdivision of the Hilbert space of state vectors and to arrive at certain quantal generalizations of the ergodic and mixing properties of classical theory, but both the enunciation of these results and the algorism leading to them - so long as one insists on mathematical rigour - are very cumbrous.

It must be observed, however, that the use of a coarse-grained cell subdivision is a consequence of the cyclic character of the time-evolution of the closed, finite systems dealt with in ergodic theory: in the classical case, this cyclic character is expressed by Poincarés theorem; in the quantal case, the discreteness of the energy spectrum leads to an almost periodic time dependence of the density operator. As a result, the idealized definitions of macroscopic quantities can only use averages taken over an infinite time, and it is then the object of the theory to express these as statistical averages, necessarily coarse-grained in view of their physical meaning. The timeevolution of infinite systems, on the other hand, is, as we have pointed out in subsection 2.2 , radically different: the classical Poincare cycle becomes of infinite duration, and the quantal energy spectrum, being continuous, allows of no almost-periodicity in time; but the correlations may lead to the occurrence of states idealized, as is usual in the theory of aperiodic processes, by (non-normalizable) state vectors with amplitudes decaying or building-up exponentially in time. This makes it possible, as we have seen, to study directly such one-sided effects of the correlations over long, but finite time intervals: the asymptotic form the density operator takes after a time of macroscopic order of magnitude can then be immediately interpreted as representing the conditions of macroscopic observation, without any need for the explicit consideration of coarse-graining. In this kinetic approach, the part of coarse-graining is played by the projection into the asymptotic subspace of our Hilbert superspace; besides its simplicity, this operation has the advantage of clearly exhibiting the fact that the macroscopic mode of description is uniquely fixed by the dynamics of the system.

### 3.3. Main features of the macroscopic aspect of the kinetic theory

The form given to the kinetic theory in section 2 has several noteworthy features. The most prominent is doubtless the clear-cut separation it effects, through the projection just mentioned, between the level of macroscopic
observation, contained in the asymptotic subspace $\tilde{I}$, and the fluctuating atomic behaviour of the system, which is fully accounted for by the density operator $\varrho(t)$ describing the dynamical behaviour in the total superspace. If the system is initially in a pure state, its density operator at any time can be factorized as a dyadic product of state vectors: in the asymptotic subspace $\tilde{\Pi}$, however, no such factorization is possible, no analogue to a state vector can be defined. Indeed, the function of the projector $\tilde{\Pi}$ is to sort out the part of the density operator that subsists after time intervals long enough to "wipe out" all initial phase relations between state vectors responsible for the fluctuations at the atomic level. In the asymptotic subspace, therefore, no "interference" of probability amplitudes occurs, but the asymptotic density operator $\tilde{\varrho}(t)$ embodies the description of any correlation effect observable at the macroscopic level.

Indeed, the formalism is not restricted to the study of the approach to thermodynamic equilibrium, but is applicable as well to systems presenting kinematic properties of macroscopic order of magnitude. It is important for the completeness of the theory that it should contain a formal criterium allowing us to recognize the type of asymptotic behaviour we may expect for a given system. This criterium is supplied by the condition of dissipativity, which gives a simple characterization of the class of systems exhibiting an irreversible approach to equilibrium. It is important to note that the dissipativity condition is amenable to explicit evaluation at least in simple cases, such as the Friedrichs model, and relates the dissipative character of the system directly to the structure of its energy spectrum.

For dissipative systems, a particularly clear picture is obtained of the origin of the irreversibility observed in their macroscopic behaviour. The projector $\tilde{\Pi}$, effecting the subdivision of the superspace into the subspaces which are the respective seats of the macroscopic and atomic evolution of the system, is invariant for time-reversal: this subdivision applies indeed to all systems, whether or not they are dissipative. The time evolution operator $\tilde{\Sigma}(t)$ in the asymptotic subspace is also time-reversal invariant; its form (48), if we use the spectral decomposition $\int \lambda \mathrm{d} P(\lambda)$ of the superoperator $L$, just amounts to a Fourier integral representation $\int \exp (-i \lambda t) d P(\lambda) \tilde{\Pi}$ of the timeevolution. The expressions (41) for $\tilde{\Sigma}(t)$ illustrate more explicitly how the asymptotic time-evolution starting from any given initial state proceeds by sequences of processes of "creation" and "destruction" of correlations between the elements of the system. The time direction in which one considers these processes is fixed by the choice of the conditions under which
we want to observe the behaviour of the system: on the information supplied by observation at a single instant, we normally base expectation of future behaviour; but the symmetry in time of the two equivalent forms (41) of $\tilde{\Sigma}(t)$ shows what retrodiction we can also make, on the basis of the same information, about the evolution of the system, on the macroscopic timescale, most likely to have led to its observed state: the sequences of creations and destructions of correlations appear inverted when, so to speak, we look back in time, and for dissipative systems we arrive at the well-known situation discussed by Ehrenfest in connexion with the $H$-theorem.*)

The collision superoperator $\Psi_{\mathscr{L}}(+0)$ does not only govern the condition of dissipativity; it also clarifies, as we have seen, the role of the dynamical invariants. In particular, it allows us, by eq. (62), to characterize the regular invariants (which, at least in typical cases, coincide with the controllable ones). This solves one of the main riddles of the kinetic theory: it was indeed never clear why the "collision operators" occurring in the usual formulations of the theory, such as the Boltzmann operator, were only in simple relation with the controllable invariants, independently of the possible existence of other invariants. At the same time, we see how decisive in this respect is the distinction between regular and singular invariants, - a distinction which can only be made for infinite systems.

Finally, it must be stressed that the macroscopic description we arrive at by projection into the $\tilde{\Pi}$ subspace is not the "classical" one: it still contains Planck's constant wherever quantal effects occur on a macroscopic scale, as in the spectral distribution of electromagnetic radiation in thermal equilibrium, or in superconductivity and superfluidity. The laws of classical physics only appear as a limiting case of this macroscopic description in which all quantal effects are neglected, i.e. formally where $\hbar$ is treated as infinitesimal.

Nevertheless, it would be a serious logical error to imagine that the procedure we have been following - starting from the quantal description of the system, obtaining by the projection $\tilde{\Pi}$ its macroscopic description, and letting in the latter $\hbar$ tend to zero - would be a deduction of classical physics

[^25]from quantum mechanics. For we must not forget that the quantal description from which we start has to be made in terms of the very concepts of classical physics. All we have done, therefore, is to prove the logical consistency of the rules by which a connexion is established between the mathematical formalism and the classical description, upon which our account of macroscopic observation must ultimately rest. Obviously, there can be no question of any formal axiomatization of such a scheme: it must be based upon some set of classical concepts (e.g. space-time localization and mo-mentum-energy) which remain unanalysed and are treated as "primitive". These concepts (and these only) must be explained by processes of measurement, i.e. prescribed manipulations of specially designed apparatus, entirely describable in classical terms. Typically quantal concepts, on the other hand, like Planck's constant or the electron spin, cannot be related directly to such purely classical measuring apparatus, - but the occurrence of quantal phenomena at the macroscopic level allows us to establish indirect connexions, involving more than one classical measurement, between quantal parameters and classical quantities, and thereby to determine with arbitrary accuracy the numerical values of the quantal parameters.*)
*) Thus, Millikan's determination of Planck's constant from the study of the ejection of electrons from metallic surfaces by light of various frequencies involves essentially two measurements: that of the light frequency and that of the corresponding kinetic energy of the ejected electrons.

## 4. Observation of individual atomic processes

### 4.1. The consistency problem of quantum mechanics

Quantum mechanics presents essentially two epistemological problems. The one, just recalled, concerns the consistency of the rules of interpretation by which the formalism is brought into relation with macroscopic observation, the other the relations of complementarity between different conditions of observation. There is nothing to add to Bohr's analysis of these relations, and we shall therefore confine ourselves to a comment, from the point of view developed in this paper, of the consistency problem. Briefly restated, this problem arises from the fact that the basic concepts used in the formulation of the laws governing individual atomic processes necessarily belong to the classical modes of description of direct macroscopic observation, which it is the aim of atomic theory to relate to the very laws of atomic behaviour. This means, as mentioned above, that these basic concepts must be regarded, from a strictly logical point of view, as "primitive". However, there is nothing to prevent us from describing on the atomic scale the process of measurement by which a value of the physical quantity denoted by any of these concepts is ascribed to an atomic system, as a dynamical process involving interactions between the atomic system observed and all the atomic constituents of the measuring apparatus, and obeying the laws of quantum mechanics. Such an analysis will only lead to the same conclusion as that resulting from the direct application of the rules of interpretation of the formalism if these rules are consistent. A test of this consistency is especially desirable with respect to the rule usually designated as the "reduction" of the wave function representing the initial state of the observed atomic system, i.e. its replacement after the measurement by another wave function expressing the information obtained by this observation. Although such a rule is obviously consonant with the statistical form of causality inherent in quantum mechanics, its relation with the dynamical process of measurement can only be
elucidated by a careful consideration of the specific function of the measuring apparatus and its implications for the course of the measuring process.

The decisive step was made by N. Boнr, ${ }^{1)}$ who pointed out that any measurement is essentially the codified registration of some characteristic signal arising from the interaction between the observed atomic system and a suitable recording device of macroscopic dimensions. Indeed, he emphasized that the very definition of a phenomenon must contain a specification of the experimental conditions under which it is observed, including the apparatus recording some kind of permanent mark allowing us to identify the process observed. Until the process has not been terminated by the registration of its permanent record, we have no basis for the use of the classical concepts corresponding to such record, and accordingly no possibility of giving any well-defined account of the process. In other words, it is precisely the recording by the apparatus which establishes the necessary link between the behaviour of an atomic system and its description in terms of concepts referring to our possibilities of observing it. Now, it is clear that the formation of a permanent mark on a recording device is an irreversible macroscopic process, retaining no other trace of the original state of the atomic system than the specific feature corresponding to the construction of the apparatus; this information modifies the conditions of observation upon which statistical predictions about the behaviour of the atomic system must henceforth be based, and it is precisely this modification which is expressed in the formal language of the theory by the assignment to the atomic system, according to the rule of "reduction", of a new wave-function, appropriate to the new conditions of observation.

Once it is realized that the wave-function of the atomic system after the measurement is a component factor in an expression representing the asymptotic state of the whole system including the measuring apparatus, it can hardly be doubted that it will have the form prescribed by the reduction rule, since the latter precisely corresponds to this asymptotic situation. As already mentioned, we are only concerned with the consistency of the use of the small set of classical concepts we have called "primitive". In quantum mechanics, these are the complementary sets defining space-time localization and momentum-energy exchange; the completion of the above argument in this case only requires, as Boнr showed, the consideration of simple dispositions of fixed or moving diaphragms. It is sufficient to discuss these, as he did, by the methods of classical optics, since the latter use an idealized representation of diaphragms which directly accounts for the irreversible modification of a wave pattern arising from its interaction with such material
bodies.*) In this connexion, it must be remembered that, although the apparatus fixing the conditions of observation, like any other macroscopic bodies, may in principle be described as large quantal systems, they must be kept outside such a description in order to fulfil their special function (otherwise, they would become themselves objects of observation); it is for this deeplying reason that their intervention is represented in the formalism of quantum mechanics by parameters denoting "external" forces and prescriptions for the selection of appropriate solutions of the fundamental equations among them the reduction rule. Disregard of this circumstance is the most frequent source of misunderstanding concerning the foundations of quantum mechanics.

The general theory of large quantal systems obviously offers another possibility of dealing with the consistency problem: one has only to apply this theory to the system formed by the atomic system under observation and the measuring apparatus described as a large assembly of atoms. This was done by the Italian physicists ${ }^{4)}$ on the basis of the form of quantal ergodic theory they had previously developed: ${ }^{8)}{ }^{* *)}$ their result is, of course, in full harmony with Bohr's argument. ${ }^{5}$ ) The kinetic approach outlined in the preceding sections allows us to discuss the issue in a more direct and simpler manner and to throw further light on the role of the measuring process in the epistemological analysis of physical theory.

### 4.2. Discussion of the measuring process

In order to analyse the course of a measuring process, we may use the schematization discussed in detail in ref. ${ }^{5}$. The main point is to arrive at a sufficiently simple and general formulation of the restrictions that have to be imposed upon the structure and dynamical behaviour of a macroscopic body in order that it may fulfil its function of measuring a specific property of a given atomic system. Its mode of interaction with the atomic system must be such as to bring it into a state observable at the macroscopic level and uniquely related (at least approximately) to the specific atomic state of interest. Without loss of generality, we avoid unessential complications by assuming

[^26]that the interaction between the atomic system and the measuring apparatus only lasts for a time short enough to allow us to disregard any dynamical change of the atomic system as a result of this interaction. The apparatus, on the other hand, reaches, at the termination of the interaction, a dynamical state which must be such as to fix the ultimate outcome of the measurement. For from the moment the interaction ceases, the two parts of the total system evolve independently, and we expect the apparatus to settle down, at the macroscopic level of observation, into a situation providing a "permanent" record*) of its specific interaction with the atomic system. This requirement imposes essential restrictions upon the constitution of the measuring apparatus and upon the interactions of its constituent elements with the atomic system under investigation. If the aim of the measurement is to ascertain whether the atomic system is in an eigenstate $\left|\varphi_{s}\right\rangle$ of the operator representing some physical quantity attached to the system, there must exist a complete orthogonal basis $|s m\rangle$ of dynamical states of the measuring apparatus such that (i) only a definite set $\{|s m\rangle\}$ of such states (denoted by a common index $s$ ) interacts with the atomic system when the latter is in a definite state $\left|\varphi_{s}\right\rangle$; (ii) the correlations between any two states $|s m\rangle,\left|s^{\prime} m^{\prime}\right\rangle$ are much weaker when they belong to different such sets $\left(s \neq s^{\prime}\right)$ than when they belong to the same set $\left(s=s^{\prime}\right.$ ). (As an example, we may think of the formation of a particle "track", in a bubble chamber or a photographic emulsion.**)

In order to show how these conditions ensure the desired functioning of the measuring device, let us examine the asymptotic time-evolution of its density supervector in its own superspace. We define the subspace $P_{o}$ by the projector

$$
P_{o}=\sum_{s} P_{o}^{(s)}, \quad P_{o}^{(s)}=\sum_{m} P_{s m} \times P_{s m},
$$

and, accordingly, the correlation subspace by the projector

$$
P_{c}=\sum_{s s^{\prime}} P_{c}^{\left(s s^{\prime}\right)}, \quad P_{c}^{\left(s s^{\prime}\right)}=\sum_{m m^{\prime}}^{\prime} P_{s m} \times P_{s^{\prime} m^{\prime}}
$$

the summation $\sum^{\prime}$ extending over all values of $m$ and $m^{\prime}$ if $s \neq s^{\prime}$ and all different values of $m$ and $m^{\prime}$ if $s=s^{\prime}$. The superoperator $\Psi(t)$ given by eq. (21) and the asymptotic superoperators $\theta, \eta$ derived from it by eqs. (20)
*) By "permanent" we do not imply that the state in question is one of actual thermodynamic equilibrium, but only that it lasts long enough for macroscopic observation.
**) The interaction of a particle with the medium gives rise at a certain point (corresponding to a state $\left|\varphi_{S}\right\rangle$ in which the particle has a definite "position") to a local fluctuation (represented by the set $\{|s m\rangle\rangle$ ) around which a bubble or a spot develops (leading to the asymptotic density $\tilde{\varrho}_{s}(\mathrm{M})(t)$ defined on p .37$)$. The condition (ii) expresses the requirement that the successive bubbles or spots formed by the passage of the particle through the medium be sufficiently distinct from each other for a recording of the corresponding positions of the particle.
will essentially effect transitions from any subspace $P_{o}^{(s)}$ to the same subspace: for other transitions, on account of the condition (ii) above, will be much less probable. Moreover, if we consider the mutually orthogonal subspaces defined by the projectors $P\left(s s^{\prime}\right)=P_{o}^{(s)} \delta_{s s^{\prime}}+P_{c}^{\left(s s^{\prime}\right)}$, the leading terms of the superoperators of destruction and creation of correlations will be those linking any subspace $P^{(s s)}$ with itself (i.e. the subspace $P_{o}{ }^{(s)}$ with the correlation subspace $P_{c}^{(s s)}$ ); next in importance will be the links between subspaces $P^{\left(s s^{\prime}\right)}$ and $P^{\left(s s^{\prime \prime}\right)}$ for values of $s^{\prime}$ and $s^{\prime \prime}$ in a small interval around $s$. Therefore, if we start from any initial density supervector $\varrho^{(M)}$ of the measuring apparatus, and only retain the leading terms, the asymptotic time-evolution of its projection $P^{\left(s s^{\prime}\right)} \varrho^{(\mathrm{M})}$ will take the form

$$
\begin{equation*}
\tilde{\Sigma}(t) P^{\left(s s^{\prime}\right)} \varrho^{(\mathrm{M})}=\delta_{s s^{\prime}} P^{(s s)} \tilde{\varrho}^{(\mathrm{M})}(t) \equiv \delta_{s s^{\prime}} \tilde{\varrho}_{s}^{(\mathrm{M})}(t): \tag{66}
\end{equation*}
$$

this formula expresses a clear-cut asymptotic trend of the measuring system towards definite states $\tilde{\varrho}_{s}{ }^{(\mathrm{M})}(t)$ uniquely associated with the eigenstates $\left|\varphi_{s}\right\rangle$ which are the objects of the measurement.*)

After this preparation, the discussion of the measuring process is readily performed. Let the initial state of the atomic system be represented by a superposition $\sum_{s} c_{s}\left|\varphi_{s}\right\rangle$ of the eigenstates $\left|\varphi_{s}\right\rangle$; the resulting density supervector

$$
\varrho^{(\mathrm{S})}=\sum_{s s^{\prime}} \varrho_{s s^{\prime}}^{(\mathrm{S})}, \quad \varrho_{s s^{\prime}}^{(\mathrm{S})}=c_{s} c_{s^{\prime}}^{*}\left|\varphi_{s}\right\rangle\left\langle\varphi_{s^{\prime}}\right|
$$

exhibits the correlation between the states $\left|\varphi_{s}\right\rangle$ arising from definite phase relations between the coefficients $c_{s}, c_{s^{\prime}}^{*}$. The initial form of the density supervector of the total system formed by the atomic system and the apparatus (i.e., let us recall it, the form this supervector takes immediately after the two constituents of the total system have interacted) is easily set up in conformity with our condition (i): to each component $\varrho_{s s^{\prime}}^{(S)}$ there corresponds a component $P^{\left(s s^{\prime}\right)} \varrho^{(\mathrm{M})}$ of the apparatus density supervector. The total density supervector is thus initially

[^27]$$
\sum_{s s^{\prime}} \varrho_{s s^{\prime}}^{(\mathrm{S})} \cdot P^{\left(s s^{\prime}\right)} \varrho^{(\mathrm{M})}
$$
and each factor evolves independently in its own superspace: the timeevolution of the atomic system is governed by its Liouville superoperator $T^{(\mathrm{S})}(t)=\exp \left\{-i L^{(\mathrm{S})} t\right\}$; as to the apparatus, we are interested in its evolution at the macroscopic level, described in its asymptotic subspace by the superoperator $\tilde{\Sigma}(t)$. Adopting the idealized situation expressed by eq. (66), we therefore obtain at time $t$ the total density supervector
$$
\sum_{s} T^{(\mathrm{S})}(t) \varrho_{s s}^{(\mathrm{S})} \cdot \tilde{\varrho}_{s}{ }^{(\mathrm{M})}(t)
$$

From this expression a density supervector making explicit reference only to the atomic system may be derived by averaging it over the apparatus superspace, i.e. by taking its trace with respect to the apparatus basis; we may simply ascribe the same limiting value to all the $\operatorname{tr} \tilde{\varrho}_{s}{ }^{(\mathrm{M})}(t)$ and normalize it to unity:

$$
\lim _{t \rightarrow \infty} \operatorname{tr} \tilde{\varrho}_{s}{ }^{(\mathrm{M})}(t)=1
$$

This gives us for the density supervector of the atomic system, after a time sufficient for the recording of a permanent mark on the apparatus, the expression

$$
\begin{equation*}
\sum_{s}\left|c_{s}(t)\right|^{2}\left|\varphi_{s}\right\rangle\left\langle\varphi_{s}\right|, \tag{67}
\end{equation*}
$$

from which every explicit reference to the apparatus has disappeared, and whose form agrees with the prescription of the reduction rule.

The way in which this result has been derived makes its meaning quite clear. In the first place, it is essentially an asymptotic result, and there is no question of its contradicting any consequence of the time-dependent Schrödinger equation. Secondly, the only interactions involved in the whole process are the specific interaction of short duration between the atomic system and the apparatus and the long sequence of interactions it triggers off between the constituent atoms of the apparatus; there is no question whatsoever of any non-physical intervention of any kind upon the atomic system : the whole measuring process is a purely automatic registering operation, obeying only the laws of quantum mechanics, and its outcome is accordingly in full harmony with these laws. Let us here emphasize again that the treatment of the measuring apparatus as a quantal system we have performed has no other purpose than exhibiting the consistency of the conceptual framework of quantum mechanics, in which formalism and rules of interpretation in terms of classical concepts form an inseparable whole. Thirdly, the difference between the "reduced" density (67) and that of the system before the
measurement simply reflects the change in our information about the system brought about by this measurement; the occurrence of such a difference is no peculiarity of quantum mechanics (though the particular form it takes is of course a specifically quantal one) - it is common to all statistical situations and in fact an essential component of the concept of probability.

### 4.3. The role of the observer

Statistical causality has often been misrepresented as implying the intrusion of a "subjective" element into the description of the phenomena; this epistemological error (which was not made by the founders of the theory of probabilities) arises from an insufficient analysis of the conditions under which knowledge of the phenomena is obtained. The inclusion of a specification of the conditions of observation into the account of the phenomena is no arbitrary decision, but, as we have insistently stressed, a necessity imposed by the very laws governing the course of these phenomena and the mechanism of their observation, and thereby an indispensable part of their objective description, since it ensures that such a description will be common to all observers placed in the specified conditions. It is in order to make this objectivity quite apparent that we have analysed, in the preceding subsection, the observation process as a purely physical one, limited to the automatic registration of a record, which need not even be read.

Obviously, such an analysis touches only one side of the process of acquisition of objective knowledge. This process is not complete until a reading of the record has actually occurred, i.e. until the information it contains has been stocked into the brain of some observer. This "psychological" side of the cognitive process is obviously just as objective as the other, since it is the same for any conceivable observer, but the question arises whether it can legitimately be separated as sharply as we have done from the purely physical registration process. It would seem that our understanding of the fundamental biological processes has now reached a stage allowing us to give a definite answer to this question.

We must above all realize that there is a large class of physical and chemical dissipative processes, occurring far from the thermodynamic equilibrium conditions, which present structural inhomogeneities quite foreign to the familiar physical phenomena observed at or near equilibrium, but analogous to typical features of biological systems. ${ }^{28,29)}$ It has been shown, for example, that chemical reactions essential for the metabolism of living systems, as well as for the regulation of genetic and evolutionary processes, can be treated in detail in terms of usual chemical kinetics, and involve branches of the solution of the non-linear kinetic equations which do not
belong to the classical thermodynamic description of near-equilibrium situations, but only appear under conditions far from equilibrium. ${ }^{30,}{ }^{31}$ ) Now, thermodynamics, both in its classical and its more general form just mentioned, is a mode of description adapted to the behaviour of macroscopic systems in the asymptotic $\tilde{\Pi}$ subspace; indeed, it has been explicitly established ${ }^{32)}$ that the thermodynamic description can be derived from the kinetic equation associated with the time-evolution operator $\Sigma(t)$. It is natural to conclude from these considerations that the distinction between "living" and "non-living'" systems appears to be part of their description in $\tilde{\Pi}$-space, and accordingly cannot be based on any quantal description on the atomic scale. An analogy which may perhaps clarify the significance of this remark is the distinction between laminar and turbulent motion, which correspond to two types of solution of the Navier-Stokes equation: as this equation belongs to the macroscopic level - it is a consequence of the kinetic equation - we cannot characterize the difference between these two types of flow by means of the formalism of quantum mechanics. Likewise, it would seem that the characteristics of "life" cannot be formulated at the atomic level but are essentially macroscopic. Incidentally, this circumstance is sufficient to dismiss all "paradoxical" situations (such as the famous example ascribed to Schrödinger) which one would allegedly encounter when attempting to treat living systems by the methods of quantum mechanics. In such cases, just as in the general problem of observation, a correct epistemological analysis can only be developed at the macroscopic level of description.

If we accept this general inference from our present knowledge of biology, we do not see any special role to be attributed to a "living" observer in the discussion of the consistency problem of quantum mechanics: the only condition the intervention of such an observer has to fulfil is to be amenable to physical description at the macroscopic level. Now, we may confidently assume that the sense organs of an animal register signals from the physical environment in essentially the same way as material apparatus, and that the storage of these signals and their incorporation into sensory-motor schemes is also the result of physical and chemical processes of the type commonly observed in biology. *) Since all the organs involved are of macroscopic order of magnitude, their activity can in principle be entirely described in the asymptotic subspace $\Pi$ of the appropriate superspace, like the functioning of any physical measuring apparatus.

[^28]
## 5. General conclusion

Perhaps the most significant general result of our approach is the introduction of generalized projection superoperators, made possible through the consideration of superspace. This generalization involves the concept of timereversal invariance which replaces the usual one of self-adjointness, to which it reduces in the absence of dissipation. These new projectors allow us to give a precise characterization of the macroscopic level of description of general quantal systems, and to formulate quantitatively the conditions under which a given system will exhibit the properties belonging to this level: a formulation obviously susceptible to experimental test (for example, we may verify whether a system is in thermodynamical equilibrium). These questions actually amount to an extension of the scope of quantum mechanics, which has only been outlined in this paper and deserves a more detailed treatment. In a sense, the question of the definition of a macroscopic level of quantum mechanics may be considered as a simple illustration of this general method, which applies as well to a large class of other problems.

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## Appendix

## Matrix representation in superspace

Although we have not made use in the text of any explicit matrix representation of supervectors and superoperators, such a representation might be helpful in concrete applications. We therefore collect in this appendix simple practical rules for writing down such matrix components.

A supervector $A$ is represented by its matrix elements in the form

$$
A=\sum_{m m^{\prime}} P_{m} A P_{m^{\prime}}=\sum_{m m^{\prime}}\langle m| A\left|m^{\prime}\right\rangle P_{m m^{\prime}}
$$

where

$$
P_{m m^{\prime}}=|m\rangle\left\langle m^{\prime}\right|, \quad P_{m m^{\prime}}^{+}=P_{m^{\prime} m} .
$$

In this notation, any superoperator $O$ is a sum of factorizable superoperators:

$$
O=\sum_{\substack{m m^{\prime} \\ n n^{\prime}}} O_{m m^{\prime}, n n^{\prime}} P_{m n} \times P_{n^{\prime} m^{\prime}},
$$

and with the adopted order of the indices one has

$$
\begin{aligned}
& \langle m| O A\left|m^{\prime}\right\rangle=\sum_{n n^{\prime}} O_{m m^{\prime}, n n^{\prime}}\langle n| A\left|n^{\prime}\right\rangle, \\
& (O Q)_{m m^{\prime}, n n^{\prime}}=\sum_{p p^{\prime}} O_{m m^{\prime}, p p^{\prime}} Q_{p p^{\prime}, n n^{\prime}} .
\end{aligned}
$$

The components of the adjoint superoperator are

$$
O_{m m^{\prime}, n n^{\prime}}^{\dagger}=O_{n n^{\prime}, m m^{\prime}}^{*}
$$

and the transposition gives

$$
\langle m| A O\left|m^{\prime}\right\rangle=\sum_{n n^{\prime}}\langle n| A\left|n^{\prime}\right\rangle O_{n^{\prime} n, m^{\prime} m}
$$

The adjoint symmetry of the superoperator $O$ implies the relations

$$
O_{m m^{\prime}, n n^{\prime}}=O_{m^{\prime} m, n^{\prime} n}^{*}
$$

between its components.

# A STUDY OF ENERGY LEVELS <br> and Coriolis coupling in odd-mass WOLFRAM NUCLEI BY MEANS OF ( $d, p$ ) AND ( $d, t$ ) REACTIONS 

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## Synopsis

The energy levels of ${ }^{179} \mathrm{~W},{ }^{181} \mathrm{~W},{ }^{183} \mathrm{~W},{ }^{185} \mathrm{~W}$ and ${ }^{187} \mathrm{~W}$ have been investigated by means of ( $d, p$ ) and ( $d, t$ ) reactions. The deuteron energy was 12.1 MeV and the charged reaction products were analyzed in a magnetic spectrograph at $60^{\circ}, 90^{\circ}$ and $125^{\circ}$. The results established detailed level schemes and greatly improved the understanding of the level structure in these nuclei. All the $N=5$ Nilsson orbitals in an energy range of about 4 MeV have been identified. In addition, several $N=6\left(i_{13 / 2}\right)$ Nilsson states have been located by combining the present results with those of a concurrent $\left({ }^{3} \mathrm{He}, \alpha\right)$ reaction study. A quantitative analysis of the Coriolis coupling of the $N=5$ orbitals was performed. It was found that many gross discrepancies between the experimental cross sections and those calculated using the Nilsson model and the distorted-wave Born approximation could be eliminated or reduced by inclusion in the cross section calculations of the Coriolis interaction with reduced coupling matrix elements. In particular, the highly distinctive systematics of the cross sections in different isotopes could be reproduced. An energy-dependent systematic reduction of the matrix elements which satisfactorily accounts for most of the experimental observations is suggested.

## 1. Introduction

TThis investigation continues a series ${ }^{1-4)}$ performed in this laboratory in the past few years. The previous work has investigated several deformed rare earth nuclei by means of the $(d, p)$ and ( $d, t$ ) reactions. The location and properties of single particle neutron states and the rotational bands built on them have been studied in a systematic manner. The results have demonstrated that the simple Nilsson model, with pairing, coupled to a standard set of DWBA calculations is quite successful as a tool for the interpretation of low-lying levels in deformed nuclei. Certain deviations from this simple scheme, such as the mixing of single-particle states or the coupling to collective excitations, were also qualitatively considered.

The present investigation continues this program with a study of the odd wolfram nuclei. In addition, a quantitative analysis is presented here of the Coriolis mixing ${ }^{5)}$ among the Nilsson orbitals and its effects on energies and cross sections. This mixing sometimes alters energies by as much as a few hundred keV and cross sections by orders of magnitude. The presence of Coriolis mixing is frequently manifested by the occurrence of widely varying inertial parameters of the different rotational bands. Accordingly, one test of the adequacy of a mixing analysis is that inertial parameters for the unperturbed bands should approach both each other and the neighbouring even-even nucleus value. Coriolis coupling often can significantly alter the expected relative population cross sections for the successive levels of a rotational band. In such cases, this so-called finger-print pattern becomes unrecognizable and hence the direct orbital identification difficult. In the present investigation a large number of such deviations from the simple Nilsson scheme could be accounted for with the inclusion of the Coriolis interaction. It has been frequently found ${ }^{5-10)}$ that the Coriolis matrix elements predicted from the Nisson model are inadequate and need to be adjusted empirically in order to fit the experimental results. The present data also require such adjustments, and an investigation has been made of the properties of the basic strength of the Coriolis interaction.

The data obtained by the ( $d, t$ ) reaction have been supplemented by a study of the $\left({ }^{3} \mathrm{He}, \alpha\right)$ reaction which, at an angle of $60^{\circ}$, preferentially populates hole states requiring high orbital angular momentum transfer. This is the case for the $N=6$ states originating from the $i_{13} / 2$ spherical shell model state. Their associated rotational bands have nearly all their strength in the $I=13 / 2+$ members. Despite having, therefore, no easily recognizable fingerprint pattern, their identification is rendered much easier with the combination of the $\left({ }^{3} \mathrm{He}, \alpha\right)$ and $(d, t)$ reactions. The analysis of the $\left({ }^{3} \mathrm{He}, \alpha\right)$ studies is being published separately ${ }^{11)}$ although the main results will be cited here for completeness.

Previous studies by Erskine and Siemsen ${ }^{12-14)}$ of ${ }^{183} \mathrm{~W},{ }^{185} \mathrm{~W}$ and ${ }^{187} \mathrm{~W}$ using the ( $d, p$ ) reaction alone located several low-lying Nilsson orbitals in these nuclei and showed that the observed transfer cross sections could be satisfactorily explained by including the Coriolis interaction in the theoretical cross section calculations. Our results are in general agreement with these earlier findings.

## 2. Theoretical considerations

The simple equations describing the transfer reactions studied here as well as those concerning the Coriolis interaction have been given elsewhere ${ }^{15)}$. We shall partly repeat them to establish a notation and terminology for the discussion to follow.

In the special case of a single-neutron stripping or pickup reaction on an even-even spin-zero target proceeding by a single step process to a state of $\operatorname{spin} I=j$ of a rotational band built on a given Nilsson orbital, the differential cross section may be written as the product of the intrinsic cross section for the neutron transfer with orbital angular momentum $l$, the $C_{j l}^{2}$ coefficient characterizing the Nilsson orbital, and a pairing factor $P$ :

$$
\begin{equation*}
\frac{d \sigma}{d \Omega}(\theta)=2 \varphi_{l}(\theta) \cdot C_{j l}^{2} \cdot P^{2} \tag{1}
\end{equation*}
$$

where $j=l \pm \frac{1}{2}$. The intrinsic reaction cross section $\varphi_{l}(\theta)$ for the specified reaction is the normalized DWBA cross section

$$
\begin{equation*}
\varphi_{l}(\theta)=\mathrm{N}^{( \pm)} \cdot \sigma_{l}^{D W B A}(\theta) \tag{2}
\end{equation*}
$$

The $\sigma_{l}(\theta)$ are calculated once, for all $l$-values and for both the $(d, p)$ and ( $d, t$ ) reactions by a standard DWBA code. The normalization factors are taken as $N^{(+)}=1.5$ for the $(d, p)$ and $N^{(-)}=3.0$ for the $(d, t)$ reaction.

The $C_{j l}$ factors are the expansion coefficients of the Nilsson wave functions on a basis of spherical wave functions. Any pure Nilsson orbital is specified by a set of these coefficients from $C_{j=K, l}$ to $C_{j=N+\frac{1}{2}, l}, N$ here being the principal quantum number of the Nilsson orbital and $K$ the angular momentum projection on the nuclear symmetry axis; $l$ and $N$ are of equal parity. This sequence of coefficients gives, by eq. (1), the relative transfer cross sections into the successive members of a rotational band, called a "fingerprint pattern", which is used as a tool for identification of such orbitals.

The factor $P$ in eq. (1) is the occupation amplitude, $U$ or $V$, for a stripping or pickup reaction, respectively. It is assumed to be constant for the various rotational members of a band. According to the pairing theory, it may be calculated from the gap parameter $\Delta$ and the excitation energy $E$ of the band head $(I=K)$ by the relations

$$
\begin{equation*}
E=\sqrt{(\varepsilon-\lambda)^{2}+\Delta^{2}}-\sqrt{\left(\varepsilon_{0}-\lambda\right)^{2}+\Lambda^{2}} \tag{3}
\end{equation*}
$$

and

$$
P^{2}=\left\{\begin{array}{l}
U^{2}  \tag{4}\\
V^{2}
\end{array}\right\}=\frac{1}{2}\left(1 \pm \frac{\varepsilon-\lambda}{\sqrt{(\varepsilon-\lambda)^{2}+\Delta^{2}}}\right)
$$

Here, $\varepsilon$ is the single particle Nilsson energy, with $\varepsilon_{0}$ being that of the ground state, $\lambda$ is the energy of the Fermi surface, and $\Delta$ is half the energy gap and is taken to be 750 keV from the empirical even-odd mass differences in the wolfram nuclei. Wherever in the interpretation of the data in this work pairing effects are important, they have been calculated from eqs. (3) and (4).

With the inclusion of band mixing, the cross section to a given level is not specified solely by one $C_{j l}$ coefficient but by a set of products, $a_{i n} C_{j l}^{(i)}$, of the admixed amplitudes $a_{i n}$ of the level $i$ into the level $n$ times the $C_{j l}$ coefficient for the $i^{\text {th }}$ orbital. In this case, the cross section becomes

$$
\begin{equation*}
\frac{d \sigma_{n}(\theta)}{d \Omega}=2 \varphi_{l}(\theta) \cdot\left(\sum_{i} a_{i n} C_{j l}^{(i)} P_{i}\right)^{2} \tag{5}
\end{equation*}
$$

Because of the coherent summation, relatively small admixtures can have drastic effects on the cross sections. In what follows we shall apply eq. (5) to the case of Coriolis mixing.

The collective Hamiltonian involves the Coriolis term which couples an odd particle to the rotational motion

$$
\begin{equation*}
V_{P R C}=-\frac{\hbar^{2}}{2 \mathfrak{J}}\left(J_{+} j_{-}+J_{-j+}\right) \tag{6}
\end{equation*}
$$

where $\mathcal{J}$ is the moment of inertia and $J_{ \pm}$and $j_{ \pm}$are standard angular momentum projection raising and lowering operators connecting states differing by one unit in the $K$ quantum number. In eq. (6), $\hbar^{2} / 2 \mathfrak{J}$ plays the role of a basic coupling constant determining the strength of the Coriolis mixing.

With the inclusion of pairing, the full Coriolis matrix element between two states of angular momentum $I$ belonging to bands with projection quantum numbers $K$ and $K+1$, takes the form

$$
\left.\begin{array}{l}
<I, K\left|V_{P R C}\right| I, K+1>= \\
-\frac{\hbar^{2}}{2 \mathfrak{J}} \eta_{K} \eta_{K+1}<K|j-| K+1>\sqrt{(I-K)(I+K+1)}\left(U_{K} U_{K+1}+V_{K} V_{K+1}\right) \tag{7}
\end{array}\right\}
$$

where

$$
\begin{equation*}
<K|j-| K+1>=\sum_{j} C_{j l}^{K} C_{j l}^{K+1} \sqrt{(j-K)(j+K+1)} . \tag{8}
\end{equation*}
$$

Expressions for mixing amplitudes and perturbed energies are given in e.g. ref. ${ }^{5)}$. The last factor in eq. (7), reflecting the effects of pairing, tends to diminish the interaction for states on opposite sides of the Fermi level. The two factors $\eta_{K}$ and $\eta_{K+1}$ are attenuation factors and are equal to unity in the Nilsson model but are included here to allow for any alteration of the matrix elements as may be empirically required. As mentioned above, previous investigations ${ }^{5-10)}$ of Coriolis coupling have indeed revealed the need for adjustments (generally reductions) in the matrix elements as calculated from the Nilsson model. The use of two attenuation factors in eq. (7) does not necessarily imply that we ascribe the reduction to the individual wave functions entering the matrix element, which in fact has been previously suggested ${ }^{16)}$. Alternatively, various authors have speculated that $\hbar^{2} / 2 \mathfrak{J}$ is not a constant but an off-diagonal operator ${ }^{6)}$ or that the pairing factor does not adequately reflect the effects of the pairing correlations ${ }^{10)}$. In any case, we have studied the amount of attenuation empirically required without investigating all its possible sources and systematics in detail.

It might be noted here finally that if the mixing amplitudes become large, it is rather meaningless to speak of a given state with quantum numbers $I K\left|N n_{z} \Lambda\right|$ having certain admixtures from other states. This, in fact, occurs among some $N=6$ orbitals and one cannot speak of a specific Nilsson orbital occurring at a certain energy, but only of the unperturbed posi-
tions of the various orbitals required to produce, after mixing, the final spectrum of thoroughly mixed states. In the $N=5$ shell, with which we shall be mainly concerned here, such strong mixing rarely occurs and the states are therefore labelled by the Nilsson quantum numbers corresponding to the largest amplitude in the wave function. The full specification for each state is given by the wave functions tabulated in the appendix.

## 3. Experimental Procedure and Results

### 3.1. Experimental Techniques

The experimental techniques resemble very much those of previous studies at this laboratory ${ }^{1-4}$. A 12.08 MeV deuteron beam of intensity from 0.3 to $1 \mu \mathrm{~A}$ was obtained from the Niels Bohr Institute's tandem accelerator. Targets of the four even wolfram isotopes ${ }^{180,182,184,186} \mathrm{~W}\left(\approx 50 \mu \mathrm{~g} / \mathrm{cm}^{2}\right)$ were prepared by direct deposition with an isotope separator on $\approx 50 \mu \mathrm{~g} / \mathrm{cm}^{2}$ carbon foil by means of a retardation technique ${ }^{17)}$. The charging material for the ion source was its own wolfram filament. The isotopic enrichment achieved was $\geq 95 \%$ except for the ${ }^{180} \mathrm{~W}$ target which was $65 \%$ enriched. The reaction products were analyzed in a broad range magnetic spectrograph. It was possible to record the $(d, p),(d, t)$ and $\left(d, d^{\prime}\right)$ reactions simultaneously in different regions on the photographic plates. Aluminium absorbers were applied for particle discrimination in regions where the different spectra overlapped. The energy resolution, at $\theta=125^{\circ}$, was 7 to 8 keV fwhm for the triton spectra, and 10 to 12 keV fwhm for the proton spectra which were recorded in a region of the focal plane where the dispersion is smaller. Measurements on all isotopes were made at $60^{\circ}, 90^{\circ}$ and $125^{\circ}$. The beam current was recorded in a Faraday cup 10 cm behind the target. The total charge per exposure was between 5000 and $60000 \mu \mathrm{C}$.

### 3.2. Spectra and Cross Section Tables

Typical spectra are shown in figs. 1 to 8 for both deuteron-induced reactions on each of the four targets studied. Quantum numbers are indicated for all peaks assigned. Contaminant peaks are labelled with the contaminating nuclide. The ( $\left.{ }^{3} \mathrm{He}, \alpha\right)$ spectra are shown in fig. 9 . They clearly demonstrate the selectivity of this reaction. The degree of confidence for each assignment is given in the level-diagram for each nucleus (figs. 10 to 14). Adopted level energies and cross sections as well as Nilsson assign-

Table 1. Levels populated in ${ }^{179} \mathrm{~W}$.

| $\begin{gathered} \text { Energy } \\ \text { keV } \end{gathered}$ | $\begin{aligned} & \text { Assignment } \\ & I K \pi\left[N n_{z} \Lambda\right] \end{aligned}$ | Experim. cross sect. $\begin{gathered} (d, t) \mu b / s r \\ 90^{\circ} \end{gathered}$ | $\begin{aligned} & Q \text {-red. cross sect. } \\ & \qquad \begin{array}{c} (d, t) \mu b / s r \\ 90^{\circ} \end{array} \end{aligned}$ |
| :---: | :---: | :---: | :---: |
| 0 | 7/2 7/2-[514] | $\sim 3$ | $\sim 3$ |
| 222* | $1 / 21 / 2-[521]$ | 183 | 218 |
| 305* | $3 / 21 / 2-[521]$ | 41 | 53 |
| 318* | $5 / 21 / 2-[521]$ | 44 | 58 |
| ~390 |  | $\sim 5$ | $\sim 6$ |
| 430* | 5/2 5/2-[512] | 9 | 14 |
| 468 | 13/2 9/2+[624] $\dagger$ | 28 | 44 |
| 508* | 7/2 1/2-[521] | 56 | 90 |
| 532* | 7/2 5/2-[512] | 115 |  |
| 533* | $9 / 21 / 2-[521]$ | 115 | 189 |
| ~ 560 |  | $\sim 4$ | $\sim 7$ |
| 689 | $3 / 21 / 2-[510]$ | 11 | 22 |
| 722 |  | 6 | 12 |
| 748 |  | 11 | 23 |
| 788 | $5 / 21 / 2-[510]$ | 13 | 27 |
| ~816 | $11 / 2 \quad 1 / 2-[521]$ | $\sim 4$ | $\sim 9$ |
| ~914 |  | $\sim 18$ | $\sim 40$ |
| 958 |  | 32 | 85 |
| 1031 |  | 7 | 22 |
| ~ 1073 |  | 28 | 86 |
| ~ 1295 |  | 8 | 34 |

* Energy from $\gamma$-ray measurements.
$\dagger 13 / 2+$ assignment suggested by ( $d, t$ ) cross section angular distribution.
ments are listed in tables 1 to 5 . In addition to the measured cross sections, the $Q$ reduced differential cross sections at $90^{\circ}$ are included in the same tables (see section 3.4).


### 3.3. Gross Section Normalization and Error Assignments

Normalization of exposures made on the same target was based on the integrated beam current and, independently, on measurements of elastically scattered deuterons using a monitor counter set at $90^{\circ}$ to the incident beam. The absolute cross sections, for each angle, were evaluated from comparison with the sum of elastic and inelastic deuteron cross sections at 12 MeV which were obtained from short exposures ( 5 to $300 \mu \mathrm{C}$ ) before and after each run. The deuteron cross sections were taken ${ }^{15)}$ to be 530 ,

Table 2. Levels populated in ${ }^{181} \mathrm{~W}$.

| Energy keV | $\begin{aligned} & \text { Assignment } \\ & I K^{\pi}\left[N n_{z} \Lambda\right] \end{aligned}$ | Experimental cross section |  |  |  | $Q$-reduced cross section |  | Inferred $l$-value |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $(d, p) \mu b / s r$ | $(d, t) \mu b / s r$ |  |  | $(d, p) \mu b / s r$ | (d,t) $\mu \mathrm{b} / \mathrm{sr}$ |  |
|  |  | $90^{\circ}$ | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $90^{\circ}$ | $90^{\circ}$ |  |
| 0 | 9/2 9/2 + [624] | 1.9 | 9 | 15 | 10 | 3 | 13 | 4 |
| 113* | 11/2 9/2+[624] |  | $\sim 1.6$ | $\sim 1.6$ | 2.2 |  | $\sim 1.5$ |  |
| 250* | 13/2 9/2 + [624] | 18 | 12 | 46 | 52 | 27 | 48 | $6 \dagger$ |
| 366* | $5 / 25 / 2-[512]$ | $<1$ | 9 | 10 | 10 | $<2$ | 11 | 3 |
| 385* | $1 / 21 / 2-[521]$ | 14 | 233 | 243 | 184 | 20 | 288 | 1 |
| 409* | $7 / 27 / 2-[514]$ | $<2$ | 11 | 19 | 21 | $<3$ | 23 | 3 |
| 450* | $3 / 21 / 2-[521]$ | 96 | 76 | obsc | 64 | 135 | ~ 95 | (1) |
| 476* | 7/2 5/2-[512] | 37 | 116 | 191 | 165 | 51 | 246 | 3 |
| 488* | $5 / 21 / 2-[521]$ | 8 | 49 | 82 | 51 | 11 | 107 | 3 |
| ~ 527 | $9 / 27 / 2-[514]$ |  | 9 | 24 | 34 |  | 33 | $h$ |
| 529* | $3 / 21 / 2-[510]$ | ~ 102 |  |  |  | $\sim 140$ |  |  |
| 560* | $5 / 21 / 2-[510]$ | 122 | 10 | 16 | 17 | 164 | 23 | 3 |
| $\sim 611$ | $9 / 25 / 2-[512]$ | <1 | <5 | 3 | 3 | <1 | 4 |  |
| 642 | $7 / 21 / 2-[521]$ | $\sim 38$ | 19 | 46 | 42 | $\sim 50$ | 70 | 3,h |
| 662* | $7 / 27 / 2-[503]$ | 226 | 14 | 29 | 21 | 296 | 45 | 3 |
| 715 |  | $<10$ | 7 | 20 | 17 | <14 | 33 | 3 |
| 726* | $3 / 23 / 2-[512]$ | 83 | 5 | 7 | $\sim 5$ | 107 | 11 | 1,3 |
| 777 | 11/2 5/2-[512] |  | $<1$ | 4 | 6 |  | 7 | $h$ |
| 807* | $5 / 23 / 2-[512]$ | 102 | 2.5 | 7 | 5 | 126 | 13 | 1,3 |
| 937 | 7/2 3/2-[512] | $\sim 56$ |  |  | $\sim 3$ | $\sim 67$ |  |  |
| 996 | $9 / 2+, N=6$ |  | 14 | $\sim 24$ | 26 |  | $\sim 56$ | 3 |
| ~ 1012 |  |  | $\sim 2$ | $<2$ | 5 |  | $<4$ |  |
| 1084 |  |  | <1 | 5 | 10 |  | 13 | $h$ |
| 1124 | $13 / 2+, N=6$ |  | 5 | 20 | 32 |  | 51 | $6 \dagger$ |
| 1191 |  | $<9$ | 21 | 43 | 32 | $<10$ | 125 | 3 |
| 1252 |  | 190 | 4 | 9 | 7 | 204 | 27 | (3) |
| ~ 1274 |  |  | 5 | 8 | 8 |  | 26 | 3 |
| 1318 |  |  | $<3$ | 7 | 8 |  | 22 | 3,h |
| 1354 |  |  | 11 | 26 | 24 |  | 92 | 3 |
| 1369 |  |  | 3 | 6 | 5 |  | $\sim 21$ | 3 |
| 1426 |  |  | 8 | 18 | 16 |  | 72 | 3 |
| 1502 |  |  |  | 5 | 4 |  | $<20$ |  |
| 1652 |  |  | $\sim 6$ | 16 | obsc |  | 88 |  |

*Energy from $\gamma$-ray measurements.
$\dagger l=6$ from $\left({ }^{3} \mathrm{He}, \alpha\right)$ data.

Table 3. Levels populated in ${ }^{183} \mathrm{~W}$.

| Energy keV | Assignment$I K^{\pi}\left[N n_{z} \Lambda\right]$ | Experimental cross section |  |  |  |  |  | Q-reduced cross section |  | $\begin{gathered} \text { In- } \\ \text { ferred } \\ l \text {-value } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $(d, p) \mu b / s r$ |  |  | (d,t) $\mu \mathrm{b} / \mathrm{sr}$ |  |  | $\begin{aligned} & (d, p) \\ & \mu b / s r \end{aligned}$ | $\begin{gathered} (d, t) \\ \mu b / s \Gamma \end{gathered}$ |  |
|  |  | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $90^{\circ}$ | $90^{\circ}$ |  |
| 0 | 1/2 1/2-[510] | 5 | 6 | 2.8 | 9 | 9 | 3 | 8 | 5 |  |
| 47* | $3 / 21 / 2-[510]$ | 280 | 195 | 86 | 304 | 266 | 104 | 264 | 150 | 1 |
| 99* | $5 / 21 / 2-[510]$ | 197 | 151 | 85 | 154 | 177 | 83 | 202 | 103 | 3 |
| 207* | $7 / 21 / 2-[510]$ | 214 | 111 | 65 | 112 | 116 | 51 | 142 | 72 | 1 |
| 209* | $3 / 2 \mathrm{3} / 2-[512]$ | 214 | 111 | 65 | 112 | 116 | 51 | 142 | 72 | 1 |
| $292 *$ | $5 / 23 / 2-[512]$ | 129 | 77 | 52 | 37 | 50 | 23 | 96 | 35 | 3 |
| 309* | $9 / 21 / 2-[510]$ | 13 | 8 | 15 | 3 | 10 | 9 | 11 | 7 | $h$ |
| 412* | $7 / 23 / 2-[512]$ | 92 | 72 | 50 | 40 | 62 | 36 | 87 | 44 | 3 |
| 453* | $7 / 27 / 2-[503]$ | 245 | 238 | 138 | 68 | 98 | 58 | 284 | 72 | 3 |
| 487 | 13/2 11/2+[615] | 17 | 30 | 34 | 9 | 35 | 33 | 35 | 26 | $6 \dagger$ |
| $\sim 553$ | $9 / 23 / 2-[512]$ | $<3$ | 4 | 4 | $<1$ | <1.3 | 1 | 4 | $<1$ |  |
| $\sim 596$ | $9 / 2 \quad 7 / 2-[503]$ | 2.9 | obsc | 2.6 |  |  | 1 | $\sim 3$ | $\sim 1$ |  |
| 623 | $9 / 29 / 2+[624]$ |  |  | 1.5 | 8 | 16 | 10 | $\sim 2$ | 13 | 4 |
| 742 | 11/2 3/2-[512] | $<5$ | 4 | 5 |  | 1.4 | 2.8 | 4 | 1.3 | $h$ |
| 906 | $5 / 25 / 2-[512]$ | 5 | 5 | 1.9 | 10 | 18 | 11 | 6 | 19 | 3,1 |
| 936 | $1 / 21 / 2-[521]$ | 38 | 15 | 11 | 285 | 342 | 158 | 15 | 364 | 1 |
| 960 | 13/2 9/2-[624] |  |  |  | 11 | 38 | 29 |  | 41 | $6 \dagger$ |
| 1002 | $7 / 25 / 2-[512]$ | 38 | 29 | 17 | 112 | 207 | 128 | 29 | 237 | 3 |
| 1029 | $3 / 21 / 2-[521]$ | 3 | 2.7 | 1.2 | 45 | 46 | 27 | 2.6 | 54 | 1 |
| 1056 | $5 / 21 / 2-[521]$ |  |  |  | 37 | 56 | 35 |  | 66 | 3 |
| 1072 | $7 / 2 \quad 7 / 2-[514]$ | 17 | 17 | 12 | 47 | 79 | 52 | 16 | 91 | 3 |
| 1128 | $9 / 25 / 2-[512]$ | 1 | 3 | 3 | 4 | 14 | 15 | 2.8 | 18 | $h$ |
| 1154 |  | 467 | 292 | 142 | 11 | 16 | 10 | 275 | 22 | 1 |
| 1219 | $9 / 2 \quad 7 / 2-[514]$ | 2 | 4 | 5 | 4 | 21 | 16 | 3 | 29 | $h$ |
| 1233 |  | 31 | 28 | 19 | 1.4 | 4 | 1.8 | 25 | 5 | 3 |
| 1265 | $7 / 2 \quad 1 / 2-[521]$ |  |  | 1.0 | $\sim 15$ | 47 | 31 |  | 69 | (3) |
| 1281 | 11/2 5/2-[512] |  |  |  | $\sim 3$ | $\sim 3$ | 4 |  | 4 |  |
| ~ 1314 | $9 / 21 / 2-[521]$ |  |  |  | $<2$ | 5 | 5 |  | 8 |  |
| 1339 |  |  |  |  | $\sim 3$ | 5 | $\sim 3$ |  | 7 |  |
| 1342 |  | 29 | 15 | 14 |  |  |  | 14 |  | (3) |
| ~1375 |  |  |  |  | 7 | 11 | 9 |  | 19 | 3 |
| 1376 |  | 11 | 6 | 4 |  |  |  | 5 |  |  |
| 1390 | $9 / 29 / 2-[505] ?$ | 28 | 28 | 23 |  |  |  | 25 |  | 3,h |
| 1397 | 11/2 7/2-[514] |  |  |  | $\sim 3$ | 9 | 7 |  | 15 | $h$ |
| 1441 |  |  |  |  |  | 2.7 | 2.2 |  | 5 |  |
| 1443 |  | 11 | 11 | 5 |  |  |  | 9 |  | (1) |
| 1468 |  |  |  |  | $\sim 5$ | $\sim 2$ | 1.2 |  | $\sim 3$ |  |
| 1476 |  | 268 | 263 | 126 | 7 | 13 | 6 | 232 | 24 | 1,3 |

Table 3 (continued).

\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow{3}{*}{Energy keV} \& \multirow{3}{*}{$$
\begin{aligned}
& \text { Assignment } \\
& I K^{\pi}\left[N n_{z} \Lambda\right]
\end{aligned}
$$} \& \multicolumn{6}{|c|}{Experimental cross section} \& \multicolumn{2}{|l|}{Q-reduced cross section} \& \multirow{3}{*}{$$
\begin{gathered}
\text { In- } \\
\text { ferred } \\
\text { l-value }
\end{gathered}
$$} <br>
\hline \& \& \multicolumn{3}{|c|}{$(d, p) \mu b / s r$} \& \multicolumn{3}{|c|}{(d,t) $\mu \mathrm{b} / \mathrm{sr}$} \& $$
\begin{aligned}
& (d, p) \\
& \mu b / s r
\end{aligned}
$$ \& $$
\begin{gathered}
(d, t) \\
\mu b / s r
\end{gathered}
$$ \& <br>
\hline \& \& $60^{\circ}$ \& $90^{\circ}$ \& $125^{\circ}$ \& $60^{\circ}$ \& $90^{\circ}$ \& $125^{\circ}$ \& $90^{\circ}$ \& $90^{\circ}$ \& <br>
\hline 1489 \& \multirow{37}{*}{$13 / 2+, N=6$
$9 / 2+, N=6$

$13 / 2+, N=6$} \& 37 \& 20 \& 21 \& 2.2 \& \& 2.3 \& 17 \& \& <br>
\hline 1514 \& \& $<2$ \& $<2$ \& $\sim 5$ \& \& \& \& $\sim 2$ \& \& <br>
\hline 1550 \& \& \& \& \& 7 \& 13 \& 13 \& \& 26 \& $6 \dagger$ <br>
\hline 1558 \& \& 190 \& 150 \& 67 \& \& \& \& 124 \& \& 1 <br>
\hline 1562 \& \& \& \& \& 11 \& 21 \& 23 \& \& 43 \& 3,h <br>
\hline 1583 \& \& 19 \& 25 \& 19 \& \& \& \& 21 \& \& 3,h <br>
\hline 1592 \& \& \& \& \& 19 \& 32 \& 21 \& \& 67 \& 3 <br>
\hline 1631 \& \& 131 \& 100 \& 50 \& \& \& \& 81 \& \& 1 <br>
\hline 1650 \& \& \& \& \& $<4$ \& 9 \& 7 \& \& 20 \& <br>
\hline ~ 1651 \& \& 25 \& 20 \& 10 \& \& \& \& 16 \& \& 1 <br>
\hline 1679 \& \& \& \& \& 4 \& 8 \& 7 \& \& 19 \& 3 <br>
\hline 1687 \& \& 73 \& 71 \& 43 \& \& \& \& 56 \& \& 3 <br>
\hline 1692 \& \& \& \& \& 4 \& 8 \& 3 \& \& 18 \& <br>
\hline 1711 \& \& \& \& \& 3 \& 7 \& 11 \& \& 17 \& $6 \dagger$ <br>
\hline 1723 \& \& 87 \& 107 \& 75 \& \& \& \& 83 \& \& 3 <br>
\hline 1737 \& \& \& \& \& 6 \& 7 \& 5 \& \& 17 \& 1 <br>
\hline 1740 \& \& 87 \& 62 \& 35 \& \& \& \& 48 \& \& 1 <br>
\hline 1763 \& \& \& \& \& 7 \& 12 \& 11 \& \& 30 \& 3 <br>
\hline 1790 \& \& 118 \& 67 \& 36 \& \& \& \& 52 \& \& 1 <br>
\hline 1792 \& \& \& \& \& $\sim 3$ \& 7 \& 5 \& \& 19 \& <br>
\hline 1816 \& \& 119 \& 138 \& 118 \& \& \& \& 104 \& \& 3,h <br>
\hline 1822 \& \& \& \& \& 7 \& 16 \& 8 \& \& 43 \& 3 <br>
\hline 1827 \& \& 260 \& 130 \& 77 \& \& \& \& 99 \& \& 1 <br>
\hline 1847 \& \& 328 \& 173 \& 115 \& \& \& \& 130 \& \& 1 <br>
\hline 1950 \& \& 129 \& 117 \& 93 \& \& \& \& 86 \& \& 3 <br>
\hline 1967 \& \& \& \& \& 1.9 \& 5 \& 5 \& \& 17 \& 3,h <br>
\hline 1969 \& \& 63 \& 52 \& $<48$ \& \& \& \& 38 \& \& 1 <br>
\hline 1989 \& \& 49 \& 37 \& $<37$ \& \& \& \& 27 \& \& 1 <br>
\hline 1989 \& \& \& \& \& 3 \& 7 \& 4 \& \& 24 \& <br>
\hline 2014 \& \& 88 \& 56 \& 42 \& \& \& \& 40 \& \& 1,3 <br>
\hline 2016 \& \& \& \& \& 9 \& 15 \& 11 \& \& $\sim 54$ \& 3,1 <br>
\hline 2050 \& \& 31 \& 28 \& 23 \& \& \& \& 20 \& \& 3 <br>
\hline 2068 \& \& 74 \& 55 \& 32 \& \& \& \& 38 \& \& 1 <br>
\hline 2097 \& \& 39 \& 28 \& 18 \& \& \& \& 19 \& \& 3 <br>
\hline 2137 \& \& \& \& \& \& $\sim 15$ \& 10 \& \& $\sim 54$ \& <br>
\hline 2134 \& \& 110 \& 68 \& 41 \& \& \& \& 46 \& \& 1 <br>
\hline 2216 \& \& \& \& \& \& $\sim 12$ \& 5 \& \& $\sim 42$ \& <br>
\hline
\end{tabular}

* Energy from $\gamma$-ray measurements.
$\dagger l=6$ from $\left({ }^{3} \mathrm{He}, \alpha\right)$ data.

Table 4. Levels populated in ${ }^{185} \mathrm{~W}$.

| $\begin{gathered} \text { Energy } \\ \mathrm{keV} \end{gathered}$ | $\begin{aligned} & \text { Assignment } \\ & I K^{\pi}\left[N n_{z} \Lambda\right] \end{aligned}$ | Experimental cross section |  |  |  |  |  | $Q$-reduced cross section |  | $\begin{gathered} \text { In- } \\ \text { ferred } \\ l \text {-value } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $(d, p) \mu b / s r$ |  |  | ( $d, t$ ) $\mu \mathrm{b} / \mathrm{sr}$ |  |  | $\begin{aligned} & (d, p) \\ & \mu b / s r \end{aligned}$ | $\begin{gathered} (d, t) \\ \mu b / s r \end{gathered}$ |  |
|  |  | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $90^{\circ}$ | $90^{\circ}$ |  |
| 0 | $3 / 23 / 2-[512]$ | 17 | 4 | $\sim 2$ | 3 | $<1$ | $<1$ | 5 | $<1$ |  |
| $24 *$ | $1 / 21 / 2-[510]$ | ~ 1.6 | 3 | $\sim 3$ | 5 | 5 | 3 | 4 | 2.7 |  |
| $66 *$ | $5 / 23 / 2-[512]$ | 287 | 257 | 90 | 415 | 409 | 221 | 301 | 207 | 3 |
| 94* | $3 / 21 / 2-[510]$ | 445 | 307 | 88 | 707 | 597 | 275 | 357 | 308 | 1 |
| 174* | $7 / 23 / 2-[512]$ | 10 | ~ 10 | 1.3 | 3 | 2.4 | 1.5 | ~11 | 1.3 |  |
| 188* | $5 / 21 / 2-[510]$ | $<3$ | $\sim 4$ | 0.6 | 14 | 19 | 9 | $\sim 4$ | 11 | 3 |
| 244* | 7/2 7/2-[503] | 243 | 287 | 97 | 209 | 278 | 160 | 316 | 154 | 3 |
| 302 | $9 / 23 / 2-[512]$ | 12 | 10 | 6 | 7 | 19 | 19 | 11 | 11 | $h$ |
| 334 | $7 / 21 / 2-[510]$ | 97 | 98 | 39 | 121 | 170 | 105 | 104 | 99 | 3 |
| 384 | 13/2 11/2+[615] | 15 | 28 | 17 | 17 | 53 | 46 | 30 | 32 | $6 \dagger$ |
| 391* | 9/2 7/2-[503] |  |  |  |  |  | $\sim 5$ |  | $\sim 3$ |  |
| $\sim 478$ | 11/2 3/2-[512] |  |  |  |  |  | $\sim 0.5$ |  | $\sim 0.4$ |  |
| $\sim 492$ | 9/2 1/2-[510] |  |  |  |  | $\sim 1$ | $\sim 1.0$ |  | $\sim 0.8$ |  |
| ~ 570 | 11/2 7/2-[503] |  |  | 1.2 |  | 2.1 | 4 | $\sim 5$ | 1.4 | $h$ |
| 666 |  | 100 | 56 | 17 | 16 | 16 | 10 | 54 | 11 | 1 |
| 706 | 11/2 1/2-[510] | $\sim 8$ | 5 | 2.8 | $\sim 2$ | 5 | 7 | 5 | 4 | $h, 3$ |
| 716 | $9 / 29 / 2+[624]$ |  | 3 |  | 11 | 19 | 13 | 3 | 15 | 3,h |
| 733 |  | 156 | 101 | 28 | 48 | 59 | 33 | 95 | 45 | 1(3) |
| ~ 789 | $9 / 29 / 2-[505]$ | 25 | 27 | 18 | 4 | 12 | 8 | 25 | 10 | $h, 3$ |
| $\sim 801$ |  | 29 | 34 | 8 | 1.1 | 1.6 | 1.3 | 31 | 1.3 |  |
| 833 |  | 13 | 11 | 1.5 | 1.1 | 1.6 | 1.6 | 10 | 1.3 | (1) |
| 888 | $5 / 25 / 2-[512]$ | $<2$ | $<3$ | $\sim 0.7$ | 17 | 16 | 12 | $<3$ | 14 | 3 |
| 904 |  | $<5$ | $<2$ | 4 | 3 | 10 | 4 | $<2$ | 9 |  |
| 921 |  |  |  |  | 2.7 | 5 | 3 |  | 5 | 3 |
| 986 | 7/2 5/2-[512] | 33 | 33 | 13 | 135 | 222 | 158 | 32 | 206 | 3 |
| 1008 | 1/2 1/2-[521] | 106 | 73 | 26 | 334 | 485 | $\sim 170$ | 62 | 386 | 1 |
| 1013 | $1 / 2-(3 / 2-[512], \gamma)$ | 106 | 73 | 26 | 334 | 485 | ~ 77 | 62 | 386 | 1 |
| 1020 | 13/2 9/2 + [624] |  |  |  |  | $\sim 23$ | 18 |  | ~ 19 | $6 \dagger$ |
| 1040 | $3 / 2-(3 / 2-[512], \gamma)$ | 27 | 23 | 4 | 68 | 83 | 26 | 20 | 80 | 1 |
| 1058* | 7/2 7/2-[514] | $\sim 18$ | 17 | 7 | 44 | 81 | 60 | 15 | 80 | 3 |
| 1073 | $5 / 2-(3 / 2-[512], \gamma)$ |  |  |  | 9 | 17 | 7 |  | 17 | 3,1 |
| 1106 | $3 / 21 / 2-[521]$ |  |  |  | 31 | 42 | 21 |  | 43 | 1,3 |
| 1107 |  | $\sim 35$ | $\sim 44$ | $\sim 6$ |  |  |  | $\sim 37$ |  | 1,3 |
| 1118 | $\begin{array}{ll} 5 / 2 & 1 / 2-[521] \\ 9 / 2 & 5 / 2-[512] \end{array}$ |  |  |  | 26 | 39 | 25 |  | 40 | 3 |
| 1120 |  | 111 | 99 | 41 |  |  |  | 81 |  | 3,1 |

(continued)

Table 4 (continued).

| Energy <br> keV | $\begin{aligned} & \text { Assignment } \\ & I K \pi\left[N n_{z} \Lambda\right] \end{aligned}$ | Experimental cross section |  |  |  |  |  | $Q$-reduced cross section |  | $\begin{gathered} \text { In- } \\ \text { ferred } \\ \text { l-value } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $(d, p) \mu b / s r$ |  |  | $(d, t) \mu b / s r$ |  |  | $\begin{aligned} & (d, p) \\ & \mu b / s r \end{aligned}$ | $\begin{gathered} (d, t) \\ \mu b / s r \end{gathered}$ |  |
|  |  | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $90^{\circ}$ | $90^{\circ}$ |  |
| 1149 |  | 96 | 74 | 21 |  |  |  | 65 |  | 1 |
| 1154 | $7 / 2-(3 / 2-[512], \gamma)$ |  |  |  | 22 | 30 | 20 |  | 28 | 3,1 |
| 1185 |  | 433 | 284 | 86 |  | $<3$ |  | 229 | $<3$ | 1 |
| ~ 1219 | 9/2 7/2-[514] |  |  |  | $\sim 5$ | 17 | 12 |  | 19 | (h) |
| 1222 |  | 437 | 315 | 91 | $\sim 5$ | $\sim 10$ | 5 | 251 | $\sim 11$ | 1 |
| ~ 1279 |  | 24 | ~ 26 | $\sim 10$ |  |  |  | 22 |  | (3) |
| 1290 |  | 244 | 197 | 63 | 10 | 18 | 9 | 154 | 21 | 1 |
| 1317 |  |  |  |  | 5 | 14 | 8 |  | 17 |  |
| 1317 |  | 65 | 74 | 31 |  |  |  | 57 |  | 3 |
| 1335 | 7/2 1/2-[521] |  |  |  | 11 | obsc | 19 |  | $\sim 25$ |  |
| 1343 |  | 19 | 23 | 10 |  |  |  | 17 |  | 3 |
| 1346 |  |  |  |  | 5 | obsc | 4 |  |  |  |
| 1361 | $9 / 21 / 2-[521]$ |  |  |  | 2.3 | $\sim 9$ | 2 |  | ~11 |  |
| 1382 |  |  |  |  | 6 | 12 | 6 |  | 15 | 1,3 |
| ~ 1402 |  |  |  |  | 7 | 28 | 23 |  | 37 | $h, 3$ |
| ~ 1410 |  |  |  |  | 4 | $\sim 3$ | $\sim 2$ |  | 4 |  |
| 1428 |  | 111 | 66 | 19 | 3 | 7 | 4 | 49 | 9 | 1 |
| 1445 |  | 49 | 43 | 22 |  |  |  | 32 |  | (3) |
| 1448 |  |  |  |  | 23 | 34 | 20 |  | 48 | 3,1 |
| 1501 |  | $\sim 36$ | 21 | 8 |  |  |  | 15 |  | 1,3 |
| 1503 |  |  |  |  | 16 | 36 | 19 |  | 54 | 3,1 |
| 1542 |  | 1074 | $\sim 570$ | 181 | 9 | 14 | 10 | $\sim 391$ | 22 | 1 |
| 1561 | $13 / 2+, N=6$ |  |  |  | 11 | 32 | 26 |  | 51 |  |
| 1561 |  | 284 | 254 | 140 |  |  |  | 183 |  | (3) |
| 1603 |  | 12 | 19 | 4 |  |  |  | 13 |  |  |
| 1623 |  | 29 | 31 | 7 |  |  |  | 22 |  | 3,h |
| 1627 |  |  |  |  | 4 | 7 | 4 |  | 9 | $6 \dagger$ |
| 1646 |  |  |  |  | $<2$ | $<5$ | 4 |  | $<8$ |  |
| 1663 |  | 50 | 38 | 18 |  |  |  | 26 |  | 1,3 |
| 1666 | $9 / 2+, N=6$ |  |  |  | 19 | 25 | 19 |  | 44 | 1,3 |
| 1677 |  | 76 | 85 | $\sim 22$ |  |  |  | 58 |  | 3 |
| ~1683 |  |  |  |  | $\sim 4$ | $\sim 5$ | 6 |  | $\sim 9$ |  |
| 1699 |  | 24 | 40 | 12 |  |  |  | 27 |  |  |
| 1701 |  |  |  |  | 5 | 10 | 7 |  | 18 | 3 |
| $1722$ |  | 28 | $\sim 26$ | 5 |  |  |  | $\sim 18$ |  | 1 |
| 1728 |  |  |  |  | 9 | 13 | 9 |  | 25 | 1,3 |

(continued)

Table 4 (continued).

| Energy keV | $\begin{aligned} & \text { Assignment } \\ & I K^{\pi}\left[N n_{z} \Lambda\right] \end{aligned}$ | Experimental cross section |  |  |  |  |  | Q-reduced cross section |  | $\begin{gathered} \text { In- } \\ \text { ferred } \\ l \text {-value } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $(d, p) \mu b / s r$ |  |  | $(d, t) \mu b / s r$ |  |  | $\begin{aligned} & (d, p) \\ & \mu b / s r \end{aligned}$ | $\begin{gathered} (d, t) \\ \mu b / s r \end{gathered}$ |  |
|  |  | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $90^{\circ}$ | $90^{\circ}$ |  |
| 1745 | $13 / 2+, N=6$ | 63 | 48 | 15 |  |  |  | 32 |  | 1 |
| 1800 |  | 42 | 33 | 9 |  |  |  | 22 |  | 1 |
| ~ 1830 |  | $\sim 72$ | $\sim 39$ | $\sim 11$ |  |  |  | ~ 25 |  | 1 |
| 1845 |  | ~ 105 | $\sim 24$ | $\sim 31$ |  |  |  | $\sim 22$ |  |  |
| 1846 |  |  |  |  | 4 | ~ 30 | 24 |  | $\sim 64$ | $6 \dagger$ |
| 1860 |  |  |  |  | 7 | $\sim 24$ | 11 |  | $\sim 52$ |  |
| 1874 |  |  |  |  | 4 | $\sim 5$ | 5 |  | $\sim 11$ |  |
| 1886 |  | $\sim 36$ | 33 | 9 |  |  |  | 21 |  | 1 |
| 1904 |  | 16 | 19 | $<4$ |  |  |  | 12 |  |  |
| 1915 |  |  |  |  | 7 | 16 | 7 |  | 38 |  |
| 1937 |  |  |  |  | 6 | 13 | 11 |  | 30 | 3 |
| 1952 |  |  |  |  | 8 | 22 | 14 |  | $\sim 53$ | 3,1 |
| 1959 |  | 83 | $\sim 41$ | 25 |  |  |  | $\sim 26$ |  |  |
| 1986 |  |  |  |  | 9 | 11 | $\sim 9$ |  | 28 | 1 |
| 2031 |  | $\sim 88$ | $\sim 61$ | $\sim 18$ |  |  |  | $\sim 38$ |  | 1 |
| ~ 2038 |  |  |  |  | $\sim 7$ | $\sim 8$ | 9 |  | $\sim 20$ |  |

* Energy from $\gamma$-ray measurements.
$\dagger l=6$ from $\left({ }^{3} \mathrm{He}, \alpha\right)$ data.

84 and $20 \mathrm{mb} / \mathrm{sr}$ at $60^{\circ}, 90^{\circ}$ and $125^{\circ}$, respectively. These values are in reasonable agreement with a recent measurement ${ }^{18}$.

Cross sections were determined from the total number of tracks in the peaks. The high level densities often required the use of an unfolding procedure which was based on the experimental peak shape in each spectrum. Estimated uncertainties on absolute cross sections greater than $20 \mu b / s r$ are about $\pm 20 \%$ while for smaller cross sections they might be as high as $\pm 50 \%$, especially at $60^{\circ}$. Relative cross sections of well resolved peaks within each spectrum are estimated to be accurate within $\pm 10 \%$. The excitation energies were determined from the peak centroids as a weighted average of the results at all three angles and, where possible, of both deuteron induced reactions. Where energies are already known, the agreement is generally very close. We assign errors of $\pm 6 \mathrm{keV}$ per MeV of excitation to well resolved peaks with $90^{\circ}$ cross section of $20 \mu b / s r$ or more.

Table 5. Levels populated in ${ }^{187} \mathrm{~W}$.

| Energy keV | $\begin{aligned} & \text { Assignment } \\ & I K^{\pi}\left[N n_{z} \Lambda\right] \end{aligned}$ | Experimental cross section |  |  | $Q$-reduced cross section | Inferred <br> $l$-value |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | (d,p) $\mu \mathrm{b} / \mathrm{sr}$ |  |  | (d,p) $\mu \mathrm{b} / \mathrm{sr}$ |  |
|  |  | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $90^{\circ}$ |  |
| 0 | $3 / 23 / 2-[512]$ | 69 | 34 | 14 | 37 | 1 |
| 77* | $5 / 23 / 2-[512]$ | 231 | 201 | 108 | 213 | 3 |
| 205* | $3 / 21 / 2-[510]$ | 437 | 268 | 126 | 272 | 1 |
| 303* | $5 / 21 / 2-[510]$ | 30 | 21 | 14 | 21 | 3 |
| 329 | 9/2 3/2-[512] | <2 | $\sim 5$ | 10 | $\sim 5$ | $h$ |
| 351 | 7/2 7/2-[503] | 278 | 219 | 137 | 211 | 3 |
| 366 | $13 / 211 / 2+[615]^{\text {a }}$ | $<9$ | $<35$ | ~ 29 | $\sim 34$ | $h$ |
| 432* | 7/2 1/2-[510] | 77 | 75 | 48 | 71 | 3 |
| 598 | $9 / 29 / 2-[505]^{\text {a }}$ | 16 | 26 | 26 | 23 | h |
| 641* | $5 / 25 / 2-[503]$ ? | 122 | 103 | 60 | 90 | 3 |
| ~ 731 |  | 3 | $\sim 5$ | 4 | $\sim 4$ |  |
| 782* |  | 535 | 310 | 145 | 260 | 1 |
| 816* |  | 641 | 406 | 195 | 336 | 1 |
| 853 |  | 207 | 125 | 63 | 102 | 1 |
| 866* |  | $\sim 50$ | ~ 62 | ~ 25 | $\sim 50$ | (3) |
| 892* |  | 54 | 41 | 20 | 33 | 1,3 |
| 961 |  | 30 | 27 | 20 | 21 | 3 |
| 980 |  | 78 | 56 | 32 | 44 | 1,3 |
| 998 |  | $\sim 6$ | ~ 9 | 3 | $\sim 7$ |  |
| 1034 |  | 8 | 7 | 4 | 5 |  |
| 1072 |  | 54 | 53 | 36 | 40 | 3 |
| 1087 |  | $\sim 21$ | 20 | 11 | 15 | 3 |
| 1114 |  | $\sim 7$ | 13 | 9 | 10 | (h) |
| 1139 |  | 30 | 19 | 8 | 14 | 1 |
| 1196 |  |  | 15 |  | 11 |  |
| 1234 |  | 70 | 52 | $\sim 45$ | 37 | 3 |
| 1267 |  | 15 | 19 | $\sim 26$ | 14 | $h$ |
| 1313 |  | 456 | 242 | 112 | 170 | 1 |
| 1349 |  | 218 | 170 | 73 | 118 | 1 |
| 1361 |  | 123 | 121 | 75 | 84 | 3 |
| 1384 |  | 293 | 186 | 101 | 127 | 1 |
| 1416 |  | 135 | 84 | ~ 58 | 57 | 3,1 |
| 1426 |  | 202 | 245 | ~ 121 | 166 |  |
| 1479 |  | 40 | 45 | 23 | 30 | 3,1 |
| 1494 |  | 25 | 11 | 4 | 8 | 1 |
| 1537 |  | 583 | 332 | 156 | 217 | 1 |
| 1566 |  | $\sim 55$ | 53 | 24 | 35 | 1,3 |

(continued)

Table 5 (continued).

| $\begin{gathered} \text { Energy } \\ \text { keV } \end{gathered}$ | Assignment$I K^{\pi}\left[N n_{z} \Lambda\right]$ | Experimental cross section |  |  | $Q$-reduced cross section | Inferred $l$-value |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $(d, p) \mu b / s r$ |  |  | $(d, p) \mu b / s r$ |  |
|  |  | $60^{\circ}$ | $90^{\circ}$ | $125^{\circ}$ | $90^{\circ}$ |  |
| 1591 |  | 296 | 167 | 85 | 107 | 1 |
| 1602 |  | ~ 99 | 79 | ~ 33 | 51 | (1) |
| 1633 |  | $\sim 24$ | 18 | 17 | 11 | (3) |
| 1673 |  | 29 | ~ 11 | 6 | $\sim 7$ | 1 |
| 1691 |  | $\sim 11$ | 14 | 7 | 9 |  |
| 1719 |  | 99 | 118 | 54 | 73 |  |
| 1749 |  | 41 | 48 | 22 | 30 |  |
| 1771 |  | 46 | ~ 21 | 14 | ~ 13 |  |
| 1825 |  | 108 | 59 | 37 | 35 | 1 (3) |
| 1844 |  | $\sim 43$ | 20 | 11 | 12 | 1 |
| $\sim 1907$ |  | obsc | $\sim 88$ | 48 | $\sim 51$ |  |
| $\sim 1917$ |  | obsc | $\sim 50$ | $\sim 23$ | $\sim 29$ |  |
| $\sim 1941$ |  | obsc | $\sim 60$ | 29 | $\sim 34$ |  |
| $\sim 2017$ |  | obsc | $\sim 60$ | 35 | $\sim 34$ |  |

* Energy from $\gamma$-ray measurements.
a The assignments of these two levels could be reversed (cf. sect. 4.7).

