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Mathematisk-fysiske Meddelelser. I, 14.

ON THE REACTION BETWEEN
HYDROGEN AND BROMINE

BY

J. A. CHRISTIANSEN



KØBENHAVN

HOVEDKOMMISSIONÆR: ANDR. FRED. HØST & SØN, KGL. HOF-BOGHANDEL

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ON THE REACTION BETWEEN HYDROGEN AND PROMYLE

By E. J. MANNING

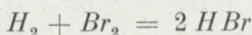


ROBINSON

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I.

M. BODENSTEIN and S. C. LIND¹ have shown that the (isothermal) reaction



goes on according to the equation

$$\frac{dx}{dt} = k_1 \frac{(a-x)(b-x)^{\frac{1}{2}}}{m + \frac{x}{b-x}}$$

Here they denote by a and b the original concentrations of hydrogen and bromine respectively, and by $2x$ the concentration of the hydrogen-bromide formed. Consequently the equation can be rewritten

$$\frac{D}{Dt} C_{HBr} = 2k_1 \frac{C_{H_2} \cdot C_{Br_2}^{\frac{1}{2}}}{2m + \frac{C_{HBr}}{C_{Br_2}}} \quad (1)$$

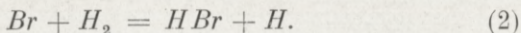
This equation is the empirical expression of the facts found by these authors. The denominator tells us that the reaction-velocity decreases with increasing concentration of hydrogen-bromide, but not below a certain limit, and further that it is the ratio between the concentrations of hydrogen-bromide and bromine, not the absolute value of the first, that determines the velocity-decrement.

The authors have further shown that such gases as carbon-tetrachloride, air, and steam have no influence on the velocity, while iodine has a still greater action.

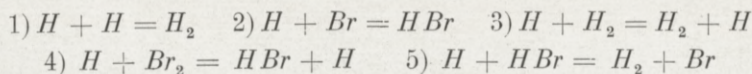
¹ Z. physik. Ch. 57 p. 168 (1907).

We will now show that by the aid of these data we can draw very definite conclusions concerning the mechanism of the reaction considered.

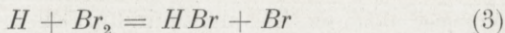
Let us suppose — in accordance with BODENSTEIN and LIND — that the bromine also by these relatively low temperatures (225°—301° C) to a certain degree is dissociated in atoms. This assumption is in concordance with the form of the numerator in equation (1) when we further suppose the primary reaction to be



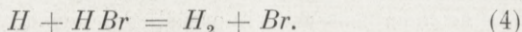
But from a number of facts¹ we know that an atom of hydrogen forms a very reactive system, and consequently we may expect it to react in one of the following five ways:



in a time which is comparable with the time of describing a free path. The possibilities 1) and 2) will occur extremely seldom on account of the small concentrations of the atoms, while the occurrence of 3), a possibility which is not altogether to be denied, will make no alterations at all in the state of the whole system. The only two ways left for the hydrogen-atom to react in are consequently



or



As is well known, the equilibrium $2 \text{Br} \rightleftharpoons \text{Br}_2$ is reached almost instantly, and so the atoms of bromine formed by the reactions (3) and (4), or those used up by the reaction (2), cannot alter the concentration of atoms of bromide (at constant C_{Br_2}).

If now we denote by P_3 and P_4 respectively the relative

¹ Compare f. inst. I. LANGMUIR Journ. am. chem. Soc. **36** p. 1711 (1914).

probabilities for the occurrences of the reactions (3) and (4), we can write

$$P_3 + P_4 = 1, \quad (5)$$

$$\frac{P_3}{P_4} = K \frac{C_{Br_2}}{C_{HBr}} \quad (6)$$

where K probably depends on the temperature but not on C_{Br_2} and C_{HBr} .

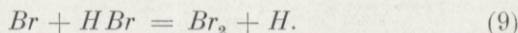
If we further let P' and P'' respectively denote the probabilities per unit time for an atom of bromine to react with a hydrogen-molecule according to (2), or with a molecule of hydrogen-bromide according to (9) (see below), the velocity of the formation of hydrogen-bromide must be

$$\frac{d}{dt} C_{HBr} = C_{Br} \cdot P' (1 + P_3 - P_4) \quad (7)$$

and the velocity of the opposing reaction

$$- \frac{d}{dt} C_{HBr} = C_{Br} \cdot P'' (1 + P_4 - P_3). \quad (8)$$

In the latter equation we have supposed that the primary reaction by the dissociation is



This assumption is a necessary consequence of our theory concerning the mechanism of formation, and of the requirement that the condition of equilibrium shall be of the well known form.

