Walther Nernst, "Thermodynamic Calculation of Chemical Affinities"

General Comments

Among the various changes in energy, those that are associated with the course of chemical processes have always been conspicuous because of their magnitude. Therefore, the application of classical thermodynamics to processes of this type has met with particular success. Nowadays, no intensive investigation of a chemical equilibrium is regarded as complete if it does not make use of the two main laws of heat theory.

To be sure, a purely thermodynamic approach will never be entirely satisfactory, if only because the question of reaction velocity is entirely outside its field; and one will always have to make sure that, in addition to thermodynamics, the principles of atomistics are included. Atomistics has explained a number of processes in an entirely satisfactory manner, especially in the form of the kinetic theory of gases, as, for example, the work done by a gas in its expansion, or the transfer of heat through a gas. But if we ask about the accomplishments of atomistics in the mechanical explanation of chemical processes, we must admit openly that everything that has so far been attempted in this field has not only remained incomplete but must be considered basically faulty.

Certainly the explanation of the law of constant and multiple proportions and the marvelous systematics, especially of organic compounds, are tremendous achievements of atomistics purely in the field of chemistry; but these applications are not of a mechanical nature and have hardly any relation to the manner in which two atoms combine in a compound, with the magnitude of the forces that enter in, and with the change in energy thus determined. Not only in chemical processes, but also in the probably simpler phenomena of steam formation, fusion, and the transformation of various modifications, the same gap exists.

The principal fault in the ideas considered up to now seems to lie in the fact that, for example, in the consideration of steam formation, one simply calculated the work to be done in the dislocation of a molecule of liquid from the interior of the liquid phase into the gaseous space, using the theory of potentials. This formulation is questionable, however, because even a small change in the state of motion of the molecule can undoubtedly exert a great effect under certain conditions; but we do not know how this is to be taken into account—a fact which, of course, cannot justify the silent neglect that has generally been practiced up to now.

Of no lesser significance is a second circumstance that plays a decisive role specifically in the chemical processes themselves, for, as Planck has shown, the laws of mechanics undergo a thorough transformation if one is dealing with the motion of atoms about their resting position. Here, also, we can only say at this time that the neglect of Planck's quantum theory (or perhaps of any other, future theory which also leads to Planck's radiation formula) had to place the stamp of incompleteness on all previous attempts at explaining chemical processes mechanically. Certainly, we do not know yet how the new views should be taken into account in this matter; nevertheless, we have made progress in being able to state with certainty now: Something mysterious is hidden within the laws of atom mechanics which is explained in part by radiation theory, in part by the more recent studies of specific heats, and which apparently must be thoroughly understood before a mechanical treatment of chemical processes will be possible. Thus, we know, for example, that the laws of motion of

a double star are quite different from those of a diatomic gas, and we can at least indicate broadly in what sense the laws of pure mechanics are modified in the second case.

There is only one temperature point at which we can probably use the laws of mechanics safely; namely, when the motion of the atoms has completely stopped, i.e., at absolute zero temperature. Without doubt the laws of ordinary potential theory can be applied here; the heat formation that corresponds to the dislocation of the atoms from one state (e.g., in the form of free elements) to another state (e.g., in the form of a chemical combination) can be regarded as the equivalent of the forces exerted here; in other words, at absolute zero the chemical affinity must be equal to the heat formation.

Now, the second heat law gives quite a general relation between the maximum work A, which we previously designated as the sum of all forces produced in the chemical process under consideration and to which we shall refer below, as usual, briefly as "chemical affinity,"[2] and the heat developed, U:

$$(1) \qquad A - U = T \frac{dA}{dT}$$

Since we observed above that the left side of the equation disappears at absolute zero, we can write:

$$\lim\left(T \frac{dA}{dT}\right) = 0 \qquad \text{for } T = 0.$$

But, according to this equation, even at $T = 0$, dA/dT (its negative value is also called "entropy") can still possess a finite value and can even be infinitely large; it must, however, be of less than first order.

Equation (1) contains the complete application of the two heat laws to chemical processes; as has been shown especially by Helmholtz, all that the older thermodynamics was able to teach can be demonstrated clearly by means of it. Therefore it will be useful to go into it a little more thoroughly.

U can be looked up in thermochemical tables for room temperature, and we now want to refer to the well-known law that U can be calculated for arbitrary other temperatures from the specific heats.

A can essentially be determined by two methods, both of which were already used by Helmholtz; namely, by measurement of the chemical equilibrium or of the electromotive force.