The ( $d, p$ ) cross sections at $60^{\circ}$ for ${ }^{182} \mathrm{~W},{ }^{184} \mathrm{~W}$ and ${ }^{186} \mathrm{~W}$ targets were determined earlier ${ }^{12)}$ by similar techniques with accuracies comparable to those assigned here. For ${ }^{187} \mathrm{~W}$, the two sets of results agree fairly well. However, the deviations for ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$, on the average, are more nearly a factor of 1.3 to 1.8 .

### 3.4. Q-Reduction and DWBA Calculations

It is necessary to consider the $Q$-dependence of the transfer reactions when comparing theoretical cross section predictions to experimental results. Since initially most of the Nilsson assignments and hence the $Q$-values for the transfer into these orbitals are not known, it is convenient to calculate all theoretical cross sections at standard $Q$-values, namely, +3.0 MeV for the $(d, p)$ reaction, and -2.0 MeV for the ( $d, t$ ) reaction. All experimental cross sections are reduced to these standard $Q$-values by means of the theoretical $Q$-dependence calculated from the DWBA. The theoretical $Q$ dependence is quite similar for the different $l$ transfers (fig. 15) and there-

Table 6. Optical model parameters for the DWBA calculations.

| Particle | $V$ <br> $(\mathrm{MeV})$ | $W$ <br> $(\mathrm{MeV})$ | $r_{0}$ <br> $(f)$ | $a$ <br> $(f)$ | $r_{0}^{\prime}$ <br> $(f)$ | $a^{\prime}$ <br> $(f)$ | $r_{C}$ <br> $(f)$ |
| :--- | ---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Proton. . . . . . | 55.0 | 17.5 | 1.25 | 0.65 | 1.25 | 0.47 | 1.25 |
| Deuteron ..... | 104.5 | 17.3 | 1.15 | 0.81 | 1.34 | 0.68 | 1.15 |
| Triton ....... | 154.0 | 12.0 | 1.10 | 0.75 | 1.40 | 0.65 | 1.25 |
| Bound State <br> $\quad$ Neutron ..... | a | - | 1.25 | 0.65 | - | - | - |

a Searched on to fit empirical binding energies.

Table 7. Differential single particle transfer cross sections calculated from the DWBA.
$\left(\theta=90^{\circ} ; Q(d, t)=-2 \mathrm{MeV} ; Q(d, p)=3 \mathrm{MeV}\right)$.
fore an average $Q$-dependence could be used. The latter is also shown, for each angle and reaction, in fig. 15. This gives rise to two sets of cross sections, the actual measured ones and a set of $Q$-reduced cross sections that, according to the DWBA, would have occurred if each transition had had the standard $Q$-value. Whenever cross section values are discussed below, unless otherwise noted, they refer to the $Q$-reduced differential cross sections at $90^{\circ}$.

The optical potential parameters used (see table 6) are those calculated for a spherical target nucleus of mass and charge 183 and 74 from the standard ${ }^{19-20)}$ prescriptions. In agreement with the results of Siemssen and Erskine ${ }^{14)}$ who made more extensive ( $d, p$ ) angular distribution measurements, this has been found to be a better procedure than to use parameters obtained by fitting the deuteron elastic scattering cross section data. A recent ( $t, d$ ) investigation ${ }^{21)}$ suggests the superiority of this procedure for the ( $d, t$ ) reaction as well.


Fig. 1. Triton spectrum for the reaction ${ }^{180} \mathrm{~W}(d, t)^{179} \mathrm{~W}$ at $125^{\circ}$.
It should finally be noted that the DWBA calculations give strong diffraction patterns for low even $l$ transfers and at high $Q$-values, which sensitively depend on slight changes of the optical model parameters and probably are not physical. An arbitrary but consistent smoothing procedure ${ }^{3)}$ was applied to the calculated angular distributions prior to the extraction of the single-particle transfer cross sections used for calculation of the theoretical fingerprint patterns. The resulting (normalized) singleparticle transfer cross sections are given in table 7 .

### 3.5. Gross Section Angular Distributions and $l$ values

Since the angular distributions are relatively structureless at this low bombarding energy, the cross section ratios from the three angles of measurement, $60^{\circ}, 90^{\circ}$ and $125^{\circ}$, provided an important guide in estimating the transferred $l$-values. For the states of previously known spin an parity, it has been found that the three experimental reduced cross section ratios $\sigma\left(60^{\circ}\right) / \sigma\left(90^{\circ}\right), \sigma\left(125^{\circ}\right) / \sigma\left(90^{\circ}\right)$ and $\sigma\left(125^{\circ}\right) / \sigma\left(60^{\circ}\right)$ fall into separate classes corresponding to $l=1,3$ and $\geq 5$ transfers (fig. 16). For example, in the ( $d, t$ ) reaction, the ratio $\sigma\left(125^{\circ}\right) / \sigma\left(90^{\circ}\right)$ for $l=1,3$ and $\geq 5$ transfers ex-

Table 8. $Q$-values and neutron separation energies for $W$ nuclei.

| $\begin{gathered} \text { Mass } \\ \mathrm{A} \end{gathered}$ | $\begin{gathered} Q(d, t) \\ \mathrm{A} \rightarrow \mathrm{~A}-1 \\ \mathrm{keV} \end{gathered}$ | $\begin{gathered} Q(d, p) \\ \mathrm{A}-1 \rightarrow \mathrm{~A} \\ \mathrm{keV} \end{gathered}$ | $\begin{gathered} S_{n}(d, t) \\ \mathrm{keV} \end{gathered}$ | $S_{n}(d, p)$ <br> keV | $\begin{aligned} & S_{n} \text { from } \\ & \text { mass tables }{ }^{22)} \\ & \text { keV } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 180 | $-2155 \pm 15$ |  | $8413 \pm 15$ |  |  |
| 181 |  | $4468 \pm 15$ |  | $6693 \pm 15$ | $6947 \pm 36$ |
| 182 | $-1809 \pm 10$ |  | $8067 \pm 10$ |  | $7987 \pm 22$ |
| 183 | $57 \pm 15$ | $3979 \pm 10$ | $6201 \pm 15$ | $6204 \pm 10$ | $6187 \pm 3$ |
| 184 | $-1154 \pm 10$ | $5187 \pm 15$ | $7412 \pm 10$ | $7412 \pm 15$ | $7418 \pm 19$ |
| 185 |  | $3533 \pm 10$ |  | $5758 \pm 10$ | $5748 \pm 5$ |
| 186 | - $939 \pm 10$ |  | $7197 \pm 10$ |  | $7213 \pm 43$ |
| 187 |  | $3240 \pm 10$ |  | $5465 \pm 10$ | $5460 \pm 5$ |

hibits values in the ranges $0.5-0.8,0.8-1.5$ and $3.0-6.0$ respectively. For the few transitions known to involve $l=4$ transfer, this ratio is somewhat higher than the average value which has been observed for $l=3$ transfers. However, with the limited angular distribution data available it was generally not possible to distinguish reliably between adjacent $l$-values.

For states of previously unknown spin and parity, $l$ transfer values have been inferred from the experimental angular distributions only when all three cross section ratios indicate the same angular momentum transfer. In some other cases, where the experimental data are less clearcut, no unique $l$ has been assigned although preferences are indicated. The angular distributions for all states which are populated with moderate to strong intensity in the $(d, p)$ and ( $d, t$ ) reactions on ${ }^{186} \mathrm{~W}$ are displayed in fig. 17, which illustrates the classification of the observed transitions into three distinct categories. The inferred $l$-values for all the nuclei studied are indicated in tables 1 to 5 . The symbol " $h$ " is used for $l \geq 5$.

The aforementioned uncertainty of $\pm 1$ unit of angular momentum in the inferred $l$-values was not a very serious limitation for the hole states since no even parity orbitals with strong population cross sections of low $l$-transfer are expected for the wolfram nuclei; the important even parity states are those originating from the $i_{13 / 2}$ spherical state which are populated predominantly with $l=6$ transfer and which have, in any case, been identified by the $\left({ }^{3} \mathrm{He}, \alpha\right)$ reaction studies. On the other hand, our inability to use the angular distribution data for parity assignment was a definite drawback in interpreting the ( $d, p$ ) spectra.


Fig. 2. Triton spectrum for the reaction ${ }^{182} \mathrm{~W}(d, t)^{181} \mathrm{~W}$ at $125^{\circ}$.

### 3.6. Ground State $Q$ Values

In all spectra the ground state or a low-lying state of known excitation energy is well populated and hence the $Q$-values can be accurately determined. These results are listed in table 8, together with the neutron separation energies $S_{n}$ calculated from the relations

$$
S_{n}(A)=6.258 \mathrm{MeV}-Q_{(d t)}(A \rightarrow A-1)
$$

and

$$
S_{n}(A)=2.225 \mathrm{MeV}+Q_{(d p)}(A-1 \rightarrow A)
$$

Also included are the results obtained from the reactions with a ${ }^{183} \mathrm{~W}$ target. The agreement with the 1964 mass tables ${ }^{22)}$ is fairly good except for the ${ }^{181} \mathrm{~W}$ neutron separation energy for which the present result is about 250 keV lower than the earlier value. The mass of ${ }^{179} \mathrm{~W}$ was not previously known.

## 4. Nilsson Assignments

The energy level systematics of well studied neighbouring nuclei provided a starting point for the interpretation of the observed level spectra as they indicated which orbitals were likely to occur as low energy excitations in


Fig. 3. Proton spectrum for the reaction ${ }^{180} \mathrm{~W}(d, p)^{181} \mathrm{~W}$ at $90^{\circ}$.
the wolfram nuclei. For each expected orbital a search was made for the corresponding band which was required to have reasonable rotational spacings and to exhibit absolute cross sections and a fingerprint pattern resembling those calculated from the DWBA and the Nilsson model. In this search the spin restrictions implied by the inferred $l$-values and the observed ratios of $(d, p)$ to ( $d, t$ ) cross-sections were also kept in mind. Several straightforward identifications resulted. For example, the $1 / 2$ - [521] and $5 / 2-[512]$ bands appeared in all the ( $d, t$ ) spectra with fingerprint patterns closely resembling those expected (figs. 18 a and b). For some other bands, e.g. the $7 / 2-[514]$ band, only tentative identifications were possible at first as the observed cross sections bore little resemblance to the predicted fingerprint patterns (fig. 18 c). In many cases subsequent Coriolis coupling calculations explained the apparent deviations from theory satisfactorily and solidified the assignments. The striking effects which can arise from strongly coupled bands are illustrated in fig. 19 where the observed cross sections for the close lying $1 / 2-$ [510] and $3 / 2-[512]$ bands, which were identified in all the ( $d, p$ ) spectra, are compared with the fingerprint patterns calculated with no mixing included.

The assignments made are listed in tables 1 to 5 and in the level schemes


Fig. 4. Triton spectrum for the reaction ${ }^{184} \mathrm{~W}(d, t)^{183} \mathrm{~W}$ at $125^{\circ}$.
of figs. 10 to 14 . All supporting arguments will not be discussed for each assignment since these are often similar and similar also to those used in previous studies. Detailed comments on the assignments and on the Coriolis mixing calculations are given in later sections.

In the ( $d, t$ ) spectra essentially all states up to about 1400 keV excitation energy were assigned along with a few tentative even parity assignments at higher excitation energies. The experimental data for the higher lying states are however of poorer quality since the ( $d, t$ ) cross sections are smaller for the more negative $Q$-values (fig. 15).

At the deformation of the wolfram nuclei the Nilsson model predicts a distinct energy gap above the neutron number 118 . In the ( $d, p$ ) spectra essentially all Nilsson orbitals below this gap were identified at excitation energies below 700 keV . The spectra clearly exhibit a reduced level density in the energy region above these states. The orbitals expected at higher excitation energies could, however, not be localized individually due to the complexity of the spectra (sect. 4.9).

The detailed discussion below therefore is limited to the negative parity Nilsson orbitals $7 / 2-[514], 5 / 2-[512]$ and $1 / 2-[521]$, which occur as hole excitations, the $1 / 2-[510]$ and $3 / 2-[512]$ orbitals near the Fermi surface and the $7 / 2-[503]$ and $9 / 2-[505]$ orbitals which are particle excitations in


Fig. 5. Proton spectrum for the reaction ${ }^{182} \mathrm{~W}(d, p)^{183} \mathrm{~W}$ at $125^{\circ}$.
the wolfram nuclei. In addition, the strongly mixed $i_{13} / 2$ even parity orbitals $11 / 2+[615], 9 / 2+[624], 7 / 2+[633], 5 / 2+[642], 3 / 2+[651]$ and $1 / 2+[660]$ are discussed together in a single section. These orbitals span an energy interval of about 4.5 MeV of the Nilsson diagram, and no other orbitals are expected in this energy region.

The energy levels in ${ }^{179} \mathrm{~W}$ were populated only through the ( $d, t$ ) reaction. Most of the observed states up to 900 keV of excitation have been assigned. These assignments are in general agreement with the results of a recent ${ }^{179}$ Re decay study ${ }^{23)}$.

The analysis of the reaction data for ${ }^{181} \mathrm{~W}$ was greatly aided by a parallel study of the ${ }^{181} R e$ decay ${ }^{24)}$. In ${ }^{181} \mathrm{~W}$, the strongly mixed $1 / 2-[510]$ and $1 / 2-[521]$ bands occur close together but on opposite sides of the Fermi surface, thus giving rise to rather unusual mixing effects. Although it has been possible to account satisfactorily for many of the observed effects with a Coriolis treatment, some anomalies remain (see section 5.4), and in general the population cross sections and level energies in ${ }^{181} \mathrm{~W}$ are not as well understood as in the other nuclei. In the $(d, t)$ spectrum, most groups up to 1200 keV have been assigned, and in the ( $d, p$ ) spectrum, all those groups which could definitely be attributed to ${ }^{181} \mathrm{~W}$. Due to the presence of other W isotopes in the ${ }^{180} \mathrm{~W}$ target, the $(d, p)$ spectrum was particularly complex. The analysis


Fig. 6. Triton spectrum for the reaction ${ }^{186} \mathrm{~W}(d, t)^{185} \mathrm{~W}$ at $125^{\circ}$.
was therefore limited to states below 1200 keV , and the ( $d$,p) cross sections into ${ }^{181} \mathrm{~W}$ are less accurately determined.

Extensive level schemes for ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$ were established using both the ( $d, p$ ) and ( $d, t$ ) reactions. All the observed hole states up to 1400 keV have been interpreted, but the high excitation energy portions of the $(d, p)$ spectra are not well understood. The low lying levels of ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$ were previously investigated in numerous radioactive decay studies, and the reaction data fully confirm the conclusions reached in the more recent investigations ${ }^{25-27)}$.

All energy levels below 600 keV populated in ${ }^{187} \mathrm{~W}$ by the ( $d, p$ ) reaction have been assigned. Our results are in good agreement with those of ErSkine's earlier reaction study ${ }^{12)}$ although two additional high $K$ orbitals have been located in the present work.

### 4.1. The 7/2-[514] Orbital

In ${ }^{179} \mathrm{~W}$, the $7 / 2-[514]$ orbital forms the ground state. Only the $7 / 2-$ state of the band could be observed in the ( $d, t$ ) spectra because of target contamination.

In ${ }^{181} \mathrm{~W}$, the $7 / 2-[514]$ band head was previously known ${ }^{28)}$. In addition, the $9 / 2$ - member of the band has been identified in the ( $d, t$ ) spectra.


Fig. 7. Proton spectrum for the reaction ${ }^{184} \mathrm{~W}(d, p)^{185} \mathrm{~W}$ at $125^{\circ}$.

In ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$, the band has been identified at approximately 1 MeV of excitation. It has not been observed in ${ }^{187} \mathrm{~W}$ which could be populated by the ( $d, p$ ) reaction only.

The observed fingerprint patterns are quite different from the predicted one which has equally populated $7 / 2$ and $9 / 2$ states (fig. 18 c). The sharp variations in population cross sections for the $7 / 2$ state are ascribed to coupling with the close-lying strong $7 / 25 / 2-[512]$ state, as will be discussed in sect. 5 .

### 4.2. The $1 / 2-[521]$ Orbital

The $1 / 2-[521]$ band is easily identified because of the strongly populated $1 / 2$ and the comparatively strong $3 / 2,5 / 2$ and $7 / 2$ band members. Furthermore, the band has a characteristic decoupling parameter of about 0.8 .

In ${ }^{179} \mathrm{~W}$ the band was already known ${ }^{23)}$ and is confirmed by the reaction data.

In ${ }^{181} \mathrm{~W}$ the $1 / 2-[521]$ band head is found at 385 keV , and the higher band members up to $I=7 / 2$ can clearly be identified. However, the observed decoupling parameter of $a=0.48$ is significantly smaller than found in the
other wolfram nuclei. This definite assignment conflicts with the previous suggestion ${ }^{28)}$ of $1 / 21 / 2-[510]$ for the 385 keV state.

In ${ }^{183} \mathrm{~W}$ the band is easily identified with the band head at 936 keV .
In ${ }^{185} \mathrm{~W}$ the assignment is also rather straightforward with the band head at 1008 keV , but a significant reduction of the total intensity (fig. 18 a ) compared to ${ }^{183} \mathrm{~W}$ is obvious. However, in ${ }^{185} \mathrm{~W}$ several groups around 1 MeV have energy spacings and $l$-values which together are suggestive of an additional $K=1 / 2$ band. It is tentatively proposed that the $1 / 2-[521]$ strength in ${ }^{185} \mathrm{~W}$ is split, and that approximately one third of it contributes to a K-2 gamma vibration at 1013 keV based on the $3 / 2-[512]$ ground state. The smaller decoupling parameter $(a=0.2)$ of this latter tentative $K=1 / 2$ band supports this interpretation.

In ${ }^{187} \mathrm{~W}$ the band is too far below the Fermi surface to be populated in the $(d, p)$ reaction.

### 4.3. The 5/2-[512] Orbital

This orbital is characterized by the large population of the $7 / 2-$ rotational member.

In ${ }^{179} \mathrm{~W}$ and ${ }^{181} \mathrm{~W}$ the band was already known ${ }^{23,28)}$ and it has been confirmed by the $(d, t)$ data. In ${ }^{181} \mathrm{~W}$, the $9 / 2-$ and $11 / 2-$ band members have also been located in the present work.

In ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$ the band is identified around 900 keV and has in both cases been definitely localized.

The band has not been seen in ${ }^{187} \mathrm{~W}$.
It is consistently observed that the $5 / 2$ member is populated with a cross section 50 to 100 times larger than the $0.2 \mu \mathrm{~b} / \mathrm{sr}$ predicted by the Nilsson model. A similar enhancement was earlier found in the rare earth region for this state.

### 4.4. The $1 / 2-[510]$ Orbital

The $1 / 2-[510]$ band is excepted to be characterized by a very strong $3 / 2-$ group and a moderately strong $5 / 2$ - group. In the wolfram nuclei, this band is strongly perturbed by the near-lying $3 / 2-[512]$ band (fig. 19 a ).

In ${ }^{179} \mathrm{~W}$ a tentative identification of the hand head has been made at $\sim 627 \mathrm{keV}$. A previous assignment ${ }^{23)}$ at 704.9 keV leading to $3 / 2$ and $5 / 2$ states at 768.7 and 806.9 keV is not consistent with the present data which show no peaks at these energies in contrast to expected cross sections of $10-20 \mu \mathrm{l} / \mathrm{sr}$.

In ${ }^{181} \mathrm{~W}$ the band head is placed at 457.7 keV . The identification of the


Fig. 8. Proton spectrum for the reaction ${ }^{186} \mathrm{~W}(d, p)^{187} \mathrm{~W}$ at $125^{\circ}$.
band is based on the combined information from the present reaction data and the parallel investigation of the ${ }^{181}$ Re decay ${ }^{24)}$. An earlier ${ }^{28)}$ assignment at 746 keV is incompatible with the reaction data as well as the more recent decay results.

In ${ }^{183} \mathrm{~W}$ and ${ }^{187} \mathrm{~W}$ the $1 / 2-[510]$ orbital was previously known ${ }^{28)}$, and the assignments are confirmed by the present reaction data.

In ${ }^{185} \mathrm{~W}$, an earlier companion study ${ }^{26}$ ) of 185 mW decay, which utilized some of the present reaction data, established the location of the $1 / 2-$ [510] band as well as the $3 / 2-[512]$ and $11 / 2+[615]$ bands discussed below.

### 4.5. The 3/2-[512] Orbital

This orbital is characterized by strong $3 / 2-$ and $5 / 2-$ groups, but in the $W$ nuclei the band is strongly perturbed (fig. 19 b ) by coupling to the $1 / 2-[510]$ band discussed above.

In ${ }^{179} \mathrm{~W}$ the band has not been observed, but it has been identified in ${ }^{181} \mathrm{~W}$ where it was not previously known.

In ${ }^{183} \mathrm{~W}$ the reaction data confirm the previously well established assignment. All rotational members up to $I=9 / 2$ were clearly observed. A high l-group which is observed at 742 keV in both reactions is tentatively assigned as the $11 / 2$ - rotational state.


Fig. 9. Alpha-particle spectra for the reactions ${ }^{182} \mathrm{~W}\left({ }^{3} \mathrm{He}, \alpha\right)^{181} \mathrm{~W},{ }^{184} \mathrm{~W}\left({ }^{3} \mathrm{He}, \alpha\right)^{183} \mathrm{~W}$ and ${ }^{186} \mathrm{~W}\left({ }^{3} \mathrm{He}, \alpha\right)^{185} \mathrm{~W}$ at $60^{\circ}$.

In ${ }^{185} \mathrm{~W}$ the band members up to $I=7 / 2$ were located in the 185 mW decay study in agreement with the present reaction data. The latter also established the $9 / 2$ - and, tentatively, the $11 / 2$ - member.

In ${ }^{187} \mathrm{~W}$, the $(d, p)$ spectrum clearly shows the $3 / 2-, 5 / 2-$ and $9 / 2-$ members of the $3 / 2-[512]$ ground state band. Because of mixing, the cross section for the $7 / 2$ - state is expected to be small (cf. table 17 and fig. 28) and the state could not be observed because of a fairly high back-ground in this region of the spectrum. The calculated perturbed energy of 186.5 keV agrees with earlier $(n, \gamma)$ results ${ }^{29)}$, although such a state has not been observed in a more recent $(n, \gamma)$ investigation ${ }^{30)}$.

### 4.6. The 7/2-[503] Orbital

The $7 / 2-[503]$ orbital occurs as a particle excitation in the wolfram nuclei and is thus mainly observed in the ( $d, p$ ) reaction. The Nilsson model predicts strong population for the $7 / 2-$ state only.

In ${ }^{181} \mathrm{~W}$ a group at 662 keV is assigned to this orbital, in disagreement with a previous ${ }^{28)}$ assignment (at 807.9 keV ) but in accord with the recent decay study ${ }^{24)}$.


Fig. 10. Level scheme for ${ }^{179} \mathrm{~W}$. The letters A, B, C denote certain, probable and tentative assignments, respectively. Hole excitations are shown to the left, particle excitations to the right. Band members established in other studies but not observed in the transfer reactions are indicated by dashed lines. The unassigned levels in the energy region where assignments were made are shown above the ground band with their particle or hole character indicated.

The present results agree with earlier proposed assignments ${ }^{27,28)}$ in ${ }^{183} \mathrm{~W},{ }^{185} \mathrm{~W}$ and ${ }^{187} \mathrm{~W}$, and some additional high spin band members have been identified.

It is worthy of note that the population cross sections for the $7 / 27 / 2-[503]$ state in the $(d, t)$ reactions were consistently $40-80 \mu b$ larger than the values calculated from the pairing factor (cf. tables $14-16$ in the appendix). It is possible that this reflects an admixture of the $7 / 25 / 2-[512]$ hole state which has a large $C_{j l}$ coefficient and is also coupled to the $7 / 2-[503]$ orbital through a large matrix element, although our present treatment of Coriolis coupling and pairing does not predict ( $d, t$ ) cross sections of the observed magnitude.

### 4.7. The $9 / 2-[505]$ Orbital

The $9 / 2-[505]$ orbital is difficult to place since only the $9 / 2$ state should be populated and by the ( $d, p$ ) reaction only. However, in ${ }^{189} \mathrm{Os}$ and ${ }^{191} \mathrm{Os}$ the state occurs ${ }^{28)}$ in the ground state region and it therefore is expected at moderate excitation energies in the wolfram nuclei.

In ${ }^{183} \mathrm{~W}$ the lowest candidate for the $9 / 2-[505]$ state is observed at 1390


Fig. 11. Level scheme for ${ }^{181} \mathrm{~W}$. See caption to Fig. 10.
keV and is tentatively assigned as such although several higher lying levels (e.g. at 1582 keV ) cannot be ruled out. The fact that the $13 / 2+[606]$ and the $j_{15} / 2$ Nilsson orbitals which have the same cross section characteristics might also occur in this energy region further complicates this assignment.

In ${ }^{185} \mathrm{~W}$ the assignment at 789 keV is somewhat more definite. Below 1300 keV only the two states at 716 keV and 789 keV have approximately the expected cross section and an angular distribution showing high angular momentum transfer. Of these, the 789 keV is more strongly populated in the $(d, p)$ reaction than in the $(d, t)$ reaction and is therefore preferred for the $9 / 2-[505]$ assignment. Furthermore, the $716 \mathrm{keV}(d, t)$ group has an $l=4$ type angular distribution and is most probably the $9 / 29 / 2+[624]$ level.

In ${ }^{187} \mathrm{~W}$, two groups with high angular momentum transfer are observed, at 366 keV and 598 keV . These two groups probably belong to the $9 / 2$ $9 / 2-[505]$ and the $13 / 211 / 2+[615]$ particle excitations, but it is difficult to distinguish between them since both states are expected to be populated with cross sections of 30 to $60 \mu b / s r$. Energy systematics of the $11 / 2+[615]$ orbital would suggest the lower state to be the $13 / 2+$ state and it is shown as such in the figures although there are some problems with this choice of assignments. For example, with the $9 / 2-[505]$ state placed at 598 keV , a mixing calculation predicts that the $9 / 29 / 2-[505]$ and the $9 / 27 / 2-[503]$ states should receive comparable cross sections of 20 to $30 \mu b / s r$. The ( $d, p$ ) spectrum shows no indication of the latter state; its cross section is certainly


Fig. 12. Level scheme for ${ }^{183} \mathrm{~W}$. See caption to Fig. 10.
less than $5 \mu b / s r$. A further difficulty is our failure* to observe an isomeric state in ${ }^{187} \mathrm{~W}$, analogous to the 100 seconds $11 / 211 / 2+[615] E 3$ isomer ${ }^{26)}$ at 197.8 keV in ${ }^{185} \mathrm{~W}$. In summary, although the two observed high spin levels probably represent the $13 / 211 / 2+[615]$ and $9 / 29 / 2-[505]$ states, no clear choice between the alternative interpretations can be made here.

### 4.8. The $N=6$ Orbitals from the $i_{13 / 2}$ Shell

For the seven $N=6$ orbitals with $K=1 / 2$ to $K=13 / 2$ stemming from the $i_{13} / 2$ spherical state only the $13 / 2+$ rotational band members are predicted to be populated with appreciable cross sections. As mentioned before, these states are difficult to isolate by the $(d, t)$ or by the ( $d, p$ ) reaction alone. However, those lying below the Fermi surface are clearly identified ${ }^{11)}$ by the combined information from the $(d, t)$ and the $\left({ }^{3} \mathrm{He}, \alpha\right)$ reactions. In the wolfram nuclei the Fermi surface is situated close to the $11 / 2+[615]$

[^29]

Fig. 13. Level scheme for ${ }^{185} \mathrm{~W}$. See caption to Fig. 10.
orbital and one therefore expects to observe six $13 / 2+$ states in a pick-up reaction. However, at excitation energies up to 4 MeV only four $13 / 2+$ states appear in the $\left({ }^{3} \mathrm{He}, \alpha\right)$ spectra for ${ }^{185} \mathrm{~W}$ and ${ }^{183} \mathrm{~W}$, and only two for ${ }^{181} \mathrm{~W}$ where the Fermi surface is closer to the $9 / 2+[624]$ orbital. The total observed $l=6$ cross section, though, in each case sums up to the total cross section predicted for all the $13 / 2+$ states.

A mixing calculation ${ }^{11)}$ starting from a conventional Nilsson model does not remotely reproduce either the energies or cross sections, or even the number of states observed. Furthermore, it is easily seen that the alteration required is a general compression of the unperturbed energy spacings for the low $K$-value orbitals. Nilsson model calculations which include a hexadecapole or $\varepsilon_{4}$ deformation ${ }^{34)}$ demonstrate that the energies for those orbitals in the wolfram region are indeed strongly compressed relative to the case with $\varepsilon_{4}=0$. A Coriolis mixing calculation using the band head energies calculated from the Nilsson model with inclusion of an $\varepsilon_{4}$ deformation $\left(\varepsilon_{4}=+0.06\right)$ correctly accounts for the observed number of states in ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$ and gives reasonable values for energies and cross sections. In ${ }^{181} \mathrm{~W}$ it predicts three states with strong population ${ }^{11)}$.

Due to the reduced energy spacing, the higher lying orbitals mix more


Fig. 14. Level scheme for ${ }^{187} \mathrm{~W}$. See caption to Fig. 10. The assignments of the two levels labelled B* may be reversed (cf. Sect. 4.7).
strongly and hence lose essentially all their cross section. The experimental energies for all three nuclei could be reproduced almost exactly by only minor alterations of the Nilsson model ${ }^{34)}$ single particle energy spacings. The calculated cross sections are then also in good agreement with experiment.

Hexadecapole deformations have previously been established from inelastic scattering of deuterons ${ }^{35)}$ and, more recently, of $\alpha$-particles ${ }^{36)}$. The evidence adduced here is an independent confirmation as it does not depend on the details of the reaction mechanism but only on the single particle level energy spacings and the relative sizes of cross sections.

Coriolis fits to the $13 / 2+$ states identified and to other $N=6$ states known from previous studies of the wolfram nuclei suggested approximate energies for the $9 / 2+$ band members which are the only additional states expected with measurable cross sections. Because of the strong mixing there are usually few such states, and it was possible in most cases to locate corresponding groups in the spectra.

In ${ }^{179} \mathrm{~W}$, where no $\left({ }^{3} \mathrm{He}, \alpha\right)$ data are available, the lowest lying $13 / 2+$ state is observed at 468 keV by the ( $d, t$ ) reaction with at least twice the cross section for a pure Nilsson state. A similar ( $d, t$ ) cross section enhancement is observed for the lowest $13 / 2+$ state in the other wolfram nuclei. The $9 / 2$ and $11 / 2$ members of the $9 / 2+[624]$ band in ${ }^{179} \mathrm{~W}$ have been previously ${ }^{23)}$ placed at 308.7 keV and 421.2 keV . The latter of these states is, however, not confirmed in a recent study ${ }^{37)}$ of the ${ }^{178} \mathrm{Hf}(\alpha, 3 n \gamma){ }^{179} \mathrm{~W}$ reaction.

In ${ }^{181} \mathrm{~W}$, where the $9 / 2+[624]$ orbital is the ground state, only two $13 / 2+$ states are observed, at 250 keV and 1124 keV , but with a cross section sum


Fig. 15. Theoretical $Q$-dependence of the transfer reaction cross sections. The average $Q$ dependence used for $Q$-reduction of the measured cross sections is shown in the lower part of the figure.
corresponding to that of the five $13 / 2+$ hole states expected. A $7 / 2+$ state at 954 keV has been assigned in decay studies ${ }^{24)}$ and a $9 / 2+$ state at 996 keV has been tentatively assigned on the basis of the coupling calculations ${ }^{11)}$.

In ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$ four $13 / 2+$ states have been identified as mentioned above. Also, the $9 / 2+[624]$ band head is clearly observed in the spectra for both nuclei. The state was known previously ${ }^{25)}$ in ${ }^{183} \mathrm{~W}$, and it was here identified in ${ }^{185} \mathrm{~W}$ at 716 keV (cf. sect. 4.7.). In each nucleus, one further $9 / 2+$ state has been tentatively assigned mainly on the basis of the calculations. The $11 / 2+[615]$ band head was known previously from radioactive decay studies ${ }^{25},{ }^{26)}$ in both nuclei.

The states of ${ }^{187} \mathrm{~W}$ could not be studied by pick-up reactions. The position of the lowest $13 / 2+$ state is discussed in sect. 4.7.


Fig. 16. The reduced cross section angular distributions for previously assigned states populated with $\sigma_{\exp }\left(90^{\circ}\right)>20 \mu b / s r$ in the $(d, p)$ and $(d, t)$ reactions on the ${ }^{186} \mathrm{~W}$ target.


Fig. 17. The reduced cross section angular distributions for all states populated with $\sigma_{\exp }\left(90^{\circ}\right)>20 \mu b / s r$ in the $(d, p)$ and $(d, t)$ reactions on the ${ }^{186} \mathrm{~W}$ target. The inferred $l$-transfer values are indicated.

### 4.9. High-lying Particle Excitations

As discussed in the preceding sections the majority of groups observed below 1 MeV of excitation can be explained in a quantitative manner. Only a few groups of appreciable intensity remain unassigned, e.g. the 666 keV and 733 keV levels in ${ }^{185} \mathrm{~W}$ which are populated strongly in both the ( $d, p$ ) and ( $d, t$ ) reactions.

As mentioned earlier, the Nilsson model predicts a distinct energy gap above neutron number 118 and this is reflected in the corresponding region of all the ( $d, p$ ) spectra by a sharp reduction in level density. A number of unassigned groups above this energy gap suggests possible fractionation of strong particle excitations. Several such excitations are expected according to the Nilsson model among which are the orbitals $1 / 2+[651], 3 / 2+[642]$, $3 / 2-[501], 5 / 2-[503]$ and $1 / 2-[501]$. Of these, the two positive parity orbitals arising from the $g_{9} / 2$ spherical state have generally been difficult to locate although a few tentative identifications have been made in rare earth nuclei ${ }^{2}$. The difficulties may be partly attributed to the fact that Nilsson model predictions for these orbitals are highly sensitive to the values of the


Fig. 18. (a), (b) and (c). Theoretical and experimental intensity patterns for the $1 / 2-[521]$, $5 / 2-$ [512], and $7 / 2-$ [514] bands in the odd W nuclei.
parameters $\delta, \varkappa$ and $\mu$ adopted. Calculations ${ }^{38)}{ }^{34)}$ with slightly different $\varkappa$ - and $\mu$-values lead to entirely dissimilar fingerprint patterns (fig. 20). The Coriolis matrix element between the bands and the value of the decoupling parameter for the $K=1 / 2$ band are also drastically affected by the choice of Nilsson parameters. The most substantial evidence for the identification of these orbitals is available for the ${ }^{175} \mathrm{Yb}$ nucleus ${ }^{39)}$ where the two bands are located 500 to 1000 keV above the $3 / 2-[512]$ band. In the less deformed wolfram nuclei, the bands are expected to lie even higher above the $3 / 2-$ [512] band than in ${ }^{175} \mathrm{Yb}$ and accordingly it seems likely that some of the unassigned ( $d, p$ ) groups in the 1 to 2 MeV excitation energy range correspond to members of the bands in question. A recent ( $p, p^{\prime}$ ) study ${ }^{40}$ ) indicates an excitation energy of approximately 1300 keV for the $g_{9} / 2$ strength in ${ }^{185} \mathrm{~W}$. However, no specific assignments have been possible, partly because of the aforementioned uncertainties in band characteristics and partly because our angular distribution results do not clearly indicate the parity of the observed states.


Fig. 19. (a) and (b). Theoretical and experimental intensity patterns for the $1 / 2-[510]$ and $3 / 2-[512]$ bands in the odd W nuclei.


Fig. 20. Fingerprint patterns for the $1 / 2+[651]$ and $3 / 2+[642]$ bands calculated using the Nilsson model parameters of Refs. 38 and 34.

In contrast to the orbitals just discussed, the $3 / 2-[501], 5 / 2-[503]$ and $1 / 2-[501]$ orbitals all converge towards lower energies with decreasing nuclear deformation. Very large ( $d, p$ ) cross sections (500 to $1000 \mu b / s r$ ) are predicted for these states and the corresponding groups should be expected to appear prominently in the $(d, p)$ spectra. In fact, none of the unexplained peaks in the spectra exceeds $300 \mu b / s r$. The only conclusion which can be drawn from the data is that the strength of these orbitals is spread over several groups. It should be noted that bands tentatively identified with the $3 / 2-[501]$ orbital in hafnium ${ }^{41)}$ and osmium ${ }^{42)}$ nuclei are populated with $(d, p)$ cross sections considerably smaller than those predicted for this band.

Arguments can be made in favour of interpreting the 641 keV state in ${ }^{187} \mathrm{~W}$ as the $5 / 2-[503]$ band head. The results of a neutron capture gammaray study ${ }^{30}$ ) provide support for the assignment, as the state in question was observed to de-excite predominantly to the $7 / 27 / 2-[503]$ level; in
 indicate $I^{\pi}=5 / 2$ - for that state. However, the $(d, p)$ cross section is five times lower than predicted and for this reason the assignment cannot be made with conviction.

The apparent fractionation of the high-lying $N=5$ particle excitations seems to be a quite general feature for the hafnium, wolfram and osmium nuclei ${ }^{41,42)}$. It is probably significant that at the deformations of these nuclei the three pairs of quasi-intersecting orbitals $3 / 2-[501]-3 / 2-[761]$, $5 / 2-[503]-5 / 2-[752]$ and $1 / 2-[501]-1 / 2-[770]$ occur close together. A recent theoretical study ${ }^{44}$ ) of $\Lambda N=2$ mixing in which a hexadecapole term was included in the nuclear deformation indicates that very strong mixing occurs between these pairs of orbitals in the wolfram region which may in part be the explanation for the observed fractionation.

### 4.10. Comparison of Experimental and Calculated Transfer Strengths

An overall measure of the agreement between the experimental data and the DWBA predictions is obtained by comparing the total observed cross section to the values calculated for these states. This comparison is given in table 9 . The ratios $S$ of the observed and theoretical cross sections for the individual Nilsson orbitals are calculated from the total cross section into all rotational members of each particular band; the effects of Coriolis mixing are included in these numbers. More detailed results for the individual band members are contained in tables 13 to 17 .

As was discussed in the preceding section it was not possible to locate the higher lying particle excitations expected from the Nilsson diagram. The

Table 9. Ratios $S=\sigma_{90^{\circ}}^{e x p} / \sigma_{90^{\circ}}^{\text {calc }}$ of experimental and calculated cross section for the $N=5$ Nilsson orbitals.

| Nilsson orbital | $S(d, p)$ |  |  |  |  | $S(d, t)$ |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | ${ }^{181} \mathrm{~W}$ | ${ }^{183} \mathrm{~W}$ | ${ }^{185} \mathrm{~W}$ | ${ }^{187} \mathrm{~W}$ | ${ }^{179} \mathrm{~W}$ | ${ }^{181} \mathrm{~W}$ | ${ }^{183} \mathrm{~W}$ | ${ }^{185} \mathrm{~W}$ |  |
| $9 / 2-[505] \ldots .$. | - | 0.38 | 0.40 | 0.52 | - | - | - | $(2.5)^{\mathrm{a}}$ |  |
| $7 / 2-[503] \ldots$. | 0.91 | 0.77 | 0.91 | 0.57 | - | 1.07 | 1.44 | 2.13 |  |
| $3 / 2-[512] \ldots$. | 0.64 | 0.72 | 1.13 | 1.07 | - | 1.33 | 1.23 | 1.22 |  |
| $1 / 2-[510] \ldots .$. | 0.55 | 1.10 | 1.58 | 2.05 | 1.02 | 0.24 | 1.07 | 0.89 |  |
| $5 / 2-[512] \ldots .$. | 0.56 | $(4.0)^{\mathrm{a}}$ | $(3.9)^{\mathrm{a}}$ | - | 0.76 | 0.91 | 1.14 | 1.03 |  |
| $1 / 2-[521] \ldots .$. | 1.04 | $(1.0)^{\mathrm{a}}$ | $(<2.7)^{\mathrm{a}}$ | - | 0.85 | 1.06 | 1.01 | 0.67 |  |
| $7 / 2-[514] \ldots$. | $<0.3$ | $(2.9)^{\mathrm{a}}$ | $(3.0)^{\mathrm{a}}$ | - | $0 b 5 c$ | 0.74 | 1.14 | 0.82 |  |
| Total $^{\mathrm{b}} \ldots \ldots .$. | 0.70 | 0.88 | 1.15 | 1.03 | 0.82 | 0.92 | 1.09 | 0.93 |  |

a The numbers in brackets refer to Nilsson bands which by the particular reaction are weakly populated.
b The $S$-values given in this line refer to the total cross section for all assigned groups.
experimental data show an increased ( $d, p$ ) strength for the higher mass numbers suggesting that these orbitals lie highest in ${ }^{183} \mathrm{~W}$. The total unassigned $90^{\circ}$, $Q$-reduced ( $d, p$ ) cross section below 2 MeV of excitation is $1.5 \mathrm{mb}, 2.1 \mathrm{mb}$, and 2.7 mb in ${ }^{183} \mathrm{~W},{ }^{185} \mathrm{~W}$, and ${ }^{187 \mathrm{~W}}$, respectively.

### 4.11. Single Particle Level Scheme

All Nilsson orbitals identified are compiled in fig. 21 which gives the band head excitation energies in the different wolfram nuclei. Particle excitations are shown above, hole excitations below the ground state. Except for the hole states in ${ }^{179} \mathrm{~W}$ the Nilsson states occur in a fairly regular sequence.

An attempt to extract the corresponding single particle level schemes is shown in fig. 22 where the nuclei are arranged in order of increasing deformation. Also shown are the Nilsson model predictions ${ }^{34}$ ) for ${ }^{187} \mathrm{~W}$ and ${ }^{179} \mathrm{~W}$. The experimental level schemes were placed such that the $1 / 2-[510]$ orbital varies smoothly in energy from ${ }^{187} \mathrm{~W}$ to ${ }^{179} \mathrm{~W}$. The experimental single particle energy spacings were obtained by eq. (3) from the band head excitation energies, corrected for the (usually small) effects of Coriolis mixing and from the adopted Fermi surface locations discussed in sect. 5.2. Since the latter could be determined only approximately, the level spacings close to the Fermi surface might not be very accurate. The rather irregular behaviour of the $9 / 2+[624]$ and $7 / 2-[514]$ orbitals might in part be at
tributed to such uncertainties. However, the discontinuities of the deeper lying hole states cannot be explained in that way.

The variation in the energy spacing of the $7 / 2-[503]$ orbital relative to the $3 / 2-[512]$ and $1 / 2-[510]$ orbitals is somewhat unexpected. In contrast to predictions this spacing decreases towards larger deformations; in ${ }^{181} \mathrm{~W}$ the $7 / 2-[503]$ state even lies below the $3 / 2-[512]$ orbital. This result may be related to the hexadecapole contribution to the nuclear deformation. It is noted that two recent theoretical investigations ${ }^{34,45)}$ appear to lead to conflicting conclusions as to the relative variation of the hexadecapole term in the wolfram nuclei, which result in opposite trends for the $7 / 2-$ [503] single particle energy through these nuclei. The observed energy variation is in accord with a hexadecapole term increasing towards higher mass numbers as predicted in ref. ${ }^{45)}$. A similar variation of the hexadecapole term is indicated by the results of a recent $\left(d, d^{\prime}\right)$ study ${ }^{46)}$.

## 5. Coriolis Coupling of the $N=5$ Orbitals

The Coriolis mixing calculations discussed here concern the odd parity $N=5$ Nilsson orbitals*. These orbitals, which were treated separately in sects. 4.1 to 4.7 , are coupled with matrix elements which typically are of the order of 100 keV . As the seven orbitals considered are observed within a range of excitation of approximately 1 MeV , it is clear that the coupling in several cases will be of decisive importance for the observed spectra. The values of $\langle | j-| \rangle$ entering the matrix elements of eq. (7) for the orbitals of the wolfram region are compiled in table 10 .

Table 10. Theoretical values of $\langle K| j-|K+1\rangle$ and of $-a_{1} / 2$ for the orbitals identified in the wolfram nuclei.
(The Nilsson model parameters are $\delta=0.22, \chi=0.0637, \mu=0.42^{48)}$ ).

|  | $9 / 2-[505]$ | $7 / 2-[503]$ | $3 / 2-[512]$ | $1 / 2-[510]$ | $5 / 2-[512]$ | $1 / 2-[521]$ | $7 / 2-[514]$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $9 / 2-[505]$ |  | -0.973 |  |  |  |  | 2.847 |
| $7 / 2-[503]$ | -0.973 |  |  | 2.858 |  |  |  |
| $3 / 2-[512]$ |  |  | 0.951 | 0.045 | 2.546 |  |  |
| $1 / 2-[510]$ |  | 2.858 | 0.045 | -0.003 |  | -2.541 |  |
| $5 / 2-[512]$ |  | 2.546 | -2.541 |  |  | -1.151 |  |
| $1 / 2-[521]$ |  |  |  |  |  |  |  |
| $7 / 2-[514]$ | 2.847 |  |  |  |  |  |  |

[^30]The wolfram nuclei are favourable for an extensive test of the mixing effects because of the completeness of the experimental material. Thus all the odd parity orbitals expected from the Nilsson diagram have been identified, and energies and cross sections are known for about 20 levels of these odd parity bands in each nucleus.

In the mixing calculations, the unperturbed band head energy, the rotational energy parameter $A_{K}$ and the decoupling parameter $a_{1 / 2}$ for each band were considered as unknowns to be determined from the experimental level energies. The Coriolis coupling matrix elements on the other hand, were fixed by the Nilsson value (eq. (7)) with definite prescriptions for the empirical attenuation coefficients $\eta$ which will be discussed below. The number of experimentally known level energies always exceeded the number of unknows. Final values for the unperturbed band head energies and rotational parameters were determined by a fitting procedure which was interrupted when the level energies were reproduced to within an accuracy of about 1 keV . The most stringent test of the calculations centred on the comparison of the experimental cross sections with those calculated using the mixed wave functions obtained by fitting the excitation energies.

### 5.1. Methods of Calculations

The Coriolis coupling calculations were performed with an Algol code that diagonalized the interaction matrix and calculated the perturbed energy eigenvalues and wave functions as well as the transfer reaction cross sections. The input includes the single particle cross sections $\varphi_{l}$ and the inertial strength parameter $\hbar^{2} / 2 \mathfrak{F}$ entering the matrix elements as well as, for each band, the band head energy, the rotational energy parameters $A_{K}$ and $a_{1 / 2}$, the empirical attenuation factor $\eta_{K}$, the occupation amplitudes $U$ and $V$, and the Nilsson wave function. The inertial strength parameter $\hbar^{2} / 2 \mathfrak{J}$ is taken as the average of the values derived from the $2+$ energies in the neighbouring even nuclei. The occupation amplitudes were calculated for each orbital from the unperturbed band head energies and the Fermi surface location $\lambda$ by eqs. (3) and (4). The Nilsson wave functions used were those calculated for the Nilsson parameters $\delta=0.22, \chi=0.0637$ and $\mu=0.420^{48)}$.

All the observed negative parity bands were included in the calculations (see fig. 21 for the bands included for each nucleus). Tests were made of the effects of unobserved bands by including them in separate calculations both at their Nilsson energies and at strongly reduced energies and with exaggerated coupling strengths to obtain limits on their effects. Only


Fig. 21. Bandhead energies of the Nilsson orbitals identified by neutron transfer. Points at negative energies indicate hole states.
the $5 / 2-[523]$ band had appreciable effects on the lower lying levels and even here no serious alterations occurred.

### 5.2. Fermi Surface Location

As the coupling matrix elements and the calculated cross sections both depend on the $U$ 's and $V$ 's, it was necessary to estimate the energy $\lambda$ of the Fermi surface for each nucleus. The convenient prescription locating it at the ground state proved to be insufficient for the low lying orbitals. The Fermi surfaces were approximately determined by comparing ratios of ex-


Fig. 22. Single particle level schemes for the odd W nuclei extracted from the experimental bandhead energies and the adopted Fermi surface locations. The Nilsson model predictions are from Ref. 34.
perimental ( $d, p$ ) and ( $d, t$ ) cross sections for certain low lying states with the theoretical values calculated as a function of the parameter $\lambda$. The levels chosen for these determinations were those least affected by mixing from high lying states and with large and accurately known cross sections. As the low lying states themselves are usually strongly mixed, the theoretical ratios had to be evaluated with all mixing effects included.

The procedure used is illustrated in fig. 23 for the ${ }^{183} \mathrm{~W}$ nucleus. In this case the most suitable states are the $3 / 21 / 2-[510]$ and $5 / 21 / 2-[510]$ states, and in the figure the experimental and calculated ratios of $(d, t)$ to ( $d, p$ ) cross sections for these states are compared. The results indicate that in this nucleus the Fermi surface is located about 150 keV below the
$1 / 2-[510]$ band head. A similar procedure was used in the cases of ${ }^{181} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$. No ( $d, p$ ) data are available for ${ }^{179} \mathrm{~W}$ and so the Fermi surface was placed at the ground state; since, however, essentially no mixing occurs in this nucleus the placement is not crucial. In ${ }^{187} \mathrm{~W}$ where no ( $d, t$ ) data exist, the Fermi surface was also placed at the ground state. The adopted Fermi surface locations which were subsequently used in all calculations are indicated in fig. 22.

### 5.3. Empirical Coriolis Coupling Strength

As mentioned in sect. 2, it has empirically been found that the Coriolis matrix elements calculated from the Nilsson model generally are too large. Hence the attenuation factors $\eta_{K}$ were introduced in eq. (7). The product $\eta_{K} \cdot \eta_{K+1}$ is the attenuation for the Nilsson coupling strength between the orbitals with projection quantum numbers $K$ and $K+1$. As already mentioned the inertial strength parameter $\hbar^{2} / 2 \mathfrak{J}$ also entering in (7) was kept at its value in the even isotopes, and all deviations between theory and experiment are thus included in the $\eta_{K} \cdot \eta_{K+1}$ factor.

Fits to the observed energies were attempted with a variety of attenuation prescriptions, and the calculated cross sections were compared to experiment. Semiquantitative criteria for good and bad agreement between theoretical and experimental cross sections were adopted and these were used consistently in judging whether the execution of a new calculation had brought about an overall improved agreement between theory and experiment. In this way the attenuation factors to be discussed below were arrived at.

Initial coupling calculations performed with full coupling strength ( $\eta_{K} \cdot \eta_{K+1}=1$ ) in ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$ gave good agreement with experimental results for the strongly mixed low lying $1 / 2-[510]$ and $3 / 2-[512]$ bands. However, difficulties were encountered for several high lying states in these nuclei; although the inclusion of mixing improved the agreement between calculated and experimental cross sections, it was impossible to reproduce the experimental energies. Calculations performed at half and quarter strengths (i.e. $\eta_{K} \cdot \eta_{K+1}=0.5$ and 0.25 ) did reproduce the experimental energies and also the cross section agreement was improved. Still better agreement was, however, obtained by the use of full strength for all matrix elements except those involving either or both the $7 / 2-[514]$ and $5 / 2-[512]$ bands. In the wolfram nuclei the latter two orbitals predominantly mix with each other and the ratio of transfer cross sections for their $7 / 2-$ states is critically dependent upon the amount of mutual mixing. In order to re-


Fig. 23. Fermi surface location in ${ }^{183} \mathrm{~W}$. The result is indicated by an arrow.
produce the experimental cross sections for these two $7 / 2-$ states in ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$, a rather strong attenuation $\left(\eta_{5 / 2} \cdot \eta_{7 / 2}=0.25\right)$ is required. A good overall description for the experimental data in ${ }^{183} \mathrm{~W}$ was obtained by using full coupling strength for all matrix elements except those involving the two orbitals mentioned which were each kept at an attenuation of $\eta=0.5$. An identical procedure also gave good results for ${ }^{185} \mathrm{~W}$ where the Nilsson states occur at similar excitation energies as in ${ }^{183} \mathrm{~W}$.

For both nuclei slightly better results were actually obtained if the matrix elements connecting the $1 / 2-[521]$ orbital with the bands in the ground state region were also reduced. This reduction, however, arises naturally out of the attenuation prescription which subsequently evolved and was finally adopted.

However, application of the same attenuations in ${ }^{181} \mathrm{~W}$ gave very poor results. In this nucleus, the $5 / 2-[512]$ and $7 / 2-[514]$ bands occur at about 400 keV excitation, and the strongly attenuated coupling strength ( $\eta_{5 / 2} \cdot \eta_{7 / 2}$ $=0.25$ ) required in ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$ could not bring the calculated cross sections into agreement with the data; a smaller reduction in coupling strength was indicated $\left(\eta_{5 / 2} \cdot \eta_{7 / 2} \simeq 0.50\right)$. In addition, the coupling strength for the $1 / 2-[510]$ and $1 / 2-[521]$ bands which also occur close together at about 400 keV excitation in ${ }^{181} \mathrm{~W}$ had to be substantially attenuated in order to obtain even fair agreement with experiment.

The required attenuations for the pairs of orbitals just discussed are shown in fig. 24 a. These results suggest that the same matrix element requires different attenuations in different nuclei. Guided by the results shown in fig. 24 a, we therefore performed coupling calculations in which each wave function was attenuated with an $\eta_{K}$ decreasing linearly with the excitation energy of the band head. The specific slope chosen was determined


Fig. 24. (a) Empirical Coriolis matrix-element attenuation factors in different wolfram nuclei shown as a function of the average excitation energy of the two admixed bands. (b) Energy dependence of the attenuation factors $\eta_{K}$ adopted in the coupling calculations.
by requiring that the calculated ratio of ( $d, t$ ) cross sections into the $7 / 2$ $7 / 2-[514]$ and $7 / 25 / 2-[512]$ states in ${ }^{183} \mathrm{~W}$ should be identical to the measured ratio. With the $\eta_{K}$ fixed by this prescription, an identical energy dependence was used for ${ }^{179}, 183-187 \mathrm{~W}$; a slightly stronger decrease was optimal for ${ }^{181} \mathrm{~W}$ (see fig. 24 b ). The same empirical rule for $\eta_{K}$ also gave optimal results for the positive parity states in these nuclei ${ }^{11)}$. Other prescriptions for the $\eta_{K}$ factors also yield improved agreement with experiment but the best agreement was obtained with that described here.

The adopted attenuation prescription is arbitrary to the extent that it is based on the transfer cross sections to two particular strongly coupled states. Indeed our analysis leaves unexplained appreciable systematic deviations between experimental and calculated cross sections for a few other states. That no such deviations occur for the two crucial $7 / 2-$ states was inherently assumed in arriving at the specific attenuation prescription. In


Fig. 25. Calculated and experimental (d,t) cross sections for the $1 / 2-[510]$ and $3 / 2-[512]$ bands in ${ }^{185} \mathrm{~W}$.
any case, it is clear that certain matrix elements must be substantially attenuated in order to reproduce the observed energies and cross sections.

At present, the origin of this attenuation and the variation in different nuclei is not understood, but the prescription adopted here might be given the physical rationale that small contributions from many higher lying unobserved bands not included among the basis states tend to affect the observed states at higher excitation energy more than those near the ground state. A difficulty, however, is that an attenuation of the decoupling parameter for the $1 / 2-[521]$ band is not simultaneously observed, nor are the cross sections for high lying bands generally diminished. It may be best to treat the above prescription as only an empirical rule; it may merely sim-
$1 / 2^{-}$[510] band


Fig. 26. Calculated and experimental cross sections for the $1 / 2-[510]$ and $3 / 2-$ [512] bands in ${ }^{183} \mathrm{~W},{ }^{185} \mathrm{~W}$ and ${ }^{187} \mathrm{~W}$. The unperturbed fingerprint patterns which are essentially identical for both the $(d, p)$ and $(d, t)$ reactions are shown above. (In ${ }^{187} \mathrm{~W}$ the $1 / 21 / 2-[510]$ and $7 / 2$ $3 / 2-[512)$ state were not observed; the experimental ( $d, p$ ) cross sections are less than $8 \mu b / s r$ ).
ulate a dependence of the Coriolis coupling strength on parameters not considered in the present calculations.

Once the attenuation prescription was chosen, the coupling calculations


Fig. 27. Calculated and experimental $(d, p)$ cross sections for the $1 / 2-[521]$ band in ${ }^{181} \mathrm{~W}$.
were performed to reproduce the observed excitation energies only. Using the wave functions obtained from this energy fit, and with no further variation of parameters, the cross sections were calculated and compared with the experimental values. The results are given in the following section.

### 5.4. Analysis of Results for Coriolis Coupled Bands

All the unperturbed, the Coriolis perturbed, and the measured energies and cross sections are given in tables 13 to 17 to which reference should be made for numerical results. The figures discussed below illustrate some of the more striking consequences of the mixing.

As was mentioned in sect. 4 it is often found that the experimentally observed fingerprint patterns bear little resemblance to those calculated with no mixing included (cf. figs. 18 and 19). A specific example, the ( $d, t$ ) cross sections for the $1 / 2-[510]$ and $3 / 2-$ [512] bands in ${ }^{185} \mathrm{~W}$, is shown in fig. 25 where the inclusion of Coriolis mixing in the calculation brought about a spectacularly improved agreement between calculated and experimental cross sections. In this nucleus the effects of mixing are particularly


Fig. 28. Cross section systematics of members of the $3 / 2-[512]$ band in ${ }^{181} \mathrm{~W}$ to ${ }^{187} \mathrm{~W}$. The experimental cross sections are normalized with the indicated multiplicative numbers (see discussion in Sect. 5.4).
drastic since the two bands lie very close together. In ${ }^{183} \mathrm{~W}$ and ${ }^{187} \mathrm{~W}$, where these bands also occur at low excitation energies, the coupling calculations were similarly successful in accounting for all the observed cross sections (fig. 26).

Another example of Coriolis coupling having a striking influence on the population cross sections is seen in ${ }^{181} \mathrm{~W}$, where the $1 / 2-[510]$ and $1 / 2-[521]$ bands occur at similar excitation energies but on opposite sides of the Fermi surface. In the $(d, p)$ spectra, the $3 / 2-$ and $7 / 2-$ members of the $1 / 2-[521]$ band are seen with much larger intensities than expected from pairing


Fig. 29. Cross section systematics of members of the $1 / 2-[510]$ band in ${ }^{181} \mathrm{~W}$ to ${ }^{187} \mathrm{~W}$. See caption to Fig. 28.
theory while the $1 / 2-$ and $5 / 2-$ members have about the expected intensities. The two $K=1 / 2$ bands are coupled by a fairly large matrix element and the resulting particle hole mixing effects are illustrated in fig. 27 for the $(d, p)$ cross sections into the members of the $1 / 2-[521]$ band. It is a consequence of the signs and relative magnitudes of the $C_{j l}$ coefficients and the mixing amplitudes that in this case only certain states are populated with large cross sections in both ( $d, p$ ) and ( $d, t$ ) reactions; the two cross sections arise from the different parts of the wave function which retain their respective occupation amplitudes in the mixed states. Some other features of the ${ }^{181} \mathrm{~W}$ analysis are however less satisfactory, e.g. the anomalous


Fig. 30. Cross section systematics of members of the $7 / 2-[514]$ band in ${ }^{179} \mathrm{~W}$ to ${ }^{185} \mathrm{~W}$. See caption to Fig. 28.
decoupling parameters obtained for the unperturbed $K=1 / 2$ bands (table 11). Even more disturbing is the poor agreement between calculation and experiment for the strongly populated $3 / 21 / 2-[510]$ state (table 14 ). This disagreement is, in fact, the largest discrepancy between theory and experiment encountered in the present work and is probably not associated with Coriolis coupling.

It has been observed that the $(d, t)$ cross sections for particle states and the $(d, p)$ cross sections for hole states are generally larger than predicted by pairing theory (cf. table 9). These observations may reflect the individually small contributions from neglected states on the opposite of the Fermi surface.

An important aspect of this study is the investigation of certain coupling matrix elements in several nuclei. Due to the different relative excitation energies of the Nilsson bands the coupling of the same bands can give rise


Fig. 31. Cross section systematics of members of the $5 / 2-[512]$ band in ${ }^{179} \mathrm{~W}$ to ${ }^{185} \mathrm{~W}$. See caption to Fig. 28.
to distinctive cross section variations from nucleus to nucleus. Systematic cross section examinations of this kind tend to distinguish between coupling effects and deviations from theory arising from other sources; the latter are expected to vary little with mass number. It is indeed found that the absolute cross sections for certain states deviate systematically in all nuclei from the calculated values. The deviation may be due to deficiencies in the Nilsson wave functions or to second order (coupled channel) effects in the reaction mechanism. Empirical normalization factors were therefore applied in figs. 28 to 31 to remove these deviations.

The cross section systematics for the $3 / 2-[512]$ band and its prominent mixing partner, the $1 / 2-[510]$ band are shown in figs. 28 and 29. The pairing theory predicts a smooth cross section variation of about a factor two through the wolfram nuclei, whereas the observed cross sections vary by factors of 10 to 100 . The sudden change in all cross sections from ${ }^{183} \mathrm{~W}$

Table 11. Observed and unperturbed energy parameters $A_{K}$, in keV, and $a_{1 / 2}$ (in paranthesis) for negative parity rotational bands in the wolfram nuclei.

| Nilsson band | ${ }^{179} \mathrm{~W}$ |  | ${ }^{181} \mathrm{~W}$ |  | ${ }^{183} \mathrm{~W}$ |  | ${ }^{185} \mathrm{~W}$ |  | ${ }^{187} \mathrm{~W}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | observed ${ }^{\text {a }}$ | unper- <br> turbed | observed $^{\mathrm{a}}$ | unper- <br> turbed | observed ${ }^{\text {a }}$ | unper- <br> turbed | $\left\|\begin{array}{c} \text { op- } \\ \text { served } \end{array}\right\|$ | unper- <br> turbed | observed ${ }^{a}$ | unper- <br> turbed |
| 7/2-[503] |  |  |  |  | 15.8 | 16.1 | 16.4 | 16.9 |  |  |
| $3 / 2-[512]$ |  |  | 16.2 | 16.7 | 16.6 | 16.1 | 13.1 | 16.2 | 15.5 | 17.0 |
| $1 / 2-[510]$ |  |  | 15.0 | 13.1 | 13.0 | 14.4 | 21.1 | 18.8 | 19.7 | 17.6 |
|  |  |  | (0.59) | (0.71) | (0.19) | (0.16) | (0.11) | (0.09) | (0.00) | (-0.04) |
| $5 / 2-[512]$ | 14.5 | 14.1 | 15.7 | 13.5 | 13.8 | 13.9 | 14.0 | 14.0 |  |  |
| $1 / 2-[521]$ | 15.2 | 16.0 | 14.6 | 17.0 | 18.2 | 17.5 | 16.7 | 15.9 |  |  |
|  | $(0.82)$ | $(0.79)$ | $(0.48)$ | $(0.40)$ | (0.70) | (0.72) | (0.86) | (0.90) |  |  |
| 7/2-[514] | 13.3 | 13.6 | 13.3 | 15.9 | 16.3 | 16.1 | 17.8 | 17.6 |  |  |
| A average | 14.3 | 14.6 | 15.0 | 15.2 | 15.5 | 15.7 | 16.5 | 16.6 | 17.6 | 17.3 |
| A even ${ }^{\text {b }}$ |  | 17.4 |  | 17.0 |  | 17.6 |  | 19.5 |  | 21.9 |

a Extracted from experimental energies of lowest two (for $K=1 / 2$ three) band members.
b Average of $A$-values for the two neighbouring even nuclei.
to ${ }^{185} \mathrm{~W}$ is caused by the interchange of the positions of the two orbitals. In ${ }^{181} \mathrm{~W}$ and ${ }^{183} \mathrm{~W}$, the $1 / 2-[510]$ band lies below the $3 / 2-[512]$ band while in ${ }^{185} \mathrm{~W}$ and ${ }^{187} \mathrm{~W}$ their positions are reversed. The Coriolis mixing merely gives rise to a redistribution of population cross section between the states of equal angular momentum $I$ without altering the total cross section to that $I$. This feature is most readily seen for the $I=5 / 2$ states of the two bands.

The $7 / 2-[514]$ and $5 / 2-[512]$ Nilsson orbitals, which form another pair of strongly coupled bands, are illustrated in figs. 30 and 31. The predominant feature of their mixing appears in the $7 / 2-$ band members which have very different $C_{j l}$ coefficients. The coupling therefore affects the $7 / 2$ $5 / 2-[512]$ state, which has the large $C_{j l}$ value, only slightly, while the same mixing amplitude causes a drastic cross section alteration for the $7 / 2$ $7 / 2-[514]$ state.

A less specific but broader view of the Coriolis mixing is provided by the data shown in table 11. Here the rotational energy parameters for the negative parity bands in the wolfram nuclei are given together with the values for the corresponding unperturbed bands. Ideally the removal of
all coupling effects should cause the inertial parameters for the various bands to converge towards a single value. The fact that the unperturbed band parameters listed in the table are clearly more closely grouped than the perturbed values provides reassurance that the Coriolis coupling treatment used here is generally correct. The additional expectation that the inertial parameters of the decoupled bands should approach the value for the neighbouring even nucleus is realized to a much lesser extent. Although a slight tendency in that direction is discernible, the overall effect is less than startling. This particular departure from theoretical expectations has been observed in other nuclei ${ }^{49)}$ and is not currently understood.

## 6. Conclusions

The level structure of the five odd mass wolfram nuclei ${ }^{179} \mathrm{~W}$ to ${ }^{187} \mathrm{~W}$ has been investigated by the ( $d, p$ ), ( $d, t$ ) and ( $\left.{ }^{3} \mathrm{He}, \alpha\right)$ neutron transfer reactions. The results considerably increase the knowledge about these nuclei and provide the material for a more detailed understanding of the single particle level structure over an energy range of about 4 MeV . All Nilsson states expected in this region have been identified.

A number of unassigned groups in the ( $d, p$ ) spectra above $\sim 1 \mathrm{MeV}$ excitation energy suggest that the strong particle excitations expected above the $N=118$ energy gap are fractionated; this phenomenon may be associated with strong $\Delta N=2$ mixing.

A quantitative analysis of the Coriolis coupling between the $N=5$ Nilsson orbitals has been performed. In most cases, the inclusion of the Coriolis interaction has greatly improved the agreement between calculated and experimental cross sections. In particular, several rather tentative assignments have been solidified by examining the effects of the mixing on the theoretical cross sections. The detailed analysis has revealed that overall satisfactory agreement can be obtained for both level energies and population cross sections only if certain coupling matrix elements are reduced below their Nilsson model values. An energy dependent systematic attenuation of the matrix elements which satisfactorily accounts for the experimental observations is suggested here, but other attenuation schemes are also feasible. Attempts ${ }^{50}$ ) to provide a theoretical basis for explaining the need for attenuated Coriolis matrix elements, revealed in these and in other experimental investigations, have not thus far been successful.

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## 7. Appendix

Table 12. Nilsson wave functions ( $C_{j l}$-values for the wolfram nuclei). ( $\delta=0.22, x=0.0637, \mu=0.42^{48}$ ) .

| $K^{\pi}\left[N n_{z} \Lambda\right]$ | $C_{1 / 2,1}$ | $C_{3 / 2,1}$ | $C_{5 / 2,3}$ | $C_{7 / 2,3}$ | $C_{9 / 2,5}$ | $C_{11 / 2,5}$ |
| :---: | ---: | ---: | ---: | ---: | ---: | ---: |
| $9 / 2-[505] \ldots$. |  |  |  |  | 0.9975 | 0.0713 |
| $7 / 2-[503] \ldots$. |  |  |  | 0.9367 | -0.3358 | 0.0995 |
| $3 / 2-[512] \ldots$. |  | 0.3794 | 0.8153 | 0.2831 | 0.3275 | 0.0627 |
| $1 / 2-[510] \ldots$. | 0.0210 | -0.6763 | 0.5862 | -0.3427 | 0.2768 | 0.0671 |
| $5 / 2-[512] \ldots$. |  |  | -0.0234 | 0.8362 | -0.5249 | 0.1570 |
| $1 / 2-[521] \ldots$. | -0.5101 | 0.3452 | 0.4726 | 0.4310 | 0.4440 | 0.1198 |
| $7 / 2-[514] \ldots$. |  |  |  | 0.3226 | 0.9378 | 0.1281 |

Table 13. Comparison of unperturbed, Coriolis coupled and experimental cross sections in ${ }^{179} \mathrm{~W}\left(\theta=90^{\circ}\right)$.

| State ${ }^{\text {a }}$ | Energy (keV |  | $\sigma(d, t) \mu b / s r$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{aligned} & \text { Per- } \\ & \text { turbed } \end{aligned}$ | Experimental | Unperturbed | $\begin{aligned} & \text { Per- } \\ & \text { turbed } \end{aligned}$ | Experimental |
| 1/2 1/2-[510]. | 627 |  | 0.0 | 0.2 |  |
| $3 / 2$ | 689.3 | 689 | 10.5 | 28.9 | 22 |
| 5/2 | 788.0 | 788 | 10.9 | 19.4 | 27 |
| 5/2 5/2-[512]. | 430.3 | 430.3 | 0.2 | 0.2 | 14 |
| 7/2 | 531.6 | 531.5 | 250.8 | 259.5 | 189 |
| 9/2 | 661.6 |  | 13.3 | 9.6 |  |
| 1/2 1/2-[521]. | 221.8 | 221.7 | 242.2 | 242.1 | 218 |
| 3/2 | 304.7 | 304.6 | 110.7 | 123.2 | 53 |
| 5/2 | 317.8 | 318.2 | 74.4 | 68.8 | 58 |
| 7/2 | 508.5 | 508.4 | 61.9 | 66.6 | 90 |
| 9/2 | 534.2 | 532.7 | 8.7 | 7.8 | obsc |
| 11/2 | 822.2 | ~ 816 | 0.6 | 0.6 | $\sim 9$ |
| 7/2 7/2-[514]. | 0.0 | 0.0 | 21.1 | 12.2 | $\sim 3$ |
| 9/2 | 119.2 | 119.8 | 23.8 | 27.2 | obsc |
| 11/2 | 265.0 | 264.7 | 0.4 | 0.3 |  |

[^31]Table 14. Comparison of unperturbed, Coriolis coupled and experimental cross sections in ${ }^{181} \mathrm{~W}\left(\theta=90^{\circ}\right)$.

| State ${ }^{\text {a }}$ | Energy (keV) |  | $\sigma(d, p) \mu b / s r$ |  |  | $\sigma(d, t) \mu b / s r$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Per- <br> turbed | Experimental | Unperturbed | Perturbed | Exper- <br> imental | Unperturbed | $\begin{aligned} & \text { Per- } \\ & \text { turbed } \end{aligned}$ | Experimental |
| 7/2 7/2-[503].. | 661.8 | 661.8 | 373 | 316 | 296 | 24 | 2.7 | 45 |
| $9 / 2$ | (813.3) |  | 7 | 6 |  | 0.4 | 0 |  |
| 3/2 3/2-[512].. | 726.2 | 726.2 | 158 | 178 | 107 | 10 | 8 | 11 |
| $5 / 2$ | 811.0 | 807.3 | 284 | 251 | 126 | 16 | 10 | 13 |
| 7/2 | 931.2 | 937 | 34 | 37 | $\sim 67$ | 1.9 | 0.3 |  |
| 1/2 1/2-[510].. | 457.6 | 457.6 | 0.5 | 0.1 |  | 0.0 | 6 |  |
| $3 / 2$ | 529.6 | 529.3 | 485 | 365 | $\sim 140$ | 47 | 9 |  |
| $5 / 2$ | 561.9 | 560.4 | 142 | 177 | 164 | 13 | 66 | 23 |
| 7/2 | 729.8 |  | 49 | 8 |  | 4 | 12 |  |
| 5/2 5/2-[512].. | 365.5 | 365.5 | 0.0 | 0.0 |  | 0.2 | 0.2 | 11 |
| $7 / 2$ | 475.5 | 475.5 | 35 | 84 | 51 | 254 | 291 | 246 |
| $9 / 2$ | 618.0 | ~ 611 | 2.1 | 9 | $<1$ | 13 | 5 | 4 |
| 11/2 . | 792.6 | 777 | 0.2 | 0.1 |  | 1.2 | 0.1 | 7 |
| 1/2 1/2-[521].. | 385.3 | 385.2 | 31 | 31 | 20 | 265 | 259 | 288 |
| $3 / 2$ | 450.8 | 450.2 | 14 | 114 | 135 | 121 | 161 | 95 |
| $5 / 2$ | 487.2 | 488.3 | 10 | 9 | 11 | 82 | 35 | 107 |
| $7 / 2$ | 639.5 | 642 | 9 | 46 | $\sim 50$ | 67 | 62 | 70 |
| $9 / 2 \quad$. | 804.1 |  | 1.4 | 7 |  | 10 | 8 |  |
| 7/2 7/2-[514].. | 409.2 | 409.0 | 5 | 12 | $<3$ | 38 | 23 | 23 |
| $9 / 2$. | 523.3 | ~ 527 | 6 | 0.1 |  | 43 | 51 | 33 |

[^32]NT. 15
Table 15. Comparison of unperturbed, Coriolis coupled and experimental cross sections in ${ }^{183} \mathrm{~W}\left(\theta=90^{\circ}\right)$.

| State ${ }^{\text {a }}$ | Energy (keV) |  | $\sigma(d, p) \mu b / s r$ |  |  | $\sigma(d, t) \mu b / s r$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Per- turbed | Experimental | Unperturbed | $\begin{aligned} & \text { Per- } \\ & \text { turbed } \end{aligned}$ | Experimental | Unperturbed | Per- <br> turbed | Experimental |
| 9/2 9/2-[505].. | 1390.4 | 1390 | 64.0 | 64.6 | 25 | 1.8 | 1.2 |  |
| 7/2 7/2-[503].. | 453.1 | 453.1 | 357.3 | 363.7 | 284 | 37.6 | 48.3 | 72 |
| 9/2 | 595.3 | $\sim 596$ | 7.0 | 8.0 | ~3 | 0.6 | 1.3 | $\sim 1$ |
| 3/2 3/2-[512].. | 208.7 | 208.8 | 138.2 | 207.6 | $131{ }^{\text {b }}$ | 29.1 | 60.1 | 58 b |
| $5 / 2$ | 292.5 | 291.7 | 248.8 | 184.0 | 96 | 48.1 | 34.4 | 35 |
| 7/2 | 410.4 | 412.1 | 30.0 | 48.5 | 87 | 5.8 | 16.7 | 44 |
| $9 / 2$ | 556.3 | ~ 553 | 6.0 | 3.9 | 4 | 1.0 | 1.0 | $<1$ |
| 11/2 | 740.0 | 742 | 0.2 | 0.4 | 4 | 0.0 | 0.1 | 1.3 |
| 1/2 1/2-[510].. | 0.0 | 0.0 | 0.3 | 0.4 | 8 | 0.2 | 0.6 | 5 |
| $3 / 2$ | 45.1 | 46.5 | 334.0 | 268.9 | 264 | 194.9 | 178.5 | 150 |
| $5 / 2$ | 99.7 | 99.1 | 97.8 | 163.4 | 202 | 52.4 | 65.0 | 103 |
| 7/2 | 207.5 | 207.0 | 33.4 | 17.7 | $11^{\text {b }}$ | 17.9 | 15.0 | $14^{\text {b }}$ |
| $9 / 2$ | 309.7 | 309.0 | 3.3 | 5.5 | 11 | 1.6 | 1.6 | 7 |
| $5 / 25 / 2-[512] \ldots$ | 905.8 | 906 | 0.0 | 0.0 | 6 | 0.2 | 0.2 | 19 |
| 7/2 | 1002.5 | 1002 | 16.6 | 7.9 | 29 | 269.3 | 217.3 | 237 |
| $9 / 2$ | 1128.1 | 1128 | 1.2 | 1.2 | 2.8 | 14.1 | 24.6 | 18 |
| 11/2 | 1282.5 | 1281 | 0.1 | 0.0 |  | 1.3 | 0.8 | 4 |
| 1/2 1/2-[521].. | 936.5 | 936 | 15.3 | 15.2 | 15 | 279.9 | 279.5 | 364 |
| $3 / 2$ | 1027.9 | 1029 | 7.0 | 2.8 | 2.6 | 128.2 | 113.6 | 54 |
| $5 / 2$ | 1055.5 | 1056 | 5.1 | 4.3 |  | 86.0 | 87.1 | 66 |
| 7/2 | 1268.2 | 1265 | 4.3 | 1.8 |  | 71.5 | 63.8 | 69 |
| $9 / 2 \quad$. | 1318.5 | ~ 1314 | 0.7 | 0.6 |  | 10.1 | 10.1 | 8 |
| 7/2 7/2-[514].. | 1072.3 | 1072 | 2.0 | 3.8 | 16 | 40.3 | 81.5 | 91 |
| $9 / 2$ | 1218.6 | 1219 | 2.6 | 3.0 | 3 | 45.3 | 34.8 | 29 |
| 11/2 . . | 1396.8 | 1397 | 0.0 | 0.1 | $<3.6$ | 0.8 | 1.3 | 15 |

a See table 13.
b The $7 / 21 / 2-[510]$ state at 207 keV and the $3 / 23 / 2-[512]$ state at 209 keV were not resolved. The experimental cross sections listed here and also used in figs. 28 and 29 were obtained by dividing the total observed cross section in the ratio indicated by the calculations.