P' and P'' are determined by

$$P' = k' C_{H_2} \quad (10)$$

and
$$P'' = k'' C_{HBr}. \quad (11)$$

In these equations we denote by k' and k'' the velocity constants defined in the usual way, and so they may be expected to depend on the temperature, but not on the concentrations.

From the equations (7), (8) and (5) we get the total velocity of formation

$$\frac{D}{Dt} C_{HBr} = 2 C_{Br} [P' (1 - P_4) - P'' P_4]$$

and by elimination of P' , P'' and P_4

$$\begin{aligned} \frac{D}{Dt} C_{HBr} &= 2 C_{Br} \left(K k' C_{H_2} \frac{C_{Br_2}}{C_{HBr}} - k'' C_{HBr} \right) : \left(1 + K \frac{C_{Br_2}}{C_{HBr}} \right) \\ &= 2 C_{Br} \left(K k' C_{H_2} - k'' \frac{C_{HBr}^2}{C_{Br_2}} \right) : \left(\frac{C_{HBr}}{C_{Br_2}} + K \right). \end{aligned} \quad (12)$$

Now by the experiments considered k'' is vanishing compared with k' , and as we furthermore have

$$\frac{C_{Br}^2}{C_{Br_2}} = K_b, \quad (13)$$

equation (12) can be rewritten

$$\frac{D}{Dt} C_{HBr} = 2 K k' K_b^{\frac{1}{2}} \frac{C_{H_2} \cdot C_{Br_2}^{\frac{1}{2}}}{K + \frac{C_{HBr}}{C_{Br_2}}}. \quad (14)$$

It is evident that equations (1) and (14) are identical in form, and so we have got an explanation of the empirical equation of BODENSTEIN and LIND.

The action of iodine vapour cannot be explained in an analogous way. But it seems quite natural to me to suppose, as the said authors¹ have a little hesitatingly done, that added iodine diminishes the concentration of bromine molecules and consequently also of bromine atoms in forming JBr , especially when we remember that the iodine in these experiments was added in considerable excess.

Comparing (1) and (14) we get

$$K = 2 m \quad (15)$$

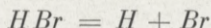
and

$$k' = \frac{1}{2} k_1 : \left(m K_b^{\frac{1}{2}} \right). \quad (16)$$

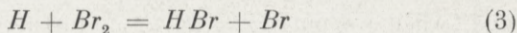
¹ l. c. p. 188.

The authors have determined k_1 by a series of temperatures. Whether m depends on the temperature can hardly be decided from the experiments in question. The authors use the value 5.00 for the temperatures investigated¹. It is determined, as far as can be seen, from the experiments at 301°.3 C.

It is interesting to note that this theory is founded on the kinetic measurements alone, and without use of WARBURG's results concerning the photolysis of hydrogen-bromide² which were unknown to me when I first worked it out, and yet the agreement is complete. WARBURG has shown, not only that hydrogen-atoms formed by the primary reaction



react with hydrogen-bromide, according to equation (4), but it also appears from his experiments that the reaction



goes on, since he has found that the quantity of hydrogen-bromide dissociated per unit time depends on the velocity of the gas-current passing the insolation cell. This phenomenon he ascribes to organic matter used in the building up of the cell, but after the theory here developed it seems doubtless that the reaction (3) is also active in this direction.

If we suppose it to be the only significant cause it is possible in this way to determine K independently of the kinetic measurements. If by n we denote the number of hydrogen-atoms primarily formed, and by M the number of hydrogen-bromide-molecules disappeared, we get

$$M = n(1 + P_4 - P_3) = 2n P_4$$

and again

$$M \left(K + \frac{C_{HBr}}{C_{Br_2}} \right) = 2n \frac{C_{HBr}}{C_{Br_2}}. \quad (17)$$

From this equation it is possible to determine K if $\frac{C_{HBr}}{C_{Br_2}}$ is

¹ l. c. p. 180.

