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ON THE CONCEPT OF HEAT

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CONTENTS

I. Introduction	3
II. The Energetic Theory. ⁷⁷	
1. Work and Energetic Heat Evolution	5
2. The Energetics of Thermal Conduction	13
3. The Fundamental Equation	17
III. The Classical Concept of Heat.	
1. General Classical Aspects	19
2. The Spatial Process	30
3. The Chemical Process	48
4. The Thermal Process	61
IV. Conclusion	73



I. Introduction.

The old conception of heat as a substance has long ago been superseded by other ideas about the "nature" of heat. That heat is "motion", i. e. kinetic energy of the elementary particles of matter, has become the view generally accepted in all modern expositions of thermodynamics. The theory which maintains this idea is referred to as the "mechanical" or "dynamic" theory of heat.

But, it must be asked, what is it that is interpreted as the mechanical energy of the elementary particles of matter? The contention that heat is a mode of motion certainly conveys some other meaning than merely that of a definition. If this contention is to possess any physical meaning at all, there must exist already a fixed macroenergetic heat concept, to which such a microenergetic interpretation may be applied. In other words: the molecular interpretation of the "nature" of heat must be preceded by the unambiguous definition of a macroscopic concept with which, from one angle or other, one may wish to associate the term "heat". The significance of such a concept will depend upon the rigour and generality of the laws to which it is subject.

It is doubtless generally assumed that such a universal macroscopic heat definition has actually long ago been safely established. At any rate in the numerous expositions of thermodynamics and heat theory now existing apparently

no uncertainty or vagueness is encountered in the formal treatment of the fundamental chapters in which the concept of heat is introduced. A closer analysis, however, will show that the formal certitude and assurance which characterise the different methods by which heat, like the fundamental concept of work, is introduced in thermodynamics, does not imply a corresponding certainty and unambiguity in the logical comprehension of this concept. It is not perhaps a mere accident, therefore, that a true definition of heat invariably seems to be missing in the text books of thermodynamics. There is much to indicate that heat is generally regarded as a concept so elementary and familiar to the student of thermodynamics that a further penetration into its nature and an establishment of the clear and unequivocal definition which is otherwise required when introducing a new physical concept is not necessary. It is undoubtedly as a consequence of this attitude that untenable views concerning heat have established themselves, and that the development of the heat concept as well as attempts to formulate the elementary energetic basic phenomena as a whole have not so far been fully successful.

In some previous papers, to which reference will be made in the sequel, it has been attempted to give a logical description of these elementary basic phenomena. It has been possible to establish a general work principle adequately accounting for an important group of particularly simple energetic phenomena. In the cases where the work principle is no longer sufficient to describe the phenomena encountered there appears another fundamental law which can be directly formulated by means of the concept of heat, or more especially, of energetic heat evolution. In some particular respects this new concept may be described

as being identical with heat in the classical sense. In the domains in which the classical concepts are obscure or intrinsically inconsistent such a conformity will be lacking, and the problem will arise of confronting and comparing the old ideas with the new.

It is the object of the present paper to formulate and consolidate the new concept of heat on the basis of such a comparison. While in some fields, for instance in all that concerns the heat engine, the doctrines of heat are fairly consistently and uniformly presented in the various expositions, there are other cases, mostly relating to phenomena of a spatial and chemical nature, in which the formulation and interpretation of the experimental evidence regarding heat are widely divergent. In such cases it is deemed necessary to supply a more detailed documentation in order to elucidate the true character of the classical postulates.

II. The Energetic Theory.

1. Work and Energetic Heat Evolution.

In the previous papers¹⁾ the macroscopic changes in nature have been shown to consist of two groups of phenomena. The first of these groups comprises the various basic processes, i. e. processes which can be described as transport of certain "energetic quantities" from one state to another. Such processes may also be designated as partial processes of the first order. The second group comprises processes in which energetic quantities are generated or produced. These we shall describe as partial processes of the second order. As shown by experience, how-

¹⁾ J. N. BRØNSTED: D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XV, No. 4 (1937) and XVI, No. 10 (1939). Phil. Mag. (7) **29**, 449 (1940). J. Physical Chem. **44**, 699 (1940).

ever, only the thermal quantity entropy is subject to generation. In making this distinction we are essentially referring to stationary systems, the relation of the phenomena of motion to the mechanical basic processes, and thus to energetics as a whole, being exhaustively dealt with in the science of mechanics.

It has further been shown to be characteristic of the basic process that the processes described in traditional thermodynamics as reversible only consist of partial processes of this kind, whereas the irreversible processes comprise partial processes of both kinds. Accordingly reversible processes must be considered to be of greater simplicity than irreversible processes and should, preferably, form the introductory chapter in an exposition of thermodynamics.

Primarily, the various basic processes are characterised by the nature and the amount of the quantity transported. Furthermore, they are characterised by the states between which the transport takes place, the potential in these states being the fundamentally decisive property. The relation between quantity and potential is represented by the work expression:

$$\delta A = (P_1 - P_2) \delta K, \quad (1)$$

where δA is the loss of work associated with the transport of the quantity δK , and P_1 and P_2 the potentials conjugate to this quantity in the initial and final states respectively. For example, in agreement with this general equation, we may write for the thermal basic process, which is of particular importance in this connection:

$$\delta A = (T_1 - T_2) \delta S, \quad (2)$$

δS being the amount of entropy transported and T_1 and T_2 the thermal potential, i. e. the temperature in the two states

between which the entropy transport takes place. It is important to note that the course of the basic process is determined solely on the basis of its given terminal states, independently of the path.

The physical significance of equation (1) is given by the work principle, expressed by:

$$\Sigma \delta A_1 = 0 \quad (3)$$

and established as the universal fundamental law for reversible processes. Starting from the existing definition of a quantity, i. e. the existing methods for comparing amounts of quantity of the same kind, equations (1) and (2) will permit the establishment of a scale for the conjugate potential on the basis of a conventional standard state. The conformity with (3) which on selection of suitable units for the energetic factors involved is generally observed for all kinds of work involved in reversible processes, is the experimental basis for the validity of the work principle.

The expressions set up, in accordance with their form, are valid for differential processes, i. e. processes of such slight extent that the two potentials involved are not appreciably affected in the course of the process. It is obvious that the two states 1 and 2, the potentials of which enter into the work expression, are of equal importance for the determination of the basic process and the magnitude of the work. Loss and gain of work are therefore restricted to systems in which both these states are included, i. e. systems describable as closed with regard to quantity. In the traditional treatment "work" is often spoken of in a different sense, the supply or removal of a volume δv (but hardly of any other quantity!) being identified with the

supply or expenditure of work $p\delta v$. This, however, must be considered as an unfortunate terminology, since it is apt to confuse two forms of energy which are fundamentally different in character. The energy of the form $P\delta K$ involved in the communication of a quantity and designated as neutral or equipotential energy¹⁾ is of a purely formal character, and excluded from participating in any energetic transformation. Only when K is entropy may such neutral energy appear in conjunction with the basic process as a form of energy for which the energy principle has any validity or meaning.

In the special case of $P_1 = P_2$, i. e. when the transport of a quantity takes place between two states in which the corresponding potential has the same value, the basic process is described as neutral. Such a process may take place without being accompanied by other processes. If the potentials differ from each other, the basic process is described as active, and in that case it will always be accompanied by other partial processes, which are either of the first or the second order, according to whether the total process is reversible or irreversible.

On the view advanced in the present paper, a reversible process, when not consisting in a neutral transport as described above, will comprise at least two basic processes. If each of these takes place in a separate system, the system in which the basic process is positive may be said to give off work to the system in which the basic process is negative. The two systems are said to be in work communication. It is obvious that in such a rever-

¹⁾ BRØNSTED: D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XV, No. 4, p. 13 (1937); XVI, No. 10, p. 57 (1939).

sible process work received or supplied will generally cause alterations of all potentials in the fractional systems in question, for which reason there has formerly been a tendency to put a different interpretation on such changes based upon the assumption of an intrinsic correlation between rise of temperature and evolution of heat. The complete reversibility, however, which characterises the phenomena described here is only to be found in coupled basic processes and will exclude a description which permits the participation of any energetic concepts other than work.

For processes of finite dimensions the loss of work is:

$$\Sigma A_i = \Sigma \int_2^1 P_i dK_i = 0. \quad (4)$$

If the reversible change of the system is made to take place in communication with work reservoirs, ΣA_i for the system will be a single-valued function of state. A system which remains unchanged with respect to its content of quantity can thus be characterised by a work function or potential energy E_p depending only on the state and given by:

$$E_{p_1} - E_{p_2} = \Sigma A_i. \quad (5)$$

It is thus possible from the point of view given here to offer a uniform and exhaustive description of the reversible processes on the basis of the concepts of quantity, potential and work, without "heat" entering at any point. More especially the reversible thermal processes may be completely described by means of the simple concepts of entropy and temperature. It is only when passing on to the irreversible processes that phenomena occur which may give rise to the formation of a new thermal concept.

As already mentioned, the irreversible processes comprise processes of both the first and the second order. This means that they are composed of basic processes in conjunction with the generation of entropy. We likewise find that the work principle is no longer valid since the total loss of work has always the same sign, which is conventionally fixed as being positive. By this convention we also obtain a rational fixation of the sign for the partial processes constituting the total reversible process as well as for the potential differences involved.

Experience having established that irreversible processes are characterised by a loss of work and a production of entropy, and this experience having been exalted into a postulate of unrestricted validity, the next step in the analysis must consist in a quantitative comparison of these two magnitudes. As the result of such an examination we shall find a very simple state of affairs, as long as the temperature of the entropy production is constant, the amount of entropy produced being proportional to the loss of work. Hence, such experiments would warrant the assumption of an equivalence of work and entropy, but the basis of such an assumption would fail if the temperature at which the entropy is generated, were changed, for in that case the same loss of work is found to generate an amount of entropy decreasing with increasing temperature. In investigating the closer correlation between the three magnitudes involved, viz. production of entropy, loss of work, and temperature, it must be remembered that according to classical thermodynamics the latter is based upon an already existing heat conception, at which we have not yet arrived by the method adopted here, and that, similarly, temperature according to the thermal scale defined in a

previous paper¹⁾ is based upon a heat definition. Only the energetic scale, which rests upon the work principle, is independent of the concept of heat and thus available for the purpose in question.

However, according to its derivation the energetic scale is a scale of temperature differences, i. e. a temperature scale, based upon an arbitrary zero. A temperature established on such a conventional basis cannot enter as a factor in the expression for a law of nature. Experiments on the irreversible evolution of entropy however show the following equation to be generally valid:

$$\delta A = T \delta S'' \quad (6)$$

in which δA is the loss of work, irrespective of its nature, $\delta S''$ the increase in entropy during the process, and T the absolute energetic temperature. This is defined as the energetic temperature read from a zero which is fixed on the basis of (6), introducing into this equation the experimental values of δA and $\delta S''$ of a single, arbitrarily chosen experiment. The T thus determined is in agreement with the Kelvin scale and the thermal scale mentioned above.

The result described here may also be expressed in the following way: Let t be the temperature in the energetic

¹⁾ BRØNSTED: D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XVI, No. 10, 25 (1939). The thermal temperature T is defined by the equation:

$$\frac{T_1}{T_2} = \frac{t_1 t''}{t_2 t'}$$

where T_1 and T_2 are the temperatures in the thermal scale of two heat reservoirs R_1 and R_2 and t_1 and t_2 are empirical changes in temperature (or another potential) read on two arbitrary potentiometers in R_1 and R_2 respectively, and caused by a reversible transport of entropy from one reservoir to the other. t' and t'' are corresponding changes caused by an irreversible heat transport using the same potentiometers as in the reversible case. The t 's are supposed to be small.

scale read from an arbitrary zero. Let δA be the loss of work and $\delta S''$ the production of entropy in a series of arbitrary irreversible processes. It is possible then to find a number t^* , such that the equation:

$$\delta A = (t + t^*) \delta S'' \quad (7)$$

is generally satisfied. $t + t^*$ is then the absolute temperature of the system, and t^* the absolute temperature of the conventional zero. It is obvious that δA and $\delta S''$ in equations (6) and (7) should be expressed in the same units as were used in applying the work principle to reversible thermal processes.

Equation (6) provides the basis for the creation of a new thermal concept. While entropy enters in the reversible thermal processes as a transportable quantity, the amount of entropy which leaves the initial state being equivalent to the amount of entropy which is received in the final state, a similar simple correlation between the loss of work and the production of entropy is no longer valid in the irreversible processes. What is proportional to the loss of work in these processes is not the entropy production, but the product of the entropy production and the absolute temperature. It is this macroenergetic concept, TdS , which is introduced in the energetic theory under the term heat, or, more precisely, as the energetic heat evolution. Using for this concept the symbol Q'' , we have by definition:

$$\delta Q'' = T \delta S'', \quad (8)$$

or by introduction of (6)

$$\delta A = \delta Q''. \quad (9)$$

It is true of any physical concept that only in fulfilling a certain phenomenologic law or regularity has it acquired

an actual meaning or *raison d'être*. For the heat concept, as introduced here, its simple relation to the loss of work constitutes this phenomenologic law. Equation (9) expresses this relation as the equivalence of the loss of work and the evolution of heat. Only the proportionality of these magnitudes is of course directly observable. It is the proportionality between the loss of work and the evolution of heat manifesting itself irrespective of the nature of the irreversible process which in a previous paper was introduced into energetics as the equivalence principle. There, it was also stated that the equivalence between heat and work is of a quantitative, but not of a genetic character, the sign of the basic process and of $\delta Q''$ being always positive. This postulate was introduced into energetics as the heat principle.