Table 16. Comparison of unperturbed, Coriolis coupled and experimental cross sections in ${ }^{185} \mathrm{~W}\left(\theta=90^{\circ}\right)$.

| State ${ }^{\text {a }}$ | Energy (keV) |  | $\sigma(d, p) \mu b / s r$ |  |  | $\sigma(d, t) \mu b / s r$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{aligned} & \text { Per- } \\ & \text { turbed } \end{aligned}$ | Exper- <br> imental | Unperturbed | Per- <br> turbed | Exper- <br> imental | Unperturbed | $\begin{aligned} & \text { Per- } \\ & \text { turbed } \end{aligned}$ | Exper- <br> imental |
| 9/2 9/2-[505] | 789.0 | 789 | 66 | 61.6 | 25 | 3.3 | 3.9 | 10 |
| 7/2 7/2-[503] | 243.5 | 243.5 | 334.2 | 341.3 | 316 | 58.1 | 72.2 | 154 |
| $9 / 2$ | 391.0 | 390.9 | 6.4 | 10.2 |  | 1.0 | 2.1 | ~ 3 |
| 11/2 | 571.2 | ~ 570 | 0.5 | 0.5 | $\sim 5.6$ | 0.1 | 0.2 | 1.4 |
| $3 / 23 / 2-[512]$ | 0.0 | 0.0 | 107.2 | 29.6 | 5 | 58.8 | 1.7 | 1 |
| $5 / 2$ | 67.9 | 66.1 | 194.8 | 247.3 | 301 | 97.2 | 173.2 | 207 |
| 7/2 | 172.5 | 173.8 | 23.4 | 7.2 | 11 | 11.7 | 1.0 | 1.3 |
| $9 / 2$ | 305.4 | 302 | 4.7 | 6.5 | 11 | 2.1 | 4.5 | 11 |
| 11/2 | 478.3 | $\sim 478$ | 0.2 | 0.1 |  | 0.1 | 0.0 | $\sim 0.4$ |
| $1 / 21 / 2-[510]$ | 23.6 | 23.6 | 0.2 | 0.2 | 4 | 0.3 | 0.9 | 2.7 |
| $3 / 2$ | 93.8 | 93.8 | 180.0 | 261.8 | 357 | 343.2 | 422.6 | 308 |
| 5/2 | 188.2 | 188.2 | 52.7 | 0.3 | ~ 4 | 92.4 | 14.1 | 11 |
| $7 / 2$ | 335.7 | 334 | 18.0 | 36.5 | 104 | 31.6 | 54.8 | 99 |
| $9 / 2$ | 492.8 | ~ 492 | 1.8 | 0.0 |  | 2.7 | 0.1 | $\sim 0.8$ |
| 11/2 | 717.6 | 706 | 0.1 | 0.2 | 5 | 0.2 | 0.4 | 4 |
| 5/2 5/2-[512] | 888.3 | 888 | 0.0 | 0.0 | $<3$ | 0.2 | 0.2 | 14 |
| 7/2 | 986.1 | 986 | 16.9 | 7.7 | 32 | 268.2 | 208.1 | 206 |
| 9/2 | 1113.8 | $\sim 1118$ | 1.2 | 1.1 |  | 14.1 | 24.2 | $\sim 20^{\text {c }}$ |
| 1/2 1/2-[521] | 1013.0 | $\sim 1008$ | 13.9 | 13.9 | $<62$ | 281.0 | 280.5 | $\sim 266^{\text {b }}$ |
| $3 / 2$ | 1105.8 | 1106 | 6.4 | 2.8 |  | 128.7 | 106.8 | $\sim 43$ |
| $5 / 2$ | 1118.0 | $\sim 1118$ | 4.7 | 3.8 |  | 86.4 | 88.7 | $\sim 20^{\text {a }}$ |
| 7/2 | 1334.3 | 1335 | 3.9 | 1.6 |  | 71.8 | 59.7 | $\sim 25$ |
| 9/2 | 1358.4 | 1361 | 0.5 | 0.6 |  | 10.1 | 10.3 | 11 |
| 7/2 7/2-[514] | 1058.3 | 1058.3 | 2.1 | 4.1 | 15 | 40.3 | 86.2 | 80 |
| $9 / 2$ | 1218.9 | ~ 1219 | 2.7 | 1.2 |  | 45.3 | 33.5 | 19 |

a See table 13.
b Intensity of $1 / 21 / 2-$ [521] component estimated from $125^{\circ}$ cross sections.
c Unresolved doublet. Total observed cross section equals $40 \mu b$.

Table 17. Comparison of unperturbed, Coriolis coupled and experimental cross section in ${ }^{187} \mathrm{~W}\left(\theta=90^{\circ}\right)$.

| State ${ }^{\text {a }}$ | Energy (keV) |  | $\sigma(d, p) \mu b / s r$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Perturbed | Experimental | Unper- <br> turbed | Per- <br> turbed | Experimental |
| 9/2 9/2-[505] | 598.2 | 598 | 62.5 | 43.9 | 23 |
| 7/2 7/2-[503] | 350.6 | 350.6 | 346.0 | 346.0 | 211 |
| 9/2 | 482.3 |  | 6.7 | 25.2 |  |
| $3 / 23 / 2-[512]$ | 0.0 | 0.0 | 84.2 | 53.9 | 37 |
| $5 / 2$ | 77.5 | 77.5 | 151.6 | 178.6 | 213 |
| 7/2 | 186.5 |  | 18.3 | 9.1 | $<8$ |
| 9/2 | 329.3 | 329 | 3.7 | 4.7 | $\sim 5$ |
| 1/2 1/2-[510] | 149.3 | 145.7 | 0.1 | 0.1 | $<8$ |
| $3 / 2$ | 204.8 | 204.9 | 121.2 | 151.6 | 272 |
| $5 / 2$ | 304.1 | 303.2 | 35.5 | 8.4 | 21 |
| 7/2 | 432.1 | 432.4 | 12.1 | 21.3 | 71 |
| $9 / 2$ | $607.4$ |  |  |  |  |
| 11/2 | 805.7 |  |  |  |  |

a See table 13.

Table 18. Mixing amplitudes ( $a_{i n} \times 100$ ) calculated for the $1 / 2-$ states.

| $K^{\pi}\left[N n_{z} \Lambda\right]$ | $A$ | $E(\mathrm{keV})$ | $1 / 2-[510]$ | $1 / 2-[521]$ |
| :---: | :---: | :---: | :---: | :---: |
| $1 / 2-[510] \ldots \ldots \ldots \ldots$ | 185 | 24 | -100 | +02 |
|  | 183 | 0 | -100 | +02 |
| $1 / 2-[521] \ldots \ldots \ldots \ldots$ | 181 | 458 | -99 | -16 |
|  | 185 | 1008 | +02 | +100 |
|  | 183 | 936 | +02 | +100 |
|  | 181 | 385 | -16 | +99 |
|  | 179 | 222 | -04 | +100 |

Table 19. Mixing amplitudes ( $a_{i n} \times 100$ ) calculated for the $3 / 2$ - states.

| $K^{\pi}\left[N n_{z} \Lambda\right]$ | $A$ | $E(\mathrm{keV})$ | $3 / 2-[512]$ | $1 / 2-[510]$ | $1 / 2-[521]$ |
| :---: | :---: | ---: | ---: | ---: | ---: |
| $3 / 2-[512] \ldots \ldots \ldots \ldots$ | 187 | 0 | -99 | -16 |  |
|  | 185 | 0 | +94 | +33 | +01 |
| $1 / 2-[510] \ldots \ldots 3$ | 209 | -99 | +15 | -03 |  |
|  | 181 | 726 | -100 | +05 | +05 |
|  | 187 | 205 | -16 | +99 |  |
| $1 / 2-[521] \ldots \ldots \ldots$ | 94 | +33 | -94 | +05 |  |
|  | 185 | 47 | -15 | -99 | +03 |
|  | 181 | 529 | -06 | -95 | -30 |
|  | 179 | 689 | -03 | -100 | -09 |
|  | 185 | 1106 | -03 | +04 | +100 |
|  | 183 | 1029 | -03 | +04 | +100 |
|  | 181 | 450 | +04 | -30 | +95 |
|  | 179 | 305 | +03 | -09 | +100 |

Table 20. Mixing amplitudes ( $a_{i n} \times 100$ ) calculated for the $5 / 2-$ states.

| $K^{\pi}\left[N n_{z} \Lambda\right]$ | $A$ | $E(\mathrm{keV}$ | $3 / 2-[512]$ | $1 / 2-[510]$ | $5 / 2-[512]$ | $1 / 2-[521]$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $3 / 2-[512] \ldots .$. | 187 | 77 | -97 | -23 |  |  |
|  | 185 | 66 | +91 | +42 | +00 | +02 |
|  | 183 | 292 | +98 | -20 | +00 | +06 |
| $1 / 2-[510] \ldots$. | 181 | 807 | -100 | +06 | +00 | +07 |
|  | 187 | 303 | -23 | +97 |  |  |
|  | 185 | 188 | -42 | +90 | -00 | -08 |
|  | 183 | 99 | +20 | +98 | +00 | -05 |
| $5 / 2-[512] \ldots$. | 181 | 560 | -09 | -85 | +00 | -52 |
|  | 179 | 788 | -05 | -99 | +00 | -11 |
|  | 185 | 888 | -00 | +00 | +100 | -00 |
| $1 / 2-[521] \ldots .$. | 183 | 906 | -00 | +00 | +100 | -00 |
|  | 181 | 366 | -00 | -00 | -100 | -00 |
|  | 179 | 430 | -00 | +00 | -100 | +00 |
|  | 185 | 1118 | -05 | +07 | +00 | +100 |
|  | 183 | 1056 | +05 | -06 | -00 | -100 |
|  | 181 | 488 | +03 | -53 | -00 | +85 |
|  | 179 | 318 | +04 | -12 | +00 | +99 |

Table 21. Mixing amplitudes $\left(a_{i n} \times 100\right)$ calculated for the $7 / 2$ - states.

| $K^{\pi}{ }_{\left[N n_{z} \Lambda\right]}$ | A | $E(\mathrm{keV})$ | $\begin{aligned} & 7 / 2- \\ & {[503]} \end{aligned}$ | $\begin{aligned} & 3 / 2- \\ & {[512]} \end{aligned}$ | $\begin{aligned} & 1 / 2- \\ & {[510]} \end{aligned}$ | $\begin{aligned} & 5 / 2- \\ & {[512]} \end{aligned}$ | $\begin{aligned} & 1 / 2- \\ & {[521]} \end{aligned}$ | $\begin{aligned} & 7 / 2- \\ & {[514]} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 7/2-[503]. | 187 | 351 | $+100$ | $+00$ | $+00$ |  |  |  |
|  | 185 | 244 | $+100$ | -00 | -00 | + 05 | + 00 | $-00$ |
|  | 183 | 453 | $+100$ | -00 | $+00$ | + 05 | - 00 | - 00 |
|  | 181 | 662 | + 98 | -00 | -00 | - 19 | - 00 | - 03 |
| 3/2-[512] . . | 187 | (186) | + 00 | -95 | $-30$ | + 00 | + 02 | + 00 |
|  | 185 | 174 | + 00 | +91 | $+42$ | + 00 | + 02 | $+00$ |
|  | 183 | 412 | - 00 | -96 | $+26$ | - 00 | - 08 | + 00 |
|  | 181 | 937 | - 00 | -99 | $+10$ | + 00 | + 13 | + 00 |
| $1 / 2-[510] \ldots$ | 187 | 432 | + 00 | -30 | $+95$ | - 00 | - 11 | + 00 |
|  | 185 | 334 | + 00 | -41 | $+90$ | - 00 | - 11 | + 00 |
|  | 183 | 207 | + 00 | $+27$ | $+96$ | + 00 | - 05 | + 00 |
|  | 181 | (730) | + 00 | +16 | + 79 | - 00 | + 59 | + 00 |
| $5 / 2-[512] \ldots$ | 185 | 986 | - 05 | -00 | $+00$ | + 98 | - 00 | - 19 |
|  | 183 | 1002 | - 05 | -00 | $+00$ | + 98 | - 00 | - 17 |
|  | 181 | 476 | - 17 | -00 | $-00$ | - 79 | - 00 | - 59 |
|  | 179 | 532 |  | -00 | $-00$ | -100 | + 00 | - 07 |
| 1/2-[521] $\ldots$ | 185 | 1335 | + 00 | +06 | -09 | - 00 | - 99 | + 00 |
|  | 183 | 1265 | + 00 | +06 | -07 | - 00 | $-100$ | + 00 |
|  | 181 | 642 | - 00 | +04 | -61 | - 00 | $+\quad 79$ | + 00 |
|  | 179 | 508 |  | +05 | $-20$ | + 00 | + 98 | + 00 |
| 7/2-[514] . . | 185 | 1058 | + 01 | $+00$ | $+00$ | - 19 | + 00 | - 98 |
|  | 183 | 1072 | + 01 | $+00$ | $+00$ | - 17 | + 00 | - 99 |
|  | 181 | 409 | - 09 | -00 | $-00$ | - 58 | - 00 | + 81 |
|  | 179 | 0 |  | +00 | $+00$ | - 07 | + 00 | $+100$ |

Table 22. Mixing amplitudes $\left(a_{i n} \times 100\right)$ calculated for the $9 / 2$ - states.

| $K^{\pi}\left[N n_{z} \Lambda\right]$ | A | $E(\mathrm{keV})$ | $\begin{aligned} & 9 / 2- \\ & {[505]} \end{aligned}$ | $\begin{aligned} & 7 / 2- \\ & {[503]} \end{aligned}$ | $\begin{aligned} & 3 / 2- \\ & {[512]} \end{aligned}$ | $\begin{aligned} & 1 / 2- \\ & {[510]} \end{aligned}$ | $\begin{aligned} & 5 / 2- \\ & {[512]} \end{aligned}$ | $\begin{aligned} & 1 / 2- \\ & {[521]} \end{aligned}$ | $\begin{aligned} & 7 / 2- \\ & {[514]} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $3 / 2-[505]$ | 187 | 598 | - 95 | - 33 | $+00$ | $+00$ |  |  |  |
|  | 185 | 789 | $-100$ | - 07 | $+00$ | $+00$ | -01 | $+00$ | -04 |
|  | 183 | 1390 | $+100$ | + 01 | +00 | $+00$ | $-00$ | +00 | -04 |
| 7/2-[503] | 187 | (482) | - 33 | + 95 | $+00$ | $+00$ |  |  |  |
|  | 185 | 391 | - 07 | + 99 | $-00$ | $-00$ | $+08$ | $+00$ | $-00$ |
|  | 183 | 595 | - 01 | $+100$ | $-00$ | $+00$ | +08 | $-00$ | $-00$ |
|  | 181 | (813) |  | - 97 | $+00$ | $+00$ | $+25$ | $+00$ | $+05$ |
| $3 / 2-[512]$ | 187 | 329 | + 00 | + 00 | $+94$ | +34 |  |  |  |
|  | 185 | 302 | + 00 | - 00 | -89 | -45 | $-00$ | -03 | $+00$ |
|  | 183 | 553 | + 00 | - 00 | $-96$ | $+26$ | $-00$ | -11 | $+00$ |
| $1 / 2-[510]$ | 187 |  | + 00 | + 00 | -34 | $+94$ |  |  |  |
|  | 185 | 492 | - 00 | + 00 | -44 | $+88$ | $-00$ | $-15$ | $+00$ |
|  | 183 | 309 | + 00 | + 00 | $-27$ | -96 | $-00$ | $+07$ | $+00$ |
| $5 / 2-[512]$ | 185 | 1118 | + 00 | - 08 | $-00$ | $+00$ | $+98$ | $-00$ | $-20$ |
|  | 183 | 1128 | - 00 | - 08 | $-00$ | $+00$ | $+98$ | $-00$ | $-20$ |
|  | 181 | $\sim 611$ |  | - 21 | $-00$ | $-00$ | -64 | $-00$ | $-74$ |
|  | 179 | $(662)$ |  |  | $-00$ | $-00$ | -99 | $+00$ | $-10$ |
| $1 / 2-[521]$ | 185 | 1361 |  |  | -09 | $+13$ | $+00$ | +99 | $+00$ |
|  | 183 | 1314 | + 00 | + 00 | -09 | $+09$ | $+00$ | $+99$ | $+00$ |
|  | $181$ | (804) |  | + 00 | $+15$ | $+59$ | $-00$ | +79 | $-00$ |
|  | 179 |  |  |  | $+06$ | $-20$ | $+00$ | +98 | $+00$ |
| 7/2-[514] | 185 |  | $+04$ |  | $+00$ | $+00$ | $-20$ | $+00$ | $-98$ |
|  | 183 | 1219 | - 04 | + 01 | $+00$ | $+00$ | $-20$ | $+00$ | $-98$ |
|  | $181$ | $\sim 527$ |  | - 15 | $-00$ | $-00$ | $-72$ | $-00$ | $+67$ |
|  | 179 | 120 |  |  | $-00$ | $+00$ | $-10$ | $+00$ | $+99$ |

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HANS MAASS

# ÜbER DIE FOURIERKOEFFIZIENTEN der Eisensteinreihen Zweiten 

 gRadesDet Kongelige Danske Videnskabernes Selskab Matematisk-fysiske Meddelelser 38, 14


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## Synopsis

Die in Mat. Fys. Medd. Dan. Vid. Selsk. 34, no. 7 (1964) vom Verfasser begonnene Analyse der Fourierkoeffizienten $a_{k}(T)$ der Eisensteinreihen zweiten Grades vom Gewicht $k$ wird fortgesetzt. Es werden Koeffizientenrelationen vom Teilersummentypus begründet, mit denen die Berechnung der Koeffizienten $a_{k}(T)$ zu nicht-primitiven $T$ auf solche zu primitiven $T$ zurückgeführt wird. Auf Grund multiplikativer Eigenschaften der Fourierkoeffizienten ergeben sich erste Beispiele von Zetafunktionen, die mit Hilfe der Koeffizienten $a_{k}(T)$ definiert sind und Eulersche Produktentwicklungen besitzen. Ein in der zitierten Arbeit formulierter Satz ererfährt hier eine Berichtigung.

In einer älteren Arbeit über »Die Fourierkoeffizienten der Eisensteinreihen zweiten Grades« (Mat. Fys. Medd. Dan. Vid. Selsk. 34, no. 7 (1964)) habe ich für die Fourierkoeffizienten $a_{k}(T)$ der Eisensteinreihe zweiten Grades

$$
G_{-k}(Z)=\sum_{\{C, D\}}|C Z+D|^{-k} \quad(k \equiv 0(\bmod 2), k>3),
$$

wobei über ein volles System von 2-reihigen nicht-assoziierten teilerfremden symmetrischen Matrizenpaaren $C, D$ summiert wird und $Z$ eine symmetrische komplexe Matrix mit positivem Imaginärteil bezeichnet, einige allgemeine Eigenschaften bewiesen. Diese Untersuchung bedarf einer Berichtigung insofern, als Satz 2 loc. cit., wie H. L. Resnikoff und R. L. Saldaña festgestellt haben, unzureichend begründet und zum Teil fehlerhaft ist. Die Elimination des Fehlschlusses in der Beweisführung von Satz 2 bereitet indessen keine Mühe und ergibt das folgende korrigierte Resultat.

$$
\begin{aligned}
& \text { Satz: Es sei } 2 T=\left(\begin{array}{cc}
2 t_{0} & t_{1} \\
t_{1} & 2 t_{2}
\end{array}\right)>0 \\
& \qquad e=e(T)=\text { g.g.T. }\left(t_{0}, t_{1}, t_{2}\right), \Delta=\Delta(T)=|2 T|
\end{aligned}
$$

Dann ist $a_{k}(T)$ durch $e$ und $\Delta$ eindeutig bestimmt:

$$
\begin{equation*}
a_{k}(T)=\beta_{k}(e, \Delta) \tag{1}
\end{equation*}
$$

und es gilt für jede Primzahl $p \geqq 2$ :

$$
\begin{gather*}
\beta_{k}\left(p e, p^{2} \Delta\right)=\left(1+p^{k-1}+\left\{\delta_{p}\left(-\Delta e^{-2} p^{-2}\right)-\left(\frac{-\Delta e^{-2}}{p}\right)\right\} p^{k-2}+p^{2 k-3}\right) \beta_{k}(e, \Delta)- \\
-\left\{p-\left(\frac{-\Delta e^{-2}}{p}\right)\right\} p^{k-2} \beta_{k}\left(p^{-1} e, \Delta\right)-\delta_{p}\left(-\Delta e^{-2} p^{-2}\right) p^{k-2} \beta_{k}(p e, \Delta)-  \tag{2}\\
-p^{2 k-3} \beta_{k}\left(p^{-1} e, p^{-2} \Delta\right),
\end{gather*}
$$

wobei $\delta_{p}(x)$ durch (5) erklärt und generell $\beta_{k}(e, \Delta)=0$ ist, wenn eine der Bedingungen $e \equiv 0(\bmod 1), \Delta e^{-2} \equiv 0$ oder $3(\bmod 4)$ verletzt ist.

Beweis: Wir schließen mit vollständiger Induktion nach

$$
h(T)=\sum_{p \geqq 2} v_{p},
$$

der Exponentensumme zur Primfaktorzerlegung

$$
\Delta(T)=\prod_{p \geqq 2} p^{v_{p}}
$$

Ist $h(T) \leqq 1$, so ist notwendig $e(T)=1$, also $T$ primitiv. Auf Grund von Satz 1 loc. cit. ist dann festzustellen, da $\beta a_{k}(T)$ durch $\Delta$ eindeutig bestimmt ist. D.h. (1) braucht nur noch für nicht-primitive $T>o$ bewiesen zu werden. Wir nehmen nun an, daß bei gegebenem $T$ bereits

$$
a_{k}(S)=\beta_{k}(e(S), \Delta(S))
$$

gilt, sofern $h(S) \leqq h(T)$ ist. Da $a_{k}(T)$ gegenüber unimodularen Transformationen $T \rightarrow T(U)$ invariant ist, können wir ohne Beschränkung der Allgemeinheit $T$ bezüglich $p$ immer so normiert annehmen, daß $t_{0}(e(T))^{-1}$ zu $p$ prim ist. Wir knüpfen wieder an die allgemeine Beziehung an

$$
\begin{align*}
& a_{k}(p T)=\left(1+p^{k-1}\right)\left(1+p^{k-2}\right) a_{k}(T)-p^{2 k-3} a_{k}\left(\frac{1}{p} T\right)-  \tag{3}\\
& \quad-p^{k-2} a_{k}\left(\frac{1}{p} T\left[\begin{array}{ll}
1 & 0 \\
0 & p
\end{array}\right]\right)-p^{k-2} \sum_{U=0}^{p-1} a_{k}\left(\frac{1}{p} T\left[\begin{array}{ll}
u & p \\
1 & 0
\end{array}\right]\right)
\end{align*}
$$

die sich aus der Heckeschen Operatorentheorie ergab. Hier ist $a_{k}(S)=0$ zu setzen, falls $e(S)$ nicht ganz ist. Man bestätigt nun gemäß Induktionsschluß, da $\beta$

$$
\begin{aligned}
a_{k}(T) & =\beta_{k}(e, \Delta), a_{k}\left(\frac{1}{p} T\right)=\beta_{k}\left(p^{-1} e, p^{-2} \Delta\right) \\
& a_{k}\left(\frac{1}{p} T\left[\begin{array}{ll}
1 & 0 \\
0 & p
\end{array}\right]\right)=\beta_{k}\left(p^{-1} e, \Delta\right)
\end{aligned}
$$

ist. Genauer muß nun auf den Fall

$$
S=\frac{1}{p} T\left[\begin{array}{ll}
u & p \\
1 & 0
\end{array}\right] \quad \text { mit } \quad \Delta(S)=\Delta(T)
$$

eingegangen werden. Es sei $2 S=\left(\begin{array}{cc}2 s_{0} & s_{1} \\ s_{1} & 2 s_{2}\end{array}\right)$ und $e_{p}(S)$ die größte $p$-Potenz, welche $e(S)$ teilt, so daß $t_{0}\left(e_{p}(T)\right)^{-1}$ zu $p$ prim ist. Aus

$$
s_{0}=p^{-1}\left(t_{0} u^{2}+t_{1} u+t_{2}\right), s_{1}=2 t_{0} u+t_{1}, s_{2}=p t_{0}
$$

entnimmt man die Teilbarkeitsrelationen

$$
e_{p}(T) / p e_{p}(S) \quad \text { und } \quad e_{p}(S) / p e_{p}(T)
$$

so daß

$$
e_{p}(S)=p^{v} e_{p}(T) \quad \text { mit } \quad|\nu| \leqq 1
$$

gilt. Zufolge

$$
\frac{e(S)}{e_{p}(S)}=\frac{e(T)}{e_{p}(T)}
$$

ist damit gleichwertig

$$
e(S)=p^{v} e(T) \quad \text { mit } \quad|v| \leqq 1
$$

Jedenfalls ist also

$$
a_{k}(S)=\beta_{k}\left(p^{v} e, \Delta\right)
$$

Der Exponent $v$ möge, wenn $u$ alle Restklassen mod $p$ durchläuft, genau $A_{v}(T)$ mal vorkommen. Es genügt, $A_{v}(T)$ für $v= \pm 1$ zu berechnen. Vermöge

$$
\sum_{|v| \leqq 1} A_{v}(T)=p
$$

ist dann auch $A_{0}(T)$ bekannt. Wir beginnen mit

1. $v=1$. Wegen der Normierung von $T$ ist $A_{1}(T)$ die Anzahl der Restklassen $u \bmod p$, die das System der Kongruenzen

$$
\begin{aligned}
2 t_{0} u+t_{1} & \equiv 0 \quad\left(\bmod p e_{p}(T)\right) \\
t_{0} u^{2}+t_{1} u+t_{2} & \equiv 0 \quad\left(\bmod p^{2} e_{p}(T)\right)
\end{aligned}
$$

befriedigen. Wir setzen $t_{\mu}=e_{p}(T) r_{\mu}(\mu=0,1,2)$ und erhalten die gekürzten Kongruenzen

$$
\begin{aligned}
2 r_{0} u+r_{1} & \equiv 0 \quad(\bmod p) \\
r_{0} u^{2}+r_{1} u+r_{2} & \equiv 0 \quad\left(\bmod p^{2}\right)
\end{aligned}
$$

Damit gleichwertig ist wegen $p \nmid r_{0}$ das System
mit

$$
\begin{equation*}
2 r_{0} u+r_{1} \equiv 0(\bmod p),\left(2 r_{0} u+r_{1}\right)^{2} \equiv-\Delta_{p}\left(\bmod p^{2+\varkappa_{p}}\right) \tag{4}
\end{equation*}
$$

$$
\begin{array}{r}
\Delta_{p}=4 r_{0} r_{2}-r_{1}^{2}=\left(e_{p}(T)\right)^{-2} \Delta(T), \\
\varkappa_{p}=\left\{\begin{array}{l}
2 \text { für } p=2, \\
0 \text { für } p>2 .
\end{array}\right.
\end{array}
$$

Notwendig und hinreichend für die Lösbarkeit von (4) ist

$$
\Delta_{p} \equiv \begin{cases}0 & \left(\bmod p^{2}\right) \\ \text { für } p>2 \\ 0 \text { oder }-4(\bmod 16) & \text { für } p=2\end{cases}
$$

was dasselbe bedeutet wie

$$
\Delta e^{-2} \equiv \begin{cases}0 & \left(\bmod p^{2}\right) \\ \text { für } p>2 \\ 0 \text { oder }-4(\bmod 16) & \text { für } p=2\end{cases}
$$

Ist diese Bedingung erfüllt, so gibt es genau eine Restklasse $u \bmod p$, welche (4) befriedigt. Wir setzen

$$
\delta_{p}(x)=\left\{\begin{array}{ll}
1, \text { wenn }\left\{\begin{array}{lr}
x=0 & (\bmod 1) \\
\text { für } p>2 \\
x \equiv 0 & \text { oder } 1(\bmod 4)
\end{array} \text { für } p=2,\right. \tag{5}
\end{array}\right\}
$$

Ersichtlich ist dann

$$
\begin{equation*}
A_{1}(T)=\delta_{p}\left(-\Delta e^{-2} p^{-2}\right) \tag{6}
\end{equation*}
$$

2. $v=-1$. Wegen $e_{p}(T) / s_{\mu}(\mu=1,2)$ ist $A_{-1}(T)$ die Anzahl der Restklassen $u \bmod p$ mit

$$
t_{0} u^{2}+t_{1} u+t_{2} \equiv \equiv 0\left(\bmod p e_{p}(T)\right)
$$

oder

$$
r_{0} u^{2}+r_{1} u+r_{2} \not \equiv 0(\bmod p)
$$

was mit

$$
\left(2 r_{0} u+r_{1}\right)^{2} \not \equiv-\Delta_{p}\left(\bmod p^{1+\varkappa_{p}}\right)
$$

gleichwertig ist.
Zufolge $p \nmid r_{0}$ ist Falle $p>2$ die Funktion $A_{-_{1}}(T)$ auch gleich der Anzahl der Restklassen $u \bmod p$ mit

$$
u^{2} \equiv-\Delta e^{-2}(\bmod p)
$$

Eine Abzählung liefert

$$
\begin{equation*}
A_{-1}(T)=p-1-\left(\frac{-\Delta e^{-2}}{p}\right) \quad \text { für } \quad p>2 . \tag{7}
\end{equation*}
$$

Im Falle $p=2$ wird

$$
\left(2 r_{0} u+r_{1}\right)^{2} \equiv-\Delta_{2}(\bmod 8)
$$

gefordert.
a) $r_{1} \equiv 0(\bmod 2) \mathrm{ergibt}$

$$
r_{0} u+\frac{r_{1}}{2} \equiv\left(r_{0} u+\frac{r_{1}}{2}\right)^{2} \equiv-\frac{\Delta_{2}}{4}(\bmod 2)
$$

mithin $A_{-1}(T)=1$. Der vorliegende Fall ist gekennzeichnet durch

$$
\Delta_{2} \equiv 0(\bmod 4) \Leftrightarrow \Delta e^{-2} \equiv 0(\bmod 4) \Leftrightarrow\left(\frac{-\Delta e^{-2}}{2}\right)=0
$$

b) $r_{1} \equiv 1(\bmod 2)$ ergibt für alle $u$ die Bedingung

$$
1 \equiv\left(2 r_{0} u+r_{1}\right)^{2} \text { 丰 }-4 r_{0} r_{2}+1(\bmod 8)
$$

also $A_{-1}(T)=2$ bzw. 0, falls $r_{0} r_{2} \equiv 1$ bzw. $0(\bmod 2)$. Im vorliegenden Fall ist $A_{-1}(T)>0$ genau dann, wenn

$$
\Delta_{2} \equiv 3(\bmod 8) \Leftrightarrow \Delta e^{-2} \equiv 3(\bmod 8) \Leftrightarrow\left(\frac{-\Delta e^{-2}}{2}\right)=-1
$$

Zusammenfassend stellen wir nun fest, daß (7) auch für $p=2$ gilt.
Damit ergibt sich schließlich

$$
A_{0}(T)=1+\left(\frac{-\Delta e^{-2}}{p}\right)-\delta_{p}\left(-\Delta e^{-2} p^{-2}\right)
$$

Die Relation (3) läßt sich jetzt umschreiben in

$$
\begin{gathered}
a_{k}(p T)=\left(1+p^{k-1}+\left\{\delta_{p}\left(-\Delta e^{-2} p^{-2}\right)-\left(\frac{-\Delta e^{-2}}{p}\right)\right\} p^{k-2}+p^{2 k-3}\right) \beta_{k}(e, \Delta)- \\
-\left\{p-\left(\frac{-\Delta e^{-2}}{p}\right)\right\} p^{k-2} \beta_{k}\left(p^{-1} e, \Delta\right)-\delta_{p}\left(-\Delta e^{-2} p^{-2}\right) p^{k-2} \beta_{k}(p e, \Delta)- \\
-p^{2 k-3} \beta_{k}\left(p^{-1} e, p^{-2} \Delta\right) .
\end{gathered}
$$

Hieraus ist ersichtlich, daß $a_{k}(p T)$ durch

$$
e(p T)=p e \quad \text { und } \quad \Delta(p T)=p^{2} \Delta
$$

eindeutig bestimmt ist, so daß nun auch

$$
a_{k}(p T)=\beta_{k}\left(p e, p^{2} \Delta\right)
$$

gesetzt werden kann. Damit ist der Induktionsbeweis für den formulierten Satz erbracht.

Mit vollständiger Induktion nach $h(T)$ beweist man schließlich

$$
\beta_{k}(e, \Delta)=\sum_{\substack{t^{2} / \Delta \\ t>0}} b_{k}(e, \Delta, t) \beta_{k}\left(1, \Delta t^{-2}\right)
$$

mit gewissen ganz rationalen Koeffizienten $b_{k}(e, \Delta, t)$. Die übrigen Sätze der ursprünglichen Arbeit behalten also ihre Gültigkeit.

Die festgestellten Eigenschaften der Fourierkoef fizienten $a_{k}(T)=\beta_{k}(e, \Delta)$ gestatten nunmehr, die tiefer liegende Relation

$$
\begin{equation*}
\beta_{k}(e, \Delta)=\sum_{0<t / e} t^{k-1} \beta_{k}\left(1, \Delta t^{-2}\right) \tag{8}
\end{equation*}
$$

zu beweisen, die R. L. Saldaña auf Grund umfangreicher Koeffiziententabellen in seiner Master's Dissertation »The Fourier coefficients of Siegel modular forms of degree two« (Rice University, Houston, Texas, January 1971) als Vermutung formuliert hat. Meiner ursprünglichen Arbeit kann für $\beta_{k}(1, \Delta)$ mit $\Delta \equiv 0$ oder $3(\bmod 4), \Delta>0$ noch folgende Darstellung entnommen werden: Es sei $d=d(\Delta)$ die Diskriminante des imaginär-quadratischen Zahlkörpers $Q(\sqrt{-\Delta})$, $p^{b}$ die höchste Potenz der Primzahl $p$, welche $\Delta$ teilt, und $j=\left[\frac{b-1}{2}\right]$ oder $\left[\frac{b-2}{2}\right]$, je nachdem $p>2$ oder $p=2$ ist. Mit einer nur von $d$ abhängigen $Z a h l \omega_{k}(d)$ ist dann

$$
\left.\begin{array}{c}
\beta_{k}(1, \Delta)=\omega_{k}(d) b_{k}(\Delta), \\
b_{k}(\Delta)=\left(\frac{\Delta}{|d|}\right)^{k-\frac{3}{2}} \prod_{p / 2 \Delta}\left(\left\{1-\left(\frac{d}{p}\right) p^{1-k}\right\} \sum_{\mu=0}^{j} p^{\mu(3-2 k)}+\left(\frac{d}{p}\right)^{2} p^{(j+1)(3-2 k)}\right) \tag{9}
\end{array}\right\}
$$

Der Beweis für (8) wird mit vollständiger Induktion nach $v=v(e)=\sum_{p} v_{p}$, der Exponentensumme zur Primfaktorzerlegung $e=\prod_{p} p^{v} p$, geführt. Für $v=0$ ist nichts zu beweisen. Sei also $v>0$ und (8) richtig für Exponentensummen kleiner als $\nu$. Wir wählen eine Primzahl $p$ mit $e=p^{h} e_{1}, p \nmid e_{1}, h>0$ und setzen $\Delta=e^{2} D=p^{2 h} e_{1}{ }^{2} D$. Der Induktionsschlu $\beta$ erlaubt den Ansatz

$$
\begin{aligned}
\beta_{k}\left(e_{1}, \Delta\right) & =\sum_{0<t / e_{1}} t^{k-1} \beta_{k}\left(1, \Delta t^{-2}\right) \\
\beta_{k}\left(e p^{-1}, \Delta p^{-2}\right) & =\sum_{0<t / e p^{-1}} t^{k-1} \beta_{k}\left(1, \Delta(p t)^{-2}\right)
\end{aligned}
$$

Gleichwertig mit (8) erweist sich somit

$$
\beta_{k}\left(p^{h} e_{1}, p^{2 h} e_{1}^{2} D\right)=\beta_{k}\left(e_{1}, p^{2 h} e_{1}^{2} D\right)+p^{k-1} \beta_{k}\left(p^{h-1} e_{1}, p^{2(h-1)} e_{1}^{2} D\right), \quad(10)_{\mathrm{h}}
$$

was nun im Rahmen der vollständigen Induktion nach $v$ durch vollständige Induktion nach $h$ bewiesen wird.

Wir beginnen mit der Betrachtung des Falles $h=1$. Auf Grund von (2) erweist sich

$$
\begin{equation*}
\beta_{k}\left(p e_{1}, p^{2} e_{1}^{2} D\right)=\beta_{k}\left(e_{1}, p^{2} e_{1}^{2} D\right)+p^{k-1} \beta_{k}\left(e_{1}, e_{1}^{2} D\right) \tag{10}
\end{equation*}
$$

als gleichwertig mit

$$
\left.\begin{array}{rl}
(1+ & \left.\left\{\delta_{p}\left(-D p^{-2}\right)-\left(\frac{-D}{p}\right)\right\} p^{k-2}+p^{2 k-3}\right) \beta_{k}\left(e_{1}, e_{1}^{2} D\right)-  \tag{11}\\
& -\delta_{p}\left(-D p^{-2}\right) \beta_{k}\left(p e_{1}, e_{1}^{2} D\right)=\beta_{k}\left(e_{1}, p^{2} e_{1}^{2} D\right)
\end{array}\right\}
$$

Es sei $p^{b}$ die höchste $p$-Potenz, welche $D$ teilt. Zur Verdeutlichung werde (11) b an Stelle von (11) geschrieben. Der Beweis für (11)b wird nun mit einer dritten (und letzten) Induktion, nämlich vollständiger Induktion nach $b$ erbracht. Die Gleichung

$$
\begin{equation*}
\left(1-\left(\frac{-D}{p}\right) p^{k-2}+p^{2 k-3}\right) \beta_{k}\left(e_{1}, e_{1}^{2} D\right)=\beta_{k}\left(e_{1}, p^{2} e_{1}^{2} D\right) \tag{11}
\end{equation*}
$$

ist gemäß (8) eine unmittelbare Folge der Relationen

$$
\left(1-\left(\frac{-D}{p}\right) p^{k-2}+p^{2 k-3}\right) \beta_{k}\left(1, e_{1}^{2} t^{-2} D\right)=\beta_{k}\left(1, p^{2} e_{1}^{2} t^{-2} D\right) \quad \text { für } t / e_{1} \text {, }
$$

die auf Grund von (9) als richtig erkannt werden können. Damit ist (11) $)_{0}$ beweisen. Die folgende Relation

$$
\begin{equation*}
\left(1+p^{2 k-3}\right) \beta_{k}\left(e_{1}, e_{1}^{2} D\right)=\beta_{k}\left(e_{1}, p^{2} e_{1}^{2} D\right) \tag{11}
\end{equation*}
$$

wird analog auf die Beziehungen

$$
\left(1+p^{2 k-3}\right) \beta_{k}\left(1, e_{1}^{2} t^{-2} D\right)=\beta_{k}\left(1, p^{2} e_{1}^{2} t^{-2} D\right) \quad \text { für } t / e_{1}
$$

zurückgeführt, die ebenfalls mit Hilfe von (9) zu beweisen sind, wobei zu beachten ist, daß $b=1$ notwendig $p>2$ zur Folge hat.

Wir setzen nun voraus, daß $b \geqq 2$ und (11) $h_{-2}$ oder, gleichwertig damit,

$$
\beta_{k}\left(p e_{1}, e_{1}^{2} D\right)=\beta_{k}\left(e_{1}, e_{1}^{2} D\right)+p^{k-1} \beta_{k}\left(e_{1}, e_{1}^{2} D\right)
$$

gültig ist. Damit reduziert sich

$$
\begin{gather*}
\left(1+\delta_{p}\left(-D p^{-2}\right) p^{k-2}+p^{2 k-3}\right) \beta_{k}\left(e_{1}, e_{1}^{2} D\right)-  \tag{11}\\
-\delta_{p}\left(-D p^{-2}\right) \beta_{k}\left(p e_{1}, e_{1}^{2} D\right)=\beta_{k}\left(e_{1}, p^{2} e_{1}^{2} D\right)(b \geqq 2)
\end{gather*}
$$

auf

$$
\beta_{k}\left(e_{1}, p^{2} e_{1}{ }^{2} D\right)=\left(1+p^{2 k-3}\right) \beta_{k}\left(e_{1}, e_{1}{ }^{2} D\right)-\delta_{p}\left(-D p^{-2}\right) p^{2 k-3} \beta_{k}\left(e_{1}, e_{1}{ }^{2} p^{-2} D\right) .
$$

Mit Hilfe von (8) läßt sich diese Beziehung auf den Fall $e_{1}=1$ zurückführen. Ohne Beschränkung der Allgemeinheit kann also vorübergehend $e_{1}=1$ gesetzt werden. Wir brauchen dann nur noch

$$
\begin{equation*}
\beta_{k}\left(1, p^{2} D\right)=\left(1+p^{2 k-3}\right) \beta_{k}(1, D)-\delta_{p}\left(-D p^{-2}\right) p^{2 k-3} \beta_{k}\left(1, p^{-2} D\right) \tag{12}
\end{equation*}
$$

zu bestätigen, was mit Hilfe von (9) ohne weiteres möglich ist, wenn man folgendes beachtet: Es ist

$$
d(D)=d\left(p^{2} D\right)=d\left(p^{-2} D\right),
$$

und $b_{k}(D), b_{k}\left(p^{2} D\right), b_{k}\left(p^{-2} D\right)$ unterscheiden sich nur in den $p$-Faktoren. Demnach ist

$$
\left.\begin{array}{c}
p^{2 k-3}\left(\left\{1-\left(\frac{d}{p}\right) p^{1-k}\right\} \sum_{\mu=0}^{j+1} p^{\mu(3-2 k)}+\left(\frac{d}{p}\right)^{2} p^{(j+2)(3-2 k)}\right)= \\
=\left(1+p^{2 k-3}\right)\left(\left\{1-\left(\frac{d}{p}\right) p^{1-k}\right\} \sum_{\mu=0}^{j} p^{\mu(3-2 k)}+\left(\frac{d}{p}\right)^{2} p^{(j+1)(3-2 k)}\right)-  \tag{13}\\
-\delta_{p}\left(-D p^{-2}\right)\left(\left\{1-\left(\frac{d}{p}\right) p^{1-k}\right\} \sum_{\mu=0}^{j-1} p^{\mu(3-2 k)}+\left(\frac{d}{p}\right)^{2} p^{j(3-2 k)}\right)
\end{array}\right\}
$$

zu prüfen, wobei $j=\left[\frac{b-1}{2}\right]$ oder $\left[\frac{b-2}{2}\right]$, je nachdem $p>2$ oder $p=2$ ist. Nun ist $\delta_{p}\left(-D p^{-2}\right)=1$ mit Ausnahme des Falles $p=2,-D \equiv 8$ oder 12 (mod 16), der $b=2$ oder 3 , mithin $j=0$ und zudem $\left(\frac{d}{2}\right)=0$ nach sich zieht, woraus die Gültigkeit von (13) erhellt. Der Beweis für (10) ${ }_{1}$ ist damit erbracht.

Wir beweisen $(10)_{\mathrm{h}}$ für $h \geqq 2$, indem wir für den Term auf der linken Seite sowie den zweiten Term auf der rechten Seite von (10) $)_{\mathrm{h}}$ die durch (2) gegebenen Darstellungen eintragen. Mit Hilfe von (10) ${ }_{\mathrm{h}-1}$ und (10) ${ }_{\mathrm{h}-2}$, sofern $h \geqq 3$ ist, führen wir die so erhaltene Relation über in

$$
\left.\begin{array}{c}
\beta_{k}\left(e_{1}, p^{2 h} e_{1} D\right)= \\
\left(1+p^{2 k-3}\right) \beta_{k}\left(e_{1}, p^{2(h-1)} e_{1}^{2} D\right)-p^{2 k-3} \beta_{k}\left(e_{1}, p^{2(h-2)} e_{1}{ }^{2} D\right)(h \geqq 2) . \tag{14}
\end{array}\right\}
$$

Die Reduktion auf den Fall $e_{1}=1$ erfolgt nach mehrmals angewendetem Verfahren mit Hilfe von (8). Die Gleichung (10) für $h \geqq 2$ erweist sich somit gleichwertig mit der Relation
$\beta_{k}\left(1, p^{2 h} D\right)=\left(1+p^{2 k-3}\right) \beta_{k}\left(1, p^{2(h-1)} D\right)-p^{2 k-3} \beta_{k}\left(1, p^{2(h-2)} D\right)(h \geqq 2)$,
die sich mit Hilfe von (9) in analoger Weise verifizieren läßt wie die Relation (12). Mit $(10)_{\mathrm{h}}$ ist schließlich auch (8), das Ziel unserer Ausführungen, bewiesen.

Schließlich sei noch auf den multiplikativen Charakter der in (9) definierten Zahlfunktion $b_{k}(\Delta)$ hingewiesen: Für Diskriminanten $d$ imaginärquadratischer Zahlkörper gilt

$$
\begin{equation*}
b_{k}\left(e_{1}{ }^{2} e_{2}{ }^{2}|d|\right)=b_{k}\left(e_{1}{ }^{2}|d|\right) b_{k}\left(e_{2}{ }^{2}|d|\right), \text { falls }\left(e_{1}, e_{2}\right)=1 \tag{16}
\end{equation*}
$$

ist. Man braucht sich nur klar zu machen, daß der p-Beitrag in der Produktdarstellung von $b_{k}\left(e^{2}|d|\right)$ bei gegebener Diskriminante $d$ nur von der höchsten Potenz von $p$ abhängt, welche $e$ teilt, und $\operatorname{daß} b_{k}(|d|)=1$ ist. Zufolge

$$
\beta_{k}\left(1, e^{2}|d|\right)=\omega_{k}(d) b_{k}\left(e^{2}|d|\right)=\beta_{k}(1,|d|) b_{k}\left(e^{2}|d|\right)
$$

erweist sich daher der Quotient

$$
\chi(e)=\frac{\beta_{k}\left(1, e^{2}|d|\right)}{\beta_{k}(1,|d|)}
$$

als multiplikativ:

$$
\chi\left(e_{1} e_{2}\right)=\chi\left(e_{1}\right) \chi\left(e_{2}\right) \quad \text { für } \quad\left(e_{1}, e_{2}\right)=1,
$$

womit eine weitere Vermutung von R. L. Saldaña verifiziert ist.
Äquivalent mit (8) ist im Falle $\Delta=|d|$ die Identität
wobei

$$
\begin{equation*}
\zeta_{k}^{*}(s, d)=\zeta(s+1-k) \zeta_{k}(s, d) \tag{17}
\end{equation*}
$$

$$
\begin{equation*}
\zeta_{k}(s, d)=\sum_{n=1}^{\infty} \beta_{k}\left(1, n^{2}|d|\right) n^{-s}, \zeta_{k}^{*}(s, d)=\sum_{n=1}^{\infty} \beta_{k}\left(n, n^{2}|d|\right) n^{-s} \tag{18}
\end{equation*}
$$

und $\zeta(s)$ die Riemannsche Zetafunktion ist. Die erste dieser Funktionen gestattet vermöge (16) die Produktdarstellung

$$
\zeta_{k}(s, d)=\beta_{k}(1,|d|) \prod_{p} \sum_{v=0}^{\infty} b_{k}\left(p^{2 v}|d|\right) p^{-v s},
$$

wobei $p$ alle Primzahlen durchläuft. Die Berechnung der p-Faktoren in diesem Produkt führt zu einem überraschend einfachen Ergebnis. Es sei
$p^{b}$ die höchste Potenz von $p$ welche $d$ teilt, und $j=\left[\frac{b-1}{2}\right]$ oder $\left[\frac{b-2}{2}\right]$,
je nachdem $p>2$ oder $p=2$ ist. Dann gilt

$$
b_{k}\left(p^{2 v}|d|\right)=p^{v(2 k-3)}\left(\left\{1-\left(\frac{d}{p}\right) p^{1-k}\right\}_{\mu=0}^{j+v} p^{\mu(3-2 k)}+\left(\frac{d}{p}\right)^{2} p^{(j+v+1)(3-2 k)}\right)
$$

Nach Aufsummierung aller auftretenden geometrischen Reihen ergibt sich

$$
\begin{gathered}
=\frac{1-\left(\frac{d}{p}\right) p^{1-k}}{1-p^{3-2 k}}\left\{\frac{\sum_{\nu=0}^{\infty} b_{k}\left(p^{2 v}|d|\right) p^{-v s}}{1-p^{-s+2 k-3}}-\frac{1}{1-p^{-s}}\right\}+\left(\frac{d}{p}\right)^{2} \frac{p^{(j+1)(3-2 k)}}{1-p^{-s}} \\
=\frac{1-\left(\frac{d}{p}\right) p^{-s+k-2}}{\left(1-p^{-s}\right)\left(1-p^{-s+2 k-3}\right)}
\end{gathered}
$$

ausnahmslos für alle Primzahlen $p$, mithin

$$
\begin{equation*}
\zeta_{k}(s, d)=\beta_{k}(1,|d|) \frac{\zeta(s) \zeta(s+3-2 k)}{L\left(s+2-k,\left(\frac{d}{*}\right)\right)} \tag{19}
\end{equation*}
$$

wobei $L\left(s,\left(\frac{d}{*}\right)\right)$ die $L$-Reihe zum Charakter $\left(\frac{d}{*}\right)$ mod $d$ bezeichnet. Damit haben wir das erste Beispiel einer Zetafunktion, die mit Hilfe von Fourierkoeffizienten einer Modulform zweiten Grades definiert ist und die eine Eulersche Produktentwicklung besitzt.

Hinsichtlich der Frage nach den Eulerprodukten, die den Modulformen höheren Grades zugeordnet werden können, eröffnen sich hier neue Perspektiven.

Zusatz bei der Korrektur:
Auf die von A. N. Andrianov in Trudy mat. Inst. Steklov 112,73-94 (1971) in russischer Sprache publizierte Arbeit mit ihren weitreichenden Ergebnissen sei hier nachdrücklich hingewiesen. Ein Autorreferat in englischer Sprache unter dem deutschen Titel ,,Dirichletreihen mit Eulerschem Produkt in der Theorie der Siegelschen Modulformen zweiten Grades’’ findet man im Zbl. für Math. 224 unter Nr. 10027. Ich wurde auf diese ideenreiche Arbeit, in der Probleme gelöst werden, die seit Jahrzehnten anstehen, durch das angegebene Referat aufmerksam.

# PHOTO-ELECTRON SPECTRA INDUCED BY X-RAYS OF above 600 NON-METALLIC COMPOUNDS CONTAINING 77 ELEMENTS 

Det Kongelige Danske Videnskabernes Selskab Matematisk-fysiske Meddelelser 38, 15


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## Synopsis

The chemical shift $\mathrm{d} I$ of the ionization energy $I$ of the inner shells is not only dependent on the oxidation state of a given element, but also on the ligands. Even for a fixed oxidation state, $\mathrm{d} I$ has been shown to vary between 2 and 8 eV in a comparative study of all elements which are neither noble gases nor strongly radioactive. However, this conclusion is, to some extent, modified by reproducible positive potentials on non-conducting samples which have been measured between 1 and 4 V in typical cases and compared with the theory for almost ionic cubic crystals and with experiments with mixtures of non-conducting powdered $\mathrm{MgF}_{2}, \mathrm{BaSO}_{4}$ and $\mathrm{ThF}_{4}$ and metals such as $\mathrm{Au}, \mathrm{Tl}_{2} \mathrm{O}_{3}$ and CuS . The widths and highly varying intensities of photo-electron signals are theoretically discussed. The $d$ and $f$ shells of transition and post-transition group atoms give relatively intense signals even for $I$ between 8 and 30 eV since the 1486.6 eV photons most readily ionize shells with small average radii. Interesting relations can be established with electron transfer spectra and optical electronegativities.

The effects of interelectronic repulsion produce multiple signals when the groundstate has positive $S$. Special satellites occur in copper(II), lanthanum(III) and other lanthanide compounds. A systematic study is made of alkaline metal, tetra-alkylammonium, tetraphenylarsonium, methylene blue and $\mathrm{Co} \mathrm{en}_{2} \mathrm{Cl}_{2}{ }^{+}$salts of several anions. The adaptation of the electronic density of the neighbour atoms in the ionized system contribute to $\mathrm{d} I$ which cannot be explained exclusively on the basis of fractional atomic charges and the Madelung potential.

## Introduction

The ionization energy $I$ of inner shells or delocalized penultimate molecular orbitals can be determined as the difference between $\mathrm{h} v$ of monoenergetic photons and the kinetic energy $\mathrm{E}_{\text {kin }}$ of the electron ejected. Since about 1963, such measurements are performed on gaseous samples [107] using the resonance line of helium at 21.2 eV or of $\mathrm{He}^{+}$at 40.8 eV . This has allowed the confirmation of previous conclusions of M.O. theory, in particular for diatomic and triatomic molecules. The resolution 0.01 eV can be achieved, allowing accurate measurement of the vibrational structure, but only moderate I values can be evaluated. Photons originating in an aluminium anti-cathode have $\mathrm{h} v=1486.6 \mathrm{eV}$ (or in a magnesium anti-cathode 1253.6 eV ) permitting $I$ to be measured in a much larger interval, but the resolution obtained is not much better than 1 eV . Such soft X-rays have also been used on gaseous atoms and molecules [98], but an important advantage is that also the surface of solid samples can be studied. The original instrument in Uppsala [97] and another in Berkeley [45] use magnetic deflection for determining $\mathrm{E}_{\mathrm{kin}}$ whereas the commercial instruments available from at least five companies use electrostatic deflection allowing a much more compact construction. In January 1971, we received a Varian IEE-15 photo-electron spectrometer using 1486.6 eV photons. As discussed below, the values $I^{*}$ recorded by the apparatus are slightly smaller (usually 2 to 5 eV ) than $I$ relative to vacuo, and under our standard conditions of 100 eV analyzer energy, $I^{*}$ between 0 and 1382 eV can be measured, and the sharp peaks (not broadened for special reasons) have the sum of the half-width $\delta(-)$ toward lower $I$ and $\delta(+)$ toward higher $I$ between 1.9 eV and 2.0 eV . Recent reviews of X-ray induced photo-electron spectra have appeared [38, 43] and can be compared with the weak chemical effects on X-ray spectra [30].

We decided to compare a large number of non-metallic, mainly inorganic, compounds, containing all those elements which are neither noble gases nor strongly radioactive in order to facilitate future work with all
kinds of related compounds. Two years ago, it was felt that one of the major applications of photo-electron spectrometry would be the distinction between non-equivalent atoms of the same element. In 1928, Stelling[100] found that the X-ray absorption edges have 8 to 11 eV higher energy in sulphur (VI) than in sulphur ( - II ), also in thiosulphate where the central atom has the former oxidation state and the terminal sulphur atom the latter. Actually, $\mathrm{S}_{2} \mathrm{O}_{3}^{-2}$ was one of the first examples of a dramatic effect of non-equivalent atoms found in Uppsala [36], and it is seen from Table 3 that the separation of the two 2 p signals is 6.0 eV which is attenuated in the gold (I) thiosulphate complexes to 5.5 eV in $\mathrm{Na}_{3}\left[\mathrm{Au}\left(\mathrm{S}_{2} \mathrm{O}_{3}\right)_{2}\right]$ and 5.3 eV in $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Au}\left(\mathrm{S}_{2} \mathrm{O}_{3}\right)_{2}\right]$ having the terminal sulphur atom bound to a gold atom. The corresponding separation is 4.3 eV in tetrathionate $\mathrm{O}_{3} \mathrm{SSSSO}_{3}{ }^{-2}$ having two of each kind of sulphur atoms. However, many other compounds containing mixed oxidation states [95] such as $\mathrm{Pb}_{3} \mathrm{O}_{4}$ and $\mathrm{U}_{3} \mathrm{O}_{8}$ at most show slightly broadened signals, and whereas the dark blue $\mathrm{Cs}_{4}\left(\mathrm{Sb}^{I I I} \mathrm{Cl}_{6}\right)\left(\mathrm{Sb}^{\mathrm{V}} \mathrm{Cl}_{6}\right)$ shows a detectable splitting 1.8 eV of the $\mathrm{Sb}_{3} \mathrm{~d}_{3 / 2}$ signal (in Table 14) this is not much compared with the range of chemical shifts 6.8 eV for antimony $(\mathrm{V})$ and 3.3 eV for antimony (III) varying the ligating atoms from fluorine to sulphur. Said in other words, the chemical shift $\mathrm{d} I$ depends more upon the nature of the neighbour atoms than on the oxidation state of the element considered.

The main conclusion of this study of 617 samples is that a given element in the same oxidation state varies $I$ of the inner shells between 2 and 8 eV (the latter, maximum interval occurs [62] for fluorine ( -I ), but both Mg (II), $\mathrm{P}(\mathrm{V}), \mathrm{S}(\mathrm{VI}), \mathrm{Ni}(\mathrm{II}), \mathrm{Cu}(\mathrm{II}), \mathrm{Br}(-\mathrm{I}), \operatorname{Rh}(\mathrm{III}), \mathrm{Sb}(\mathrm{V}), \mathrm{La}(I I I), \operatorname{Re}(\mathrm{VII})$ and $\mathrm{Pt}(\mathrm{IV})$ show intervals above 5 eV$)$. It is true that the elements able to change their oxidation state by eight units [56] such as nitrogen [41] and sulphur [77] show large ranges of $\mathrm{d} I$ above 10 eV . However, the separation according to oxidation state is by no means clear-cut. Thus, the perchlorates in Table 4 have their 2 p signals distributed over 2.5 eV , the lower limit being 5 eV above the higher limit of the interval for chlorides which is itself 4.6 eV wide. The only exceptions to the statement of minimum interval 2 eV are Tb (III), Ho (III) and Tm (III) of which only two compounds have been studied here, and Sc(III) with three.

There was a time when it was believed that $\mathrm{d} I$ indicates the oxidation number though the strong influence of the Madelung potential was emphasized early [27]. This hypothesis was refuted by Kramer and Klein [70, 71] showing that $I(\mathrm{Fe} 3 \mathrm{p})$ of highly covalent iron(III) compounds such as $\mathrm{Fe}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3}$ is below $\mathrm{Fe}(\mathrm{CO})_{5}$ and salts of $\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}^{+2}$ though even larger $I$ values are observed for the less covalent iron(III) complexes $\mathrm{FeF}_{6}^{-3}$
and $\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}^{+3}$. One might have argued that the important variable is the fractional charge of the central atom [52], but our results show that this cannot be the whole truth. As discussed below, our 59 potassium salts cannot seriously be suspected for strong deviations from the charge +1 of $\mathrm{K}(\mathrm{I})$, and the observed interval 4 eV of $I$-values varies, on the whole, in the opposite direction of the changes of the Madelung potential acting on the cation. Other conclusions of our work relate to half-widths and relative intensities of photo-electron signals and to multiple signals either due to effects of interelectronic repulsion (when the groundstate has positive total spin quantum number $S$ ) or to satellites of the kind prominent in copper(II), lanthanum(III) and the earlier lanthanides. Further on, it is of obvious interest to the chemist to obtain as much information as possible about the valence region with $I$ below 50 eV . However, the non-conducting samples involve difficult problems of intrinsic calibration, as we shall discuss at first.

## Orbital Energies Relative to the Vacuo Zero-point and Internal References

Metallic samples brought in electric contact with the apparatus do not produce serious difficulties. The instrument records the number of photoelectrons counted as a function of their kinetic energy $\mathrm{E}_{\text {kin }}$, and since the work-function of the metallic copper used in the analyzer is said to be 4.6 eV , an ionization energy $I^{*}$ relative to this prevailing Fermi level is indicated by the simple relation $I^{*}=1482.0 \mathrm{eV}-\mathrm{E}_{\mathrm{kin}}$. Gold has a strong signal due to the eight $4 \mathrm{f}_{7 / 2}$ electrons ( $I^{*}$ has been carefully determined to be 83.8 eV in Uppsala) and is one of the few metals not showing covering oxide, hydroxide or carbonate layers. Hence, a Varian instrument like ours [113] has been used to measure the small changes from $I^{*}=83.15 \mathrm{eV}$ for pure Au to 83.45 eV for the alloy $\mathrm{Au}_{0.05} \mathrm{Ag}_{0.95}$ and 84.5 eV in $\mathrm{AuAl}_{2}$ and $\mathrm{AuGa}_{2}$. All gaseous hydrocarbons (containing single, double or triple bonds, but only hydrogen and carbon bound to a given carbon atom) have $I(\mathrm{C} 1 \mathrm{~s})$ only a few tenths eV below the value 290.8 eV for $\mathrm{CH}_{4}$, and it was suggested [60] to use the aliphatic hydrocarbon (polymerized isoprene) on the adhesive side of one-sided scotch tape ( 15 mm 600 P from the 3 M company) as internal standard having $I=290 \mathrm{eV}$ relative to vacuo and to define the scotch tape correction $\mathrm{C}_{\text {st }}$ as the difference between 290 eV and the lowest $I^{*}$ (C1s) recorded by the instrument when a sample covers some $300^{\circ}$ of a cylindrical surface $60^{\circ}$ of which consists of scotch tape without sample. The purpose of this definition is to evaluate $I=I^{*}+\mathrm{C}_{\text {st }}$ of all the other signals measured.

It may be noted that double-sided scotch tape (a poly-ether) or certain brands containing polyvinylchloride are not suitable, because of adjacent shoulders on the carbon signal, due to carbon atoms bound to oxygen or Cl .

Tables 1 to 19 gives the $\mathrm{C}_{\text {st }}$ values (without brackets) and $I$-values (shoulders in parentheses) for 617 compounds and other samples in order of increasing atomic number of the elements $\mathrm{Li}, \mathrm{Be}, \mathrm{B}, \mathrm{N}, \mathrm{F}, \mathrm{Na}$ to $\mathrm{Cl}, \mathrm{K}$ to $\mathrm{Br}, \mathrm{Rb}$ to I, Cs to Nd, Sm to Bi , Th and U. For some elements, the oxidation number is given as a super-script Roman numeral for all the compounds where it is defined[56]; in some other cases, only relatively exceptional oxidation states are indicated. Table 20 gives some weak signals measured of 22 selected samples. Each sample has an identification number. Figure 1 gives typical spectra between $I=0$ and 250 eV of compounds mainly containing elements between iodine and osmium, whereas Figure 2 gives spectra between $I=0$ and 450 eV of compounds mainly containing elements between platinum and uranium.

There is no doubt that the $I$-values evaluated in this way do not correspond exactly to the ionization energies relative to vacuo. The main reason [97] is that the non-conducting sample becomes positive because it looses photoelectrons, and a quasi-stationary equilibrium is soon established where electrons come back to the sample, but in insufficient number, maintaining a potential $V$ decreasing the kinetic energy of the ejected electrons to $\mathrm{E}_{\mathrm{kin}}-\mathrm{V}$ corresponding to an apparent higher ionization energy $I=I^{\prime}+\mathrm{V}$ where $I^{\prime}$ would be the ionization energy relative to vacuo in absence of this charging effect. Actually, the physicists [44] at Brookhaven National Laboratory made experiments with a metallic cylinder covered with $\mathrm{BaSO}_{4}$ on which thin layers of gold or palladium were evaporated. The $I^{*}$ value of $\mathrm{Au}_{4} \mathrm{f}_{7 / 2}$ of the isolated gold turned out to be 1.6 eV higher than when the gold was in electric contact with the sample holder. Further on, this difference was increased to 2.2 eV if an external potential of -1.6 V was imposed on the sample holder, whereas the difference decreased to 1.2 eV if the external potential was +1.6 V . It may be noted that $I^{*}$ of the "connected" gold varied perfectly linearly, $82.8,81.2$ and 84.3 eV in the three cases, whereas the "isolated" gold varied less, $84.4,83.4$ and 85.5 eV in the three cases. These values are all 1 eV too low in the sense that they refer to 82.8 eV derived from X-ray spectra by Bearden and Burr [3].

When we measured gold powder distributed in a dense way on scotch tape, two independent measurements both gave $I^{*}=83.15 \mathrm{eV}, \mathrm{C}_{\text {st }}=5.4 \mathrm{eV}$ and $I=88.55 \mathrm{eV}$. If the work-function of gold is $4.8 \mathrm{eV}, I=88.6 \mathrm{eV}$ confirming the choice of 290.0 eV . A cylinder made from 0.2 mm thick gold plate


Figure 1. Photo-electron spectra of fourteen selected compounds in the region of $I$ below 250 eV . The scale of intensities is not identical, and an arbitrary amount of background counts have been subtracted in each region. Elements between $Z=53$ (iodine) and $Z=76$ (osmium) are mainly considered.
showed $I^{*}=83.75 \mathrm{eV}$ again in good agreement with the Uppsala value. A piece of scotch tape glued to this cylinder showed $I^{*}=283.9 \mathrm{eV}$ but we do


Figure 2. Photo-electron spectra of fourteen selected compounds in the region of $I$ below 450 eV . One or two carbon 1s signals are seen, as discussed in the text. Elements between $Z=78$ (platinum) and 92 (uranium) are mainly considered.
not ascribe physical significance to the corollary $\mathrm{C}_{\text {st }}=6.1 \mathrm{eV}$. During 12 hours of continued measurements, we varied the X -ray potential from its standard value $(9000 \mathrm{~V})$ to 6000 V and the X -ray filament current from its
standard value ( 70 mA ) to 50 and 30 mA in various combinations in order to study the effect of varying radiation density. The number of electrons counted varied by a factor of six. The sample measured was a powdered mixture of (equimolar quantities) of $2.4 \mathrm{~g} \mathrm{BaSO}_{4}, 3.0 \mathrm{~g} \mathrm{ThF}_{4}$ and 2.0 g Au on one-sided scotch tape. The two non-conducting and the metallic constituent were chosen in order to avoid mutual chemical reactions. $I^{*}(\mathrm{C} 1 \mathrm{~s})$ varied from 285.25 eV at the beginning to 285.05 eV at the lowest irradiation level and back to 285.1 eV at the standard conditions. The corresponding drift of the F 1 s , Ba3d and Th4f signals was a decrease, at most between 0.45 and 0.75 eV , and showing a certain hysteresis in the sense that $I$ did not return fully to the original values when the standard conditions were restored. A positive result of this experiment is that the gold powder only had a very small influence on the signals of the atoms in the isolators (it may be noted that $\operatorname{Th} 4 \mathrm{f}_{7 / 2}$ and $\mathrm{Au} 4 \mathrm{~d}_{5 / 2}$ are adjacent and measured in the same region, as is also true for Th5d $\mathrm{d}_{5 / 2}$ and the two Au4f signals) and the $I$ values are only marginally larger of pure $\mathrm{BaSO}_{4}$ or $\mathrm{ThF}_{4}$ on scotch tape. On the other hand, it cannot be denied that the "isolated" gold was brought in a state comparable to that described above[44], $I^{*}$ varied from 86.65 to 86.25 eV during the experiment, 2.9 to 2.5 eV above the gold alone. One conclusion is that this charging effect hardly depends on the X-ray density in the interval varied here, but is induced by a much lower level of irradiation [65].

It is known from the statistical treatment of a mixture of isolating and metallic grains of comparable size that the bulk electric conductivity rather suddenly raises in a narrow interval as a function of the percentage of the metallic grains. We seem to have arrived at both sides of this interval when measuring two mixtures of magnesium(II) fluoride and thallium(III) oxide. Actually, dark brown $\mathrm{Tl}_{2} \mathrm{O}_{3}$ is a physical metal, and it was found surprising that $I$ is some 2 to 4 eV lower than of the thallium(I) compounds ( $c f$. Table 19). A mixture $6 \mathrm{MgF}_{2}: 2 \mathrm{Au}: \mathrm{Tl}_{2} \mathrm{O}_{3}$ (having $I^{*}\left(\mathrm{Au} 4 \mathrm{f}_{7 / 2}\right)=83.1 \mathrm{eV}$ ) conserves this "metallic" situation whereas $\mathrm{Tl}_{2} \mathrm{O}_{3}$ must be isolated having $I 3 \mathrm{eV}$ higher in the mixture $16 \mathrm{MgF}_{2}: 2 \mathrm{Au}: \mathrm{Tl}_{2} \mathrm{O}_{3}$ (where the gold signal has $\left.I^{*}=86.7 \mathrm{eV}\right)$. The effect is less dramatic on the mixture $5 \mathrm{MgF}_{2}: 1 \mathrm{CuS}$ increasing $I^{*}$ of the lowest copper 2 p signal 2.2 eV and $I 1.5 \mathrm{eV}$ relative to CuS alone (cf. Table 8).

One might lose the hope of evaluating these charging effects increasing the apparent $I$-values of non-conducting samples some 2 to 4 eV relatively to "connected" metallic samples. However, there is one way out, as pointed out by Bremser and Linnemann [8]. The carbon 1 s signal is frequently accompanied by a shoulder or separate signal at 2 to 4 eV higher $I^{*}$. It was
felt for some time that this shoulder might be due to alcohols $\left(\mathrm{CH}_{3} \mathrm{OH}\right.$ is known [98] to have $I 1.9 \mathrm{eV}$ higher than $\mathrm{CH}_{4}$ ) either originating from residual organic solvents from the preparation of the samples, from filter paper fibers (cellulose is a poly-alcohol) or from the action of strong oxidants (such as $\mathrm{PbO}_{2}$ or $\mathrm{Cs}_{2} \mathrm{RhCl}_{6}$ ) on the hydrocarbon. However, this is not too probable in all cases because of the variable distance of this shoulder. On the other hand, this signal is situated at $I^{*}$ between 289 and 290 eV in several fluorides, at first suggesting carbonate impurities. Again, this is not plausible because an actual carbonate C 1 s signal has been observed at $I^{*}=291.5 \mathrm{eV}$ in $\mathrm{Li}_{2} \mathrm{CO}_{3}$, 291.9 eV in the complex no. 9 discussed in the experimental section, 291.2 eV in $\mathrm{Ag}_{2} \mathrm{CO}_{3}, 292.7 \mathrm{eV}$ in $\mathrm{CdCO}_{3}, 291.9 \mathrm{eV}$ in $\mathrm{PbCO}_{3}$ and 292.4 eV in the salt of $\operatorname{Th}\left(\mathrm{CO}_{3}\right)_{5}^{-6}$. These values may be compared with $I=297.6 \mathrm{eV}$ for [98] gaseous $\mathrm{CO}_{2}$. As a matter of fact, the carbonates mentioned show three signals. A reasonable working hypothesis is that the middle signal of carbonate and the left-hand signal (highest $I^{*}$ ) of many other compounds are due to the adhesive hydrocarbon on the sample in contrast to the right-hand signal due to scotch tape without adherent sample. Correspondingly, the $\mathrm{C}_{\text {st }}$ columns in Tables $1-20$ contain values in sharp brackets obtained as the difference between 290 eV and $I^{*}$ of the left-hand signal. In the following, we call $I^{*}$ plus $\mathrm{C}_{\text {st }}$ in sharp brackets $I^{\prime}$, and we call the difference between the two $\mathrm{C}_{\text {st }}$ values for $\partial$.

The question is now whether $\partial$ is a reasonable measure of the charging effects and whether $I^{\prime}$ has the physical significance of an ionization energy of an orbital in an uncharged solid relative to vacuo. One of the arguments [60] for $\mathrm{C}_{\text {st }}$ based on the choice of 290 eV was the good agreement with the Madelung potential $V_{\text {Mad }}$ added to the ionization energy [4,81] of gaseous $\mathrm{X}^{-}$and subtracted from the ionization energy [82] of gaseous $\mathrm{M}^{+}$or $\mathrm{M}^{+2}$ with exception of iodides and caesium salts having $I$ of the loosest bound shells some 1 to 2 eV higher than excepted. Table 21 gives the new $I^{\prime}$ values. They agree definitely less well with the simple Madelung theory; thus, the 15 alkali metal halides have on the average $\mathrm{I}^{\prime}(\mathrm{M}) 2.4 \mathrm{eV}$ too low and $I^{\prime}(\mathrm{X})$ 1.8 eV too low. However, Mott and Gurney [84] give the ionization energies 10.17 eV for $\mathrm{NaCl}, 9.49 \mathrm{eV}$ for KCl and 9.00 eV for KBr in astonishing agreement with our $I^{\prime}$ values, in particular when it is realized that presently known values of the electron affinity of Cl and Br atoms are 0.15 eV lower. It may be noted that Mott and Gurney do not use the Madelung potential but the heats of formation of the crystal from gaseous ions (hence including a certain amount of core-core repulsion in decreased $I$ ) and they have to add contributions around 1.5 eV from electric polarizability of the groundstate.


Figure 3. Explanation of almost constant positive potential $V$ on the surface of non-metallic samples under X-ray irradiation. As discussed in the text, V can be identified with the difference $\partial$ between the two carbon 1 s signals indicated as the difference between $\mathrm{C}_{\mathrm{st}}$ and the value in sharp brackets in Tables 1-19.

One may ask the question why the charging effects remain roughly constant over a wide interval of X-ray densities, and Figure 3 suggests an explanation. All the apparent $I$ values are the sum of the $I^{\prime}$ valid for the neutral crystal and a potential $V$ determined by the condition that the lower limit of the empty conduction band is brought down just below the Fermi level of the adjacent metallic objects with the result that electrons can be supplied at a reasonable rate to replace the ejected photo-electrons. When identifying $\partial$ with V , it is easy to understand why most fluorides have large values close to 4 eV , whereas most compounds measured have V between 1 and 2 eV which are difficult to detect as distinct shoulders in the carbon 1 s region. Actually, if this explanation is perfectly valid, it would be better to cover the scotch tape completely with the sample and make no attempt to observe the pure hydrocarbon. The first ten compounds measured by us (see $\mathrm{K}_{2} \mathrm{ReCl}_{6}, \mathrm{~K}_{2} \mathrm{OsCl}_{6}$ and $\mathrm{KNiF}_{3}$ ) were treated this way and produced low $\mathrm{C}_{\text {st }}$ values close to 3.7 eV . However, we doubt that this would be a very accurate technique, though it is surprising how narrow are distinct left-hand
signals indicating a well-defined situation of the "isolated" hydrocarbon. Another interesting corollary is that the energy gap, the difference between the highest filled orbitals and the lower limit of the conduction band should be exactly $(I-4.8 \mathrm{eV})$ in this model. This is why the last column of Table 21 gives this quantity showing good agreement with the values obtained from absorption spectra of the crystals [54], the photo-conductivity usually setting in about 0.5 eV above the maximum of the first strong absorption band.

There is no doubt that $\partial$ does not represent the average energy between the top of the valence band and the bottom of the lowest conduction band, (that is half the energy gap disregarding band width) as frequently said[105] to be the Fermi level of a semi-conductor. Actually, $\partial$ can be larger than half the energy gap, as can be seen from the specific examples 2.7 eV for CuO , 2.4 eV for $\mathrm{ZnS}, 2.0 \mathrm{eV}$ for $\mathrm{GaS}, 2.8 \mathrm{eV}$ for $\mathrm{Ag}_{3} \mathrm{PO}_{4}, 1.9 \mathrm{eV}$ for $\mathrm{AgBr}, 2.6 \mathrm{eV}$ for $\mathrm{CdO}, 1.5 \mathrm{eV}$ for CdS and 3.4 eV for $\mathrm{PbI}_{2}$. Langer and Vesely [73] argue that their results (also obtained with a Varian IEE-15 spectrometer) for $\mathrm{ZnO}, \mathrm{ZnS}, \mathrm{ZnSe}, \mathrm{ZnTe}$, and the corresponding cadmium(II) and mercury (II) compounds are compatible with the conventional definition of the Fermi level, identifying the difference between $I^{\prime}$ and $I^{*}$ with the top of the valence band plus half the energy gap $[109,110]$.

If we define $I^{\prime}$ by subtracting $\partial$ (in the cases where two carbon 1 s signals have been detected) from the $I$-values, we reach smaller chemical shifts (roughly two-thirds as large as in Tables 1 to 20) because $\partial$ is particularly large for fluorides and small (and not detectable) for sulphides and many complexes of organic ligands. It is perhaps not superfluous to note that large chemical shifts are known for gaseous nitrogen compounds [31] where $I=I^{\prime}=417.0 \mathrm{eV}$ for N 1 s of $\mathrm{NOF}_{3}, 414.2 \mathrm{eV} \mathrm{NF} 3,412.5 \mathrm{eV}$ for the central and 408.6 for the terminal nitrogen atom of NNO, 409.9 eV for $\mathrm{N}_{2}, 406.8 \mathrm{eV}$ for $\mathrm{HCN}, 405.6 \mathrm{eV}$ for $\mathrm{NH}_{3}, 405.1 \mathrm{eV}$ for $\mathrm{CH}_{3} \mathrm{NH}_{2}$ and 404.7 eV for $\mathrm{N}\left(\mathrm{CH}_{3}\right)_{3}$. Actually, the $I$-values in Table 1 are $405 \pm 1 \mathrm{eV}$ for coordinated ammonia and ethylenediamine and $404 \pm 1 \mathrm{eV}$ for coordinated cyanide. These values (which do not refer to fluorides) may be rather representative and only about 1 eV above the $I^{\prime}$ values. For certain elements, the corrections with $\partial$ almost cancels the chemical shift. Thus, $I^{\prime}($ Li1s $)=60.7 \mathrm{eV}$ for LiF, 60.2 eV for $\mathrm{Li}_{2} \mathrm{CO}_{3}$ and 60.0 eV for $\mathrm{Li}_{3} \mathrm{PO}_{4}$ though it is probably close to 58 eV for $\mathrm{Li}_{2} \mathrm{SO}_{4}$ and $\mathrm{Li}_{3} \mathrm{Co}(\mathrm{CN})_{6}$. Again, $I^{\prime}(\mathrm{Be} 1 \mathrm{~s})=120.8 \mathrm{eV}$ for $\mathrm{BeF}_{2}, 119.6 \mathrm{eV}$ for $\mathrm{K}_{2} \mathrm{BeF}_{4}$ (two independent measurements agree, like in the case of LiF), 119.3 eV for $\mathrm{BeO}, 118.5 \mathrm{eV}$ for the carbonate complex no. 9 and somewhere between 117 and 118 eV for $\left[\mathrm{Be}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right] \mathrm{SO}_{4}$.