² Berichte Berliner Akad. 1916 (I) p. 314.

small compared with K . For great values* of this fraction equation (17) is equivalent with

$$M = 2n, \quad (17a)$$

which WARBURG has shown to be in accordance with experiment, when n is determined by the aid of EINSTEIN'S law on the photochemical equivalent.

Finally we will try to apply quite analogous considerations to the formation and dissociation of hydrogen-iodide, although these reactions according to BODENSTEIN¹ are regularly bimolecular.

We can transform (12) in

$$\frac{D}{Dt} C_{HJ} = \frac{2C_J}{C_{HJ} + KC_{J_2}} (Kk' C_{H_2} \cdot C_{J_2} - k'' C_{HJ}^2)$$

and, when we put $C_J = K_J^{\frac{1}{2}} \cdot C_{J_2}^{\frac{1}{2}}$, further in

$$\frac{D}{Dt} C_{HJ} = \frac{2K_J^{\frac{1}{2}}}{\frac{C_{JH}}{C_{J_2}^{\frac{1}{2}}} + KC_{J_2}^{\frac{1}{2}}} (Kk' C_{H_2} \cdot C_{J_2} - k'' C_{HJ}^2).$$

Now the quantity $\frac{C_{HJ}}{C_{J_2}^{\frac{1}{2}}} + KC_{J_2}^{\frac{1}{2}}$ has a minimum (when $\frac{C_{HJ}}{C_{J_2}} = K$), and consequently it may be difficult to see whether the factor outside the parenthesis is necessary to express the results exactly or not, especially as it seems to be rather difficult to determine the constants with any great accuracy.

It follows from the above equation that, when C_{J_2} is very small, we should have

$$\frac{D}{Dt} C_{HJ} = -2K_J^{\frac{1}{2}} \cdot k'' \cdot C_{HJ} \cdot C_{J_2}^{\frac{1}{2}}$$

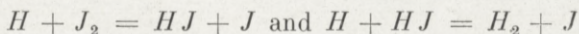
i. e. the reaction should be autocatalysed by the iodine formed.

¹ Z. phys. Ch. **20** (1899) p. 295.

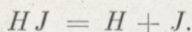
That it is really so, is suggested by a curve from BODENSTEIN'S work on the dissociation of hydriodic acid¹. Inspection shows that without a point of inflection a curve cannot be drawn through the points found by experiments (dissociation curve) and the zero point of the coordinates.

If now these points were determined very exactly, this would definitely show that the said explanation was the right one. Unfortunately however, it seems that the results are hardly sufficient to draw this conclusion.

The same author has found² that the photolysis of hydrogen-iodide is simply monomolecular, but as the vapour-pressure of iodine is very small at ordinary temperature, and consequently the ratio $\frac{C_{HJ}}{C_{J_2}}$ great, this gives us no other information as to the mechanism of the process (compare eq. (17) and (17 a)), than this, that the reactions



are both possible as secondary processes, when the primary one is supposed to the



In a recent paper WARBURG³ has shown the occurrence of the lastnamed two reactions.

II.

In this section we shall use the numerical values found by the said authors to calculate the critical energies according to MARCELIN⁴, and in this and the next draw some further conclusions from the results.

¹ Z. physik. Ch. **13** (1894) p. 111.

² Z. physik. Ch. **22** (1897) p. 23.

³ Ber. Berliner Akademie 1918 p. 300.

⁴ Ann. de Phys. **3** (1915) p. 120.

From eq. (12) we get

$$K_{HBr} = \frac{C_{H_2} \cdot C_{Br_2}}{C_{HBr}^2} = \frac{k''}{K \cdot k'} \quad (18)$$

where K_{HBr} is the equilibrium-constant for the hydrogen-bromide-dissociation. We further found

$$k' = \frac{k_1}{K K_b^{\frac{1}{2}}} \quad (19)$$

and so

$$k'' = \frac{k_1}{K_b^{\frac{1}{2}}} \cdot K_{HBr}. \quad (20)$$

According to I. W. CEDERBERG¹

$$\log K_{HBr} = -\frac{5294}{T} - 0.88.$$

Instead of that we will place

$$\log K_{HBr} = -\frac{5294}{T} - 0.98 \quad (21)$$

which gives a somewhat better agreement with the found values.

