ON THE

THERMODYNAMICS
OF
CHEMICAL PROCESSES.

BY

PROFESSOR H. VON HELMHOLTZ.

PART I.

Ueber die Thermodynamik der chemischen Prozessen. Sitzungsbericht der Akademie der Wissenschaften zu Berlin, 2nd February, 1882; also 'Wissenschaftliche Abhandlungen von H. Helmholtz,' vol. ii. pp. 958–978.

PREVIOUS investigations on the work-value of chemical processes relate almost exclusively to the quantities of heat appearing or vanishing during the formation and decomposition of compounds. Now alterations in the state of aggregation and in the density of the substances concerned are indissolubly connected with most chemical changes. Of these last, however, we know certainly that they are capable of producing or consuming work in two different forms, to wit: first in the form of heat, secondly in the form of other kinds of work convertible without limit. A store of heat is not, as is well known from Carnot's law—more precisely expressed by Clausius—convertible without limit into other work-equivalents. We can only bring this about in any case, and even then only partially, by allowing the untransformed residue of the heat to pass over into a body of lower temperature. We know that in the case of fusion, vaporization, expansion of gases, &c., heat can even be extracted from surrounding bodies at the same temperature, to pass over into work of other forms. Since such changes, as already said, are indissolubly connected with most chemical processes, this circumstance clearly proves that, even in the case of chemical changes, the origin of these two forms of work-equivalents must be examined, and they must be considered from the point of view of Carnot's law. It has long been known that there are chemical processes which occur spontaneously and proceed without external force, and in which cold is produced. Of these processes the customary theoretical treatment, which deals only with the heat developed as the measure of the work-value of the chemical forces of affinity, can give no satisfactory account*. They appear rather as processes which take place in opposition to the forces of affinity. In general, however, this view, which I have myself adopted in my earlier papers, is certainly justified. There is no question that, especially in those cases in which powerful forces of affinity act, the greater development of heat coincides with the stronger affinity, so far as the latter is to be recognized by means of the formation and decomposition of chemical compounds. But the two do not coincide in all cases. If we now take into consideration that chemical forces can produce not merely heat but also other forms of energy, the latter even without the necessity of any change of temperature in the interacting substances being set up corresponding to the magnitude of the effect, as, for example, in the case of the production of work by a galvanic battery; then it appears to me unquestionable that, even in the case of chemical processes, a distinction must be made between the parts of their forces of affinity capable of free transformation into other forms of work, and the parts producible only as heat. In what follows I shall, for the sake of brevity, distinguish these two parts of the energy as the "free" and as the "bound" energy. We shall see later that processes spontaneously originating and proceeding without the help of any external force, when the system is at rest and is maintained at a constant uniform temperature, can take place only in such a direction as to cause diminution of free

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* B. Rathke, "On the Principles of Thermal Chemistry," *Abhandl. d. Naturforsch.-Ges. zu Halle*, Bd. xv.

energy. In this category will also be reckoned chemical processes originating spontaneously and proceeding at constant temperature. On the assumption of the unrestricted applicability of Clausius's law, it would therefore be the value of the free energy, not that of the total energy made known by development of heat, which especially determines the direction in which chemical affinity can become active.

As a rule the calculation of the free energy can be carried out only for such changes as are perfectly reversible in a thermodynamic sense. This is the case with many solutions and mixtures which, within certain limits, can be formed in all proportions. To such are related, *e. g.*, the researches on solutions of salts and gases undertaken by G. Kirchhoff*. On the other hand, among chemical combinations in the narrower sense, taking place by fixed equivalents, the electrolytic changes between unpolarized electrodes afford an important example of reversible processes. In fact, I myself have been led to the theory of free chemical energy, about to be set forth here, by the question of the connexion between the electromotive force of such a battery and the chemical changes going forward within it. Then also questions obtruded themselves as to how, whether, and when the latent heat of the gases developed during decomposition of water, or the heat set free during the crystallizing out of a salt produced by electrolysis, has or has not an influence on the electromotive force. The communication made by me, Nov. 26, 1877, "On Galvanic Currents originated by differences of Concentration" (*Wiss. Abh.* Bd. i. No. xliv.), falls clearly into this department.