Table 22 gives $I^{\prime}(\mathrm{F} 1 \mathrm{~s})$ and $I^{\prime}\left(\mathrm{K} 2 \mathrm{p}_{3 / 2}\right)$ of 48 fluorine[62] and 29
potassium compounds. There is no doubt that the reproducibility is far better, some 0.2 eV , than the 0.7 eV we find for repeated measurements of $I$-values. In all fairness, it must be added that we have most frequently repeated compounds where the position of the right-hand signal of C1s was doubtful the first time, and the repetition almost always has increased the $I$-value. When compounds are repeated under good conditions at some months' interval, the reproducibility seems to be close to 0.4 eV . The conclusions from Table 2 and 5 are not modified strongly, essentially the same order of compounds is found, though the scale is compressed. It must be remembered that the lower $I$-values of potassium salts do not have known $\partial$ values; Table 5 probably ends with $I^{\prime}$ close to 296 eV since no metallic sample containing potassium has been measured.

It is also striking that $I^{\prime}$ of iodates varies less, and in a more regular way, than $I$ of Table 15 . Thus, $I^{\prime}\left(\mathrm{I}_{3 \mathrm{~d}_{5 / 2}}\right)$ varies from 629.8 to 628.9 eV in the order Hf, Th, Y, In, Ni, Sm, Eu, La, Pr, Nd, Pb, UO2, Gd, Ho, Ca, Tm, Zn, Zr, $\mathrm{Er}, \mathrm{Ce}, \mathrm{Yb}, \mathrm{Ag}, \mathrm{Ba}, \mathrm{Hg}, \mathrm{Tl}, \mathrm{K}, \mathrm{Cu}$ and Lu. It is also interesting to compare $I^{\prime}$ (Th4f $\mathrm{f}_{7 / 2}$ ) for eight mixed oxides (of which several are black [53] and should conduct to some extent) varying from 339.5 to 338.25 eV with the average 338.9 eV . The higher $I^{\prime}=341.8 \mathrm{eV}$ for $\mathrm{ThF}_{4}$ and 341.0 eV for $\mathrm{Th}\left(\mathrm{IO}_{3}\right)_{4}$ shows that even thorium (IV) have perceptible chemical shifts. The oxidized powdered metallic thorium with $I^{\prime}=339.3 \mathrm{eV}$ and $\partial=3.5 \mathrm{eV}$ shows that it has hardly any effect if a non-conducting sample is metallic inside. Since the 4 f signals are so important for the understanding of the lanthanides, Table 23 gives $I^{\prime}$ (4f) when they can be evaluated.

Though $I^{\prime}$ undoubtedly is a better approximation to ionization energies relative to vacuo than $I$ in the case of highly isolating samples, a few conceptual difficulties remain. For instance, it is not easy to accept the accessible hydrocarbon not covered by sample as a kind of metal, establishing its $I^{\prime}=I^{*}+4.8 \mathrm{eV}$ whereas the "isolated" hydrocarbon of the surface of isolating samples shows $I^{*}=I+\partial-4.8 \mathrm{eV}$. This is not an easy question to answer by experimentation in the laboratory. The propensity of establishing electric equilibrium may perhaps only develop under the X-ray irradiation. It is more difficult to understand why $\mathrm{C}_{\text {st }}$ in Tables 1 to 20 does not remain constant but shows systematic variations. Thus, the high $\mathrm{C}_{\text {st }}$ values between 5.2 and 6 eV usually develop when the sample is a metallic powder. One explanation is that the electric equilibrium is so distorted in this case that some of the photo-electrons and secondary (Auger etc.) electrons emitted fix on the scotch tape, much in the same way as on amber, making the surface negative to the extent of about 1 eV . We do not have an absolute guaranty
that the parameters $\mathrm{C}_{\mathrm{st}}=5.4 \mathrm{eV}$ and $I=290.0 \mathrm{eV}$ compatible with our measurements of gold powder on scotch tape really refers to neutral hydrocarbon ; it might have, for instance, $I^{\prime}=291 \mathrm{eV}$ and a potential $\mathrm{V}=-1 \mathrm{eV}$. On the other hand, the typical values of $\mathrm{C}_{\text {st }}$ around 4 eV (most frequently due to adjacent left-hand and right-hand signals) may also be explained as $\mathrm{V}=+1 \mathrm{eV}$ on the scotch tape without coverage. It is somewhat difficult to understand why the $\partial$ values of caesium salts are so large in Table 21 since they are not expected to have particularly large energy gaps. As a matter of fact, the high $\partial$ values tend to cancel the unusually high $I$ values of caesium salts previously discussed [60], the $I^{\prime}$ values rather being on the low side. This might be interpreted as an effect of the highly polarizable Cs+ ${ }^{+}$on the thin layer of the hydrocarbon. If this layer becomes particularly difficult to ionize, it may be that Table 21 underestimates $I^{\prime}$ of caesium salts. On the other hand, the $I$-values of tetraphenylarsonium and methylene blue salts of anions seem low, and of tetraphenylborates of cations. It may be that these salts have low $\partial$ values because the conjugated constituents readily become "metallic", that is sufficiently conducting, under the influence of X-rays. This tendency reaches its climax in copper (II) phthalocyanine combining a doubtless small $\partial$ with a high $\mathrm{C}_{\text {st }}$.

From a practical point of view, one may ask what one can do to make $I^{*}$ values measured physically more significant. We believe that this is a very difficult problem outside the cases where $\partial$ can be measured and where they are accepted as indicators of $I^{\prime}=I^{*}$ plus the difference between 290 eV and $I^{*}$ of the left-hand C1s signal. In mixtures, $\partial$ is determined by the major constituent, as seen from the values around 3 eV for gold mixed with sufficient amounts of non-conducting powders such as $\mathrm{MgF}_{2}, \mathrm{BaSO}_{4}$ and $\mathrm{ThF}_{4}$. We do not believe in the beneficial effects of nets or decorations of metal attempting electric connection with non-conducting samples. An argument against this possibility is the measurement of $5 \mathrm{MgF}_{2}$ : 1 CuS where $I^{*}$ of the lowest copper 2 p signal increases 2.2 eV relative to CuS on scotch tape, $I$ increases 1.5 eV (since $\mathrm{C}_{\text {st }}$ decreases from 5.5 to 4.8 eV ) but $\partial$ is as large as 4.0 eV , a characteristic property of magnesium fluoride. It is even probable that a mixture of two non-conducting materials have their individual $\partial$ values, so internal standards such as admixed LiF or $\mathrm{MgF}_{2}$ would only produce representative $I$ values in sofar the measured compound does not have a different $\partial$. This attitude would bring $I$-values of non-conducting samples in the same systematic difficulties as activity coefficients making the mass-action law rather tautological. Thin films, say of organic compounds, on a metallic support, such as gold, probably have their $I^{*}$ values
changing dramatically as a function of thickness of the film. Many of these difficulties are less serious by the comparison of related compounds, but one has to worry about the extent of similar conductivity in the experiment in the sense of comparable $\partial$ values. The only compound found to have $\partial$ above 5.0 eV is $\mathrm{LuF}_{3}$, but other closed-shell cations form fluorides lacking a positive electron affinity having high $\partial$ and may also increase $\mathrm{C}_{\text {st }}$ by pushing off electrons to the scotch tape.

## The Individual Elements

A comparison of $I^{*}(\mathrm{Be} 1 \mathrm{~s})$ of $\mathrm{BeF}_{2}, \mathrm{BeO}$ and Be is shown in the first ESCA book [97]. $I^{*}(\mathrm{~F} 1 \mathrm{~s})=686.1$ and $I^{*}(\mathrm{Li} 1 \mathrm{~s})=56.9 \mathrm{eV}$ reported [39] for LiF are about 4 eV below our $I^{\prime}$ values and $I^{*}(\mathrm{Be} 1 \mathrm{~s})=114.2 \mathrm{eV}$ for BeO is 5 eV below. The Berkeley group [42] has made a careful study of many boron compounds showing a chemical shift 8.4 eV between $\mathrm{NaBF}_{4}$ and $\mathrm{B}_{4} \mathrm{C}$. Certain boron compounds [9] have also been measured in connection with the use of LiF as an internal standard. We have also studied a few salts of $\mathrm{BF}_{4}^{-}$and $\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}^{-}$showing a chemical shift of 7 to 8 eV .

We do not here discuss carbon compounds specifically [13, 34]. Nitrogen compounds have been extensively discussed in literature[41, 97]. The spreading 3.5 eV of $I$-values for nitrates in Table 1 would probably be only 2 eV in $I^{\prime}$, but the order as a function of the cations would be approximately the same. It has already been noted [32] that coordinated NO shows higher $I$ than ammonia, as seen here in the cases of $\mathrm{Ru}(\mathrm{NO}) \mathrm{Cl}_{5}^{-2}$ and $\mathrm{Fe}(\mathrm{CN})_{5} \mathrm{NO}^{-2}$. A comparative study has been made (assuming $I^{*}(\mathrm{~N} 1 \mathrm{~s})=406.9 \mathrm{eV}$ of $\mathrm{KNO}_{3}$ ) of quaternary ammonium salts [47] but our measurements do not allow a clear distinction between $\mathrm{NH}_{4}{ }^{+}$and various tetra-alkylammonium salts, and we believe that most of the spreading (above 3 eV ) of $I$-values observed is a function of the accompanying anion. We find the lowest $I$ (N1s) for the nitrogen end of pseudohalogens such as $\mathrm{CN}^{-}$and $\mathrm{SeCN}^{-}$, and we do not detect any significant difference between sulphur- and nitrogenbound thiocyanate. Coordinated azide might conceivably show three N1s signals, and actually, $\mathrm{Pt}\left(\mathrm{N}_{3}\right)_{6}^{-2}$ has the middle atom of each ligand producing $I=407.7 \mathrm{eV}$ whereas the nitrogen atom bound to platinum(IV) produces a shoulder to the left of the peak at $I=403.8 \mathrm{eV}$ due to the terminal nitrogen atom. Similar effects are observed [76] in a rhenium(II) complex of $\mathrm{N}_{2}$, whereas rhenium(I) produces two distinct signals separated by 2.0 eV . We do not here discuss oxygen ; adsorbed water and superficial hydroxo groups are a considerable problem for a significant interpretation.

Fluorine has the oxidation state $\mathrm{F}(-\mathrm{I})$ in all its compounds. It has been discussed separately [62] how the $I$-values of fluorides in Table 2 span 7.9 eV . The lower extreme is CsF , and its vanishing $\partial$ may have something to do with its highly hygroscopic nature. Quite generally, salt hydrates (frequently loosing their water very slowly even under a high vacuo [106]) and even compounds recently prepared from aqueous solution tend to show small $\partial$ values. Though the detectable double C1s signals only allow $I^{\prime}$ (F1s) in Table 22 to vary 4.6 eV , the inclusion of the small $\partial$ for RbF and assuming $\partial=0$ in CsF extends this interval slightly, and it would be 7.2 eV when including the $I=695.0 \mathrm{eV}$ for gaseous $\mathrm{CF}_{4}$. The strongly hydrogen-bound ammonium salts of fluoro anions generally have lower $I$ (and $\partial$ ) than the corresponding potassium salts.

Though the $I$ variation of sodium (I) is 4 eV , the dependence on anions does not show a clear-cut trend except the tendency (contrary to the idea of a Madelung potential) for small anions to induce the highest $I$ (Na1s). However, the corrected $I^{\prime}$ values do not show this trend. $I^{\prime}=1076.4$ or 1076.7 eV for $\mathrm{NaF}, 1076.8$ for $\mathrm{NaCl}, 1076.9$ for NaBr and 1077.4 eV for NaI (to be compared with values between 1076.8 and 1076.0 eV for the acidic selenite, stannate and antimonate) are all smaller than the minimum value 1077.5 eV for the tetraphenylborate.

We find a variation 6.5 eV of $I(\mathrm{Mg} 1 \mathrm{~s})$ between the fluoride and the phthalocyanine. Apparently, the corresponding variation of $I^{\prime}$ values is only about 3 eV . When Mg (II) is coordinated exclusively to four, six or eight oxygen atoms [33], a variation of $I$ can be observed which may perhaps, to the first approximation, indicate varying $\mathrm{Mg}-\mathrm{O}$ distances. Photo-electron spectrometry is a scalar technique in the sense of the properties of a given atom not directly being influenced by the angular distribution of the neighbour atoms, though their electronegativity and distance have a great influence. Here, we only report two aluminium compounds, because Oscar Pitton is working on a larger, comparative study of aluminium oxidized surfaces. The only silicate we have measured is the mineral pollucite. It is seen how $I$ is slightly smaller than in salts of $\mathrm{SiF}_{6}^{-2} ; I^{\prime}(\mathrm{Si} 2 \mathrm{p})$ is 1.8 eV lower in pollucit than in $\mathrm{K}_{2} \mathrm{SiF}_{6}$. Several silicon compounds are reported in literature [86] to have chemical shifts above 7 eV . The corresponding shift [89] between $\mathrm{NH}_{4} \mathrm{PF}_{6}$ and CrP is 8.5 eV . Most other studies of P 2 p signals have concentrated on phosphonium salts [102] and phosphines $\mathrm{R}_{3} \mathrm{P}$ free [14, 83] or coordinated to platinum (II) and on $\mathrm{R}_{3} \mathrm{PO}, \mathrm{R}_{3} \mathrm{PS}$ and $\mathrm{R}_{3} \mathrm{PS}$ e, where the typical range of variation is 2 eV . As seen from Table 2, we find an $I$ interval of 6.6 eV and $I^{\prime}$ cannot vary less than 5 eV . Though it can be discussed whether
$\mathrm{PR}_{4}^{+}$contains $\mathrm{P}(\mathrm{V})$, the variation $\mathrm{PF}_{6}^{-}>\mathrm{PO}_{4}^{-3}>(\mathrm{RO})_{2} \mathrm{PS}_{2}^{-}$occurs for the latter oxidation state.

Probably no other element has been as much studied by photo-electron spectrometry as sulphur [77, 97] Table 3 gives $I\left(\mathrm{~S}_{2} \mathrm{p}_{3 / 2}\right)$ of 98 compounds. In most cases, we do not indicate the number of water molecules in sulphates in view of the fact shown by Tovborg Jensen [106] of slow establishment of most hydration equilibria. Thus, Madame Watelle pointed out to us the difference between $\mathrm{CuSO}_{4}, 3 \mathrm{H}_{2} \mathrm{O}$ and $\mathrm{CuSO}_{4}, 5 \mathrm{H}_{2} \mathrm{O}$. Our variation 4.8 eV of the $I$-values of sulphates may be overestimated because of the systematically low $\partial$ values in hydrated crystals. Thus, $I$ of anhydrous, almost insoluble sulphates are high, but $I^{\prime}\left(\mathrm{S}_{2} \mathrm{p}_{3 / 2}\right)$ are only 173.6 eV for $\mathrm{SrSO}_{4}, 173.8 \mathrm{eV}$ for $\mathrm{EuSO}_{4}$ and 173.9 eV for $\mathrm{BaSO}_{4}$ to be compared with $I=180.4 \mathrm{eV}$ for gaseous $\mathrm{SF}_{6}$ and $I^{\prime}$ between 174.1 and 174.3 eV for the hydrated sulphates of La (III), Eu(III), Gd(III) and U(IV). The lower limit of $I^{\prime}$ for sulphates seems to be close to 172 eV but is, of course, difficult to determine. Instances of highly non-equivalent sulphur atoms were discussed in the introduction. Thio-ethers $\mathrm{R}_{2} \mathrm{~S}$ fall in the wide gap between typical S (VI) and S (-II) compounds, here having $I$ between 169.3 and 172.1 eV . Methylene blue cations contain one heterocyclic sulphur atom falling in the same category. $I$-values between 168.5 and 170 eV are under some suspicion for being due to superficial oxidation of the samples to elemental sulphur. Unfortunately, the charging effects prevent a reliable determination of $S_{8}$ alone. Many double sulphides and salts of tetra-thio anions were prepared by Müller and Diemann and discussed elsewhere [85]. Both such compounds, thiocyanate complexes and [55] dithiocarbamates $\mathrm{R}_{2} \mathrm{NCS}_{2}^{-}$and dithiophosphates $(\mathrm{RO})_{2} \mathrm{PS}_{2}^{-}$have their $I\left(\mathrm{~S}_{2} \mathrm{p}_{3 / 2}\right)$ values in the rather narrow interval from 169 to 166.8 eV and, undoubtedly, have low (if not vanishing) $\partial$ values. The valence region between $I=9$ and 30 eV of sulphate (and of related anions such as the isoelectronic perchlorate) show an interesting structure [18, 91] due to the seven sets of delocalized M.O., and we are going, separately, to discuss this aspect of our results. To the first approximation, five of these sets correspond to oxygen 2 p and two sets to oxygen 2 s orbitals.

There is a clear-cut gap 5 eV in Table 4 of $I\left(\mathrm{Cl} 2 \mathrm{p}_{3 / 2}\right)$ values between perchlorates and chlorides. Like it is the case for nitrates, the total width 2.5 eV of $I$-values may be somewhat illusory, though $\partial$ for most perchlorates is small. The width 4.6 eV for chlorides must also be influenced by charging effects. Thus, $I^{\prime}\left(2 \mathrm{p}_{3 / 2}\right)=203.9 \mathrm{eV}$ for NaCl and 203.8 eV for $\mathrm{CsSbCl}_{6}$ are larger than for $\mathrm{RbCl}(203.3)$ and $\mathrm{CsCl}(202.8)$ and there is little doubt that highly covalent chlorides such as $\mathrm{Rb}_{2} \mathrm{PtCl}_{6}(204.3), \mathrm{Au}_{2} \mathrm{Cl}_{6}$ and Bengal Rosa B
(representing a non-volatile organic compound with $\mathrm{C}-\mathrm{Cl}$ bond like the derivatives studied by Clark [13]) have even higher $I^{\prime}$. On the other hand, ionic chlorides of large cations (such as $\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{6}^{+3}$ ) and chloro complexes with large cations have both the lowest $I$ and $I^{\prime}$ values (the latter close to 202 eV ) in agreement with the Madelung theory.

The $I$ values of potassium are given in Table 5 and the $I^{\prime}\left(2 \mathrm{p}_{3 / 2}\right)$ in Table 22. As already discussed [62], their variation is (with the exception of the iodide) essentially a question of the hard or soft character of the anion according by Pearson. We return to this question below. We have only measured a few calcium, scandium and titanium compounds, they show familar trends. $I^{\prime}\left(\mathrm{Ti} 2^{2} \mathrm{p}_{3 / 2}\right)=466.9 \mathrm{eV}$ for $\mathrm{K}_{2} \mathrm{TiF}_{6}$ and 463.5 eV for $\mathrm{TiO}_{2}$ may be noted. Our ten vanadium compounds do not show a spectacular dependence on the oxidation state, but the sulphur-containing compound has a remarkably low set of $I$-values. Recently, the $I$ values (obtained by adding 4.8 eV to $I^{*}$ relative to the Fermi level of gold) of $\mathrm{V}_{2} \mathrm{O}_{3}$ have been reported as 528.8 eV for $\mathrm{V} 2 \mathrm{p}_{1 / 2}, 521.3 \mathrm{eV}$ for $\mathrm{V} 2 \mathrm{p}_{3 / 2}, 74.8 \mathrm{eV}$ for $\mathrm{V} 3 \mathrm{~s}, 46.7 \mathrm{eV}$ for V 3 p and 6.0 eV for V 3 d , both below and above the temperature where it becomes metallic [46].

The variation of $I^{*}(\mathrm{Cr} 3 \mathrm{p})$ reported by the Berkeley group [42] involved a higher limit 48.7 eV for $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ and 43.5 eV for $\mathrm{Cr}_{2} \mathrm{O}_{3}$, with $\mathrm{Cr}(\mathrm{CO})_{6}$ in the middle having $I^{*}=45.8 \mathrm{eV}$. Our results show a total width of $I\left(2 \mathrm{p}_{3 / 2}\right)$ variation 7.3 eV and of $I(3 \mathrm{p}) 8.2 \mathrm{eV}$. The intervals corresponding to $\mathrm{Cr}(\mathrm{VI})$ and $\operatorname{Cr}($ III $)$ overlap slightly. With exception of the high $\partial=3.2 \mathrm{eV}$ for $\mathrm{K}_{2}\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$ these conclusions would be similar for $I^{\prime}$. Chromium (III) is the first case of strong effects of interelectronic repulsion to be discussed in the section below.

We believe that the sets of two signals of permanganates are due to superficial reduction to $\mathrm{Mn}(\mathrm{IV})$ at lower $I$, and the variation of $I\left(\mathrm{Mn} 2 \mathrm{p}_{3 / 2}\right)$ is 5.9 eV . However, the positions of signals belonging to Mn(II), Mn(III) and Mn(IV) are insufficiently different to allow safe conclusions to be drawn regarding the mixed oxides studied by Feitknecht and kindly put at our disposal. Similar comments can be made about iron(II) and iron(III) showing the overall tendency $\mathrm{Fe}(\mathrm{III})(S=5 / 2)>\mathrm{Fe}(\mathrm{III})(S=1 / 2)>\mathrm{Fe}(\mathrm{II})$ $(S=2)>\mathrm{Fe}(\mathrm{II})(S=0)$ but also dependent on the nature of the ligands. Kramer and Klein [70] studied the wide variation of $I^{*}(\mathrm{Fe} 3 \mathrm{p})$ of iron(III) complexes, and Prussian blue (of which the idealized formula isK $\left[\mathrm{Fe}(\mathrm{CN})_{6} \mathrm{Fe}\right]$ containing the octahedral chromophores low-spin $(S=0) \mathrm{Fe}(\mathrm{II}) \mathrm{C}_{6}$ and high-spin $\left.(S=5 / 2) \mathrm{Fe}(\mathrm{III}) \mathrm{N}_{6}\right)$ has been studied by Leibfritz and Bremser [75] and by Wertheim and Rosencwaig [115]. Mixed cyanide complexes in-
volving $\mathrm{Fe}, \mathrm{Co}, \mathrm{Ni}, \mathrm{Cu}, \mathrm{Ru}, \mathrm{Pd}, \mathrm{Cd}, \mathrm{Os}$, Ir and Pt are prepared by Andreas Ludi, and though some are included in the Tables here for comparison, they are going to be discussed more thoroughly by us. Other instances of mixed oxidation states are $\mathrm{K}_{0.5} \mathrm{FeF}_{3}[10]$ containing equal amounts of high-spin Fe (II) and Fe (III), and the biferrocene(II, III) picrate [20] where Fe (III) has $I=3.4 \mathrm{eV}$ higher than $\mathrm{Fe}(\mathrm{II})$. We have had difficulties of detecting individual spectra in mixed oxides. However, it is beyond doubt that $\mathrm{Fe}_{3} \mathrm{O}_{4}$ also contains iron(II). This is not a perfectly trivial statement, because magnetite is a physical metal at room temperature ascribed by Verwey to rapid electron exchange between Fe (II) and Fe (III) on the octahedral sites. Our interval 5.7 eV of $I\left(\mathrm{Fe}_{2} \mathrm{p}_{3 / 2}\right)$ is only weakly affected by charging effects since $\partial$ of the ammonium salt no. 70 is small.

Our 42 cobalt compounds exemplify the case previously noted for $\mathrm{Tl}_{2} \mathrm{O}_{3}$ and $\mathrm{PbO}_{2}$ compared with $\mathrm{Tl}(\mathrm{I})$ and $\mathrm{Pb}(\mathrm{II})$, viz. that the lower oxidation state Co (II) on the whole has higher $I$-values than Co(III). It must be admitted that $I^{\prime}\left(2 \mathrm{p}_{3 / 2}\right)$ of $\mathrm{CoF}_{2}$ is only 787.8 eV , but only eight cobalt(III) complexes have higher $I$, and probably none higher $I^{\prime}$. Thus, $\mathrm{Cs}_{3} \mathrm{Co}(\mathrm{CN})_{6}$ has $I^{\prime}=787.0 \mathrm{eV}$, a value which might conceivably be valid for the lithium salt too, but not for the potassium and tetra-ethylammonium salts. We have precipitated many anions with the yellow $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}^{+3}$ and the green trans[Coen $\left.\mathrm{Cl}_{2}\right]^{+}$The interval of $I$-variation is 3.4 and 1.4 eV , respectively. The former interval cannot conceivably be due to charging effects alone, since $\partial$ is at most 1.9 eV . The acetylacetonates and the complexes of sulphurcontaining ligands having strong covalent bonding according to the visible absorption spectra [55] show the lowest $I$-values.

It has previously been discussed [60] how high-spin ( $S=1$ ) nickel(II) complexes show four signals in the 2 p region, whereas low-spin $(S=0)$ diamagnetic complexes show only two signals, as normally expected. We return below to this question, and here, we only consider the range of chemical shifts being 7.5 eV for the $I$-values of paramagnetic and 3.7 eV for $I\left(\mathrm{Ni}^{2} \mathrm{p}_{3 / 2}\right)$ of diamagnetic $\mathrm{Ni}(\mathrm{II})$. However, the former estimate is not quite realistic, since $I^{\prime}$ is known to be 862.6 eV for $\mathrm{KNiF}_{3}, 862.3 \mathrm{eV}$ for $\mathrm{NiF}_{2}, 4 \mathrm{H}_{2} \mathrm{O}$ and 860.1 eV for pale green (almost stoichiometric) NiO. Unfortunately, $\partial$ cannot be measured for most other nickel(II) compounds, but the lower limit of $I^{\prime}$ is below 858 eV .

The interpretation of the complicated photo-electron spectra of copper compounds is intimately connected with the satellites to be discussed below. Reliable $I^{\prime}\left(\mathrm{Cu}^{2} \mathrm{p}_{3 / 2}\right)$ values are 941.1 eV for $\mathrm{CuF}_{2}, 2 \mathrm{H}_{2} \mathrm{O}, 938.8 \mathrm{eV}$ for CuO , 938.3 eV for synthetic torbernite (no. 242), 937.8 eV for CuCN and 936.6 eV
for the copper(I) iodo complex no. 60. Our seven zinc(II) compounds show a moderate variation 2.8 eV , and almost the same variation of $I^{\prime}$ occurs in view of the almost constant $\partial$. Vesely and Langer [109] report a mild variation of $I$ of all the inner shells $\mathrm{ZnO}<\mathrm{ZnS} \sim \mathrm{ZnSe}>\mathrm{ZnTe}$ within half an eV . Our five gallium compounds only vary $I$ within 1.5 eV , including the yellow semiconductor [105] GaS having direct Ga-Ga bonds. The lowest $I^{\prime}\left(\mathrm{Ga}^{2} \mathrm{p}_{3 / 2}\right)=1122.6 \mathrm{eV}$ for $\mathrm{Ga}_{2} \mathrm{O}_{3}$ is still 2 eV above $I$ for metallic gallium. We may shortly note $I^{\prime}(\mathrm{Ge} 2 \mathrm{p} 3 / 2)=1226.3 \mathrm{eV}$ for $\mathrm{K}_{2} \mathrm{GeF}_{6}$ and 1225.2 eV for $\mathrm{GeO}_{2}$. Arsenic is the last element for which an aluminium anti-cathode allows the detection of the $2 \mathrm{P}_{3 / 2}$ signal. Though $I$ varies by 4.1 eV , the interval of $I^{\prime}$ is smaller since $I^{\prime}=1331.4 \mathrm{eV}$ for $\mathrm{LaAsO}_{4}, 1330.9$ for $\mathrm{NdAsO}_{4}, 1331.0$ for $\mathrm{YbAsO}_{4}$ but 1331.6 eV for $\mathrm{K}_{2} \mathrm{HAsO}_{4}$. The ten tetraphenylarsonium salts probably have $I^{\prime}$ somewhat below 1330 eV . $I^{*}\left({\left.\mathrm{As} 3 \mathrm{~d}_{5 / 2}\right)}\right.$ ) values between 147.6 eV for $\mathrm{KAsF}_{6}$ and 140.4 eV for $\mathrm{Zn}_{3} \mathrm{As}_{2}$ have been reported [99]. These authors use $I^{*}\left(\mathrm{~Pb}_{4} \mathrm{f}_{7 / 2}\right)=138.3 \mathrm{eV}$ of $\mathrm{Pb}_{3} \mathrm{O}_{4}$ as internal standard.

Selenium has attracted some interest [104] because of the close chemical analogies with sulphur. A roughly monotonic increase of $I$-values (to the extent of 5 eV ) as a function of the oxidation state increasing from $\mathrm{Se}(-\mathrm{II})$ to Se (VI) is observed. We find also a range of $I$-values close to 8 eV though it must be noted that $I^{\prime}\left(\mathrm{Se}_{3} \mathrm{p}_{3 / 2}\right)$ is only 171.7 eV for both measurements of $\mathrm{BaSeO}_{4}$. It is expected that $I$ of bromates are some 6 eV higher than of the corresponding bromides. Our $I$ interval of 5 eV of 26 bromides includes, at the higher limit, caesium (I) salts (with lower $I^{\prime}$ ) and dibromosuccinic acid having $\mathrm{C}-\mathrm{Br}$ bonds. The influence of the Madelung potential on electrovalent bromides is discussed in Table 21.

No characteristic conclusion can be drawn about the moderate variation 2.6 eV of $I\left(\mathrm{Rb} 3 \mathrm{p}_{3 / 2}\right)$ in ten rubidium (I) salts. When the $I^{\prime}$ values are considered, it is one of the elements closest to show no chemical shifts. The same is true for strontium(II), where the observation of the $3 \mathrm{p}_{1 / 2}$ signal is made difficult due to the adjacent C1s signal. The $I$-intervals of yttrium(III) are almost 5 eV but it must be noted that $I^{\prime}\left(\mathrm{Y} 2 \mathrm{p}_{3 / 2}\right)=307.8 \mathrm{eV}$ for $\mathrm{YF}_{3}$ and 307.0 eV for $\mathrm{Y}\left(\mathrm{IO}_{3}\right)_{3}$ probably are not much above $\mathrm{Y}_{2} \mathrm{O}_{3}$. Comparable comments can be made about zirconium(IV) and niobium(V). The actual $I^{\prime}$ intervals occurring in our compounds seem to be close to 3 eV in the three latter elements. It must be noted that the fluorides have distinctly the highest $I^{\prime}$ values.

We find a rather moderate $I$-variation of molybdenum(VI) compounds with the lowest values of tetrathiomolybdates [85] comparable with Mo(III). Swartz and Hercules [103] report a $I^{*}$ variation 1.7 eV between fifteen
$\mathrm{Mo}(\mathrm{VI})$ compounds including many heteropolymolybdates, and $\mathrm{MoO}_{2} \mathrm{aca}_{2}$ at the lower end, below $\mathrm{MoCl}_{5}$ and $\mathrm{MoO}_{2}$. These authors have succeeded in measuring $I^{*}$ of freshly cleaned molybdenum, 6 eV below that of $\mathrm{Na}_{2} \mathrm{MoO}_{4}$. Comparable signal positions are found for cooled $\mathrm{Mo}(\mathrm{CO})_{6}$.

It is rather difficult to study the 3 d region of ruthenium compounds because of coincidences with the scotch tape main at $I=290.0 \mathrm{eV}$, with other carbon 1 s signals at higher $I$ and with the replica signal at an apparent $I=280.2 \mathrm{eV}$ induced by the small intensity of so-called aluminium $\mathrm{K} \alpha_{3}$ $\left(1 \mathrm{~s} 2 \mathrm{~s}^{2} 2 \mathrm{p}^{5} \rightarrow 1 \mathrm{~s}^{2} 2 \mathrm{~s}^{2} 2 \mathrm{p}^{4}\right)$ photons $(1496.4 \mathrm{eV})$ present in the X-ray source. Though the 3 p signals are weaker, they are more readily identified. $I^{*}\left(3 d_{5 / 2}\right)$ $=284.4 \mathrm{eV}$ for $\mathrm{BaRu}^{\mathrm{VI}_{4}}$, 282.2 eV for $\left[\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{6}\right]\left(\mathrm{BF}_{4}\right)_{3}, 279.8 \mathrm{eV}$ for $\left[\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{I}_{2}$ and 279 eV for Ru are reported [74] in a study of the dehydrogenation product of Ruen ${ }_{3}^{+2}$ forming $\mathrm{C}=\mathrm{N}$ double bonds. We believe in a roughly monotonic variation with the oxidation state and accept unusually high $I$ in the perruthenate, ascribing the shoulders at lower $I$ to reduced species in analogy to permanganate.
$\mathrm{K}_{3} \mathrm{RhF}_{6}$ has exceptionally high $I$, even $I^{\prime}\left(\mathrm{Rh}_{3} \mathrm{~d}_{5 / 2}\right)=317.3 \mathrm{eV}$ is considerably larger than 314.7 eV for $\mathrm{Cs}_{2}\left[\mathrm{Rh}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{Cl}_{5}\right]$. Probably, our dark green [48] $\mathrm{Cs}_{2} \mathrm{RhCl}_{6}$ was reduced to the latter species. Many rhodium(III) complexes of sulphur-containing ligands have $I$ comparable to the metal, but we do not believe that they have been transformed superficially. The compound $\left[\mathrm{Rhns}_{3}\right]_{2} \mathrm{Ni}\left(\mathrm{ClO}_{4}\right)_{2}$ supplied by Walter Schneider has three bidentate ligands forming the chromophore fac-Rh(III) $\mathrm{N}_{3} \mathrm{~S}_{3}$ but each sulphur atom forms a bridge to the central $(S=1)$ nickel atom forming octahedral $\mathrm{Ni}(\mathrm{II}) \mathrm{S}_{6}$.

Palladium compounds have been studied [72] having $I^{*}\left(3 d_{5 / 2}\right)=340.3$ eV for $\mathrm{K}_{2} \mathrm{PdCl}_{6}, \mathrm{Pd}(\mathrm{II})$ varying from 339.6 eV for $\mathrm{Pd}(\mathrm{CN})_{2}$ and 339.2 eV for $\mathrm{K}_{2} \mathrm{Pd}(\mathrm{CN})_{4}$ down to 336.6 eV for $\mathrm{PdI}_{2}$ (the metal has 335.7 eV ) stressing the dependence of $I$ on the electronegativity of the ligating atoms though cyanide has remarkable high $I$ as also seen in Table 13 in the case of $\operatorname{Pd}(\mathrm{CN})_{6}^{-2}$ prepared by Ludi [79]. The range of $I$ for $\mathrm{Pd}(\mathrm{II})$ is 2.15 eV , and metallic Pd slightly below. Our fifteen silver(I) compounds show a similar $I$ range of 2.9 eV probably moderated to slightly above 1 eV in $I^{\prime}$. One of the most stable silver(II) compounds, the peroxodisulphate of the tetrakis (pyridine) complex shows a lower $I$ than $\mathrm{Ag}_{2} \mathrm{SO}_{4}$ but it seems to represent a mixture of $\mathrm{Ag}(\mathrm{I})$ and $\mathrm{Ag}(\mathrm{II})$. A weak satellite of the $\mathrm{Ag} 3 \mathrm{~d}_{5 / 2}$ signal can be perceived, this would be an interesting analogy to Cu (II) discussed below.

The $I$ variation 2.6 eV of cadmium(II) compounds do not follow a very clear-cut order of ligands but is compatible with the weak variation

CdO $>$ CdS $\sim$ CdSe reported by Vesely and Langer [109]. Indium(III) compounds vary $I$ to the extent 3.7 eV , the highest $I^{\prime}\left(\operatorname{In} 3 \mathrm{~d}_{5 / 2}\right)=450.8 \mathrm{eV}$ is represented by both the sulphate and the fluoro complex. Metallic indium may have been successfully measured in the sample having $I=448.8 \mathrm{eV}$. Among the $\mathrm{tin}(\mathrm{IV})$ compounds, $\mathrm{Cs}_{2} \mathrm{SnBr}_{6}$ has exceptionally high $I$ but $I^{\prime}\left(\operatorname{Sn} 3 \mathrm{~d}_{5 / 2}\right)$ is only 492.4 and 492.6 eV in the two measurements. Metallic tin evidently was oxidized, and the lowest $I$ is observed for tetraphenyltin, which fortunately enough was not too volatile.

The measurements of the (otherwise very strong) antimony $3 \mathrm{~d}_{5 / 2}$ signal are sometimes dif ficult because of almost coinciding signals from oxygen 1 s . We base our discussion on Sb3d $\mathrm{d}_{3 / 2}$ having overlapping intervals of $\mathrm{Sb}(\mathrm{V})$ and Sb (III). The total $I$ width of these two intervals is 6.8 eV and 3.3 eV , but as usual, $\partial$ of the fluoro complexes is rather large, and the $I^{\prime}$ variation of $\mathrm{Sb}(\mathrm{V})$ is between 547.7 eV for $\mathrm{CsSbF}_{6}$ (still well above 545.7 eV for $\mathrm{CsSbCl}_{6}$ and 545.0 eV for $\mathrm{NaSb}(\mathrm{OH})_{6}$ ) and somewhat below 544 eV for $\mathrm{Na}_{3} \mathrm{SbS}_{4}$. The $I\left(3 \mathrm{~d}_{5 / 2}\right)$ range of tellurium compounds is 6.8 eV in agreement with the $I^{*}$ variation between 576.8 eV for $\mathrm{TeO}_{3}$ and 572.4 eV for $\mathrm{Na}_{2} \mathrm{Te}$ reported by Swartz, Wayne and Hercules [104].

It was mentioned above how 28 iodates (excepting those of $\operatorname{Co}$ (II) and $\mathrm{Bi}(\mathrm{III}))$ vary $I^{\prime}\left(\mathrm{I}_{3} \mathrm{~d}_{5 / 2}\right)$ within the narrow interval 629.8 to 628.9 eV . On the average, iodates have $I$ about 4 eV and $I^{\prime}$ about 5 eV above those of the corresponding iodides. The range of $I$-values for iodides is rather large, 3.7 eV , including the C-I bond in Bengal Rosa B. Large cations produce low $I$-values (in qualitative agreement with the Madelung potential) and a low $I^{\prime}=622.0 \mathrm{eV}$ has been observed in $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{I}$. The less covalent iodides have the higher $I$-values, but tend, at the same time, to have larger $\partial$ decreasing $I^{\prime}$. Thus, KI having $I^{\prime}=623.8 \mathrm{eV}$ and RbI 624.6 eV have a higher $I^{\prime}$ than CsI ( 623.3 eV ) but lower than $\operatorname{AgI}(625.2 \mathrm{eV})$.

Our 34 caesium (I) salts show a spreading 4.8 eV of $I\left(3 \mathrm{~d}_{5 / 2}\right)$. Generally, the monatomic anions (and $\mathrm{SbF}_{6}^{-}$) produce the high $I$-values, whereas the polyatomic anions (soft in the sense of Pearson) have low $I$-values in analogy to potassium salts in Table 22. However, $I^{\prime}\left(\operatorname{Cs} 3 \mathrm{~d}_{5 / 2}\right)$ is between 728.9 and 729.1 eV for $\mathrm{CsCl}, \mathrm{CsBr}, \mathrm{CsI}, \mathrm{CsNO}_{3}, \mathrm{CsReO}_{4}$ and $\mathrm{Cs}_{2} \mathrm{PtCl}_{6}$ which is a rather unexpected coincidence, whereas $I^{\prime}$ is close to 729.8 eV for $\operatorname{CsSbF}_{6}$, pollucite and conceivably for the tetraphenylborate. Though
 785 eV for the five cases where $\partial$ has been determined.

The 3 d region of lanthanum (III) shows four signals though the closedshell groundstate has $S=0$. We have ascribed this unusual effect [63] to
electron transfer from the neighbour atoms to the empty 4 f shell of La becoming highly stabilized in the ionized system lacking a 3d electron. We return to this problem in the section on satellites. The chemical shift of $I$-values is 6 eV in Table 17, but the extreme values of $I^{\prime}\left(\mathrm{La}^{2} \mathrm{~d}_{5 / 2}\right)=842.3 \mathrm{eV}$ for $\mathrm{LaF}_{3}$ and 838.9 eV for $\mathrm{La}_{2} \mathrm{O}_{3}$ only differ by 3.4 eV .

Also the photo-electron spectra of cerium compounds are unexpectedly complicated. The most plausible explanation is that otherwise stable cerium (IV) compounds always contain some Ce(III) in the surface (whether due to simple reduction or to attack by the carbon dioxide of air forming carbonates) and that $I$ of the inner shells is 16 eV higher of Ce(IV) than of Ce(III). This is a most spectacular difference from the previous elements where a change of the oxidation state by one unit do not usually produce a chemical shift above 2 eV . Actually, this shift is even larger than in the cases of europium and terbium in Table 17. The double signals of cerium (III) compounds are most probably due to effects of interelectronic repulsion, the groundstate having $S=1 / 2$. However, it is not excluded that some of the signals are electron transfer satellites like in the case of La(III). Black $\mathrm{Pr}_{6} \mathrm{O}_{11}$ should consist of a mixture of two-thirds $\operatorname{Pr}(\mathrm{IV})$ and a third $\operatorname{Pr}$ (III), but we observe only weak signals at approximately 15 eV higher $I$ due to $\operatorname{Pr}(I V)$. As far goes $\operatorname{Pr}(I I I)$, the chemical shift are rather similar to La(III), but the 3 d signals have shoulders toward lower $I$. This is a phenomenon only known from neodymium(III) compounds too, and a possible explanation has been suggested by Christiane Bonnelle that the electron transfer satellites correspond to lower energy of the ionized system than the conventional ionization process. The probability of electron transfer becomes negligible for elements heavier than Nd , the 4 f shell having a much smaller average radius than the orbitals delocalized on the neighbour atoms. However, it is also conceivable that effects of interelectronic repulsion combined with strong relativistic effects (spin-orbit coupling) in the 3 d shell produces an unexpected distribution of the probability of forming the many possible energy levels of $3 d^{9} 4 f^{2}$ in $\operatorname{Pr}$ (III) and of $3 d^{9} 4 f^{3}$ in Nd (III) (cf. the $4 d^{9} 4 f^{q}$ configuration treated theoretically by $\operatorname{SUGAR}^{[101]}$ and compared with soft X-ray absorption spectra of 4 f group metals). $I^{\prime}\left(3 \mathrm{~d}_{5 / 2}\right)$ varies only slightly more than 1 eV for Nd (III). The same is true for our four samarium (III) compounds having $I^{\prime}=1088.6 \mathrm{eV}$ for $\mathrm{SmF}_{3}$ and 1087.7 eV for $\mathrm{Sm}_{2} \mathrm{O}_{3}$.

The strong chemical shift between europium(III) and Eu(II) has been known [26, 27] since 1967. Here, our $\mathrm{EuSO}_{4}$ could not be measured without some superficial Eu(III) ; the chemical shift is 11 eV for $3 \mathrm{~d}, 9 \mathrm{eV}$ for 4 d and 7 eV for 4 f , as discussed below. The variation of $I\left(3 \mathrm{~d}_{5 / 2}\right)$ is 2.5 eV between
$\mathrm{EuF}_{3}$ and $\mathrm{Eu}_{2} \mathrm{O}_{3}$ and the corresponding variation of $I^{\prime}$ is 1.6 eV . The chemical shift $\mathrm{d} I$ is 3.6 eV between $\mathrm{GdF}_{3}$ and $\mathrm{Gd}_{2} \mathrm{O}_{3}$ and $\mathrm{d} I^{\prime}$ is 2.0 eV . The weakly asymmetric 3 d signals of Sm (III), Eu(III) and Gd(III) can be ascribed to effects of interelectronic repulsion; there are no perceptible satellites.

Brown $\mathrm{Tb}_{4} \mathrm{O}_{7}$ should contain equal amounts of Tb (IV) and Tb (III). With exception of the 4 f signal of $\mathrm{Tb}(\mathrm{IV})$, the higher oxidation state cannot be detected. Professor Georg Brauer was so kind as to send us a sample of fox-red $\mathrm{TbO}_{2}$ prepared by exhaustive extraction of $\mathrm{Tb}_{4} \mathrm{O}_{7}$ with acetic acid [6]. Though the cubic unit cell parameter and chemical analysis shows a deviation from the stoichiometry $\mathrm{TbO}_{2}$ by less than one percent, we find Tb (IV) and Tb (III) signals superposed like in the case of $\mathrm{CeO}_{2}$. The chemical shift is 10.6 eV in the case of the 3 d shell. Since we did not succeed in measuring the $3 \mathrm{~d}_{5 / 2}$ signal of holmium, which should be on the limit of the instrument, dysprosium is the last element showing this signal. $\mathrm{Dy}_{2} \mathrm{O}_{3}$ and DyVO $\mathrm{O}_{4}$ differ 1.9 eV in $I$ and 1.1 eV in $I^{\prime}$.

Ho(III), Er(III) and Tm(III) show comparable shift in the fluoride, iodate and oxide of the very broad 4 d signals[5] and of the 4 f signals to be discussed below. A systematic comparison of ten ytterbium (III) compounds indicates $\mathrm{d} I$ of the lowest 4 d signal 5.5 eV between the fluoride and the oxide and $I^{\prime}$ varies from 192.2 eV in $\mathrm{YbF}_{3}$ to somewhere below 188 eV in $\mathrm{Yb}_{2} \mathrm{O}_{3}$. In Table 23 are given $I^{\prime}(\mathrm{Yb} 4 \mathrm{f})$. Lutetium(III) compounds have simpler photo-electron spectra (since the closed-shell groundstate has $S=0$ ). It is very important for the understanding of the 4 f group that $I(4 \mathrm{~d})$ increases 17 eV from Lu(III) to the isoelectronic Hf(IV) and $I(4 \mathrm{f})$ increases 9 eV . This shows that the end of the lanthanides is more a question of the oxidation state than of a definite atomic number (such as 71) and constitutes an analogy to the huge chemical shifts between Ce(III) and Ce(IV) or between Tb (III) and $\mathrm{Tb}(\mathrm{IV})$. The chemical shifts $\mathrm{d} I$ are 2.9 eV for $4 \mathrm{~d}_{5 / 2}$ and 2.4 eV for $4 \mathrm{f}_{7 / 2}$ of hafnium (IV) compounds. As usually, the variation of $I^{\prime}$ must be somewhat smaller. The corresponding range of $\mathrm{d} I$ is 3.0 eV for $4 \mathrm{~d}_{5 / 2}$ and 2.9 eV for $4 \mathrm{f}_{7 / 2}$ of tantalum $(\mathrm{V})$ compounds. Whereas the 4 f signals of the lanthanides up to Yb (III) has a structure due to the multiple levels possible of $4 \mathrm{f}^{\mathrm{q}-1}$, the splitting of the 4 f signal starting from $\mathrm{Hf}(\mathrm{IV})$ is simply due to the two $j$-levels $5 / 2$ and $7 / 2$ which are known to be separated 1.3 eV in ytterbium(III) compounds [50] from near infra-red spectra and 1.46 eV in gaseous $\mathrm{Lu}^{+4}$.

The chemical effects on the photo-electron spectra of tungsten(VI) compounds are closely similar to those of molybdenum(VI). The $I$ range of rhenium (VII) compounds is 6.1 eV both in the case of $4 \mathrm{~d}_{5 / 2}$ and $4 \mathrm{f}_{7 / 2}$. The high $I$ values for $\mathrm{CsReO}_{4}$ and $\mathrm{TIReO}_{4}$ are diminuished by $\partial=3.1$ and 2.5 eV ,
respectively. As a matter of fact, the $I^{\prime}$ values of these two perrhenates are the same as of $\mathrm{KReO}_{4}$ within 0.2 eV . However, even if $\partial$ were zero for the methylene blue and the tetraphenylarsonium perrhenates, $I^{\prime}(4 \mathrm{f})$ would be 0.5 eV lower. The four rhenium(IV) compounds studied have somewhat lower $I$ values with $I\left(4 \mathrm{f}_{7 / 2}\right)$ varying 1.2 eV .

It is rather difficult to study the 4 d region of osmium compounds because of interference with the carbon 1 s signals and their $\mathrm{K} \alpha_{3}$ replica. However, we have studied $I(4 \mathrm{f})$ of sixteen complexes, iodo-chloro-osmates (IV) kindly supplied by Preetz and Homborg [61] and the double cyanides by Ludi. It is a general characteristic that $\partial$ is below 2 eV and cannot be measured with exception of the osmium(VIII) nitrido complex $\mathrm{K}\left[\mathrm{OsO}_{3} \mathrm{~N}\right]$. On the whole, the $I$ increase follows the order Os(II) $<\mathrm{Os}$ (IV) $<\mathrm{Os}$ (VI) $<\mathrm{Os}$ (VIII) but the intervals of the oxidation states Os (II) and Os (IV) overlap strongly. Similar conclusions can be reached regarding $\operatorname{Ir}$ (III) and $\operatorname{Ir}$ (IV) where total variation of $I\left(4 \mathrm{f}_{7 / 2}\right)$ is 3.1 eV but where the ligands (sulphurcontaining ligands $<$ amines $<\mathrm{Cl}^{-}<\mathrm{CN}^{-}$) are of greater importance than the oxidation state. It must be added that iridium(IV) chloro and bromo complexes may loose elemental halogens in the vacuo.

Several authors have studied photo-electron spectra of platinum complexes, in particular involving bonds to carbon and to phosphorus. The Uppsala group [19] using $I^{*}=285 \mathrm{eV}$ for C 1 s as internal standard report $I^{*}\left(\mathrm{Pt}_{\mathrm{f}}^{7 / 2}\right)=73.4 \mathrm{eV}$ for $\mathrm{L}_{2} \mathrm{PtCl}_{2}$ and 71.7 eV for $\mathrm{PtL}_{4}$ (where L is triphenylphosphine $\left.\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\right)$ whereas the metal has 71.2 eV . Clark, Adams and Briggs [14] study related complexes such as $I^{*}=71.2 \mathrm{eV}$ for $\mathrm{L}_{2} \mathrm{Pt}\left(\mathrm{CH}_{3}\right)_{2}$ and 72.2 eV for $\mathrm{L}_{2} \mathrm{PtCl}_{2}$ using $I^{*}\left(\mathrm{Au}_{4} \mathrm{f}_{7 / 2}\right)=84.0 \mathrm{eV}$ of gold supports as internal standard. These authors find $I^{*}=284.7$ for the carbon and 71.1 eV for metallic Pt. Riggs [94] also uses $I^{*}=285 \mathrm{eV}$ as internal standard and reports $I^{*}=75.9 \mathrm{eV}$ for $\mathrm{K}_{2} \mathrm{Pt}^{\mathrm{IV}} \mathrm{Cl}_{6}, 74.0 \mathrm{eV}$ for $\mathrm{K}_{2} \mathrm{Pt}^{\mathrm{II}}(\mathrm{CN})_{4}, 73.4 \mathrm{eV}$ for $\mathrm{K}_{2} \mathrm{Pt}^{\mathrm{II}}$ $\mathrm{Cl}_{4}, 73.3 \mathrm{eV}$ for $\left(\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{3} \mathrm{P}\right)_{2} \mathrm{Pt}^{\mathrm{II}} \mathrm{Cl}_{2}$ and 71.6 eV for $\mathrm{Pt}^{0} \mathrm{~L}_{4}$ among thirteen other platinum complexes. His $I^{*}$ values are about 6 eV below the $I$ values in Table 19 suggesting charging effects of the order of magnitude 1 eV . Our $I$ intervals for $\mathrm{Pt}(\mathrm{IV}) 5.6 \mathrm{eV}$ and for Pt (II) 1.7 eV overlap almost completely, but this is due to the hexa-iodo complexes no. 37, 114 and 358. The $I^{\prime}\left(\mathrm{Pt}_{4} \mathrm{f}_{7 / 2}\right)$ are 80.4 eV for $\mathrm{K}_{2} \mathrm{PtCl}_{6}, 80.75 \mathrm{eV}$ for $\mathrm{Rb}_{2} \mathrm{PtCl}_{6}$ and 80.8 eV for $\mathrm{Cs}_{2} \mathrm{PtCl}_{6}$ suggesting a weak residual stabilization by the larger, more polarizable alkali ions, and 79.8 eV for the slightly more covalent $\mathrm{Cs}_{2} \mathrm{PtBr}_{6}$. It is probable that $I=I^{\prime}$ for $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{6}$ and $\mathrm{Tl}_{2} \mathrm{PtCl}_{6}$ because of too little noncovered scotch tape. There is no doubt that salts of $\mathrm{PtI}_{6}^{-2}$ have lower $I$-values in contrast to alkaline metal iodides.

Gold is very popular because of its absence of superficial oxidation. Taken at their face value, the $I$-values of Table 19 suggest $I$ of Au(III) complexes some 5.3 eV above the metal. However, because of the charging effects discussed above, the $I^{\prime}$ shift may be less than 3 eV . The salts of $\mathrm{AuCl}_{4}^{-}$and $\mathrm{AuBr}_{4}^{-}$deteriorate under the measurement perhaps more by loosing free halogen in the vacuo (and remaining as $\mathrm{AuCl}_{2}^{-}$and $\mathrm{AuBr}_{2}^{-}$) than by photo-chemical decomposition. We believe the lower $I$ values developing are due to $\mathrm{Au}(\mathrm{I})$ rather than to the metal. $\mathrm{K}\left[\mathrm{Au}(\mathrm{CN})_{2}\right]$ does not change its photo-electron spectrum. It is, of course, conceivable that its signals coincide with those of "isolated" metal.

Our 8 mercury (II) compounds show moderate $\mathrm{d} I$ within 2 eV . We were restricted in the choice by the volatility of many compounds and of the element. This may not only maintain pressures above $3.10^{-6}$ torr, but the vapours destroy the photomultiplier receiving the electrons. Fadley and Shirley [28] studied the valence band ( $I^{*}$ below 10 eV ) of twelve metallic elements and also HgO , noting the separation 1.6 eV between the two components $I^{*}(5 \mathrm{~d})=13.6$ and 12.0 eV . It is not yet known whether the corresponding splitting 3.1 eV of Au also is due to spin-orbit coupling alone, or whether it is due to "ligand field" non-equivalence of two and three d-like orbitals in this cubic crystal, or finally to collective effects producing two energy bands (or at least two maxima of probability of ionization by the X -rays). The corresponding separation is far smaller in metallic silver and has not been detected in copper. The gaseous $\mathrm{HgCl}_{2}, \mathrm{HgBr}_{2}$ and $\mathrm{HgI}_{2}$ have been studied by Eland [25], their lowest $I(5 \mathrm{~d})$ occurs at $16.8,16.4$ and 15.9 eV, respectively. Our $I$ values fall in this interval, whereas the lowest $I^{\prime}$ is 14.1 eV for $\mathrm{Hg}\left(\mathrm{IO}_{3}\right)_{2}$ and 14.0 eV for $\mathrm{HgO} . \mathrm{HgF}_{2}$ behaves rather different from most fluorides and have been discussed elsewhere [67a].

Our 21 thallium(I) compounds span an $I\left(4 \mathrm{f}_{7 / 2}\right)$ interval of 2.8 eV . A few of the previously given values [60] have been revised when the C1s signals were better characterized. It is seen that $\mathrm{Tl}_{2} \mathrm{O}_{3}$ has $I$ almost 3 eV below the average thallium(I). However, this dark brown compound (crystallizing in the cubic C-type [53] like lemon-yellow $\mathrm{In}_{2} \mathrm{O}_{3}$, white $\mathrm{Y}_{2} \mathrm{O}_{3}$ and most of the heavier rare earths) is a physical metal, and when diluted in isolating compounds such as $\mathrm{MgF}_{2}$, it turns out to have $I$ in the middle of the univalent compounds (like the salts containing $\mathrm{TlCl}_{6}^{-3}$ ) though $I^{\prime}$ remains 122.9 eV ( to be compared with 124.5 eV for $\mathrm{TlReO}_{4}, 123.75 \mathrm{eV}$ for $\mathrm{Tl}_{2} \mathrm{MoO}_{4}$ and 123.6 eV for $\mathrm{Tl}_{2} \mathrm{CO}_{3}$ ). Like it is also true in the analogous case of $\mathrm{PbO} \mathrm{O}_{2}$, the $I(5 \mathrm{~d})$ values vary parallel to the $I(4 \mathrm{f})$ values. Our fifteen lead(II) compounds show an $I\left(4 \mathrm{f}_{7 / 2}\right)$ interval of 3.9 eV , but the $I^{\prime}$ values vary less. They are, for a few selected cases, $144.1\left(\mathrm{PbF}_{2}\right), 144.0\left(\mathrm{PbCl}_{2}\right) 143.75\left(\mathrm{PbBr}_{2}\right)$,
$143.35\left(\mathrm{PbI}_{2}\right), 144.7\left(\mathrm{~Pb}\left(\mathrm{NO}_{3}\right)_{2}\right)$ and $144.35 \mathrm{eV}\left(\mathrm{Pb}\left(\mathrm{IO}_{3}\right)_{2}\right)$. On the whole, the lead (IV) compounds have the lower $I$-values, as previously pointed out for $\mathrm{PbO}_{2}$. The high $I$-value for $\mathrm{Cs}_{2} \mathrm{PbCl}_{6}$ seems to be a common property of caesium salts (with exception of the fluoride) and actually, $I^{\prime}=144.3 \mathrm{eV}$ similar to lead (II) iodate. $I^{\prime}$ for $\mathrm{PbO}_{2}$ is somewhat below 143 eV . We only detect slightly broadened signals of $\mathrm{Pb}_{3} \mathrm{O}_{4}$ at $I$ slightly below PbO , and actually, minium has been suggested [99] as internal standard. It is not quite certain that bismuth $(\mathrm{V})$ has been observed in our nominal $\mathrm{Bi}_{2} \mathrm{O}_{4}$ and $\mathrm{NaBiO}_{3}$; if it has, the signals have almost the same positions as of Bi (III) in contrast to arsenic and antimony, but in analogy with thallium and lead. The $I\left(\mathrm{Bi}_{4} \mathrm{f}_{7 / 2}\right)$ range is 2.9 eV for our nine $\mathrm{Bi}(\mathrm{III})$ compounds; $I^{\prime}=165.7$ eV for the fluoride and 164.15 eV for the oxide show a distinct difference.

Besides 8 stoichiometric thorium(IV) compounds, we have measured six mixed oxides [53] which have also kindly been measured by Proctor and Wilson in the Varian laboratories in Palo Alto, Cf. and by Bremser and Linnemann in Darmstadt. It was mentioned above how the $I^{\prime}$ values vary only slightly less (by 3.5 eV ) than $I\left(4 \mathrm{f}_{7 / 2}\right)$ by 3.9 eV , but $I^{\prime}$ for the oxides fall in a narrower interval. In the case of uranium compounds, it is not easy to know whether certain mixed oxides are not superficially oxidized to U(VI). Certain uranyl salts show weak satellites to the left, probably of electron transfer type to the empty 5 f shell in analogy to the stronger satellites of La(III) 3d signals. As later discussed with Cornelius Keller, uranium (V) in mixed oxides show strong satellites at 8 eV higher $I$ than the $4 \mathrm{f}_{5 / 2}$ signal. It may seem somewhat worrying that the strong 4f signals of $\mathrm{UO}_{2} \mathrm{SO}_{4}, 3 \mathrm{H}_{2} \mathrm{O}$ and $\mathrm{U}\left(\mathrm{SO}_{4}\right)_{2}, 4 \mathrm{H}_{2} \mathrm{O}$ almost coincide, but the uranium (IV) compound has a pronounced structure with maxima at 5 eV higher $I$, probably due to effects of interelectronic repulsion. The salt of $\mathrm{UCl}_{6}^{-2}$ has the lowest $I$ values observed, whereas $\mathrm{K}_{2} \mathrm{UF}_{6}$ occurs in the middle of the uranyl salts. This constitutes a major difference from the chemical shift about 16 eV between cerium(IV) and Ce(III) with none and one 4 f electron. The $I$ interval of U(VI) is 2.1 eV , the highest $I^{\prime}\left(4 \mathrm{f}_{7 / 2}\right)=388.1 \mathrm{eV}$ occurs for $\mathrm{CsUO}_{2}\left(\mathrm{NO}_{3}\right)_{3}$.

The separation between $4 \mathrm{f}_{5 / 2}$ and $4 \mathrm{f}_{7 / 2}$ signals from hafnium to uranium has previously been discussed [64]. Its variation for a given element, at most 0.1 eV , is on the limit of the experimental uncertainty.

## General Trends in the Chemical Shift as a Function of Neighbour Atoms and the Manne Effect

To the first approximation, the chemical shifts $\mathrm{d} I$ in inner shells follow the general ideas (partly based on the nephelauxetic effect derived from
excited levels of d and f shells containing from two to $4 l$ electrons) of fractional atomic charges $[52,56]$ in transition group and post-transition group elements, the fluorides having the highest fractional charges of the central atom and ligands containing elements of low electronegativity, such as sulphur, producing the lowest fractional charges due to more pronounced covalent bonding. The same type of behaviour was also found in Uppsala [34] for gaseous and solid carbon compounds, the effect of hydrogen and carbon neighbour atoms being almost identical. It was early recognized that $\mathrm{d} I$ is smaller than the theoretical values obtained by interpolation between gaseous ions $\mathrm{M}^{+}, \mathrm{M}^{+2}, \ldots$ where the change of $I$ per unit of charge is approximately $<\mathrm{r}^{-1}>$ in atomic units of the valence shell being depopulated. This theoretical slope is between 10 and 20 eV , and hence, the typical chemical shift $\mathrm{d} I=5 \mathrm{eV}$ corresponds to charges between 0.25 and 0.5 which would be almost incompatible with the visible absorption spectra [59]. However, the negative charges on adjacent atoms produce a Madelung potential counteracting $\mathrm{d} I$ by a large amount which, in a binary molecule $M X_{N}$, is proportional to the fractional charge of $M$ and inversely proportional to the internuclear distance M-X. In Table 21, the Madelung potential in the alkali metal halides vary between 12.52 eV in LiF and 6.41 eV in CsI. Hence, it is quite conceivable that the fractional charges are several times larger than supposed if the Madelung potential is neglected. Only in the 4 f group, such as the cases Ce(III), Ce(IV); Eu(II), Eu(III) and Tb(III), Tb(IV), the observed $d I$ are not much below the theoretical slope close to 20 eV .

The low $I$-values of transition and post-transition group oxides agree with the pronounced nephelauxetic effect (a common exception to both effects is NiO$)[51,56]$ though it is not generally believed by chemists that oxides have particularly low fractional atomic charges. What is stranger is that cyanides have unusually high $I$-values (this becomes even more striking when $I^{\prime}$ are considered, decreasing the fluoride values) as noted [72, 94] by several authors. This may be taken as an argument for $\pi$-back-bonding to empty orbitals of cyanide, increasing the positive charge of the central atom. It is also true that carbon monoxide complexes tend to have rather high $I$-values (though they lack significant Madelung potentials) but a difference is that much independent evidence suggests that the $\pi$-back-bonding becomes progressively more important when the central atom oxidation state becomes more negative in a series such $\mathrm{Ni}(\mathrm{CO})_{4}, \mathrm{Co}(\mathrm{CO})_{4}^{-}$and $\mathrm{Fe}(\mathrm{CO})_{4}^{-2}$ whereas even palladium (IV) in $\operatorname{Pd}(\mathrm{CN})_{6}^{-2}$ presents a rather extreme, high $I$-value. Several authors $[15,16,117]$ have discussed metallo-organic compounds, in particular of chromium, and their fractional charges. In view of
the variation of $I$-values of potassium, this is perhaps a difficult conclusion to draw. The opinion that iron(II) in $\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ has a negative fractional charge is based on $I^{*}\left(\mathrm{Fe} 2 \mathrm{p}_{3 / 2}\right)$ being 710.8 eV to be compared with 713.0 eV in $\mathrm{Fe}(\mathrm{CO})_{5}$. We find $I^{*}=711.7 \mathrm{eV}$ for $\mathrm{FeC}_{2} \mathrm{O}_{4}, 2 \mathrm{H}_{2} \mathrm{O}$ and 707.6 eV for [Fedip $] \mathrm{Br}_{2}$ and our conclusion would only be that the central atom in ferrocene is less positive than in iron(0) carbonyl but perhaps more positive than in the dipyridyl complex.

A less dramatic but more universal trend than the high $I$-values of cyanides is a general tendency for complexes of neutral ligands (water, ammonia, amines, etc.) to have lower $I$-values of the central atoms than chloro complexes, in contrast to the nephelauxetic effect and chemical consensus. It may be that crystals involving strong hydrogen bonds, as has already been mentioned in the case of ammonium salts of fluoro complexes, have intrinsically small $\partial$ values. However, one has to accept that the general variation of $I$ of inner shells of d group complexes as a function of the ligands is somewhat similar, but by no means identical, with the nephelauxetic series [51, 56] . The situation is quite different in the case of cations not forming covalent bonds at all.

Extrapolating the comparison of potassium and caesium salts, we have made a systematic study of several anions with tetra-alkylammonium ions $\mathrm{NR}_{4}^{+}$(where we have concentrated on the smallest, $\mathrm{R}=\mathrm{CH}_{3}$, and $\mathrm{R}=\mathrm{n}-$ $\mathrm{C}_{4} \mathrm{H}_{9}$ which can be obtained in a high degree of purity) and with $\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}^{+}$precipitating many large anions as crystalline salts which are soluble in organic solvents. As a student with Jannik Bjerrum, one of us started work in 1950 on the precipitation of anions (most frequently forming weakly soluble caesium salts) with the green "praseo" ion trans- $\left[\mathrm{Coen}_{2} \mathrm{Cl}_{2}\right]^{+}$ (a somewhat analogous anion is the raspberry-red "reineckeate" trans-$\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]^{-}$; the salt no. 100 is extraordinary by being off-white; the complementary colours of the cation and the anion compensate almost exactly, also intensity-wise). Here, we also study salts of the univalent methylene blue cation. We bought it as the chloride (though some commercial samples are the tetrachlorozincate) and in spite of the very high $\varepsilon \sim 10^{5}$, many anions precipitate it so quantitatively that the supernatant solution hardly is pale blue. Thus, the blue-violet perchlorate, blue perrhenate, slightly greenish blue tetraphenylborate and blackish blue reineckeate and hexa-iodoplatinate can be prepared.

The decrease of $I$-values with increasing radius of the cation agrees qualitatively with the Madelung potential. There is little doubt that the total expression for the Madelung potential is a fairly good approximation, and
for instance, $I\left(\mathrm{~K}_{2} \mathrm{p}_{3 / 2}\right)$ for gaseous $\mathrm{K}^{+}$is probably close to 306 eV obtained by adding 8 eV to the $I^{\prime}$ values in Table 22 though it is striking how frequently $\partial$ seems to cancel variations in the Madelung potential. Quite generally, the differential variation from one salt to another seems to be less well represented. In particular, in ten caesium salts (excepting the fluoride), the $I$ values of the strongest signal of twelve elements are, on the average, 1.3 eV higher than of the analogous ten potassium salts, whereas one would have expected a decrease about 0.8 eV due to the Madelung potential. It is seen from Table 21 how caesium salts tend to have high $\partial$ values, and the six cases of $I^{\prime}$ values known do not vary ( 0.0 eV ) on the average from caesium to potassium salts. Said in other words, the Madelung theory underestimates $I^{\prime}$ values of caesium salts some 0.8 eV and $I$ some 2 eV . It was suggested [27] in 1968 that the highly polarizable salts are more difficult to ionize because of the groundstate polarization.

However, there is no doubt that one also encounters an effect of polarizability of opposite sign, decreasing the $I^{*}$ values observed of the sharp peaks in the photo-electron spectra. In the case of the neon atom, the ionization energy of a 1 s electron in the Hartree-Fock wave-function maintaining the "frozen" orbitals of the other nine electrons is calculated to be 891.7 eV in disagreement with the observed value 870.2 eV . On the other hand, if a Hartree-Fock calculation for the ionized system $\mathrm{Ne}^{+}$is performed [108] with the constraint that the electron configuration is $1 \mathrm{~s}^{2} \mathrm{~s}^{2} 2 \mathrm{p}^{6}$ but allowing the radial functions of the eight outer electrons to adapt (contract) the energy difference relative to the Hartree-Fock groundstate is 868.6 eV . When the two minor corrections of relativistic effects on the 1 s energy and the correlation effect in the pair of 1 s electrons in the groundstate are added, 870.6 eV is obtained. One can now ask the question whether a FranckCondon principle is valid for the other electrons. The agreement between the experimental $I$ and the difference between the two Hartree-Fock functions suggests that the other electrons have time to adapt during the ionization of the 1 s shell. However, this adaptation is improbable for other reasons, and the problem was finally resolved by Manne and $\AA b e r g[80]$. In the neon photo-electron spectrum, many satellites occur between $I=900$ and 1000 eV . Though individually, they are weaker than 4 percent of the primary signal at 870.2 eV , the integrated intensity of all these satellites (due to shake-up forming excited levels such as $1 \mathrm{~s} 2 \mathrm{~s}^{2} 2 \mathrm{p}^{5} 3 \mathrm{p}$ and shake-off loosing two or three electrons such as $1 \mathrm{~s} 2 \mathrm{~s}^{2} 2 \mathrm{p}^{5}$ or $1 \mathrm{~s} 2 \mathrm{~s} 2 \mathrm{p}^{5}$ ) is about a quarter of the intensity of the primary signal. The important point is now that the baricenter of all this structure including the primary signal occurs at 886 eV , close to the

Koopmans value assuming "frozen" orbitals. Hence, the ionization process can be described as "sudden" in the sense that the instantaneously formed $1 \mathrm{~s} 2 \mathrm{~s}^{2} 2 \mathrm{p}^{6}$ decays to the hundreds of alternatives among which one alternative, the "adapted" $1 \mathrm{~s} 2 \mathrm{~s}^{22} 2 \mathrm{p}^{6}$ (which would have been formed by an adiabatic process in the electron system) accounts for 80 percent of the squared amplitude. In the Copenhagen representation of quantum mechanics, it is normally said that quantum jumps do not take any time at all. However, this is a non-relativistic statement; it takes light $10^{-18}$ sec to cross an atom with a diameter of $3 \AA$, and it can hardly be argued that the primary process of photo-ionization can be more rapid. On the other hand, good arguments are available that this process is not slower than $10^{-17}$ sec.

We suspect that this Manne effect occurs also for electrons in adjacent atoms in solids and not only for outer electrons in the same atom. For relativistic reasons, there is a limit for how distant atoms have the time to be informed about the primary ionization process, and in practice, we believe the first two or three layers of neighbour atoms to be the most important. Hence, the higher $I$ values of $\mathrm{K} 2 \mathrm{p}_{3 / 2}$ in salts of fluoro complexes relative to pseudohalide complexes may be connected with the larger deformability adapting to the ionized system in the latter case. In solids, we observe only the primary signal, and the numerous satellites due to shake-up and to shakeoff are swamped by the intense background due to inelastically scattered electrons. Anyhow, the neon atom may perhaps be somewhat exceptional by allowing eight electrons to be stabilized 2.5 eV each by the contraction in the adapted anti-Koopmans ionized state, and it may be that the inter-atomic Manne effect in most polyatomic systems amounts to some 5 eV perhaps combined with an intra-atomic Manne effect between 15 and 30 eV . It is obvious that a differential change of 2 eV of the inter-atomic Manne effect can contribute significantly to the range of $I$ values observed. Colloquially speaking, this effect can be considered to indicate the extent to which the ionized system has the capability to develop additional covalent bonding within a very short time.

## The Widths and Radiative Half-lifes

The typical photo-electron signal, when corrected for a much intenser background, is a Gaussian error-curve. With our standard conditions of 100 V analyzer potential (not giving the best resolution, but the strongest signals) the one-sided half-width $\delta(-)$ toward lower $I$-values is between 0.95 and 1.0 eV . We frequently run into asymmetric and somewhat broadened
signals which must be due to the superposition of two or more adjacent signals. Unfortunately, it is very difficult to calculate backwards from the observed spectrum to a unique choice of two components. In particular, one encounters the problem of great importance for visible spectra of solutions that two Gaussian curves with the same $\delta$ add to a curve almost looking like a new Gaussian with a slightly larger $\delta$, if the two maxima are of comparable heights and a not too far distance, say below $1.28 \delta$. Claus Schäffer has investigated this problem thoroughly explaining how many adjacent energy levels predicted in "ligand field" theory cannot conceivably be resolved. Thus, the function $\exp \left(-x^{2} / 2\right)$ (which is frequently tabulated for the use by statisticians) has $\delta=(2 \ln 2)^{1 / 2}=1.177$. When two identical Gaussians have their maxima situated at $x_{1}=-\varkappa$ and at $x_{2}=+\varkappa$, their sum forms an almost perfect Gaussian for small $x$ having its maximum at $x=0$ and the half-width

$$
\begin{equation*}
\delta=1.177\left(1+0.589 \varkappa^{2}+\ldots\right) \tag{1}
\end{equation*}
$$

where 0.589 is half the numerical constant 1.177. The important point is the quadratic singularity in $x$; it is not possible to calculate backwards from an experimental spectrum with its usual uncertainty inherent in all such measurements to a reliable value of $x$; once $x$ is small, it might equally well be half as large or zero indicating only one Gaussian component of the signal. The sum curve has a flat maximum with vanishing second differential quotient for $\varkappa=1$; for this value, curvature at $x=0$ is due exclusively to the fourth and subsequent (even) differential quotients. When $x$ is larger, two maxima with a minimum in the middle develop.

There are good reasons to believe that the observed $\delta$ of our signals can be described as the square-root of the sum of squared contributions from differing sources of signal broadening. Fadley and Shirley [29] pointed out that the two 4 d signals of lutetium (III) fluoride each have $2 \delta=4.23 \mathrm{eV}$ due to short radiative half-life of the ionized system $4 d^{9} 4 f^{14}$ where a $4 f$ electron rapidly jumps down in the 4 d vacancy forming the lowest configuration $4 d^{10} 4 f^{13}$ of Lu(IV) (which then picks up an electron from the surroundings less rapidly). According to Heisenberg's uncertainty principle, the doublesided half-width $2 \delta$ should be 0.46 eV if the radiative half-life is $10^{-15} \mathrm{sec}$ and 4.6 eV for $10^{-16} \mathrm{sec}$, the product of the two quantities remaining constant. We have also found $\delta=2.1 \mathrm{eV}$ for Lu4d signals of $\mathrm{Lu}_{2} \mathrm{O}_{3}$ and $\mathrm{Lu}\left(\mathrm{IO}_{3}\right)_{3}$. In the heavier elements, $\delta$ of the 4 d signal remains roughly constant and is 2.0 eV in $\mathrm{HfO}_{2}, 2.1 \mathrm{eV}$ in $\mathrm{K}_{2} \mathrm{HfF}_{6}, 2.3 \mathrm{eV}$ in powdered Au and in $\mathrm{HgO}, 2.4 \mathrm{eV}$ in $\mathrm{PbSO}_{4}, 2.2 \mathrm{eV}$ in $\mathrm{BiF}_{3}, 2.5 \mathrm{eV}$ in $\mathrm{Th}\left(\mathrm{IO}_{3}\right)_{4}, \mathrm{UO}_{2}\left(\mathrm{IO}_{3}\right)_{2}$ and $\mathrm{Cu}\left(\mathrm{UO}_{2}\right)_{2}\left(\mathrm{PO}_{4}\right)_{2}$.

Hence, the half-life of these states lacking a 4 d electron is between 1 and 1.3 times $10^{-16}$ sec.

Quite generally, most of the intense signals observed by us have $\delta$ close to the standard value 1.0 eV . This is particularly true for the 4 f signals of elements above tungsten [64] whereas the 4 f signals of ytterbium(III) are broadened by effects of interelectronic repulsion (separating terms of $4 \mathbf{f}^{12}$ ) and of lutetium (III) and hafnium (IV) by spin-orbit coupling not sufficiently resolved. Since a half-life $10^{-15} \mathrm{sec}$ would increase $\delta$ by 0.06 eV , this is the lower limit where Heisenberg uncertainty broadening becomes perceptible. Many of the lower $l$ values correspond to broadened signals, and we are now going to discuss them in the order s, p, d.