The values of K_b we know at different temperatures from a series of measurements, which we also owe to BODENSTEIN². His expression for K_p , the equilibrium-constant at constant pressure as a function of the temperature, is, however, a little complicated, while the simple expression

$$\log K_b = -\frac{9960}{T} + 3.31_2 \quad (22)$$

(the concentrations reckoned in Mols per l.) agrees with the experimental results to almost the same degree of accuracy.

¹ Die thermodynamische Berechnung chem. Affiniteten a. s. o. Upsala (1916) p. 84.

² Z. für Elektroch. **22** (1916) p. 337.

A graph with $1/T$ as abscissæ and $\log K_b$ as ordinates will show that the deviations from the straight line are hardly greater than the experimental errors.

Finally BODENSTEIN and LIND's results¹ can be expressed as follows

$$\log k_1 = -\frac{9220}{T} + 14.99$$

where the concentrations are reckoned in 1/22.4 Mols per l. and time in minutes. To transform to Mols per l. and seconds we write

$$\begin{aligned} \log k_1 &= -\frac{9920}{T} + 14.99 - \log 60 + \frac{1}{2} \log 22.42 = \\ &= -\frac{9220}{T} + 13.89. \end{aligned} \quad (23)$$

From the equations (20) to (23) we get

$$\log k'' = -\frac{9564}{T} + 11.22$$

or

$$k'' = 1.66 \cdot 10^{11} \cdot e^{-\frac{43700}{RT}} l^{+1} \cdot Mol^{-1} \cdot sec^{-1} \quad (24)$$

where R is the gas-constant reckoned for one Mol. As will be remembered, we denote by k'' the chance per unit time for a bromine-atom to react with a hydrogen-bromide molecule, when the concentration of the latter is 1 Mol per l.

To compare, we will calculate the chance per unit time for a bromine atom to collide with a hydrogenbromide-molecule.

According to JEANS¹, the chance per unit time for a molecule 1 to collide with a molecule 2 is

$$2 \nu_2 S_{12}^2 \sqrt{2\pi RT \frac{m_1 + m_2}{m_1 m_2}}$$

¹ l. c.

² Dynamical Theory of Gases 2nd ed. p. 267, eq. 738.

where ν_2 is the number of molecules per cm^3 , $S_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ where σ_1 and σ_2 respectively are the diameters of the two molecules and m_1 and m_2 the corresponding masses.

When the concentration of hydrogenbromide is 1 Mol per l. we have $\nu_2 = \nu_{HBr} = 6,1 \cdot 10^{20}$. Further we will assume $\frac{1}{2} \sigma_{Br} = 1,4 \cdot 10^{-8} \text{cm}$ and $\frac{1}{2} \sigma_{HBr} = 2 \cdot 10^{-8}$. Here we have placed $\sigma_{Br} = \frac{1}{2} \sigma_{Cl_2}$ with use of the value for σ_{Cl_2} from JEANS *ibid.* p. 341 and $\sigma_{HBr} = \frac{1}{2}(\sigma_{Cl_2} + \sigma_{H_2})$ so that $\frac{1}{2} \sigma_{HBr} = 2,0 \cdot 10^{-8}$, and finally $m_1 = 80 = m_2$. With these values we get

$$s'' = 2 \cdot 6,1 \cdot 10^{20} \cdot 3,4^2 \cdot 10^{-16} \sqrt{2 \pi \cdot 8,31 \cdot 10^7 \cdot \frac{2}{80}}$$

which gives

$$s'' = 5,1 \cdot 10^9 \sqrt{T}.$$

Now we transform eq. (24) into an equation of the form

$$k'' = A \sqrt{T} \cdot e^{-\frac{B}{RT}} \quad (24a)$$

remembering, that (23) is an empirical expression of the experimental results between 225° and 301°C .

As will be well known, equations of the forms (24) and (24 a) are very nearly equivalent, when the temperature-interval is not very great. Calculation gives

$$\log k'' = -\frac{9470}{T} + \frac{1}{2} \log T + 9,68$$

$$k'' = 4,9 \cdot 10^9 \sqrt{T} \cdot e^{-\frac{43300}{RT}} = s'' \cdot e^{-\frac{43300}{RT}} \quad (24b)$$

Equation (24 b) combined with the equation for s'' makes it probable that it is possible to calculate the reaction velocity *a priori* when B in the factor $e^{-\frac{B}{RT}}$ in (24a) can be measured in some way or other, and the molecule-diameters are known from viscosity measurements or other quantities depending on the mean free path¹.