In a constant galvanic element under the condition of a current-strength so vanishingly small that the development of heat in the connecting wire, proportional to the resistance and to the square of the current-strength, can be neglected as a vanishing quantity of the second order, the processes going on are perfectly reversible, and must obey the thermodynamic laws of reversible processes. If we have a galvanic element of uniform absolute temperature θ (*i. e.* temperature reckoned from —273° C. as zero-point of the scale), its condition will be

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* Pogg. *Ann.* ciii. pp. 177 & 206, civ. p. 612.

altered if the quantity of electricity $d\epsilon$ go through, owing to the fact that a chemical change occurs proportional to this quantity $d\epsilon$; and we can treat the state of the element as defined by the quantity ϵ of electricity which has traversed it in a definite direction assumed as positive. If the ends of the constant battery be connected with the two plates of a condenser of very great capacity which is charged to a difference of potential p, then the transfer of the quantity $d\epsilon$ from the negative to the positive plate of the condenser will correspond to an addition $p\,.\,d\epsilon$ to the store of electrostatic energy present. Let us denote at the same time by dQ the quantity of heat which we must communicate to (or, if negative, withdraw from) the galvanic element, in order to keep its temperature constant during the said transfer of $d\epsilon$, by U the total store of energy contained in it, which we can look on as a function of θ and ϵ, and by $\mathfrak{J}$ the mechanical equivalent of the unit of heat; then according to the law of the Constancy of Energy:—

$$\mathfrak{J}\,.\,dQ=\frac{\partial U}{\partial \theta}\,.\,d\theta+\left(\frac{\partial U}{\partial \epsilon}+p\right).\,d\epsilon. \quad . \quad . \quad . \qquad (1)$$

On the other hand, we shall obtain, according to the Carnot-Clausius principle, a function of the variables θ and ϵ, named by Clausius the entropy of the system, the variation dS of which is

$$dS=\frac{1}{\theta}\,.\,\mathfrak{J}\,.\,dQ=\frac{1}{\theta}\,.\,\frac{\partial U}{\partial \theta}\,.\,d\theta+\frac{1}{\theta}\left[\frac{\partial U}{\partial \epsilon}+p\right]d\epsilon, \quad . \quad . \qquad (1a)$$

whence

$$\frac{\partial S}{\partial \theta}=\frac{1}{\theta}\,.\,\frac{\partial U}{\partial \theta}, \qquad \frac{\partial S}{\partial \epsilon}=\frac{1}{\theta}\left[\frac{\partial U}{\partial \epsilon}+p\right].$$

Thence it follows that

$$\frac{\partial^2 S}{\partial \theta\,.\,\partial \epsilon}=\frac{1}{\theta}\,.\,\frac{\partial^2 U}{\partial \theta\,.\,\partial \epsilon}=\frac{1}{\theta}\left[\frac{\partial^2 U}{\partial \epsilon\,.\,\partial \theta}+\frac{\partial p}{\partial \theta}\right]-\frac{1}{\theta^2}\left[\frac{\partial U}{\partial \epsilon}+p\right],$$

or

$$\theta\,.\,\frac{\partial p}{\partial \theta}=\frac{\partial U}{\partial \epsilon}+p.$$

We can therefore now write equation (1):—

$$\mathfrak{J}\,.\,dQ=\frac{\partial U}{\partial \theta}\,.\,d\theta+\theta\,.\,\frac{\partial p}{\partial \theta}\,.\,d\epsilon, \quad . \quad . \quad . \quad . \qquad (1^\circ)$$

wherein the last term gives the mechanical equivalent of that quantity of heat which we must supply to the galvanic element during the passage of $d\epsilon$ in order to keep its temperature constant. In fact, if in equation (1°) we put the variation of temperature $d\theta$ equal to zero, we have

$$\theta \cdot \frac{\partial p}{\partial \theta} \cdot d\epsilon = \mathfrak{J} \cdot dQ.$$

The quantity of heat developed in this way is in most cases relatively small, and with powerfully acting cells would be difficult to detect among the much greater quantities of heat which are proportional to the resistance of the conductor and the square of the current-strength. There are besides differences of heating at the two electrodes, which in their manner of appearance are similar to Peltier's phenomenon in the case of thermoelectric currents, even though they are perhaps of different origin. On the other hand, it may be ascertained much more easily, and with greater accuracy, whether the electromotive force of a constant galvanic element diminishes or increases with rise of temperature.

Investigations of the latter kind have been undertaken by Lindig[*]; unfortunately they chiefly refer to a case that is not strictly reversible, namely Daniell's cells in which the zinc is in contact with dilute sulphuric acid, which must therefore, when the current is reversed, develop hydrogen on the zinc. Really reversible Daniells, in which the zinc is in contact with zinc-sulphate solution, show, according to researches lately undertaken by me, a diminution of electromotive force with increasing temperature, if the zinc solution be of moderate or great concentration; an increase, on the contrary, in very dilute solution. Between these two alternatives there is a limit at which the electromotive force is sensibly independent of the temperature. With concentrated copper solution this occurs when the zinc solution has a specific gravity of about 1·04.