Parrett [88] discussed the uncertainty width of 1 s holes as a function of $Z$. The radiative width due to $2 \mathrm{p} \rightarrow 1 \mathrm{~s}$ X-ray fluorescence is $Z^{4} \cdot 1 \cdot 2 \cdot 10^{-6} \mathrm{eV}$, but the observed width in $\mathrm{eV}(0.5$ for $\mathrm{Ar}, 1.5$ for $\mathrm{Cu}, 3.0$ for $\mathrm{Kr}, 7.5$ for Ag and 54 for Au ) is larger because of competing processes, such as the emission of Auger electrons. We find some 1 s signals significantly broadened, such as 1.3 eV for several lithium(I) salts and 1.1 eV for beryllium(II). We do not believe that this is due to half-lifes below $10^{-15}$ sec for so low $Z$ values, but rather a dependence of $I$ on the internuclear distance producing a broadened signal according to Franck and Condon's principle, having the maximum at the "vertical" transition with unchanged distances, like the broadening (with frequent vibrational structure) one finds in the photo-electron spectra of gaseous molecules [107] when a strongly bonding (or anti-bonding) electron is removed. It is of obvious importance for the use of carbon 1 s signals as internal standards to consider their $\delta$ values, in view of eq. (1), as an indicator of closely adjacent signals. As a matter of fact, the pure scotch tape hydrocarbon shows $\delta=0.95 \mathrm{eV}$. Many nitrogen 1s signals have $\delta=1.0 \mathrm{eV}$ but it must be noted that in other cases, larger values may be observed though no obviously non-equivalent nitrogen atoms are involved. This may again be connected with Franck-Condon-broadening. Fluorine 1s signals vary between 1.2 and 1.4 eV . On the other hand, most sodium(I) salts have $\delta$ close to 1.05 eV . Finally, $\mathrm{Mg}(\mathrm{II})$ shows $\delta=1.4 \mathrm{eV}$.
$\delta$ of 2 s signals is difficult to evaluate in fluorides because of the rapidly varying background, but seems to be close to 1.5 eV as it is also in Mg (II). The Al2s signal in $\mathrm{Na}_{3} \mathrm{AlF}_{6}$ has $\delta=1.3 \mathrm{eV}$. This value increases to 2.0 eV for $\mathrm{CaF}_{2}$ and 2.1 eV for $\mathrm{Ca}\left(\mathrm{IO}_{3}\right)_{2}$ and seems to be as large as 3.5 eV for $\mathrm{BaCrO}_{4}$.
$\delta$ of the 3 s signal is 1.6 eV in $\mathrm{CaF}_{2}$ and 2.4 eV in $\mathrm{SrF}_{2}$. In the 3 d group, effects of interelectronic repulsion produce two broad signals (see Table 20) when the groundstate has positive $S$.
$\delta$ of the 4 s signal in $\mathrm{BaF}_{2}$ is 2.0 eV . According to Cohen et al. [17], the intrinsic width of the lanthanide 4 s signals (again split by interelectronic repulsion) corresponds to $\delta \sim 3 \mathrm{eV}$.
$\delta$ of fluorine 2 p in $\mathrm{CaF}_{2}, \mathrm{SrF}_{2}$ and $\mathrm{BaF}_{2}$ is close to 1.5 eV but is difficult to evaluate in other compounds, partly because of adjacent I-values of delocalized M.O. The 2 p signal has $\delta=1.3 \mathrm{eV}$ in Mg (II) and 1.2 eV in Al (III) but becomes difficult to measure in the following elements because of the perceptible spin-orbit coupling. When the two $j$-values are sufficiently distinct again, $\delta$ is 1.0 to 1.1 eV in $\mathrm{K}(\mathrm{I})$ and $\mathrm{Ca}(\mathrm{II}) . \mathrm{Cr} 2 \mathrm{p}$ has $\delta=1.1 \mathrm{eV}$ in $\mathrm{BaCrO}_{4}$ but the subsequent elements have slightly broadening due to positive $S$ of the groundstate, though diamagnetic Co(III) has $\delta=1.05 \mathrm{eV}$. Similar moderate $\delta \sim 1.1 \mathrm{eV}$ can be seen in Zn (II) and Ga(III).
$\delta$ of calcium 3p in $\mathrm{CaF}_{2}$ is 1.3 eV . When not broadened by effects of interelectronic repulsion, the 3 d group has $\delta$ of 3 p signals close to 1.5 eV , whereas $\delta=1.6$ for $\mathrm{Ge}(\mathrm{IV})$ and 1.4 eV for $\mathrm{As}(\mathrm{V})$. In $\mathrm{Se}, \mathrm{Br}, \mathrm{Rb}$ and $\mathrm{Sr}, \delta$ is also close to 1.5 eV . Y (III), $\mathrm{Zr}(\mathrm{IV})$ and $\mathrm{Ru}(\mathrm{III})$ show 1.8 eV and $\mathrm{CdF}_{2} 1.9$ eV , whereas the value finally increases to 2.9 eV in $\mathrm{BaF}_{2}$.
$\delta$ of 4 p in $\mathrm{SrF}_{2}$ is 1.4 eV and seems to be as low as 1.0 eV in $\mathrm{YF}_{3}$. It then increases rapidly, being about 2 eV in Rh (III), 3 eV in Pd (II), 4 eV in Ag (I) and close to 5 eV in $\mathrm{Cd}(\mathrm{II})$. This increase does not continue, $\delta=2.7 \mathrm{eV}$ for Au and as narrow as 1.3 eV for Ba (II).
$\delta$ of the 5 p signal has only been measured to 1.3 eV in $\mathrm{BaF}_{2}$ and about 1.4 eV in Au .
$\delta$ of the 3 d signal is difficult to measure as long it remains in the region with $I$ below 20 eV . It is 1.2 eV in Ga (III), 1.1 eV in $\mathrm{Ge}(\mathrm{IV})$ and 1.3 eV in $\mathrm{As}(\mathrm{V})$. It is possible that a part of this broadening must be ascribed to beginning spin-orbit splitting. $\delta$ is 1.15 eV in bromides, 1.0 eV for Mo (VI) and Rh (III) and as low as 0.95 eV for $\mathrm{Pd}(\mathrm{II})$ and $\mathrm{Ag}(\mathrm{I})$. It then increase slightly to 1.05 eV in Cd (II), about 1.2 eV in tellurium, 1.15 eV in both iodides and iodates, 1.05 eV in $\mathrm{Cs}(\mathrm{I})$ and 1.2 eV in $\mathrm{Ba}(\mathrm{II})$. The signal at lowest $I$ in La(III) has $\delta=1.5 \mathrm{eV}$ whereas the broad and somewhat asymmetric signals of Sm (III), Eu (III), Gd (III) and Dy (III) all are close to 2.5 eV .
$\delta$ of the 4 d signal of $\mathrm{Ag}(\mathrm{I})$ is 1.5 eV , perhaps due to "ligand field" effects of differing energy of the five 4 d orbitals. $\delta$ decreases to 1.0 eV in $\mathrm{CdF}_{2}$ and is 1.1 eV for $\mathrm{Cs}(\mathrm{I})$ and $\mathrm{Ba}(\mathrm{II})$ having a clear-cut separation between the two $j$-values. All the lanthanides have asymmetric (and frequently irregular) shape, $\delta$ is 1.5 eV in La(III), 3.2 eV in Nd (III), 1.7 eV in Eu (III) and 2.3 eV in Gd (III). The following elements all have $\delta$ around 2 eV . The relatively
sharp signal of Yb (III) at lowest $I$ (cf. Fig. 1) has $\delta=1.9 \mathrm{eV}$. It was discussed above how $\delta$ slowly increases from 2.1 to 2.5 eV in the elements from lutetium to uranium.
$\delta$ of the 5 d signal is 1.0 eV in $\mathrm{Pb}(\mathrm{II}), 1.1 \mathrm{eV}$ in $\mathrm{Th}(\mathrm{IV})$ and 1.3 eV in U(VI).

The general conclusion is that the half-width only becomes spectacularly large (above 2 eV ) for several ns-signals when $Z$ increases, in the rather isolated case of 3 p in $\mathrm{BaF}_{2}$, for all 4 p signals when $Z$ larger than 45 and for all 3 d and 4 d signals for $Z$ above 60 . It is even possible to maintain that only 4 p and 4 d signals have a pronounced propensity toward high $\delta$. The physical explanation may be that the half-lifes only are shorter than $2.10^{-16} \mathrm{sec}$ when $n(l+1)$ electrons are present to fill the $n l$ vacancy. If this condition for extremely short half-life is valid, $1 \mathrm{~s}, 2 \mathrm{p}, 3 \mathrm{~d}$ and 4 f signals should never become exceedingly broad. The 3 p signal broadens in the presence of 3 d electrons, but this is not a convincing argument for the hypothesis. However, it is striking that the 4 p signal broadens tremendously in the interval from Rh(III) to Cd(II) where the number of 4 d electrons available increase from six to ten. In this case, $\delta$ decreases slightly in the heavier elements barium and gold, whereas $\delta$ remains almost constant of the 4 d signal once the 4 f shell is filled, starting with $\mathrm{Lu}(\mathrm{III})$ and $\mathrm{Hf}(\mathrm{IV})$. There are good reasons to believe that the 5 d signal would broaden in transuranium elements once many 5 f electrons are present.

One may ask whether $\delta$ is influenced by chemical effects. There is a distinct tendency to sharp (and as we see below, higher) peaks of alkaline metal ions compared with the broader, slightly lower peaks of the isoelectronic halides. Such an effect might be connected with Franck-Condon broadening being more important for the anions. We do not know a clear-cut case of the same element (conserving the same value of $S$ ) varying $\delta$ as a function of the neighbour atoms, with exception of the nitrogen and oxygen 1 s signals mentioned above.

## Relative Signal Intensities

In stoichiometric compounds, the relative intensities (expressed as the difference of counts/sec between the maximum and the interpolated background) of different elements, or for that matter, different shells of the same element, do not reproduce better than 20 percent. Hence, the instrument is not perfectly suited for quantitative analysis, though it can be of great interest to obtain information about relative concentrations (even within a


Figure 4. Intensities of photo-electron signals from the $n l$ shells in different elements (as a function of $Z$ ) relative to fluorine 1 s . As discussed in ref. [67] this is not better determined than within a factor 1.3. When two $j$-signals are seen, the maximum at lower $I$ due to the higher $j$ is considered; otherwise, the observed maximum is simply used.
factor 1.5) of elements in the outermost $30 \AA$ of a solid sample. Wagner [112] studied the strongest signal (usually the highest $I$ among the alternatives 1 s , $2 \mathrm{p}_{3 / 2}, 3 \mathrm{~d}_{5 / 2}$ and $4 \mathrm{f}_{7 / 2}$ ) of 43 elements relative to fluorine 1 s . In the following, we use the colloquial abbreviation "w" for this unit. We are also interested in the less intense signals and find a variation by a factor of 1000 . Figure 4
shows the relative intensities as a function of $Z$. It must once more be emphasized that they may be some 30 percent wrong. In practice, we established a set of secondary standards, such as 0.4 w for $\mathrm{N} 1 \mathrm{~s}, 2.0 \mathrm{w}$ for Na1s, 4.0 w for $\mathrm{I}_{3} \mathrm{~d}_{5 / 2}$ and 6.5 w for $\mathrm{Cs} 3 \mathrm{~d}_{5 / 2}$. We agree with Wagner that C1s has 0.27 w and that iodine (at least in iodides) represents a relative minimum of the curve between antimony and caesium. Most of our values differ less than 25 percent from those given by WAGNER. It may be added that his $\mathrm{K}_{4} \mathrm{Ni}(\mathrm{CN})_{6}$ most probably is $\mathrm{K}_{2} \mathrm{Ni}(\mathrm{CN})_{4}$ dividing the nickel intensity by two.

An attractive hypothesis also suggested by WaGNER[112] is that the number of photo-electrons counted in a given signal is proportional to the number of X-ray photons absorbed by a given shell (anyhow, the yield of electrons not suffering inelastic scattering is low, since the penetration depth of the soft X-rays is about 100 times deeper than the surface layer allowing photo-electrons to escape). If the typical absorption edges where the molar extinction coefficient is proportional to $v^{-3}$ (in agreement with an argument by Kramers based on the correspondence principle) are extrapolated to large $v$, the signal intensity should be proportional to $(2 j+1) I^{2}$ where $(2 j+1)$ is the number of electrons producing the $n l j$ signal. However, this argument is only valid for s- and perhaps for p - electrons. For higher $l$, the probability of absorption of a high-energy photon is far larger, and we have proposed that the intensity is proportional to the product of three factors, $(2 j+1)$, the average $\left\langle\mathrm{r}^{-2}\right\rangle$ of the shell being ionized, and a kind of squared effective nuclear charge. Actually, Watson was as kind as to supply $\left.<\mathrm{r}^{-2}\right\rangle$ values for Hartree-Fock functions, and the third factor seems remarkably invariant [67].

Since small average radii favour photo-ionization by the X-rays, the $d$ and $f$ shells at the end of the transition groups and in the subsequent posttransition elements show rather strong signals, as also seen on Fig. 1 and 2. This is rather fortunate, because the number of valence electrons can be rather overwhelming. This number is 32 in each sulphate or perchlorate anion, 40 in acetylacetonate and 120 in tetraphenylborate, whereas the methylene blue cation presents 126 valence electrons. In particular, hydrocarbons have a virtually flat photo-electron spectrum in the region of $I$ below 20 eV showing a vanishing probability of ionizing carbon 2 p orbitals. In oxides, the 2 s signal close to 30 eV has the intensity 0.02 w whereas 2 p is on the limit of detection. $\mathrm{F} 2 \mathrm{~s}(0.04 \mathrm{w})$ and $\mathrm{F} 2 \mathrm{p}(0.02 \mathrm{w})$ are quite perceptible.

On the whole, the curves on Fig. 4 are smoothly increasing as a function of $Z$ until the limit 1382 eV of $I$ is reached. However, there is pronounced
tendency for the transition groups to have too weak signals. In view of what we said about probability for a given shell to absorb the photon, one would consider the product of the height and the width to be the important quantity, but this distinction would make little actual difference. Even the satellites to be discussed below and the multiple signals due to effects of interelectronic repulsion would not change the intensities by more than a factor of three, whereas an extrapolation of the 3 d intensity on Fig. 4 would arrive at 10 to 20 w for Sm to Dy. However, we have indicated the two highly different sets of intensities for $\mathrm{Cu}(\mathrm{I})$ and $\mathrm{Cu}(\mathrm{II})$ on Fig. 4. Most of these differences can only be qualitatively understood as an increased probability of secondary processes (such as emission of electrons in broad shake-up and shake-off signals at higher $I$ ) since the probability of inelastic scattering should only depend on the kinetic energy of the electron.

Obviously, the identification of $n l j$-values for a given signal is an important problem. Usually, there is no ambiguity when comparing with literature, but one has to realize that the Uppsala tables [97] based partly on $I^{*}$ measurements relative to the Fermi level and partly on the critical analysis of X-ray spectra by Bearden and Burr [3], besides chemical shifts, shows unexplained irregularities up to 5 eV . This can most readily be seen from the plot [66] of $\mathrm{d} I / \mathrm{d} Z$ as a function of $Z$, especially in the lanthanides. However, we have had no serious difficulties with identifying given shells (except due to coincidences with stronger signals or their $\mathrm{K} \alpha_{3}$ replica) with the exception of the $6 p$ signals of thorium and uranium. The Uppsala tables supposed to give $I^{*}$ of metallic elements relative to the Fermi level indicate Th6p $\mathrm{p}_{1 / 2}$ at 49 and Th6p3/2 at 43 eV whereas the values for uranium should be 43 and 33 eV . It is obvious that this must be wrong for at least one of the two elements. We find a sharp signal with $I=27.2 \mathrm{eV}$ and $I^{\prime}=23.6 \mathrm{eV}$ for $\mathrm{ThF}_{4}$ and $I=24.3$ and $I^{\prime}=20.7 \mathrm{eV}$ for $\mathrm{ThO}_{2}$ and ascribe it to $6 \mathrm{p}_{3 / 2}$. When compared with $I=10.75 \mathrm{eV}$ of the radon atom measured by Ebbe Rasmussen, it is probable that $I$ is close to 55 eV for $\mathrm{Th}^{+4}$, and the Madelung potential would decrease this value by 30 eV in fully ionic $\mathrm{ThO}_{2}$. It is seen in Table 21 that the difference 25 eV is expected to be slightly higher than the actual $I$. The spin-orbit separation is 3.8 eV in $\mathrm{Rn}^{+}$, and it is quite conceivable that it has increased to 6 eV in thorium, but we are not able to see a signal close to 30 eV in $\mathrm{ThO}_{2}$ because of the oxygen 2 s signal having $I=31.3$ and $I^{\prime}=27.7 \mathrm{eV}$. We have not succeeded in identifying the 6 p signals in uranium compounds; some of them have a weak signal with $I \sim 54 \mathrm{eV}$ which seems rather high. This problem needs further studies.

It is frequently argued in literature [7] that Auger electrons with the kinetic energy $\mathrm{E}_{\mathrm{kin}}$ can produce signals in our type of spectrometer with the
apparent $I^{*}=(1482 \mathrm{eV})-\mathrm{E}_{\text {kin }}$. Wagner [111] even reports that these signals may be almost as intense as genuine photo-electron signals between 0.2 and 1 w . Usually, we did not detect Auger signals. However, they have been found in $\mathrm{MgF}_{2}$, NaF and NaI, where they are particularly strong. The kinetic energy is 645.6 and 645.5 eV for the strongest fluorine signal, respectively, 979.3 eV and 983.2 eV for sodium, and 1169.3 eV for magnesium. It can be argued that $\partial=3.9,4.3$ and 3.7 eV should be added in order to correct for the positive charge of the three samples. On the other hand, graphite and many other samples have very broad Auger signals. Some low apparent $I^{*}$ are in eV 381 for $\mathrm{As}(\mathrm{V}), 191 \mathrm{BaSeO}_{4}, 183 \mathrm{KSeCN}, 104 \mathrm{Er}_{2} \mathrm{O}_{3}$ and 46.6 for $\mathrm{Tm}_{2} \mathrm{O}_{3}$.

## Satellites and Multiple Signals due to Interelectronic Repulsion

When the groundstate has positive $S$, the ionized system has lower energy for ( $S+1 / 2$ ) than for ( $S-1 / 2$ ), essentially because of the lower interelectronic repulsion $\left\langle\mathrm{r}_{12}^{-1}\right\rangle$ in the former case. This effect was detected in Uppsala [97, 98] for gaseous $\mathrm{O}_{2}(S=1)$ and $\mathrm{NO}(S=1 / 2)$ having their 1 s signals split to the extent of about 1 eV . Also solid chromium (III) $(S=3 / 2)$ and manganese(II) and iron(III) ( $S=5 / 2$ ) show this effect [29]. From a theoretical point of view, the situation is the most clear-cut if one of the two partly filled shells consists of an s orbital containing one electron, such as $s d^{q}$ or $\mathrm{sf}^{\mathrm{q}}$ in which case the intensity ratio between the two signals is $(S+1) / S$, the ratio between the degeneracy numbers, and their distance $(2 S+1) \mathrm{K}_{\mathrm{av}}$ where $\mathrm{K}_{\mathrm{av}}$ is the average value [56] of the exchange integral of the twoelectron operator between the s orbital and the five d or the seven $f$ orbitals (the formation of an average value is not strictly necessary when one of the orbitals is spherically symmetric). This phenomenon has been observed [17] for the 4 s and 5 s signals of lanthanides and seen in Table 20 as the separation 3.4 eV in the Cr 2 s signals of $\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}\left(\mathrm{NCS}_{4}^{-}, 4.8 \mathrm{eV}\right.$ in the Co3s signals of $\mathrm{CoF}_{2}$ and 2.8 eV in the Ni3s signals of $\mathrm{NiF}_{2}, 4 \mathrm{H}_{2} \mathrm{O}$. Hence, $\mathrm{K}_{\mathrm{av}}(2 \mathrm{~s}, 3 \mathrm{~d})=0.85$ eV in Cr (III), $\mathrm{K}_{\text {av }}(3 \mathrm{~s}, 3 \mathrm{~d})=1.2 \mathrm{eV}$ in $\mathrm{Co}(\mathrm{II})$ and 0.93 eV in $\mathrm{Ni}(\mathrm{II})$, all of the same order of magnitude as the spin-pairing energy parameter $D$ (representing $7 \mathrm{~K}_{\mathrm{av}}(3 \mathrm{~d}, 3 \mathrm{~d}) / 6$ ) for the partly filled 3 d shell. We return in the next section to the partly filled shell itself. Between Gd(III) and Tm(III), $\mathrm{K}_{\mathrm{av}}(4 \mathrm{~s}, 4 \mathrm{f})=1.1 \mathrm{eV}$ and $\mathrm{K}_{\mathrm{av}}(5 \mathrm{~s}, 4 \mathrm{f})$ increases from 0.4 to 0.5 eV in the series $\operatorname{Pr}(\mathrm{III})$ to $\mathrm{Dy}(\mathrm{III})[17]$.

The 2 p signals in the 3 d group are stronger (see Fig. 4) but the many states of the configuration $2 \mathrm{p}^{5} 3 \mathrm{~d}^{4}$ may produce several signals. The splitting has the order of magnitude 2 eV in Cr (III), 4 eV in Mn (II), 8 eV in Fe (III)
but only 3 eV in Fe (II) and 5 eV in Co (II). Apparently, $\mathrm{K}_{\mathrm{av}}$ (2p, 3d) increases in direction of the later members of the 3 d group. However, the strong deviations from Russell-Saunders coupling in the 2 p shell exclude the possibility of evaluating this parameter, the $120.6=720$ states of $2 \mathrm{p}^{5} 3 \mathrm{~d}^{7}$ are far wider distributed than to the extent of $4 \mathrm{~K}_{\mathrm{av}}\left(2_{\mathrm{p}}, 3 \mathrm{~d}\right)$. We still believe that the corresponding splitting 6 eV of the two 2 p signals of high-spin $(S=1)$ nickel(II) compounds are due to effects of interelectronic repulsion separating the $45.6=270$ states of $2 \mathrm{p}^{5} 3 \mathrm{~d}^{8}$. Rosencwaig, Wertheim and Guggenheim [96] suggest that these multiple signals are satellites of the same kind as the copper(II) signals discussed in the next paragraph. We do not believe that the main origin of the four Ni2p signals is such satellites, in part because only two strong signals are observed in the case of diamagnetic $(S=0)$ nickel(II) complexes [60] and also because the separation is 17.2 eV in the latter case, whereas the distance between the first and third signal of paramagnetic Ni (II) is close to 17.7 eV . It is known that the chemical variation [64] of spin-orbit splitting is on the limit of experimental uncertainty, normally below 0.1 eV , and the increase from 17.2 to about 17.7 eV is what one would expect of effects of interelectronic repulsion, as first noted by Helmer comparing $\mathrm{Cr}_{2} \mathrm{O}_{3}$ with $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$. This does not prevent that the unusually strong left-hand components of the 2 p signals of the acetylacetonate $\mathrm{Ni}(\text { aca })_{2}$ $\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$ (probably dehydrating to $\mathrm{Ni}_{3} \mathrm{aca}_{6}$ in vacuo) may partly be due to electron transfer satellites of the kind discussed below in the case of La (III) in view of the strongly reducing character of acetylacetonate ligands derived from electron transfer spectra in the visible and the ultra-violet [49].

Novakov [87] detected satellites 8 to 10 eV to the left of 2 p signals of copper compounds. It was originally reported that also copper (I) compounds such as $\mathrm{CuCl}, \mathrm{CuI}$ and $\mathrm{Cu}_{2} \mathrm{O}$ show satellites. However, we believe that these satellites really belong to $\mathrm{Cu}(\mathrm{II})$ in superficial oxidation products. Actually, the non-oxidizable $\mathrm{CuCN}, \mathrm{Cu}_{2} \mathrm{HgI}_{4}$ and $\left[\mathrm{Nien}_{2}\right]\left(\mathrm{CuI}_{2}\right)_{2}$ show just two strong signals like the isoelectronic Zn (II) and Ga(III). At present, the origin of the copper(II) satellites is not perfectly clear. Though Cu(II) is rather oxidizing, it is not too probable that they are due to electron transfer like in La(III) because similar strong satellites are not observed in Rh(III) and Pd(II). Further on, their distance from the main signals is smaller in the fluoride. The numerical value 8 to 10 eV is slightly below the ionization energy of the 3 d electrons suggesting shake-off (simultaneous ionization of a 2 p and a 3 d electron by the same photon, in contrast to consecutive emission of Auger electrons) or shake-up, the 3 d electron simultaneously jumping to a low-lying empty orbital such as 4 s . The former alternative seems less plausible
in view of the central field becoming more negative, increasing the effective $I(3 \mathrm{~d})$. The fundamental difficulty for both alternatives is that copper(I) has a 3 d shell easier to excite than $\mathrm{Cu}(\mathrm{II})$. This might be explained away if a selection rule holds that such satellites are only conspicuous when the groundstate has positive $S$. Anyhow, diamagnetic Ni (II) and Pd (II) do not show satellites, though both electron transfer and $d$ shake-up should be equally possible. One way out of this difficulty would be to connect the satellites with the presence of a strongly $\sigma$-anti-bonding $\left(\mathrm{x}^{2}-\mathrm{y}^{2}\right)$ electron delocalized to a large extent on the ligands [58]. The quadratic $\mathrm{d}^{8}$ systems have the $\left(x^{2}-y^{2}\right)$ orbital empty. It must be noted that octahedral high-spin Mn (II), Fe (II), Co (II) and Ni (II) also contain two $\sigma$-anti-bonding electrons, one $\left(x^{2}-y^{2}\right)$ and one $\left(3 z^{2}-r^{2}\right)$. It might then be argued that these systems show weaker satellites because the delocalization is less pronounced, and at smaller distance from the main signal because $I(3 \mathrm{~d})$ is smaller, except of Fe(III). Outside the elements from manganese to copper, very few cases of distinctly $\sigma$-anti-bonding electrons occur in the groundstate, though they are the origin of most of the excited levels treated in "ligand field" theory [59]. We tend to believe that shoulders or residual asymmetry of the main 2 p signals of Cu (II) are due to effects of interelectronic repulsion, and that the distant satellites have a rather specific origin. Quite generally, copper(II) complexes of pseudo-halides [80a] and the oxidized surface of copper-nickel alloys [12] show satellites, and it becomes an interesting question whether diamagnetic quadratic Cu (III) also shows satellites. We have precipitated the periodato complex (no. 67) and find somewhat ambiguous evidence of much weaker satellites probably belonging to a superficially reduced impurity of Cu(II). Similar results have been obtained by Steggerda and us for $\mathrm{Cu}($ III ) biguanide complexes. One might have hoped that the silver (II) complex $\mathrm{Agpy}_{4}^{+2}$ shows illustrating analogies. Actually, the 3 d signals hardly have any satellites, whereas 3 p shows doubtful broad satellites.

Lorquet and Cadet [78] and their colleague Momigny pointed out that the intensity of shake-up satellites is a quantitative measure for the extent of configuration interaction in the groundstate. Thus, the configuration $1 \mathrm{~s}^{2} 2 \mathrm{p}^{2}$ contributes 0.15 of the squared amplitude of the groundstate ${ }^{1} \mathrm{~S}$ of the beryllium atom (the preponderant configuration of which is $1 \mathrm{~s}^{2} 2 \mathrm{~s}^{2}$ ) and correspondingly, fairly strong Rydberg series in the auto-ionizing continuum above the first ionization limit $\left(1 \mathrm{~s}^{2} 2 \mathrm{~s}\right)$ converge to the excited configuration $1 \mathrm{~s}^{2} 2 \mathrm{p}$ of $\mathrm{Be}^{+}$The carbon 1 s and oxygen 1 s signals of carbon monoxide complexes of zerovalent chromium, iron, nickel and tungsten show satellites at 5.4 to 6.0 eV higher $I^{*}$. According to Barber, Connor and Hillier [2]
the occurrence of these satellites indicates a poor description of the groundstate by a Hartree-Fock M.O. configuration, and they ascribe the satellites to the valence bond structure $\mathrm{M}^{+}(\mathrm{CO})_{\mathrm{N}}^{-}$This is somewhat analogous, but not exactly equivalent, to our opinion of "inverted electron transfer" satellites from the d-like orbitals of the central atom to the empty orbitals of the ligands (again stabilized by the 1 s hole on either the carbon or the oxygen atom). Similar satellites have been observed in other metallo-organic compounds [89a] but one has to be rather cautious regarding the possibility of superficial admixture of other compounds and of charging effects of the $\partial$ type discussed above.

We have already discussed the satellites in the closed-shell system La(III) due to electron transfer $\lambda^{-1} 3 d^{9} 4 \mathrm{f}$ where $\lambda$ denotes a M.O. localized on adjacent atoms. There is little doubt that electron transfer satellites also contribute to some structure in Ce, Pr and Nd compounds, though Nd (III) may be determined by effects of interelectronic repulsion alone in $3 \mathrm{~d}^{9} 4 \mathrm{f}^{3}$, and that $\lambda^{-1} 4 f^{13} 5 \mathrm{f}$ occur with low intensity in uranium(VI). Nevertheless, our conclusion is that strong satellites are rather uncommon and are concentrated on a few elements in definite oxidation states such as Cu (II) and La(III).

## The Valence Region and Optical Electronegativities

For the chemist, one of the most interesting problems to be studied by photo-electron spectrometry is the valence region with $I$ below 50 eV . Somewhat exceptionally, the fluorine 2 s signals [98] are split by ligandligand interactions [64] to the extent of 3.5 eV in $\mathrm{CF}_{4}$ and 4.9 eV in $\mathrm{SF}_{6}$ but usually, chemical effects of this kind are only observed for $I$ below 40 eV . The resolution is far better in gaseous molecules than in solid samples, and with exception of d and f shells, the signals are rather weak when induced by X-rays. The optical electronegativity was introduced [50,57] with the purpose of describing electron transfer spectra where an electron is transferred from one or more reducing ligands to an oxidizing central atom. The Pauling values $\varkappa_{\mathrm{opt}}=3.9\left(\mathrm{~F}^{-}\right), 3.0\left(\mathrm{Cl}^{-}\right), 2.8\left(\mathrm{Br}^{-}\right)$and $2.5\left(\mathrm{I}^{-}\right)$can be obtained for the halide ligands if each unit of $\chi_{\text {opt }}$ corresponds to the wavenumber difference $30000 \mathrm{~cm}^{-1}$ or 3.7 eV . It was pointed out [54] that most gaseous halides [107] have their lowest ionization energy

$$
\begin{equation*}
I=\left(1+3.7 \varkappa_{\mathrm{opt}}\right) \mathrm{eV} \tag{2}
\end{equation*}
$$

close to 15.4 eV for fluorides, 12.1 eV for chlorides, 11.3 eV for bromides
and 10.2 eV for iodides. It is seen from Table 21 that the almost ionic halides have $I$ values without corrections for charging effects close to eq. (2) whereas $I^{\prime}$ is lower. One may conclude that rather covalent halides have slightly higher ionization energies than ionic solids though normally below the values [82] for the gaseous atoms $17.42(\mathrm{~F}), 12.97(\mathrm{Cl}), 11.81(\mathrm{Br})$ and 10.45 (I) eV.

The partly filled d shell has $I$ values between 8 and 12 eV in most cases. The variation with the ligands for a given element in the same oxidation state may, to some degree, be an illusion when $I^{\prime}$ are considered. One might have hoped for a determination of the sub-shell energy difference $\Delta$ (which is known from visible spectra [56] to be about 1 eV in these cases) from the 3 d ionization energies of octahedral cobalt(II) and nickel(II) complexes, though it is by no means evident that the same $\Delta$ value would be obtained from $I$ differences as from the excitation energies studied by "ligand field" theory. However, our present results are on the limit of the experimental uncertainty. The two sub-shells of $\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ containing four and two d-like electrons have $I=6.9$ and $7.2 \mathrm{eV}[107]$. By the way, the chromium (II) methylcyclopentadienide $\mathrm{Cr}\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{CH}_{3}\right)_{2}$ has $[22] I=5.55$ and 6.9 eV , the former value being the lowest known for any gaseous molecule (whereas solid alkali metals have $I$ close to 2 eV ). Nevertheless, the d-group molecules have not been particularly informative for our purposes; Cox, Evans, Hamnett and Orchard [21] found $I=9.41 \mathrm{eV}$ for the single 3 d electron of gaseous $\mathrm{VCl}_{4}$. It is interesting that the loosest bound M.O. of $\mathrm{PF}_{3}$ corresponding to the lone-pair has $I=12.3 \mathrm{eV}$ whereas $\mathrm{Ni}\left(\mathrm{PF}_{3}\right)_{4}$ has $I=9.55$ eV for six of the 3 -like electrons and 10.58 eV for the other sub-shell containing four electrons [35]. These values may be compared with $I=8.8$ and 9.7 eV for the two similar sub-shells of $\mathrm{Ni}(\mathrm{CO})_{4}$. Recently, the separation between halogen $n$ p and copper 3d signals has been reported [69] for solid $\mathrm{CuCl}, \mathrm{CuBr}$ and CuI . What is particularly interesting is a shoulder towards lower $I$ of the latter signal possibly representing the separation between the two sub-shells in the tetrahedral chromophore in close analogy to the isoelectronic $\mathrm{Ni}(0)$ complexes.

It is beyond doubt that $I$ (3d) of zinc (II) compounds is some 5 eV higher than corresponding nickel(II) and copper(II), and $I(3 \mathrm{~d})$ of gallium(III) some 16 eV higher than cobalt(III). This is a most striking difference from the lanthanides with comparable $I(4 \mathrm{f})$ of gadolinium (III) and lutetium (III) and $I(4 \mathrm{f})$ only increasing about 2 eV from $\mathrm{Yb}(\mathrm{III})$ to $\mathrm{Lu}(\mathrm{III})$. Actually, $I(4 \mathrm{f})$ is higher of $\mathrm{TbO}_{2}$ than of $\mathrm{HfO}_{2}$. Said in other words, there is an absolute sense in which the closed-shell character of Zn (II) and Ga(III) shows up as
considerably higher $I(3 \mathrm{~d})$ than of the partly filled shell in preceeding elements having the same oxidation state. The valence region of metallic $\mathrm{Fe}, \mathrm{Co}, \mathrm{Ni}$, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt and Au have been studied both by BaEr et al. [1] and by Fadley and Simpley [28]. There is no doubt that in many $d$ group compounds, $I$ of the partly filled shell is comparable or higher than $I$ of the loosest bound ligand orbitals. It might be felt a somewhat paradoxical situation, but the point is that partly filled shells with small average radii have large differences between the ionization energy and the electron affinity, and the main condition for a well-defined oxidation state with an integral number of electron in the partly filled shell is that its electron affinity is significantly smaller than the ionization energy of any of the ligand orbitals.

Wertheim and Hüfner [116] studied several d group oxides, concluding in almost coincidence of oxygen 2 p and central atom 3 d signals. It was even argued that metallic $\mathrm{ReO}_{3}$ has a weak shoulder at $I^{*} \sim 1 \mathrm{eV}$ due to rhenium 5 d electrons. However, the $I^{*}$ values reported seem to be some 8 eV below our $I$ values. Though it is seen from Table 21 that the Madelung theory is not perfectly valid, it is interesting to note that a change from $310^{\circ} \mathrm{K}$ to $500^{\circ} \mathrm{K}$ produced an increase of the distances between potassium K3s and K3p and chlorine (3p) signals in KCl in excellent agreement with the result 0.13 eV calculated from the change of the Madelung potential by the thermal expansion whereas the similar heating of LiF produced an increase of the distance $I(\mathrm{Li} 1 \mathrm{~s})-I(\mathrm{~F} 2 \mathrm{~s})$ two-thirds and $I(\mathrm{Li} 1 \mathrm{~s})-I(\mathrm{~F} 2 \mathrm{p})$ half the calculated value 0.18 eV [10a].

Wertheim, Rosencwaig, Cohen and Guggenheim [114] found that anhydrous fluorides $\mathrm{MF}_{3}$ have a weak signal corresponding to $I$ (M4f) being slightly lower than $I(\mathrm{~F} 2 \mathrm{p})$ for $\mathrm{M}=\mathrm{Ce}, \mathrm{Pr}$ and Nd . When $I$ (M4f) increases for $M=S m$, Eu and Gd, the (now weaker) fluorine 2 p signal is masked and does not contribute significantly to the observed spectrum for heavier M (cf. Fig. 4). However, the subsequent $\mathrm{M}=\mathrm{Tb}, \mathrm{Dy}, \mathrm{Ho}$, Er, Tm and Yb have two signals which can be ascribed, to the first approximation, to the lower energy of the terms of $4 \mathrm{f}^{q-1}$ having ( $S+1 / 2$ ) relative to the terms having $(S-1 / 2)$ decreased from the groundstate of $4 \mathrm{f}^{\mathrm{q}}$. The distribution of intensities on these signals can, in principle, be calculated from the coefficients of fractional parentage [22] and the separation 3.8 eV between the two signals of the $4 f^{13}$ system Yb (III) is considerably larger than the pure spin-pairing energy $2 D=1.6 \mathrm{eV}$ but agrees with the well-known distribution $[50]$ of the energy levels of $4 \mathrm{f}^{12}$, Tm(III) being isoelectronic with Yb (IV). The authors at Bell[114] did not want to pronounce themselves about the absolute $I$ values and the extent of the charging effects. It is seen from Table 23 that
$I^{\prime}(4 \mathrm{f})=15.3 \mathrm{eV}$ for both $\mathrm{GdF}_{3}$ and $\mathrm{LuF}_{3}$. This may conceivain'y be slightly less than real $I$, but the values in Tables 17 and 18 are too large due to charging effects. Hagström and collaborators [37, 40] measured photoelectron spectra of metallic lanthanides. When the conditional oxidation state [56] is M [II], the $I^{*}$ values relative to the Fermi level are low, such as 2.0 eV for europium and 2.7 and 1.4 eV (split by spin-orbit coupling) for ytterbium. Other elements are $\mathrm{M}[I I I]$ and show the structure expected for the terms of $4 \mathrm{f}^{\mathrm{q}-1}$. Thus, $I^{*}=7.8 \mathrm{eV}$ for gadolinium. Since the work-function of this metal is said $[24]$ to be $3.2 \mathrm{eV}, I(\mathrm{Gd} 4 \mathrm{f})=11.0 \mathrm{eV}$ relative to vacuo. The chemical shift from $I^{\prime}=15.3 \mathrm{eV} \mathrm{GdF}_{3}$ and 13.6 eV in $\mathrm{Gd}_{2} \mathrm{O}_{3}$ to the metal, or from $I^{\prime}=6.9 \mathrm{eV}$ for $\mathrm{EuSO}_{4}$ to $I$ close to 4 eV for Eu are quite normal for other elements too. The adiabatic ionization energy of europium (II) aqua ions derived from $\left(\mathrm{E}_{0}+4.5\right) \mathrm{eV}$ where $\mathrm{E}_{0}$ is the standard oxidation potential [59, 66] is 4.1 eV , and demonstrates a difference between "vertical" processes obeying the Franck-Condon principle and chemical equilibria. The variation of $I(4 \mathrm{f})$ with the number of 4 f electrons is in excellent agreement with the spin-pairing energy theory [59, 66] and the compounds of M (III) are close to follow eq. (2) for M (IV), as one would expect.

From a theoretical point of view, it is fascinating that $I$ (M4f) is larger or comparable with the ionization energies of the loosest bound, filled orbitals of the ligands, even in fluorides, since it is evident from the visible absorption spectra $[50,53]$ that the nephelauxetic effect (giving a higher limit of the extent of covalent bonding in the sense of delocalization of the partly filled shell $[56,59]$ ) is below 10 percent, and actually below 3 percent in almost all cases. It cannot be concluded in this case that comparable central atom and ligand ionization energies are a sufficient condition for strong covalent bonding. Presumably, the much smaller electron affinity $\mathrm{E}_{\mathrm{A}}$ than ionization energy $I$ of the 4 f shell may be connected with this paradox ${ }^{1}$, and the situation in the metallic elements is also that the 4 f shell does not get invaded by the conduction electrons though $I^{*}$ is positive, i.e. $I$ is larger than $\mathrm{E}_{\mathrm{F}}$, because $\mathrm{E}_{\mathrm{A}}$ is far smaller than the Fermi level $\mathrm{E}_{\mathrm{F}}$. The extent of covalent bonding in highly heteronuclear cases may be determined by $I$ of the ligands and $\mathrm{E}_{\mathrm{A}}$ of the partly filled shell. It may also be argued [59] that the diagonal elements of M.O. theories represent the Mulliken electronegativity $\left(I+\mathrm{E}_{\mathrm{A}}\right) / 2$ rather

[^33]than $I$. It should be remembered that the covalent bonding has the extent which minimizes the total energy of the whole molecule or polyatomic ion. Seen from this angle, photo-electron spectrometry determining "vertical", ionization energies complements the information derived from visible and ultra-violet spectra $[57,59]$ about excitations in a most helpful and unexpected way.

## Experimental

The Varian IEE-15 photo-electron spectrometer has been described [7]. With exception of the samples of metallic Ni, Ga, In, Sn and Pt, we measured powdered samples covering about five-sixths of a cylinder covered with one-sided scotch tape [60] (15 mm broad, no. 600P from the Company 3M) normally using the analyzer potential 100 V .
Among the samples, we bought from :
American Potash (Lindsay Division) 455, 525, 526, 531, 533, 534, 536, 537, $539,541,543,544,545,546,547$ and 551.
British Drug Houses the Anala R 5, 19, 21, 22, 27, 183, 193, 262, 325, 355, $365,419,461,477,489,572,573,601$ and the $1,13,23,28,76,97,145$, $171,196,197,200,201,203,212,213,217,221,223,224,229,231,232$, $236,249,258,274,285,293,329,351,356,363,367,371,372,379$, $389,391,393,394,396,397,400,407,408,409,418,444,478,479$, $484,487,511,512,521,564,568,588,590,591,592,594,598$ and 602.
Dodge Fibers 181.
Drijfhout (Amsterdam) 51, 72, 323, 328, 332, 352, 357, 362, 366, 465, 468, 483, 486, 596 and 600.
Fluka (Buchs, SG) the puriss. 15, 82, 167, 184, 190, 233, 235, 243, 255, 260, 261, 270, 290, 291, $350,384,403,425,426,427,472,481,519,552$, 560 and the $6,8,12,35,41,43,63,75,86,144,149,204,208,215,237$, $267,272,275,303,305,308,319,339,353,354,411,436,445,447,449$, $453,459,471,473,476,488,490,491,506,530,553,556,557,558,571$, 593 and 607.
Heraeus 99.
Johnson and Matthey 124.
Merck pro analysii $2,30,269,462,567,575,577,580,589$ and the 158,160 , $239,273,321,347,349,361,369,424,574,579,595$ and 597.
Métaux Précieux (Neuchâtel) 470.
Riedel de Haën 374, 399 and 416.
Schuchardt (München) 38, 45, 173, 180, 186, 188, 194, 195, 198, 202, 206,
$211,214,219,220,244,268,278,348,373,422,439,510,578,603$ and 605.

Struer (Copenhagen) and collections from DTH (Chemistry Department A). $3,10,11,209,240,283,364,387,388,401,402,423,561$ and 576.
We are grateful for the gifts of the following samples from
Lugette Balsenc (Geneva) 555 and 587.
Fred Basolo (Evanston, Ill.) 137.
Ole Bostrup (Nakskov) 131.
Georg Brauer (Freiburg-im-Breisgau) 540.
Peter Day (Oxford) 109, 146, 309, 311, 313, 318 and 341.
Marcel Delépine ( $\dagger$, Paris) 39, 103 and 108.
E. Diemann (Dortmund) 65, 280, 286, 287, 288, 295, 297, 300, 301, 383, 437, 438, 440, 458, 460, 522, 559, 569 (cf. further discussion in ref. [85]).
W. Feitknecht (Bern) 392.
R. Gut (Zürich) 182, 192 and 610.
F. Hein (Jena) 33 and 415.

George Kauffman (Fresno, Cf.) 282.
Cornelius Keller (Karlsruhe) 606.
Yukio Kondo (Tokyo) 29, 87, 117, 150, 159 and 404.
Karen Kümmel (née Jensen) 32.
Salvatore Losi (Geneva) 234, 316, 566, 599 and 604.
Anthony Lucken (Geneva) 281.
Andreas Ludi (Bern) 4, 52, 56, 57, 58, 84, 91, 104, 107, 115, 121, 132, 134, $136,140,142,143,147,148,152,153,154,156,157,161,162,164,174$, $175,176,177,385,398$ and 463.
These compounds are later to be discussed in greater detail.
Romano Pappalardo (Waltham, Mass.) 191 and 207.
W. Preetz (Kiel) 327, 334, 340, 345, 360, 516, 517 and 518 [ref. 61].

Lene Rasmussen 128 [ref. 92] and 138 [ref. 93].
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G. Watelle (Dijon) 256.

When one of us worked 1961-68 at the Cyanamid European Research Institute, Cologny (Republic of Geneva) Dieter Garthoff (now São Paulo) and Hans-Herbert Schmidtre (now Frankfurt-am-Main) prepared the following compounds: $40,44,46,49,55,61,68,71,73,79,90,92,93,110$, $111,123,129,163,165,166,168,169,170,172,178,179,185,289$ and

565, a major part of which already has been described by these two authors.

The remaining 200 compounds were prepared by ourselves. The mixed oxides [ref. 53 ] $386,457,527,528,529,532,550,582,585,586$ were made by calcination of the co-precipitated hydroxides from aqueous ammonia. A similar precipitation of lanthanide chlorides in ethanol and $\mathrm{TaCl}_{5}$ in acetonitrile with ammonia was used for the tantalates 535,538 and 548 . The orthovanadates $376,377,378$ and 380 were obtained by calcination of thoroughly mixed, stoichiometric quantities of the rare earths and no. 82.

Most of the other compounds were made from rather obvious metathetical precipitation in aqueous solution. Stock solutions of indium metal in nitric acid, rare earths in perchloric or hydrochloric acid, $\mathrm{HfO}_{2}$ in 5 M sulphuric acid etc. were used, for instance precipitating the iodates described in the text with 1 M iodic acid. A pure sample of 405 precipitated many anions, also 9, 135 and 584 from a solution of Be (II), Ce(IV) and Th(IV) in strong $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{CO}_{3}$ We give the literature $[90]$ formula $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Be} 2(\mathrm{OH})_{3}\right.$ $\left.\left(\mathrm{CO}_{3}\right)_{2}\right]$ for compound no. 9 but we suspect it for being $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}$ $\left[\mathrm{OBe}_{4}\left(\mathrm{CO}_{3}\right)_{6}\right]$ in analogy to basic beryllium acetate. Freshly prepared solutions of green trans- $\left[\mathrm{Co} \mathrm{en} \mathrm{n}_{2} \mathrm{Cl}_{2}\right] \mathrm{Cl}$ were used for precipitating the salts of this cation. Solutions of $\mathrm{PbCl}_{6}^{-2}$ were obtained from $\mathrm{PbO}_{2}$ in ice-cold 12 M HCl . The tetraphenylborates of many univalent cations are almost insoluble [11, 68], we precipitated them with 0.5 M no. 15 . The fluorides 187 and 222 were obtained by evaporating a solution of the carbonates in hydrofluoric acid in a nickel crucible. 189 and 210 were obtained by melting the dioxides with $\mathrm{KHF}_{2}$. $\mathrm{EuSO}_{4}$ was formed from 254 in $2 \mathrm{M}_{2} \mathrm{SO}_{4}$ treated with p.a. zinc. The crystalline sulphates were generally made with sulphuric acid from oxides, and from a few carbonates. Palladium(II) chemistry has been discussed $[92,93], 80$ and 81 precipitate readily by acidification of a mixture of $\mathrm{X}^{-}$and Pdphen $(\mathrm{OH})_{2}$. The black iodides 467, 479 and 514 also precipitate by adding $\mathrm{I}^{-}$to a solution of Rh (III), Pd (II) or $\mathrm{Bi}(\mathrm{III})$ in HCl . Synthetic torbernite 242 was co-precipitated according to Marie Curie.

In the tables, we use the abbreviations for the ligands and organic molecules:
aca ${ }^{-}$is deprotonated acetylacetone (or 2,4-pentanedione) coordinated to the central atom by two oxygen atoms.
aminin is 1-amino-1-aminomethylcyclohexane, coordinating with two nitrogen atoms.

Bengal Rosa B is a dyestuff $\mathrm{Na}_{2}\left[\mathrm{C}_{20} \mathrm{H}_{2} \mathrm{O}_{5} \mathrm{Cl}_{4} \mathrm{I}_{4}\right]$
curtis is the condensation product of acetone and ethylenediamine [23] coordinating with two nitrogen atoms.
daes is bis (2-aminoethyl) sulphide coordinating with two nitrogen and one sulphur atom.
den is diethylenetriamine $\mathrm{HN}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)_{2}$ able to coordinate with three nitrogen atoms.
dip is $2,2^{\prime}$-dipyridyl (or $2,2^{\prime}$-bipyridine) coordinating with two nitrogen atoms.
dmg ${ }^{-}$is deprotonated dimethylglyoxime, normally coordinating with the two three nitrogen atoms.
en is ethylenediamine (1,2-diaminoethane) $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ coordinating with two nitrogen atoms.
$\mathrm{et}_{4} \mathrm{den}$ is $\mathrm{N}, \mathrm{N}, \mathrm{N}^{\prime \prime}, \mathrm{N}^{\prime \prime}$-tetra-ethyl-diethylenetriamine coordinating with nitrogen atoms.
methylene blue is the cation ${ }_{5}^{N}\left\{\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}\left(\mathrm{CH}_{3}\right)_{2}\right\}_{2}^{+}$
$\mathrm{ns}^{-}$is deprotonated 2-mercaptoethylamine $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{~S}^{-}$coordinating with the nitrogen and the sulphur atom.
phen is 1,10 -phenanthroline coordinating with two nitrogen atoms.
phthalocyanine is a macrocyclic ligand ; it is di-deprotonated in our complexes and coordinating with four nitrogen atoms.
py is pyridine $\mathrm{C}_{5} \mathrm{H}_{5}$ Ncoordinating with the nitrogen atom.
tartrate is di-deprotonated tartaric acid bound by two oxygen atoms in our dimeric antimony(III) complex (tartar emetic). However, Anderegg kindly indicated tetra-deprotonated tartrate and no oxide ligands.
tren is tris (2-aminoethyl) amine $\mathrm{N}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)_{3}$ coordinating with four nitrogen atoms.
urea is $\left(\mathrm{NH}_{2}\right)_{2} \mathrm{CO}$. In our complexes, it is coordinated with the oxygen atom.
In almost all our sulphur-containing ligands [55] such as dithiocarbamates $\mathrm{R}_{2} \mathrm{NCS}_{2}^{-}$and dithiophosphates ( RO$)_{2} \mathrm{PS}_{2}^{-}$both sulphur atoms are coordinated. Contrary to previous belief, many nitrate complexes have two oxygen atoms coordinated to the central atom.

## Acknowledgments

We thank the many colleagues for the most interesting compounds mentioned above. The Swiss National Science Foundation provided the funds allowing the purchase of the photo-electron spectrometer.

Table 1. Photo-electron signals of lithium, beryllium, boron and nitrogen.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(1 \mathrm{~s})$ |
| :---: | :---: | :---: | :---: |
| 1 | LiF | [1.4],4.2 | 63.5 |
| 1 | repeated | [0.7],4.4 | 64.4 |
| 2 | $\mathrm{Li}_{2} \mathrm{CO}_{3}$ | [ [3.4],4.8 | 61.6 |
| 3 | $\mathrm{Li}_{3} \mathrm{PO}_{4}$ | [3.5],5.1 | 61.6 |
| 4 | $\mathrm{Li}_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ | 4.7 | 61.3 |
| 5 | $\mathrm{Li}_{2} \mathrm{SO}_{4}$ | 5.2 | 61.0 |
| 6 | $\mathrm{BeF}_{2}$ | [3],5.3 | 123.1 |
| 7 | $\mathrm{K}_{2} \mathrm{BeF}_{4}$ | . [2.5],5.3 | 122.4 |
| 7 | repeated | [2.0],5.0 | 122.6 |
| 8 | BeO | . [2.4],4.7 | 121.6 |
| 9 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Be}_{2}(\mathrm{OH})_{3}\left(\mathrm{CO}_{3}\right)_{2}\right]$ | [2.8],4.6 | 120.3 |
| 10 | $\left[\mathrm{Be}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right] \mathrm{SO}_{4}$ | 4.8 | 120.1 |
| 10 | repeated | 4.7 | 120.8 |
| 11 | $\mathrm{NH}_{4} \mathrm{BePO}_{4}$ | 4.5 | 119.5 |
| 12 | $\mathrm{Be}(\mathrm{OH})_{2}$ | 5.3 | 118.9 |
| 13 | $\mathrm{KBF}_{4}$ | [3.1], 4.6 | 202.3 |
| 14 | $\left[\mathrm{Coen}_{2} \mathrm{Cl}_{2}\right] \mathrm{BF}_{4}$. | 4.6 | 200.1 |
| 15 | $\mathrm{Na}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ | 6.6 | 193.0 |
| 16 | $\mathrm{K}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ | 5.1 | 192.9 |
| 17 | methylene blue $\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$. | 6.1 | 191.9 |
| 18 | $\mathrm{CsUO}_{2}\left(\mathrm{NO}_{3}\right)_{3}$. | [2.8],5.1 | 414.9 |
| 19 | $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$ | [2.8],5.3 | 414.8 |
| 20 | $\mathrm{RbUO}_{2}\left(\mathrm{NO}_{3}\right)_{3}$ | . [2.7],4.8 | 414.6 |
| 21 | $\mathrm{Ba}\left(\mathrm{NO}_{3}\right)_{2}$. | . [3],5.1 | 414.0 |
| 22 | $\mathrm{UO}_{2}\left(\mathrm{NO}_{3}\right)_{2}$. | 4.5 | 414 |
| 23 | $\mathrm{CsNO}_{3}$ | [3.2],4.8 | 413.5 |
| 607 | $\mathrm{Th}\left(\mathrm{NO}_{3}\right)_{4}, 5 \mathrm{H}_{2} \mathrm{O}$ | 4.4 | 413.2 |
| 24 | $\mathrm{KNO}_{3}$. | 5.1 | 413.1 |
| 25 | $\mathrm{RbNO}_{3}$. | 5.1 | 413.1 |
| 26 | $\mathrm{Mg}_{3} \mathrm{Nd}_{2}\left(\mathrm{NO}_{3}\right)_{12}, 24 \mathrm{H}_{2} \mathrm{O} \ldots$ | 4.6 | 413.1 |
| 27 | $\mathrm{Sr}\left(\mathrm{NO}_{3}\right)_{2}$ | 4.7 | 413.0 |
| 28 | $\mathrm{Cr}\left(\mathrm{NO}_{3}\right)_{3}, 9 \mathrm{H}_{2} \mathrm{O}$ | 4.6 | 412.6 |
| 29 | $\left[\mathrm{Cuen}_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}$. | 4.6 | 412.4 |
|  |  |  | \& 405.5 |
| 30 | $\mathrm{Fe}\left(\mathrm{NO}_{3}\right)_{3}, 9 \mathrm{H}_{2} \mathrm{O}$. | 4.8 | 412.2 |
| 31 | [Crurea ${ }_{6}$ ( $\left.\mathrm{NO}_{3}\right)_{3}$ | 5.3 | 412.1 |
|  |  |  | \& 405.2 |
| 32 | $\left[\mathrm{Coen}_{2} \mathrm{Cl}_{2}\right] \mathrm{NO}_{3}$ | 4.4 | 411.9 |
|  |  |  | \& 405.3 |
| 33 | $[\mathrm{Ni} \mathrm{aminin} 2]\left(\mathrm{NO}_{3}\right)_{2}$. | 4.6 | 411.4 |
|  |  |  | \& 404.8 |
| 34 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{PtI}_{6}$ | [2],4.8 | 410.0 |
| 35 | $\mathrm{Na}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{5} \mathrm{NO}\right]$ | 4.7 | (409.1) |
|  |  |  | \& 403.8 |

## Table 1. (continued).

Compound $\mathrm{C}_{\mathrm{st}}$ $I(1 \mathrm{~s})$
$36 \quad\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{CeCl}_{6}$ ..... [2.7],4.5
409.0
$37 \quad\left[\mathrm{~N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2} \mathrm{PtI}_{6}$ ..... 4.8
409.0
$38 \mathrm{NH}_{4} \mathrm{SbF}_{4}$ ..... [3.5],5.3
$39 \mathrm{~K}_{2}\left[\mathrm{Ru}(\mathrm{NO}) \mathrm{Cl}_{5}\right]$ ..... 4.8
$40 \quad\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{SeCN}$ ..... 4.6
$41 \quad\left(\mathrm{NH}_{4}\right)_{3} \mathrm{GaF}_{6}$ [3.7],5.4408.9
408.7
408.6
\& 404.2
408.5
$42 \quad\left(\mathrm{NH}_{4}\right)_{2}\left[\operatorname{In}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$ ..... [3.8],5.0

408.3
$43\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{I}$ ..... 4.9
$44 \quad\left[\mathrm{~N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right] \mathrm{SeCN}$ ..... 4.2
$45 \quad\left(\mathrm{NH}_{4}\right)_{2} \mathrm{ZrF}_{6}$ ..... 5.1
$46 \quad\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{SCN}$ ..... 5.1
$47 \quad\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right){ }_{3} \mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right]_{2} \mathrm{PtCl}_{6}$ ..... 4.6
$48 \quad\left[\mathrm{~N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{PtBr}_{6}$ ..... 4.6
$49 \quad\left[\mathrm{C}_{19} \mathrm{H}_{42} \mathrm{~N}_{2}\right]_{2}\left[\operatorname{Pt}\left(\mathrm{~N}_{3}\right)_{6}\right]$ ..... 5.3
$50 \quad\left(\mathrm{NH}_{4}\right)_{3} \mathrm{ScF}_{6}$ ..... 5.4
$289\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{3}\left[\mathrm{Ru}(\mathrm{NCS})_{6}\right]$ ..... 4.3
$51 \quad\left(\mathrm{NH}_{4}\right){ }_{2} \mathrm{PtCl}_{6}$ ..... 4.8
$52\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ ..... 4.9
$53 \quad\left[\mathrm{Ni} \mathrm{en}_{2}\right]\left(\mathrm{AgI}_{2}\right)_{2}$ ..... [2.0],4.6
$54 \quad\left[\mathrm{~N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]\left[\mathrm{Au}(\mathrm{CN})_{2} \mathrm{Br}_{2}\right]$ ..... 5.3
$11 \quad \mathrm{NH}_{4} \mathrm{BePO}_{4}$ ..... 4.5
$55 \quad\left[\mathrm{~N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right] \mathrm{ClO}_{4}$ ..... 4.8
$56 \quad\left(\mathrm{NH}_{4}\right)_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ ..... 4.8
$57 \quad\left[\mathrm{~N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ ..... 5.1
$58 \quad\left[\mathrm{~N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ ..... 5.0
59 trans- $\mathrm{Pd}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}$ ..... 4.8
$60 \quad\left[\mathrm{Ni} \mathrm{en}_{2}\right]\left(\mathrm{CuI}_{2}\right)_{2}$ ..... [2.2],4.6
$61 \quad\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{3}\left[\operatorname{Ir}(\mathrm{SCN})_{6}\right]$ ..... 4.4
$62\left[\mathrm{Ag} \mathrm{py}_{4}\right] \mathrm{S}_{2} \mathrm{O}_{8}$ ..... 4.2
$584\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{Th}\left(\mathrm{CO}_{3}\right)_{5}\right]$ ..... [2.3],4.2
$63 \quad\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{Br}$ ..... 4.9
$64 \quad\left[\mathrm{~N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{OsCl}_{6}$ ..... 5.2
408.2
408.2
\& 403.4 408.1 407.9
\& 403.1
407.9
407.8
407.7
\& 403.8 asym.
407.7
407.7
\& 403.5
407.6
407.5
\& 403.2
407.4
407.4
\& 404.3
407.3
407.3
407.2
\& 403.6
407.2
\& 403.1
407.2
\& 403.4
407.2
407.2
(407.2)
\& 403.2
\& (401.6)
407.1
407.0
407.0
407.0

## Table 1. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(1 \mathrm{~s})$ |
| :---: | :---: | :---: | :---: |
| 65 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{ReS}_{4}$ | 4.4 | 407 |
| 66 | $\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{MnBr}_{4}$ | 4.6 | 406.9 |
| 67 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{7}\left[\mathrm{Cu}\left(\mathrm{IO}_{6}\right)_{2}\right]_{3}$ | 4.7 | 406.9 |
| 68 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{3} \mathrm{IrCl}_{6}$ | 4.4 | 406.9 |
| 69 | $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{CrF}_{6}$ | 4.8 | 406.8 |
| 70 | $\left(\mathrm{NH}_{4}\right)_{2}\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$ | 4.8 | 406.8 |
| 9 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Be}_{2}(\mathrm{OH})_{3}\left(\mathrm{CO}_{3}\right)_{2}\right]$ | [2.8],4.6 | 406.8 |
| 71 | [ Rh den $\mathrm{I}_{3}$ ] | [2.4],4.6 | 406.8 |
| 72 | $\left(\mathrm{NH}_{4}\right){ }_{2} \mathrm{PdCl}_{6}$ | 5.0 | 406.8 |
| 73 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2}\left[\mathrm{Sn}(\mathrm{NCS})_{6}\right]$. | 5.0 | 406.8 |
|  |  |  | \& 403.5 |
| 74 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{IrCl}_{6}$ | 4.4 | 406.7 |
| 75 | $\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right] \mathrm{I}$ | 4.5 | 406.6 |
| 76 | $\left(\mathrm{NH}_{4}\right)_{3}\left[\mathrm{Cr}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]$ | 5.2 | 406.6 |
| 77 | $\left[\mathrm{Coen}_{2} \mathrm{Cl}_{2}\right] \mathrm{PF}_{6}$ | 4.7 | 406.6 |
| 78 | $\left[\mathrm{Coen}_{2} \mathrm{Cl}_{2}\right]_{3}\left(\mathrm{PW}_{12} \mathrm{O}_{40}\right)$ | 4.0 | 406.5 |
| 79 | $\left[\mathrm{Pd}\left(\mathrm{et}_{4} \mathrm{den}\right) \mathrm{Cl}\right] \mathrm{ClO}_{4}$ | [3.3],5.0 | 406.5 |
| 80 | [ Pd phen $\mathrm{Br}_{2}$ ] | 4.5 | 406.5 |
| 81 | [Pd phen $\mathrm{I}_{2}$ ] | 4.9 | 406.5 |
| 135 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{Ce}\left(\mathrm{CO}_{3}\right)_{5}\right]$ | 4.2 | 406.5 |
| 82 | $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{~V}_{3} \mathrm{O}_{9}$ | 4.6 | 406.4 |
| 83 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Au}\left(\mathrm{S}_{2} \mathrm{O}_{3}\right)_{2}\right]$ | 4.4 | 406.4 |
| 84 | $\mathrm{Cd}\left[\mathrm{Pd}(\mathrm{CN})_{6}\right]$. | [2.2],4.9 | 406.3 |
| 85 | Pd dmg2 | 4.4 | 406.3 |
| 86 | $\mathrm{NH}_{4}\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]$ | [3.7],5.2 | 406.2 |
|  |  |  | \& (404.9) |
|  |  |  | \& 403.6 |
| 87 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left(\mathrm{SiF}_{6}\right)_{3}$ | 4.4 | 406.2 |
| 88 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right] \mathrm{BF}_{4}$ | 4.6 | 406.1 |
| 89 | $\left[\mathrm{Co} \mathrm{en} 22_{2} \mathrm{Cl}_{2}\right] \mathrm{MnO}_{4}$ | 4.7 | 406.0 |
| 90 | $\left[\mathrm{Ph}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl} \mathrm{Cl}_{2}\right.$. | 4.6 | 406.0 |
| 91 | $\left[\mathrm{Ni}(\mathrm{CN})_{2}\left(\mathrm{NH}_{3}\right)\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{~S}\right)\right]$. | 5.5 | 405.9 |
| 92 | $\left[\mathrm{Pd}\left(\mathrm{et}_{4}\right.\right.$ den $\left.) \mathrm{Br}\right] \mathrm{ClO}_{4}$. | 4.4 | 405.9 |
| 93 | [ Pt den $\mathrm{Cl}_{3}$ ] $\mathrm{ClO}_{4}$ | 4.5 | 405.9 |
| 94 | $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{InCl}_{6}\right]$ | 5.0 | 405.8 |
| 95 | [ $\left.\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ | 5.2 | 405.8 |
| 96 | [ $\mathrm{Ni}\left(\mathrm{et}_{4}\right.$ den) Cl$] \mathrm{Cl}$. | 5.1 | 405.7 |
| 97 | CuCN | . [3.2],5.3 | 405.7 |
| 98 | $\mathrm{Cu}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}$ | 4.4 | 405.7 |
| 99 | $\left[\operatorname{Ir}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}^{2} \mathrm{Cl} 2\right.$. | 4.4 | 405.7 |
| 100 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right]\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]$ | 4.5 | 405.6 |
|  |  |  | \& (404.0) |
| 101 | [Pd phen $\mathrm{Cl}_{2}$ ] | 4.5 | 405.5 |

## Table 1. (continued).

Compound $\mathrm{C}_{\mathrm{st}}$ $I(1 \mathrm{~s})$
$102[\mathrm{Pd}$ phen 2$]\left(\mathrm{ClO}_{4}\right)_{2}$ ..... 5.1 ..... 405.5
$103 \mathrm{~K}\left[\mathrm{Ir}\right.$ py $\mathrm{Cl}_{5}$ ] ..... 4.7 ..... 405.5
$104 \mathrm{Cs}_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ ..... [2.5],4.6 ..... 405.4
$105\left[\left(\mathrm{NH}_{3}\right)_{5} \mathrm{CoO}_{2} \mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}\right]\left(\mathrm{SO}_{4}\right)_{2} \mathrm{HSO}_{4}$ ..... 5.3
405.4
$106\left[\mathrm{Rh} \mathrm{ns}_{3}\right]_{2} \mathrm{Ni}\left(\mathrm{ClO}_{4}\right)_{2}$ ..... 4.6405.4
$107 \mathrm{Rb}_{2}\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ ..... 4.6
405.4
$608 \mathrm{~K}\left[\mathrm{OsO}_{3} \mathrm{~N}\right]$ ..... [2.1],4.4 ..... 405.4
$108\left[\mathrm{Ir} \mathrm{py} 4 \mathrm{Cl}_{2}\right] \mathrm{Cl}$ ..... 4.7
$109\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{SbCl}_{6}$ ..... 4.3
$110\left[\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{NCS}\right]\left(\mathrm{ClO}_{4}\right)_{2}$ ..... 4.7
4.8
111 [ Rh den $\mathrm{Cl}_{3}$ ]
4.4
$112\left[\mathrm{Rh} \mathrm{py} 44 \mathrm{Br}_{2}\right] \mathrm{ClO}_{4}$
4.6
114 (methylene blue) ${ }_{2} \mathrm{PtI}_{6}$ ..... 5.0
$115 \mathrm{Co}\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ ..... [2],4.0
116 Ni dmg 2 ..... 4.9
$117\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4}\right]\left(\mathrm{PtCl}_{4}\right)$ ..... 4.0
$118 \mathrm{Te}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{2}\right)_{4}$ ..... 4.9
119 [Pd py $\left.{ }_{4}\right] \mathrm{SO}_{4}$ ..... 4.65
120 [Fe urea $\left.{ }_{6}\right]\left(\mathrm{ClO}_{4}\right)_{3}$ ..... 5.1
$121 \mathrm{Cu}_{3}\left[\operatorname{Ir}(\mathrm{CN})_{6}\right]_{2}, 11 \mathrm{H}_{2} \mathrm{O}$ ..... 4.5
$122 \mathrm{~K}\left[\mathrm{Ag}(\mathrm{CN})_{2}\right]$ ..... [2.7],4.5
123 [Cu den Br$] \mathrm{Br}$ ..... 4.7
$124\left[\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}$ ..... 4.7
125 methylene blue $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]$ ..... 5.0
$126 \mathrm{Cr}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{2}\right)_{3}$ ..... 5.9
$127 \mathrm{Ni}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}$ ..... 4.7
$128\left[\mathrm{Pd}\left(\mathrm{NH}_{3}\right)_{4}\right]\left(\mathrm{CH}_{3} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SO}_{3}\right)_{2}$ ..... 4.8
128 repeated ..... 4.6
$129 \mathrm{~K}_{2}\left[\mathrm{Pt}(\mathrm{SeCN})_{6}\right]$ ..... [2.7],4.8
$130 \quad\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{ReBr}_{6}$ ..... 4.6
131 [ Fe dip 3 ] $\mathrm{Br}_{2}$ ..... 5.6
$132 \mathrm{Na}_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ ..... 4.8
133 [ Ni daes $\left.{ }_{2}\right]\left(\mathrm{ClO}_{4}\right)_{2}$ ..... 4.6
$134 \mathrm{Ni}_{2}\left[\mathrm{Os}(\mathrm{CN})_{6}\right]$ ..... 5.0
17 methylene blue $\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ ..... 6.0
$136 \mathrm{Co}_{2}\left[\mathrm{Os}(\mathrm{CN})_{6}\right]$ ..... 5.0
$137 \mathrm{Ni}\left(\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$ ..... 3.7
$138 \quad[\mathrm{Ni}($ tren $) p h e n]\left(\mathrm{ClO}_{4}\right)_{2}$ ..... 4.6
139 methylene blue $\left(\mathrm{ClO}_{4}\right)$ ..... 5.1
$140 \quad \mathrm{H}_{3} \mathrm{Co}(\mathrm{CN})_{6}$ ..... 4.7405.4
405.3
405.3
\& (402.9)405.3
405.3
405.2405.2405.1405.1
405.05405.0404.95404.9404.9404.9
404.8404.75404.7
\& 403.1
404.7
404.7404.6405.2
404.6
404.5
404.4
404.4
404.4
404.4
404.3
404.3
404.3
404.3404.2
404.2

## Table 1. (continued),

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(1 \mathrm{~s})$ |
| :---: | :---: | :---: | :---: |
| 141 | $\mathrm{Co}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3}$ | 5.8 | 404.2 |
| 142 | [ Ni enr]][ $\mathrm{Ni}\left(\mathrm{CN}_{4}\right]$ | 5.0 | 404.2 |
| 143 | $[\mathrm{Pd} \mathrm{en} 2]\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.4 | 404.2 |
| 144 | $\mathrm{K}\left[\mathrm{Au}(\mathrm{CN})_{2}\right]$. | 4.5 | 404.2 |
| 145 | $\mathrm{Na}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right], 10 \mathrm{H}_{2} \mathrm{O}$ | 4.7 | 404.1 |
| 146 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{BiCl}_{6}$ | 3.6 | 404.1 |
| 147 | $[\mathrm{Ni} \mathrm{en} 3]\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]$ | 4.9 | 404.1 |
| 148 | $[\mathrm{Ni} \mathrm{en} 2]\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.4 | 404.1 |
| 149 | $\mathrm{K}_{2}\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$. | 5.1 | 404.1 |
| 150 | $[\mathrm{Ni} \mathrm{en} 3] \mathrm{SO}_{4}$ | 3.8 | 404.0 |
| 151 | [ Ni (tren)( NCS$)_{2}$ ] | 4.6 | 404.0 |
| 152 | $[\mathrm{Ni} \mathrm{en} 3]\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.4 | 404.0 |
| 153 | $\mathrm{Cu}_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]_{2}, 11 \mathrm{H}_{2} \mathrm{O}$. | 4.5 | 404.0 |
| 4 | $\mathrm{Li}_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ | 4.7 | 403.9 |
| 154 | $\mathrm{Cu}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right], 11 \mathrm{H}_{2} \mathrm{O}$. | 4.8 | 403.8 |
| 155 | $\mathrm{Co}(\mathrm{NCS})_{4} \mathrm{Hg}$ | 4.7 | 403.8 |
| 156 | $\left.[\mathrm{Ni} \mathrm{en}]_{2}\right]\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]$ | 4.1 | 403.8 |
| 157 | $[\mathrm{Ni} \mathrm{en} 3]\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]$ | 3.9 | 403.8 |
| 158 | methylene blue Cl | 5.5 | 403.7 |
| 159 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2}$ | 3.9 | 403.7 |
| 160 | $\mathrm{K}_{2}\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]$ | 4.9 | 403.7 |
| 161 | $\mathrm{Co}_{2}\left[\mathrm{Ru}(\mathrm{CN})_{6}\right]$ | 4.5 | 403.6 |
| 162 | $\mathrm{Ni}_{2}\left[\mathrm{Ru}(\mathrm{CN})_{6}\right]$ | 4.5 | 403.6 |
| 163 | $\mathrm{K}_{2}\left[\mathrm{Hg}(\mathrm{SCN})_{4}\right]$ | 5.0 | 403.6 |
| 164 | $\mathrm{Cu}_{2}\left[\mathrm{Os}(\mathrm{CN})_{6}\right]$ | 5.0 | 403.5 |
| 165 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]\left[\mathrm{Au}(\mathrm{SeCN})_{4}\right]$ | 4.8 | 403.5 |
| 166 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{3}\left[\operatorname{Ir}(\mathrm{SeCN})_{6}\right]$. | 4.1 | 403.45 |
| 167 | $\mathrm{K}_{3}\left[\mathrm{Cr}(\mathrm{NCS})_{6}\right]$ | 4.8 | 403.4 asym. |
| 168 | $\mathrm{K}_{2}\left[\mathrm{Pt}(\mathrm{SCN})_{6}\right]$ | 4.8 | 403.35 |
| 169 | $\mathrm{K}_{3}\left[\mathrm{Rh}(\mathrm{SCN})_{6}\right]$. | 4.7 | 403.3 |
| 170 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{3}\left[\mathrm{Os}(\mathrm{SCN})_{6}\right]$. | 5.2 | 403.1 |
| 170 | repeated | 4.6 | 403.6 |
| 171 | KSeCN | 3.6 | 403.1 |
| 171 | repeated. | . [3.3],5.0 | 403.9 |
| 609 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]\left[\mathrm{OsO}_{3} \mathrm{~N}\right]$ | 4.2 | 403.6 |
| 172 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2}\left[\mathrm{Cd}(\mathrm{NCSe})_{4}\right]$ | 4.5 | 403 asym. |
| 173 | Mg phthalocyanine | 5.4 | 402.9 |
| 174 | $\mathrm{Cu}_{2}\left[\mathrm{Ru}(\mathrm{CN})_{6}\right]$ | 4.4 | 402.8 |
| 175 | $\mathrm{Ru}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{3}$. | 4.9 | 402.8 |
| 176 | $\mathrm{Fe}_{4}\left[\mathrm{Ru}(\mathrm{CN})_{6}\right]_{3}$. | 4.6 | 402.7 asym. |
| 177 | $\mathrm{Fe}_{4}\left[\mathrm{Os}(\mathrm{CN})_{6}\right]_{3}$ | 4.6 | 402.7 asym. |
| 178 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{SCN}$ | 4.8 | 402.2 |
| 179 | $\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{SCN}$. | 5.3 | 401.9 |
| 180 | Cu phthalocyanine.... | 6.0 | 401.9 |

Table 2. Photo-electron signals of fluorine, sodium, magnesium, aluminium, silicon and phosphorus.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(1 \mathrm{~s})$ | $I(2 \mathrm{~s})$ | $I(2 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 181 | $\mathrm{CF}_{2}$ polymer. | 3.8 | 695.7 | - | - |
| 606 | $\mathrm{LuF}_{3}$ | .[0.3],5.5 | 695.5 | - | - |
| 182 | $\mathrm{CsSbF}_{6}$ | .[1.5],5.1 | 695.0 | 39.3 | - |
| 182 | repeated | [1.3],5.5 | 695.3 | - | - |
| - | $\mathrm{CF}_{4}$ (ref. 97) . | - | 695.0 | 43.8,40.3 | 25-16.2 |
| 183 | $\mathrm{MgF}_{2} \ldots \ldots$. | [ [0.8],5.1 | 695.0 | 39.4 | 18.3 |
| 183 | repeated | . [0.1],5.0 | 695.6 | 40.6 | 20 |
| 184 | $\mathrm{LaF}_{3}$. | . [0.0],4.7 | 694.8 | 39.1 | 18.1 |
| 185 | $\mathrm{K}_{3} \mathrm{RhF}_{6}$ | . [2.0],4.7 | 694.8 | 38.9 | 16.4 |
| 13 | $\mathrm{KBF}_{4}$ | . [3.1],4.6 | 694.0 | - | (18),16.1 |
| 13 | repeated | . [2.8],5.4 | 694.8 | 38.7 | 17.7 |
| - | $\mathrm{SF}_{6}$ (ref. 97) | - | 694.6 | 44.2-39.3 | 27-16 |
| 186 | $\mathrm{YF}_{3}$ | . [1.5],5.2 | 694.2 | 39 | 17.5 |
| 187 | TlF. | . [2.6],5.2 | 694.2 asym. | 37.3 | 13 |
| 1 | LiF | . [1.4],4.2 | 692.8 | 37.4 | 15.6 |
| 1 | repeated | . [0.7],4.4 | 694.1 | 38.0 | 16.6 |
| - | $\mathrm{CHF}_{3}$ (ref. 97) | . - | 694.1 | - | - |
| 188 | $\mathrm{CoF}_{2}$ | . [1.1],5.4 | 694.1 | 38.9 | - |
| 189 | $\mathrm{K}_{2} \mathrm{GeF}_{6}$ | . [1.3],4.7 | 694.1 | - | - |
| 190 | $\mathrm{CeF}_{3}$ | . [0.5],4.8 | 694.1 | 38.4 | 17 |
| 191 | $\mathrm{PrF}_{3}$ | . [1.5],4.9 | 694.1 | - | - |
| 192 | $\mathrm{KPF}_{6}$ | . [2.7],4.5 | 694.0 | 39.0 | 17.3,15.7 |
| 193 | NaF | . [1.2],5.0 | 692.9 | - | 16 |
| 193 | repeated | . [0.9],5.1 | 693.8 | (38) | 16.8 |
| 194 | $\mathrm{EuF}_{3}$ | . [1],4.8 | 693.8 | 37.5 | - |
| 195 | $\mathrm{ErF}_{3}$ | [1],4.5 | 693.8 | - | - |
| 196 | $\mathrm{Na}_{3} \mathrm{AlF}_{6}$ | . [1.8],4.8 | 693.7 | - | 16.0 |
| 197 | $\mathrm{SrF}_{2}$ | . [1.7],5.5 | 693.4 | 37.9 | 17.0 |
| 197 | repeated | . [1.2],5.0 | 693.7 | 38.0 | 17.1 |
| 198 | $\mathrm{GdF}_{3}$ | . [0.8],4.4 | 693.6 | 37.7 | - |
| 199 | $\mathrm{ThF}_{4}$ | . [1.3],4.9 | 693.6 | 38.7 | 17.3 |
| 200 | $\mathrm{K}_{2} \mathrm{SiF}_{6}$ | . [2.4],4.8 | 693.5 | 38.6 | 16.0 |
| 200 | repeated | . [2.4],5.0 | 693.5 | 38.8 | 16.7 |
| 201 | $\mathrm{CaF}_{2}$ | . [1.8],4.6 | 692.7 | 38.4 | 16.1 |
| 201 | repeated | . [1.3],4.5 | 693.5 | 38.6 | 16.3 |
| 202 | $\mathrm{ZrF}_{4}$ | . [1.8],4.4 | 693.5 | 37.2 | - |
| 7 | $\mathrm{K}_{2} \mathrm{BeF}_{4}$ | . [2.0],5.0 | 693.4 | 38.0 | (18),16.0 |
| 7 | repeated | . [2.5],5.3 | 692.8 | - | - |
| 203 | $\mathrm{BaF}_{2}$ | . [0.3],4.7 | 693.2 | 38.0 | 16.3 |
| 203 | repeated | . [0.1],4.4 | 693.3 | 37.9 | 16.2 |
| 77 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right] \mathrm{PF}_{6}$ | 4.7 | 692.9 | - | - |
| 204 | $\mathrm{GaF}_{3}, 3 \mathrm{H}_{2} \mathrm{O}$. | . [2.3],5.0 | 692.9 | 38.1 | 17.6 |
| 205 | $\mathrm{YbF}_{3} \ldots \ldots$. | . [2.2],4.7 | 692.9 | 38.7 | - |