Of course, dA/dT can then be found by measuring A at two slightly different temperatures.

Historical Background

Under such circumstances, the desire to derive A thermodynamically beyond equation (1) appeared quite early. The first determined effort in this direction came from Julius Thomsen, if one disregards Helmholtz' method of calculating the electromotive force of galvanic elements, which will be discussed further below. Thomsen, in his "Contributions to a Thermochemical System," emphasized repeatedly as early as 1852 that strong manifestations of chemical affinity are accompanied by intense heat formation and that chemical processes associated with heat absorption occur only rarely. He therefore arrived at the following conclusion:

"When a body falls, it develops a certain mechanical effect that is proportionate to its weight and to the space traversed. In chemical processes that take place in the usual direction, a certain effect likewise appears; but it shows itself in this instance as heat formation. The heat formation constitutes a measure of the chemical force developed in the process."

We have seen above that a chemical process may not be regarded—at least not above absolute zero—as a phenomenon of attraction, comparable to the falling of a stone; but we shall not hold this against Thomsen, in view of the fact that attempts to use this interpretation are still being made repeatedly today in spite of the kinetic theory of heat.

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Furthermore, Thomsen himself already recognized the untenability of the above concept in the early seventies, probably influenced chiefly by the results of his very ingenious method for determining the affinity between acids and bases.

We know that the same law was formulated in 1869 by the second master of thermochemistry, Berthelot, and energetically defended by him for a long time. Berthelot's formulation is the following:

"Every chemical transformation which takes place without the interposition of a foreign energy aims toward the production of that substance or that system of substances which develops the most heat."

Both formulations—the older one by Thomsen, as well as the later one by Berthelot-lead one to set $A = U$ in formula (1) for all temperatures. It is unnecessary to give the reasons for the inadmissibility of this equation again in more detail, but a reference to a remark by Horstmann will be useful for further clarification. According to him, the proof of chemical equilibrium or, what amounts to the same thing, of a reversible reaction was sufficient for refuting Berthelot's principle. Since the reaction takes place in one or the other sense, depending on the ratio of quantities of the reacting components, on one or the other side of the equilibrium, the reaction in the vicinity of chemical equilibrium must proceed in one instance according to Berthelot's principle with heat formation and in the other, certainly in opposition to that principle, with heat absorption.

We have emphasized above that the electromotive force of a galvanic element is proportional to the affinity of the process providing the current. The Thomsen-Berthelot principle, then, can also be expressed in such a way that the electromotive force of galvanic elements would have to be proportional to the heat formed per electrochemical gram element. It is of historical interest to emphasize that this formulation is found already in the famous paper by Helmholtz on the conservation of energy (1847). The method of calculation, which was only indicated there, was later carried out by William Thomson for several examples. More intensive study has shown, in agreement with our earlier observations, that one can indeed frequently calculate the electromotive force of galvanic elements very accurately from the heat formed, especially in cases where the affinity is strong, but that one may in no way speak of a strict law.

It is evident that all further progress must be tied to equation (1); a relationship must be found that is independent of the special nature of the reaction under consideration, if the uncertainty inherent in equation (1) is to be overcome.

For a certain class of reactions-namely, those where a gas is formed from one or more solid substances—Le Châtelier, Matignon, and Forcrand found the following approximate relationship: if Q designates the heat formed at constant pressure, and T', the absolute temperature at which the dissociation pressure of the gas being formed equals atmospheric pressure, then:

$$\frac{Q}{T'} = \text{approx. } 32$$

In this case, disregarding the variation of Q with temperature, the second heat law gives

$$\ln p = -\frac{Q}{RT} + \text{const}$$

We recognize immediately that Le Châtelier-Matignon's rule gives a value of approximately 32 for the undetermined integration constant multiplied by R. This rule is only approximately valid; nevertheless, it provides an important cue, and it probably deserved more attention than it was given formerly. We shall become acquainted with a more precise formulation later on.

Van't Hoff set up an equation in 1904 that was hardly satisfactory. If one wants to satisfy the effect of temperature on U by the (seemingly!) simplest equation:

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(2) $\quad U = U_0 + \alpha T,$

integrating (1) gives

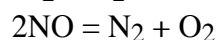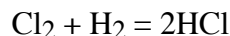(3) $\quad A = U_0 + aT + \alpha T \ln T,$

where a is the constant of integration. Van't Hoff assumed that a was small. This hypothesis is not only arbitrary but also evidently inaccurate. For, even if we assume the case that a equals zero, we only need to alter the temperature scale—i.e., divide the space between the melting and boiling points of water into a million instead of a hundred parts—and we immediately have a finite and even sizable value for a. It is hardly likely that the natural laws are guided by the fact that Celsius divided the above-mentioned temperature interval into a hundred parts and that he happened to choose water as the standard substance.