Latimer Clark's cells, in which a layer of mercurous sulphate in concentrated zinc [sulphate] solution lies on a mercury anode, and the kathode is formed of amalgamated zinc, are

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[*] Pogg. *Ann.* cxxiii. pp. 1-30, 1864.

specially adapted for accurate measurements, since the diffusion of two liquids is here avoided, and the whole can be completely sealed into glass. Their electromotive force depends on the temperature in a very remarkable manner. L. Clark* himself has asserted that the electromotive force diminishes by 0·06 per cent. for a rise of 1 degree C. The maximum of this variability occurs if powdered zinc salt be allowed to remain in contact both with the mercury among its sulphate and with the liquid zinc amalgam. I found this quantity 0·08 per cent.; with greater dilution of the zinc solution it diminished to 0·03; while, on the other hand, the electromotive force underwent considerable increase. The above formula allows us to see that in the case of this most concentrated solution the work given up as heat bears to that which appears in the electromotive force the same ratio as

$$\theta.\frac{\partial p}{\partial \theta} : p = 1 : 4{\cdot}2.$$

In this case the zinc sulphate newly formed by the current can no longer be dissolved, and its latent heat of solution is saved; accordingly there is a more powerful development of heat in the cell in spite of the weaker electromotive force. The discussion of the thermoelectric relations of solutions of crystallizable salts, which I propose to give later, shows besides universally that, in batteries of this type, diluting the solution must increase the electromotive force by an amount which increases with increasing temperature.

Batteries of a similar type, which I have frequently employed during the last year on account of their cleanliness and constancy for very small current-strengths, in which the mercurous sulphate of the Clark is replaced by mercurous chloride (calomel) and the solution of zinc sulphate by one of zinc chloride, show, on the contrary, with stronger dilution of the latter solution a real though small increase of the electromotive force, with rising temperature.

I adduce these facts since they show that very manifold relations are here apparent. The thermoelectric researches of Lindig, Bleekrode†, Bouty‡, and Gore § exhibit the abun-

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* Proc. Roy. Soc. xx. p. 444.

† Pogg. *Ann.* cxxxviii. pp. 571–604.

‡ *Almeida Journ. de Phys.* ix. p. 229.

§ Proc. Roy. Soc. 1871, Feb. 23.

dance of such differences. If, for instance, we take a central glass vessel communicating with four side vessels by means of syphon tubes all filled with the same liquid, two of the side vessels being heated, the other two cold, and if A and a denote the differences of potential between the liquid in the central tube and two unpolarizable metallic electrodes of one kind, B and b those of two electrodes of another kind, A and B referring to the heated liquid, a and b to the cold; then the electrode A joined to a gives a thermoelement, as likewise does B joined to b. Again, A and B, when joined, form a galvanic battery of higher temperature, a and b one of lower temperature. If, now, the electromotive force

$$\mathrm{A}-a>\mathrm{B}-b,$$

then also

$$\mathrm{A}-\mathrm{B}>a-b$$

and

$$(\mathrm{A}-\mathrm{B})-(a-b)=(\mathrm{A}-a)-(\mathrm{B}-b).$$

If, for example, A and a belonged to zinc amalgam, B and b to mercury covered with mercurous sulphate, all in the same zinc-sulphate solution, then I was able actually to verify the last equation by experiment.

In order to employ these and other facts safely, it appeared to me that in the first place the discussion of a somewhat generalized form of the general principles of thermodynamics was necessary, and a method of expressing them more suitable to the subject, desirable. This led to a simplified analytical treatment of their laws. I will at present limit myself to the exposition of these theoretical discussions.

§ 1. *Idea of Free Energy.*

Dynamics has attained a great simplification and generalization of its analytical developments by the employment of the idea of "potential energy" (the negative of which is termed "Force Function" by C. G. J. Jacobi, "Ergal" by Clausius, "Quantity of Tension-force" by Helmholtz). Hitherto, however, in the employment of this notion, changes of temperature have not as a rule been considered, either because the forces, the work-value of which was calculated, were entirely independent of temperature, *e. g.* Gravitation, or because the temperature could be looked on either as constant during the process investigated, or as a definite function of mechanical changes (*e.g.*, in the case of the transmission of sound as a function of the density of the gas). Of course the physical constants occurring in the value of the ergal, such as density, coefficients of elasticity, &c., may vary with temperature; and in this sense of course this quantity would be a function of the temperature. In that case, however, the constants of integration entering into the value of every ergal would have to be determined quite arbitrarily for every new temperature, and the passage from one temperature to the other could not be made. The means of doing this is nevertheless easily obtained from the two fundamental equations of thermodynamics set forth by Clausius.

This philosopher has limited himself in the first instance, in his published papers, to the case in which the state of the body is conditioned by the temperature and only one other parameter. The expression of the law for the case in which changes of different kinds can occur, in that the state of the body is conditioned by several other parameters besides the temperature, can be easily formed according to the same principle as applies in the case of a single one. In what follows I have denoted the absolute temperature by θ; the parameters defining the state of the body, but independent of each other and of the temperature, by $p_{\mathfrak{a}}$. Their number must be finite, but may be as great as we please.