Table 2. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(1 \mathrm{~s})$ | $I(2 \mathrm{~s})$ | $I(2 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 206 | $\mathrm{NdF}_{3}$ | [2],4.7 | 692.8 asym. | 37.4 | - |
| 207 | $\mathrm{SmF}_{3}$ | [2.0],5.0 | 692.8 | - | - |
| 208 | $\mathrm{K}_{2} \mathrm{NbF}_{7}$ | [3],5.0 | 692.7 | 37 | - |
| 209 | $\mathrm{KNiF}_{3}$ | 3.6 | 690.8 | 37.2 | 15.6 |
| 209 | repeated | [1.3],4.5 | 692.6 | - | - |
| 210 | $\mathrm{K}_{2} \mathrm{HfF}_{6}$ | [2.7],5.0 | 692.6 | 37.0 | - |
| 211 | $\mathrm{TaF}_{5}$ | 5.3 | 692.4 | - | (17.5),14.9 |
| - | $\mathrm{CH}_{3} \mathrm{~F}$ (ref. 97) | - | 692.4 | - | - |
| 212 | $\left[\mathrm{Zn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{SiF}_{6} \cdots \cdots$ | [2.5],4.9 | 692.2 | 38.0 | 13.6 |
| 6 | $\mathrm{BeF}_{2} \ldots \ldots . . . . . . . .$. | [3],5.3 | 692.1 | 39.0 | 16.7 |
| 213 | $\mathrm{K}_{2} \mathrm{TiF}_{6}$ | [2.4],4.5 | 692.1 | - | 15.2 |
| 214 | $\mathrm{CuF}_{2}, 2 \mathrm{H}_{2} \mathrm{O}$ | [3.0],5.2 | 692.0 asym. | - | 15.8 |
| 215 | $\mathrm{K}_{2} \mathrm{TaF}_{7}$ | [3.1],4.5 | 692.0 | - | 15 |
| 216 | $\mathrm{K}_{2}\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$. | [1.7],4.9 | 691.9 | 36.5 | 14.7 |
| 217 | $\mathrm{CdF}_{2} \ldots \ldots . . .$. | [3],4.8 | 692.1 | - | 13.7 |
| 217 | repeated | [2],4.3 | 691.9 | 36.4 | 14.5 |
| 38 | $\mathrm{NH}_{4} \mathrm{SbF}_{4}$ | [3.5],5.3 | 691.9 | 37.0 | - |
| 218 | $\mathrm{K}_{2} \mathrm{UF}_{6} \ldots \ldots . . .$. | [2.4],4.9 | 691.9 | - | - |
| 14 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right] \mathrm{BF}_{4}$ | 4.6 | 691.8 | - | - |
| 219 | $\mathrm{CeF}_{4}, \mathrm{H}_{2} \mathrm{O} \ldots$. | 4.9 | 691.8 | 36.9 | 15.6 |
| 219 | repeated | [1.7],4.5 | 692.4 | - | - |
| 220 | $\mathrm{BiF}_{3}$ | [3.3],5.4 | 691.7 | - | - |
| 221 | $\mathrm{NiF}_{2}, 4 \mathrm{H}_{2} \mathrm{O}$ | [2.6],4.7 | 691.5 | - | - |
| 41 | $\left(\mathrm{NH}_{4}\right){ }_{3} \mathrm{GaF}_{6}$. | [3.7],5.4 | 691.3 | - | - |
| 222 | RbF . . . . . . . . . . . . | 4.4 | 691.3 | 35.4 | 14 |
| 87 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left(\mathrm{SiF}_{6}\right)_{3}$ | 4.4 | 691.1 | 36.2 | - |
| 45 | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{ZrF}_{6}$. | 5.1 | 691.0 asym. | 35.5 | (16)14.1 |
| 42 | $\left(\mathrm{NH}_{4}\right)_{2}\left[\operatorname{In}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right] \ldots$ | . [3.8],5.0 | 691.0 | 35.8 | 14.2 |
| 50 | $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{ScFF}_{6} \ldots$ | 5.4 | 690.9 | 35.7 | - |
| 223 | KF | [1.7],4.15 | 690.4 | 34.8 | 14.0 |
| 224 | $\mathrm{PbF}_{2}$ | [3],4.8 | 690.1 | 36 | - |
| 610 | $\mathrm{HgF}_{2}$ | [2.5],4.5 | 690.0 | - | - |
| 69 | $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{CrF}_{6}$ | 4.75 | 689.5 | - | - |
| 70 | $\left(\mathrm{NH}_{4}\right)_{2}\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$ | 4.8 | 689.45 | 34.6 | - |
| 225 | CsF. | 4.1 | 687.8 | - | 14 |
| - | Ne (ref. 97) | - | 870.2 | 48.4 | 21.6 |
| 193 | NaF | [1.2],5.0 | 1080.2 | - | 38 |
| 193 | repeated | . [0.9],5.1 | 1080.9 | 72.4 | 39.7 |
| 226 | NaI | [ [2.8],5.6 | 1080.2 | 72.0 | 38.4 |
| 196 | $\mathrm{Na}_{3} \mathrm{AlF}_{6}$ | . [1.8],4.8 | 1080.1 | 71.6 | (37) |
| 227 | NaBr | . [2.9],5.3 | 1079.3 | 71 | 37.7 |
| 228 | NaCl . | [ [3.0],5.2 | 1079.0 | - | 37.8 |
| 15 | $\mathrm{Na}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ | 6.6 | 1078.8 | - | 37.4 |
| 230 | $\mathrm{NaZn}\left(\mathrm{UO}_{2}\right)_{3}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{9}$ | . [2.5],4.6 | 1078.4 | - | - |

Table 2. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(1 \mathrm{~s})$ | $I(1 \mathrm{~s})$ | $I(2 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 231 | $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{6}, 2 \mathrm{H}_{2} \mathrm{O}$ | 5.3 | 1078.3 | - | 37.4 |
| 232 | $\mathrm{NaHSeO}_{3}$. | [2.3], 4.7 | 1078.3 | 70.3 | - |
| 233 | $\mathrm{Na}_{2} \mathrm{WO}_{4}$. | . [3.4],5.6 | 1078,3 | - | - |
| 234 | $\mathrm{Na}_{3}\left[\mathrm{Au}\left(\mathrm{S}_{2} \mathrm{O}_{3}\right)_{2}\right]$ | 4.8 | 1078.3 | - | - |
| 235 | $\mathrm{NaIO}_{4}$ | 4.7 | 1078.2 | - | 37.3 |
| 236 | $\mathrm{Na}_{2} \mathrm{SeO}_{4}, 10 \mathrm{H}_{2} \mathrm{O}$ | [3],4.7 | 1078.0 | - | 37.5 |
| 237 | $\mathrm{Na}_{5} \mathrm{IO}_{6}$ | 5.2 | 1078.0 | - | 37.6 |
| 238 | $\mathrm{NaMg}\left(\mathrm{UO}_{2}\right)_{3}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{9}$ | [3],4.4 | 1078.0 | - | - |
| 239 | $\mathrm{NaBrO}_{3} \ldots \ldots . . . . . .$. | 5.2 | 1077.8 | - | 37.4 |
| 229 | $\mathrm{Na}\left[\mathrm{Sb}(\mathrm{OH})_{6}\right]$ | [2.5],4.4 | 1077.7 | - | - |
| 591 | $\mathrm{Na}_{2} \mathrm{TeO}_{3}$ | 5.0 | 1077.6 | - | 36.7 |
| 591 | repeated | [2.8],4.8 | 1078.0 | - | - |
| 145 | $\mathrm{Na}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right], 10 \mathrm{H}_{2} \mathrm{O}$ | 4.7 | 1077.5 | 69.9 | 37.0 |
| 132 | $\mathrm{Na}_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right] \ldots$. | 4.8 | 1077.5 | - | - |
| 592 | $\mathrm{Na}_{2}\left[\mathrm{Sn}(\mathrm{OH})_{6}\right]$ | [3],4.5 | 1077.5 | - | 36 |
| 593 | Bengal Rosa B | 4.8 | 1077.4 | - | 37 |
| 594 | $\mathrm{NaAsO}_{2}$. | 4.7 | 1077.4 | - | 37.0 |
| 595 | $\mathrm{Na}_{2} \mathrm{MoO}_{4}$ | 5.0 | 1077.4 | - | 36.7 |
| 596 | $\mathrm{Na}_{3} \mathrm{RhCl}_{6}, 12 \mathrm{H}_{2} \mathrm{O}$. | 5.0 | 1077.4 | - | 36.5 |
| 597 | $\mathrm{Na}_{2} \mathrm{HAsO}_{4}, 7 \mathrm{H}_{2} \mathrm{O}$ | 4.3 | 1077.3 | 69.5 | 36.1 |
| 598 | $\mathrm{Na}_{2}\left[\mathrm{TeO}_{2}(\mathrm{OH})_{4}\right] \ldots$. | 4.7 | 1077.3 | - | - |
| 599 | $\mathrm{Na}_{3}\left[\mathrm{Au}\left(\mathrm{SO}_{3}\right)_{2}\right]$. | .[2.7],5.4 | 1076.9 | - | - |
| 600 | $\mathrm{Na}_{2} \mathrm{IrCl}_{6}$. | 4.6 | 1076.8 | - | 36.1 |
| 600 | repeated | 4.7 | 1077.4 | - | - |
| 35 | $\mathrm{Na}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{5} \mathrm{NO}\right]$. | 4.7 | 1076.7 | 68.8 | - |
| 601 | $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ | 5.7 | 1076.5 | - | - |
| 602 | $\mathrm{Na}_{3} \mathrm{VO}_{4}, 14 \mathrm{H}_{2} \mathrm{O}$ | 4.5 | 1076.4 | - | 35.3 |
| 603 | $\mathrm{Na}_{3} \mathrm{SbS}_{4}$. | 4.3 | 1076.3 | 69.4 | 36.3 |
| 604 | $\mathrm{Na}_{7} \mathrm{H}_{4} \mathrm{Mn}\left(\mathrm{IO}_{6}\right)_{3}$. | 4.1 | 1076.2 | - | - |
| 183 | $\mathrm{MgF}_{2}$ | . [0.8],5.1 | 1314.1 | 98.9 | 60.1 |
| 183 | repeated | . [0.1],5.0 | 1314.3 | 99.9 | 60.5 |
| 183 | repeated | . [1.1],5.0 | 1313.7 | - | - |
| 403 | MgO | . [0.4],4.0 | 1311.3 | 96.5 | 57.7 |
| 26 | $\mathrm{Mg}_{3} \mathrm{Nd}_{2}\left(\mathrm{NO}_{3}\right)_{12}, 24 \mathrm{H}_{2} \mathrm{O}$ | 4.6 | 1310.1 | 95.6 | 56.5 |
| 238 | $\mathrm{NaMg}\left(\mathrm{UO}_{2}\right)_{3}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{9}$ | [3],4.4 | 1310 | - | - |
| 605 | $\mathrm{Mg}\left(\mathrm{UO}_{2}\right)_{2}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{6}$. | 5.1 | 1309.3 | - | 56.1 |
| 173 | Mg phthalocyanine | 5.4 | 1307.7 | - | - |
| 196 | $\mathrm{Na}_{3} \mathrm{AlF}_{6}$ | . [1.8],4.8 | - | 128.1 | 83.3 |
| 240 | $\mathrm{CsAlSi}_{2} \mathrm{O}_{6}$ | . [2.5],4.7 | - | 126.4 | - |
| 241 | Al, foil, + oxide | 4.3 | - | 124.5 | 79.7 |
|  |  |  |  | \& 122.6 | \& 76.9 |
| 200 | $\mathrm{K}_{2} \mathrm{SiF}_{6}$ | . [2.4],4.8 | - | - | 111.7 |
| 200 | repeated | . [2.4],5.0 | - | 163 | 112.0 |
| 212 | $\left[\mathrm{Zn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{SiF}_{6}$. | . [2.6],4.9 | - | 162 | 110 |

Table 2. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(1 \mathrm{~s})$ | $I(2 \mathrm{~s})$ | $I(2 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 87 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left(\mathrm{SiF}_{6}\right)_{3}$ | 4.4 | - | 160.8 | 109.9 |
| 240 | $\mathrm{CsAlSi}_{2} \mathrm{O}_{6}$ | . [2.5],4.7 | - | 160.8 | 109.8 |
| 192 | $\mathrm{KPF}_{6}$ | . [2.7],4.5 | - | - | 145.4 |
| 77 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right] \mathrm{PF}_{6}$ | 4.7 | - | - | 143.2 |
| 242 | $\mathrm{Cu}\left(\mathrm{UO}_{2}\right)_{2}\left(\mathrm{PO}_{4}\right)_{2}$ | . [2.0],4.6 | - | - | 141.3 |
| 243 | $\mathrm{Ag}_{3} \mathrm{PO}_{4}$ | . [1.9],4.7 | - | - | 141.1 |
| 244 | $\mathrm{CePO}_{4}$ | . [2.4],4.8 | - | - | 141.1 |
| 3 | $\mathrm{Li}_{3} \mathrm{PO}_{4}$ | . [3.5],5.1 | - | - | 140.2 |
| 11 | $\mathrm{NH}_{4} \mathrm{BePO}_{4}$ | 4.5 | - | - | 139.6 |
| 245 | $\mathrm{Ni}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{2}$ | 5.1 | - | - | 139.1 |
| 246 | $\mathrm{Ir}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{3}$ | 4.5 | - | - | 138.6 |
| 247 | $\mathrm{Co}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{3}$ | 6.4 | - | - | 138.5 |
| 248 | $\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3} \mathrm{H}\right]_{2} \mathrm{UCl}_{6}$. | 4.6 | - | - | 138.1 |
| 179 | $\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{SCN}$ | 5.3 | - | - | 137.8 |

Table 3. Photo-electron signals of sulphur (the shoulder corresponding to
$2 \mathrm{p}_{1,2}$ is not given).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(2 \mathrm{p})$ |
| :---: | :---: | :---: | :---: |
| - | $\mathrm{SF}_{6}$ (ref. 97) | - | 180.4 |
| 249 | $\mathrm{BaSO}_{4}$ | [3.2],5.9 | 177.7 |
| 249 | repeated | [1.1],5.0 | 177.8 |
| 250 | $\mathrm{La}_{2}\left(\mathrm{SO}_{4}\right)_{3}$. | [2.6],5.0 | 176.6 |
| 251 | $\mathrm{Gd}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | [2.5],4.8 | 176.6 |
| 252 | $\mathrm{U}\left(\mathrm{SO}_{4}\right)_{2}$ | [2.5],4.8 | 176.4 |
| 253 | $\mathrm{SrSO}_{4}$ | [2.5],4.9 | 176.2 |
| 254 | $\mathrm{Eu}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | [2.5],4.5 | 176.2 |
| 255 | $\mathrm{CdSO}_{4}, \mathrm{H}_{2} \mathrm{O}$ | 5.0 | 176.1 |
| 256 | $\mathrm{CuSO}_{4}, 3 \mathrm{H}_{2} \mathrm{O}$ | 5.0 | 176.0 |
| 257 | $\mathrm{Cs}_{2} \mathrm{SO}_{4}$ | 4.9 | 175.8 |
| 258 | $\mathrm{BaS}_{2} \mathrm{O}_{6}, 2 \mathrm{H}_{2} \mathrm{O}$ | 4.8 | 175.8 |
| 259 | $\mathrm{EuSO}_{4}$ | . [2.4],4.4 | 175.8 |
| 234 | $\mathrm{Na}_{3}\left[\mathrm{Au}\left(\mathrm{S}_{2} \mathrm{O}_{3}\right)_{2}\right]$ | . [2.7],4.8 | 175.8 |
|  |  |  | \& 170.3 |
| 260 | $\mathrm{Sc}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 5.3 | 175.7 |
| 261 | $\mathrm{Ga}_{2}\left(\mathrm{SO}_{4}\right)_{3}$. | 4.4 | 175.7 |
| 262 | $\mathrm{Tl}_{2} \mathrm{SO}_{4}$ | 5.1 | 175.7 |
| 263 | $\mathrm{Pr}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 4.2 | 175.6 |
| 264 | $\mathrm{PbSO}_{4}$ | 4.5 | 175.6 |
| 231 | $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{6}, 2 \mathrm{H}_{2} \mathrm{O}$ | 5.3 | 175.5 |
| 265 | $\mathrm{Y}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 4.4 | 175.5 |
| 10 | $\left[\mathrm{Be}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right] \mathrm{SO}_{4}$ | 4.8 | 175.2 |

## Table 3. (continued).

Compound $\mathrm{C}_{\mathrm{st}}$ $I(2 \mathrm{p})$
repeated4.7175.8
$266 \mathrm{Yb}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ ..... 4.2175.2
$267 \mathrm{Ce}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ ..... 4.7 ..... 175.1
$268 \mathrm{UO}_{2} \mathrm{SO}_{4}$ ..... 5.1
175.1
$269 \mathrm{VOSO}_{4}, 5 \mathrm{H}_{2} \mathrm{O}$ ..... 4.8 ..... 174.8
$270 \mathrm{CuSO}_{4}, 5 \mathrm{H}_{2} \mathrm{O}$ ..... 5.3 ..... 174.8
271 [ $\left.\mathrm{Ag} \mathrm{py} \mathrm{p}_{4}\right] \mathrm{S}_{2} \mathrm{O}_{8}$ ..... 4.2
$272 \quad \mathrm{Ag}_{2} \mathrm{SO}_{4}$ [3],4.3174.8$5 \quad 1 . \mathrm{i}_{2} \mathrm{SO}_{4}$5.2
$273 \quad\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{SO}_{4}$ ..... 4.1
174.8$274 \mathrm{PbS}\left(+\mathrm{PbSO}_{4}\right.$ ?4.2
$83\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Au}\left(\mathrm{S}_{2} \mathrm{O}_{3}\right)_{2}\right]$ ..... 4.4
$275 \mathrm{Rb}_{2} \mathrm{SO}_{4}$ ..... 4.1
$276 \mathrm{Nd}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ ..... [2.5],4.6
277 [ $\left.\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]\left(\mathrm{SO}_{4}\right) \mathrm{Cl}$ ..... 5.3
$105\left[\left(\mathrm{NH}_{3}\right)_{5} \mathrm{CoO}_{2} \mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}\right]\left(\mathrm{SO}_{4}\right)_{2} \mathrm{HSO}_{4}$ ..... 5.3
$278 \quad \mathrm{~K}_{2} \mathrm{~S}_{4} \mathrm{O}_{6}$ ..... 5.3
$110 \quad\left[\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{NCS}\right]\left(\mathrm{ClO}_{4}\right)_{2}$ ..... 4.7
$601 \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ ..... 5.7
$128\left[\mathrm{Pd}\left(\mathrm{NH}_{3}\right)_{4}\right]\left(\mathrm{CH}_{3} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SO}_{3}\right)_{2}$ ..... 4.8
128 repeated ..... 4.6
$91\left[\mathrm{Ni}(\mathrm{CN})_{2}\left(\mathrm{NH}_{3}\right)\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{~S}\right)\right]$ ..... 5.5
119 [Pd py $\left.{ }_{4}\right] \mathrm{SO}_{4}$ ..... 4.6
$599 \mathrm{Na}_{3}\left[\mathrm{Au}\left(\mathrm{SO}_{3}\right)_{2}\right]$ ..... 5.45
$150 \quad[\mathrm{Ni} \mathrm{en} 3] \mathrm{SO}_{4}$ ..... 3.8
174.7174.6
174.6
\& 167.7
174.5
\& 169.2174.4174.4
174.2
174.1
174.0
\& 169.7
173.9
173.8
\& 167.8173.3173.5
173.3
173.25
173.1173.0
$279 \quad\left[\mathrm{PtCl}_{2}\left(\mathrm{~S}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}\right]$ ..... 5.0 ..... 172.1

- $\mathrm{H}_{2} \mathrm{~S}$ (ref. 97) ..... - ..... 170.2
$280 \mathrm{Tl}_{3} \mathrm{TaS}_{4}$ ..... 4.8 ..... 170.1
281 GaS ..... [3.0],5.0 ..... 169.9
- $\mathrm{CS}_{2}$ (ref. 97) 169.8
5.2
$282 \quad\left[\operatorname{Ir}\left(\mathrm{~S}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3} \mathrm{Cl}_{3}\right]$
283 ZnS ..... [2.2],4.6
139 methylene blue $\left(\mathrm{ClO}_{4}\right)$ ..... 5.1 ..... 169.3169.6
169.4
133 [ Ni daes ${ }_{2}$ ] $\left(\mathrm{ClO}_{4}\right)_{2}$ ..... 4.6 ..... 169.3
$284 \mathrm{Au}\left(\mathrm{SCH}_{2} \mathrm{CO}_{2} \mathrm{H}\right)$ ..... 3.9 ..... 169.3
17 methylene blue[ $\left.\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ ..... 6.0 ..... 169.2
$168 \mathrm{~K}_{2}\left[\mathrm{Pt}(\mathrm{SCN})_{6}\right]$ ..... 4.8
169.1
$163 \mathrm{~K}_{2}\left[\mathrm{Hg}(\mathrm{SCN})_{4}\right]$ ..... 5.0
169.0
$155 \mathrm{Co}(\mathrm{NCS})_{4} \mathrm{Hg}$ ..... 4.7
168.9
285 CdS ..... [3.2],4.7168.9
158 methylene blue Cl ..... 5.5 ..... 168.7


## Table 3. (continued).

Compound $\mathrm{C}_{\text {st }}$ $I(2 \mathrm{p})$
$286 \mathrm{Tl}_{2}\left[\mathrm{MoO}_{2} \mathrm{~S}_{2}\right]$ ..... 4.7 ..... 168.6
$287 \mathrm{Cs}_{2} \mathrm{WS}_{4}(+\mathrm{S}$ ?) ..... 5.2
168.6
\& 165.8
$288 \mathrm{Tl}_{2} \mathrm{MoS}_{4}$ ..... 4.4 ..... 168.5
$73 \quad\left[\mathrm{~N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2}\left[\mathrm{Sn}(\mathrm{NCS})_{6}\right]$ ..... 5.0
$61\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{3}\left[\operatorname{Ir}(\mathrm{SCN})_{6}\right]$ ..... 4.4
$100\left[\mathrm{Coen}_{2} \mathrm{Cl}_{2}\right]\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]$ ..... 4.5
$98 \mathrm{Cu}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}$ ..... 4.4
$289\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{3}\left[\mathrm{Ru}(\mathrm{NCS})_{6}\right]$ ..... 4.3
$169 \mathrm{~K}_{3}\left[\mathrm{Rh}(\mathrm{SCN})_{6}\right]$ ..... 4.7
$86 \mathrm{NH}_{4}\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]$ .....  [3.7],5.2
$106\left[\mathrm{Rh} \mathrm{ns}_{3}\right]_{2} \mathrm{Ni}\left(\mathrm{ClO}_{4}\right)_{2}$ ..... 4.6
$290 \mathrm{AgS}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}$ ..... [3.3],5.1
$291 \mathrm{In}_{2} \mathrm{~S}_{3}$ ..... [3],4.7
$292 \mathrm{In}_{2}\left(\mathrm{~S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3}$ ..... [3],4.8
$167 \mathrm{~K}_{3}\left[\mathrm{Cr}(\mathrm{NCS})_{6}\right]$ ..... 4.8
$245 \mathrm{Ni}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{2}$ ..... 5.1
$46 \quad\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{SCN}$ ..... 5.1
125 methylene blue[ $\left.\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]$ ..... 5.0
293 CuS ..... 5.5
$294 \mathrm{Rh}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{\varepsilon} \mathrm{H}_{5}\right)_{2}\right)_{3}$ ..... 4.5
$295 \mathrm{Tl}_{2} \mathrm{WS}_{4}$ ..... 4.2
$170\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{3}\left[\mathrm{Os}(\mathrm{SCN})_{6}\right]$ ..... 5.2
170 repeated ..... 4.6
$296 \mathrm{~Pb}\left(\mathrm{~S}_{2} \mathrm{CN}\left(\mathrm{C}_{\varepsilon} \mathrm{H}_{5}\right)_{2}\right)_{2}$ ..... 4.2
$297 \mathrm{Tl}_{3} \mathrm{VS}_{4}$ ..... 4.7
151 [ Ni tren $(\mathrm{NCS})_{2}$ ] ..... 4.6
$298 \mathrm{As}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3}$ ..... 4.8
$299 \mathrm{Sb}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3}$ ..... 4.9
$141 \mathrm{Co}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3}$ ..... 5.8
$247 \mathrm{Co}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{3}$ ..... 6.4
$65\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{ReS}_{4}$ ..... 4.4
$300 \quad\left(\mathrm{NH}_{4}\right)_{3} \mathrm{VS}_{4}$ ..... 5.5
$178 \quad\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{SCN}$ ..... 4.8
$118 \mathrm{Te}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{4}$ ..... 4.9
$126 \operatorname{Cr}\left(\mathrm{~S}_{2} \mathrm{CN}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{2}\right)_{3}$ ..... 5.9
$301 \mathrm{Cs}_{2} \mathrm{MoS}_{4}(+\mathrm{S}$ ? ) ..... 4.1
$603 \mathrm{Na}_{3} \mathrm{SbS}_{4}$ ..... 4.3
$302 \mathrm{~Pb}\left(\mathrm{~S}_{2} \mathrm{P}\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}$ ..... 4.8
$179 \quad\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{SCN}$ ..... 5.3
$303 \mathrm{Ag}_{2} \mathrm{~S}$ ..... 4.6
$127 \mathrm{Ni}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}$ ..... 4.7
$246 \quad \operatorname{Ir}\left(\mathrm{~S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{3}$ ..... 4.5
168.5168.5168.4
168.3
168.3168.3168.2
168.2
168.2168.1168.1168.0
168.0
167.9167.9167.9
167.9
167.9
167.9168.4167.9
167.8
167.6167.6167.6
167.5
167.5
167.5
167.4167.4
167.4
167.2167.2
\& 164.5167.2
167.0

## Table 4. Photo-electron signals of chlorine (the shoulder corresponding to

 $2 \mathrm{p}_{1 / 2}$ is not given).|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: |
| 304 | $\mathrm{KClO}_{4}$ | 4.8 | 215.0 | - |
| 305 | $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]\left(\mathrm{ClO}_{4}\right)_{2}$. | 4.8 | 214.5 | - |
| 306 | [V urea ${ }_{6}$ ] $\left(\mathrm{ClO}_{4}\right)_{3}$ | 5.4 | 214.0 | - |
| 79 | $\left[\mathrm{Pd}\left(\mathrm{et}_{4} \mathrm{den}\right){\mathrm{Cl}] \mathrm{ClO}_{4}}\right.$ | [3.3],5.0 | 213.9 | - |
|  |  |  | \& 204.2 | - |
| 110 | $\left[\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{NCS}\right]\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.7 | 213.7 | - |
| 93 | $\left[\mathrm{Pt}\right.$ den $\left.\mathrm{Cl}_{3}\right] \mathrm{ClO}_{4}$ | 4.5 | 213.7 | - |
|  |  |  | \& 204.5 | - |
| 106 | $[\mathrm{Ph} \mathrm{ns} 3]_{2} \mathrm{Ni}\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.6 | 213.5 | - |
| 113 | $[\mathrm{Ni} \mathrm{en} 2]\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.6 | 213.3 | - |
| 133 | [ Ni daes $_{2}$ ] $\left(\mathrm{ClO}_{4}\right)_{2}$. | 4.6 | 213.3 | - |
| 92 | $\left[\mathrm{Pd}\left(\mathrm{et}_{4}\right.\right.$ den) $\mathrm{Br}^{\text {] }} \mathrm{ClO}_{4}$ | 4.4 | 213.2 | - |
| 120 | [Fe urea ${ }_{6}$ ] $\left.\mathrm{ClO}_{4}\right)_{3}$ | 5.1 | 213.1 | - |
| 138 | [ Ni (tren) phen] $\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.6 | 213.1 | - |
| 307 | [ Ni curtis ${ }_{2}$ ] $\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.7 | 212.8 | - |
| 102 | [ Pd phen 2 ] $\left(\mathrm{ClO}_{4}\right)_{2}$ | 5.1 | 212.8 | - |
| 55 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{\mathrm{ClO}_{4}}$ | 4.8 | 212.6 | - |
| 139 | methylene blue ( $\mathrm{ClO}_{4}$ ) | 5.1 | 212.6 | - |
| 112 | $\left[\mathrm{Rh} \mathrm{py} 4 \mathrm{Br}_{2}\right] \mathrm{ClO}_{4}$ | 4.4 | 212.5 | - |
| 308 | CsCl | [0.4],5.2 | 207.6 | 13.4 |
| 308 | repeated | [0.7],5.2 | 207.3 | 13.8 |
| 309 | $\mathrm{Cs}_{4}\left(\mathrm{InCl}_{6}\right)\left(\mathrm{SbCl}_{6}\right)$ | [3.3],4.9 | 207 | - |
| 310 | $\mathrm{Cs}_{2} \mathrm{PtCl}_{6}$ | [1.6],4.3 | 206.9 | 15.7 |
| 311 | $\mathrm{CsSbCl}_{6}$ | [2.0],5.0 | 208.8 | - |
| 312 | $\mathrm{Rb}_{2} \mathrm{PtCl}_{6}$ | [2.5],5.0 | 206.8 | 15.6 |
| 313 | $\mathrm{Cs}_{4}\left(\mathrm{SbCl}_{6}\right)\left(\mathrm{TlCl}_{6}\right)$ | [2.3],4.6 | 206.7 | - |
| 314 | $\mathrm{Cs}_{2} \mathrm{PbCl}_{6}$ | [2.1],4.9 | 206.5 | 12.5 |
| 315 | $\mathrm{Cs}_{2}\left[\mathrm{Rh}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{Cl}_{5}\right]$. | [2.0],4.9 | 206.3 | 14.0 |
| 316 | $\mathrm{Au}_{2} \mathrm{Cl}_{6}$ | 4.4 | 206.2 | 15 |
| 228 | NaCl . | [3.0],5.2 | 206.1 | 12.2 |
| 593 | Bengal Rosa B | 4.8 | 206.0 | - |
| 317 | L. aOCl | [2],4.4 | 206.0 | - |
| 318 | $\mathrm{Cs}_{4}\left(\mathrm{Sb}^{\mathrm{III}} \mathrm{Cl}_{6}\right)\left(\mathrm{Sb}^{\mathrm{V}} \mathrm{Cl}_{6}\right)$ | [3.1],4.9 | 205.9 | - |
| 319 | RbCl | [2.8],5.2 | 205.7 | 11.9 |
| 59 | $\left[\mathrm{Pd}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$. | 4.8 | 205.6 | - |
| 320 | $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ | [3],4.6 | 205.5 | 14.2 |
| 321 | KCl | [2.3],4.8 | 205.45 | 11.9 |
| 322 | $\mathrm{Cs}_{2} \mathrm{IrCl}_{6}$ | 5.7 | 205.4 | - |
| 322 | repeated | 4.9 | 205.6 | 14 |
| 323 | $\mathrm{KAuCl}_{4}$ | 3.2 | 205.4 | - |
| 324 | $\mathrm{K}_{2} \mathrm{OsCl}_{6}$ | 3.8 | 203.9 | 12.1 |
| 324 | repeated. | 5.0 | 205.3 | 13.7 |
| 325 | $\mathrm{MnCl}_{2}, 4 \mathrm{H}_{2} \mathrm{O} \ldots .$. | 4.3 | 205.2 | - |

## Table 4. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: |
| 326 | $\mathrm{Cs}_{2} \mathrm{OsCl}_{6}$. | 4.8 | 205.2 | - |
| 327 | $\mathrm{Cs}_{2}\left[\mathrm{OsCl}_{5} \mathrm{I}\right]$ | 4.4 | 205.2 | - |
| 328 | $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ | 4.4 | 205.2 | - |
| 329 | SbOCl | [2.5],4.7 | 205.1 | - |
| 330 | $\mathrm{PbCl}_{2}$. | . [2.5],4.6 | 205.1 | - |
| 331 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right]_{2} \mathrm{PbCl}_{6}$ | [3.0],5.0 | 205.1 | 11 |
| 332 | $\mathrm{K}_{2} \mathrm{PdCl}_{4}$. | 4.8 | 205.0 | - |
| 77 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right] \mathrm{PF}_{6}$ | 4.7 | 205.0 | - |
| 78 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right]_{3}\left(\mathrm{PW}_{12} \mathrm{O}_{40}\right)$. | 4.0 | 204.9 | - |
| 36 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{CeCl}_{6}$ | 4.2 | 204.9 | - |
| 64 | $\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{OsCl}_{6}$ | 5.2 | 204.8 | 11.6 |
| 89 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right] \mathrm{MnO}_{4} \ldots$ | 4.7 | 204.7 | - |
| 333 | $\mathrm{RhCl}_{3}$ | 4.9 | 204.7 | - |
| 14 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right] \mathrm{BF}_{4}$ | 4.6 | 204.6 | - |
| 39 | $\mathrm{K}_{2}\left[\mathrm{Ru}(\mathrm{NO}) \mathrm{Cl}_{5}\right] \ldots$. | [1.5],4.8 | 204.6 | - |
| 334 | $\mathrm{Rb}_{2}\left[\mathrm{OsCl}_{4} \mathrm{I}_{2}\right]$ | 4.6 | 204.6 | - |
| 335 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right] \mathrm{AuCl}_{4}$ | 5.2 | 204.6 | - |
| 600 | $\mathrm{Na}_{2} \mathrm{IrCl}_{6}$ | 4.6 | 204.5 | - |
| 600 | repeated | 4.7 | 204.9 | - |
| 596 | $\mathrm{Na}_{3} \mathrm{RhCl}_{6}, 12 \mathrm{H}_{2} \mathrm{O}$. | 5.0 | 204.4 | 12.4 |
| 51 | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{6}$ | 3.3 | 204.4 | 13.1 |
| 51 | repeated | 4.8 | 204.6 | 13.6 |
| 94 | $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{InCl}_{6}$ | 5.0 | 204.4 | - |
| 336 | $\mathrm{K}_{3} \mathrm{MoCl}_{6}$ | 4.5 | 204.3 | - |
| 337 | $\mathrm{K}_{2} \mathrm{ReCl}_{6}$ | 3.7 | 204.2 | 12.1 |
| 338 | $\mathrm{Tl}_{2} \mathrm{PtCl}_{6}$ | 2.8 | 204.2 | - |
| 339 | AgCl . | 4.8 | 204.1 | - |
| 99 | $\left[\operatorname{Ir}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2}$ | 4.4 | 204.1 | - |
| 117 | $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4}\right]\left(\mathrm{PtCl}_{4}\right)$ | 4.0 | 204.1 | - |
| 47 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right]_{2} \mathrm{PtCl}_{6}$ | 4.6 | 204.1 | 13 |
| 95 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \ldots$ | 5.2 | 204.0 | - |
| 90 | $\left[\mathrm{Rh}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2}$. | 4.6 | 204.0 | - |
| 279 | $\left[\mathrm{PtCl}_{2}\left(\mathrm{~S}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}\right] \ldots$ | 5.0 | 203.9 | - |
| 159 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2}$ | 3.9 | 203.8 | - |
| 32 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right] \mathrm{NO}_{3}$. | 4.4 | 203.8 | - |
| 109 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{SbCl}_{6}$. | 4.3 | 203.8 | - |
| 340 | $\mathrm{Cs}_{2}\left[\mathrm{OsCl}_{2} \mathrm{I}_{4}\right]$. | 5.0 | 203.8 | - |
| 72 | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{6}$ | 5.0 | 203.75 | - |
| 248 | $\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3} \mathrm{H}\right]_{2} \mathrm{UCl}_{6}$. | 4.6 | 203.75 | - |
| 111 | [ Rh den $\mathrm{Cl}_{3}$ ] | 4.8 | 203.7 | (11) |
| 108 | $\left[\operatorname{Irpy}_{4} \mathrm{Cl}_{2}\right] \mathrm{Cl}$. | 4.7 | 203.7 | - |
| 103 | $\left.\mathrm{K}[\operatorname{IrpyCl}]_{5}\right]$. | 4.7 | 203.7 | - |
| 96 | [ $\mathrm{Ni}\left(\mathrm{et}_{4}\right.$ den) Cl$] \mathrm{Cl}$. | 5.1 | 203.6 | - |
| 101 | [Pd phen $\mathrm{Cl}_{2}$ ] | 4.5 | 203.6 | - |

## Table 4. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: |
| 341 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{TlCl}_{6}$ | 3.7 | 203.6 | - |
| 146 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{BiCl}_{6}$ | 3.6 | 203.5 | - |
| 342 | $\left[\mathrm{Co} \mathrm{en} \mathrm{E}_{2} \mathrm{Cl}_{2}\right] \mathrm{ReO}_{4}$ | 5.0 | 203.5 | - |
| 343 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2} \mathrm{PtCl}_{4}$ | 5.3 | 203.5 | 11 |
| 282 | $\left[\operatorname{Ir}\left(\mathrm{S}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3} \mathrm{Cl}_{3}\right]$ | 5.2 | 203.4 | - |
| 344 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{PbCl}_{6}$. | 4.8 | 203.4 | - |
| 345 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2}\left[\mathrm{OsCl}_{4} \mathrm{I}_{2}\right]$ | 4.2 | 203.3 | - |
| 346 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{ReCl}_{6}$. | 4.9 | 203.2 | - |
| 68 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{3} \mathrm{IrCl}_{6}$ | 4.4 | 203.1 | - |
| 124 | $\left[\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2} \mathrm{Cl}_{3}$. | 4.7 | 202.95 | - |
| 74 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{IrCl}_{6} \ldots$ | 4.4 | 202.85 | - |

Table 5. Photo-electron signals of potassium, calcium, scandium, titanium and vanadium.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{~s})$ | $I(3 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| - | Ar(ref. 97) . | - | 250.6 | 248.5 | 29.3 | 15.8 |
| 189 | $\mathrm{K}_{2} \mathrm{GeF}_{6}$ | [1.3],4.7 | 304.7 | 302.0 | - | 26.0 |
| 185 | $\mathrm{K}_{3} \mathrm{RhF}_{6}$ | [2.0],4.7 | 304.4 | 301.7 | 42 | 25.7 |
| 7 | $\mathrm{K}_{2} \mathrm{BeF}_{4}$ | [2.5],5.3 | 303.8 | 301.3 | $\rightarrow$ | - |
| 7 | repeated. | [2.0],5.0 | 304.2 | 301.5 | 41.6 | 25.4 |
| 200 | $\mathrm{K}_{2} \mathrm{SiF}_{6}$. | [2.4],4.8 | 303.7 | 301.2 | 41.0 | 25.2 |
| 200 | repeated | [2.4],5.0 | 304.1 | 301.4 | 41.9 | 25.5 |
| 192 | $\mathrm{KPF}_{6}$ | [2.7],4.5 | 303.8 | 301.05 | 39.0 | 24.75 |
| 13 | $\mathrm{KBF}_{4}$ | [3.1],4.6 | 303.4 | 301.0 | 39.6 | 24.8 |
| 13 | repeated | [2.8],5.4 | 304.4 | 301.8 | 41.4 | 25.7 |
| 347 | KI | [1.6],4.7 | 303.75 | 301.0 | 40.7 | 24.8 |
| 209 | $\mathrm{KNiF}_{3}$ | 3.6 | - | 300.75 | (37.8) | 24.8 |
| 209 | repeated | [1.3],4.5 | 303.7 | 300.9 | (38) | 25.2 |
| 210 | $\mathrm{K}_{2} \mathrm{HfF}_{6}$ | [2.7],5.0 | 303.5 | 300.8 | (41) | - |
| 348 | $\mathrm{K}_{4} \mathrm{BiI}_{7}$ | [3],4.9 | 303 | 300.5 | - | 24.2 |
| 208 | $\mathrm{K}_{2} \mathrm{NbF}_{7}$ | [3],5.0 | 303.2 | 300.5 | 40 | - |
| 349 | $\mathrm{KIO}_{4}$ | [2.8],5.3 | 303.4 | 300.5 | 40.1 | 24.3 |
| 213 | $\mathrm{K}_{2} \mathrm{TiF}_{6}$ | [2.4],4.5 | 303.1 | 300.45 | (36.9) | 24.3 |
| 223 | KF | [1.7],4.15 | 303.0 | 300.35 | 40.3 | 24.15 |
| 321 | KCl | [2.3],4.8 | 303.0 | 300.3 | 40.2 | 23.9 |
| 216 | $\mathrm{K}_{2}\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$ | [1.7], 4.9 | 303.0 | 300.3 | 41 | 24.3 |
| 218 | $\mathrm{K}_{2} \mathrm{UF}_{6}$ | [2.4],4.9 | 302.9 | 300.3 | - | - |
| 350 | $\mathrm{KIO}_{3}$ | [3.2],5.3 | 303.1 | 300.2 | 40.5 | 23.8 |
| 351 | $\mathrm{K}_{2} \mathrm{HgI}_{4}$ | [2.4],4.6 | 302.6 | 300.2 | - | - |
| 608 | $\mathrm{K}\left[\mathrm{OsO}_{3} \mathrm{~N}\right] \ldots$ | [2.1],4.4 | 303 | 300.0 | 40 | 24.0 |

## Table 5. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{~s})$ | $I(3 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 352 | $\mathrm{KAuBr}_{4}$ | 3.4 | 302.65 | 300.0 | (38.3) | 22.4 |
| 320 | $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ | [3],4.6 | 302.6 | 299.9 | 39.9 | 23.7 |
| 304 | $\mathrm{KClO}_{4}$. | 4.8 | 302.5 | 299.8 | 39.9 | 23.9 |
| 353 | KBr | [3.1], 4.6 | 302.4 | 299.8 | 39.3 | 23.3 |
| 129 | $\mathrm{K}_{2} \mathrm{Pt}(\mathrm{SeCN})_{6}$ | [2.7],4.8 | 303 | 299.8 | - | 23.6 |
| 354 | $\mathrm{KSb}(\mathrm{OH})_{6}$ | 5.1 | 302.3 | 299.7 | (38) | - |
| 355 | $\mathrm{K}_{2}\left[\mathrm{Sb}_{2} \mathrm{O}_{2}\right.$ tartrate $\left.{ }_{2}\right]$ | [3],4.9 | 302.5 | 299.6 | (39) | - |
| 215 | $\mathrm{K}_{2} \mathrm{TaF}_{7}$ | [3.1], 4.5 | 302.3 | 299.6 | (36) | 23.8 |
| 356 | $\mathrm{K}_{2} \mathrm{HAsO}_{4}$ | [2.8],4.5 | 303 | 299.5 | 40 | 23.5 |
| 39 | $\mathrm{K}_{2}\left[\mathrm{Ru}(\mathrm{NO}) \mathrm{Cl}_{5}\right]$. | [1.5],4.8 | 302.1 | 299.4 | 39.4 | 23.2 |
| 357 | $\mathrm{KReO}_{4}$ | [2],3.7 | 302.1 | 299.4 | - | 23.6 |
| 358 | $\mathrm{K}_{2} \mathrm{PtI}_{6}$ | 4.6 | 302.0 | 299.4 | - | 23.6 |
| 332 | $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ | 4.8 | 301.9 | 299.3 | 39.2 | 23.2 |
| 122 | $\mathrm{K}\left[\mathrm{Ag}(\mathrm{CN})_{2}\right]$ | [2.7], 4.5 | 302.1 | 299.3 | - | - |
| 359 | $\mathrm{K}_{2} \mathrm{ReBr}_{6}$ | 4.8 | 302.1 | 299.3 | 39.4 | 22.9 |
| 360 | $\mathrm{K}_{2}\left[\mathrm{OsCl}_{2} \mathrm{I}_{4}\right]$ | 4.1 | 301.8 | 299.2 | 39.4 | 23.0 |
| 328 | $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ | 4.4 | 302 | 299.2 | - | 23.4 |
| 149 | $\mathrm{K}_{2}\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 5.1 | 301.8 | 299.1 | 38 | - |
| 361 | $\mathrm{KBrO}_{3}$ | [3.3],5.0 | 301.6 | 299.0 | - | - |
| 362 | $\mathrm{K}_{2}\left[\mathrm{OsO}_{2}(\mathrm{OH})_{4}\right]$ | 4.8 | 301.7 | 299.0 | - | - |
| 16 | $\mathrm{K}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ | 5.1 | 301.6 | 298.9 | 39.0 | 22.7 |
| 24 | $\mathrm{KNO}_{3}$. | 5.1 | 301.4 | 298.8 | 38.9 | 22.7 |
| 278 | $\mathrm{K}_{2} \mathrm{~S}_{4} \mathrm{C}_{6}$ | 5.3 | 301.4 | 298.8 | 38.5 | 22.5 |
| 337 | $\mathrm{K}_{2} \mathrm{ReCl}_{6}$. | 3.7 | 301.3 | 298.7 | 39.0 | 22.4 |
| 363 | $\mathrm{K}_{2}\left[\mathrm{TiO}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{2}\right]$. | 4.9 | 301.6 | 298.8 | - | - |
| 160 | $\mathrm{K}_{2}\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]$ | 4.9 | 301.3 | 298.8 | 38.9 | 22.9 |
| 336 | $\mathrm{K}_{3} \mathrm{MoCl}_{6}$ | 4.5 | 301.6 | 298.8 | 38.9 | 23.4 |
| 364 | $\mathrm{K}_{2} \mathrm{PtBr}_{6}$ | 2.6 | 301.45 | 298.8 | 39.4 | 23.1 |
| 364 | repeated | 5.0 | 301.7 | 299.0 | - | 23.9 |
| 144 | $\mathrm{K}\left[\mathrm{Au}(\mathrm{CN})_{2}\right]$ | 4.5 | 301.3 | 298.8 | - | - |
| 163 | $\mathrm{K}_{2}\left[\mathrm{Hg}(\mathrm{SCN})_{4}\right]$ | 5.0 | 301.5 | 298.8 | - | - |
| 365 | $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ | 5.1 | 301.3 | 298.6 | 39.0 | 22.8 |
| 366 | $\mathrm{K}_{2} \mathrm{IrBr}_{6}$. | 4.7 | 301.3 | 298.5 | 39.0 | 23.6 |
| 167 | $\mathrm{K}_{3}\left[\mathrm{Cr}(\mathrm{NCS})_{6}\right]$ | 4.8 | 301.1 | 298.4 | 38.7 | 22.6 |
| 367 | $\mathrm{K}_{3}\left[\mathrm{Cr}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]$. | 5.3 | - | 298.4 | 38.4 | 22.3 |
| 368 | $\mathrm{KMnO}_{4}$ | 5.1 | 301.1 | 298.4 | 38.5 | 22.4 |
| 324 | $\mathrm{K}_{2} \mathrm{OsCl}_{6}$ | 3.8 | 301.1 | 298.4 | 38.7 | 22.7 |
| 324 | repeated | 5.0 | 302.4 | 299.7 | - | - |
| 168 | $\mathrm{K}_{2}\left[\mathrm{Pt}(\mathrm{SCN})_{6}\right]$ | 4.8 | 301.0 | 298.3 | 38.5 | 22.5 |
| 171 | KSeCN | 3.6 | 301.0 | 298.1 | - | - |
| 171 | repeated. | [3.3],5.0 | 301.0 | 298.2 | 39 | - |
| 369 | $\mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ | 5.4 | 300.5 | 297.9 | 38.1 | 21.9 |
| 103 | $\mathrm{K}[\mathrm{IrpyCl} 5]$. | 4.7 | 301 | 297.9 | - | - |
| 201 | $\mathrm{CaF}_{2}$. | [1.8], 4.6 | 359.5 | 356.0 | - | 33.4 |
| 201 | repeated ....... | [1.3], 4.5 | 359.6 | 356.1 | 52.5 | 33.7 |

## Table 5. (continued).

|  | Compound | $\mathrm{C}_{\text {St }}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{~s})$ | $I(3 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 370 | $\mathrm{Ca}\left(\mathrm{IO}_{3}\right)_{2}$. | [2.2],4.6 | 358.2 | 354.7 | - | 32.2 |
| 371 | $\mathrm{CaCrO}_{4}$ | 4.7 | 355.7 | 352.3 | - | 30.3 |
| 260 | $\mathrm{Sc}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 5.3 | 414.6 | 410.05 | - | 39.5 |
| 50 | $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{ScF}_{6}$ | 5.4 | 414.2 | 410 | - | 39.4 |
| 372 | $\mathrm{Sc}_{2} \mathrm{O}_{3}$ | 5.0 | 413.2 | 408.75 | - | 38.3 |
| 213 | $\mathrm{K}_{2} \mathrm{TiF}_{6}$ | [2.4],4.5 | 472 | 469.0 | - | - |
| 373 | $\mathrm{Bi}_{2} \mathrm{Ti}_{2} \mathrm{O}_{7}$. | [2.3],4.7 | 473 | 465.9 | - | 45 |
| 374 | $\mathrm{TiO}_{2}$ | [3],4.8 | 471.0 | 465.3 | - | 43.6 |
| 363 | $\mathrm{K}_{2}\left[\mathrm{TiO}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{2}\right]$ | 4.9 | 470.6 | 464.7 | - | - |
| 375 | $\mathrm{Yb}_{2} \mathrm{Ti}_{2} \mathrm{O}_{7}$ | 4.6 | 469.8 | 464.1 | - | - |
| 376 | $\mathrm{YbVO}_{4}$ | [2.8],4.9 | 531 | 524.1 | - | 49.1 |
| 377 | $\mathrm{YVO}_{4}$ | 4.7 | 530 | 523.4 | - | 48.9 |
| 378 | $\mathrm{PrVO}_{4}$ | 4.8 | 530.6 | 523.0 | - | 49 |
| 269 | VOSO ${ }_{4}, 5 \mathrm{H}_{2} \mathrm{O}$ | 4.8 | 530,528 | 522.9 | - | (51),47.5 |
| 379 | $\mathrm{V}_{2} \mathrm{O}_{5}$. | [3],5.3 | 529.6 | 522.2 | - | 47.4 |
| 380 | $\mathrm{DyVO}_{4}$. | 3.4 | 529 | 522.1 | - | - |
| 380 | repeated | [1.8],4.2 | 531 | 524.2 | - | 49.8 |
| 602 | $\mathrm{Na}_{3} \mathrm{VO}_{4}, 14 \mathrm{H}_{2} \mathrm{O}$ | 4.5 | 528 | 522.0 | - | 47.0 |
| 82 | $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{~V}_{3} \mathrm{O}_{9}$ | 4.6 | 529.5 | 521.6 | 75.8 | 47.6 |
| 306 | [V urea ${ }_{6}$ ] $\left(\mathrm{ClO}_{4}\right)_{3}$. | 5.4 | 527.6 | 521.3 | - | 48,46 |
| 300 | $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{VS}_{4}$. | 5.5 | 526.6 | 519.1 | - | 43.7 |

Table 6. Photo-electron signals of chromium, manganese, iron and cobalt.

|  | Compound | $\mathrm{C}_{\mathrm{st}}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I(2 \mathrm{p} 3,2)$ | $I(3 \mathrm{p})$ | $I(3 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 81 | $\mathrm{BaCr}^{\mathrm{VI}} \mathrm{O}_{4}$. | [2.2],4.9 | 596.7 | 587.5 | 56.2 | - |
| 82 | $\mathrm{Ce}\left(\mathrm{Cr}^{\text {VI }} \mathrm{O}_{4}\right)_{2}$ | [3.0], 4.8 | 595.5 | 586.6 | 55 | - |
| 16 | $\mathrm{K}_{2}\left[\mathrm{Cr}^{\mathrm{III}}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$. | [1.7], 4.9 | (598.2),596.0 | (588.2),586.1 | (55),52.8 | 10.8 |
| 11 | $\mathrm{Hg}_{2} \mathrm{Cr}^{\text {VI }} \mathrm{O}_{4}$ | [1.8],4.0 | 595.3 | 585.9 asym | 55.2 | - |
| 71 | $\mathrm{CaCr}^{\text {VI }} \mathrm{O}_{4}$. | 4.7 | 594.1 | 584.9 | 53.7 | - |
| 93 | $\mathrm{Tl}_{2} \mathrm{Cr}^{\text {VI }} \mathrm{O}_{4}$ | 4.5 | 594 | 584.9 | 54.6 | - |
| 34 | $\mathrm{Ag}_{2} \mathrm{Cr}^{\text {VI }} \mathrm{O}_{4}$ | [3.1],5.1 | 593.9 | 584.7 | 54.3 | - |
| 35 | $\mathrm{Cd}_{3}\left[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_{6}\right]_{2}$. | [2.9],4.8 | (597),594.2 | (586),584.3 | 51.5 | - |
| 39 | $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{Cr}^{\mathrm{III}} \mathrm{F}_{6}$. | 4.8 | 594.0 | (586),583.8 | (55),51.0 | 12 |
| 28 | $\mathrm{Cr}^{\mathrm{III}}\left(\mathrm{NO}_{3}\right)_{3}, 9 \mathrm{H}_{2} \mathrm{O}$ | 4.6 | (595),593.1 | (586),583.6 | (55),50.4 | 10.6 |
| 37 | $\mathrm{K}_{3}\left[\mathrm{Cr}^{\text {III }}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]$ | 5.3 | 593.2 | (585),583.5 | 55.8,50.6 | 10.5 |
| 34 | $\left[\mathrm{Cr}^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{InCl}_{6}$ | 5.0 | 593.7 | (586),583.5 | (52),50.4 | 10.5 |
| 31 | $\left[\mathrm{Cr}^{\text {III }}\right.$ urea $\left.{ }_{6}\right]\left(\mathrm{NO}_{3}\right)_{3}$ | 5.3 | (595),592.9 | (585),583.4 | (53),49.9 | 10.7 |
| 77 | $\left[\mathrm{Cr}^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{6}\right]\left(\mathrm{SO}_{4}\right) \mathrm{Cl}$. | 5.3 | 593.1 | 583.3 | (55),50.1 | 11 |
| 36 | $\mathrm{LaCr}^{\text {III }} \mathrm{O}_{3}$ | [2.5],4.5 | (596),593.2 | (586),583.1 | - | 12 |
| )0 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right]\left[\mathrm{Cr}^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]$ | 4.5 | 593 | (585),583.0 | 50 broad | - |
| ;7 |  | 4.8 | (594),592.1 | (585),582.9 | (53),50 | 8.2 |

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Table 6. (continued).

|  | Compound | $\mathrm{C}_{\mathrm{st}}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | I(3p) | $I(3 \mathrm{~d}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 387 | $\mathrm{PbCr}^{\text {VI }} \mathrm{O}_{4}$. | 3.3 | 592.2 | 582.9 | 52.7 | - |
| 76 | $\left(\mathrm{NH}_{4}\right)_{3}\left[\mathrm{CrII}_{\left.\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]}\right.$ | 5.2 | (594),592.5 | (585),582.8 | - | - |
| 86 | $\mathrm{NH}_{4}\left[\mathrm{CrIII}^{\left.\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right] \ldots . . .}\right.$ | [3.7],5.2 | (594),592.0 | 582.8 | 50.0 | - |
| 125 | methylene blue[ $\mathrm{CrIII}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS}$ | S) $\left.{ }_{4}\right] \quad 5.0$ | 592.4 asym. | (584),582.4 | - | - |
| 388 | $\mathrm{Cr}_{2} \mathrm{O}_{3}$ | 4.2 | (594),592.3 | (584),582.3 | (51),49.5 | 8.2 |
| 126 | $\mathrm{Cr}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{2}\right)_{3}$ | 5.9 | 589.6 | 580.4 | 48.0 | - |
| 389 | Cr, powder, oxidized . . . . . . . | 4.5 | 592.7 | 582.8 | 51.3,49.6 | - |
| 390 | $\mathrm{CsMnO}_{4}$ (shoulders $\mathrm{Mn}^{\text {IV }}$ ) | [2.7],4.7 | 663.4,(660) | 652.3,(648.7) | 61.3 | - |
| 391 | $\mathrm{Ba}\left(\mathrm{MnO}_{4}\right)_{2}$ (" '") | 4.4 | 663,660.1 | 651.2,648.7 | 60,57 | - |
| 368 | $\mathrm{KMnO}_{4}$ (" '") | 5.1 | 663,659.7 | 651.2,(647.9) | 60.4,55.7 | - |
| 89 | [ $\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}$ ] $\mathrm{MnO}_{4}$ ('، '') . . . . . . | 4.7 | 662.8,659.8 | 651.4,(648.2) | 59.5,55.5 | - |
| 604 | $\mathrm{Na}_{7} \mathrm{H}_{4}\left[\mathrm{Mn}^{\text {IV }}\left(\mathrm{IO}_{6}\right)_{3}\right] \ldots . . . . . .$. | 4.1 | 658 broad | 648.4 | - | - |
| 325 | $\mathrm{MnCl}_{2}, 4 \mathrm{H}_{2} \mathrm{O}$ | 4.3 | 664.8,659.9 | 651.9,648.2 | (59),55.4) | - |
| 392 | $\alpha$-type $\mathrm{MnO}_{2}$ | 4.7 | (663),659.6 | (652),648.0 | 55.5 | - |
| 393 | $\mathrm{Mn}^{\mathrm{II}} \mathrm{C}_{2} \mathrm{O}_{4}, 2 \mathrm{H}_{2} \mathrm{O} \ldots \ldots . . . . . .$. | 4.7 | 661.3 broad | 647.7 broad | (59),55.0 | 11.3 |
| 66 | $\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{Mn}^{\text {II }} \mathrm{Br}_{4}$ | 4.6 | 663,657.8 | 650.6,646.4 | (55),53.2 | 8.5 |
| 70 | $\left(\mathrm{NH}_{4}\right)_{2}\left[\mathrm{Fe}^{\mathrm{III}}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right] \ldots \ldots .$. | 4.8 | (739.8),733.1 | (727.8),718.9 | 63.6 | 13.6,12. |
| 120 | [ $\mathrm{Fe}^{\mathrm{III}} \mathrm{urea}_{6}$ ] $\left(\mathrm{ClO}_{4}\right)_{3} \ldots \ldots . . .$. | 5.1 | (735),731.7 | (726),717.8 | 63,62 | 10.2 |
| 30 | $\mathrm{Fe}{ }^{\mathrm{III}}\left(\mathrm{NO}_{3}\right)_{3}, 9 \mathrm{H}_{2} \mathrm{O}$ | 4.8 | (735),731.0 | (724),717.6 | (64.5),62.1 | 10 |
| 394 | $\left(\mathrm{NH}_{4}\right)_{3}\left[\mathrm{Fe}^{\mathrm{III}}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right] \ldots . . . .$. | 5.0 | (729)726 | 717.5 | 63,60 | - |
| 369 | $\mathrm{K}_{3}\left[\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_{6}\right]$ | 5.4 | 728.6 | 717.1 | 60.9 | 12.7 |
| 395 | $\mathrm{Fe}^{\mathrm{III}} \mathrm{O}_{3}{ }_{3}$ | 4.4 | (739.2),730.2 | 724.8,716.6 | (65),62.3 | 13.6,10. |
| 396 | $\mathrm{Fe}_{3} \mathrm{O}_{4}$ | 5.0 | 730.5 | (719.2),716.5 | (68),61.5 | - |
| 35 | $\mathrm{Na}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{5} \mathrm{NO}\right]$ | 4.7 | 729.2 | 716.3 | 62.8 | - |
| 397 | $\mathrm{Fe}^{\left[1 \mathrm{C}_{2} \mathrm{O}_{4}, 2 \mathrm{H}_{2} \mathrm{O}\right.}$ | 4.3 | (733),729.7 | (719),716.0 | 70,67,61.3 | - |
| 398 | $\mathrm{Fe}^{\mathrm{III}} 4_{4}\left[\mathrm{Fe}^{\mathrm{II}}(\mathrm{CN})_{6}\right]_{3}$ | 5.1 | (731),726.5 | (717),713.5 | 61 | - |
| 154 | $\mathrm{CuII}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right], 11 \mathrm{H}_{2} \mathrm{O} \ldots \ldots$. | 4.8 | 727.2 | 714.2 | 60.8 | - |
| 175 | $\mathrm{Ru}^{\mathrm{III}}{ }_{4}\left[\mathrm{Fe}^{\mathrm{II}}(\mathrm{CN})_{6}\right]_{3}$ | 4.9 | 727 | 713.6 | 60.2 | - |
| 176 | $\mathrm{Fe}^{\mathrm{III}}{ }_{4}\left[\mathrm{Ru}^{\mathrm{II}}(\mathrm{CN})_{6}\right]_{3}$ | 4.6 | (731),726.8 | 717.3 | - | - |
| 177 | $\mathrm{Fe}^{\mathrm{III}}{ }_{4}\left[\mathrm{Os}^{\text {II }}(\mathrm{CN})_{6}\right]_{3} \ldots$ | 4.6 | (731),728 | 717.5,714.7 | - | - |
| 145 | $\mathrm{Na}_{4}\left[\mathrm{Fe}^{\mathrm{II}}(\mathrm{CN})_{6}\right], 10 \mathrm{H}_{2} \mathrm{O} \ldots \ldots$. | 4.7 | 727.7 | 714.7 | 61.5 | 8.2 |
| 365 | $\mathrm{K}_{4}\left[\mathrm{Fe}^{\mathrm{II}}(\mathrm{CN})_{6}\right]$. | 5.1 | 727.2 | 714.3 | 60.7 | 11.5 |
| 131 | $\left[\mathrm{Fe}^{\mathrm{II}} \mathrm{dip}_{3}\right] \mathrm{Br}_{2}$ | 5.6 | 726.0 | 713.2 | 60.6 | - |
| 188 | $\mathrm{Co}^{\mathrm{II}} \mathrm{F}_{2}$ | [1.1],5.4 | 814,808.3 | (798),792.1 | (75),71.2 | 14 |
| 104 | $\mathrm{Cs}_{3}\left[\mathrm{Co}^{\mathrm{III}}(\mathrm{CN})_{6}\right]$. | [2.5],4.6 | 804.2 | 789.1 | 71 | - |
| 115 | $\left.\mathrm{Co}^{\mathrm{II}}{ }_{[ } \mathrm{Pd}(\mathrm{CN})_{4}\right] \ldots . . . . . . . . . . . .$. | [2],4.0 | (810),804.5 | (792),788.8 | (72),68.5 | - |
| 9 | $\left[\mathrm{Co}^{\text {III }}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Be}_{2}(\mathrm{OH})_{3}\left(\mathrm{CO}_{3}\right)_{2}\right]$ | [2.8],4.6 | 803.5 | 788.6 | - | 11 |
| 67 | $\left[\mathrm{Co}{ }^{\text {III }}\left(\mathrm{NH}_{3}\right)_{6}\right]_{7}\left[\mathrm{Cu}\left(\mathrm{IO}_{6}\right)_{2}\right]_{3} \ldots \ldots$ | 4.7 | 803.5 | 788.6 | 69.3 | - |
| 584 | $\left[\mathrm{CoIII}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{Th}\left(\mathrm{CO}_{3}\right)_{5}\right] \ldots .$. | [2.3],4.2 | 803.6 | 788.6 | - | - |
| 135 | $\left.\left[\mathrm{Co}{ }^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{6}\right)\right]_{2}\left[\mathrm{Ce}\left(\mathrm{CO}_{3}\right)_{5}\right] \ldots$ | 4.2 | 803.3 | 788.3 | - | - |
| 83 | $\left[\mathrm{CoIII}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Au}\left(\mathrm{S}_{2} \mathrm{O}_{3}\right)_{2}\right] \ldots .$. | 4.4 | 803.2 | 788.2 | 69.2 | - |
| 136 | $\mathrm{Co}^{\text {II }}{ }_{2}\left[\mathrm{Os}(\mathrm{CN})_{6}\right]$ | 5.0 | 804 | (790),788.2 | (71) | - |
| 161 | $\mathrm{Co}^{\mathrm{II}}{ }_{2}\left[\mathrm{Ru}(\mathrm{CN})_{6}\right] \ldots . . . . . . . . . . . .$. | 4.5 | 804 | 788.0 | 70 | - |
| 87 | $\left[\mathrm{Co}^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left(\mathrm{SiF}_{6}\right)_{3}$. | 4.4 | 803.0 | 787.9 | 69.1 | - |

Table 6. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{p})$ | $I(3 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 32 | $\mathrm{Na}_{3}\left[\mathrm{Co}^{\text {III }}(\mathrm{CN})_{6}\right]$. | 4.8 | 802.9 | 787.9 | 69 | 10 |
| 05 | $\left[\mathrm{Co}^{\text {II }}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.8 | 809.3,804.3 | (793),787.9 | 73,70,68 | 11,9 |
| 55 | $\mathrm{Co}^{\text {II }}(\mathrm{NCS})_{4} \mathrm{Hg} \ldots .$. | 4.7 | 809.3,804.0 | 792.5,787.9 | 73,68 | , |
| 77 | $\left[\mathrm{Co}^{\text {III }} \mathrm{en}_{2} \mathrm{Cl}_{2}\right] \mathrm{PF}_{6}$. | 4.7 | 802.9 | 787.9 | 68.8 | - |
| 40 | $\mathrm{H}_{3} \mathrm{Co}^{\text {III }}(\mathrm{CN})_{6} \ldots$ | 4.7 | 802.8 | 787.8 | 68.8 | 10.7 |
| 31 | $\left[\mathrm{Co}^{\text {III }} \mathrm{en}_{2} \mathrm{Cl}_{2}\right]_{2} \mathrm{PbCl}_{6}$ | [3.0],5.0 | 802.8 | 787.7 | - | - |
| 78 | $\left[\mathrm{Co}^{\text {III }} \mathrm{en}_{2} \mathrm{Cl}_{2}\right]_{3}\left(\mathrm{PWW}_{12} \mathrm{O}_{40}\right)$ | 4.0 | 802.5 | 787.5 | 68 | - |
| 4 | $\mathrm{Li}_{3}\left[\mathrm{Co}^{\text {III }}(\mathrm{CN})_{6}\right]$. | 4.7 | 802.5 | 787.5 | 68.7 | 9.6 |
| 99 | $\mathrm{Co}^{\mathrm{III}} 2_{2} \mathrm{O}_{3} \ldots$ | [2.8],4.9 | 802.4 | 787.3 | 67.8 | - |
| 05 | $\begin{gathered} {\left[\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Co}^{\mathrm{III}}\left(\mathrm{O}_{2}\right) \mathrm{Co} \mathrm{III}\left(\mathrm{NH}_{3}\right)_{5}\right]} \\ \left(\mathrm{SO}_{4}\right)_{2} \mathrm{HSO}_{4} \ldots \ldots \ldots \ldots \ldots \end{gathered}$ | 5.3 | 802.4 | 787.3 | 68.0 | - |
| )9 | $\left[\mathrm{CoIII}_{\left.\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{SbCl}_{6} \ldots \ldots . .}\right.$ | 4.3 | 802.3 | 787.3 | 68.5 | - |
| 39 | $\left[\mathrm{CoIII}_{\left.\mathrm{en}_{2} \mathrm{Cl}_{2}\right]} \mathrm{MnO}_{4}\right.$ | 4.7 | 802.4 | 787.3 | 68.7 | - |
| j0 | $\left(\mathrm{NH}_{4}\right)_{3}\left[\mathrm{Co}^{\text {III }}(\mathrm{CN})_{6}\right]$ | 4.8 | 802.3 | 787.3 | 68.6 | - |
| ;3 | $\mathrm{Cu}_{3}\left[\mathrm{Co}^{\text {III }}(\mathrm{CN})_{6}\right]_{2}, 11 \mathrm{H}_{2} \mathrm{O} \ldots$. | 4.5 | 802.5 | 787.3 | 69 | - |
| 38 | $\left[\mathrm{CoIII}^{\text {IIn }}{ }_{2} \mathrm{Cl}_{2}\right] \mathrm{BF}_{4}$ | 4.6 | 802.2 | 787.2 | 68.6 | - |
| ;8 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{4}\right)_{4}\right]_{3}\left[\mathrm{Co}^{\text {III }}(\mathrm{CN})_{6}\right]$ | 5.0 | 802.2 | 787.2 | 68.3 | - |
| 15 | $\left[\mathrm{Co}^{\text {III }} \mathrm{en}_{2} \mathrm{Cl}_{2}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ | 5.2 | 802.2 | 787.1 | 68.1 | - |
| ;2 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{3}\left[\mathrm{Co}^{\mathrm{III}}(\mathrm{CN})_{6}\right] \ldots$ | 4.9 | 802.0 | 787.0 | 68.1 | - |
| 10 | $\mathrm{K}_{3}\left[\mathrm{Co}^{\text {III }}(\mathrm{CN})_{6}\right]$. | 4.7 | 802 | 787.0 | - | 13.4 |
| 11 | $\mathrm{Co}^{\text {II }} \mathrm{araca}_{8}$ | [3],5.0 | 808,802.4 | (793),(791),786.9 | 67 | 9.4 |
| 17 | $\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{3}\left[\mathrm{Co}^{\mathrm{III}}(\mathrm{CN})_{6}\right] \ldots$. | 5.0 | 801.8 | 786.8 | 68 | - |
| 2 | $\left[\mathrm{Co}^{\text {III }} \mathrm{en}_{2} \mathrm{Cl}_{2}\right] \mathrm{NO}_{3}$ | 4.4 | 801.6 | 786.6 | 68 | - |
| 0 | $\left[\mathrm{Co}^{\mathrm{III}} \mathrm{en}_{2} \mathrm{Cl}_{2}\right]\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]$. | 4.5 | 801.6 | 786.6 | 68.1 | - |
| 2 | $\mathrm{Co}^{\mathrm{II}}\left(\mathrm{IO}_{3}\right)_{2}$ | 3.5 | 802.5 | 786.5 | - | - |
| 2 | repeated | [2.4],4.5 | 809,803.4 | 793.3,787.9 | - | 11,(8) |
| 2 | $\left[\mathrm{Co}^{\text {III }} \mathrm{en}_{2} \mathrm{Cl}_{2}\right] \mathrm{ReO}_{4}$ | 5.0 | 801.6 | 786.5 | 67.5 | - |
| 4 | $\mathrm{Co}^{\text {III }} \mathrm{acaca}_{3}$. | 4.9 | 801.5 | 786.4 | 67.2 | 9 |
| 6 | $\left[\mathrm{Co}{ }^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{BiCl}_{6}$. | 3.6 | 801.0 | 786.1 | 67.2 | 10.1 |
| 9 | $\left[\mathrm{Co}{ }^{\text {III }}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}_{2}\right] \mathrm{Cl}$. | 3.9 | 800.4 | 785.4 | 67.5 | 9.2 |
| 5 | $\left[\mathrm{Co}{ }^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}$. | 3.9 | 800.3 | 785.2 | 67.4 | 10 |
| 7 | $\mathrm{Co}^{\mathrm{III}}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{3}$. | 6.4 | 799.6 | 784.7 | - | - |
| 1 | $\mathrm{Co}^{\text {III }}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3} \ldots \ldots . .$. | 5.2 | 799.2 | 784.1 | 66 | - |

ible 7. Photo-electron signals of nickel. High-spin complexes ( $S=1$ ) are given first, owing four signals (separated by effects of interelectronic repulsion) in the 2 p region, llowed by low-spin complexes $(S=0)$ giving only two. In iodides, $\mathrm{Ni}^{2} \mathrm{p}_{1 / 2}$ tends to coincide with $\mathrm{I}^{2} \mathrm{p}_{3 / 2}$.

| Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{p})$ | $I(3 \mathrm{~d})$ |
| :--- | :--- | :--- | :--- | :--- | :--- |

$\mathrm{KNiF}_{3}$ $3.6-882.2$
869.9,864.0
77.4
12.6

Table 7. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{p})$ | $I(3 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 209 | repeated | [1.3],4.5 | 889.8,883.7 | 871.7,865.8 | - | 12 |
| 221 | $\mathrm{NiF}_{2}, 4 \mathrm{H}_{2} \mathrm{O}$ | [2.6],4.7 | 887.8,882.5 | 870.5,864.4 | (79),76.6 | 12 |
| 612 | $\mathrm{Ni}\left(\mathrm{IO}_{3}\right)_{2}$ | [2.5], 4.9 | - ,(882.4) | 870.5,863.9 | 82,77 | (11 |
| 134 | $\mathrm{Ni}_{2}\left[\mathrm{Os}(\mathrm{CN})_{6}\right]$ | 5.2 | (887) ,880.6 | (869) ,862.9 | (78),76.2 |  |
| 406 | ${ }_{[\mathrm{Ni} \mathrm{en}}^{3} \mathrm{l} \mathrm{PtI}_{6}$ | 4.8 | 882 | 870 ,862.8 | - |  |
| 91 | $\left[\mathrm{Ni}(\mathrm{CN})_{2}\left(\mathrm{NH}_{3}\right)\left(\mathrm{C}_{4} \mathrm{H}_{4} \mathrm{~S}\right)\right] \ldots .$. | 5.5 | 887 ,880.3 | 869.8,862.7 | (78),74.9 | 10 |
| 162 | $\mathrm{Ni}_{2}\left[\mathrm{Ru}(\mathrm{CN})_{6}\right]$ | 4.5 | (886) , 880 | (869) ,862.7 | (77),75 |  |
| 407 | NiO, black. . . . . . . . . . . . . . . . | [2.2],4.9 | 887.0,880.4 | 868.5,862.6 | - | 10 |
| 408 | NiO , pale. | [2.5],4.8 | 886.8,879.9 | 868.6,862.4 | (80),75.4 | 11 |
| 409 | $\mathrm{NiC}_{2} \mathrm{O}_{4}, 2 \mathrm{H}_{2} \mathrm{O}$ | 4.3 | $886,879.9$ | 868 ,862.1 | (78),75.0 | 10 |
| 410 | [ Ni en 3 ] $\mathrm{I}_{2}$ | [2.7],4.9 | 885 ,881 | 868.2,862.1 | 79.2,74.7 |  |
| 273 | $\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{SO}_{4} \cdots \ldots . . . . .$. | 4.1 | 885.2,879.3 | 867 ,861.9 | (81),74.8 | 11 |
| 156 | [ Ni en 2$]\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]$. | 4.1 | 884 ,878.5 | 868 ,861.0 | 74 |  |
| 411 | $\mathrm{Ni}_{3} \mathrm{aca}_{6}$ | 5.3 | 884 ,878.6 | 866 ,860.9 | (77),73.6 | $\varepsilon$ |
| 142 | [ Ni en 2$]\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]$ | 5.0 | (884) ,878.2 | (867) , 860.9 | 74 |  |
| 96 | $\left[\mathrm{Ni}\left(\mathrm{et}_{4} \mathrm{den}\right) \mathrm{Cl}\right] \mathrm{Cl}$ | 5.1 | 884.5,877.9 | 866.9,860.6 | (76),73.9 |  |
| 148 | $\left[\mathrm{Ni} \mathrm{en} \mathrm{n}_{2}\right]\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.2 | (884) , 878.0 | 866.5,860.6 | $78,73.7$ |  |
| 147 | $[\mathrm{Ni} \mathrm{en} 3]\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]$ | 4.9 | (885) , 877.9 | (867) ,860.5 | (76),74.1 |  |
| 137 | $\mathrm{Ni}\left(\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$ | 3.8 | 883 ,877.8 | 865.6,860.4 | (80),74.3 |  |
| 152 | $[\mathrm{Ni} \mathrm{en} 3]\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.4 | 886 ,878.3 | 867 ,860.4 | 79,73 |  |
| 151 | [ Ni tren( NCS$)_{2}$ ] | 4.6 | 883 ,878.2 | 867 ,860.3 | 79,73 |  |
| 138 | [ Ni (tren)phen] $\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.5 | 882 ,877.8 | 866 ,860.2 | 80,73.5 |  |
| 157 | $[\mathrm{Ni} \mathrm{en} 3]\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]$. | 3.9 | 885 ,877.7 | 866.5,860.0 | 73 |  |
| 150 | [ $\mathrm{Ni} \mathrm{en}_{3}$ ] $\mathrm{SO}_{4}$ | 3.8 | 883.2,877.5 | 866.0,859.9 | (79),73.1 |  |
| 412 | [ Ni phen3] ${ }^{\left(\mathrm{ClO}_{4}\right)_{2}}$ | 5.0 | 884 ,877.6 | 867 ,859.9 | - |  |
| 133 | [ Ni daes $_{2}$ ] $\left(\mathrm{ClO}_{4}\right)_{2}$. | 4.6 | - ,877 | 866 ,859.8 | 74 |  |
| 413 | $\left[\mathrm{Ni}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{2}\right.$ phen]. | 5.2 | - ,877 | 865 ,859.6 | 73 |  |
| 106 | $[\mathrm{Ph} \mathrm{ns} 3]_{2} \mathrm{Ni}\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.6 | 882, ,876.7 | 864 ,859.4 | $\rightarrow$ |  |
| 414 | [ Ni pyridinalhydrazone 3 ] $\left(\mathrm{ClO}_{4}\right)_{2}$ | 3.0 | 881 ,876 | 865 ,858.3 | - |  |
| 53 | [ Ni en 2$]\left(\mathrm{AgI}_{2}\right)_{2} \ldots \ldots . . . . .$. | [2.0],4.6 | 881 | 862.4 | 76.2 |  |
| 60 | [ Ni en 2$]\left(\mathrm{CuI}_{2}\right)_{2} \ldots \ldots . .$. | [2.2],4.6 | 881 | 862.2 | 76 |  |
| 160 | $\mathrm{K}_{2}\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]$ | 4.9 | 878.2 | 860.8 | 74.8 |  |
| 113 | [ Ni en 2$]\left(\mathrm{ClO}_{4}\right)_{2} \ldots \ldots .$. | 4.6 | 877.6 | 860.5 | 74.4 | 1 |
| 33 | [ $\mathrm{Ni} \mathrm{aminin}_{2}$ ] $\left(\mathrm{NO}_{3}\right)_{2}$. | 4.6 | 877.2 | 860.1 | 73.8 | 1 |
| 307 | [ Ni curtis ${ }_{2}$ ] $\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.7 | 877.5 | 860.1 | 73 |  |
| 415 | [ Ni aminin $\left._{2} \mathrm{Br}\right] \mathrm{Br} \ldots . . . . . . . . .$. | 4.5 | 876.9 | 859.8 | 73.3 |  |
| 116 | $\mathrm{Ni} \mathrm{dmg}_{2}$ | 4.9 | 876.6 | 859.6 | 73.6 |  |
| 245 | $\mathrm{Ni}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{2} \ldots \ldots . . . .$. | 5.1 | 876 | 859.2 | 73.6 |  |
| 127 | $\mathrm{Ni}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}$. | 4.7 | 875.8 | 858.7 | 73.0 |  |
| 416 | $\mathrm{Ni}_{2} \mathrm{O}_{3}$ | 4.5 | 884.8,878.0 | 866.3,860.0 | (75),73.2 |  |
| 417 | Ni, powder (oxidized?) | 4.9 | 880.3,(877.6) | 862.8,(859.5) | - |  |
| 418 | Ni, foil . . . . . . . . . . . . . . . | 5.2 | 878.2,876 | 860.5,857.8 | 72.5,71 |  |