Combining the work and heat principles we conclude that no natural process permits a positive gain of work. Work can only be gained at the expense of an equivalent amount of work being lost. The task of technical science is restricted, therefore, to an efficacious transformation of the various types of work, utilizing the potential differences already existing in nature in conformity with the work principle. An exploitation of heat for the purpose of creating work is not rendered possible by the laws of nature.

2. The Energetics of Thermal Conduction.

The description of the irreversible processes given above is general and theoretically exhaustive. However, in the particular case where the quantity transported is identical with the quantity generated, inherently novel phenomena are bound to occur. These phenomena appear when bodies of different temperatures enter into direct thermal contact,

and are identical with the unique and important phenomena known as "thermal conduction" or "heat transport". We shall now analyse this process according to the principles given above for the irreversible processes.

We consider an entropy reservoir I of the temperature T_1 in thermal contact with an entropy reservoir II of the lower temperature T_2 , these temperatures being expressed in the absolute energetic scale. We suppose the connecting thermal conductor to be of such dimensions that the amount of entropy which may accumulate in it during the process may be disregarded. In this case there must enter into II an amount of entropy which is the sum of the entropy leaving I and that which is formed in the conductor during the thermal flow by virtue of its irreversibility.

Let us suppose that the amount of entropy S passes through a cross-section of the conductor in which the temperature is T . In the intervening space between this cross-section and a neighbouring one of the temperature $T - dT$ a loss of work will take place, which according to (1) is given by:

$$\delta A = -S dT. \quad (10)$$

On account of the irreversibility an amount of heat will be generated simultaneously in the same interval, which amount according to (8) is given by:

$$\delta Q'' = T dS, \quad (11)$$

where dS is the entropy produced in the interval.

Introducing the equivalence principle (9), according to which loss of work and evolution of heat are equal, we obtain:

$$-S dT = T dS, \quad (12)$$

or

$$TS = \text{constant}. \quad (13)$$

Accordingly, if during the process of conduction the amount of entropy given off by reservoir I is $\delta S'_1$, and that received by reservoir II is $\delta S'_2$, then by (13) these two quantities will satisfy the equation:

$$T_1 \delta S'_1 = T_2 \delta S'_2. \quad (14)$$

This result is verified by experiment.

In this equation, as in equation (6), we find a product of the form $T \delta S$ satisfying a law of great simplicity. Just as equation (6) supplied the basis for the formulation of the concept of heat evolution, and then on creation of this concept appeared as an expression of the law of the equivalence of heat and work, equation (14) may supply the basis for the formulation of the concept of heat communication, according to which this equation appears as an expression of the law of the irreversible transportability of heat. If the symbol Q' is used for heat communicated, equation (14) can be written as:

$$\delta Q'_1 = \delta Q'_2. \quad (15)$$

In case T_1 and T_2 are identical, (14) may also be taken as the expression for a neutral transport of entropy in conformity with the reversible character of this process.

In the changes which have been described as basic processes, we meet with a series of phenomena showing a complete mutual analogy. In the transference of heat described by (15) a process of quite a different character is encountered which is actually unparalleled by any other known natural phenomenon. The distinctive character of a heat transport as compared with the basic process may be illustrated by the statement that heat does not possess the character of an energetic quantity. According to the theory presented above, however, the process of thermal con-

duction is not a phenomenon differing by its intrinsic nature from irreversible processes in general. On the contrary, the analysis of the process of heat conduction given above shows how this phenomenon may be split into processes of the first and second order as typical of irreversible changes in general. Accordingly, the transportability principle represented by (14) or (15) is not a self-sufficing or independent law of heat, but is based upon the general equivalence principle, which in the form of (9) was introduced for its derivation.

In a previous paper¹⁾ the heat concept has been introduced on a somewhat different basis, the transportability being used as an actual definition of heat. This method is entirely justified, but the formulation of the heat concept given above possesses an advantage in being based on the phenomenon of irreversibility in general as contrasted with that of a specific thermal character.

One other essential feature related to the heat transport and distinguishing reversible and irreversible differential processes from each other should be mentioned. While in the reversible transport of a quantity δK the loss of work and the potentials involved in the work expression are given by the terminal states of the system in question, the potential for the entropy production is not necessarily identical with the temperature of the system in which the irreversible basic process takes place. It is possible, by means of special devices, to cause the production of entropy at an arbitrary temperature outside the system, and still from the same initial state to reach the same final state, the heat formed at a higher temperature being led irreversibly back to the system. In that case a loss of work resulting from the heat

1) D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XVI, No. 10 (1939).

transport in conformity with (10) will be added to the loss of work which is directly observed as a function of state; and to the heat evolution, if the entropy is formed at the temperature of the system, an equivalent evolution of heat will be added in conformity with (11). If the temperature of the system is T and the temperature at which the entropy is formed T'' , the loss of work and heat evolution will, as previously shown,¹⁾ be determined by:

$$\delta A = \delta Q'' = \delta Q \ln \frac{T''}{T}.$$

Since the final state is unaffected by possible differences in the mechanism of the process, and since the entropy transported does not belong to the initial state at all, being created during the course of the process, the additional energetic heat and work phenomena cannot be discovered from the properties of the initial and final states. Proof of their existence will only be possible through a detailed scrutiny of the special mechanism of reaction. It is essential to note that this conclusion is true of all kinds of irreversible changes.

3. The Fundamental Equation.

According to the above considerations, there are, evidently, two ways in which a system can take up heat. It can do so either by generation of heat in the system, or by communication of heat to the system. Heat taken up in the first of these ways is, as previously mentioned, always positive, i. e. heat can only be produced, not consumed. On the other hand communicated heat may obviously be either positive or negative. In either case the absorption of heat and entropy is connected by the relation:

1) D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XVI, No. 10, p. 40 (1939).

$$\delta Q = T dS. \quad (16)$$

It is characteristic of heat that it must be associated with processes or transformations, not with states. The contention of classical thermodynamics that heat is not a function of state, as are energy, quantity, and potential, also applies, therefore, to the extended concept of heat given by (16). Only under special conditions, primarily in "heat" or "entropy reservoirs", is such a dependence on state present. On the other hand, the thermal energy or the product TS , where S is the total entropy of the system, as well as the analogous products, corresponding to other forms of energy, are of course single-valued functions of the state of the system.

While the relation between heat and entropy communication is also accepted in classical thermodynamics, either, according to the point of departure, as a definition of heat or of entropy, the corresponding relation (8), which defines the heat evolution, and the expression (1), which defines the loss of work, are characteristic of the energetic theory. The equivalence principle (9) between the concepts thus established is therefore also foreign to the classical treatment. It should be made quite clear, however, that the actual content of the general equivalence principle, which according to (1) and (8) may be written:

$$\Sigma (P_1 - P_2) \delta K = T dS'', \quad (17)$$

is quite independent of any terminology by means of which the concepts involved are introduced into thermodynamics. Undoubtedly the terms "work" and "heat" employed to designate the magnitudes entering into equation (17) are adequate and consistent. If, however, objections should

be raised from a traditional point of view against such an application of these terms, this will not in the least affect the significance of our equivalence principle expressed by (17), since this equation is formulated solely by means of symbols of fully recognised significance. Regardless of any convention the equation represents a general and important principle, of which the classical "first law of thermodynamics" is only a special case. The genetic description of the energetic phenomena presented in the classical treatment as the "second law of thermodynamics" follows from it merely through the fixation of the sign of the magnitudes involved. For the special case of $dS'' = 0$, the equation represents the work principle introduced for the reversible processes. Taking into account the alternative possibilities with respect to the changes in entropy, the relation becomes:

$$\Sigma (P_1 - P_2) \delta K = T dS'' \geq 0 \quad (18)$$

and in this form is an expression of the three fundamental laws, the equivalence, heat, and work principles, which have previously been advanced as the fundamental laws of all macroenergetic phenomena¹⁾.

III. The Classical Phenomenon of Heat.

1. General Classical Aspects.

The basis of the heat concept, as historically evolved, is to be sought in the fact that thermal conduction and the simple mixing of substances of different temperatures are phenomena which are compatible with a material concept of heat. From investigations into such phenomena J. BLACK

¹⁾ Cf.: D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XVI, No. 10 (1939) and Phil. Mag. 29, 449 (1940).

succeeded in formulating the vague ideas of earlier times into a more well-founded and consistent theory in harmony with the conception of heat as a special substance, a certain elastic fluid which might be led in unchanged quantity from one place to another. Actually it is the theory of the irreversible transportability of heat that is contained in these ideas, but the general idea of the unchangeability of heat altogether was created at the same time.

Opposed to this idea of heat as an unalterable substance there early appeared the rival hypothesis that heat was an intestine commotion among the elementary particles of matter¹. RUMFORD and DAVY tried to show that heat could be formed by friction². CARNOT, however, seems to have been the first to formulate explicitly the supposition of a transition between heat and work, but his considerations on the subject³ remained unnoticed until long after the notion of the transformation, in a fixed proportion, of heat into work had been established by others. One of the pioneers in this field was the Danish scientist COLDING⁴. It is however to J. R. MAYER and J. P. JOULE that special credit should be given as the creators of the

1) See e. g. E. MACH: "Principien der Wärmelehre", 1896; M. PLANCK: "Das Princip der Erhaltung der Energie", 3. Aufl., 1913.

2) The conclusions drawn by RUMFORD and DAVY on the basis of their experiments are subjected to an interesting criticism by WILLIAM THOMSON in the article "Heat" in the Encyclopaedia Britannica, 9th Ed., 1878. Cf. Math. and Phys. Papers by Sir WILLIAM THOMSON, 3, 113 (1890).

3) S. CARNOT: "Sur la puissance motrice du feu" (Réimpression Paris 1878). Cf.: C. r. 87, p. 967 (1878).

4) L. A. COLDING: "Some Theses on the Forces". The manuscript was presented in the Royal Danish Academy of Sciences in November 1843, but was not printed until 13 years later in the "Oversigt" of the Academy No. 8, 1856. A more elaborate work: "Investigations into the General Forces in Nature and their Interdependence" appeared in D. Kgl. Danske Vidensk. Selskab, Skr., nat. og math. Afd. 5, II, p. 121 (1851). Cf. also Phil. Mag. [4] 27, 56 (1864).

transformation theory and the theory of the existence of energetic equivalence between heat and work¹⁾.

It is characteristic of these early contributions to the problem of the relation between heat and work that no reservation is made with regard to the direction of the processes in which the equivalence in question is supposed to appear. It is imagined that the inconstancy of heat appears both in the case of the production and the consumption of heat. Although the equivalence was not yet formulated as an actual "energy principle", it was the notion of reciprocity or equal genetic-energetic value of heat and work which dominated the ideas. Thus J. R. MAYER writes: "Wie die Wärme als Wirkung entsteht, bei Volumensverminderung und aufhörender Bewegung, so verschwindet die Wärme als Ursache unter dem Auftreten ihrer Wirkungen, der Bewegung, Volumensvermehrung, Lasterhebung" ²⁾ Further, in describing the function of the heat engine, he writes: "Der Aufwand von Wärme, oder die Verwandlung der Wärme in Bewegung beruht nun darauf, dass die Wärmemenge, welche von den Dämpfen aufgenommen wird, fortwährend grösser ist als die, welche von den Dämpfen bei ihrer Verdichtung an die Umgebung wieder abgesetzt wird. Die Differenz giebt die nutzbar verwendete, oder die in mechanischen Effekt verwandelte Wärme" ³⁾. "Die Leistung der Maschine ist an ein Konsumo von Wärme unzertrennlich geknüpft." ⁴⁾

1) The papers on the subject are of easiest access in: ROBERT MAYER: "Die Mechanik der Wärme", 1893, and "The Scientific Papers" of J. P. JOULE, London, 1884—87.

2) ROBERT MAYER: "Bemerkungen über die Kräfte der unbelebten Natur". Ann. Ch. Pharm. 1842; "Die Mechanik der Wärme", p. 28.

3) ROBERT MAYER: "Die organische Bewegung in ihrem Zusammenhange mit dem Stoffwechsel". 1845; "Die Mechanik der Wärme", p. 52.

4) Ibidem, p. 54.

Or, even more precisely: "Wenn wir in dieser Richtung vorgehen, und die auf mechanischem Wege entwickelte Wärmemenge, sowie die dazu verbrauchte Arbeitskraft messen, und diese Grössen mit einander vergleichen, so finden wir sofort, dass dieselben in der denkbar einfachsten Beziehung, d. h. in einem unveränderlichen geraden Verhältnisse zu einander stehen, und dass das nämliche Verhältnis auch statt hat, wenn umgekehrt mit Hilfe der Wärme wieder Arbeitskraft erzeugt wird. Diese Thatsachen in kurze klare Worte gefasst, sagen wir: "Wärme und Bewegung verwandeln sich in einander"¹⁾.

In the works of JOULE we find the same notions: His conclusions from his famous experiments on the generation of heat in chemical, electrical and mechanical processes are not confined to the directly observed phenomenon of transformation, but also include the inverse processes, in which heat is supposed to be converted into work. Thus in a paper presented at the meeting of the "British Association" in 1843 Joule wrote²⁾: "The quantity of heat capable of increasing the temperature of a pound of water by one degree of Fahrenheit's scale is equal to, and may be converted into, a mechanical force capable of raising 838 lb. to the perpendicular height of one foot". As another typical example of his ideas the following quotation from a paper of 1847 may be given³⁾: "The general rule, then, is, that wherever living force is apparently destroyed, whether by percussion, friction, or any similar means, an exact equivalent of heat is restored. The converse of

1) ROBERT MAYER: "Bemerkungen über die mechanische Äquivalent der Wärme". 1851; "Die Mechanik der Wärme", pp. 242—43.