Clausius employs for the setting forth of his general laws two functions of the temperature and of the one parameter retained by him, which he names the "Energy," U, and the "Entropy," S. These, however, are not independent of each other, but are connected together through the differential equation

$$\frac{\partial S}{\partial \theta}=\frac{1}{\theta}\cdot\frac{\partial U}{\partial \theta}.$$

It will be shown that these two can be expressed by means of differential coefficients of the ergal completely determined as a function of the temperature, so that the thermodynamical equations no longer require two functions of the variables, but only one, namely the ergal.

The function denoted by Clausius in his equations by W coincides with the ergal, so long as the temperature is unaltered; with varying temperature, however, it is more generally a many-valued function of the temperature and of the parameter. What G. Kirchhoff (*l. c.*) has termed "Quantity of Action" is the function U.

I assume in the first place a system of masses anyhow arranged, which all have the same temperature θ, and which all undergo the same temperature changes. The state of this system will then be completely determined by θ and a number of independent parameters $p_{\mathfrak{a}}$.

I denote, as Clausius does, by dQ the quantity of heat introduced by an infinitesimally small change in the state of the body, the internal energy by U. The law of the constancy of energy can be brought into the form

$$\mathfrak{J} \,.\, dQ = \frac{\partial U}{\partial \theta} . d\theta + \Sigma_{\mathfrak{a}} \left\{ \left(\frac{\partial U}{\partial p_{\mathfrak{a}}} + P_{\mathfrak{a}} \right) dp_{\mathfrak{a}} \right\} \quad . \quad . \quad . \quad (1)$$

Here $\mathfrak{J}$ denotes the mechanical equivalent of the heat-unit, and $P_{\mathfrak{a}} . dp_{\mathfrak{a}}$ the whole of the freely convertible work produced by the variation $dp_{\mathfrak{a}}$, part of which can pass over to surrounding bodies, while part may be transformed into kinetic energy of the masses of the system. This latter is moreover to be treated as *external* work in contradistinction to the internal changes of the system.

The second law of the mechanical theory of heat asserts that

$$\int \frac{\partial Q}{\theta} \,.\, d\theta = 0,$$

if the final state of the body becomes again the same as the initial state was, and if the series of changes which the body has gone through is perfectly reversible. The latter condition requires, for a system of bodies the parts of which always have their temperatures equal among themselves, only that no fresh heat be produced at the expense of other forms of energy. The above requirement cannot be complied with under the conditions mentioned unless dQ/θ is the differential of a one-valued function depending only on the temperature and on the state of the body, *i. e.* on the parameters $p_\mathfrak{a}$, one of which Clausius has named "Entropy" and denoted by S.

Therefore

$$\frac{1}{\theta} . dQ = dS = \frac{\partial S}{\partial \theta} . d\theta + \Sigma_\mathfrak{a} \left\{ \frac{\partial S}{\partial p_\mathfrak{a}} . dp_\mathfrak{a} \right\} . \quad . \quad . \qquad (1\,a)$$

From (1) and (1 *a*) follow

$$\mathfrak{J} . \frac{\partial S}{\partial \theta} = \frac{1}{\theta} . \frac{\partial U}{\partial \theta}, \qquad \mathfrak{J} \frac{\partial S}{\partial p_\mathfrak{a}} = \frac{1}{\theta} \left[\frac{\partial U}{\partial p_\mathfrak{a}} + P_\mathfrak{a} \right].$$

Thence follows

$$P_\mathfrak{a} = \frac{\partial}{\partial p_\mathfrak{a}} \left[\mathfrak{J} . \theta . S - U \right] . \quad . \quad . \quad . \quad . \qquad (1\,b)$$

Further,

$$\mathfrak{J} . \frac{\partial^2 S}{\partial \theta . \partial p_\mathfrak{a}} = \frac{1}{\theta} . \frac{\partial^2 U}{\partial \theta . \partial p_\mathfrak{a}} = \frac{1}{\theta} \left[\frac{\partial^2 U}{\partial \theta . \partial p_\mathfrak{a}} + \frac{\partial P}{\partial \theta} \right] - \frac{1}{\theta^2} \left[\frac{\partial U}{\partial p_\mathfrak{a}} + P_\mathfrak{a} \right] \quad , \qquad (1\,c)$$

From the latter equation follows again

$$\theta . \frac{\partial P_\mathfrak{a}}{\partial \theta} = \frac{\partial U}{\partial p_\mathfrak{a}} + P_\mathfrak{a} . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1\,d)$$

If now we put

$$\mathfrak{F} = U - \mathfrak{J} . \theta . S, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1\,e)$$

then $\mathfrak{F}$, like U and S, is a one-valued function of the quantities $p_\mathfrak{a}$ and θ. The functions U and S, which are only defined by the values of their differential coefficients, each contain an arbitrary additive constant. If we denote these by a and β, it follows that in the function $\mathfrak{F}$ an additive term of the form

$$[a - \beta . \mathfrak{J} . \theta]$$

remains arbitrary; in other respects this function $\mathfrak{F}$ is completely defined by equation (1 *e*).