Table 8. Photo-electron signals of copper. Satellites are observed in the 2 p region in the case of copper(II) compounds.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{p})$ | $I(3 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 214 | $\mathrm{Cu}^{\text {II }} \mathrm{F}_{2}, 2 \mathrm{H}_{2} \mathrm{O}$ | [3.0],5.2 | 971,963.5 | 950.8,943.3 | 86.0 | 13.3 |
| 256 | $\mathrm{Cu}^{\mathrm{II}} \mathrm{SO}_{4}, 3 \mathrm{H}_{2} \mathrm{O}$ | 5.0 | 962.2 | 951,947,942.1 | - | 13.0 |
| 121 | $\mathrm{Cu}^{\mathrm{II}} 3\left[\operatorname{Ir}(\mathrm{CN})_{6}\right]_{2}, 11 \mathrm{H}_{2} \mathrm{O}$ | 4.5 | 962.3 | 948,942.0 | (89), 86.7 | - |
| 613 | $\mathrm{Cu}^{\mathrm{II}}\left(\mathrm{IO}_{3}\right)_{2}$ | [2.3],4.4 | 969,961.2 | 949.1,941.7 | 85 | - |
| 419 | $\mathrm{Cu}^{\mathrm{II}} \mathrm{O}$. | [2.2],4.9 | (963.2),961.4 | 950.2,941.5 | (93.3), 85.6 | - |
| 67 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{7}\left[\mathrm{Cu}{ }^{\mathrm{III}}\left(\mathrm{IO}_{6}\right)_{2}\right]$ | 4.7 | 961.0 | 949 weak, 941.3 | 85 | - |
| 153 | $\mathrm{Cu}^{\mathrm{II}}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]_{2} 11 \mathrm{H}_{2} \mathrm{O}$. | 4.5 | 961.5 | 950,941.3 | 85 | - |
| 242 | $\mathrm{CuII}\left(\mathrm{UO}_{2}\right)_{2}\left(\mathrm{PO}_{4}\right)_{2} \ldots \ldots$ | [2.0],4.6 | 961 broad | 951,(943),940.9 | - | - |
| 29 | $\left[\mathrm{Cu}^{\text {II }} \mathrm{en}_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}$ | 4.6 | 959.9 | 949.0,940.1,(937.6) | 82.6 | 10.8 |
| 97 | $\mathrm{Cu}^{\mathrm{I}} \mathrm{CN}$ | [3.2],5.3 | 959.8 | 939.9 | 83.2 | 11.0 |
| 420 | $\mathrm{Cu}^{\mathrm{I}} \mathrm{CHg}_{4}$ | [4.3],6.1 | 959.4 | 939.6 | 82.0 | 10 |
| 123 | $\left[\mathrm{Cu}^{\mathrm{II}}\right.$ denBr]Br | 4.7 | (961.0), 959.0 | 949,939.4,(936.0) | - | - |
| 60 | $[\mathrm{Ni} \mathrm{en} 2]\left(\mathrm{Cu}^{\mathrm{I}} \mathrm{I}_{2}\right)_{2} \ldots \ldots$. | [ [2.2],4.6 | 958.8 | 939.0 | 82.4 | - |
| 98 | $\mathrm{Cu}^{\mathrm{II}}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}$ | 4.4 | 8.6,(960.6),959.0 | 948.6,(940),939.0 | 83.3 | - |
| 270 | $\mathrm{Cu}^{\mathrm{II}} \mathrm{SO}_{4}, 5 \mathrm{H}_{2} \mathrm{O}$ | 5.3 | 958.6 | (941.4),938.7 | - | - |
| 154 | $\mathrm{CuII}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right], 11 \mathrm{H}_{2} \mathrm{O}$ | 4.8 | (961.2),958.4 | 949,(941.2),938.4 | 83.3 | - |
| 164 | $\mathrm{Cu}^{\mathrm{II}} 2\left(\mathrm{Os}[\mathrm{CN})_{6}\right]$ | 5.0 | (961),958.3 | 949.2,(941.2),938.4 | 83 | - |
| 180 | $\mathrm{Cu}^{\text {II }}$ phthalocyanine | 6.0 | 966,958.2 | 947,938.2 | - | - |
| 174 | $\mathrm{CuII}_{2}\left[\mathrm{Ru}(\mathrm{CN})_{6}\right]$ | 4.4 | (960),957.4 | 948,(940),937.7 | 83 | - |
| 293 | CuS | 5.5 | (960),957.4 | 949,(939),937.3 | 81 | - |
| - | $5 \mathrm{MgF}_{2}: 1 \mathrm{CuS} \ldots . .$. | . [0.8],4.8 | (965),958.9 | 951,(941.8),938.8 | - | - |

Table 9. Photo-electron signals of zinc, gallium, germanium and arsenic.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I\left(3 \mathrm{p}_{1 / 2}\right)$ | $I\left(3 \mathrm{p}_{3 / 2}\right)$ | $1(3 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 212 | $\left[\mathrm{Zn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{SiF}_{6}$ | [2.5],4.9 | 1052.65 | 1029.5 | (101) | 97.5 | 18.9 |
| 421 | $\mathrm{Zn}\left(\mathrm{IO}_{3}\right)_{2}$. | [2.4],5.0 | 1052.4 | 1029.2 | - | - | 18.2 |
| 283 | ZnS | [2.2],4.6 | 1052.2 | 1029.0 | (97) | 94 | 18.0 |
| 230 | $\mathrm{NaZn}\left(\mathrm{UO}_{2}\right)_{3}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{9}$ | 4.6 | 1054 | 1029 | - | - | - |
| 422 | $\mathrm{Zn}\left(\mathrm{UO}_{2}\right)_{2}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{6}$. | [3.7],5.6 | 1052.0 | 1028.8 | - | - | 17.7 |
| 423 | Zn aca 2 | 5.3 | 1050.5 | 1027.4 | - | - | 16.2 |
| 424 | ZnO | 4.9 | 1049.8 | 1026.7 | (97) | 94.2 | 15.7 |
| 204 | $\mathrm{GaF}_{3}, 3 \mathrm{H}_{2} \mathrm{O}$. | [2.3],5.0 | 1153.4 | 1126.4 | 118 | 114.8 | 29.5 |
| 425 | $\mathrm{Ca}_{2} \mathrm{O}_{3}$ | [1.8],4.9 | 1152.6 | 1125.7 | 117.4 | 114.2 | 28.7 |
| 281 | GaS | [3.0],5.0 | 1151.8 | 1125.2 | - | - | 27.9 |
| 41 | $\left(\mathrm{NH}_{4}\right)_{3} \mathrm{GaF}_{6}$. | [3.7],5.4 | 1151.8 | 1125.0 | 116.7 | 113.1 | 27.6 |
| 261 | $\mathrm{Ga}_{2}\left(\mathrm{SO}_{4}\right)_{3}$. | 4.4 | 1151.9 | 1124.9 | 116 | 113 | 27.6 |
| 426 | Ga , coherent. | 4.2 | - | 1120.6 | (112) | 108.0 | 22.7 |
| 189 | $\mathrm{K}_{2} \mathrm{GeF}_{6}$ | [1.3],4.7 | 1260.9 | 1229.7 | 138.5 | 134.2 | 42.3 |
| 427 | $\mathrm{GeO}_{2}$. . | [2.1],4.7 | 1259.0 | 1227.8 | 136.7 | 132.9 | 41.0 |

Table 9. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(2 \mathrm{p}_{1 / 2}\right)$ | $I\left(2 \mathrm{p}_{3 / 2}\right)$ | $I\left(3 \mathrm{p}_{1 / 2}\right)$ | $I\left(3 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 428 | $\mathrm{LaAsO}_{4}$ | [2.0],4.7 | 1370.1 | 1334.1 | 157.0 | 152.4 | 53.3 |
| 429 | NdAsO 4 | [1.9],4.5 | 1369.7 | 1333.5 | 157.3 | 152.5 | 53.7 |
| 356 | $\mathrm{K}_{2} \mathrm{HAsO}_{4}$ | [2.8],4.5 | 1369.3 | 1333.3 | 156.5 | 151.7 | 52.9 |
| 430 | $\mathrm{YbAsO}_{4}$ | [2.5], 4.2 | 1368.8 | 1332.7 | 155.4 | 150.9 | 52.2 |
| 597 | $\mathrm{Na}_{2} \mathrm{HAsO}_{4}, 7 \mathrm{H}_{2} \mathrm{O}$ | 4.3 | 1368.4 | 1332.4 | 155.4 | 150.5 | 51.6 |
| 431 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{PtI}_{6}$ | 4.8 | 1368.3 | 1332.3 | - | - | - |
| 594 | $\mathrm{NaAsO}_{2}$ | 4.7 | 1367.9 | 1331.9 | - | - | 51.3 |
| 432 | $\mathrm{Ag}_{3} \mathrm{AsO}_{4}$ | 4.7 | 1367.9 | 1331.9 | 154.4 | 149.9 | 50.9 |
| 172 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2}\left[\mathrm{Cd}(\mathrm{NCSe})_{4}\right]$ | 4.5 | 1367.5 | 1331.4 | - | - | 50.2 |
| 344 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{PbCl}_{6}$. | 4.8 | 1367.5 | 1331.4 | - | 149.0 | 50.3 |
| 346 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{ReCl}_{6}$. | 4.9 | 1367.3 | 1331.3 | - | - | - |
| 170 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2}\left[\mathrm{Os}(\mathrm{SCN})_{6}\right]$ | 5.2 | 1367.0 | 1331.3 | - | - | - |
| 170 | repeated | 4.6 | 1367.2 | 1331.3 | 154 | 149.2 | 50.4 |
| 178 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{SCN}$ | 4.8 | 1367.1 | 1331.1 | 154 | 149.0 | 50.2 |
| 433 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{RuO}_{4}$ | 4.5 | 1367.0 | 1331.0 | - | - | 50.1 |
| 434 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{ReO}_{4}$ | 3.9 | 1366.7 | 1330.9 | - | - | - |
| 610 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]\left[\mathrm{OsO}_{3} \mathrm{~N}\right]$ | 4.2 | 1366.8 | 1330.9 | 155 | 149.3 | 50.7 |
| 166 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{3}\left[\operatorname{Ir}(\mathrm{SeCN})_{6}\right]$ | 4.1 | 1366.5 | 1330.7 | - | 149.3 | 49.7 |
| 298 | $\mathrm{As}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3} \ldots$ | 4.8 | 1365.8 | 1330.0 | 152 | 147.4 | 48.4 |

Table 10. Photo-electron signals of selenium and bromine.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{p}_{1 / 2}\right)$ | $I\left(3 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{~d})$ | $I(4 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 435 | $\mathrm{BaSeO}_{4}$ | [2.2],4.8 | 180 | 174.1 | - | - |
| 435 | repeated | [1.1],4.7 | 180.9 | 175.1 | 69.2 | - |
| 236 | $\mathrm{Na}_{2} \mathrm{SeO}_{4}, 10 \mathrm{H}_{2} \mathrm{O}$. | [3],4.7 | 179.3 | 173.5 | 67.8 | - |
| 232 | $\mathrm{NaHSeO}_{3}$. | [2.3],4.7 | 178.3 | 172.55 | 66.6 | - |
| 436 | $\mathrm{SeO}_{2}$ | 4.5 | 176.9 | 171.2 | 65.2 | - |
| 129 | $\mathrm{K}_{2}\left[\mathrm{Pt}(\mathrm{SeCN})_{6}\right]$ | 4.8 | 174.0 | 168.3 | - | - |
| 437 | $\mathrm{Tl}_{3} \mathrm{VSe}_{4}$ | 4.7 | 174 | 168.0 | - | - |
| 40 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{SeCN}$. | 4.6 | 173 | 167.0 | 61.1 | - |
| 166 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{3}\left[\operatorname{Ir}(\mathrm{SeCN})_{6}\right]$ | 4.1 | 172.7 | 166.8 | 60.4 | - |
| 171 | KSeCN . . . . . . . . . | 3.6 | 172.4 | 166.7 | 60.7 | - |
| 171 | repeated. | [3.3],5.0 | 172.1 | 166.3 | 61.9 | - |
| 438 | $\mathrm{Tl}_{3} \mathrm{NbSe}_{4}$. | 4.7 | (174),173 | (168),166.7 | - | - |
| 439 | CdSe. | [4],5.7 | 172.3 | 166.7 | 60.7 | - |
| 172 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2}\left[\mathrm{Cd}(\mathrm{NCSe})_{4}\right]$ | 4.5 | 172.5 | 166.6 | 60.6 | - |
| 440 | $\mathrm{Tl}_{3} \mathrm{TaSe}_{4}$ | 4.3 | 173 | 166.5 | - | - |
| 44 | [ $\left.\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right] \mathrm{SeCN}$. | 4.2 | 172 | 166.3 | 60.3 | - |
| 239 | $\mathrm{NaBrO}_{3}$. | 5.2 | 202.3 | 195.6 | 82.4 | - |
| 361 | $\mathrm{KBrO}_{3}$. | [3.3],5.0 | - | - | 81.5 | - |

Table 10. (continued).

|  | Compound | $\mathrm{C}_{\text {St }}$ | $I\left(3 \mathrm{p}_{1 / 2}\right)$ | $I\left(3 \mathrm{p}_{3 / 2}\right)$ | $I(3 \mathrm{~d})$ | $I(4 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 441 | $\mathrm{Cs}_{2} \mathrm{PtBr}_{6}$ | [1.5],4.8 | 197.7 | 191.1 | 78.2 | 14.5 |
| 442 | $\mathrm{Cs}_{2} \mathrm{SnBr}_{6}$ | [2.9],5.2 | - | - | 76.9 | 12.0 |
| 442 | repeated | [2.0],4.8 | 197.1 | 190.5 | 77.3 | 12.2 |
| 443 | $\left(-\mathrm{CHBrCO}_{2} \mathrm{H}\right)_{2}$ | 4.8 | 196.7 | 190.0 | 76.6 | - |
| 444 | CsBr . | [1.6],4.95 | 196.7 | 189.95 | 76.7 | 12.0 |
| 352 | $\mathrm{KAuBr}_{4}$ | 3.4 | 196.35 | 189.7 | 74.2 | (12.4) |
| 227 | NaBr | [2.9],5.3 | 196.1 | 189.5 | 76.3 | 11.4 |
| 445 | RbBr | [2.7],5.1 | 196.1 | 189.4 | 76.0 | 11.3 |
| 446 | $\mathrm{PbBr}_{2}$. | [2.7],4.9 | 195.8 | 189.2 | 76.0 | 10.7 |
| 364 | $\mathrm{K}_{2} \mathrm{PtBr}_{6}$. | 2.6 | 194.8 | 188.2 | 75.2 | 12.4 |
| 364 | repeated | 5.0 | 195.8 | 189.1 | 76.0 | 13.7 |
| 353 | KBr | [3.1],4.6 | 195.4 | 188.7 | 75.7 | 10.7 |
| 447 | AgBr | [3.4],5.3 | 195.3 | 188.7 | 75.6 | - |
| 448 | $\mathrm{Cs}_{2} \mathrm{OsBr}_{6}$ | 3.8 | 194.9 | 188.5 | 75.5 | - |
| 80 | [Pd phen $\mathrm{Br}_{2}$ ] | 4.5 | 194.9 | 188.2 | 75.1 | (11.8) |
| 359 | $\mathrm{K}_{2} \mathrm{ReBr}_{6}$ | 4.8 | 194.7 | 188.1 | 75.0 | (11.4) |
| 449 | TlBr | 4.6 | 194.7 | 188.1 | 75.0 | 10.2 |
| 450 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right] \mathrm{AuBr}_{4}$ | 5.0 | 194.6 | 188.0 | 74.9 | - |
| 451 | $\mathrm{Tl}_{2} \mathrm{OsBr}_{6}$ | 6.0 | 194.2 | 187.6 | 74.5 | - |
| 54 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]\left[\mathrm{Au}(\mathrm{CN})_{2} \mathrm{Br}_{2}\right]$ | 5.3 | 194 | 187.5 | 74.0 | - |
| 92 | $\left[\mathrm{Pd}\left(\mathrm{et}_{4} \mathrm{den}\right) \mathrm{Br}\right] \mathrm{ClO}_{4} \ldots$ | 4.4 | 194.0 | 187.3 | 74.3 | - |
| 452 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2} \mathrm{OsBr}_{6}$. | 5.1 | 193.9 | 187.2 | 74.1 | 10.6 |
| 112 | $\left[\mathrm{Rh} \mathrm{py}{ }_{4} \mathrm{Br}_{2}\right] \mathrm{ClO}_{4}$ | 4.4 | 193.7 | 187.1 | 74.1 | 10.4 |
| 130 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{ReBr}_{6}$ | 4.6 | 193.6 | 186.95 | 73.8 | (10.8) |
| 66 | $\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{MnBr}_{4}$ | 4.6 | 193.7 | 186.9 | 73.8 | (9.8) |
| 63 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{Br}$ | 4.9 | 192.5 | 186.0 | 72.7 | 8.3 |
| 131 | [ $\mathrm{Fe} \mathrm{dip} \mathrm{d}_{3} \mathrm{Br}_{2}$ | 5.6 | 192.2 | 185.9 | 72.7 | - |
| 48 | $\left[\mathrm{N}\left(\mathrm{Co}_{9} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{PtBr}_{6} \ldots$ | 4.6 | 192.6 | 185.9 | 74.9 | 12.1 |

Table 11. Photo-electron signals of rubidium, strontium, yttrium, zirconium, niobium and molybdenum.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{p}_{1 / 2}\right)$ | $I\left(3 \mathrm{p}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| - | Kr (ref. 97) | - | 222.2 | 214.4 | 94.9 | 93.7 | 14.0 |
| 445 | RbBr . | [2.7],5.1 | 254.75 | 245.8 | (119) | 117.2 | 20.9 |
| 312 | $\mathrm{Rb}_{2} \mathrm{PtCl}_{6}$ | [2.5],5.0 | 254.8 | 245.8 | (119) | 117.8 | 21.5 |
| 319 | RbCl | [2.8],5.2 | 254.5 | 245.5 | 119.4 | 117.6 | 21.4 |
| 453 | RbI | [3.1],4.8 | 253.9 | 245.0 | (118) | 116.7 | 20.5 |
| 107 | $\mathrm{Rb}_{2}\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.6 | 253.6 | 244.6 | (118) | 116.7 | 20.1 |
| 222 | RbF . | 4.4 | 253.4 | 244.4 | (117.6) | 116.5 | 19.7 |
| 25 | $\mathrm{RbNO}_{3}$. | 5.0 | 253.0 | 244.1 | (117.5) | 116.2 | 19.7 |

Table 11. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{p}_{1,2}\right)$ | $I\left(3 \mathrm{p}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 275 | $\mathrm{Rb}_{2} \mathrm{SO}_{4}$ | 4.1 | 253.1 | 244.1 | (118) | 117.1 | 19.3 |
| 334 | $\mathrm{Rb}_{2}\left[\mathrm{OsCl}_{4} \mathrm{I}_{2}\right]$ | 4.6 | 252.9 | 243.9 | (117.6) | 116.2 | 19.7 |
| 20 | $\mathrm{RbUO}_{2}\left(\mathrm{NO}_{3}\right)_{3}$ | [2.7],4.8 | 252.1 | 243.2 | - | 117.3 | - |
| 197 | $\mathrm{SrF}_{2}$ | [1.7],5.5 | - | 278.6 | 145.5 | 143.2 | 28.7 |
| 197 | repeated | [1.2],5.0 | - | 278.4 | (144.5) | 143.0 | 28.8 |
| 253 | $\mathrm{SrSO}_{4}$ | [2.5],4.9 | 287 | 277.1 | (143.1) | 141.4 | 27.1 |
| 27 | $\mathrm{Sr}\left(\mathrm{NO}_{3}\right)_{2}$ | 4.7 | 286 | 275.9 | (142.6) | 140.6 | - |
| 186 | $\mathrm{YF}_{3}$ | [1.5],5.2 | 323.4 | 311.5 | (171) | 168.5 | 35.3 |
| 454 | $\mathrm{Y}\left(\mathrm{IO}_{3}\right)_{3}$ | [2.2],4.8 | 321.3 | 309.6 | (168) | 166.3 | 33.8 |
| 265 | $\mathrm{Y}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 4.4 | 320.4 | 308.4 | (167.2) | 165.3 | 32.5 |
| 377 | $\mathrm{YVO}_{4}$ | 4.7 | - | - | (165.5) | 163.8 | 31.4 |
| 455 | $\mathrm{Y}_{2} \mathrm{O}_{3}$. | 4.6 | 319.1 | 306.9 | 165.8 | 163.6 | 32 |
| 202 | $\mathrm{ZrF}_{4}$ | [1.8],4.4 | 357.6 | 343.8 | (195.6) | 193.2 | 41.5 |
| 456 | $\mathrm{Zr}\left(\mathrm{IO}_{3}\right)_{4}$ | [2.1],4.6 | 354.5 | 341.1 | (192.9) | 190.5 | 39.3 |
| 45 | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{ZrF}_{6}$. | 5.1 | 354.6 | 340.9 | 192.7 | 190.4 | 39.5 |
| 457 | $\mathrm{Pr}_{0.2} \mathrm{Zr}_{0} \cdot 8 \mathrm{O}_{1.95}$ | 4.6 | 353.0 | 339.2 | 192 | 188.3 | 37 |
| 208 | $\mathrm{K}_{2} \mathrm{NbF}_{7}$ | [3],5.0 | 389.6 | 374.4 | 219 | 216.0 | 44.8 |
| 458 | $\mathrm{Tl}_{3} \mathrm{NbS}_{4}$ | 4.8 | 388 | 371.2 | 216 | 213.4 | 41.8 |
| 459 | $\mathrm{Nb}_{2} \mathrm{O}_{5}$ | 4.4 | 386.0 | 370.6 | 215.4 | 212.7 | 41 |
| 460 | $\mathrm{Tl}_{2} \mathrm{MoO}_{4}$. | [2.6],4.8 | - | - | 242.0 | 239.0 | - |
| 595 | $\mathrm{Na}_{2} \mathrm{MoO}_{4}$ | 5.0 | 421.8 | 404.3 | 241.9 | 238.9 | 47.4 |
| 461 | $\mathrm{H}_{3} \mathrm{PMo}_{12} \mathrm{O}_{40}$ | 4.6 | 421.9 | 404.4 | 241.7 | 238.6 | 47 |
| 462 | $\mathrm{MoO}_{3}$ | 4.6 | 421.4 | 404.0 | 241.5 | 238.5 | - |
| 286 | $\mathrm{Tl}_{2}\left[\mathrm{MoO}_{2} \mathrm{~S}_{2}\right]$ | 4.7 | 421 | 403.7 | 240.6 | 237.6 | - |
| 288 | $\mathrm{Tl}_{2} \mathrm{MoS}_{4}$. | 4.4 | 419 | 402 | 239.6 | 236.7 | 45 |
| 336 | $\mathrm{K}_{3} \mathrm{MoCl}_{6}$ | 4.5 | 419.8 | 402.3 | 240.0 | 236.5 | - |
| 301 | $\mathrm{Cs}_{2} \mathrm{MoS}_{4}$. | 4.1 | - | - | 239.0 | 235.8 | - |

Table 12. Photo-electron signals of ruthenium and rhodium. It is often difficult to detect Ru3d because of the coincidence with C1s.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{p}_{1 / 2}\right)$ | $I\left(3 \mathrm{p}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{p})$ | $I(4 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 433 | $\begin{aligned} & {\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{Ru}^{\mathrm{VII}_{\mathrm{O}_{4}} \cdots}} \\ & \quad\left(\text { shoulders } \mathrm{Ru}^{\mathrm{IV}}\right) \end{aligned}$ | 4.5 | 494.0,(490) | 472.0,(468) | - | - | 54 | - |
| 39 | $\mathrm{K}_{2}\left[\mathrm{Ru}(\mathrm{NO}) \mathrm{Cl}_{5}\right]$ | [1.5],4.8 | 492.5 | 470.3 | - | - | 53.0 | - |
| 110 | $\left[\mathrm{Ru}^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{NCS}\right]\left(\mathrm{ClO}_{4}\right)_{2}$. | 4.7 | 491.9 | 469.6 | - | - | 53 | 8. |
| 124 | $\left[\mathrm{Ru}^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}$ | 4.7 | 491.5 | 469.1 | - | 287.8 | 53.7 | 8. |
| 175 | $\mathrm{Ru}^{\mathrm{III}} 4\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{3}$ | 4.9 | 490.9 | 468.5 | - | 287 | 51 | - |
| 463 | $\left.\mathrm{Ru}^{\mathrm{III}} 4{ }_{4} \mathrm{Ru}^{\mathrm{II}}(\mathrm{CN})_{6}\right]_{3}$ | 4.6 | 490.1 | 468.4 | - | - | 52 | - |
| 464 | $\mathrm{Ru}^{\mathrm{IV}} \mathrm{O}_{2}, \mathrm{xH}_{2} \mathrm{O}$ | [2],4.7 | 490.9 | 468.3 | - | 286 | - | - |
| 162 | $\mathrm{Ni}_{2}\left[\mathrm{Ru}^{\mathrm{II}}(\mathrm{CN})_{6}\right]$ | 4.5 | 490.4 | 468.0 | - | - | 51 | - |

Table 12. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{p}_{1 / 2}\right)$ | $I\left(3 \mathrm{p}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{p})$ | $I(4 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 161 | $\mathrm{Co}_{2}\left[\mathrm{Ru}^{\text {II }}(\mathrm{CN})_{6}\right]$ | 4.5 | 490.2 | 467.9 | - | - | 51 | - |
| 289 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{3}\left[\mathrm{Ru}^{\mathrm{III}}(\mathrm{NCS})_{6}\right]$ | 4.6 | 488.6 | 467.2 | - | 285.9 | - | 8.9 |
| 289 | repeated | 4.3 | 490.3 | 468.1 | - | 286.8 | 51 | - |
| 176 | $\mathrm{Fe}_{4}\left[\mathrm{Ru}^{\mathrm{II}}(\mathrm{CN})_{6}\right]_{3}$ | 4.6 | 489.7 | 467.1 | - | 286.1 | - | - |
| 174 | $\mathrm{Cu}_{2}\left[\mathrm{Ru}^{\mathrm{II}}(\mathrm{CN})_{6}\right]$. | 4.4 | 489.4 | 466.9 | - | - | - | - |
| 465 | Ru, powder (oxidized?) | 4.3 | 489.8 | (469),467.2 | - | - | - | - |
| 185 | $\mathrm{K}_{3} \mathrm{RhF}_{6}$ | [2.0],4.7 | - | 507 | 324.8 | 320.0 | 58 | 11.9 |
| 466 | $\mathrm{Cs}_{2} \mathrm{Rh}^{\mathrm{IV}} \mathrm{Cl}_{6}$ (reduced?) | [2.3],5.0 | - | - | 322.5 | 317.7 | - | 11.3 |
| 315 | $\mathrm{Cs}_{2}\left[\mathrm{Rh}^{\text {III }}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{Cl}_{5}\right]$. | [2.0],4.9 | - | - | 322.3 | 317.6 | 57 | 11.3 |
| 90 | $\left[\mathrm{Rh}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2} \ldots \ldots$ | 4.6 | - | - | 320.8 | 316.2 | - | 9.6 |
| 71 | [ Rh den $\mathrm{I}_{3}$ ] | [2.4],4.6 | 529.6 | 505.0 | 320.9 | 316.2 | - | 10.2 |
| 596 | $\mathrm{Na}_{3} \mathrm{RhCl}_{6}, 12 \mathrm{H}_{2} \mathrm{O}$. | 5.0 | - | - | 320.5 | 315.8 | 56 | 9.5 |
| 333 | $\mathrm{RhCl}_{3}$ | 4.9 | - | - | 320.2 | 315.5 | 56 | 8.9 |
| 112 | $\left[\mathrm{Rh} \mathrm{py} 4 \mathrm{Br}_{2}\right] \mathrm{ClO}_{4}$ | 4.4 | 528.5 | 504.3 | 320.0 | 315.4 | - | 9.0 |
| 111 | [ Rh den $\mathrm{Cl}_{3}$ ] | 4.8 | - | - | 320.0 | 315.3 | 56 | 8.5 |
| 467 | $\mathrm{RhI}_{3}$ | 4.5 | - | - | 319.7 | 315.1 | - | 10 |
| 106 | $[\mathrm{Rh} \mathrm{ns} 3]_{2} \mathrm{Ni}\left(\mathrm{ClO}_{4}\right)_{2}$ | 4.6 | 528 | 503.6 | 319.3 | 314.7 | - | - |
| 169 | $\mathrm{K}_{3}\left[\mathrm{Rh}(\mathrm{SCN})_{6}\right]$. | 4.7 | 527.8 | 503.1 | 319.0 | 314.3 | - | 9 |
| 294 | $\mathrm{Rh}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3}$ | 4.5 | 528.0 | 503.8 | 318.9 | 314.3 | - | 8 |
| 468 | Rh , powder | 5.2 | 527.9 | 503.5 | 318.9 | 314.2 | 55 | - |

Table 13. Photo-electron signals of palladium and silver.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{p})$ | $I(4 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 84 | $\mathrm{Cd}\left[\mathrm{Pd}^{\mathrm{IV}}(\mathrm{CN})_{6}\right]$ | [2.2],4.9 | 355.3 | 350.0 | 65.5 | 14 |
| 107 | $\mathrm{Rb}_{2}\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.6 | 350.9 | 345.65 | 62 | 10.6 |
| 115 | $\mathrm{Co}\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | [2],4.0 | 350.7 | 345.4 | 61 | 11.0 |
| 59 | trans- $\left[\mathrm{Pd}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$. | 4.8 | 350.5 | 345.3 | - | 11.1 |
| 72 | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{Pd}^{\mathrm{IV}} \mathrm{Cl}_{6} \ldots \ldots$ | 5.0 | 349.5 | 345.3 | 62 | 9.4 |
| 149 | $\mathrm{K}_{2}\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$. | 5.1 | 350.2 | 344.9 | 61 | 10 |
| 332 | $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ | 4.8 | 350.0 | 344.7 | 60 | 10.2 |
| 469 | $\mathrm{PdI}_{2}$ | 5.1 | 349.9 | 344.6 | - | 11 |
| 79 | $\left[\mathrm{Pd}\left(\mathrm{et}_{4} \mathrm{den}\right) \mathrm{Cl}\right] \mathrm{ClO}_{4}$. | [3.3],5.0 | 349.6 | 344.4 | 60 | - |
| 81 | [Pd phen $\mathrm{I}_{2}$ ] | 4.9 | 349.6 | 344.3 | - | - |
| 80 | [Pd phen $\mathrm{Br}_{2}$ ] | 4.5 | 349.5 | 344.2 | - | 9.9 |
| 148 | $\left[\mathrm{Ni} \mathrm{en}_{2}\right]\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.4 | 349.5 | 344.2 | 61 | - |
| 85 | Pd dmg 2 | 4.4 | 349.3 | 344.1 | - | - |
| 152 | $[\mathrm{Ni} \mathrm{en} 3]\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.4 | 349.4 | 344.1 | - | - |
| 143 | $[\mathrm{Pd} \mathrm{en} 2]\left[\mathrm{Pd}(\mathrm{CN})_{4}\right]$ | 4.4 | 349.4 | 344.1 | - | - |
| 102 | [ Pd phen 2 ] $\left(\mathrm{ClO}_{4}\right)_{2}$ | 5.1 | 349.3 | 344.0 | - | 9.9 |
| 128 | $\left[\mathrm{Pd}\left(\mathrm{NH}_{3}\right)_{4}\right]\left(\mathrm{CH}_{3} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SO}_{3}\right)_{2}$ | 4.8 | 349.0 | 343.7 | - | 10 |

Table 13. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{p})$ | $I(4 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 128 | repeated | 4.6 | 349.1 | 343.8 | 60 | 9.7 |
| 92 | $\left[\mathrm{Pd}\left(\mathrm{et}_{4}\right.\right.$ den) Br$] \mathrm{ClO}_{4}$ | 4.4 | 348.9 | 343.6 | 60 | - |
| 101 | [ Pd phen $\mathrm{Cl}_{2}$ ] | 4.5 | 348.8 | 343.55 | - | 10.2 |
| 119 | $[\mathrm{Pd} \mathrm{py} 4] \mathrm{SO}_{4}$ | 4.65 | 348.8 | 343.5 | 59.5 | - |
| 470 | Pd , powder . | 4.3 | 346.9 | 341.5 | 58 | - |
| 471 | $\mathrm{AgIO}_{3}$ | [2.3],4.8 | 382.6 | 376.6 | 68 | 13.0 |
| 243 | $\mathrm{Ag}_{3} \mathrm{PO}_{4}$ | [1.9],4.7 | 382.1 | 376.1 | - | 13.3 |
| 53 | [ Ni en 2$]\left(\mathrm{AgI}_{2}\right)_{2}$ | [2.0],4.6 | 381.7 | 375.7 | 68 | - |
| 122 | $\mathrm{K}\left[\mathrm{Ag}(\mathrm{CN})_{2}\right]$. | [2.7],4.5 | 381.6 | 375.55 | - | 12.8 |
| 472 | AgI. | [3.3],5.0 | 381.5 | 375.5 | 69 | 12.7 |
| 473 | $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ | [2.6],4.6 | 381.2 | 375.1 | 66 | - |
| 474 | $\mathrm{AgReO}_{4}$ | 4.7 | 381.1 | 375.0 | 68 | 12.3 |
| 384 | $\mathrm{Ag}_{2} \mathrm{CrO}_{4}$ | [3.1],5.1 | 380.9 | 374.85 | 66 | 12.2 |
| 447 | AgBr | [3.4],5.3 | 380.8 | 374.75 | - | 11.9 |
| 475 | $\mathrm{Ag}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ | 5.3 | 380.2 | 374.2 | - | 11.5 |
| 272 | $\mathrm{Ag}_{2} \mathrm{SO}_{4}$. | [3],4.3 | 380.2 | 374.2 | - | 11.2 |
| 303 | $\mathrm{Ag}_{2} \mathrm{~S}$. | 4.6 | 380.0 | 374.0 | 66 | - |
| 290 | $\mathrm{AgS}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}$. | [3.3],5.1 | 380.0 | 374.0 | 65 | - |
| 339 | AgCl . | 4.8 | 379.9 | 373.9 | 65 | 10.8 |
| 432 | $\mathrm{Ag}_{3} \mathrm{AsO}_{4}$ | 4.7 | 379.7 | 373.7 | 65 | 11.3 |
| 271 | $\left[\mathrm{AgII}_{\mathrm{py}_{4}} \mathrm{~S}_{2} \mathrm{O}_{8}\right.$. | 4.2 | 379.6 | 373.6 | - | 11.1 |
| 476 | Ag, wool | 5.9 | 379.2 | 373.2 | 66 | - |

Table 14. Photo-electron signals of cadmium, indium, tin, antimony and tellurium. It is frequently difficult to distinguish $\mathrm{Sb}_{5} \mathrm{~d}_{5 / 2}$ from oxygen 1s.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 477 | $\mathrm{CdI}_{2}$ | [2.4],4.7 | 420.0 | 413.3 | 19.6 |
| 84 | $\mathrm{Cd}\left[\mathrm{Pd}(\mathrm{CN})_{6}\right]$. | [2.2],4.9 | 419.8 | 413.0 | 19.4 |
| 217 | $\mathrm{CdF}_{2}$ | [3],4.8 | 419.2 | 412.4 | 19.2 |
| 217 | repeated | [2],4.3 | 419.7 | 412.9 | 19.1 |
| 478 | CdO | [2.3],4.9 | 419.65 | 412.8 | 19.4 |
| 255 | $\mathrm{CdSO}_{4}, \mathrm{H}_{2} \mathrm{O}$ | 5.0 | 419.6 | 412.8 | 19.1 |
| 385 | $\mathrm{Cd}_{3}\left[\mathrm{Cr}(\mathrm{CN})_{6}\right]_{2}$ | [2.9],4.8 | 419.6 | 412.8 | 19.3 |
| 479 | $\mathrm{CdCO}_{3}$ | [2.1], 4.6 | 419.5 | 412.7 | 19.3 |
| 285 | CdS | [3.2],4.7 | 418.75 | 412.0 | 18.3 |
| 439 | CdSe. | [4],5.7 | 418.5 | 411.7 | 17.8 |
| 172 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2}\left[\mathrm{Cd}(\mathrm{NCSe})_{4}\right]$ | 4.5 | 417.5 | 410.7 | 17.2 |
| 480 | $\mathrm{In}\left(\mathrm{IO}_{3}\right)_{3}$ | [2.0], 4.8 | 460.9 | 453.3 | 26.9 |
| 481 | $\mathrm{In}_{\underline{2}}\left(\mathrm{SO}_{4}\right)_{3}$. | [2.8],5.1 | 460.7 | 453.1 | 26.6 |
| 309 | $\mathrm{Cs}_{4}\left(\mathrm{InCl}_{6}\right)\left(\mathrm{SbCl}_{6}\right)$ | [2.3],4.9 | 460.2 | 452.7 | 25.5 |

Table 14. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 42 | $\left(\mathrm{NH}_{4}\right)_{2}\left[\operatorname{In}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$. | [3.8],5.0 | 459.5 | 452.0 | 25.6 |
| 94 | $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{InCl}_{6}$ | 5.0 | 458.8 | 451.2 | 24.6 |
| 291 | $\mathrm{In}_{2} \mathrm{~S}_{3}$ | [3],4.7 | 458.4 | 450.8 | 24.8 |
| 292 | $\mathrm{In}_{2}\left(\mathrm{~S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3}$ | [3],4.8 | 457.4 | 449.8 | 23.9 |
| 482 | $\mathrm{In}_{2} \mathrm{O}_{3}$ | 5.8 | 457.2 | 449.6 | 23.0 |
| 483 | In, coherent(oxidized?) | 5.3 | 456.4 | 448.8 | 21.9 |
| 442 | $\mathrm{Cs}_{2} \mathrm{SnBr}_{6}$ | [2.9],5.2 | 503.2 | 494.7 | 34.7 |
| 442 | repeated | [2.0], 4.8 | 503.9 | 495.4 | 35.0 |
| 484 | $\mathrm{Sn}^{\text {II }} \mathrm{C}_{2} \mathrm{O}_{4}$ | 4.9 | 502.1 | 493.6 | 33.7 |
| 592 | $\mathrm{Na}_{2}\left[\mathrm{Sn}^{\text {IV }}(\mathrm{OH})_{6}\right]$ | [3],4.5 | 502 | 493.3 | 33.1 |
| 485 | $\mathrm{Sn}^{\text {IV }}{ }_{1-2 \chi} \mathrm{Sb}^{\text {III }} \mathrm{Sb}^{V_{\chi} \mathrm{O}_{2} .}$ | 5.4 | 501.0 | 492.6 | 32.6 |
| 486 | Sn, foil, oxidized | 5.0 | 500.8 | 492.3 | 31.8 |
| 73 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2}\left[\mathrm{Sn}(\mathrm{NCS})_{6}\right]$. | 5.0 | 500.7 | 492.2 | 32.3 |
| 487 | $\mathrm{SnO}_{2}$ | 5.4 | 500.5 | 492.0 | 32.1 |
| 488 | $\mathrm{Sn}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}$ | 5.1 | 499.7 | 491.2 | 31.0 |
| 182 | $\mathrm{CsSb}^{\mathrm{V}} \mathrm{F}_{6}$ | [1.3],5.5 | 551.9 | 542.4 | 46.4 |
| 318 | $\mathrm{Cs}_{4}\left(\mathrm{Sb}^{\mathrm{III}} \mathrm{Cl}_{6}\right)\left(\mathrm{Sb}^{\mathrm{V}} \mathrm{Cl}_{6}\right)$. | [3.1],4.9 | 548.9 | 538 | 42.5 |
|  |  |  | \& 547.1 |  | \& 41.4 |
| 311 | $\mathrm{CsSb}^{\mathrm{V}} \mathrm{Cl}_{6}$ | [2.0],5.0 | 548.7 | 539.1 | 44 |
| 309 | $\mathrm{Cs}_{4}\left(\mathrm{InCl}_{6}\right)\left(\mathrm{Sb}^{\mathrm{V}} \mathrm{Cl}_{6}\right)$ | [2.3],4.9 | 548.7 | 539.1 | 43.7 |
| 313 | $\mathrm{Cs}_{4}\left(\mathrm{Sb}^{\mathrm{V}} \mathrm{Cl}_{6}\right)\left(\mathrm{TlCl}_{6}\right)$ | [2.3],4.6 | 548.7 | 539 | 43.7 |
| 485 | $\mathrm{Sn}_{1-2 \chi} \mathrm{Sb}^{I I I} \mathrm{\chi}_{\chi} \mathrm{Sb}_{\chi} \mathrm{O}_{2}$ | 5.4 | 547.8 | 539 | 44 |
|  |  |  | \& 545.7 |  | \& 41.2 |
| 38 | $\mathrm{NH}_{4} \mathrm{Sb}^{\text {III }} \mathrm{F}_{4}$ | [3.5],5.3 | 547.7 | 538.3 | 43.0 |
| 354 | $\mathrm{K}\left[\mathrm{Sb}^{\mathrm{V}}(\mathrm{OH})_{6}\right]$ | 5.1 | 547.1 | 538 | 42.1 |
| 329 | $\mathrm{Sb}^{\text {III }} \mathrm{OCl}$ | [2.5],4.7 | 547.0 | 537.6 | 42.1 |
| 355 | $\mathrm{K}_{2}\left[\mathrm{Sb}^{\text {III }} \mathrm{O}_{2}\right.$ tartrate 2$]$ | [3],4.9 | 546.9 | 538 | 41.8 |
| 229 | $\mathrm{Na}\left[\mathrm{Sb}^{\mathrm{V}}(\mathrm{OH})_{6}\right]$. | [2.5],4.4 | 546.9 | 537.6 | 42.1 |
| 109 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Sb}^{\text {III }} \mathrm{Cl}_{6}$ | 4.3 | 545.4 | 536.1 | 40.8 |
| 603 | $\mathrm{Na}_{3} \mathrm{Sb}^{\text {V }} \mathrm{S}_{4}$ | 4.3 | 545.1 | 535.8 | 40.1 |
| 299 | $\mathrm{Sb}^{\mathrm{III}}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3}$ | 4.9 | 544.4 | 535.1 | 39.3 |
| 489 | $\mathrm{Te}^{\mathrm{VI}}(\mathrm{OH})_{6}$. | 5.0 | 594.4 | 583.9 | 52.7 |
| 490 | $\mathrm{Te}^{\mathrm{IV}} \mathrm{O}_{2}$. | 4.4 | 593.3 | 582.8 | 51.2 |
| 490 | repeated (oxidized) | 4.7 | 594.3 | 583.85 | 52.0 |
| 591 | $\mathrm{Na}_{2} \mathrm{Te}^{\text {IV }} \mathrm{O}_{3}$. | 5.0 | 592.8 | 582.4 | 50.8 |
| 591 | repeated | [2.8],4.8 | 593.5 | 583.05 | 51.1 |
| 598 | $\left.\mathrm{Na}_{2}\left[\mathrm{Te}^{-\mathrm{VI}_{2}} \mathrm{O}_{2} \mathrm{OH}\right)_{4}\right]$ | 4.7 | 593.7 | 581.45 | 51.7 |
| 118 | $\mathrm{Te}^{\mathrm{IV}}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{4}$ | 4.9 | 590.6 | 580.2 | 48.1 |
| 491 | $\mathrm{Al}_{2} \mathrm{Te}_{3}$ (oxidized to Te ?) | 5.3 | 587.55 | 577.1 | 45.6 |

Table 15. Photo-electron signals of iodine. The shoulder on the 4 d signal is not indicated.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{~d})$ | $I(5 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 492 | $\mathrm{Eu}\left(\mathrm{IO}_{3}\right)_{3}$ | [1.6], 4.9 | 644.4 | 632.9 | 63.6 | - |
| 493 | $\mathrm{La}\left(\mathrm{IO}_{3}\right)_{3}$. | [1.7],5.0 | 644.4 | 632.85 | 63.3 | - |
| 349 | $\mathrm{KIV}^{\mathrm{VII}} \mathrm{O}_{4} \ldots \ldots$ | [2.8],5.3 | 644.3 | 632.8 | 63.7 | - |
| 494 | $\mathrm{UO}_{2}\left(\mathrm{IO}_{3}\right)_{2} \ldots \ldots$ | [1.4],4.7 | 644.4 | 632.8 | 63.2 | - |
| 495 | $\mathrm{Sm}\left(\mathrm{IO}_{3}\right)_{3}$ | [1.5],4.6 | 644.3 | 632.75 | 63.2 | - |
| 496 | $\mathrm{Gd}\left(\mathrm{IO}_{3}\right)_{3}$ | [1.8],5.0 | 644.2 | 632.65 | 63.2 | - |
| 480 | $\mathrm{In}\left(\mathrm{IO}_{3}\right)_{3}$ | [2.0],4.8 | 644.0 | 632.5 | 62.8 | - |
| 497 | $\mathrm{Nd}\left(\mathrm{IO}_{3}\right)_{3}$ | [1.7],4.7 | 644.05 | 632.5 | 62.9 | - |
| 498 | $\operatorname{Pr}\left(\mathrm{IO}_{3}\right)_{3} \ldots \ldots$ | [1.7], 4.6 | 643.95 | 632.4 | 63.0 | - |
| 454 | $\mathrm{Y}\left(\mathrm{IO}_{3}\right)_{3}$ | [2.2],4.8 | 643.85 | 632.3 | 62.5 | - |
| 499 | $\mathrm{Th}\left(\mathrm{IO}_{3}\right)_{4}$ | [2.2],4.7 | 643.85 | 632.3 | 62.7 | - |
| 235 | $\mathrm{NaI}^{\mathrm{VII}} \mathrm{O}_{4}$. | 4.75 | 643.75 | 632.25 | 63.35 | - |
| 500 | $\mathrm{Hf}\left(\mathrm{IO}_{3}\right)_{4}$. | [2.6],5.0 | 643.7 | 632.2 | 62.7 | - |
| 501 | $\mathrm{Pb}\left(\mathrm{IO}_{3}\right)_{2}$ | [1.5],4.1 | 643.7 | 632.1 | 62.3 | - |
| 502 | $\mathrm{Ho}\left(\mathrm{IO}_{3}\right)_{3}$ | [1.6],4.2 | 643.6 | 632.05 | 62.8 | - |
| 612 | $\mathrm{Ni}\left(\mathrm{IO}_{3}\right)_{2}$ | [2.5],4.9 | 643.6 | 632.05 | 62.7 | - |
| 503 | $\mathrm{Ce}\left(\mathrm{IO}_{3}\right)_{4}$ | [1.8],4.6 | 643.55 | 632.0 | 62.4 | - |
| 421 | $\mathrm{Zn}\left(\mathrm{IO}_{3}\right)_{2}$ | [2.4],5.0 | 643.45 | 631.9 | 62.3 | - |
| 504 | $\mathrm{Yb}\left(\mathrm{IO}_{3}\right)_{3} \ldots$ | [2],4.7 | 643.4 | 631.9 | 62.3 | - |
| 370 | $\mathrm{Ca}\left(\mathrm{IO}_{3}\right)_{2}$ | [2.2],4.6 | 643.3 | 631.8 | 61.8 | - |
| 456 | $\mathrm{Zr}\left(\mathrm{IO}_{3}\right)_{4}$ | [2.1],4.6 | 643.35 | 631.8 | 62.0 | - |
| 505 | $\mathrm{Tm}\left(\mathrm{IO}_{3}\right)_{3}$ | [1.9], 4.3 | 643.3 | 631.75 | 62.4 | - |
| 614 | $\mathrm{Ba}\left(\mathrm{IO}_{3}\right)_{2} \ldots$ | [1.9],4.6 | 643.25 | 631.7 | 62.3 | - |
| 237 | $\mathrm{Na}_{5} \mathrm{I}^{\mathrm{VII}} \mathrm{O}_{6} \ldots$ | 5.25 | 643.25 | 631.65 | 62.65 | - |
| 506 | $\mathrm{TlIO}_{3}$ | [2.5],5.1 | 643.2 | 631.6 | 61.8 | - |
| 507 | $\mathrm{Er}\left(\mathrm{IO}_{3}\right)_{3}$ | [2],4.3 | 643.1 | 631.6 | - | - |
| 471 | $\mathrm{AgIO}_{3}$ | [2.3],4.8 | 643.0 | 631.5 | 61.8 | - |
| 508 | $\mathrm{Lu}\left(\mathrm{IO}_{3}\right)_{3}$ | [2],4.5 | 642.9 | 631.4 | 62.0 | - |
| 509 | $\mathrm{Bi}\left(\mathrm{IO}_{3}\right)_{3} \cdots \ldots . . . .$. | 4.1 | 642.8 | 631.3 | 61.4 | - |
| 67 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{7}\left[\mathrm{Cu}\left(\mathrm{I}^{\mathrm{VII}} \mathrm{O}_{6}\right)_{2}\right]_{3}$ | 4.7 | 642.7 | 631.2 | 61.9 | - |
| 510 | $\mathrm{Hg}\left(\mathrm{IO}_{3}\right)_{2}$ | [3.5],5.6 | 642.6 | 631.1 | 61.5 | - |
| 350 | $\mathrm{KIO}_{3}$ | [3.2],5.3 | 642.5 | 631.0 | 62.1 | - |
| 613 | $\mathrm{Cu}\left(\mathrm{IO}_{3}\right)_{2} \ldots \ldots$ | [2.3],4.4 | 642.55 | 631.0 | 61.9 | - |
| 604 | $\mathrm{Na}_{7} \mathrm{H}_{4}\left[\mathrm{Mn}\left(\mathrm{I}^{\mathrm{VII}} \mathrm{O}_{6}\right)_{3}\right]$. | 4.1 | 640.9 | 629.5 | 60.3 | - |
| 402 | $\mathrm{Co}\left(\mathrm{IO}_{3}\right)_{2}$ | 3.5 | 640.5 | 629.0 | - | - |
| 402 | repeated | [2.4],4.5 | 642.3 | 630.75 | 61.2 | - |
| 226 | NaI | [2.8],5.6 | 638.9 | 627.3 | 57.6 | 11.2 |
| 511 | $\mathrm{PbI}_{2}$ | [1.7],5.1 | 638.7 | 627.15 | 58.0 | 11.8 |
| 512 | CsI. | [1.5],5.15 | 638.55 | 627.0 | 57.95 | 11.7 |
| 347 | KI | [1.6],4.7 | 638.5 | 626.9 | 57.4 | 10.2 |
| 472 | AgI | [3.3],5.0 | 638.4 | 626.9 | 56.5 | (9.7) |
| 477 | $\mathrm{CdI}_{2}$. | [2.4],4.7 | 638.4 | 626.8 | 58.3 | 11.1 |
| 469 | $\mathrm{Pd} \mathrm{I}_{2}$. | 5.1 | 638.3 | 626.75 | 58.0 | 11.6 |

Table 15. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{~d})$ | $I(5 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 34 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{PtI}_{6}$. | 4.8 | 638.3 | 626.75 | 57.2 | 13 |
| 420 | $\mathrm{Cu}_{2} \mathrm{HgI}_{4}$. | [4.3],6.1 | 638.2 | 626.7 | 56.7 | 10.1 |
| 593 | Bengal Rosa B . | 5.1 | 638.1 | 626.5 | 57.9 | 11 |
| 406 | [ $\left.\mathrm{Ni} \mathrm{en}_{3}\right] \mathrm{PtI}_{6}$. | 4.8 | 638.0 | 626.45 | 57.0 | - |
| 453 | RbI | [3.1],4.8 | 637.9 | 626.3 | 55.6 | 10 |
| 53 | [ $\mathrm{Ni} \mathrm{en} \mathrm{I}_{2}$ ] $\left(\mathrm{AgII}_{2}\right)_{2}$ | [2.0],4.6 | 637.9 | 626.3 | 56.9 | - |
| 60 | [ $\mathrm{Ni} \mathrm{en}_{2}$ ] $\left(\mathrm{CuI}_{2}\right)_{2}$ | [2.2],4.6 | 637.7 | 626.2 | 57.0 | - |
| 348 | $\mathrm{K}_{4} \mathrm{BiI}_{7} \ldots \ldots$ | [3],4.9 | 637.7 | 626.15 | 56.9 | 10.2 |
| 351 | $\mathrm{K}_{2} \mathrm{HgI}_{4}$ | [2.4],4.6 | 637.6 | 626.1 | 57.3 | 10.6 |
| 37 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2} \mathrm{PtI}_{6}$ | [2],4.7 | 637.6 | 626.05 | 56.6 | 12 |
| 467 | $\mathrm{RhI}_{3}$ | 4.5 | 637.55 | 626.0 | 56.5 | 10 |
| 513 | $\mathrm{CsBiI}_{4}$ | [3],5.0 | 637.5 | 626.0 | 57.6 | 10.3 |
| 513 | repeated | 4.5 | 637.9 | 626.4 | 57.1 | 10.7 |
| 71 | [ Rh den $\mathrm{I}_{3}$ ] | [2.4],4.6 | 637.4 | 625.9 | 56.4 | (11.2) |
| 514 | $\mathrm{BiI}_{3}$ | [3],5.0 | 637.25 | 625.8 | 57.8 | - |
| 81 | [ Pd phen $\mathrm{I}_{2}$ ] | 4.9 | 637.2 | 625.7 | 56.2 | - |
| 75 | $\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right] \mathrm{I}$ | 4.5 | 636.9 | 625.6 | 54.1 | 8 |
| 410 | [ $\mathrm{Ni} \mathrm{en} \mathrm{n}_{3} \mathrm{I}_{2}$ | [2.7], 4.9 | 636.8 | 625.3 | 55.7 | - |
| 431 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{PtI}{ }_{6}$ | 4.8 | 636.8 | 625.3 | 56.0 | - |
| 327 | $\mathrm{Cs}_{2}\left[\mathrm{OsCl}_{5} \mathrm{I}\right]$ | 4.4 | 636.75 | 625.25 | 56.0 | - |
| 334 | $\mathrm{Rb}_{2}$ cis-[ $\mathrm{OsCl}_{4} \mathrm{I}_{2}$ ] | 4.6 | 636.65 | 625.1 | - | - |
| 358 | $\mathrm{K}_{2} \mathrm{PtI}_{6}$ | 4.6 | 636.5 | 624.9 | 56.3 | 9.6 |
| 360 | $\mathrm{K}_{2}$ cis-[ $\left.\mathrm{OsCl}_{2} \mathrm{I}_{4}\right]$ | 4.1 | 636.4 | 624.85 | 55 | - |
| 515 | TlI | 4.85 | 636.25 | 624.75 | 56.25 | 9.7 |
| 516 | $\mathrm{Cs}_{2} \mathrm{fac}-\left[\mathrm{OsCl}_{3} \mathrm{I}_{3}\right]$. | 3.5 | 636.0 | 624.4 | 56 | - |
| 114 | (methylene blue) ${ }_{2} \mathrm{PtI} \mathrm{I}_{6}$. | 5.0 | 635.8 | 624.3 | 55.2 | - |
| 517 | $\mathrm{Cs}_{2}$ trans- $\left[\mathrm{OsCl}_{2} \mathrm{I}_{4}\right] \ldots$ | 5.0 | 635.8 | 624.25 | 55.7 | 9 |
| 43 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{I}$. | [2.8],4.9 | 635.6 | 624.15 | 54.3 | 9 |
| 518 | $\mathrm{Cs}_{2} \mathrm{OsI}_{6}$ | 5.7 | 635.7 | 624.15 | 56 | 10.5 |
| 519 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right] \mathrm{I}$. | 4.7 | 635.1 | 623.6 | 54.6 | - |
| 345 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2}$ trans-[ $\left.\mathrm{OsCl}_{4} \mathrm{I}_{2}\right]$. | 4.2 | 635.1 | 623.55 | 54 | - |

## Table 16. Photo-electron signals of caesium and barium.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I\left(4 \mathrm{~d}_{3 / 2}\right)$ | $I\left(4 \mathrm{~d}_{5 / 2}\right)$ | $I(5 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| - | Xe (ref. 97) . | - | 689.0 | 676.4 | 69.5 | 67.5 | .4,12.1 |
| 182 | $\mathrm{CsSbF}_{6}$ | [1.5],5.1 | 747.7 | 733.8 | 86.8 | 84.6 | - |
| 182 | repeated | [1.3],5.5 | 747.9 | 733.9 | - | - | - |
| 308 | CsCl | [0.4],5.2 | 747.8 | 733.8 | 86.8 | 84.7 | 19.6 |
| 308 | repeated | [0.7],5.2 | 747.5 | 733.4 | 87.5 | 85.1 | 19.6 |
| 512 | CsI. | [1.5],5.15 | 746.85 | 732.75 | 86.0 | 83.7 | 18.75 |

Table 16. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I\left(4 \mathrm{~d}_{3 / 2}\right)$ | $I\left(4 \mathrm{~d}_{5 / 2}\right)$ | $I(5 \mathrm{p})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 444 | CsBr . | [1.6],4.95 | 746.3 | 732.25 | 85.7 | 83.5 | 18.3 |
| 520 | $\mathrm{CsReO}_{4}$ | [1.6],4.7 | 746.3 | 732.2 | - | 83.7 | 16.7 |
| 521 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ | [2.5],4.9 | 746.0 | 732.0 | 84.9 | 82.7 | 17.7 |
| 240 | $\mathrm{CsAlSi}_{2} \mathrm{O}_{6}$ | [2.5],4.7 | 746.05 | 732.0 | (85.7) | 83.1 | 18.3 |
| 309 | $\mathrm{Cs}_{4}\left(\mathrm{InCl}_{6}\right)\left(\mathrm{SbCl}_{6}\right)$ | [2.3],4.9 | 746.0 | 731.9 | 84.9 | 82.8 | 17.4 |
| 314 | $\mathrm{Cs}_{2} \mathrm{PbCl}_{6}$ | [2.1],4.9 | 745.8 | 731.9 | 85.4 | 83.1 | 17.9 |
| 315 | $\left.\mathrm{Cs}_{2}\left[\mathrm{Rh}^{\left(\mathrm{H}_{2} \mathrm{O}\right.}\right) \mathrm{Cl}_{5}\right]$. | [2.2],4.9 | 745.8 | 731.8 | 85.4 | 83.2 | 18 |
| 311 | $\mathrm{CsSbCl}_{6}$ | [2.0],5.0 | 745.6 | 731.7 | 85.2 | 83.1 | - |
| 310 | $\mathrm{Cs}_{2} \mathrm{PtCl}_{6}$. | [1.6],4.3 | 745.7 | 731.7 | - | - | 18 |
| 513 | $\mathrm{CsBiI}_{4}$ | [3],5.0 | 745.6 | 731.5 | - | - | _ |
| 513 | repeated | 4.5 | 745.9 | 731.9 | 85.4 | 83.3 | 18.7 |
| 313 | $\mathrm{Cs}_{4}\left(\mathrm{SbCl}_{6}\right)\left(\mathrm{TlCl}_{6}\right)$. | [2.4],4.6 | 745.5 | 731.5 | 84.8 | 82.6 | - |
| 18 | $\mathrm{CsUO}_{2}\left(\mathrm{NO}_{3}\right)_{3} .$. | [2.8],5.1 | (745.7) | 731.5 | 85.3 | 83.1 | - |
| 104 | $\mathrm{Cs}_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$. | [2.5],4.6 | 745.4 | 731.4 | 84.8 | 82.6 | 18.1 |
| 442 | $\mathrm{Cs}_{2} \mathrm{SnBr}_{6}$ | [2.9],5.2 | 745.4 | 731.4 | 85.3 | 83.0 | - |
| 442 | repeated | [2.0],4.8 | 746.2 | 732.2 | 85.6 | 83.4 | 18.4 |
| 466 | $\mathrm{Cs}_{2} \mathrm{RhCl}_{6}(?)$ | [2.3],5.0 | 745.3 | 731.3 | 84.9 | 82.7 | 18 |
| 441 | $\mathrm{Cs}_{2} \mathrm{PtBr}_{6}$ | 4.0 | 745.3 | 731.3 | - | - | 17.6 |
| 318 | $\mathrm{Cs}_{4}\left(\mathrm{Sb}^{\mathrm{III}} \mathrm{Cl}_{6}\right)\left(\mathrm{Sb}^{\mathrm{V}} \mathrm{Cl}_{6}\right)$ | [3.1],4.9 | 745.0 | 731.1 | 84.6 | 82.4 | - |
| 522 | $\mathrm{Cs}_{2} \mathrm{WSe}_{4}$. | 4.7 | 745.1 | 731.1 | - | - | - |
| 257 | $\mathrm{Cs}_{2} \mathrm{SO}_{4}$. | 4.9 | 744.8 | 730.8 | 84.1 | 81.9 | 17.1 |
| 390 | $\mathrm{CsMnO}_{4}$. | [2.7],4.7 | 744.8 | 730.8 | 84.4 | 82.2 | 17.3 |
| 287 | $\mathrm{Cs}_{2} \mathrm{WS}_{4}$ | 5.2 | 744.7 | 730.7 | 84.4 | 82.4 | - |
| 23 | $\mathrm{CsNO}_{3}$ | [3.2],4.8 | 744.55 | 730.5 | 84.2 | 81.9 | - |
| 523 | $\mathrm{Cs}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$ | 4.7 | 744.2 | 730.2 | 83.5 | 81.3 | - |
| 326 | $\mathrm{Cs}_{2} \mathrm{OsCl}_{6}$. | 4.8 | 744.05 | 730.1 | 83.5 | 81.3 | 16.0 |
| 322 | $\mathrm{Cs}_{2} \mathrm{IrCl}_{6}$ | 5.7 | 744.0 | 730.0 | 83.7 | 81.5 | - |
| 322 | repeated | 4.9 | 744.7 | 730.7 | 83.7 | 81.7 | 17 |
| 327 | $\mathrm{Cs}_{2}\left[\mathrm{OsCl}_{5} \mathrm{I}\right]$ | 4.4 | 743.9 | 729.9 | 83.7 | 81.5 | - |
| 448 | $\mathrm{Cs}_{2} \mathrm{OsBr}_{6}$ | 3.8 | 743.7 | 729.7 | 83.8 | 81.5 | - |
| 225 | CsF. | 4.1 | 743.5 | 729.5 | 83.0 | 80.7 | 16.3 |
| 340 | $\mathrm{Cs}_{2}\left[\mathrm{OsCl}_{2} \mathrm{I}_{4}\right]$. | 5.0 | 743.4 | 729.4 | (82.7) | 80.3 | - |
| 301 | $\mathrm{Cs}_{2} \mathrm{MoS}_{4}$. | 4.1 | 743.25 | 729.3 | 83.3 | 81.0 | - |
| 518 | $\mathrm{Cs}_{2} \mathrm{OsI}_{6}$ | 5.7 | 743.15 | 729.1 | 82.7 | 80.7 | - |
| 203 | $\mathrm{BaF}_{2}$ | [0.3],4.7 | 804.6 | 789.3 | 101.7 | 99.1 | 23.6 |
| 203 | repeated | [0.1],4.4 | 804.6 | 789.3 | 101.4 | 98.8 | 23.6 |
| 249 | $\mathrm{BaSO}_{4}$ | [3.2],5.9 | 804.0 | 788.7 | 101.4 | 98.8 | 22.3 |
| 249 | repeated | [1.1],5.0 | 804.3 | 789.0 | 101.3 | 98.7 | 23.3 |
| 258 | $\mathrm{BaS}_{2} \mathrm{O}_{6}, 2 \mathrm{H}_{2} \mathrm{O}$ | 4.8 | 803.0 | 787.7 | 100.2 | 97.5 | 21.8 |
| 381 | $\mathrm{BaCrO}_{4}$ | [2.2],4.9 | 803.0 | 787.7 | 100.2 | 97.7 | 22.1 |
| 435 | $\mathrm{BaSeO}_{4}$ | [2.2],4.8 | 802.85 | 787.5 | 100.2 | 97.6 | - |
| 435 | repeated | [1.1],4.7 | 804.2 | 788.9 | 101.2 | 98.7 | - |
| 609 | $\mathrm{Ba}\left(\mathrm{IO}_{3}\right)_{2}$ | [1.9],4.6 | 802.6 | 787.2 | 99.6 | 97.2 | 21.6 |
| 21 | $\mathrm{Ba}\left(\mathrm{NO}_{3}\right)_{2}$. | [3],5.1 | 802.5 | 787.0 | 99.7 | 97.1 | 21.2 |
| 391 | $\mathrm{Ba}\left(\mathrm{MnO}_{4}\right)_{2}$. | 4.4 | 801.1 | 785.8 | 98.2 | 95.7 | 20.1 |

Table 17. Photo-electron signals of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium and dysprosium.

|  | Compound | $\mathrm{C}_{\text {St }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{~d})$ | $I(5 \mathrm{p})$ | $I(4 \mathrm{f})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 34 | $\mathrm{LaF}_{3} \ldots \ldots . .$. | [0.0], 4.7 | (868),863.9 | (851.4), 847.0 | 117.1,114.3 | 29.3 asym. | - |
| Э3 | $\mathrm{La}\left(\mathrm{IO}_{3}\right)_{3}$ | [1.7],5.0 | 863.8,860.7 | 847.0,843.9 | 114.6,112.1 | - | - |
| 50 | $\mathrm{La}_{2}\left(\mathrm{SO}_{4}\right)_{3}$. | . [2.6],5.0 | 863.6,860.4 | 846.6,843.4 | 114.6,111.7 | 26 | - |
| 24 | $\mathrm{La}_{2}\left(\mathrm{CO}_{3}\right)_{3}$. | . [1.4],4.0 | 863.5,860.1 | 846.4,843.2 | 117.3,115.8 | - | - |
| 28 | $\mathrm{LaAsO}_{4}$ | [2.0],4.7 | 863.2,859.9 | 846.5,843.1 | 114.0,111.4 | - | - |
| 17 | LaOCl | [2],4.4 | 862.8,859.1 | 845.5,842.4 | 113.7,110.9 | - | - |
| 36 | $\mathrm{LaCrO}_{3}$ | [2.5],4.5 | 862.1,858.6 | 845.2,841.5 | 112.4,109.6 | 24.2 | - |
| 25 | $\mathrm{La}_{2} \mathrm{O}_{3}$, calcined. . | [2.6],4.6 | 861.9,857.2 | 844.5,840.9 | - | 24.6 | - |
| 19 | $\mathrm{CeF}_{4}, \mathrm{H}_{2} \mathrm{O}: \mathrm{Ce}^{\text {IV }}$. | 4.9 | - | 907.9 | - | - | - |
|  | Ce ${ }^{\text {III }}$ |  | 913.1 | (902,)894.4,(890.7) | ) 120.6 broad | 28.4 | - |
| 19 | repeated: $\mathrm{Ce}^{\text {IV }}$. | [1.7],4.5 | 926.0 | 907.9 | (136),132.5 | - | - |
|  | Ce ${ }^{\text {III }}$ |  | (921),913.0 | 894.3,(891) | 120.9,(118) | - | - |
| 26 | $\mathrm{CeO}_{2}: \quad \mathrm{Ce}^{\text {IV }}$. | [2.2],4.7 | - | 915.7,906.7 | - | - | - |
|  | Ce ${ }^{\text {III }}$ |  | 909 | 896.8,890.7 | - | 25.4 | - |
| 26 | repeated: $\mathrm{Ce}^{\text {IV }}$ | [2],5.0 | - | 914.8,905.8 | - | - | - |
|  | Ce ${ }^{\text {III }}$ |  | (908.4) | 896.0,890.0 | 119.6,116.3 | - | - |
| 26 | repeated: $\mathrm{Ce}^{\text {IV }}$. | [2.2],4.8 | 924.2 | 905.8 | (133),129.9 | - | - |
|  | Ce ${ }^{\text {III }}$ |  | (908.4) | 896.3,890.1 | 121.0,116.7 | - | - |
| :7 | $\mathrm{Th}_{0 \cdot 6} \mathrm{Ce}_{0 \cdot 2} \mathrm{U}_{0 \cdot 2} \mathrm{O}_{2}$ : |  |  |  |  |  |  |
|  | Ce ${ }^{\text {IV }}$ | 5.9 | - | 906.4 | - | - | - |
|  | Ce ${ }^{\text {III }}$ |  | 909 | 896,890.4 | - | - | - |
| :8 | $\mathrm{Th}_{0 \cdot 8} \mathrm{Ce}_{0 \cdot 15} \mathrm{U}_{0 \cdot 05} \mathrm{O}_{2}:$ |  |  |  |  |  |  |
|  | $\mathrm{Ce}^{\mathrm{IV}}$ | $[2.2], 4.8$ | - | 915.4,906.0 | - | - | - |
|  | Ce ${ }^{\text {III }}$ |  | 908.7 | 896.2,890.4 | - | - | - |
| :9 | $\mathrm{Ce}_{0 \cdot 5}{ }^{\mathrm{T}} 0 \cdot 5 \mathrm{O}_{2}$ | 6.1 | 908,906.1 | 895,889.8 | - | - | - |
| 13 | $\mathrm{Ce}^{\mathrm{IV}}\left(\mathrm{IO}_{3}\right)_{4} \ldots \ldots$ | [1.8],4.6 | 912,907.3 | 892,887.4 | 123,120.6,117 | - | - |
| ; | $\mathrm{Ce}^{\mathrm{IV}}\left(\mathrm{CrO}_{4}\right)_{2}: \mathrm{Ce}^{\mathrm{IV}}$. | [2.7],4.8 | 923.8 | 905.4 | - | - | - |
|  | Ce ${ }^{\text {III }}$ |  | 914.5,908.6 | 895.5,889.9 | 118.3 broad | - | - |
| 6 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{Ce}^{\text {IV }} \mathrm{Cl}_{6}$ | . [2.7],4.5 | 910.6,906.2 | 892.5,(889.0) | 118.4 broad | - | - |
| 5 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2} \mathrm{Ce}^{\text {IV }}(\mathrm{CO}$ | 3)5] : |  |  |  |  |  |
|  | Ce ${ }^{\text {VV }}$. | 4.2 | 923.1 | 904.9 | 128.6 | - | - |
|  | Ce ${ }^{\text {III }}$ |  | (913),904.9 | 895.2,889.4 | 119.5,115.5 | - | - |
| 0 | $\mathrm{Ce}^{\text {III }} \mathrm{F}_{3}$ | [0.5],4.8 | (915.5),912.2 | (897.1),893.5 | (123),119.8 | (31),28.5 | - |
| 4 | $\mathrm{Ce}^{\text {III }} \mathrm{PO}_{4} \ldots \ldots$. | [2.4],4.8 | 911.6,(910.3) | 892.8,(890) | 119,(117) | - | - |
| 0 | $\mathrm{Ce}^{\mathrm{III}}{ }_{2}\left(\mathrm{CO}_{3}\right)_{3} \ldots \ldots$ | . [2.6],4.8 | 911.6,908.2 | 892.8,890.0 | 116 broad | - | - |
| 7 | $\mathrm{Ce}^{\mathrm{III}} 2^{\left(\mathrm{SO}_{4}\right)_{3} \ldots . .}$ | 4.7 | 909.9 asym. | 889.9 asym. | 117.5 broad | - | - |
| 1 | $\mathrm{PrF}_{3}$. | [1.5],4.9 | (968.4),962.1 | 943.7 broad | (130),125.3 | 28.5 | (12.0) |
| 8 | $\operatorname{Pr}\left(\mathrm{IO}_{3}\right)_{3} \ldots \ldots$. | [1.7],4.6 | 962.2,(957) | 942.1,(937) | 125.2 | - | - |
| 1 | $\mathrm{Pr}_{6} \mathrm{O}_{11}$ | 6.5 | 962.3 | 941.6,(937.2) | - | - | - |
| 1 | repeated: $\mathrm{Pr}^{\text {IV }}$. | .[1.7],4.8 | 979.4,(973.3) | (954) | 138 | (38) | - |
|  | PrIII |  | 961.8 | 941.4,(936.4) | 125.3,(122) | 27.3 | (11) |
| 2 | $\mathrm{Th}_{0.9} \mathrm{Pr}^{\mathrm{IV}}{ }_{0 \cdot 1} \mathrm{O}_{2} \ldots$ | . [2.0],5.5 | - | 941.2,(937.5) | - | - | - |
| 3 | $\mathrm{Pr}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 4.2 | 960.8 | 940.2 | 123.7 | - | (10.8) |
| 3 | $\mathrm{Pr}_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3} \ldots \ldots$ | 3.7 | (963.5),959.3 | 938.8 | - | - | - |

Table 17. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(3 \mathrm{~d}_{3 / 2}\right)$ | $I\left(3 \mathrm{~d}_{5 / 2}\right)$ | $I(4 \mathrm{~d})$ | $I(5 \mathrm{p})$ | $I(4 \mathrm{f})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 378 | $\mathrm{PrVO}_{4}$ | 4.8 | 953.3 | 937 broad | - | - | (11) |
| 206 | $\mathrm{NdF}_{3}$ | [2],4.7 | 1013.2,(1005) | 990.3 asym. | 130.8 | 28.5 | (17), 14.9 |
| 497 | $\mathrm{Nd}\left(\mathrm{IO}_{3}\right)_{3}$ | . [1.7], 4.7 | 1013.4,(1010.3) | 990.8,(988.5) | - | - | - |
| 429 | $\mathrm{NdAsO}_{4}$ | .[1.9],4.5 | 1012.6,(1008) | 990.0,(986) | 130.5 | 27.9 | (16.5), 13.5 |
| 276 | $\mathrm{Nd}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | . [2.5],4.6 | 1012.7,(1009) | 990.0,(985) | 130.3 | 28 | (16), 13.2 |
| 534 | $\mathrm{Nd}_{2} \mathrm{O}_{3}$ | . . [2.1],5.1 | 1012.4 asym. | 989.8,(985) | 130.3 | 28 | (16.6), 13.4 |
| 26 | $\mathrm{Mg}_{3} \mathrm{Nd}_{2}\left(\mathrm{NO}_{3}\right.$ | $)_{12}, 24 \mathrm{H}_{2} \mathrm{O} \quad 4.6$ | 1011.3,(1005) | 988.8,(984) | 129.2 | - | - |
| 207 | $\mathrm{SmF}_{3}$ | . . . [2.0],5.0 | (1122),1118.5 | 1091.6 | 143.2 broad | - | (15.8), 14.1 |
| 495 | $\mathrm{Sm}\left(\mathrm{IO}_{3}\right)_{3}$ | . . . [1.5],4.6 | 1118.6 | 1091.4 | - | - | (14) |
| 535 | $\mathrm{SmTaO}_{4}$ | . . [1],4.1 | 1117.3 | 1090.4 | 144,140 | - | (16), 13.5 |
| 536 | $\mathrm{Sm}_{2} \mathrm{O}_{3}$ | . . [2.7],5.3 | (1121),1117.6 | 1090.3 | 141.3 broad | 32 | (16), 13.7 |
| 194 | $\mathrm{EuF}_{3}$ | [1],4.8 | (1177),1173.6 | (1146),1143.8 | 151.6,146.3 | 30.8 | 17.5 |
| 492 | $\mathrm{Eu}\left(\mathrm{IO}_{3}\right)_{3}$ | . . [1.6],4.9 | 1172.6 | 1143.0 | - | - | (17.6) |
| 254 | $\mathrm{Eu}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | . . . [2.5],4.5 | 1171.5 | 1141.8 | 149.8,144.4 | - | 16.0 |
| 537 | $\mathrm{Eu}_{2} \mathrm{O}_{3}$. | . . . . [1.6],4.5 | 1171.0 | 1141.3 | 148.8,143.6 | 29 | 14.9 |
| 259 | $\mathrm{Eu}^{\mathrm{II}} \mathrm{SO}_{4}$ | . . . [2.4],4.4 | 1160.6 | 1130.8 | 135 | 17.9 ? | 8.9 |
|  | (and Eu ${ }^{\text {III }}$ ) |  | \& 1171.7 | \& 1141.4 | \& 141 | - | $17.9{ }^{\circ}$ |
| 198 | $\mathrm{GdF}_{3}$ | . [0.8],4.4 | 1229.0 | 1196.6 | 157.9,152.5 | 32.0 | 18.9 |
| 496 | $\mathrm{Gd}\left(\mathrm{IO}_{3}\right)_{3}$ | . . [1.8],5.0 | 1229 | 1195.3 | 157,151.6 | - | - |
| 538 | $\mathrm{GdTaO}_{4}$ | . . [3.2],5.0 | 1227.7 | 1194.9 asym. | 156.4,151.4 | (31) | 17.4 |
| 251 | $\mathrm{Gd}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | . . . . [2.5],4.8 | 1227.8 | 1194.8 | 156.2,150.9 | - | 17.5 |
| 539 | $\mathrm{Cid}_{2} \mathrm{O}_{3}$. | . [2],4.0 | 1227.3 | 1193.0 | 154.6,149.3 | - | 15.6 |
| 540 | $\mathrm{Tb}^{\mathrm{IV}} \mathrm{O}_{2}$. | . . [2.3],5.4 | 1296 | 1260.0 | 173,166.2 | - | 27.8 |
|  | (and $\mathrm{Tb}^{\text {III }}$ ) |  | \& 1284.5 | \& 1249.4 | 158.4 | - | 18,(12) |
| 541 | $\mathrm{Tb}_{4} \mathrm{O}_{7}$ : | Tb ${ }^{\text {IV }} \ldots[2.5], 5.1$ | - | - | - | - | 27.0 |
|  |  | Tb ${ }^{\text {III }}$. | 1283.9 | 1249.1 | 158 | - | 17.2,11.1 |
| 542 | $\mathrm{Tb}(\mathrm{OH})_{3}$ | . . [2.5],5.1 | 1284.0 | 1248.9 | - | 31.3 | 18.1,(11.5) |
| 543 | $\mathrm{TbCl}_{3}$. | 4.5 | 1283.2 | 1248.1 | - | 30.8 | 17.7,11.0 |
| 544 | $\mathrm{Dy}_{2} \mathrm{O}_{3}$ | 3.3 | - | - | 163.3 broad | 36 | 16.8,(13.8),(1 |
| 544 | repeated | . . . [1.1],4.3 | 1342.5 | 1303.6 | 164.3 broad | 37 | 17.9,14.7,(12. |
| 380 | DyVO4 | 3.4 | - | - | 163.2 broad | - | - |
| 380 | repeated | . . . . [1.8],4.2 | 1340.2 | 1301.7 | 163,161 | - | 16.9,(12.0) |

Table 18. Photo-electron signals of holmium, erbium, thulium, ytterbium and lutetium.