2) Scientific Papers of JAMES PRESCOTT JOULE, I, p. 123.

3) "On Matter, Living Force, and Heat". The Scientific Papers of JAMES PRESCOTT JOULE, I, p. 265.

this proposition is also true, namely, that heat cannot be lessened or absorbed without the production of living force, or its equivalent attraction through space. Thus, for instance, in the steam engine it will be found that the power gained is at the expense of the heat of the fire, that is, that the heat occasioned by the combustion of the coal would have been greater had a part of it not been absorbed in producing and maintaining the living force of the machinery. It is right, however, to observe that this has not as yet been demonstrated by experiment. But there is no room to doubt that experiment would prove the correctness of what I have said; for I have myself proved that a conversion of heat into living force takes place in the expansion of air, which is analogous to the expansion of steam in the cylinder of the steam engine. But the most convincing proof of the conversion of heat into living force has been derived from my experiments with the electro-magnetic engine, a machine composed of magnets and bars of iron set in motion by an electric battery. I have proved by actual experiment that, in exact proportion to the force with which this machine works, heat is abstracted from the electric battery. You see, therefore, that living force may be converted into heat, and that heat may be converted into living force, or its equivalent attraction through space." "... The same quantity of heat will always be converted into the same quantity of living force".

In his well-known work on the conservation of energy¹⁾ HELMHOLTZ in the main accepts JOULE's ideas, while at the same time he particularly emphasises the mechanical

¹⁾ H. HELMHOLTZ: "Über die Erhaltung der Kraft", 1847. Ostwalds Klassiker No. 1.

conception of heat, free and latent, as "living force" and "tensional force" between the elementary particles of matter. In support of the idea of the production of "mechanical force" at the cost of heat he mentions JOULE'S experiments on the expansion of air with and without the production of work upon the surroundings, and it seems that in these experiments HELMHOLTZ sees the realisation of such a heat-work transformation. On the whole, a consumption of heat in the production of mechanical work is considered a necessary consequence of the law of the conservation of energy¹⁾. Although HELMHOLTZ is often held to have been the first to express the energy principle as a quite general law, applicable to all kinds of energy, he is in reality a stranger to the conception of the correlation between the different macroscopic forms of energy which is the main principle of the energetic theory.

The postulate of a reciprocal transformation of heat and work which is proclaimed in these early contributions to energetics as verified by experience is mainly based upon the fact that a system which undergoes a definite change gives off less or takes up more heat if work is done upon the surroundings during the process, than if this is not the case. That such a postulate can be based on this perfectly correct observation is, however, an entirely unjustified contention, since the observation only concerns the numerical, not the genetic correlation between the different kinds of energy. Nevertheless, the reciprocity postulate has exercised a decisive influence on the entire development of the concept of heat, and has been maintained, although in a modified form, right down to the

¹⁾ Cf. also WILLIAM THOMSON, *Mathematical and Physical Papers* 3, 236 (1890).

present time. To such an extent, indeed, has this idea of the conversion of heat into work become an integral part of the existing theories, that the historiography of later times has not even paused at this primitive fallacy in the establishment of the fundamental laws of thermodynamics. As late as 1849 WILLIAM THOMSON questioned the validity of JOULE'S proof of the reciprocal transformation of heat and work. Having acknowledged JOULE'S discovery concerning the production of heat he adds: "No experiment however is adduced in which the converse operation is exhibited"¹). But this, according to REYNOLDS²) is the only doubt which has ever been thrown on the sufficiency of JOULE'S demonstration. A modification of this view, however, was introduced shortly afterwards by CLAUSIUS and by WILLIAM THOMSON himself.

It was only natural that during the time immediately following JOULE'S fundamental experiments efforts should be made to establish a theory of the heat engine, based on the new principle of equivalence. The functioning of this engine, which seems to correlate heat and work in a particularly striking and significant manner, had been interpreted by CARNOT from entirely different points of view. While CARNOT had regarded a transfer of heat from a higher to a lower temperature as the basis of the mechanical work done by the engine, the newly established equivalence principle seemed to require an expenditure of heat as an indispensable condition of the work done. The difficulty of reconciling these two ideas was clearly recognised by WILLIAM THOMSON³). It was CLAUSIUS who

1) WILLIAM THOMSON: *Mathem. and Phys. Papers* I, p. 102 (1882).

2) OSBORNE REYNOLDS: *Memoirs of JAMES PRESCOTT JOULE*, Manchester Lit. a. Philos. Soc. 1892, p. 122.

3) W. THOMSON: *An Account of CARNOT'S Theory of the Motive Power of Heat*, Edinb. Trans. 16, 541 (1849).

first brought forward the alleged solution of this problem in advancing a conception of the functioning of the heat engine which aimed at reconciling the conflicting ideas.

According to the ideas of CLAUSIUS the mechanical production of work takes place at the cost of heat, the functioning of the engine being accompanied by an expenditure of heat of the same magnitude as the gain of work. In this respect there is conformity with the MAYER-JOULE principle. The new idea introduced by CLAUSIUS is that simultaneously with this heat-work transformation a compensating parallel reaction takes place in which heat is transported from a higher to a lower temperature.

In the previous papers the conception of CLAUSIUS has been subjected to a critical analysis and it will also be dealt with in more detail in one of the later chapters of the present paper. Here we shall only observe that it has exercised a considerable influence on the conception of heat as a work-producing form of energy, since not only in the case of the thermal process, with which we are here concerned, but quite generally "compensating processes" have been claimed to take place when heat is supposedly expended in the production of work. This conception of the work-producing property of heat, which is based upon the equivalence principle in its classical form, but adds a new feature of an essentially irrational character, is still prevalent at the present day. Nevertheless in numerous processes in which a transformation of heat into work is claimed to take place, the compensation process, although virtually recognised as necessary, is left entirely out of consideration.

As has been previously¹⁾ shown, the function of the heat

¹⁾ D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XV, No. 4 (1937).

engine is easily interpretable on the basis of the work principle in conformity with Equation (2)¹⁾. It was explicitly proved that in the thermal process, no expenditure of heat takes place any more than in other reversible processes, the idea of heat being conceived in conformity with the classical view as representing a form of energy. In a later section this question will be more closely analysed and illustrated in connection with the discussion of the CLAUSIUS theory.

As already stated, from a purely phenomenologic angle the traditional notion of heat transport and heat communication is in agreement with the ideas of the present exposition. This agreement is plainly revealed in equations (12) and (13), the validity of which is accepted also in classical thermodynamics, where they serve to define the concept of entropy. The essence of traditional ideas is the postulate that the amount of heat leaving one heat reservoir in a process of irreversible thermal communication is equal to the amount of heat taken up by the other heat reservoir. It is worth noticing, however, that such a postulate cannot be advanced as a result of an empirical observation concerning heat, unless this concept has been previously defined on a different basis. The actual facts behind the classical postulate do not permit a comparison of the two amounts of heat entering into the classical formulation, but can be expressed by the following postulate:

If two heat reservoirs, i. e. two material systems open to changes by communication of entropy only, are in a state of irreversible thermal communication, this process comprising merely the two reservoirs, not the surroundings, then the change in one reservoir accompanying a

¹⁾ D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XV, No. 4 (1937).

given change in the other reservoir is independent of the path by which the thermal communication takes place.

If the changes observed in the reservoirs are described as due to a transport of heat, then obviously it can only be ascertained by experience that a given amount of heat lost in one reservoir is always connected with a constant amount of heat gained in the other reservoir. Equality of these two amounts of heat is outside the possibility of experimental verification. The contention, therefore, that they are equal, although not justified by any actual demonstration, cannot lead to any conflict with experience, for on account of the irreversibility of the process of heat conduction it is impossible to subject the postulate to any experimental test.

Quite different from this, however, is the position of the classical theory as regards the phenomena of production and consumption of heat. According to the energetic theory, these phenomena should be interpreted in conformity with equation (6), which defines the evolution of heat by means of its relation to the entropy produced. As previously emphasised, on the classical view this equation will not define any amount of heat, except in certain particularly simple cases. This is revealed in a striking manner by the fact that the "heat evolution", contrary to the production of entropy, is supposed to be able to have either a positive or a negative sign. If we ask how then is formulated the classical definition of the concept of heat evolution, we encounter however the very peculiar fact that classical thermodynamics does not contain any general and universally accepted definition whatever of this concept, and that in various

quarters entirely different conceptions of heat evolution are advocated in the individual cases. Although such a lack of clarity is understandable at the moment when the very idea of the "conservation of energy" is intuitively brought into existence and therefore does not in any way reduce the importance of the achievements due to the creators of the principle of the equivalence of heat and work, the persistent absence of clarity with regard to the fundamental concepts which characterises the development in the succeeding time has had fatal consequences in the system of classical thermodynamics.

This uncertainty with regard to the concept of heat is, as previously mentioned, closely connected with the fact that the traditional treatment of the problem of heat generation does not make any distinction at all between reversible and irreversible processes. From the establishment of the equivalence theory right down to modern times, such phenomena as heat evolution by elastic compression and heat evolution by friction figure as co-ordinated and fundamentally identical phenomena. It is in this respect that the contrast between the traditional conception and the energetic theory manifests itself in the most marked and striking manner.

It is also a remarkable fact that in many domains of thermodynamics heat has not yet been entirely disentangled from the notions of the caloric theory, which attributes to heat the properties of a material quantity. In his well-known "Theory of Heat" MAXWELL¹⁾ after describing some of the properties of heat says: "We have therefore the right to speak of heat as a measurable quantity, and to treat it mathematically like other measurable quantities

¹⁾ J. CL. MAXWELL, "Theory of Heat", 5 Ed., 7 (1877).

so long as it continues to exist as heat". This statement presupposes the possibility of a heat-work-transformation and also recognises the fact that heat is not a function of state. Nevertheless it is assumed by MAXWELL — and this assumption is, as will appear from numerous instances in recent thermodynamic literature¹⁾, still commonly accepted — that heat can be treated as a property of a system in the sense that by investigating the state before and after an irreversible change of the system it would be possible to determine the amount of heat developed during that change. Such a view is actually the basis of CLAUSIUS' theory of the heat engine, of the classical interpretation of the transport of heat, and many other energetic phenomena. As already stated in chapter II. 3, heat does not, according to the energetic theory, possess the character of such a property, which is a simple consequence of the general definition of heat given by equation (II. 16).

In the following sections the principal basic processes i. e. the processes of a spatial, thermal, and chemical nature, are considered separately. The treatment comprises the necessary documentation with respect to the classical conceptions and interpretations of these processes combined with a critical analysis based on the view-points of the energetic theory.

2. The Spatial Process.

The spatial basic process in its differential form consists in the transference of a volume from one pressure to another. The process can be carried out for example by the infinitesimal displacement of a piston which separates two material states of different pressures. In the integral

¹⁾ See e. g. C.W. MILLER, "Introduction to Physical Science", p. 90 (1935).

basic process the change of state in question is given finite dimensions, whereby also the pressures in the two states separated by the piston undergo finite changes. In physics processes of this kind are designated in different ways according to the nature of the circumstances, for instance as expansion, dilatation, compression and contraction.

According to the energetic theory, no caloric or heat phenomenon is involved in the reversible course of these processes while the irreversible course is accompanied by an evolution of heat. The classical interpretation is quite different. In order to provide a clear and indisputable basis for the subsequent analysis it will be necessary to elucidate the historical status by means of a comprehensive documentation. Therefore we shall first quote a number of passages illustrating the ideas of the creators of the energy principle, or of authoritative expositions of thermodynamics on the subject of the spatial changes in gases or liquids.

J. R. MAYER¹⁾, dealing with natural processes in which different types of energy are interconverted, says: "Verwandlung von mechanischem Effekt in Wärme bei der Kompression elastischer Flüssigkeiten, bei Stoss und Reibung" . . . "Die Verwandlung der Wärme in mechanischen Effekt erfolgt bei der Ausdehnung der Gasarten unter einem Drucke"

J. P. JOULE²⁾: "From them" (JOULE'S principles) "we may infer that the steam while expanding in the cylinder, loses heat in quantity exactly proportional to the mechanical force which it communicates by means of the piston".

1) J. R. MAYER, "Mechanik der Wärme", p. 72.

2) J. P. JOULE, Scientific Papers I, 189. Cf. also p. 23 of the present article.

In a biography of JOULE J. G. CROWTHER¹⁾ says: "By these experiments JOULE proved to a high accuracy the assumption previously made by MAYER, that in the compression of air the whole of the work done is converted into heat".

H. v. HELMHOLTZ: When water evaporates, a weight being lifted by the expansion, more heat must be added than if the same process of expansion takes place without any production of work: "Wir haben hier also eine Verwandlung von Wärme in mechanische Energie²⁾".

Furthermore³⁾ "Giebt der Stempel nach, so wird durch den Druck des Gases mechanische Arbeit geleistet, und die im Dampf bei der Ausdehnung verschwindende Wärme wird zur Leistung dieser Arbeit verwendet". And: "Suchen wir bei der Ausdehnung eines Gases nach dem Äquivalent für den Gewinn an mechanischer Energie, so finden wir ihn in dem Wärmeverbrauch, der sich in der Abkühlung des Gases äussert".

H. C. ØRSTED. In a communication: "Experiments on the Heat developed by Water when compressed"⁴⁾ he says: "About $\frac{1^\circ}{40}$ centigrade is developed in the water for each atmosphere applied".