The equations (1 *b*) fall therefore into the form

$$P_\mathfrak{a} = - \frac{\partial \mathfrak{F}}{\partial p_\mathfrak{a}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1\,f)$$

i. e. *in all transformations taking place at constant temperature the function* $\mathfrak{F}$ *expresses the value of the potential energy or of the ergal.*

By differentiating equation (1 *e*) with respect to θ we obtain

$$\frac{d\mathfrak{F}}{d\theta}=\frac{\partial U}{\partial\theta}-\mathfrak{J}.S-\mathfrak{J}.\theta.\frac{\partial S}{\partial\theta}.$$

Since, however, as already remarked in relation to (1 *a*),

$$\mathfrak{J}.\frac{\partial S}{\partial\theta}=\frac{1}{\theta}.\frac{\partial U}{\partial\theta},$$

our equation reduces to

$$\frac{\partial\mathfrak{F}}{\partial\theta}=-\mathfrak{J}.S; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1g)$$

whence, in consideration of (1 *e*), follows immediately

$$U=\mathfrak{F}-\theta.\frac{\partial\mathfrak{F}}{\partial\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\,h)$$

These two equations therefore supply the values of the two functions U and S (Energy and Entropy according to Clausius) in terms of differential coefficients of $\mathfrak{F}$.

From them it follows that

$$\frac{\partial U}{\partial\theta}=-\theta.\frac{\partial^2\mathfrak{F}}{\partial\theta^2}=\mathfrak{J}.\theta.\frac{\partial S}{\partial\theta}.$$

This is the above-mentioned connexion between the functions S and U by means of a differential equation, which is therefore immediately satisfied by our expression of them in terms of the function $\mathfrak{F}$.

With the parameters p_a maintained constant, equation (1) gives

$$\mathfrak{J}.dQ=\frac{\partial U}{\partial\theta}.d\theta.$$

The quantity $\partial U/\partial\theta$ expresses therefore, even in our generalized case, the heat-capacity of the system with contant parameters (calculated for the whole of the masses belonging to the system taken together). We will denote this by Γ. Thus

$$\mathfrak{J}.\Gamma=-\theta.\frac{\partial^2\mathfrak{F}}{\partial\theta^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\,i)$$

Since Γ, like θ, is an essentially positive quantity, it follows from this that $\partial^2\mathfrak{F}/\partial\theta^2$ is essentially negative, and that therefore the quantities $(-\partial\mathfrak{F}/\partial\theta)$ and $(\mathfrak{F}-\theta\,.\,\partial\mathfrak{F}/\partial\theta)$ with increasing temperature and constant parameters must proceed to positively increasing values. These are the quantities $(\mathfrak{J}\,.\,\mathrm{S})$ and U.

We obtain further, for calculating the values of $\mathfrak{F}$ with increasing temperature and constant parameters,

$$\frac{\partial^2\mathfrak{F}}{\partial\theta^2}=-\mathfrak{J}\,.\,\frac{\partial \mathrm{S}}{\partial\theta}=-\,\mathfrak{J}\,.\,\frac{1}{\theta}\,.\,\Gamma.$$

Since

$$\theta\,.\,\frac{\partial^2\mathfrak{F}}{\partial\theta^2}=\frac{\partial}{\partial\theta}\,.\left[\theta\,.\,\frac{\partial\mathfrak{F}}{\partial\theta}-\mathfrak{F}\right]=-\mathfrak{J}\,.\,\Gamma,$$

we obtain, by integration, for the difference of the two values of $\mathfrak{F}$ which correspond to the same system of parameters but to two different temperatures, distinguished by the suffixes 1 and 0,

$$\mathfrak{F}_1-\mathfrak{F}_0=\mathfrak{J}\left\{(\theta_0-\theta_1)\mathrm{S}_0+\int_{\theta_0}^{\theta_1}\Gamma\left(1-\frac{\theta_1}{\theta}\right)d\theta\right\}. \qquad (1\,k)$$

The values of $\mathfrak{F}_0$ and S_0, to be chosen arbitrarily, constitute the two above-mentioned arbitrary constants.

For an interval of temperature such that within it Γ can be looked on as constant we should have

$$\mathfrak{F}_1-\mathfrak{F}_0=\mathfrak{J}\,.(\Gamma-\mathrm{S}_0)(\theta_1-\theta_0)-\mathfrak{J}\,.\,\Gamma\,.\,\theta_1\,.\log\left(\frac{\theta_1}{\theta_0}\right). \qquad (1\,l)$$

Hence it results that the value of $\mathfrak{F}_1$, even for the absolute zero-point of temperature, $\theta=0$, would remain finite, even though the value of Γ remain finite up to that point; while the value of

$$\frac{\partial\mathfrak{F}}{\partial\theta}=-\mathfrak{J}\,.\,\mathrm{S}_1$$

would be infinite at the limit $\theta=0$, unless at this limit the value of Γ, referred to absolute temperature, were vanishingly small. On the other hand, the product $(\theta_1\,.\,\mathrm{S}_1)$ even with finite Γ will at the limit, $\theta=0$, become equal to zero.