The earlier attempts to go beyond equation (1) thus were unsuccessful; but at least the problem had been sharply formulated. The clearest position taken, next to Helmholtz, was probably that of Le Châtelier as early as in 1888. I want to reproduce his words here:[3]
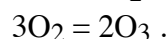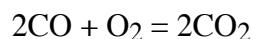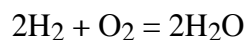
"It is very probable that the integration constant, like the other coefficients of the differential equation, is a definite function of certain physical properties of the reacting substances. The determination of the nature of the function would lead to complete knowledge of the laws of equilibrium. Independently of new experimental data, it would determine a priori the complete equilibrium conditions which correspond to a given chemical reaction; up to now, it has not been possible to determine the exact nature of this constant."

If I may now discuss my part in the solution of the problem, it seemed noteworthy to me from the beginning that, for an erroneous law of nature, Berthelot's rule still is too frequently applicable to be ignored entirely, and therefore I had already emphasized in the first edition of my textbook of theoretical chemistry (1893) "that it is quite possible that Berthelot's principle, in a clearer

form, may at some time again become important." It was particularly noticeable that for solid substances, affinity and heat formation frequently coincide. It was clear from the beginning, on the other hand, that the identification of these two magnitudes actually becomes meaningless for gaseous systems, for the maximum work depends on the initial and final concentrations of the reacting gases, while the heat formation is entirely independent of these. Thus, the question arose whether a relationship between heat formation and chemical equilibrium could be found empirically, at least for comparable reactions such as:

$\qquad$ $Cl_2 + H_2 = 2HCl$
$\qquad$ $2NO = N_2 + O_2$

or:

$\qquad$ $2H_2 + O_2 = 2H_2O$
$\qquad$ $2CO + O_2 = 2CO_2$
$\qquad$ $3O_2 = 2O_3$.

Therefore, together with a large number of collaborators, and guided by such considerations, about ten years ago I undertook the determination of equilibriums in gases, on which only very little, and usually uncertain, observed material was previously available.

Thermodynamic Considerations

In its application to gaseous systems, the second heat law leads to the following result. Experience teaches us that the specific heats vary only slowly with temperature, so that it is suitable and convenient, to begin with, to assume an expression of the form

(4) $\quad c = c_0 + aT + bT^2 + ...$

to be valid; c_0 would thus be the specific heat at very low temperatures.

Furthermore, since, according to a law by Kirchhoff, the temperature dependence of the heat of reaction U is determined by the specific heats of the substances participating in the reaction, we can also set

(5) $\quad U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + ... ,$

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where U_0 is the heat of reaction near absolute zero.

Substituting in the equation of the reaction isochore

$$U = RT^2 \frac{d\ln K}{dT}$$
(6)

and integrating, we easily find

$$\ln K = -\frac{U_0}{RT} + \frac{\alpha}{R}\ln T + \frac{\beta}{R}T + \frac{\gamma}{2R}T^2 + ... + I$$
(7)

where I is the constant of integration.

The right-hand side of equation (7) thus contains, besides the constant of integration, only pure thermal magnitudes (heat of reaction, specific heat, or, respectively, its temperature coefficients); but the second heat law says nothing at all about the integration constant itself.

At very low temperatures, the effect of all other members disappears, and we obtain

$$RT \ln K = -U_0,$$

i.e., we can here calculate the equilibrium from the heat of reaction U_0; at finite temperatures, however, first the effect of $\alpha T \ln T$ and RTI, and then also that of the remaining members will be noticeable.

From the experimental point of view, we arrive at the problem that the behavior of gases cannot be measured at lower temperatures because they cease to remain capable of existing in significant concentrations.

If we now consider the opposite of gaseous equilibrium namely, a reaction between solid substances only—a limiting transition to absolute zero seems entirely possible in theoretical as well as experimental respects. And here it is noticeable that Berthelot's principle frequently fits quite well, especially if one is dealing with relatively great reaction heats. Thus, the conjecture forced itself upon me (1906) that this is a matter of a limiting law of such a kind that A and U not only become equal at absolute zero but approach each other asymptotically. Thus we should have:

$$\lim \frac{dA}{dT} = \lim \frac{dU}{dT}$$
(8) (for $T = 0$);

but it is to be noted that the above equation is applicable, to begin with, only to pure solid or liquid substances; at absolute zero, gases stop being capable of existing, and the behavior of solutions must still be investigated more closely.