L. A. COLDING⁵⁾: "When heat expands a vapour or a gas, then the temperature decreases if no heat is supplied during the expansion. But the activity is not therefore lost,

1) J. G. CROWTHER, "British Scientists in the 19th Century", p. 183 (1935).

2) H. v. HELMHOLTZ, Vorles. über theor. Phys. I, 2 p. 224 (1898).

3) H. v. HELMHOLTZ, Ibid. VI, pp. 171—173 (1903).

4) H. C. ØRSTED, D. Kgl. Danske Vidensk. Selskab, Overs. for the year 1845, p. 117 (1846).

5) L. A. COLDING, D. Kgl. Danske Vidensk. Selskab, Skr., nat. og math. Afd. 5, II, p. 130 (1851).

since an amount of motion has been produced during the expansion. If a gas or liquid is compressed, an amount of motion is consumed in the process, but this amount has not disappeared either; it also manifests itself in other forms as heat etc.”.

H. V. REGNAULT¹⁾ after mentioning experiments to measure the evolution of heat in the compression of water says: “Je conclus de ces expériences que la chaleur dégagée par une pression subite de 10 atmosphères sur l'eau, est incapable d'élever sa température de $\frac{1}{50}$ de degré centigrade”.

REGNAULT thus imagines that the compression is associated with an evolution of heat, which increases the temperature of the compressed liquid.

G. A. HIRN²⁾: “Tout corps qu'on comprime s'échauffe”. “... il y a donc réellement production de chaleur dans un gaz qu'on comprime, et disparition de chaleur dans un gaz qui se détend, et non pas simplement manifestation de ce qui y existait déjà”.

JOHN TYNDALL³⁾: “Heat is known to be developed when air is compressed”. As an experimental proof of this he mentions the experiment that vapours of carbon disulfide in air ignite when the mixture is compressed. The increase of temperature is obviously interpreted as an evolution of heat in the gaseous mixture.

R. CLAUSIUS⁴⁾: “Ein permanentes Gas verschlucht, wenn es sich bei konstanter Temperatur ausdehnt, nur so viel

1) H. V. REGNAULT, Mémoires de l'Académie Royale des Sciences, Paris. 21, 462 (1847).

2) G. A. HIRN, “Théorie Mécanique de la Chaleur” (2^{me} Ed.), 1865.

3) JOHN TYNDALL, “Heat Considered as a Mode of Motion”, London 1865, p. 27.

4) R. CLAUSIUS, “Mechanische Wärmetheorie” I, 46 (1876).

Wärme, wie zu der äusseren Arbeit verbraucht wird”.

L. BOLTZMANN¹⁾. The heat amount dQ is added to a gas, increasing temperature and volume. “Wir setzen $dQ = dQ_1 + dQ_4$, wobei dQ_1 die auf Erhöhung der Molekularenergie verwendete, dQ_4 aber die auf äussere Arbeitsleistung verwendete Wärme darstellt”.

WILHELM OSTWALD²⁾. On the subject of the isothermal expansion of gas he says: “Wir haben hier den idealen Grenzfall der schon mehrfach erwähnten Maschine zur Umwandlung von Wärme in mechanische Energie ohne Temperaturdifferenz vor uns”.

M. PLANCK³⁾. Discussing CLAUSIUS' conceptions concerning the expansion of air in the case of the expanding gas being perfect, he declares: “Dann wird also alle äussere Arbeit lediglich auf Kosten der Wärme des Gases geleistet”.

PLANCK⁴⁾ strongly emphasises the fact that heat is transformed into work during the expansion of an ideal gas. After mentioning the particularly simple energetic relations of these substances he says: “Lässt man nun ein ideales Gas sich unter Arbeitsleistung ausdehnen, und verhindert man die Abkühlung des Gases durch gleichzeitige Zuleitung von Wärme aus einem Wärmebehälter von höherer Temperatur, so behält das Gas mit seiner Temperatur zugleich auch seine Energie unverändert bei, und man kann sagen, dass durch den Prozess die vom Reservoir abgegebene Wärme vollständig in Arbeit verwandelt

1) L. BOLTZMANN, “Vorlesungen über Gastheorie” I, p. 54 (1923).

2) W. OSTWALD, “Lehrbuch d. allgemeinen Chemie” II. I. p. 32 (1910).

3) M. PLANCK, “Das Princip der Erhaltung der Energie” p. 63 (1913).

4) M. PLANCK, “Thermodynamik”, 1. Aufl., p. 74 (1897); 9. Aufl., p. 80 (1930).

worden ist, ohne dass sonst irgendwo ein Energieumsatz stattgefunden hat. Gegen diesen Ausspruch lässt sich nicht das mindeste Tatsächliche einwenden". Further, discussing the compression of air, he writes: "Leitet man nun, um das Gas auch auf seine alte Temperatur zurückzubringen die Kompressionswärme bei konstant gehaltenem Volumen ab". This statement seems to imply that a "heat of compression" is involved in the experiment in any case, even if no heat is led away from the system, which is in accordance with the above quotation from "Das Princip der Erhaltung der Energie".

J. BERTRAND¹⁾: Air is compressed without any rise of temperature when connected with a reservoir: "qui impose la température constante T_2 , en recueillant toute la chaleur produite par la compression".

B. WEINSTEIN²⁾: "Wie bemerkt, wandelt sich Wärme in jede andere Energie um, und wird von jeder anderen Art Energie hervorgerufen Erwärmt man ein Gas, so dehnt es sich aus, kühlt man es ab, so zieht es sich zusammen". The latter part of the quotation exemplifies the validity of the first part.

A. WASSMUTH³⁾: "Komprimiert man ein Gas, so steigt seine Temperatur, weil die aufgewendete Arbeit in Wärme umgesetzt wird".

Considering the compression of water below 4° , which takes place adiabatically and is accompanied by a decrease in temperature, he writes⁴⁾: "Wird keine Wärme von aussen

1) J. BERTRAND, "Thermodynamique", p 28 (1887).

2) B. WEINSTEIN, "Thermodynamik und Kinetik der Körper", I p. 14 (1901).

3) A. WASSMUTH, "Müller-Pouillet's Lehrb. d. Physik" III. 4 (1907), p. 645.

4) Ibidem, p. 688.

zugeführt, . . . und doch das Volum verkleinert, so muss die, wie wir sehen, hierzu nötige Wärme aus dem Innern des Körpers selbst genommen werden".

H. POINCARÉ¹⁾: The cooling effect of an expanding gas is explained as an expenditure of heat associated with a production of work: "La chaleur abandonnée par le gaz est transformée en travail".

A. EUCKEN²⁾. As an example of the equivalence of heat and work he mentions the expansion of a gas at constant temperature in thermal contact with the surroundings. Processes of this kind are accompanied by "Nebeneffekte" (CLAUSIUS' compensations), in the present case the change in the volume of the gas. For perfect gases, however, he finds "dass die bei der Expansion eines Gases gewonnene mechanische Energie tatsächlich der verbrauchten Wärmemenge äquivalent ist". Thus heat is expended to produce an equivalent amount of work.

W. C. McLEWIS³⁾: "During the process of isothermal compression, the heat which is produced and evolved is absorbed by the surroundings . . .".

Furthermore⁴⁾: "The source of the energy which has been used in the work of expansion if the temperature has been maintained constant, is the heat which has been drawn from the surroundings. If we had enclosed the gas in a "heat tight" case and allowed it to do work we should have found that its temperature would have fallen. In the latter case the work is done at the expense of the

1) H. POINCARÉ, "Thermodynamique", p. 82 (1923).

2) A. EUCKEN, Müller-Pouillet: Lehrb. d. Physik III. 1. pp. 113—14 (1926).

3) W. C. McLEWIS, "A System of Physical Chemistry" II; "Thermodynamics", p. 19 (1920).

4) Ibidem, pp. 3—4.

heat energy in the gas itself". With regard to the isothermal expansion he says: "what we have actually done is to transform heat energy into mechanical energy".

Again¹⁾ concerning the isothermal expansion: "the heat which had to be added . . . was quantitatively converted into the work done".

J. EGGERT²⁾. Discussing the expansion or compression of a gas he declares: ". . . verliert oder gewinnt das Gas—auch das ideale—jetzt ebensoviel Wärme, wie der Stempel an mechanischer Arbeit empfängt oder leistet". This applies to both isothermal and adiabatic processes.

K. JELLINEK³⁾ considers the expansion of a gas which overcomes an external pressure thus doing work at the same time as supplying kinetic energy to a heavy piston. If this takes place when the gas is in thermal contact with a large water bath, "so haben wir als Quelle der mechanischen Arbeit und kinetischen Energie die von dem Wasserbad auf das Gas übergehende äquivalente Wärmemenge anzusehen".

In a later publication⁴⁾ the same author says: "Da bekanntlich die gesamte Energie W bei der Expansion sich nicht ändert, so erkennt man, dass als Quelle für die geleistete Arbeit nur eine Wärmemenge $Q = A$ in Frage kommt, die aus dem Wärmebad in das Gasmol hineinfließt".

D. A. MACINNES⁵⁾: "The isothermal expansion of a perfect gas is therefore a means for converting heat into work quantitatively".

1) Ibidem, p. 9, footnote.

2) J. EGGERT, "Lehrb. d. physik. Chemie" I, p. 32 (1926).

3) K. JELLINEK, "Lehrb. d. physik. Chemie" I, p. 84 (1914).

4) K. JELLINEK, "Kurzes Lehrbuch der physikalischen Chemie", 31 (1938).

5) D. A. MACINNES, "The Principles of Electrochemistry", 97 (1939).

R. A. HOUSTOUN¹⁾ considering the reversible gas expansion: "... According to the first principle of thermodynamics this heat is used for two purposes: 1. It does external work. 2. It increases the intrinsic energy of the substances".

From the above quotations it will be evident that the reversible compression and expansion of gases and liquids is regarded in classical thermodynamics as exemplifying processes in which a transformation of work into heat and of heat into work takes place. In a large number of the cases quoted it is without doubt that the reciprocal transformation of heat and work is imagined to be directly associated with the adiabatic change of volume, i. e. that heat is imagined to be created or consumed within the working system itself communicating with the surroundings only as regards volume. It is positively stated that it is the change of temperature which is an indicator of the supposed production or consumption of heat in such systems. HELMHOLTZ for instance states clearly that the consumption of heat manifests itself through the fall in the temperature of the expanding gas. In his paper of 1847²⁾ he also expresses a doubt as to the correctness of CLAPEYRON's law of the relation between the heat of compression and the thermal coefficient of expansion³⁾, obviously arguing that if the "force" is to be maintained, the work of compression must result in a positive evolution of heat and, consequently, in a positive rise of temperature.

1) R. A. HOUSTOUN, "An Introduction to Mathematical Physics", 170 (1920).

2) HELMHOLTZ: "Über die Erhaltung der Kraft", Ostwalds Klassiker No. 1, p. 27.

3) E. CLAPEYRON, Journ. de l'Ecole polytechnique, 14, 23. Cahier 153 (1834).

In other cases quoted above the experiment in question is carried out isothermally the heat phenomenon being recorded in a heat reservoir communicating with the reacting gas. Whether this modification of the experiment is regarded by the authors as a necessary condition for the heat manifestation is not clear. It is natural, however, to interpret the superaddition of a heat reservoir merely as an attempt to record and, if possible, measure, by means of an ordinary calorimetric arrangement, an amount of heat, which is also in the absence of this means considered as generated or consumed. It would certainly be quite irrational to assume that a neutral passage of heat between the system and the heat reservoir should be able in any way to influence the contingency of a heat generation. That such a view, however, is actually to be found in the thermodynamic literature appears from a recent paper by F. H. MACDOUGALL¹⁾, who holds the opinion that the heat generation in a system can be generally identified with the amount of heat given off to the surroundings by the system during the process. On this view, which is considered by its author to be in harmony with traditional thermodynamics, no generation of heat by friction, electrical discharge or combustion etc. should take place, if only the system in question were adiabatically isolated from the surroundings!

With regard to the magnitude of the amount of heat produced or consumed a general and clear conception only seems to exist in the case of the system being a perfect gas. In that case the heat evolved is identified with the external mechanical loss of work. If this be designated as δA , and if δQ_a be the amount of heat produced:

1) F. H. MACDOUGALL, Journ. Phys. Chem. **44**, 713 (1940).

$$\delta A = \delta Q_a \quad (1)$$

in conformity with the principle of the equivalence of heat and work. In the case considered the evolution of heat equals the isothermal emission of heat δQ_i :

$$\delta Q_a = \delta Q_i, \quad (2)$$

whence:

$$\delta A = \delta Q_i. \quad (3)$$

It is the latter of these equations which has been verified by experiment, both the terms involved being completely energetically defined.

If the system is not a perfect gas one should expect the above-mentioned argument by HELMHOLTZ to involve as a logical consequence that the heat produced should be equivalent to the work of compression. Experience, however, shows only too plainly that for imperfect systems equation (3) is no longer satisfied. For liquids it will generally be very far from satisfied, δA and δQ_i during the compression having even in certain cases different signs, while during the expansion, at pressure <0 , such a deviation as regards the sign is almost universal. Classical thermodynamics therefore does not draw the conclusion mentioned above. It would be natural to investigate, on the basis of the classical argument, whether the invalidity of Equation (3) is due to the invalidity of (1) or (2) or possibly to that of both these equations. This problem, however, does not appear to be explicitly formulated in the classical considerations. In spite of unanimity with regard to the existence of a generation of heat in the case of volume changes in general, the fundamental question of its magnitude has not been subjected to investigation. On the other hand a conventional practice has been established in this

domain which in reality accepts equation (2) and rejects equation (1). This means that equivalence between heat and work is no longer claimed, since it is believed that the heat produced by the compression of an imperfect gas or liquid does not equal the work of compression, but equals the heat given off if the same infinitesimal change of volume were to take place isothermally. It is not improbable that this convention has been established owing to a confusion of the concepts of heat production and heat communication, as is obviously the case in the arguments of F. H. MACDOUGALL, quoted above.