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(4 \mathrm{~d})$ | $I(5 \mathrm{p})$ | $I(4 \mathrm{f})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 502 | $\mathrm{Ho}\left(\mathrm{IO}_{3}\right)_{3}$ | [1.6],4.2 | (172), 170.4 | - | 17.8,(15.4),(13) |
| 545 | $\mathrm{Ho}_{2} \mathrm{O}_{3}$. | [2.3],4.9 | (174),169.4 | 32 | 16.9,(13) |
| 195 | $\mathrm{ErF}_{3}$ | [1],4.5 | plateau +178.8 | 34.4 | 18.7,(15.7) |
| 507 | $\mathrm{Er}\left(\mathrm{IO}_{3}\right)_{3}$. | [2],4.3 | plateau +177.1 | - | 17.5,(16),(13.8) |

Table 18. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I(4 \mathrm{~d})$ | $I(5 \mathrm{p})$ | $I(4 \mathrm{f})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 546 | $\mathrm{Er}_{2} \mathrm{O}_{3}$ | [1.6],4.7 | plateau +177 | 34 | 17,5,(14) |
| 505 | $\mathrm{Tm}\left(\mathrm{IO}_{3}\right)_{3}$ | [1.9],4.3 | plateau +185.1 | - | 17.2,(13.8) |
| 547 | $\mathrm{Tm}_{2} \mathrm{O}_{3}$ | [2.3],5.1 | (187),184.5 | 34 | 17.7,(13.6) |
| 547 | repeated | [1.6],4.2 | 197,184.2 40 | 40.8,33.4 | 16.9,(13.4) |
| 205 | $\mathrm{YbF}_{3}$ | [2.2],4.7 | 216,209,202,194.7 | 35.4 | 20.5,16.7 |
| 504 | $\mathrm{Yb}\left(\mathrm{IO}_{3}\right)_{3}$ | [2],4.7 | 214,207.3,199.2,193.9 | 9 | (20),16.0 |
| 548 | $\mathrm{YbTaO}_{4}$ | [1.9],4.7 | 207,(200),193.3 | - | 19.4,15.7 |
| 549 | $\mathrm{Yb}_{2}\left(\mathrm{WO}_{4}\right)_{3}$ | [2.5],4.3 | 205,198,193.0 | - | 19.1,15.1 |
| 550 | $\mathrm{Yb}_{2} \mathrm{Hf}_{2} \mathrm{O}_{7}$ | [2.2],4.7 | 208,200,193.1 | - | 18.7,15.0 |
| 266 | $\mathrm{Yb}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 4.2 | 206,(199),192.4 | 33 | 18.4,14.6 |
| 430 | $\mathrm{YbAsO}_{4}$ | [2.5],4.2 | 205,199,192.4 | 33 | (18.8),14.6 |
| 376 | $\mathrm{YbVO}_{4}$. | [2.8],4.9 | 205,199,192.2 39 | 39.9,33.5 | 18.2,14.3 |
| 375 | $\mathrm{Yb}_{2} \mathrm{Ti}_{2} \mathrm{O}_{7}$ | 4.6 | 205,199,191.4 | 32.7 | 17.5,13.7 |
| 551 | $\mathrm{Yb}_{2} \mathrm{O}_{3}$ | 3.8 | (210),203.3,(196),189. | 9.233 .1 | (17.6),13.6 |
| 606 | $\mathrm{LuF}_{3}$ | [0.3],5.5 | 218.6,208.7 | 38.5 | 20.5 |
| 606 | repeated. | [0.4],4.9 | 217.6,207.6 44 | 44.9,37.8 | 19.7 |
| 508 | $\mathrm{Lu}\left(\mathrm{IO}_{3}\right)_{3}$ | [2],4.5 | 214.8,204.8 | - | 16.8 |
| 552 | $\mathrm{Lu}_{2} \mathrm{O}_{3} \ldots$ | [2.7],4.8 | 213.9,203.9 | 35.0 | 16.0 |

Table 19. Photo-electron signals of the elements hafnium to uranium. It is often to difficult to detect $\operatorname{Re} 4 \mathrm{~d}_{3 / 2}$ and Os 4 d because of coincidences with C1s.

| . 0 | $\mathrm{K}_{2} \mathrm{Hf} \mathrm{F}_{6}$ | . [2.7],5.0 | 232.9 |
| :---: | :---: | :---: | :---: |
| 10 | $\mathrm{Hf}\left(\mathrm{IO}_{3}\right)_{4}$ | [2.6],5.0 | 232.6 |
| 3 | $\mathrm{HfO}_{2}$ | [2.2],4.5 | 231.5 |
| 0 | $\mathrm{Yb}_{2} \mathrm{Hf}_{2} \mathrm{O}_{7}$ | . [2.2],4.7 | 231.4 |
| 4 | $\mathrm{Hf}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CHOHCO} 2\right)_{4}$ | 5.0 | 230.2 |
| 5 | Hf, powder, oxidized. | 5.0 | - |
| 5 | $\mathrm{K}_{2} \mathrm{TaF}_{7}$ | [3.1],4.5 | 250.7 |
| 8 | $\mathrm{GdTaO}_{4}$ | . [3.2],5.0 | 250.6 |
| 1 | $\mathrm{TaF}_{5}$ | 5.3 | 250.2 |
| 8 | $\mathrm{YbTaO}_{4}$ | . [1.9],4.7 | 250.1 |
| 5 | $\mathrm{SmTaO}_{4}$ | [1],3.9 | - |
| 6 | TaC (oxidized?) | . [2.8],5.1 | 249.2 |
| 7 | $\mathrm{Ta} \cdot \mathrm{O}_{5} \ldots \ldots$. | . [2.8],4.9 | 248.8 |
| 0 | $\mathrm{Tl}_{3} \mathrm{TaS}_{4}$ | 4.8 | 248.6 |
| 0 | $\mathrm{Tl}_{3} \mathrm{TaSe}_{4}$ | 4.3 | 247.8 |
| 8 | Ta, powder, oxidized. | 4.7 | 248.7 |
| 9 | $\mathrm{Yb}_{2}\left(\mathrm{WO}_{4}\right)_{3}$ | 4.3 | 267.1 |
| 3 | $\mathrm{Na}_{2} \mathrm{WO}_{4}$. | . [3.4],5.6 | 267.3 |

Table 19. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(4 \mathrm{~d}_{3 / 2}\right)$ | $I\left(4 \mathrm{~d}_{5 / 2}\right)$ | $I\left(4 \mathrm{f}_{5 / 2}\right)$ | $I\left(4 \mathrm{f}_{7 / 2}\right)$ | $I(5 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 559 |  | 2.9],4.8 | 266.7 | 254.1 | 44.2 | 42.7 | - |
| 78 | $\left[\mathrm{Co} \mathrm{en}_{2} \mathrm{Cl}_{2}\right]_{3}\left(\mathrm{PW}_{12} \mathrm{O}_{40}\right) \ldots$ | 4.0 | - | - | 44.7 | 42.7 | - |
| 560 | $\mathrm{H}_{3} \mathrm{PW}_{12} \mathrm{O}_{40} \cdots \cdots . . .$. | 4.0 | 265 | 252.8 | 43.0 | 41.1 | - |
| 287 | $\mathrm{Cs}_{2} \mathrm{WS}_{4} \ldots \ldots . . . . . . . .$. | 5.2 | 265 | 252.6 | 42.7 | 40.9 | - |
| 295 |  | 4.5 | 264.2 | 251.7 | 41.5 | 39.5 | - |
| 561 | W, powder, oxidized . . . | 4.5 | 265.6 | 253.1 | 43.2 | 41.3 | - |
| 520 | $\mathrm{CsReO}_{4} \ldots \ldots . .$. | [1.6],4.7 | 287 | 273.7 | 56.5 | 54.3 | - |
| 562 | $\mathrm{TlReO}_{4} \cdots$. . . . . . . . . . . [2. | 2.6],5.1 | 286 | 273.2 | 56.1 | 53.9 | - |
| 474 | $\mathrm{AgReO}_{4} \cdots \cdots . . . . . . . .$. | 4.7 | 286 | 272.6 | (55.5) | 53.4 | - |
| 357 |  | [2],3.7 | 286.2 | 272.5 | 55.1 | 52.9 | - |
| 563 | methylene blue ( $\mathrm{ReO}_{4}$ ) .. | 4.5 | 284 | 270.3 | 53.1 | 50.7 | - |
| 434 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right] \mathrm{ReO}_{4} \ldots \ldots$. | 3.9 | 284 | 272 | (53.0) | 50.6 | - |
| 337 | $\mathrm{K}_{2} \mathrm{ReCl}_{6}$ | 3.7 | 282.9 | 268.7 | 51.5 | 49.1 | 9.7,(8) |
| 359 | $\mathrm{K}_{2} \mathrm{ReBr}_{6} \ldots \ldots . . . . .$. | 4.8 | - | 269.0 | 51.4 | 49.0 | 8.9 |
| 65 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right] \mathrm{ReS}_{4} \cdots \cdots$. | 4.4 | 280 | 267.6 | (50.8) | 48.2 | - |
| 130 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{ReBr}_{6} \ldots \ldots$. | 4.6 | - | 267.8 | 50.4 | 47.9 | 8.2 |
| 346 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{ReCl}_{6} \ldots \ldots$. | 4.9 | - | 267 | 50.1 | 47.9 | - |
| 607 | $\mathrm{K}\left[\mathrm{Os}^{\mathrm{VIII}} \mathrm{O}_{3} \mathrm{~N}\right] \ldots . . . . .[2$ | 2.1],4.4 | - | - | 66.2 | 63.7 | - |
| 608 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]\left[\mathrm{Os}^{\text {VIII }} \mathrm{O}_{3} \mathrm{~N}\right]$. | 4.2 | - | - | 63.9 | 61.3 | - |
| 362 | $\mathrm{K}_{2}\left[\mathrm{Os}{ }^{\text {VI }} \mathrm{O}_{2}(\mathrm{OH})_{4}\right] \ldots . .$. | 4.8 | - | - | 63.2 | 60.7 | 10 |
| 326 | $\mathrm{Cs}_{2} \mathrm{Os}^{\text {IV }} \mathrm{Cl}_{6}$. | 4.8 | - | - | 62.4 | 59.8 | 9 |
| 327 | $\mathrm{Cs}_{2}\left[\mathrm{Os}^{\mathrm{IV}} \mathrm{Cl}_{5} \mathrm{I}\right] \ldots . . . .$. | 4.4 | - | 286 | 62.2 | 59.2 | 9.6 |
| 448 | $\mathrm{Cs}_{2} \mathrm{Os}^{\text {IV }} \mathrm{Br}_{6}$ | 3.8 | 301.6 | - | 61.8 | 59.1 | 9.8 |
| 324 | $\mathrm{K}_{2} \mathrm{Os}^{\text {IV }} \mathrm{Cl}_{6} \ldots \ldots . .$. | 3.8 | - | 286.3 | 61.6 | 58.9 | 10.6,(8. |
| 324 | repeated . . . . . . . . . . . | 5.0 | - | 287 | 62.8 | 59.9 | 10.8, (8. |
| 64 | $\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{Os}^{\text {IV }} \mathrm{Cl}_{6} \ldots$. | 5.2 | - | - | 62.4 | 58.6 | 9.1, (7. |
| 334 | $\mathrm{Rb}_{2}$ cis-[ $\left.\mathrm{Os}^{\text {IV }} \mathrm{Cl}_{4} \mathrm{I}_{2}\right] \ldots .$. | 4.6 | - | - | 61.1 | 58 | 9.0 |
| 136 | $\mathrm{Co}_{2}\left[\mathrm{Os}^{\mathrm{II}}(\mathrm{CN})_{6}\right]$ | 5.0 | 300.4 | 285 | 60.6 | 57.9 | - |
| 134 | $\mathrm{Ni}_{2}\left[\mathrm{Os}^{\mathrm{II}}(\mathrm{CN})_{6}\right] \ldots . . .$. | 5.2 | 301.0 | 285 | 60.6 | 57.9 | - |
| 451 | $\mathrm{Tl}_{2} \mathrm{Os}^{\text {IV }} \mathrm{Br}_{6} \ldots \ldots .$. | 6.0 | 301 | 285 | 60.7 | 57.9 | 8.8 |
| 452 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2} \mathrm{Os}^{\text {IV }} \mathrm{Br}_{6} \ldots \ldots$ | 5.1 | - | - | 60.3 | 57.5 | 8.5 |
| 345 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2}$ trans-[ $\left.\mathrm{Os}^{\mathrm{IV}} \mathrm{Cl}_{4} \mathrm{I}_{2}\right]$ | ] 4.2 | - | - | 60.0 | 57.5 | - |
| 170 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{3}\left[\mathrm{Os}^{\mathrm{III}}(\mathrm{SCN})_{6}\right]$ | 4.6 | - | - | 59.8 | 57.1 | - |
| 518 | $\mathrm{Cs}_{2} \mathrm{Os}^{\text {IV }} \mathrm{I}_{6} \ldots \ldots . . . . . . .$. | 5.7 | - | - | 59.8 | 57 | - |
| 340 | $\mathrm{Cs}_{2}$ trans-[ $\left.\mathrm{Os}^{\text {IV }} \mathrm{Cl}_{2} \mathrm{I}_{4}\right] \ldots$. | 5.0 | - | 284.9 | 59.6 | 56.5 | 9,(8) |
| 177 | $\mathrm{Fe}_{4}\left[\mathrm{Os}^{\text {II }}(\mathrm{CN})_{6}\right]_{3}$ | 4.6 | - | - | 58.4 | 55.8 | - |
| 322 | $\mathrm{Cs}_{2} \mathrm{Ir}^{\mathrm{IV}} \mathrm{Cl}_{6} \ldots \ldots$. | 4.9 | 321 | 306 | 73.5 | 70.7 | 10.6 |
| 121 | $\mathrm{Cu}_{3}\left[\mathrm{Ir}^{\mathrm{III}}(\mathrm{CN})_{6}\right]_{2}, 11 \mathrm{H}_{2} \mathrm{O}$. | 4.5 | 320 | 305.4 | 72.9 | 70.0 | - |
| 103 | $\mathrm{K}\left[\mathrm{Ir}^{\mathrm{IV}} \mathrm{pyCl}_{5}\right] \ldots . . . . .$. | 4.7 | 319.5 | 303.7 | 71.9 | 68.9 | - |
| 600 | $\mathrm{Na}_{2} \mathrm{Ir}^{\mathrm{IV}} \mathrm{Cl}_{6} \ldots \ldots . .$. | 4.6 | - | 303.7 | 71.2 | 68.6 | - |
| 600 | repeated . . . . . . . . . . . | 4.7 | 319 | 304 | 71.6 | 68.9 | - |
| 99 | $\left[\operatorname{Ir}{ }^{\mathrm{III}}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2} \ldots .$. | 4.4 | 319.5 | 303.7 | 71.5 | 68.65 | 9.2 |
| 366 | $\mathrm{K}_{2} \mathrm{Ir}^{\mathrm{IV}} \mathrm{Br}_{6} \ldots \ldots .$. | 4.7 | - | - | 71.1 | 68.6 | 8.7 |
| 74 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{Ir}^{\text {IV }} \mathrm{Cl}_{6} \ldots \ldots$. | 4.4 | - | 303.9 | 71.3 | 68.5 | - |

Table 19. (continued).

|  | Compnund | $\mathrm{C}_{\text {st }}$ | $I\left(4 \mathrm{~d}_{3 / 2}\right)$ | $I\left(4 \mathrm{~d}_{5 / 2}\right)$ | $I\left(4 f_{5 / 2}\right)$ | $I\left(4 \mathrm{f}_{7 / 2}\right)$ | $I(5 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 08 | $\left[\mathrm{Ir}^{\text {III }} \mathrm{py}_{4} \mathrm{Cl} \mathrm{Cl}_{2}\right] \mathrm{Cl}$ | 4.7 | 319.3 | 303.8 | 71.15 | 68.2 | 8.5 |
| 32 | $\left[\mathrm{Ir}^{\mathrm{III}}\left(\mathrm{S}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{3} \mathrm{Cl}_{3}\right] \ldots$. | 5.2 | - | 303 | 70.5 | 67.5 | - |
| 31 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{3}\left[\mathrm{Ir}^{\mathrm{III}}(\mathrm{SCN})_{6}\right] .$. | 4.4 | 318 | 301.4 | 70.3 | 67.4 | - |
| 38 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{3} \mathrm{Ir}^{\text {III }} \mathrm{Cl}_{6} \ldots \ldots$. | 4.4 | - | - | 69.8 | 67.1 | - |
| 36 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{3}\left[\mathrm{Ir}^{\mathrm{III}}(\mathrm{SeCN})_{6}\right]$ | 4.1 | 316 | 299 | 69.8 | 67.0 | - |
| 16 | $\mathrm{Ir}^{\mathrm{III}}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{3} \mathrm{H}_{7}\right)_{2}\right)_{3} \ldots \ldots$. | 4.5 | 318.1 | 302.3 | 69.8 | 66.85 | - |
| 10 | $\mathrm{Cs}_{2} \mathrm{PtCl}_{6} \ldots \ldots \ldots \ldots . .$. | [1.6],4.3 | - | - | (86.3) | 83.5 | 12.4 |
| 12 | $\mathrm{Rb}_{2} \mathrm{PtCl}_{6} \ldots \ldots$ | [2.5],5.0 | - | - | 86.5 | 83.25 | 12.1 |
| 11 | $\mathrm{Cs}_{2} \mathrm{PtBr}_{6} \ldots \ldots$ | [1],4.0 | - | - | (85) | 82.8 | 11.5 |
| 20 | $\mathrm{K}_{2} \mathrm{PtCl}_{6}$. | [3],4.6 | 342.0 | 325.0 | 85.25 | 82.0 | 10.9 |
| )3 | [Pt den $\mathrm{Cl}_{3}$ ] $\mathrm{ClO}_{4} \ldots \ldots .$. | 4.5 | 340.4 | 323.3 | 84.5 | 81.4 | - |
| 34 | $\mathrm{K}_{2} \mathrm{PtBr}_{6} \ldots$ | 2.6 | 340.0 | 323.2 | 83.7 | 80.4 | 9.8 |
| ; 4 | repeated .............. | 5.0 | 341.2 | 324.3 | 84.6 | 81.3 | 10.5 |
| 17 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right]_{2} \mathrm{PtCl}_{6}$ | 4.6 | - | - | 84.2 | 81.0 | 9.2 |
| ; 8 | $\mathrm{Tl}_{2} \mathrm{PtCl}_{6} \ldots \ldots . . . . . .$. | 2.8 | 341.6 | 323.0 | 84.2 | 81.0 | 10.0 |
| ;1 | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{6}$ | 3.3 | 340.9 | 323.7 | 84.15 | 80.9 | 9.6 |
| i1 | repeated | 4.8 | 340.8 | 324.0 | 84.4 | 81.1 | 10.0 |
| 4 | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]_{2} \mathrm{PtI}_{6} \ldots \ldots$ | [2],4.8 | - | 323 | 84.1 | 80.8 | 10.4 |
| ;9 | $\mathrm{K}_{2}\left[\mathrm{Pt}(\mathrm{SeCN})_{6}\right] \ldots . . .$. | [2.7],4.8 | 340 | 323.4 | 83.9 | 80.6 | 10 |
| 6 | $\left[\mathrm{Ni} \mathrm{en}_{3}\right] \mathrm{PtI}_{6}$. | 4.8 | - | - | 83.8 | 80.5 | - |
| 8 | $\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{PtBr}_{6}$ | 4.6 | - | - | 83.6 | 80.4 | 9.3 |
| 8 | $\mathrm{K}_{2}\left[\mathrm{Pt}(\mathrm{SCN})_{6}\right]$ | 4.8 | 339.6 | 322.5 | 83.1 | 80.0 | 10.9,(9) |
| 1 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{PtI}_{6}$ | 4.8 | - | 323 | 83.2 | 80.0 | - |
| 9 | $\left[\mathrm{C}_{19} \mathrm{H}_{42} \mathrm{~N}_{2}\right]_{2}\left[\mathrm{Pt}\left(\mathrm{N}_{3}\right)_{6}\right] \ldots$. | 5.3 | 338 | 321 | 83.0 | 79.8 | - |
| 8 | $\mathrm{K}_{2} \mathrm{Pt}^{\text {II }} \mathrm{Cl}_{4}$ | 4.4 | 339.2 | - | 82.6 | 79.4 | 9.4 |
| 6 | $\left[\mathrm{Ni} \mathrm{en}_{2}\right]\left[\mathrm{Pt}^{\mathrm{II}}(\mathrm{CN})_{4}\right]$ | 4.1 | 339.5 | 322.1 | 82.4 | 79.3 | - |
| 9 | $\left[\mathrm{Pt}^{\text {II }}\left(\mathrm{S}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2} \mathrm{Cl}_{2}\right] \ldots$. | 5.0 | 338.6 | 321.6 | 81.9 | 78.7 | - |
| 7 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2} \mathrm{PtI}_{6}$ | 4.7 | - | - | 81.9 | 78.7 | 9.5 |
| 8 | $\mathrm{K}_{2} \mathrm{PtI}_{6}$ | 4.6 | 338 | 321.5 | 81.2 | 78.4 | 9.6 |
| 7 | $\left[\mathrm{PtII}\left(\mathrm{NH}_{3}\right)_{4}\right]\left[\mathrm{Pt}^{\mathrm{II}} \mathrm{Cl}_{4}\right] \ldots$. | 4.0 | 338.3 | 321.2 | 81.55 | 78.25 | - |
| 4 | (methylene blue) ${ }_{2}\left(\mathrm{PtI}_{6}\right) .$. | 5.0 | - | - | 81.1 | 77.9 | 8.2 |
| 3 | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right]_{2} \mathrm{Pt}^{\text {II }} \mathrm{Cl}_{4} \ldots \ldots$. | 5.3 | 338 | 320.2 | 80.9 | 77.7 | 8.3 |
| 1 | Pt , foil | 5.7 | 337.3 | 320.3 | 80.1 | 76.8 | 10.1 |
| 3 | $\mathrm{Au}_{2} \mathrm{Cl}_{6}$. | 4.4 | 361.8 | 343.6 | 97.9 | 94.6,92.0 | 11.8 |
| 3 | $\mathrm{KAu}^{\mathrm{III}} \mathrm{Cl}_{4}$. | 3.2 | - | 344.4 | 97.4 | 93.85 | - |
| 3 | $\mathrm{KAu}^{\mathrm{III}} \mathrm{Cl}_{4}, 1^{\mathrm{h}}$ later $\ldots .$. | 3.2 | - | - | 97.2 | 93.8,(91.2) | - |
| 2 | $\mathrm{KAu}^{\text {III }} \mathrm{Br}_{4}\left(+\mathrm{Au}^{\mathrm{I}}\right) \ldots .$. | 3.4 | - | - | (97.6),95.1 | (93.5),91.8 | 9.8 |
| t | $\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{4}\right]\left[\mathrm{Au}^{\text {III }}(\mathrm{CN})_{2} \mathrm{Br}_{2}\right]$ | 5.3 | 362 | 343.4 | 96.7 | 93.3 | - |
| ; | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right] \mathrm{Au}^{\mathrm{III}} \mathrm{Cl}_{4} \ldots \ldots$ | 5.2 | 360.8 | 342.8 | 96.8 | 93.4 | - |
| t | $\mathrm{Na}_{3}\left[\mathrm{Au}^{\mathrm{I}}\left(\mathrm{S}_{2} \mathrm{O}_{3}\right)_{2}\right]$. | 4.8 | 361.1 | 343.1 | 96.35 | 92.8 | - |
| , | $\left[\mathrm{N}\left(\mathrm{C}_{4} \mathrm{H}_{9}\right)_{4}\right] \mathrm{Au}^{\text {III }} \mathrm{Br}_{4}$. | 4.9 | 360.7 | 342.4 | 95.8 | 92.4(90) | - |
| ; | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Au}^{\mathrm{I}}\left(\mathrm{S}_{2} \mathrm{O}_{3}\right)_{2}\right] \ldots$ | 4.4 | 360.0 | 342.3 | 95.0 | 91.4 | - |
|  | $\mathrm{K}\left[\mathrm{Au}^{\mathrm{I}}(\mathrm{CN})_{2}\right] \ldots . . . . . .$. | 4.5 | 360.1 | 342.0 | 94.9 | 91.2 | 10.5 |
|  | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]\left[\mathrm{Au}^{\text {III }}(\mathrm{SeCN})_{4}\right]$ | 4.8 | 359 | 342.0 | 94.5 | 90.9 | - |

Table 19. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(4 \mathrm{~d}_{3 / 2}\right)$ | $I\left(4 \mathrm{~d}_{5 / 2}\right)$ | $I\left(4 \mathrm{f}_{5 / 2}\right)$ | $I\left(4 \mathrm{f}_{7 / 2}\right)$ | $I(5 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 284 | $\mathrm{Au}^{\mathrm{I}} \mathrm{S}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$ | 3.9 | 359.6 | 341.6 | 94.45 | 90.8 | - |
| 599 | $\mathrm{Na}_{3}\left[\mathrm{Au}^{\mathrm{I}}\left(\mathrm{SO}_{3}\right)_{2}\right]$. | 5.4 | 359.4 | 341.3 | 94.4 | 90.8 | 10.7 |
| 566 | Au, powder | 5.4 | 358.1 | 339.9 | 92.2 | 88.55 | 10.8,8.0 |
| - | Au , powder ( $\mathrm{BaSO}_{4}+\mathrm{T}$ | $\begin{aligned} & \left.\mathrm{F}_{4}\right) \\ & {[1.7], 4.8} \end{aligned}$ | - | 342.1 | 95.2 | 91.3 | , |
| - | $6 \mathrm{MgF}_{2}: 2 \mathrm{Au}: \mathrm{TI}_{2} \mathrm{O}_{3}$. | 5.6 | - | - | 92.6 | 88.8 | - |
| - | $16 \mathrm{MgF}_{2}: 2 \mathrm{Au}: \mathrm{Tl}_{2} \mathrm{O}_{3}$. | [2],4.2 | - | - | 94.5 | 90.9 | - |
| - | $2 \mathrm{BaSO}_{4}: 2 \mathrm{Au}: \mathrm{Tl}_{2} \mathrm{O}_{3}: 2$ | $\begin{aligned} & \mathrm{hF}_{4} \\ & {[1.0], 4.8} \end{aligned}$ | - | - | - | 92.9 | - |
| 567 | HgO . | [3.2],5.5 | 386.4 | 367.1 | 112.6 | 108.55 | - |
| 567 | repeated | [2.5],4.8 | 386.4 | 367.0 | 112.3 | 108.25 | (17.7),16.3 |
| 610 | $\mathrm{HgF}_{2}$ | [2.5],4.5 | 386.3 | 366.8 | 112.55 | 108.5 | 17.7,16.3 |
| 611 | $\left(\mathrm{Hg}_{2}\right) \mathrm{CrO}_{4} \cdots \cdots$. | [1.8], 4.0 | 386.2 | 366.8 | 112.25 | 108.2 | (17.9),16.5 |
| 510 | $\mathrm{Hg}\left(\mathrm{IO}_{3}\right)_{2} \ldots . . . .$. | [3.5],5.6 | 386.1 | 366.6 | 111.95 | 107.9 | (17.6),16.2 |
| 351 | $\mathrm{K}_{2} \mathrm{HgI}_{4} \ldots \ldots . .$. | 4.6 | 385 | 366.2 | 111.85 | 107.8 | - |
| 420 | $\mathrm{Cu}_{2} \mathrm{HgI}_{4} \ldots \ldots . .$. | . [4.3],6.1 | 386 | 366.7 | 111.9 | 107.8 | - |
| 163 | $\mathrm{K}_{2}\left[\mathrm{Hg}(\mathrm{SCN})_{4}\right] \ldots .$. | 5.0 | 384 | 365.2 | 110.85 | 106.75 | - |
| 155 | $\mathrm{Co}(\mathrm{NCS})_{4} \mathrm{Hg}$. . . . . . . | 4.7 | 384.4 | 364.9 | 110.6 | 106.55 | - |
| 187 | TIF . . . . . . . . . . . . . | [2.6],5.2 | - | - | 131.6 | 127.2 | (24.2), 22.0 |
| 562 | $\mathrm{TlReO}_{4} \ldots \ldots . . . .$. | . [2.6],5.1 | 414.5 | 393.7 | 131.45 | 127.0 | 23.9,21.8 |
| 506 | $\mathrm{TlIO}_{3} \ldots \ldots . . . . . . .$. | . [2.5],5.1 | - | - | 131.4 | 126.95 | 23.9,21.7 |
| 262 | $\mathrm{Tl}_{2} \mathrm{SO}_{4}$ | 5.1 | - | - | 131.15 | 126.7 | 23.6,21.4 |
| 313 | $\mathrm{Cs}_{4}\left(\mathrm{SbCl}_{6}\right)\left(\mathrm{Tl}^{\mathrm{III}} \mathrm{Cl}_{6}\right) \ldots$ | . [2.3],4.6 | - | - | 130.9 | 126.45 | (23.6),21.4 |
| 559 | $\mathrm{Tl}_{2} \mathrm{WO}_{4} \ldots \ldots$. | . [2.9],4.8 | - | - | 130.8 | 126.35 | (23.4),21.1 |
| 460 | $\mathrm{Tl}_{2} \mathrm{MoO}_{4} \ldots \ldots . .$. | . [2.6],4.8 | 413.3 | 392.0 | 130.4 | 125.95 | (23.1),20.8 |
| 568 | $\mathrm{Tl}_{2} \mathrm{CO}_{3} \ldots \ldots . . . .$. | . [2.4],4.7 | 413.7 | 392.8 | 130.35 | 125.9 | (22.8),20.7 |
| 286 | $\mathrm{Tl}_{2}\left[\mathrm{MoO}_{2} \mathrm{~S}_{2}\right]$ | 4.7 | 413.3 | - | 130.1 | 125.65 | (23),20.4 |
| 569 | $\mathrm{Tl}_{2}\left[\mathrm{WO}_{2} \mathrm{~S}_{2}\right]$. | 4.5 | - | - | 130.05 | 125.65 | (22.7),20.5 |
| 280 | $\mathrm{Tl}_{3} \mathrm{TaS}_{4}$ | 4.8 | - | - | 130.05 | 125.6 | (22.8),20.8 |
| 383 | $\mathrm{Tl}_{2} \mathrm{CrO}_{4}$ | 4.5 | - | - | 129.95 | 125.55 | (22.8),20.4 |
| 449 | TlBr . . . . . . . . . . | 4.6 | - | - | 129.9 | 125.45 | 22.2,20.1 |
| 288 | $\mathrm{Tl}_{2} \mathrm{MoS}_{4}$ | 4.4 | 412.5 | - | 129.75 | 125.3 | (22.5),20.2 |
| 458 | $\mathrm{Tl}_{3} \mathrm{NbS}_{4}$ | 4.8 | - | - | 129.7 | 125.25 | (22.3),20.1 |
| 438 | $\mathrm{Tl}_{3} \mathrm{NbSe}_{4}$. | 4.7 | - | - | 129.7 | 125.25 | (23),20.3 |
| 295 | $\mathrm{Tl}_{2} \mathrm{WS}_{4}$. | 4.5 | - | - | 129.6 | 125.15 | 21.8,19.5 |
| 570 | $\mathrm{Tl}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]$. | 5.0 | 412.9 | 392.0 | 129.55 | 125.1 | 22.1,19.8 |
| 515 | TlI | 4.85 | 412.1 | 391.5 | 129.4 | 125.05 | 23.4,20.4 |
| 338 | $\mathrm{Tl}_{2} \mathrm{PtCl}_{6}$ | 2.8 | 412.0 | 391.0 | 129.15 | 124.7 | 19.7 |
| 440 | $\mathrm{Tl}_{3} \mathrm{TaSe}_{4}$ | 4.3 | - | - | 129.1 | 124.65 | (22.2),19.9 |
| 341 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{\text {Tl }}{ }^{\mathrm{III}} \mathrm{Cl}_{6}$. | 3.7 | - | - | 129.0 | 124.6 | - |
| 451 | $\mathrm{Tl}_{2} \mathrm{OsBr}_{6}$ | 6.0 | - | - | 128.75 | 124.4 | $21.1,19.1$ |
| 571 | $\mathrm{Tl}^{\mathrm{III}} 2_{2} \mathrm{O}_{3}$ | 4.4 | - | - | 127.35 | 123.0 | - |
| 571 | repeated | 5.4 | 410.9 | 390.0 | 127.05 | 122.7 | 20,18.0 |
| - | $6 \mathrm{MgF}_{2}: 2 \mathrm{Au}: \mathrm{Tl}_{2} \mathrm{O}_{3}$. | 5.6 | - | - | 127.2 | 122.85 | - |
| - | $16 \mathrm{MgF}_{2}: 2 \mathrm{Au}: \mathrm{Tl}_{2} \mathrm{O}_{3} \ldots$ | . [2],4.2 | - | - | 129.4 | 125.0 | - |

Table 19. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(4 \mathrm{~d}_{3 / 2}\right)$ | $I\left(4 \mathrm{~d}_{5 / 2}\right)$ | $I\left(4 \mathrm{f}_{5 / 2}\right)$ | $I\left(4 \mathrm{f}_{7 / 2}\right)$ | $I(5 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| - | $2 \mathrm{BaSO}_{4}: 2 \mathrm{Au}: \mathrm{Tl}_{2} \mathrm{O}_{3}: 2 \mathrm{ThF}_{4}$ |  |  |  |  |  |  |
|  |  | [1.0], 4.8 | - | - | 131.1 | 126.7 | - |
| 19 | $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$ | . [2.8],5.3 | - | 422.2 | 152.1 | 147.2 | 30.9,28.3 |
| 14 | $\mathrm{Cs}_{2} \mathrm{~Pb}^{\mathbf{I V}} \mathrm{Cl}_{6}$ | . [2.1],4.9 | - | - | 151.95 | 147.1 | 30.5,27.8 |
| 01 | $\mathrm{Pb}\left(\mathrm{IO}_{3}\right)_{2}$. | [1.5],4.1 | - | - | 151.85 | 146.95 | 30.6,28.0 |
| 11 | $\mathrm{PbI}_{2} \ldots$ | . [1.7],5.1 | - | - | 151.7 | 146.75 | 30.4,28.0 |
| 64 | $\mathrm{PbSO}_{4}$ | 4.5 | 443.2 | 420.7 | 150.95 | 146.1 | 29.8,27.2 |
| 30 | $\mathrm{PbCl}_{2}$ | . [2.5],4.6 | - | - | 151.0 | 146.1 | 29.3,26.8 |
| 46 | $\mathrm{PbBr}_{2} \ldots \ldots . . . .$. | . [2.7],4.9 | - | - | 150.85 | 145.95 | 29.4,26.9 |
| 24 | $\mathrm{PbF}_{2}$ | [3],4.8 | - | - | 150.75 | 145.9 | 29.6,27.1 |
| 72 | $\mathrm{Pb}_{3}(\mathrm{OH})_{3}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{3}$ | 5.2 | - | - | 150.8 | 145.85 | - ,27.2 |
| 31 | $\left[\mathrm{Co} \mathrm{en} 2 \mathrm{Cl}_{2}\right]_{2} \mathrm{~Pb}^{\text {IV }} \mathrm{Cl}_{6}$. | [3.0],5.0 | - | - | 150.7 | 145.85 | 29.4,26.7 |
| 73 | $\mathrm{Pb}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{2}, 2 \mathrm{H}_{2} \mathrm{O} \ldots$ | 4.9 | - | - | 150.0 | 145.1 | 28.9,26.3 |
| 74 | $\mathrm{PbCO}_{3} \ldots \ldots$. | 3.2 | - | - | 149.8 | 145.0 | - |
| 74 | PbS | 4.2 | - | - | 149.85 | 145.0 | 28.9,26.3 |
| 44 | $\left[\mathrm{As}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right]_{2} \mathrm{~Pb}^{\mathrm{IV}} \mathrm{Cl}_{6}$. | 4.8 | - | - | 149.2 | 144.25 | - ,25.2 |
| 75 | PbO | 3.3 | - | - | 149.0 | 144.15 | - |
| 96 | $\mathrm{Pb}\left(\mathrm{S}_{2} \mathrm{CN}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}$. | 4.2 | - | - | 148.9 | 144.0 | 26.6,24.2 |
| 76 | $\mathrm{Pb}^{\mathrm{II}} 2^{\mathrm{Pb}}{ }^{\text {IV }} \mathrm{O}_{4}$. | 3.6 | - | - | 148.8 | 143.9 | - |
| 87 | $\mathrm{PbCrO}_{4}$ | 3.3 | - | - | 148.6 | 143.75 | 27,25.0 |
| J2 | $\mathrm{Pb}\left(\mathrm{S}_{2} \mathrm{P}\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{2}\right)_{2}$. | 4.8 | - | - | 148.2 | 143.3 | (26.5), 24.3 |
| 77 | $\mathrm{PbO}_{2}$ | 4.4 | - | - | 147.2 | 142.4 | - |
| 77 | repeated | 5.0 | 440.6 | 418.4 | 148.0 | 143.1 | 27,24.4 |
| 20 | $\mathrm{BiF}_{3}$ | . [3.3],5.4 | 474.7 | 450.9 | 173.1 | 167.8 | 37.6,34.7 |
| 78 | $\mathrm{Bi}^{\text {III }} \mathrm{Bi}^{\mathrm{V}} \mathrm{O}_{4}$ | . [2.3],4.8 | 474.0 | 450.1 | 172.5 | 167.15 | 37.3,34.4 |
| )9 | $\mathrm{Bi}\left(\mathrm{IO}_{3}\right)_{3} \ldots \ldots$. | 4.1 | - | - | 172.3 | 166.95 | $36.7,33.9$ |
| 73 | $\mathrm{Bi}_{2} \mathrm{Ti}_{2} \mathrm{O}_{7} \ldots \ldots . .$. | . [2.3],4.7 | 473 | 449.8 | 172.2 | 166.9 | 36.9,34.0 |
| 79 | $\mathrm{Bi}_{2} \mathrm{O}_{3}$ | . [2.1],4.7 | - | - | 172.2 | 166.85 | 36.8,33.8 |
| 30 | $\mathrm{NaBi}^{\text {V }} \mathrm{O}_{3}$ | 4.55 | - | - | 171.8 | 166.5 | - |
| 14 | $\mathrm{BiI}_{3}$ | [3],5.0 | - | - | 171.8 | 166.5 | (36.8),33.7 |
| 13 | $\mathrm{CsBiI}_{4}$ | [3],5.0 | - | - | 171.6 | 166.3 | (36.5), 33.7 |
| . 3 | repeated | 4.5 | 473 | 449.3 | - | - | 36.4,33.3 |
| 31 | BiOI. . . . . . . . . . . | . [2],5.05 | - | - | 171.4 | 166.1 | - |
| 18 | $\mathrm{K}_{4} \mathrm{BiI}_{7}$ | [3],4.9 | 472.6 | 449.1 | 171.3 | 166.0 | 35.8,32.9 |
| 16 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{BiCl}_{6}$. | 3.6 | - | - | 170.2 | 164.9 | 35,31.9 |
| 19 | $\mathrm{ThF}_{4}$ | [1.3],4.9 | 723.5 | 686.1 | 354.75 | 345.4 | 104.15,97.3 |
| 5 | $\mathrm{Th}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{2}$ | [1.9],4.6 | 722.6 | 685.1 | 353.45 | 344.1 | 103.1,96.2 |
| 19 | $\mathrm{Th}\left(\mathrm{IO}_{3}\right)_{4}$ | [2.2],4.7 | 722.4 | 684.3 | 352.85 | 343.5 | 102.4,95.55 |
| ;2 | $\mathrm{Th}_{0.95} \mathrm{U}_{0.05} \mathrm{O}_{2}$ | . [2.3],6.4 | - | - | 352.35 | 343.0 | - |
| ; 3 | $\mathrm{ThO}_{2} \ldots$ | . [1.0],4.6 | 720.6 | 683.4 | 352.0 | 342.65 | 101.5,94.5 |
| ; 4 | $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left[\mathrm{Th}\left(\mathrm{CO}_{3}\right)_{5}\right]$ | . [2.3],4.2 | 720.7 | 683.0 | 351.8 | 342.45 | - |
| 7 | $\mathrm{Th}_{0 \cdot 6} \mathrm{Ce}_{0 \cdot 2} \mathrm{U}_{0 \cdot 2} \mathrm{O}_{2} \ldots$ | [2.8],5.9 | - | - | 351.4 | 342.1 | - |
| . 2 | $\mathrm{Th}_{0.9} \mathrm{Pr}_{0 \cdot 1} \mathrm{O}_{2} \ldots \ldots$ | . [2.0],5.5 | - | - | 351.1 | 341.8 | - |
| 6 | $\mathrm{Thaca}_{4}$ | [2.3],4.3 | 720.0 | 682.5 | 351.1 | 341.75 | 100.8,94.0 |
| 5 | $\mathrm{Th}_{0.5} \mathrm{Eu}_{0.5} \mathrm{O}_{1.75} \ldots$. | . [2.3],5.8 | - | - | 351.1 | 341.75 | - |

Table 19. (continued).

|  | Compound | $\mathrm{C}_{\text {st }}$ | $I\left(4 \mathrm{~d}_{3 / 2}\right)$ | $I\left(4 \mathrm{~d}_{5 / 2}\right)$ | $I\left(4 \mathrm{f}_{5 / 2}\right)$ | $I\left(4 \mathrm{f}_{7 / 2}\right)$ | $I(5 \mathrm{~d})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 586 | $\mathrm{Th}_{0 \cdot 8} \mathrm{Ce}_{0 \cdot 1} \mathrm{U}_{0 \cdot 1} \mathrm{O}_{2} \ldots$ | [2.6],4.8 | - | - | 351.0 | 341.7 | - |
| 528 | $\mathrm{Th}_{0.8} \mathrm{Ce}_{0 \cdot 15} \mathrm{U}_{0.05} \mathrm{O}_{2}$ | . [2.2],4.8 | 720.3 | 682.4 | 351.0 | 341.7 | 100.8,93.9 |
| 607 | $\mathrm{Th}\left(\mathrm{NO}_{3}\right)_{4}, 5 \mathrm{H}_{2} \mathrm{O}$ | 4.4 | 720.3 | 682.8 | 351.0 | 341.65 | 100.3,93.6 |
| 617 | $\mathrm{Th}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CHOHCO} 2\right)_{4}$ | 4.3 | 719.7 | 682.4 | 350.85 | 341.5 | 100.4,93.5 |
| 587 | Th, powder, oxidized. | [2.3],5.7 | - | - | 352.0 | 342.7 | - |
| 494 | $\mathrm{UO}_{2}\left(\mathrm{IO}_{3}\right)_{2} \ldots \ldots$. | [1.4],4.7 | 791.1 | 748.8 | 401.7 | (394),390.8 | 115.2,106.9 |
| 18 | $\mathrm{CsUO}_{2}\left(\mathrm{NO}_{3}\right)_{3}$. | [2.8],5.1 | 790.3 | 746 | (405),401.2 | (394),390.4 | - ,106.6 |
| 242 | $\mathrm{Cu}\left(\mathrm{UO}_{2}\right)_{2}\left(\mathrm{PO}_{4}\right)_{2}$ | . [2.0],4.6 | 790.8 | 747.9 | 400.9 | 390.0 | 114.7,106.3 |
| 20 | $\mathrm{RbUO}_{2}\left(\mathrm{NO}_{3}\right)_{3} \ldots$ | [ [2.7], 4.8 | 790.0 | 747.4 | (404),400.6 | (393),389.7 | - |
| 230 | $\mathrm{NaZn}\left(\mathrm{UO}_{2}\right)_{3}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{9}$ | . [2.5],4.6 | 790 | 747.8 | 400.4 | 389.6 | 114.0,105.5 |
| 218 | $\mathrm{K}_{2} \mathrm{U}^{\text {IV }} \mathrm{F}_{6}$ | . [2.4],4.9 | 790 asym. | . 747.5 | 407.3,400.4 | 396.7,389.5 | - |
| 238 | $\mathrm{NaMg}\left(\mathrm{UO}_{2}\right)_{3}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{9}$ | . [3],4.4 | 789.5 | 747.4 | 400.4 | (393),389.5 | 114.2,105.4 |
| 422 | $\mathrm{Zn}\left(\mathrm{UO}_{2}\right)_{2}\left(\mathrm{CH}_{3} \mathrm{CO}_{2}\right)_{6} \ldots$ | [3.7],5.6 | - | - | 400.2 | 389.4 | - |
| 528 | $\mathrm{Th}_{0.8} \mathrm{Ce}_{0 \cdot 15} \mathrm{U}_{0.05} \mathrm{O}_{2} \ldots$ | . [2.2],4.8 | - | - | 400.1 | 389.2 | - |
| 527 | $\mathrm{Th}_{0 \cdot 6} \mathrm{Ce}_{0 \cdot 2} \mathrm{U}_{0 \cdot 2} \mathrm{O}_{2} \ldots \ldots$ | . [2.8],5.9 | - | - | 400.05 | 389.15 | - |
| 588 | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{U}_{2} \mathrm{O}_{7}$. | 4.7 | 789.0 | 747.1 | 399.9 | 389.05 | - |
| 529 | $\mathrm{Ce}_{0.5} \mathrm{U}_{0.5} \mathrm{O}_{2}$ | 6.1 | - | - | 399.5 | (397),388.8 | - |
| 268 | $\mathrm{UO}_{2} \mathrm{SO}_{4}, 3 \mathrm{H}_{2} \mathrm{O}$ | 5.1 | 789.4 | 746.9 | 399.6 | 388.8 | 113.3,104.8 |
| 252 | $\mathrm{U}\left(\mathrm{SO}_{4}\right)_{2}, 4 \mathrm{H}_{2} \mathrm{O}$ | [2.5],4.8 | 789 | 747.0 | 405,399.5 | 393.8,388.7 | 113,107,104.8 |
| 252 | repeated | 4.8 | (795),789.7 | (752.4),747.0 | 405.2,398.9 | 393.9,389.0 | 113.4,108,105. |
| 22 | $\mathrm{UO}_{2}\left(\mathrm{NO}_{3}\right)_{2} 6 \mathrm{H}_{2} \mathrm{O}$ | 4.0 | 790 | 746.8 | 399.5 | (392),388.65 | 113,105.0 |
| 586 | $\mathrm{Th}_{0 \cdot 8} \mathrm{Ce}_{0 \cdot 1} \mathrm{U}_{0 \cdot 1} \mathrm{O}_{2} \ldots$ | [2.6],4.8 | - | - | 399.5 | 388.6 | - |
| 589 | $\mathrm{U}^{\mathrm{IV}} \mathrm{O}_{2}$ | 3.6 | 787.9 | 745.4 | 398.1 | 387.3 | - |
| 590 | $\mathrm{U}_{3} \mathrm{O}_{8}$. | 4.1 | (794),787.5 | (750.7),745.3 | 398.0 | 387.2 | - |
| 248 | $\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3} \mathrm{H}\right]_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{Cl}_{6} .$. | 4.6 | 787 | 746.2 | 396.6 | 386.0 | - |

Table 20. Various weak photo-electron signals from 22 selected compounds.

|  | Compound | $\mathrm{C}_{\text {st }}$ |  |
| :---: | :---: | :---: | :---: |
| 403 | MgO | [0.4],4.0 | $I(\mathrm{O} 2 \mathrm{~s})=29.6 \mathrm{I}(\mathrm{O} 2 \mathrm{p})=14$ |
| 388 | $\mathrm{Cr}_{2} \mathrm{O}_{3}$ | 4.2 | $I(\mathrm{O} 2 \mathrm{~s})=28.3 I(\mathrm{O} 2 \mathrm{p})=11.5 I(\mathrm{Cr} 3 \mathrm{~d})-8.2$ |
| 395 | $\mathrm{Fe}_{2} \mathrm{O}_{3}$ | 4.4 | $I(\mathrm{O} 2 \mathrm{~s})=28.4 I(\mathrm{O} 2 \mathrm{p}), I(\mathrm{Fe} 3 \mathrm{~d})=13.6,10.6$ |
| 304 | $\mathrm{KClO}_{4}$ | 4.8 | $I(\mathrm{Cl2s})=285.3$ |
| 321 | KCl | [2.3],4.8 | $I(\mathrm{Cl} 2 \mathrm{~s})=276.7 \quad I(\mathrm{Cl} 3 \mathrm{~s})=(22.1)$ |
| 320 | $\mathrm{K}_{2} \mathrm{PtCl}_{6}$ | [3],4.6 | $I(\mathrm{Cl} 2 \mathrm{~s})=276.4$ |
| 324 | $\mathrm{K}_{2} \mathrm{OsCl}_{6}$ | 5.0 | $I(\mathrm{Cl2s})=276.2$ |
| 201 | $\mathrm{CaF}_{2}$ | [1.3],4.5 | $I(\mathrm{Ca} 2 \mathrm{~s})=448.0 \quad I(\mathrm{Ca} 3 \mathrm{~s})=52.5$ |
| 370 | $\mathrm{Ca}\left(\mathrm{IO}_{3}\right)_{2}$ | [2.2], 4.6 | $I(\mathrm{Ca} 2 \mathrm{~s})=446.4$ |
| 306 | [Vurea ${ }_{6}$ ] $\left.\mathrm{ClO}_{4}\right)_{3}$. | 5.4 | $I(\mathrm{O} 2 \mathrm{~s})=31.8 I(\mathrm{~V} 3 \mathrm{~d})=11.1$ |
| 381 | $\mathrm{BaCrO}_{4}$ | [2.2],4.9 | $I(\mathrm{Cr} 2 \mathrm{~s})=708.5 \quad I(\mathrm{O} 2 \mathrm{~s})=30.1$ |
| 216 | $\mathrm{K}_{2}\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$ | [1.7],4.9 | $I(\mathrm{Cr} 2 \mathrm{~s})=707.2$ broad $I(\mathrm{Cr} 3 \mathrm{~s})=88.6,84.3$ |
| 86 | $\mathrm{NH}_{4}\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{NCS})_{4}\right]$ | [3.7],5.2 | $I(\mathrm{Cr} 2 \mathrm{~s})=706.6,703.2$ |

Table 20. (continued).


Table 21. Comparison of $I^{\prime}$ Values (corrected for charging effects) with the calculated values $I_{\text {calc }}$ from atomic ionization energies and Madelung potentials. $\partial$ is defined in the text the distance between the two carbon 1 s signals.

|  | $\partial$ | $I^{\prime}(\mathrm{M})$ | $I_{\text {calc }}$ | $I^{\prime}(\mathrm{X})$ | $I_{\text {calc }}$ | $I-4.8$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| LiF. | 2.8,3.7 | 60.7 | 63.12 | 12.85 | 12.92 | 10.8,11.8 |
| NaF. | 4.2 | 35.5 | 36.43 | 12.8 | 14.26 | 12.0 |
| NaCl . | 2.2 | 35.6 | 38.37 | 10.0 | 12.53 | 7.4 |
| NaBr | 2.4 | 35.3 | 39.84 | 9.0 | 11.81 | 6.6 |
| NaI | 2.8 | 35.6 | 39.52 | 8.4 | 10.83 | 6.4 |
| KF | 2.4 | 21.7 | 22.20 | 11.5 | 12.82 | 9.2 |
| KCl | 2.5 | 21.4 | 23.63 | 9.4 | 11.60 | 7.1 |
| KBr | 1.5 | 21.8 | 23.98 | 9.2 | 11.00 | 5.9 |
| KI | 3.1 | 21.7 | 24.51 | 7.9 | 10.17 | 6.2 |
| RbCl | 2.4 | 19.0 | 19.64 | 9.5 | 11.25 | 7.1 |
| RbBr . | 2.4 | 18.5 | 19.97 | 8.9 | 10.67 | 6.5 |
| RbI | 1.7 | 18.8 | 20.43 | 8.3 | 9.91 | 5.2 |
| CsCl | 4.8,4.5 | 15.0 | 18.0 | 9.0 | 10.7 | 8.6,9.0 |
| CsBr . | 3.35 | 15.0 | 18.27 | 8.7 | 10.2 | 7.2 |
| Csi | 3.65 | 15.1 | 18.7 | 8.1 | 9.5 | 6.9 |
| MgO | 3.6 | 54.1 | 56.24 | 9 | - | - |
| $\mathrm{CaF}_{2}$. | 2.75,3.2 | 30.6 | 35.56 | 13.3 | 18.75 | 11.3,11.5 |
| $\mathrm{SrF}_{2}$. | 3.8,3.8 | 25.0 | 29.3 | 13.3 | 17.70 | 12.2,12.3 |
| $\mathrm{BaF}_{2}$ | 4.4,4.3 | 19.3 | 28.0 | 11.9 | 16.93 | 11.5,11.4 |
| ZnS | 2.4 | 15.6 | 19.72 | - | - | - |
| CdO | 2.6 | 16.8 | 16.04 | - | - | - |
| CdS | 1.5 | 16.8 | 18.78 | - | - | - |
| AgBr | 1.9 | 10.0 | 14.77 | - | - | - |
| $\mathrm{CdF}_{2}$ | 1.8 | 17.4 | 22.0 | 11.9 | 18.9 | 8.9 |
| $\mathrm{HgF}_{2}$. | 2.0 | 14.3 | 19.1 | - | - | - |

Table 22. $I^{\prime}$ of fluorine and potassium compounds. Sometimes, two independent determinations have been performed.

|  | $\partial$ | $I^{\prime}(\mathrm{F} 1 \mathrm{~s})$ |  | $\partial$ | $I^{\prime}(\mathrm{F} 1 \mathrm{~s})$ |  | $\partial$ | $I^{\prime}\left(\mathrm{K} 2 \mathrm{p}_{3 / 2}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{KBF}_{4}$ | 1.5,2.6 | 692.5,692.2 | $\mathrm{CoF}_{2}$ | 4.3 | 689.8 | $\mathrm{KBF}_{4}$ | 1.5,2.6 | 299.5,299.2 |
| $\mathrm{KPF}_{6}$ | 1.8 | 692.2 | $\mathrm{CuF}_{2}, 2 \mathrm{H}_{2} \mathrm{O}$ | 2.2 | 689.8 | $\mathrm{KPF}_{6}$ | 1.8 | 299.2 |
| $\mathrm{K}_{3} \mathrm{RhF}_{6}$ | 2.7 | 692.1 | $\left[\mathrm{Zn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{SiF}_{6}$ | 2.3 | 689.8 | $\mathrm{K}_{3} \mathrm{RhF}_{6}$. | 2.7 | 299.0 |
| $\mathrm{CsSbF}_{6}$ | 3.6,4.2 | 691.4,691.1 | $\left(\mathrm{NH}_{4}\right)_{2}\left[\mathrm{In}\left(\mathrm{H}_{2} \mathrm{O}\right)\right.$ |  |  | $\mathrm{K}_{2} \mathrm{SiF}_{6}$ | 2.4,2.6 | 298.8,298.8 |
| $\mathrm{K}_{2} \mathrm{SiF}_{6}$ | 2.4,2.6 | 691.1,690.9 |  | 1.2 | 689.8 | $\mathrm{K}_{2} \mathrm{GeF}_{6} \ldots \ldots$ | 3.4 | 298.6 |
| $\mathrm{ZrF}_{4}$ | 2.6 | 690.9 | $\mathrm{CeF}_{3}$ | 4.3 | 689.8 | $\mathrm{K}_{4} \mathrm{BiI}_{7}$. | 1.9 | 298.6 |
| $\mathrm{MgF}_{2}$ | 4.3,4.9 | 690.7,690.7 | $\mathrm{SmF}_{3}$ | 3.0 | 689.8 | $\mathrm{K}_{2} \mathrm{BeF}_{4}$ | 3.0,2.8 | 298.5,298.5 |
| $\mathrm{Na}_{3} \mathrm{AlF}_{6}$. | 3.0 | 690.7 | $\mathrm{BiF}_{3}$. | 2.1 | 689.8 | $\mathrm{K}_{2} \mathrm{NbF}_{7} \ldots \ldots$ | 2.0 | 298.5 |
| $\mathrm{K}_{2} \mathrm{GeF}_{6}$ | 3.4 | 690.7 | $\mathrm{SrF}_{2}$. | 3.8,3.8 | 689.9,689.7 | $\mathrm{K}_{2} \mathrm{HfF}_{6} \ldots \ldots$ | 2.3 | 298.5 |
| $\mathrm{K}_{2} \mathrm{NbF}_{7} \ldots$ | 2.0 | 690.7 | $\mathrm{CeF}_{4}, \mathrm{H}_{2} \mathrm{O} \ldots$ | 2.8 | 689.6 | $\mathrm{K}_{2} \mathrm{TiF}_{6}$ | 2.1 | 298.4 |
| $\mathrm{PrF}_{3}$ | 3.4 | 690.7 | $\mathrm{CdF}_{2}$ | 2.3,1.7 | 689.6,689.3 | $\mathrm{K}_{2} \mathrm{PtCl}_{6} \ldots \ldots$ | 1.6 | 298.3 |
| $\mathrm{K}_{2} \mathrm{TaF}_{7}$ | 1.4 | 690.6 | NaF . | 4.2,3.8 | 689.6,689.1 | KBr . | 1.5 | 298.3 |
| $\mathrm{YF}_{3}$ | 3.7 | 690.5 | $\mathrm{NiF}_{2}, 4 \mathrm{H}_{2} \mathrm{O} \ldots$ | 2.1 | 689.4 | $\mathrm{K}_{2} \mathrm{TaF}_{7} \ldots \ldots$ | 1.4 | 298.2 |
| $\mathrm{YbF}_{3}$ | 2.5 | 690.4 | $\mathrm{KNiF}_{3}$ | 3.2 | 689.4 | $\mathrm{KIO}_{3} \ldots \ldots$ | 2.1 | 298.1 |
| LiF | 2.8,3.7 | 690.0,690.4 | $\mathrm{K}_{2} \mathrm{UF}_{6}$ | 2.5 | 689.4 | $\mathrm{KIO}_{4} \ldots \ldots$. | 2.5 | 298.0 |
| $\mathrm{K}_{2} \mathrm{BeF}_{4}$ | 3.0,2.8 | 690.4,690.0 | $\mathrm{BaF}_{2}$ | 4.3,4.4 | 689.0,688.8 | $\mathrm{K}_{2} \mathrm{HgI}_{4} \ldots \ldots$ | 2.2 | 298.0 |
| $\mathrm{ErF}_{3}$ | 3.5 | 690.3 | $\mathrm{K}_{2}\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$ | 3.2 | 688.7 | KF. | 2.4 | 297.9 |
| $\mathrm{LuF}_{3}$ | 5.2 | 690.3 | $\mathrm{PbF}_{2}$ | 1.7 | 688.4 | KI | 3.1 | 297.9 |
| $\mathrm{K}_{2} \mathrm{Hf} \mathrm{F}_{6}$. | 2.3 | 690.3 | $\mathrm{HgF}_{2}$. | 2.0 | 688.0 | KCl | 2.5 | 297.8 |
| $\mathrm{GaF}_{3}, 3 \mathrm{H}_{2} \mathrm{O}$. | 2.7 | 690.2 | KF. | 2.4 | 687.9,687.6 | $\mathrm{K}_{2} \mathrm{HAsO}_{4} \ldots$ | 1.7 | 297.8 |
| $\mathrm{LaF}_{3}$. | 4.7 | 690.1 |  |  |  | $\mathrm{K}_{2} \mathrm{UF}_{6}$ | 2.5 | 297.8 |
| $\mathrm{NdF}_{3}$ | 2.7 | 690.1 |  |  |  | $\mathrm{KNiF}_{3} \ldots \ldots$. | 3.2 | 297.7 |
| $\mathrm{CaF}_{2}$. | 3.2,2.7 | 690.3,690.0 |  |  |  | $\mathrm{K}\left[\mathrm{OsO}_{3} \mathrm{~N}\right]$ | 2.3 | 297.7 |
| $\mathrm{K}_{2} \mathrm{TiF}_{6}$. | 2.0 | 690.0 |  |  |  | $\mathrm{K}_{2} \mathrm{Pt}(\mathrm{SeCN})_{6}$ | 2.1 | 297.7 |
| $\mathrm{NH}_{4} \mathrm{SbF}_{4} \ldots$ | 1.7 | 690.0 |  |  |  | $\mathrm{KAg}(\mathrm{CN})_{2} \ldots$ | 1.8 | 297.5 |
| $\mathrm{EuF}_{3}$ | 3.8 | 690.0 |  |  |  | $\mathrm{KBrO}_{3} \ldots \ldots$ | 1.7 | 297.3 |
| $\mathrm{GdF}_{3}$ | 3.6 | 690.0 |  |  |  | $\mathrm{K}_{2}\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{F}_{5}\right]$ | 3.2 | 297.1 |
| $\mathrm{ThF}_{4}$ | 3.6 | 690.0 |  |  |  | KSeCN | 1.7 | 296.5 |
| $\mathrm{BeF}_{2} \ldots \ldots$ | 2.3 | 689.8 |  |  |  | $\mathrm{K}_{2}\left[\mathrm{Ru}(\mathrm{NO}) \mathrm{Cl}_{5}\right]$ | 3.3 | 296.1 |

Table 23. $I^{\prime}$ (4f) of compounds of lanthanides, hafnium and tantalum.

|  | $\partial$ | $I^{\prime}(4 \mathrm{f})$ |  | $\partial$ | $I^{\prime}(4 \mathrm{f})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{PrF}_{3}$ | 3.4 | 10.3,(8.6) | $\mathrm{ErF}_{3}$ | 3.5 | 15.2,(12.2) |
| $\mathrm{NdF}_{3}$ | 2.7 | 12.2 | $\mathrm{Er}\left(\mathrm{IO}_{3}\right)_{3}$ | 2.3 | 15.2,(14),(11.5) |
| $\mathrm{NdAsO}_{4}$ | 2.6 | 10.9 | $\mathrm{Er}_{2} \mathrm{O}_{3}$ | 3.2 | 14.4,(11) |
| $\mathrm{Nd}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 2.1 | 11.1 | $\mathrm{Tm}\left(\mathrm{IO}_{3}\right)_{3}$ | 2.4 | 14.8,(11.4) |
| $\mathrm{Nd}_{2} \mathrm{O}_{3}$ | 3.0 | 10.4 | $\mathrm{Tm}_{2} \mathrm{O}_{3}$ | 2.8 | 14.9,(10.8) |
| $\mathrm{SmF}_{3}$ | 3.0 | 11.1 | $\mathrm{YbF}_{3}$ | 2.5 | 18.0,14.2 |
| $\mathrm{Sm}_{2} \mathrm{O}_{3}$ | 2.6 | 11 | $\mathrm{Yb}\left(\mathrm{IO}_{3}\right)_{3}$ | 2.7 | 17,13.3 |
| $\mathrm{EuF}_{3}$ | 3.8 | 13.7 | $\mathrm{Yb}_{2}\left(\mathrm{WO}_{4}\right)_{3}$ | 1.8 | 17.3,13.3 |
| $\mathrm{Eu}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 2.0 | 14 | $\mathrm{YbTaO}_{4}$ | 2.8 | (16.6),12.9 |
| $\mathrm{Eu}_{2} \mathrm{O}_{3}$. | 2.9 | 12.0 | $\mathrm{YbAsO}_{4}$ | 1.7 | (17),12.9 |
| $\mathrm{EuSO}_{4}$ | 2.0 | 6.9 | $\mathrm{Yb}_{2} \mathrm{Hf}_{2} \mathrm{O}_{7}$ | 2.5 | (16),12.5 |
| $\mathrm{GdTaO}_{4}$ | 1.8 | 15.6 | $\mathrm{YbVO}_{4}$ | 2.1 | 16.1,12.2 |
| $\mathrm{GdF}_{3}$ | 3.6 | 15.3 | $\mathrm{LuF}_{3}$ | 5.2, | 15.3,15.2 |
| $\mathrm{Gd}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | 2.3 | 15.2 | $\mathrm{Lu}\left(\mathrm{IO}_{3}\right)_{3}$ | 2.5 | 14.3 |
| $\mathrm{Gd}_{2} \mathrm{O}_{3}$. | 2.0 | 13.6 | $\mathrm{Lu}_{2} \mathrm{O}_{3}$ | 2.1 | 13.9 |
| $\mathrm{TbO}_{2}$ | 3.1 | 24.7 | $\mathrm{K}_{2} \mathrm{HfF}_{6}$ | 2.3 | (25.2), 23.7 |
| $\mathrm{Tb}_{4} \mathrm{O}_{7}$ | 2.6 | 24.4,14.6,8.5 | $\mathrm{Hf}\left(\mathrm{IO}_{3}\right)_{4}$ | 2.4 | (24.9), 23.2 |
| $\mathrm{Tb}(\mathrm{OH})_{3}$ | 2.6 | 15.5,8.9 | $\mathrm{HfO}_{2}$ | 2.3 | 22.7 |
| $\mathrm{Dy}_{2} \mathrm{O}_{3}$ | 3.2 | 14.7,11.5,(9.1) | $\mathrm{Yb}_{2} \mathrm{Hf}_{2} \mathrm{O}_{7}$ | 2.5 | (23.6),21.9 |
| $\mathrm{DyVO}_{4}$. | 2.4 | 14.5,(9.6) | $\mathrm{K}_{2} \mathrm{TaF}_{7}$ | 1.4 | (36),34.3 |
| $\mathrm{Ho}\left(\mathrm{IO}_{3}\right)_{3}$ | 2.6 | 15.2,(12.8),(10.5) | $\mathrm{YbTaO}_{4}$ | 2.8 | (33.6),31.8 |
| $\mathrm{Ho}_{2} \mathrm{O}_{3}$ | 2.6 | 14.3,(10.6) | $\mathrm{Ta}_{2} \mathrm{O}_{5} \ldots$ | 2.1 | (33.0),31.2 |

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[^0]:    * If a fast particle travels through water, the modification to $\cos \theta$ ( $\theta$ being the Cerenkov angle in the rest system) introduced by the quantum theory will amount to approximately $10^{-6}$.

[^1]:    * Assume $k_{0}=0, f_{0}=0$. Then from (4.23a, b) we get $x(\boldsymbol{k} \cdot \boldsymbol{V})^{2}=\boldsymbol{k}^{2}, \boldsymbol{k} \cdot \boldsymbol{f}=x \boldsymbol{k} \cdot \boldsymbol{V} \boldsymbol{f} \cdot \boldsymbol{V}$. Combining these we obtain $\boldsymbol{k} \cdot \boldsymbol{f} \boldsymbol{k} \cdot \boldsymbol{V}=\boldsymbol{k}^{2} \boldsymbol{f} \cdot \boldsymbol{V}$, which means that $\boldsymbol{f}$ lies in the plane determined by $\boldsymbol{k}$ and $\boldsymbol{k} \times \boldsymbol{V}$, i. e. $\boldsymbol{f}=c_{1} \boldsymbol{k} \times \boldsymbol{V}+c_{2} \boldsymbol{k}$. The solution parallel to $\boldsymbol{k}$ must however be excluded since it runs into conflict with eq. ( 4.23 c ) in the directions determined by $k_{0}=0$. There remains the solution $\boldsymbol{f}=c_{1} \boldsymbol{k} \times \boldsymbol{V}$, i.e. there is only one polarization vector in this plane.

[^2]:    ${ }^{*} \varepsilon_{0123}=1$.

[^3]:    ${ }^{8}$ ) See ref.s (10) and (11).

[^4]:    ${ }^{9}$ ) The theorem, initially stated by Bochner, ref. (1), has been generalised by Schwartz, ref.s (5) and (14).

[^5]:    ${ }^{10}$ ) See ref. (3).
    ${ }^{11}$ ) See ref. (4).

[^6]:    * Tabulated data received by private communication.

[^7]:    * Bonderup kindly sent us his computation of the shell-corrections.

[^8]:    ${ }^{4} 1 \mathrm{~d}=6 \mathrm{H}$ (large hours) $=6,0^{\circ}$ (time degrees). The large hour is a unit introduced for the sake of convenience in the modern literature; the Babylonian unit is the time degree (uŠ).

    5 There is no distinction between anomalistic and sidereal year in Babylonian astronomy.
    ${ }^{6}$ cf. Aaboe [2].
    ${ }^{7}$ cf. Aaboe [1] and [2].
    ${ }^{8}$ v. d. Waerden [1], p. 148 f., Aaboe [1] and [2].
    ${ }^{9}$ Whenever a value of $\Phi$ exceeds $2,13,20$ it is replaced by $2,13,20$, and whenever it is smaller than $1,58,31,6,40$ it is replaced by $1,58,31,6,40$ (see Aaboe [1]).

[^9]:    ${ }^{13}$ Aaboe [2].

[^10]:    15 For the table converting $\Phi$ into G see ACT p. 60 ; for the $\Phi-\Lambda$ table see Aaboe [2], p. 22.

[^11]:    ${ }^{9}$ ) Not every capacity $c$ has the property that $c^{*}$ is sequentially order continuous from below, cf. $\S 5.6$ below. On the other hand the capacities encountered in potential theory do have this property under very general circumstances.

[^12]:    $\left.{ }^{11}\right)$ By the hereditary convex closure of a set $\mathscr{S} \subset \mathscr{M}^{+}$is meant the smallest hereditary, convex and vaguely closed subset of $\mathscr{M}^{+}$containing $\mathscr{S}$.
    ${ }^{12}$ ) For any $\mu \in \mathscr{T}$ the trace $\nu$ of $\mu$ on $\{x \in X \mid f(x)>0\}$ belongs to $\mathscr{T}$ since $\mathscr{T}$ is hereditary. For $f \in \mathscr{T}^{0}$ we thus obtain $f^{+} \in \mathscr{T}^{0}$ because $\mu\left(f^{+}\right)=v(f) \leq 1$ for every $\mu \in \mathscr{T}$.

[^13]:    ${ }^{13}$ ) The convexity of $\mathscr{S}$ follows from the positive definite character of the kernel $G$. Mat.Fys. Medd. Dan.Vid.Selsk. 38, no. 7 .

[^14]:    a) ref. 34).
    b) ref. 39).

[^15]:    * An equation of motion of type of (2.20) is often called the backward equation, (2.13) being the forward equation.

[^16]:    * Note that in infinite space the function $a(x, t)$ will usually tend to zero everywhere, but it can tend to an equilibrium function $a^{0}(x)$ in the sense that $a(x, t) / a\left(x^{\prime}, t\right) \rightarrow a^{0}(x) / a^{0}\left(x^{\prime}\right)$.

[^17]:    *) For a discussion of these conditions and their extension to finite quantal systems, see in particular refs. ${ }^{7,8}$ ).

[^18]:    *) A monograph by I. Prigogine, C. George and F. Henin, dealing with these problems, is in preparation.

[^19]:    *) The matrix representation of the superoperators defined in this subsection is given in the Appendix.

[^20]:    *) The proof is given here as an example of the calculus of factorizable superoperators. Putting $L_{1}=-i L t / \hbar, H_{1}=-i H t / \hbar$, we have

[^21]:    *) The distinction between regular and singular invariants also applies to classical systems; the first mention of it occurs in a paper by P. Résibois and I. Prigogine, ${ }^{20}$ ) devoted to classical dilute gases. Cf. also ref. ${ }^{6}$ ).

[^22]:    *) We must exclude from consideration in this respect the time-evolution superoperator $\exp \left(-i L_{00} t\right)$; e.g., for homogeneous systems, where $P_{0}=\Sigma_{m} P_{m} \times P_{m}$, one has $L_{00}=0$.

[^23]:    *) This result was first derived by I. Prigogine, C. George and F. Henin. ${ }^{14}$, ${ }^{15}$ )

[^24]:    *) Clearly, the density distribution $\hat{\varrho}(t)$ includes only those fluctuations that cannot be detected under the given conditions of observation. For instance, the usual fluctuations around the thermodynamic equilibrium state can be derived from the corresponding asymptotic distribution density $\check{\varrho}(\infty)$ and are therefore contained in the asymptotic subspace $\tilde{\Pi}$.
    **) In the preceding argument, we have started from the construction of an asymptotic solution of the Liouville equation and shown that it corresponds to a "subdynamics". A different point of view may be adopted $:^{22},{ }^{23}$ ) we may first study the conditions enabling us to separate the density supervector into two components evolving independently, and then discuss under which conditions one of the components represents an asymptotic solution of the Liouville equation. The conception of subdynamics may be extended to relativistic dynamical systems, for which R. Balescu and L. Brenig ${ }^{24}$ ) have shown that the projector $\tilde{\Pi}$ commutes with the ten generators of the Poincaré group.

[^25]:    *) It must be observed, in this connexion, that while both $\tilde{\varrho}(t)$ and $\varrho(t)$ appear as functions of the same time variable $t$, and in fact as solutions of the same Liouville equation, their time variations may be extremely different: $\varrho(t)$ exhibits variations at the rate of atomic processes, whereas the variations of $\tilde{\varrho}(t)$ may look quite smooth in comparison. This circumstance may be made quite explicit, as shown by L. Lanz, L. A. Lugiato and G. Ramella, ${ }^{25}$ ) at the unavoidable cost of formal complication: one must then renounce using the asymptotic time-displacement superoperator $\theta$ acting at any time, but introduce a similar superoperator, whose action is only defined for an arbitrary finite sequence of separate instants.

[^26]:    *) Somewhat less elementary is the case of quantum electrodynamics, owing to the necessity of taking account of all retardation effects in the measurement of a field component; in this case also, the consistency of the formalism could be established by a detailed analysis, ${ }^{2}$ ) in which advantage was taken of the smallness of the coupling between electro-magnetic fields and distributions of electric charge and current.
    **) More recently, they have given some consideration to the problem from the point of view of their own kinetic theory, but made no attempt at a detailed examination of the issues involved. ${ }^{26}$ )

[^27]:    *) It should be stressed that the approximation (66) is sufficient for the analysis of the most general measuring process of physical interest. The case envisaged by Wigner's theorem ${ }^{27}$ ), in which the system formed by the atomic object and the measuring apparatus has an additive invariant, only occurs if the quantity to be measured is precisely such an invariant, or commutes with it, and an idealization of the type (66) is then in accordance with the theorem. If, however, the quantity to be measured does not commute with the additive invariants, Wigner's theorem has no relevance, for it is an obvious physical requirement that any sueh invariance should be destroyed by coupling the apparatus to a suitable external system of infinite extension. For instance, while a momentum measurement of infinite accuracy may be performed by means of an elastic collision of the atomic object with a freely moving test-body, the spatial localization of the object requires the test-body to be rigidly attached to some body of infinite mass serving as a spatial system of reference. It is worth pointing out how well adapted the $\tilde{\Pi}$-space representation is to a concise and general account of the process of measurement.

[^28]:    *) Of great interest in this respect is the experimental evidence showing that the memory of a specific sensory-motor scheme can be stored in the form of a coded macromolecule.

[^29]:    * In the $\gamma$-spectrum recorded with a $G e(L i)$ counter immediately after thermal neutron activation of ${ }^{186} \mathrm{~W}$ the expected isomer was not observed ${ }^{32}$. If one assumes a capture cross section ratio for the formation of the ground state and the isomeric state comparable to those found ${ }^{33}$ ) for this isomer in ${ }^{183} \mathrm{~W}$ and ${ }^{185} \mathrm{~W}$ the upper limit for the half life of the $11 / 2+[615]$ isomer in ${ }^{187} \mathrm{~W}$ is $T_{1 / 2} \leqslant 10$ seconds.

[^30]:    * Some of the results discussed in this section have been reported previously ${ }^{47}$ ).

[^31]:    a Unestablished band members with calculated cross sections less than $1 \mu b / s r$ are omitted.

[^32]:    a Unestablished band members with calculated cross sections less than $1 \mu b / s r$ are omitted.

[^33]:    ${ }^{1}$ Taking the extreme form of $I^{\prime}(4 \mathrm{f})$ about 25 eV in $\mathrm{Tb}(\mathrm{IV})$ and about 9 eV in $\mathrm{Tb}($ III) (cf. Table 23) with $(96 \mathrm{D} / 13)=6 \mathrm{eV}$ due to spin-pairing energy differences and 10 eV is the difference between one-electron ionization energy and affinity. It is noted that the ligand ionization energy is slightly larger than the electron affinity of $\operatorname{Tb}(I V)$ which is almost as large as the ionization energy of $\mathrm{Tb}(\mathrm{III})$ and identical if disregarding the consequences of the Franck-Condon principle.