In the calculation of the work of physical processes the indeterminateness of these two constants offers no disadvantage, since we always have to do only with the difference of the work-values corresponding to two different states and temperatures of the body. Since the quantity S, which, as to its dimensions, corresponds to a specific heat, increases for each quantity of heat communicated to the system, we will assume the value of S_0 always so chosen that the value of S remains positive for every attainable degree of cold. I shall therefore continue to employ the symbol $\mathfrak{J}.S$ as an essentially positive quantity, instead of the negatively marked value $(-\partial\mathfrak{F}/\partial\theta)$.

When the values $\mathfrak{F}_0$ and S_0 are adopted for a state of the body chosen as the normal condition, all values of $\mathfrak{F}$ are determinate, as the above shows, if the capacity Γ be known for a single system of values of the parameters, and the work from this to every other system can be calculated for each constant temperature.

For isothermal changes the function $\mathfrak{F}$ coincides, as we have seen, with the value of the potential energy for work-values convertible without limit. I propose therefore to style this quantity the "free energy" of the system of bodies.

The quantity

$$U=\mathfrak{F}-\theta\frac{\partial\mathfrak{F}}{\partial\theta}=\mathfrak{F}+\mathfrak{J}.\theta.S$$

can be distinguished, as before, as the "total (internal) energy;" possible *vis viva* of the masses of the system remains excluded from both $\mathfrak{F}$ and U, so far as it belongs to the freely convertible work-equivalents, and not to heat. Then we may distinguish the quantity

$$U-\mathfrak{F}=-\theta.\frac{\partial\mathfrak{F}}{\partial\theta}=\mathfrak{J}.\theta.S$$

as the "bound energy."

If we compare the value of the bound energy,

$$U-\mathfrak{F}=\mathfrak{J}.\theta.S$$

with equation (1 *a*),

$$dQ=\theta.dS,$$

it results that the bound energy expresses the mechanical equivalent of that quantity of heat which must be conveyed into the body at temperature θ in order to raise its entropy to the value S.

It is to be remarked that all these values of U, $\mathfrak{F}$, S express only their excesses above the values corresponding to the normal condition, to which we refer as the starting-point of the calculation, since we do not possess the data for going back to the absolute zero-point of temperature.

In this department, finally, we require an expression in order to clearly distinguish the quantity hitherto designated in theoretical mechanics as *vis viva*, or actual energy, from the work-equivalent of heat, which is itself to be regarded for the most part as *vis viva* of invisible molecular motions. I would propose to distinguish the first as "*vis viva of regular motion.*" I call that "regular motion" in which the components of velocity of the moving masses can be viewed as differentiable functions of the space-coordinates. "Irregular motion," again, would be that in which the motion of each single particle need bear no kind of similarity to that of its neighbour. We have every reason to believe that the motion constituting heat is of the latter kind; and in this sense the quantity of entropy should be distinguished as the *measure of the irregularity*. With our means of observation, gross as they are in comparison with molecular structure, only regular motion can be freely reconverted into other forms of energy*.

§ 2. *The Production of Work expressed by means of the Free Energy.*

After it has been settled how the function $\mathfrak{F}$ is to be formed, and how the two functions U and S are to be derived from it, it is easy also to express the two other quantities, dW and dQ, present in Clausius's equations, though they are no longer generally integrable.

In order to shorten the notation we will distinguish the variations which any function of the coordinates undergoes if the parameters p_a change, but not the temperature, by the symbol δ, but the complete variation, in which the tempera-

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* Whether such conversion be impossible in view of the fine structure of living organic tissues appears to me to be still an open question, the importance of which in the economy of nature is obvious.

ture also changes, by d. For any function ϕ of $p_\mathfrak{a}$ and θ therefore

$$\delta\phi=\Sigma_\mathfrak{a}\left[\frac{\partial\phi}{\partial p_\mathfrak{a}}\delta p_\mathfrak{a}\right], \qquad d\phi=\delta\phi+\frac{\partial\phi}{\partial\theta}\,.\,d\theta.$$

Accordingly the freely convertible external work is

$$\begin{aligned} dW&=\Sigma(P_\mathfrak{a}\,.\,dp_\mathfrak{a})=-\delta\mathfrak{F}\\ &=-d\mathfrak{F}+\frac{\partial\mathfrak{F}}{\partial\theta}\,.\,d\theta=-d\mathfrak{F}-\mathfrak{J}\,.\,S\,.\,d\theta. \quad . \quad . \quad (1\,m)\end{aligned}$$

The quantity of heat simultaneously flowing in would be, according to equation (1),

$$\mathfrak{J}\,.\,dQ=dU-\delta\mathfrak{F};$$

or, making use of the value of U found in (1 *h*),

$$\begin{aligned}\mathfrak{J}\,.\,dQ&=d\mathfrak{F}-d\left[\theta\,.\,\frac{\partial\mathfrak{F}}{\partial\theta}\right]-\delta\mathfrak{F}\\ &=-\theta\,.\,d\left[\frac{\partial\mathfrak{F}}{\partial\theta}\right]=\theta\,.\,\mathfrak{J}\,.\,dS, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\,n)\end{aligned}$$

as (1 *a*) and (1 *g*) give.