This conventional determination of the generation of heat by compression, however, leads to a decided dilemma. If with HELMHOLTZ and the other classical authors we consider an expenditure of heat in the perfect expanding gas as the genetic equivalent of the external mechanical gain of work, measured for instance by the displacement of a weight perpendicular to the earth's surface, and if analogously we consider an evolution of heat as the genetic equivalent of a mechanical loss of work of the same kind by the compression, without introducing in any of the cases the spatial work as part of the transformation, we cannot, if the system under consideration deviates only infinitesimally from ideality, give an entirely different interpretation of the process. If the spatial work is excepted from the calculation in the case of a perfect system, it cannot possibly enter into it if the system is imperfect. But if this be so, an equivalent for the amount of work, positive or negative, by which the external work exceeds the expenditure of heat is obviously not available. The above-mentioned conventional estimation of the heat of compression and expansion in non-ideal systems is therefore contradictory

to the preceding classical interpretation of the spatial process and must virtually, logically analysed, be described as constituting a rupture of the principle of the equivalence between heat and work.

Classical thermodynamics makes no attempt to solve this difficulty, but evades it by introducing a new concept which represents neither work nor heat nor any other defined form of energy. Having accepted as a fact that the two magnitudes involved in (3) are no longer equivalent, the measures taken in an attempt to restore the balance consist in introducing a third term dE , writing:

$$dE = \delta A - \delta Q \quad (4)$$

and ascribing to this new term such a value that (4) is satisfied. This value is designated as the increase in internal energy of the reacting system.

It is beyond the scope of the present paper to give a detailed discussion of the content and significance of equation (4) and the concept of energy defined thereby. We may find it appropriate to describe work and heat as forms of energy but, as pointed out elsewhere,¹⁾ energy, even according to classical conceptions, may suffer alterations from other sources than through the communication of work and heat. What concerns us in the present connection is the fact that this new concept does not contribute to the solution of the problem under consideration here. This problem consists in establishing the general principles governing the transformations of the various forms of energy which are all of them already defined by strict and unambiguous definitions. The summary and unspecified character of the concept

¹⁾ BRØNSTED, D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XVI, No. 10, p. 50 (1939).

of internal energy makes it useless as a means of interpreting natural phenomena and establishing these general principles.

The difficulties which seem to surround the classical treatment of the simple spatial process may be ascribed to several reasons. In the first place the correlation between the change of temperature and the amount of heat in a system with the character of a calorimeter has been transferred quite automatically and without any theoretical consideration to systems of a different character. The intimate connection between the change of temperature and the supply of heat in a system of calorimetric character is due solely to the fact that entropy is the only independently variable quantity involved in the experiment. If other quantities, such as volume, are also made independently variable, the change of temperature will of course no longer depend on the supplied heat alone. Furthermore not only temperature, but also any other potential in the system will depend upon the communicated heat. The classical method of calculating heat is therefore irrational, partly because it is irrational to give precedence to temperature as compared with other quite analogous energetic potentials, partly because it is irrational and unjustifiable to transfer a correlation which is valid for simple cases to cases of a composite nature. The establishment of such a practice, not only in the case of the spatial process considered here, but quite generally, has been made possible only by the fact previously pointed out that the concept of heat generation is used in classical thermodynamics without any clear definition.

A second reason for the obscurity of the classical interpretation of the spatial basic process is due to the uncertainty with which the various types of work involved in

the process are recorded and enumerated. The compression of a gas requires some mechanical arrangement, a work reservoir, in which work is lost, for example by the lowering of a load. By the compression a volume is transferred from a higher to a lower pressure. With the latter process, however, the traditional treatment does not seem to associate any work, or rather, by virtue of a quite obscure reasoning, seems to mix it up with the work in the reservoir into a single "work of compression", the sign of which is hardly specified. Thus it is made possible to introduce heat as an equivalent for the work of compression and to clear the way for the theory of the reversible heat evolution. The obscurity of the argument actually excludes a pertinent discussion and is strongly contrasted with the simple and straightforward interpretation of the energetic theory.

Finally we shall have to consider the application of the theory of "compensations" to the case of the spatial processes. MAYER and JOULE, as already stated, believed in an unrestricted reciprocal transformation of heat and work. Later, it was enunciated by CLAUSIUS and WILLIAM THOMSON that although heat may be transformed into work, a parallel "compensating" reaction is required to make this transformation possible. The impossibility of the uncompensated transformation of heat has been formulated by OSTWALD as the impossibility of a perpetual motion machine of the second order¹⁾. With regard to the spatial processes considered here the majority of authors, however, do not make reference to any proviso concerning the heat-work transformation. It seems that such reference has only been made unambiguously by EUCKEN who, in dealing with a perfect gas, declares the volume change of the gas to be the com-

1) W. OSTWALD, Lehrbuch der allgemeinen Chemie II. I. p. 478.

compensating process: "Der Nebeneffekt, der mit diesem Vorgange verknüpft ist, besteht hier in der Volumenänderung des Gases". Strangely enough EUCKEN describes this compensation as "harmless" ("unschädlich"), an expression which is not immediately intelligible. Beyond this only very few authors reveal any kind of recognition of the necessity of a compensating reaction. For example, when PLANCK states that the heat given off by the expansion of a perfect gas is completely transformed into work, "ohne dass sonst irgendwo ein Energieumsatz stattgefunden hat", then this very positive assertion must be supposed to imply that PLANCK—like EUCKEN—though regarding the expansion of the gas as a compensating reaction, does not consider this worthy of any special mention, because the process takes place "without any energy transformation whatsoever", and possibly, for that reason, may be considered as "harmless".

This assumption, that the proof of the possibility of the transformation of heat into work—or more precisely: the transformation of heat from a single heat reservoir into work in an external work reservoir—can be based on the "harmlessness" of the compensating process, or, according to PLANCK, on the fact that no transformation of energy takes place in the compensating gas expansion, must, however, be characterised as illusory. What, in fact, is the substance of the contention that no transformation of energy takes place? Obviously it cannot be meant to express that the energy in the expanding gas does not change, for if heat is transformed into work in accordance with the equivalence principle, the change of energy in the compensating reaction must always be zero, if conflict with the energy principle is to be avoided. The meaning, then, apparently can only be that no transformation of energy of one

form into energy of another form takes place in the expansion. But, if the volume of the gas is increased by dv , this volume being taken for instance from a surrounding vacuum, then if the pressure is p , the system, not only according to the present theory, but also according to classical conceptions, will lose an amount of energy of the magnitude $p dv$ and of the particular form which is determined by the nature of the quantity, i. e. volume or spatial energy. The total energy in the compensating system having undergone no change, energy in another form must have been created simultaneously. Of this form there can be no doubt. In fact, since the compensating gas expansion is irreversible, entropy according to all stand-points has increased by a certain amount dS , which is tantamount to an increase of energy for the system of $T dS$. The compensating process is therefore clearly associated with a "transformation of energy", i. e. a loss of one form of energy and a gain of another. The expression for this transformation in the compensating process:

$$p \delta v \rightarrow T \delta S,$$

in conjunction with the expression for the main process:

$$T \delta S \rightarrow \delta A,$$

where δA is the external gain of work, shows that the term $T \delta S$ disappears in the total reaction, and that for describing this process there only remains the expression for the work principle:

$$p \delta v \rightarrow \delta A.$$

In these considerations we have been using for the products $p dv$ and $T dS$ the term "energy". This cautious mode of expression has been resorted to in order to avoid of-

fending against traditional phraseology and thus possibly diverting the reader's attention from the essential points in the argument. As $p dv$ is associated with the basic process of displacing a volume from one pressure to another and the factor dS in the product TdS is entropy generated by the irreversible expansion, the two products are of course according to the terminology of the energetic theory describable as work and heat respectively. Regardless of any terminology, however, the above reasoning shows conclusively that the spatial process considered is interpretable solely by the work principle of the energetic theory. The classical contention that heat enters into the energy transformation of the spatial process is therefore wholly unfounded. This result naturally applies no less to those formulations that entirely ignore the claim for compensations than to those which accept their presence without drawing the conclusions which they logically entail.

Since the processes here considered are reversible, "compensations" in the heat-work transformation will of course require "compensations" in the reverse process also. There would be reasons, therefore, to distinguish between two kinds of compensations, positive and negative, respectively. It is clear that the "negative" compensations would prevent heat from entering into the process of compression, just as the "positive" compensations, according to the proof given above, prevent heat from entering into the process of expansion. Thus we are obliged, even when following the classical views as closely as possible, entirely to exclude the phenomenon of heat from the reversible spatial process. If a transformation of heat into work were really to form part of these processes, then the presence of compensations would come into conflict with the generally accepted prin-

ciple that work may be transformed into heat without reservation.

Finally it should be mentioned that such phenomena as the stretching of a wire and changes of surface areas are closely related to the spatial process in imperfect systems. These phenomena have played an essential part in thermodynamic considerations but will not be discussed in the present paper, as their treatment does not offer any new aspect of special importance.

3. The Chemical Process.

The chemical basic process comprises not only the chemical reactions proper, which are characterised by certain fixed numbers of conversion, but all processes in which various forms of substance are transferred from one state to another. Even the transport of a substance from a pure state under given conditions of temperature and pressure to a pure state under other conditions of temperature and pressure is a chemical process according to this terminology. While the spatial and thermal processes involve only a single quantity, volume and entropy respectively, the chemical phenomena are more varied, as every chemical component has to be regarded as a separate quantity. It is not necessary that a chemical component should be what chemists describe as a "chemical individual". It may be an arbitrary group of substances capable of entering into the structure of the system. In principle, the amount of a component may enter also with a negative sign in a chemical component transformation. Further it should be noted that the chemical component is generally associated with the spatial and thermal quantities, i. e. with volume and entropy. The chemical basic process, which is defined by the nature and

amount of the transported component as well as by the chemical potentials in the states involved, is therefore in general associated with a simultaneous spatial and thermal basic process. The formal complications which might result herefrom in the energetic treatment are generally eliminated by a conventional definition of the composition of these quantity assemblies¹⁾. Even without such conventions they will disappear in the case of changes taking place at temperature and pressure homogeneity.

Finally may be mentioned another difference, which makes the treatment of the chemical process, as contrasted with the spatial process, more complicated. While only a single quantity, that is entropy, was admitted in the latter process as a neutral addition to the reacting system, a similar access will be generally supposed to exist both for entropy and volume in the treatment of the chemical process.

Just like the basic process in general the chemical process also can be differential or integral. The simplest differential chemical process consists in the transport of a single component between two different states, the amounts involved being of such dimensions that only infinitesimal changes in these states ensue; whereas the corresponding integral process is defined as a process of such extent that finite changes in these states take place even if these changes affect only infinitesimal fractions of the total system. When chemical processes are included it is particularly striking that a differential process may be carried out by way of an integral mechanism. It will be possible, for example, to substitute the differential basic process in which a given

¹⁾ Cf. W. GIBBS, Collected Works I. BRØNSTED, D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XV, No. 4, p. 18 (1937).

infinitesimal volume δv of a gas is transferred from the pressure p_1 to the pressure p_2 by an integral chemical process in which the gas contained in the volume dv is transferred to the gas of pressure p_1 , the pressure in δv falling to zero, and then gas from the pressure p_2 is transferred to dv , the pressure in this volume rising from zero to p_2 . However, this does not lead to any uncertainty regarding the concept of differential change, since a process which is differential with respect to a certain quantity, cannot also be differential with respect to another quantity.

According to the energetic theory an irreversible chemical process, like any other irreversible process, will cause an energetic evolution of heat. This applies for instance to the evaporation of a liquid in non-equilibrium with its vapour, or to the dissolution of a salt in water under decrease in temperature. On the other hand no caloric phenomenon will be associated with the reversible chemical process according to this theory. The traditional conception differs entirely from this view. For instance, with the reversible change of states it generally associates a caloric phenomenon i. e. a production or consumption of heat. CAVENDISH¹⁾, already, speaks of a generation of heat as being associated with the condensation of vapour, and recently W. JÄGER²⁾ as examples of processes in which other forms of energy are transformed into heat mentions changes in the state of aggregation and allotropic transformation and dissociation. This caloric effect is usually spoken of as "latent heat". Actually the distinction made between latent heat effects at constant temperature and reversible processes

¹⁾ Cf. J. CL. MAXWELL, "Theory of Heat", 5th Ed. 72 (1877). MAXWELL himself apparently did not share this view of a generation of heat in these processes.

²⁾ W. JÄGER, "Handbuch der Physik" (Geiger u. Scheel), IX, 474 (1926).

in which the temperature varies is unjustified, and all these reversible processes should logically be included in the general traditional idea relating heat generation to change of temperature. Precisely in the domain of chemistry, through the conventions and practice of thermochemistry, this idea of a simple correlation between heat and temperature has been demonstrated as particularly obvious. In the conventional language "evolution" and "absorption" of heat is the amount of heat which in the chemical process must be removed from or transferred to the reacting system, in order that its temperature may remain constant during the experiment. If the course of the reaction is irreversible, and also partly in the reversible case, these magnitudes are jointly designated as "Varmetoning"¹⁾, a term introduced by JULIUS THOMSEN. As distinct from energetic heat evolution the classical heat phenomenon has been described in a previous paper as thermometric²⁾.