¹ Comp. LEWIS: *Journ. Chem. Soc.* 113 p. 471 (1918) and numerous papers by M. TRAUTZ in the *Zeitschr. für anorg. und allgem. Chemie.*

As for the present we are unable to calculate „ B ” otherwise than by direct determination of the velocity at different temperatures, this circumstance is at present of small practical value.

With reference to the foregoing calculations some remarks are necessary. In the first instance, it is unfortunately not possible to get a similar expression for k' , because we do not know, as mentioned before, whether K is dependent upon temperature or not.

The value of the first factor in eq. (24) depends to a very high degree on the form chosen for the velocity-constant as a function of temperature, and it is for that reason rather uncertain, because the right form to choose has not been established as yet. On the other hand the conclusions drawn from it may be supposed to be substantially correct, if namely we think of eq. (24) as an empirical expression for the velocity-constant in the temperature-interval mentioned. Of course this is only true with reservation, because in using eq. (22) together with (23) we have extrapolated from the temperature-interval 1075° to 1558° (abs.) between which temperatures BODENSTEIN has measured the degrees of dissociation of bromine to temperatures about 550° (abs.). It is not easy to control the correctness of this extrapolation in the case considered, but in other cases, such an extrapolation is known to give remarkably correct results.

The same remarks will also apply to the determination of „ B ” the “critical energy” according to MARCELIN, but by comparing for instance eq. (24) and (24 b) it is seen, that the influence is rather small, the difference between the two values being only about 400 cal. so that it seems improbable that the error should reach for instance $2 \times RT$ or 2000 cal.

III.

We have found that the critical energy at the reaction $Br + HBr = Br_2 + H$ is 43700 cal. (24). This means that the difference between the mean energy of a reacting

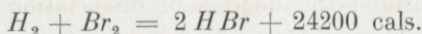
complex Br, HBr and the sum of the mean energies of an atom of bromine and a hydrogen-bromide-molecule in the temperature-interval mentioned is 43700 cal.

When we now write



where by Br, H, HBr and Br_2 respectively we denote the atoms and molecules in their mean state at the temperature in question, we express by this equation that the reacting Br, HBr complexes have received from the surroundings an energy of 43700 cal. (per Mol.) either as radiation or by collision (or both united), and that during their transformation into an atom of hydrogen and a bromine-molecule they again lose on an average x cal. either as kinetic energy or as radiation emitted (and perhaps again absorbed by neighbouring molecules.)

Now the heat of dissociation for hydrogen is $\div 84000$ cal. according to LANGMUIR¹, while the analogous number for bromine is $\div 45500$ cal. (equation (22)). Further we used above the equation



and from these three data we get $x = 12400$ cal., a quantity greater than zero with an amount much greater than the possible error.

This result is interesting, because it shows that it is not permissible to use the measurement of the temperature-coefficient of the velocity-constant of this reaction to determine the heat of dissociation of for instance hydrogen, which is by no means self-evident. It follows that the energy absorbed in the formation of the reacting complex is greater than that necessary to bring the system from the original to the final state ($Br + HBr \rightarrow Br_2 + H$).

¹ Journ. am. chem. Soc. **37** (1915) p. 417.

But if this is often the case, it seems that it is generally not correct to use measurements in systems where thermodynamical equilibrium between the reacting complexes and the surrounding molecules cannot be expected to be established in calculating the reversible heats of dissociation (and formation).