By these determinations of dQ and dW the fundamental equations of the system set forth in (1) and (1 *a*) are identically satisfied even for the case of several parameters, and with them also all the results deduced from them by Clausius and other physicists.

If we have to do with cyclic processes, we can calculate the work in the form taken from (1 *m*)

$$dW=-d\mathfrak{F}-\mathfrak{J}\,.\,S\,.\,d\theta. \quad . \quad . \quad . \quad . \quad (1\,m)$$

If the series of changes entered upon be of the special kind during which S can be exhibited as a one-valued function of θ, in some such form as

$$S=\frac{\partial\sigma}{\partial\theta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where σ is only a function of θ, then

$$dW=d\mathfrak{F}-\mathfrak{J}\,.\,d\sigma\,;$$

and since the right-hand side is a perfect differential, the left is so also, consequently for a series of changes returning upon itself

$$\int dW = 0.$$

In this case it is therefore not necessary that, during return to the initial condition, exactly the same system of values of the parameters $p_{\mathfrak{a}}$ should exist for every value of θ as during departure therefrom, but only that for each value of θ the same value of S should always recur. So far the cyclic process without work has here a greater freedom than in the case of the single parameter.

On the other hand, it is in this case clear that

$$\int_1^2 dW = \mathfrak{F}_1 - \mathfrak{F}_2,$$

even if equation (2) continues to hold during the alteration and

$$\theta_2 = \theta_1,$$

but the parameters $p_{\mathfrak{a}}$ have different values at the end from those at the commencement.

The simplest case of equation (2) is that of the *adiabatic* variation

$$S = \text{const.}$$

Then

$$\int_1^2 dW = \mathfrak{F}_1 - \mathfrak{F}_2 + \mathfrak{J} \,.\, S \,.\, (\theta_1 - \theta_2).$$

If the constant S_0 contained in the values of $\mathfrak{F}$ and S be so chosen that the value herein contained shall be $S=0$, then likewise the external work is given simply by the difference between the values of $\mathfrak{F}$ for the beginning and end of the change. It is then only needful to eliminate the temperature from the value of $\mathfrak{F}$ by means of the equation

$$\frac{\partial \mathfrak{F}}{\partial \theta} = 0.$$

Work can therefore, as equation (1 *m*) shows, only be produced, even in the case of several parameters, by means of a complete cyclic process, if the integral

$$\int S \,.\, d\theta < 0,$$

or

$$\int \theta \,.\, dS > 0,$$

i. e. the rise of θ must chiefly take place with the smaller values of S, while the growth of S, or positive values of dQ, must accompany the higher values of θ. The values of the parameters can in that case undergo every kind of alteration compatible with the values of S determined for each value of θ.

Transformation of Free into Bound Work.

The value of the bound work, which I will denote by $\mathfrak{G}$, is

$$\mathfrak{G} = \mathfrak{J} \,.\, \theta \,.\, S;$$

its variation therefore

$$\begin{aligned} d\mathfrak{G} &= \mathfrak{J} \,.\, \theta \,.\, dS + \mathfrak{J} \,.\, S \,.\, d\theta \\ &= \mathfrak{J} \,.\, dQ + \mathfrak{J} \,.\, S \,.\, d\theta. \end{aligned}$$

On the other hand,

$$\begin{aligned} d\mathfrak{F} &= \delta\mathfrak{F} + \frac{\partial \mathfrak{F}}{\partial \theta} \,.\, d\theta \\ &= -dW - \mathfrak{J} \,.\, S \,.\, d\theta. \end{aligned}$$

That is, therefore, $\mathfrak{G}$ increases in the first place uniformly at the expense of the introduced heat dQ, secondly in the case of rise of temperature by the amount $\mathfrak{J} \,.\, S \,.\, d\theta$ at the expense of the free energy. The free energy is diminished by this last amount and by the amount of the external work performed, as is shown immediately by the equation

$$-\frac{\partial \mathfrak{F}}{\partial \theta} \,.\, d\theta = \mathfrak{J} \,.\, S \,.\, d\theta.$$

Thereby also the variation of $\mathfrak{F}$ which corresponds to the variation of θ maintains its significance as production of work, and the "*entropy*" S appears as *the heat-capacity for heat produced at the expense of the free energy during adiabatic change.*

In all *isothermal* changes, in which $d\theta = 0$, work is produced only at the expense of the free energy. The bound energy changes in that case at the expense of the incoming or outgoing heat.