We shall first examine the reversible chemical process, which in its simplest form consists in the transport of a substance from one state to another. If the chemical potential of the component in the initial and final states is μ_1 and μ_2 respectively and δn the amount of substance transported, then the loss of work in the process will be:

$$\delta A_{\text{ch}} = (\mu_1 - \mu_2) \delta n, \quad (5)$$

the same amount of work being gained simultaneously in an annexed work reservoir. Processes of this kind can be carried out in a particularly simple manner by means of

1) JULIUS THOMSEN, *Termokemiske Resultater*, 2 (1905). *Thermochemischen Untersuchungen I*, 5 (1882). In German: *Wärmetönung*. For this word there seems to be no adequate equivalent in English or French.

2) BRØNSTED, *D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd.*, XV, No. IV, p. 39 (1937).

a galvanic concentration cell in which the transformation under consideration is electromotively active. In principle, however, the electromotive method may be used also more generally for determining chemical work. If the cell serves for differential charging of a condenser the potential of which is equal to that of the cell, the chemical work may be said to be transformed into electric work. Also, if the electric work is only intermediate, being a link in the production of mechanical or chemical forms of work or even in the irreversible heat evolution, the electric gain of work may be regarded as directly coupled with the chemical loss of work, so that it will be possible in all instances to describe adequately the reversible function of the cell as a chemical-electrical work-transformation. What is essential is of course only the fact that the reversible process can be interpreted as a transformation of chemical work into external work of some form or other depending on the experimental conditions.

In conformity with thermodynamic practice the chemical system which constitutes the cell is considered as closed with regard to chemical components. Whether it is otherwise closed as regards quantity, or whether during the differential process under consideration it is in quantity communication with the surroundings is without significance for the above interpretation. The supply of entropy or of volume in infinitesimal amounts from outside will not cause any alteration of the nature of the infinitesimal transformation of work, and the corresponding neutral energy terms $T\delta S$ og $p\delta v$ will not have any share whatsoever in the external gain of work. The latter is in all cases determined by the chemical loss of work alone in conformity with equation (II. 1). It

should be specially noted that for this reason it will not be possible to find in energy or in other thermodynamic functions comprising such energy terms a universal basis for the determinations of chemical work or the corresponding electromotive force. Before entering upon the discussion of such attempts, however, it will be appropriate to consider the application of the classical views in the particularly simple instance of the substance transported in the chemical basic process obeying the simple gas laws. It is possible, in various ways, to make this transport electromotively active in a reversible concentration cell. If the cell functions isothermally, in communication with a work reservoir and a heat reservoir of the temperature of the cell, an amount of heat numerically equivalent to the accumulated work will be removed from the heat reservoir. The whole arrangement will thus be quite analogous to an isothermal and reversible expansion of air¹⁾, and the classical ideas, if consistently maintained, should lead to identical interpretations of the two phenomena. In conformity with the above considerations concerning the spatial process, the function of the cell should therefore be interpreted as a transformation of heat from the heat reservoir into work in the work reservoir, this imaginary process being rendered possible through the simultaneous, compensating cell-reaction consisting in an irreversible transference of substance from a higher to a lower chemical potential. This consistent interpretation, however, is not to be found in the traditional treatment. An interpretation, if given at all, is generally to the effect that a "work of dilution" associated with the process of the cell appears as electric energy. This work

¹⁾ This analogy was first pointed out by W. GIBBS, *Collected Works* I, 339 (1928). Cf. also V. v. TÜRIN, *Z. physik. Ch.* 5 343 (1890).

of dilution is identical with the chemical loss of work in the energetic theory.

When dealing with such chemical processes of a more complex nature as take place in the ordinary "chemical cells", the situation is much more complicated. Although the treatment of this subject is extremely varied in classical thermodynamics, it may be said to possess the general characteristic that heat, explicitly or implicitly, is supposed to enter as a partial genetic equivalent of the electric gain of work. This view, again, has developed from the earlier attempts to interpret the function of the cell on the basis of its irreversible thermometric heat evolution.

According to the so-called THOMSON rule¹⁾, which actually was developed already by JOULE²⁾ and by HELMHOLTZ³⁾, the electric energy supplied by a galvanic cell is measured by what is now called the thermometric heat evolution. JULIUS THOMSEN⁴⁾, for instance, carried out experiments to test the validity of this rule. Its incorrectness was fully recognised in later theoretical investigations especially by HELMHOLTZ⁵⁾, and appears plainly from the energy equation for the reversible cell process:

$$\delta A_{\text{ch}} = T dS - p dv - dE, \quad (6)$$

expressing that the total or internal energy of the system is altered partly by virtue of the chemical loss of work δA_{ch}

1) WILLIAM THOMSON, Phil. Mag. [4] **2**, 429 (1851).

2) JOULE, Phil. Mag. **19**, 260 (1841), **20**, 92 (1842), "Scientific Papers" 60, 81 (1884).

3) HELMHOLTZ, "Über die Erhaltung der Kraft", 1847, Ostw. Klass. No. 1. p. 34 (1915).

4) JULIUS THOMSEN, D. Kgl. Danske Vidensk. Selskab, Skr., nat. og math. Afd. 5. V, p. 155 (1861), Ann. d. Physik u. Chemie N. F. **11**, 246 (1880).

5) HELMHOLTZ, Sitzungsber. d. Berl. Akad. 1882 p. 22, Ges. Abh. II. 598.

and partly by virtue of the amounts of entropy and volume taken up from outside sources. As the irreversible thermometric loss of heat is given by:

$$-T dS' = \delta Q' = -(dE + p dv), \quad (7)$$

(6) may also be written:

$$\delta A_{\text{ch}} = T dS + \delta Q' = T dS''. \quad (8)$$

It will be seen that the chemical loss of work and the equivalent external electric gain of work in the reversible cell function equals the thermometric loss of heat, if under the given conditions the process takes place without any change of entropy, and that this loss of work is equal to the loss of energy, if the volume also remains constant. As the JOULE-THOMSON rule involves constancy of temperature and pressure, it will therefore ordinarily be valid only in the quite special cases where these conditions coincide.

As to equation (6) it is evident that it does not give, nor can it give, any contribution to the solution of the problem as to how the function of the galvanic cell should be interpreted, since by introducing the unspecified concept of internal or total energy, the distinction between the different forms of energy, which is the requisite condition of such an interpretation, is abandoned. The equation only serves to represent a numerical correlation between amounts of energy, without considering the presence of any genetic relation. It may be said to pertain to the realm of functional energetics or energetics of states, as contrasted with energetics of processes.

The same argument applies to the relation between chemical work and another important function, the ψ -function of GIBBS, which was also independently established by HELMHOLTZ in his paper of 1882, and was called by him

the free energy and denoted by F ¹⁾. This function is defined by the equation:

$$F = E - TS. \quad (9)$$

According to HELMHOLTZ it is an expression for the internal "work store" of the system, its ability to carry out work at constant temperature. Comparison of equations (6) and (9), differentiated at constant temperature, however gives:

$$dF = -p dv - \delta A_{\text{ch}}, \quad (10)$$

from which it appears that the change in free energy comprises not only the chemical work δA_{ch} , but also a term $p dv$, which does not possess the character of work as given by (5) and is actually intransformable energy. Only if the external pressure is zero, will the term $p dv$ possess an active form, capable of representing work, but this particular condition is not involved in the characterisation of the free energy; on the contrary, the free energy is generally used as a work function at pressure and temperature homogeneity. The GIBBS ζ - or G-function also, defined by:

$$G = E - TS + pv, \quad (11)$$

will only under special conditions measure the chemical work, namely when the pressure and temperature are constant within the system. The question of the free energy and the relation of the other thermodynamic functions to the heat-work concept will, however, be discussed elsewhere, and we shall here only emphasise the fact pointed out in Section II.1 that all terms of the form PdK represent neutral energy, i. e. energy which is not transformable and to which no character of work can be ascribed. That the term $p dv$ is generally small in galvanic processes and

¹⁾ Later HELMHOLTZ in his lectures exchanged the symbol F for the symbol H . "Vorlesungen über theoretische Physik" **6**, 267 (1903).

practically without significance has of course theoretically no influence on the argument.

If we introduce this condition in (6), i. e. if we assume $p dv$ to be negligible, the isothermal loss of energy and the thermometric loss of heat are equal and accordingly (6) and (8) will coincide. It is generally under this simplifying condition that classical thermodynamics, after recognising the incorrectness of the JOULE-THOMSON rule, looks for an interpretation of the chemical process in the galvanic cell, attempting to specify the forms of energy from which the electric work of the cell originates. In this way, in conflict with the views of the energetic theory, heat is introduced as a partial equivalent for the electric work in the reversible function of the cell.

According to the generally adopted view the electric work is gained at the cost of the "chemical energy" of the cell, this energy being "converted" into work and heat. The concept of "chemical energy" is not clearly defined, but its magnitude, according to thermodynamic practice and terminology, is fixed by the thermometric heat evolution at the irreversible cell process, or eventually by the total isothermal change of energy¹⁾. In the reversible process this "chemical energy" is supposed to be transformed into electric work. The electric work, however, does not represent the total loss of energy in the cell, since the two amounts need not be equal. Their difference is supposed to appear as "heat". Here two possibilities are present, the "heat" appearing either adiabatically in a closed system or isothermally in communication with the surroundings. Thus "chemical energy" is imagined to be present in the cell and to be transformed into external electric work in the

1) Cf. e. g. W. NERNST, "Theoretische Chemie", 8.—10. Aufl., 816 (1921).

cell process, and, in case the difference between chemical energy and work is positive, into heat as well. If the difference is negative, the chemical energy available will not suffice as an equivalent for the work, and in that case the surplus of work is supposed to be formed from "heat". The interpretation is thus quite similar to that employed in the case of the spatial process, a heat-work transformation being supposed to take place in spite of the reversibility of the process, and a certain form of energy, described as "chemical" but without definition, being involved in the interpretation.

These ideas, which are still maintained even in modern expositions of chemical thermodynamics, can be traced back to the earliest attempts to arrive at a more correct understanding of the electric cell phenomena than was given by the JOULE-THOMSON rule. Among these, investigations by F. BRAUN¹⁾ occupy a prominent place. According to this author the electric work can be created at the expense of an equivalent amount of heat resulting from the chemical process in the cell. The chemical energy supplied by the process is of the same form as heat. Only part of this energy, however, is ordinarily transformed into electric work. The rest of the "chemical heat" remains in the cell. A characteristic feature of this reasoning is the introduction of the concept of "electromotive efficiency" ("Nutzeffekt"), to designate the ratio between the work gained and the heat evolved, work being quite generally identified with "die von dem betr. chemischen Process in elektrische Energie, d. h. in mechanische Arbeit verwandelbare Wärmemenge". There are cases, however, in which the electric

¹⁾ F. BRAUN, *Ann. d. Physik u. Chemie*, N. F. **5**, 182 (1878), **16**, 561 (1882), **17**, 632 (1882).

work is greater than the heat evolution, and accordingly, the efficiency is greater than unity. In such cases the view advanced by BRAUN leads to the conclusion that work is created from heat consumed in the interior of the chemical system.

The investigations of S. CZAPSKI¹⁾, which have also played an essential part in the verification of the equations of HELMHOLTZ, as a main result lead to the conclusion "dass diejenige Elemente, die nicht alle chemische Wärme in Stromarbeit umsetzen, eine mit wachsender Temperatur abnehmende elektromotorische Kraft haben, und umgekehrt diejenigen, welche zum Teil auf Kosten ihres eigenen Wärmehalts arbeiten, eine mit der Temperatur wachsende Kraft". This statement is based on the same view that the production of work in the chemical process is associated with and dependent upon an expenditure of heat. Similarly A. GOCKEL²⁾ speaks about the "fraction of heat in the chemical process which is transformed into electric work" and about the "amounts of heat appearing or disappearing at the poles of the cell".

Ideas such as those described here have remained unchanged right down to the present time and are still the basis of authoritative expositions of the thermodynamics of chemical reactions³⁾. They are sharply contrasted with the theory of the chemical basic process advanced in the introduction of this section, according to which heat is excluded from any participation in reversible processes.

Closely related to the chemical processes in reversible galvanic cells are the phenomena appearing at the passage

1) S. CZAPSKI, Ann. d. Physik u. Chemie, N. F. **21**, 209 (1884).

2) A. GOCKEL, Ann. d. Physik u. Chemie N. F. **24**, 618 (1885).

3) Cf. C. DRUCKER, "Handbuch der Experimentalphysik" (Wien-Harms)

of an electric current through the junctions of metallic conductors, as we are here dealing with the transference of electric charges from one medium to another. HELMHOLTZ¹⁾, already, supposed that a direct relation existed in these phenomena between the electric energy and heat, and extended this view to include also the thermoelectric Thomson-effect²⁾. He regards the reversible passage of current as heat-generating, so that in these combinations electric energy is transformed into heat or vice versa. This view, which is also held by WILLIAM THOMSON³⁾, is adhered to in modern expositions⁴⁾, the usual conclusion being drawn from temperature changes to caloric effects. In this, it is overlooked that a thermoelectric cell is not a system of calorimetric character. This question, however, will not be discussed any further here, since the energetics of thermoelectric phenomena will be subjected to a more detailed treatment in another connection.