This objection will probably not apply to the explosion method of determining heat-effects, on account of the very small time necessary for thermodynamical equilibrium to be established¹ (MAXWELL'S time of relaxation), when we suppose that the radiating energy emitted during the explosion is practically totally absorbed by the gas-mass itself, but it seems possible to me that it is applicable to LANGMUIR'S determination of the heat of dissociation of hydrogen. This work comprises a very great amount of theoretical and experimental material and so it is not possible to discuss it here in detail, but I think that his method of proceeding can be summarized as follows:

The heat loss from an electrically heated incandescent tungsten wire in hydrogen is determined at a series of different temperatures. From experiments at lower temperatures the heat loss owing to conduction, convection, and radiation is calculated. The difference between the found heat loss and that calculated represents the heat used to dissociate some of the hydrogen-molecular striking the wire. From experiments under varied circumstances the degree of dissociation is found, and from these data the heat of dissociation is calculated. In this calculation it must be tacitly assumed, that the hydrogen-atoms coming from the wire have a mean energy corresponding to the temperature of the wire, and that no extra radiation is emitted during the process, which is, according to LANGMUIR², a

¹ JEANS l. c. p. 260.

² Journ. am. chem. Soc. **38** p. 1145 (1916).

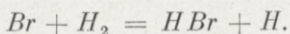
little complicated, for instance during the absorption of the hydrogen-molecules on the wire¹.

Of course only experiment can decide whether such effects are to be excluded or not, but according to the calculations above they seem at least possible. It appears that they will bring about a too high value of the dissociation heat compared with the "reversible" value. As is well known the latter has been calculated by N. BOHR² in a purely theoretical way at 62000 cal. (when we place BOHR's „ W_0 ” = $3,29 \cdot 6,55 \cdot 10^{-12}$ Erg.) As will be seen, the difference can perhaps be explained as shown above.

Using BOHR's value, we get in equation (25) $x = 23400$ or

$$Br + HBr + 43700 \text{ cal.} = Br_2 + H + 23400 \text{ cal.} \quad (25a)$$

As mentioned before it is not possible to calculate the critical energy for the reaction



We can only tell, 1) that the chance at 574° abs. for a hydrogen-atom to react with molecule of bromine is ten times as great as the chance that it will react with a hydrogenbromide-molecule, and 2) that if by W_1 and W_2 respectively we denote the energy-differences between the complex $HHBr$ in the critical state (MARCELIN) and the systems $H_2 + Br$ and $HBr + H$, we shall find

$W_2 - W_1 = 3900$ cal. (when $H_2 = 2H - 62000$ cal.)
or $W_2 - W_1 = \div 7100$ cal. (when $H_2 = 2H - 84000$ cal.)

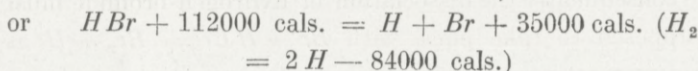
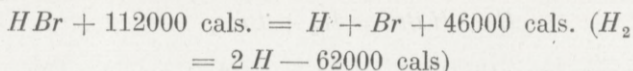
It is not to be denied that, in this case, the result found by means of LANGMUIR's value is in better concordance with ordinary chemical instinct.

It will perhaps be of interest to note that from WAR-

¹ l. c.

² Phil. Mag. [6] 26 (1913) p. 857

BURG's¹ experiments on the photolysis of hydrogen-bromide we get



the wavelength of the light used being $\lambda = 0.253 \mu$.

Also in this case it is evident, that the energy absorbed is considerably greater than that necessary to separate the atoms reversibly.

In the above pages we have gained a rather definite view of the mechanism of the reaction considered.

To illustrate it still better, we could take a step further in assuming that the molecule of hydrogen-bromide is constituted substantially as a hydrogen-molecule and the bromine-atom substantially as a hydrogen-atom according to N. BOHR².

The critical state can then be supposed to be one in which three electrons constitute a ring in plane with one bromine-kernel, while the other and the hydrogen-kernel are located at a certain distance on either side of this plane. As will be seen a complex of this configuration can equally easily be transformed in either $Br_2 + H$ or $HBr + Br$, and according to MARCELIN³ the critical state is just that, which all reacting complexes pass during the transformation from the original to the final state.

Summary.

In section I it is shown, that it can be concluded from BODENSTEIN and LIND's experiments on the formation of hydrogen-bromide that the reaction occurs as a result of the following

¹ l. c. ² l. c. ³ l. c.

an experimental examination of the reaction $COCl_2 = CO + Cl_2$, which according to BODENSTEIN and DUNANT¹ is autocatalysed (by chlorine?).

Finally I wish to express my thanks to Prof. Dr. E. BILLMANN, the director of this laboratory, for the interest he has shown in this paper.

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¹ Z. für physik. Ch. **61** p. 437 (1908).

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