In all *adiabatic* changes, in which $dQ=0$, work is produced at the expense both of the free and of the bound energy.

In all other cases we can regard the facts as if all external work were supplied at the expense of the free energy, all loss of heat at the expense of the bound energy, and finally during every rise of temperature in the system free energy were transformed into bound to the amount stated.

The last change can also occur even in the case of irreversible processes, through the transformation of free energy into *vis viva,* and of this, by friction-like processes, partly or wholly into heat. If the latter be the case,

$$dQ=dU$$

simply; accordingly the heat given up in passing from the initial state denoted by the suffix (1) to the final state denoted by (2) will be

$$\mathfrak{J} \cdot Q=U_1-U_2.$$

This is the quantity determined by the investigations hitherto made into the absorption of heat during chemical processes, the temperatures in the initial and final states being the same. The free work in isothermal transformation, viz.

$$W=\mathfrak{F}_1-\mathfrak{F}_2,$$

is essentially different from this, and cannot therefore be found by merely determining the total evolution of heat, as I have already remarked in the introduction.

Condition of Equilibrium and Direction of Changes spontaneously occurring.

Since in the case of infinitesimally small changes the quantity $\delta\mathfrak{F}$ conditioned by the variation of the parameters alone comes into consideration for every production of freely convertible work, being wholly independent of the value of the simultaneously occurring temperature-change $d\theta$, we therefore obtain in the first place that, without access of reversible external work-equivalents, to which also the *vis viva* of regular motion would belong, a positive value of $\delta\mathfrak{F}$ increasing with the time δt cannot arise. Under such conditions the ratio $\delta\mathfrak{F}/\delta t$ can only be zero or negative. Persistence in the given state would thus be secured if for all changes of the parameters possibly occurring at the then existing temperature

$$\delta\mathfrak{F} \geqq 0.$$

If, through rise of temperature, a point can be reached at which $\delta\mathfrak{F}$ begins to pass through zero to negative values, the phenomenon of dissociation would here occur with chemical compounds. Below this point, however, $\delta\mathfrak{F}$ must increase with falling temperature, *i. e.* the differential coefficient

$$\frac{\partial}{\partial\theta}\left[\delta\mathfrak{F}\right]=\delta\left[\frac{\partial\mathfrak{F}}{\partial\theta}\right]=-\mathfrak{J}\,.\,\delta\mathrm{S}$$

must have negative values, δS therefore must be positive. Since now, for $d\theta=0$,

$$dQ=\theta\,.\,dS,$$

it results that all chemical compounds which dissociate at high temperatures must evolve heat, at least in the parts of the thermometric scale lying close under the dissociation temperature, if they are formed in a reversible manner, but must render heat latent if they be decomposed.

The reverse will be true of such as separate into their constituents in the cold, as *e. g.* solutions of crystallizable salts.

With these general results the above-mentioned observations on galvanic elements actually agree.

Finally, collecting together once more the essential relations of the function $\mathfrak{F}$, from which its physical significance and properties are derived, they are the following :—

1. All external reversible work corresponds to change of the function $\mathfrak{F}$ conditioned by change of the parameters:

$$dW=-\delta\mathfrak{F}.$$

2. The differential coefficient $\partial\mathfrak{F}/\partial\theta$ can only be changed by bringing up fresh heat dQ. By "fresh heat" I understand such as is either communicated from surrounding bodies,

or is freshly produced through the transformation of freely convertible work-equivalents into heat:

$$d\left[\frac{\partial\mathfrak{F}}{\partial\theta}\right]=-\frac{1}{\theta}\cdot\mathfrak{J}\cdot dQ.$$

In this case it is to be noticed that in transformation of dW into heat dQ,

$$dW=\mathfrak{J}\cdot dQ.$$

3. The differential coefficient

$$\frac{\partial^2\mathfrak{F}}{\partial\theta^2}=-\mathfrak{J}\cdot\frac{1}{\theta}\cdot\Gamma,$$

is necessarily always negative.

That Γ is necessarily positive is tacitly assumed in all thermodynamical investigations, but an essential condition for this is that only transfer of heat from bodies at a higher to those at a lower temperature can produce work.

If the relations to each other of several bodies or systems of bodies at different temperatures be dealt with, the function $\mathfrak{F}$ for each single one is entirely independent of that for the others. Their relations to each other are only given by the fact that they can reciprocally communicate free energy and heat *inter se,* and in the case of reversible processes both pass over unchanged in amount; in that of irreversible processes, as already noted, work can be transformed into heat. For such transferences the new condition of reversibility is added, according to which transfer of heat may take place only between bodies at the same temperature. In all these relations, no change is produced by the generalization here carried out and the changed mode of expressing principles.

Supplementary Appendix.—It has perhaps not been insisted on above with sufficient clearness, that the laws developed only hold if the parameters be so chosen that, if they be constant, change of temperature is not accompanied by any production of work.