The energetic phenomena connected with the chemical basic process have been studied by numerous other methods besides the electrochemical method specially dealt with above. It is generally found that the classical treatment introduces caloric effects, i. e. heat evolution and heat absorption, in processes of a reversible course, such as phase transitions, processes of dissociation and chemical reactions in general, regardless of the fact that these phenomena imply certain conditions, for instance constancy of temper-

1) HELMHOLTZ, "Über die Erhaltung der Kraft". Ostw. Klass. No. 1, p. 43.

2) HELMHOLTZ, "Vorlesungen über die theoretische Physik" VI, 263 (1903).

3) WILLIAM THOMSON, "Mathematical and Physical Papers" I, 246 (1882).

4) Cf. K. BAEDECKER, "Die elektrische Erscheinungen in metallischen Leitern", p. 77 (1911). WEINSTEIN, "Thermodynamik und Kinetik" III, 348 (1905). NERNST, "Theoretische Chemie", 10. Aufl., 814 (1921). E. LANGE, "Handbuch der Experimentalphysik" (Wien-Harms) 12, 2. Teil, 327 (1933).

ature for the course considered. In the majority of cases it must be presumed that an actual heat-work transformation is presupposed, as for instance when it is claimed that the heat of combustion of carbon may be almost completely transformed into external work¹⁾, or that heat is consumed in the process of chemical dissociation²⁾. The heat involved here is always thermometric heat effects which do not enter into any energy transformation but are merely of communicative significance. In agreement with the main aspect of the classical theory the irreversible mixing of perfect gases is assumed to take place without any evolution of heat, because it is accompanied by no temperature change. These ideas, however, are so widely disseminated and familiar that a particular documentation concerning such phenomena may presumably be omitted.

4. The Thermal Process.

The thermal basic process consists in the passage of entropy from one temperature to another. If the amount of entropy δS passes from a heat reservoir R_1 of the temperature T_1 to a heat reservoir R_2 of the temperature T_2 , a thermal work:

$$\delta A_{\text{th}} = (T_1 - T_2) \delta S \quad (12)$$

is lost, and, in case of reversibility an equivalent amount of work of another kind, for instance mechanical, is gained. This description of the thermal process is completely exhaustive, since no independent phenomena other than those mentioned participate in the process. It is a principal point in the energetic theory that no caloric phenomenon is comprehended in the reversible process. No loss

1) W. NERNST, "Theoretische Chemie", 5^{te} Aufl. p. 698 (1907).

2) Ibidem, p. 602.

of heat therefore will take place when the heat engine is operating, an equivalent for the mechanical work gained being provided solely by the entropy transport.

The concept of a thermal basic process does not form part of classical thermodynamics, its ideas in this field being embodied in the theory of the heat engine. This theory is so familiar and generally accepted that further documentation beyond that given in previous papers¹⁾ will not be needed. We may therefore directly proceed to an analysis of the classical theory as presented by CLAUDIUS.

By way of introduction it should be pointed out that the contention of CLAUDIUS of a heat-work transformation in the function of the heat engine is based on the idea that heat is motion of the elementary particles of matter. "Wenn dieses richtig ist", he says²⁾, "so muss sich auf die Wärme auch der allgemeine Satz der Mechanik anwenden lassen, dass eine vorhandene Bewegung sich in Arbeit umsetzen kann und zwar so, dass der Verlust an lebendiger Kraft der geleisteten Arbeit proportional ist". It is claimed therefore "dass zur Erzeugung von Arbeit, nicht bloss eine Änderung in der Verteilung der Wärme sondern auch ein wirklicher Verbrauch von Wärme nötig sey". This necessity of an expenditure of heat in the production of work is emphatically insisted upon in the classical theory and on the whole appears as the new idea by means of which the difficulties connected with CARNOT's view³⁾ might be duly removed.

That the "general laws of mechanics" do not take us far towards the solution of the problem of heat-work rela-

1) J. N. BRØNSTED, D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XV, No. 4, p. 47 (1937).

2) R. CLAUDIUS, Pogg. Ann. 79, 370 (1850).

3) Cf. WILLIAM THOMSON, Edinb. Transact. 16, 541 (1849).

tions is however a fact that appears clearly from CLAUSIUS' own treatment. Reference to these laws therefore seems rather pointless or even misleading particularly if it be kept in mind that the procedure of CLAUSIUS is otherwise based exclusively on what is described in the present paper as the macroenergetic view, entirely disregarding existing theories of the micro-structure of matter.

If we make a record of the phenomena which are directly observable as a result of the function of the heat engine operating for example by means of a CARNOT cycle in a direction which we shall describe as positive, the issue is as follows:

1. The heat or entropy reservoir R_1 of the temperature T_1 gives off an amount of heat δQ_1 and an amount of entropy δS , interrelated by the equation:

$$\delta Q_1 = T_1 \delta S. \quad (13)$$

2. The heat or entropy reservoir R_2 of the temperature T_2 receives an amount of heat δQ_2 and an amount of entropy δS , interrelated by the equation:

$$\delta Q_2 = T_2 \delta S. \quad (14)$$

3. In a mechanical work reservoir an amount of work δA_m , given by:

$$\delta A_m = \delta Q_1 - \delta Q_2 \quad (15)$$

or:

$$\delta A_m = (T_1 - T_2) \delta S \quad (16)$$

is accumulated.

This is what may be phenomenologically established. Classical thermodynamics, however, does not content itself with this description, but looks for a genetic interpretation of the phenomena from a more complicated energetic standpoint. While the present theory views the process as a transport of entropy, a contention which

merely forms a record of the observed phenomena, the function, according to the traditional view of CLAUSIUS, consists in the transformation of an amount of heat $\delta Q_1 - \delta Q_2$ into work, the heat being taken for instance from the reservoir R_1 , and a supplementary transport of heat δQ_2 from R_1 to R_2 . Thus in addition to the heat-work transformation a parallel heat transport takes place, which is regarded as a compensation for the main process: "Die eine aus dem Körper K_1 stammende Wärmemenge Q ($= \delta Q_1 - \delta Q_2$) ist in Arbeit verwandelt, und die andere Wärmemenge Q_2 ($= \delta Q_2$) ist aus dem Körper K_1 in den kälteren Körper K_2 übergegangen"¹⁾. In the thermal process the presence of such a compensation has become particularly appreciated as a condition for the realisation of the heat-work-transformation.

If the direction of the cycle is reversed the work δA , will on this view be transformed into heat at the temperature T_1 , while simultaneously heat δQ_2 is led from T_2 to the higher temperature T_1 . It is the impossibility of the latter process as an isolated phenomenon which is established by CLAUSIUS as a special principle exceeding the sphere of the energy principle, and it is the simultaneous work-heat transformation which is introduced as a "compensation" that enables heat to pass from a lower to a higher temperature.

The thermal work relation has found another classical expression in the following well-known postulate by WILLIAM THOMSON²⁾: "It is impossible, by means of inanimate

¹⁾ R. CLAUSIUS: "Die mechanische Wärmetheorie" I, p. 75 (1876). Cf. also H. v. HELMHOLTZ, *Wiss. Abhandl.* **3**, 120 (1895), M. PLANCK, "Thermodynamik", 1st Ed., p. 60 (1897), and 9th Ed., p. 66 (1930).

²⁾ WILLIAM THOMSON, *Trans. Roy. Soc. Edinb.* 1851; *Phil. Mag.* 4 1852. "Mathematical and Physical Papers" I, 174, 511 (1882).

material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects". The formulation must be interpreted as expressing the impossibility of the heat-work transformation as an isolated phenomenon, while at the same time conceding the possibility of such a process when accompanied by compensating changes.

Of the two parts into which the reversible function of the heat engine is traditionally divided the main process, i. e. the transformation of heat into work, is imaginary, while the compensating heat transport is irreversible. The imaginary processes are not known to have been subjected to special consideration in classical thermodynamics, but the irreversible processes are well characterised and familiar phenomena. It is natural therefore to commence our analysis by considering the irreversible heat transport.

As stated above, an irreversible process can always be described as a basic process associated with the formation of entropy. If the entropy ΔS is generated in a reservoir of calorimetric character at temperature T , the amount of heat $T\Delta S$ formed simultaneously can be determined by measurements on the reservoir before and after the process. If, however, the irreversible process is given merely by the initial and final states of the bodies involved, in which case we shall say that the process is terminally defined, the heat evolution will not be fixed. For the heat, equivalent to the work of the basic process considered, may have been formed in a reservoir at the higher temperature T' and from there have been conducted to the reservoir of temperature T , thus causing additional heat to be produced by the irreversible heat transport. The reason for this indetermin-

ation of the heat evolution is to be found in the fact that the entropy generated does not form part of the initial state and that the basic processes acting in the case of irreversibility are not therefore terminally established.

The heat transport is an irreversible process describable by the amount of heat Q passing from the reservoir R_1 to the reservoir R_2 and the temperatures T_1 and T_2 of these reservoirs. Owing to the general relation:

$$Q = T_1 S_1 = T_2 S_2 \quad (17)$$

the amount of entropy S_1 leaving R_1 and the amount of entropy S_2 arriving in R_2 during the heat transport are terminally determined. Furthermore the generation of entropy is fixed by:

$$\Delta S = S_2 - S_1 = Q \frac{T_1 - T_2}{T_1 T_2} \quad (18)$$

or

$$\Delta S = S_1 \frac{T_1 - T_2}{T_2} = S_2 \frac{T_1 - T_2}{T_1}. \quad (19)$$

This terminal definition of the increase of entropy exemplifies the general character of entropy as a function of state.

In accordance with the above statements concerning irreversible processes in general there are present, however, in the heat transport certain important magnitudes which are not given as functions of state. The same heat transport, describable by Q , T_1 and T_2 , may therefore be carried out by means of various basic processes. In all cases these consist in entropy transports. As contrasted with the entropy produced, however, the amount of entropy transported is not terminally fixed. Nor is this the case with the temperature of the entropy generation. But, as is easily seen, these two indeterminate magnitudes are not independent of each other.

If the entropy transported in the basic process is denoted by S and the temperature of formation for ΔS by T , then, by equation (II, 17), which expresses the equivalence principle, we may write:

$$(T_1 - T_2) S = T \Delta S, \quad (20)$$

$T \Delta S$ being the energetic heat evolution. (20) can be rewritten as:

$$S = \frac{T}{T_1 - T_2} \Delta S = \frac{T}{T_1 T_2} Q \quad (21)$$

or

$$S = S_1 \frac{T}{T_2} = S_2 \frac{T}{T_1}. \quad (22)$$

These equations express the correlation existing between the variables S and T . If T has been chosen $= T_1$, the entropy ΔS being produced in R_1 , the entropy of the basic process is given by:

$$S = \frac{T_1}{T_1 - T_2} \Delta S = S_2. \quad (23)$$

If on the other hand $T = T_2$, ΔS is produced in R_2 and:

$$S = \frac{T_2}{T_1 - T_2} \Delta S = S_1. \quad (24)$$

$T = T_1$ and $T = T_2$ represent two special instances of the realisation of the heat transport. But actually the heat transport can be accomplished in an infinite number of ways, since the generation of entropy is not confined to one of the temperatures T_1 or T_2 , but can be distributed over the two reservoirs R_1 and R_2 in arbitrary proportions. This method can be made use of for instance by introducing a third heat reservoir R of the temperature T , in which ΔS is produced. The process is then completed by transferring ΔS , in fractions $\Delta S'$ and $\Delta S''$ from R to the reservoirs R_1 and R_2 respectively. This transference should not involve any irreversible phenomenon, i. e. it must

consist of two basic processes in which loss and gain of work are equal. This condition can be expressed by:

$$\Delta S = \Delta S' + \Delta S''$$

$$(T_1 - T) \Delta S' = (T - T_2) \Delta S''$$

whence:

$$\Delta S' = \Delta S \frac{T - T_2}{T_1 - T_2} = S \frac{T - T_2}{T} \quad (25)$$

and

$$\Delta S'' = \Delta S \frac{T_1 - T}{T_1 - T_2} = S \frac{T_1 - T}{T} \quad (26)$$

the distribution ratio $\frac{x}{1-x}$, given by:

$$\frac{x}{1-x} = \frac{T - T_2}{T_1 - T}, \quad (27)$$

being completely arbitrary. If the evolution and transference of entropy are continuous, the reservoir R may be given infinitesimal dimensions, so that its addition does not constitute any real change of the system. Obviously $\Delta S'$ and $\Delta S''$ can also be formed directly in R_1 and R_2 in the ratio given by x or T , without having to pass through an R-reservoir. In both cases on the analogy of (20) we obtain:

$$(T_1 - T_2) S = T_1 \Delta S' + T_2 \Delta S''$$

or for the entropy transport in dependence of x :

$$S = \frac{xT_1 + (1-x)T_2}{T_1 - T_2} \Delta S = \frac{xT_1 + (1-x)T_2}{T_1 T_2} Q. \quad (28)$$

The distribution of the entropy over the two temperatures T_1 and T_2 is thus genetically equivalent to its formation at the temperature T , if this temperature is correlated with the distribution ratio by equation (27).

If not the heat Q , but the entropy S is given in the process of heat transport, ΔQ , the energetic heat evolution, and not ΔS , will be directly defined. Since

$$\Delta Q = T \Delta S, \quad (29)$$

it will not be possible in this case, either, to calculate the temperature of the entropy formation. This is in conformity with the universal law that entropy evolution is determined by the total process and heat evolution by the basic process.

Combining (18) and (20) and (29) we may also write for the heat evolution:

$$\Delta Q = Q (T_1 - T_2) \frac{T}{T_1 T_2} = (T_1 - T_2) S = A_{th}, \quad (30)$$

where T is defined by (27) and A_{th} is the thermal loss of work.

Having thus analysed the auxiliary process of heat transport we shall now proceed to consider the imaginary main process. As previously mentioned, this process, according to CLAUSIUS, is a heat-work transformation in which work is gained at the expense of heat taken from a heat reservoir. The temperature T of this heat reservoir is not given. In the usual treatment one puts $T = T_1$ or $T = T_2$. We shall first, however, consider the general case of the temperature T being arbitrarily chosen. According to CLAUSIUS¹⁾ the heat expended is then calculated in the following way.

If in a reversible thermal process the amounts of heat Q_0 , Q_1 and Q_2 are given off by 3 heat reservoirs R_0 , R_1 and R_2 of the temperatures T_0 , T_1 and T_2 respectively, the relation:

$$\frac{Q_0}{T_0} + \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad (31)$$

is generally valid. Putting $Q_1 = -Q_2 = Q$, the process, as regards R_1 and R_2 , may be considered a transport of the heat Q from T_1 to T_2 , while Q_0 , taken at the temperature T_0 , is being transformed into work. Equation (31) may then be written:

¹⁾ CLAUSIUS, "Die mechanische Wärmetheorie" I, 89, 97 (1876).

$$Q_0 = Q (T_1 - T_2) \frac{T_0}{T_1 T_2} = A_m. \quad (32)$$

The transference of the amount of heat Q from T_1 to T_2 will thus involve a transformation into mechanical work A_m of an amount of heat Q_0 given by (32) and consumed in a reservoir of temperature T_0 . If a special term is desired for this imaginary magnitude, Q_0 might appropriately be designated as the energetic heat consumption.

On the basis of the general expression (32) we obtain for the special cases of $T = T_1$ or T_2 , the special forms for the expenditure of heat:

$$Q_0 = Q \frac{T_1 - T_2}{T_2} \quad (33)$$

and

$$Q_0 = Q \frac{T_1 - T_2}{T_1} \quad (34)$$

respectively. These expressions indicate the amounts of heat expended in the production of work at T_1 and T_2 .

As regards the correlation between entropy and heat supplied to or removed from a heat reservoir, no distinction has been made by CLAUSIUS or other classical authors between the case in which entropy and heat are communicated and that in which these magnitudes are developed or consumed in the reservoir. Even if it is not explicitly stated, classical thermodynamics must therefore be supposed to maintain that there exists the same relation between heat and entropy in the case of the imaginary process under consideration as that universally accepted for the process of communication. The consumption of entropy S_0 corresponding to Q_0 in equations (32), (33) and (34) is then obtained on division of Q_0 by T_0 , T_1 and T_2 respectively. We obtain in all 3 cases:

$$S_0 = Q \frac{T_1 - T_2}{T_1 T_2}, \quad (35)$$

i. e. a value which is independent of the temperature at which the entropy is consumed. This expression is identical with the expression (18) for the evolution of entropy in the process of heat transport.

The result obtained may also be expressed in the following way. Since the total function of the heat engine involves no change of entropy, it is known beforehand that the expenditure of entropy in the imaginary process and the evolution of entropy in the compensation process must be identical. The entropy given by (18) will therefore be consumed concurrently with the amount of heat expressed by (32). This means that the relation between heat consumed and entropy which was supposed above to be accepted in the classical treatment, actually follows as a necessary consequence of the classical assumptions.

On the basis of these considerations the partial processes in the classical theory of the heat engine are thus seen to resolve themselves as follows:

The imaginary process is split into two partial processes, the first being a basic mechanical process representing the gain of work A_m , the second being a consumption of entropy S_0 taking place at an indeterminate temperature T_0 . The energetic consumption of heat Q_0 given by $Q_0 = T_0 S_0$, is synonymous with this expenditure of entropy.

Similarly the irreversible compensating process is split into two partial processes, the first being a basic thermal process consisting in a transport of the entropy S from T_1 to T_2 , and representing the loss of work A_{th} , the second being an evolution of entropy ΔS taking place at an indeterminate temperature T . The energetic heat evolu-

tion $\Delta Q = T\Delta S$ is synonymous with this evolution of entropy.

According to equation (32) the mechanical gain of work A_m is identical with the thermal loss of work A_{th} defined by equation (30), in perfect accordance with the demands of the energetic theory. In addition to these equivalent work phenomena which, jointly, give a complete account of the empirical function of the heat engine, the classical theory, according to the analysis offered, postulates the consumption of a certain amount of entropy in the main process and an evolution of the same amount of entropy in the compensating process. These changes, if occurring at unequal temperatures, would constitute a transport of entropy from one temperature to another and thus represent an amount of thermal work for which no energetic equivalent is available in the operation of the heat engine. Such a phenomenon would be at variance with the energy principle also in its traditional formulation. Accordingly the alleged formation and consumption of entropy must occur at the same temperature.

The recognition of this circumstance, however, entirely removes the basis of the classical interpretation, according to which the function of the heat engine consists in a heat-work transformation. If an expenditure of entropy of the same magnitude as a simultaneous evolution of entropy were to take place in different sections of the system but at the same temperature, then these processes would completely cancel and the attribution of any kind of reality to the separate phenomena would have no physical sense. Similarly one cannot attribute any reality to the concurrent phenomena of creation and consumption of the equal thermal energies $T\Delta S$

and $T_0\Delta S$, no matter what terminology is used for designating these energy terms. The classical doctrine that $T\Delta S$ is converted into work while at the same time $T\Delta S$ is generated as a consequence of the irreversible heat transport would be quite parallel to supposing that the turning of a loaded balance in a state of equilibrium might be interpreted as a process in which one of the loads were raised at the cost of an amount of heat supplied irreversibly by the lowering of the other. Assertions of this kind are physical absurdities which must be excluded from rational science. In accordance with the energetic theory we are therefore justified in contending that no heat is consumed in the operation of the heat engine and that the classical theory of the thermal production of mechanical work is based on a misinterpretation of experimental realities.

IV. Conclusion.

This concluding section contains a recapitulation of the more essential ideas to which we have been led through the present investigation. Some results arrived at or implied in the previous articles regarding the concepts of heat and work are also included.

1. The fundamental thermal concepts are defined on the basis of calorimetric phenomena. It is a requisite of the application of the calorimetric method that the various basic processes are interdistinguishable. A calorimeter, describable also as a heat or entropy reservoir, is a system the changes of which are due solely to its taking up or giving off entropy. A standard calorimeter serves to define amounts of entropy taken up or given off by it in communication with the surroundings.

2. Any irreversible process is conceivable as a transport of energetic quantities in connection with generation of entropy. If δK is the quantity transported and if it passes from a potential P_1 to a potential P_2 , these potentials being conjugate to the quantity considered, then the relation:

$$(P_1 - P_2) \delta K = T dS \quad (1)$$

where dS is the increase in entropy and T the absolute energetic temperature at which the entropy is generated, is found to be universally valid. This fundamental law of nature forms the basis for the creation of a new thermal concept TdS which is called heat. Since the generation of entropy is bound to irreversible changes and is always positive, the concept of heat is essentially that of a heat generation.

The increase in entropy dS is defined as the amount of entropy to be added to the reacting system in order to reproduce the irreversible process reversibly. It is measured by means of the standard calorimeter from which it may be reversibly transferred.

3. The product $(P_1 - P_2) \delta K$ represents work in a generalised sense. Equation (1) identifies the loss of work and the heat evolution. It is an expression, therefore, of the generalised law of energetic equivalence. In a world of reversible processes $dS = 0$, and all energetic phenomena would be describable in terms of work. In such a world there would be no rational basis for the creation of a concept of heat.

4. It is the obvious phenomenologic similarity between terms on the left hand side of equation (1) and the corresponding dissimilarity between these terms and the right hand side product TdS that has led to the new terminology

by which the terms heat and work have acquired a clear and unequivocal meaning. Classical thermodynamics does not accept the terms heat and work in the same sense. This of course does not affect the validity or significance of equation (1). The question of terminology is one of convenience and logical adaptation, not one of truth or untruth.

5. In addition to the law of the equivalence of heat and work which is recognised by classical thermodynamics in some particular instances, heat is generally characterised by the law of heat conduction. The actual contents of this law are given by the equation:

$$T_1 \delta S_1 = T_2 \delta S_2. \quad (2)$$

It has been shown, however, that equations (1) and (2) are not independent, the process of heat conduction being a special case of the process of heat generation, and that no new thermal concept, therefore, can be established on equation (2). This demonstration is of some significance, since it is the object of science to reduce as far as possible the number of axiomatic postulates upon which it rests. What is called heat transport is either simply an isothermal transport of entropy or in case of temperature inhomogeneity it is such a transport associated with a heat generation in conformity with equation (1).

6. If the law expressed by (2) is being described as the law of heat conduction or heat transport, this involves that the addition of the entropy δS to a system of temperature T is synonymous to the addition of an amount of heat $T \delta S$. If the system is a calorimeter it is customary and permissible to say that the amount of heat in the calorimeter has increased by $T \delta S$. Heat in this sense is not, however,

comprised in the definition of heat by equation (1) from which it differs fundamentally, but must be ranged with other energies of the type PdK for which no law of transformation — and also no special designations — exist. It pertains to what might be called functional energetics or energetics of state. This kind of energetics is concerned with changes in partial or fractional systems with no reference to simultaneously effected alterations in other fractional systems and is of quite formal character. Work and heat as energetic realities are dealt with in the energetics of processes. This branch of science is concerned with the interconversion and equivalence of the various forms of energy and is characterised by disregarding no part of the phenomena involved in the total change. It deals with closed or isolated systems. Indiscriminate application of the functional heat concept within the energetics of processes is a regrettable feature of classical thermodynamics.

7. If a system of pressure p receives a volume δv from an external source, traditional thermodynamics claims an amount of work $p\delta v$ to be “done” by the system, although this “work” is intransformable and the change, therefore, comes within the domain of “functional energetics”. As in the case of heat this traditional terminology involves the danger of confusing intrinsically incommensurable concepts and is actually to a considerable extent responsible for the inconsistency of classical thermodynamic ideas.

8. Reversible processes are considered by classical thermodynamics as processes with which there may be associated a transformation of heat into work or vice versa. This view is not compatible with a consistent and general definition of the concepts of heat and work. Nor is this the

case with the traditional postulates that irreversible processes involving substances which obey the ideal gas laws occur without heat evolution.

9. The heat which according to the classical view is consumed in a reversible spatial process may be taken from a heat reservoir or from the expanding system itself. In the first case the conclusion concerning a heat-work transformation is based upon the sort of fallacy of argument which was indicated under 6. In either case it is made possible by the obscurity of the classical definition of the phenomena of generation and consumption of heat and the lack of precision in what is called the "work of expansion".

10. Chemical work according to traditional ideas originates partly in "chemical energy" concealed in the system and measurable as an irreversible thermometric heat evolution, partly in heat taken from an external source. The concept of "chemical energy" is, however, completely undefined and that of chemical heat-work transformation meets with the same obstacles as the heat-work transformation in the spatial process.

The traditional interpretations of chemical and spatial processes involving substances which obey the perfect gas laws are entirely incongruous in spite of the obvious similarity of the processes.

11. The proposition of the impracticability of an uncompensated heat-work transformation, though frequently violated in the treatment of an isolated problem, seems to be generally adopted within classical thermodynamics. On the other hand, classical thermodynamics has set up and strongly advocates the doctrine that a heat-work transformation is actually realisable if supported by some sort of concurrent compensation. The nature of this

compensation is, however, not specified, in fact it has received but a very cursory attention in the historic evolution of the theory of heat.

Concerning this crucial contention in classical thermodynamics it has been shown above that the moment a heat consumption is postulated as an equivalent for the production of work, such as is the case in any imaginary classical process, the compensation, simultaneously necessitated, will emerge automatically in the shape of an irreversible process involving as such a generation of heat. Moreover the heat expended and the heat generated prove to be equal and to appear at the same temperature. Consequently the two caloric phenomena will cancel completely and there will be left no source of caloric nature for the production of work. This argument does not depend upon any terminologic circumvention, the term heat in both cases standing for energy members of the form $T\Delta S$ of quite unambiguous significance.

12. The classical notion of a generation or absorption of heat is closely bound up with the appearance of temperature changes in the reacting system. For instance, when the reaction involves a fall in temperature, heat is supposed to disappear. If heat is to be taken as a form of energy, such a view is incompatible with the principle of energetic equivalence and is therefore an obstacle to the formation of a rational and consistent concept of heat.

13. The function of the heat engine has been of decisive significance for the comprehension of heat. According to CARNOT a passage of heat from a higher to a lower temperature constituted an equivalent for the work gained by the engine. In the theory of CLAUSIUS the function of the engine was claimed to be a compensated heat-work transformation.

The energetic theory, finally, views the function as a work-work transformation exclusively controlled by the work principle.

In conformity with the general postulate that the concept of heat is foreign to reversible processes and that the theory of energetic compensation is illusory, special evidence has been brought forward to show that also in the case of a thermal process no heat is consumed in the mechanical performance of work.

14. Heat is a macroscopic entity. The maintenance of a concept of heat is vindicable only through the existence of macroenergetic phenomena and the fulfilment of macroenergetic laws. The question as to the "nature" of heat is without object. The contention that heat is "motion" or energy of molecular motion, no less than the contention that heat is a fluid, is incompatible with the classical thesis that heat does not possess the character of a single-valued function of state.