We recognize further that equation (8) combined with (1) gives

$$\lim \frac{dA}{dT} = 0 , \qquad \lim \frac{dU}{dT} = 0 \text{ (for } T = 0).$$

The relationship

$$\lim \frac{dU}{dT} = 0 \text{ (for } T = 0)$$

teaches us that the atomic heats of the elements and compounds must be strictly additive at low temperatures; already in the first practical applications of my theorem I was led to the conjecture that all of them must converge toward very small values at low temperatures. The experimental and theoretical studies of recent times have, as we know, not only confirmed this conjecture but even made it into a certainty that the specific heats of all solid substances converge toward zero at low temperatures.

We shall make use of this below, and we shall find the following equation to be strictly valid for low temperatures, if we include the very important result that was confirmed theoretically by Debye and experimentally by Eucken and, quite recently, also by Schwers and myself, that the specific heat changes in proportion to the third power of the absolute temperature at low temperatures:

$$\text{(14)} \quad U = U_0 + \delta T^4, \qquad A = U_0 - \frac{\delta}{3}T^4 .$$

In the discussion of the following examples, we shall limit ourselves to a graphic representation, and I shall give references to the appropriate publications for the specific numerical material. It is even quite possible and, in many cases, practicable, to determine

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the relationship between affinity and heat of reaction by purely graphic means.

We shall assume, for example, that the heat of reaction was measured for a single arbitrary temperature and that we know the specific heats of the reacting solid substances down to very low temperatures. By assuming the T^3 law for the very low temperatures that are inaccessible to measurement, we are then in a position to draw the heat of reaction as a function of temperature with great accuracy down to absolute zero.

The integral of the equation

$$A - U = T \frac{dA}{dT}$$

(1)

is

$$A = -T \int_0^T \frac{U}{T^2} dT + cT$$

(15)   ;

for $T = 0$, we have

$$A = U_0;$$

i.e., as was already mentioned, Berthelot's law is valid here without restriction. However, for higher temperatures the value of the integration constant c becomes decisive, and the second heat law leaves this value undetermined.
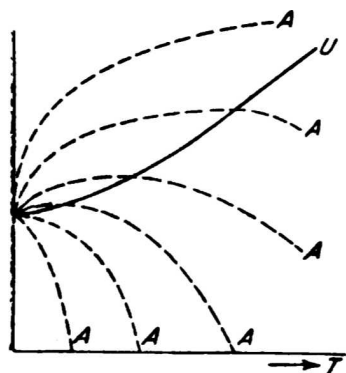

Fig. 1.

Figure 1 shows this. The solid curve U represents the dependence of the heat formed on the absolute temperature; thus U_0 is the value this quantity assumes at absolute zero; then each of the dotted curves A is a solution of the above equation, and one sees at once that there is no point, and therefore no value for A, through which we could not draw an A

curve out of the entire set of curves. In other words, every arbitrary value of the affinity A is compatible with any experimentally given shape of the heat formation, so that the second heat law abandons us here to a large extent. It gives us a precise answer only for absolute zero, since the curves for heat formation and affinity intersect here so that both quantities become identical, as Berthelot had assumed to be the case for all temperatures.

But if we now include the new heat law, the A curve must run parallel to the U curve at absolute zero; in other words, from the infinite set of A curves one, and only one, is fixed as being possible.

If we wish to determine it, not by calculation from equation (15), in which c must be set equal to zero according to the new law, but by purely graphic means, we must first, starting at absolute zero, draw it parallel to the U curve; the further direction is given at every point by the equation

$$\tan \alpha = \frac{dA}{dT} = \frac{A - U}{T}.$$

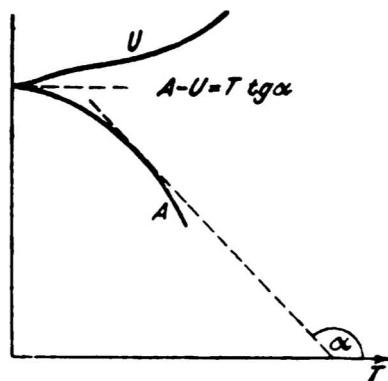With some practice, the A curve can be drawn quickly and with sufficient accuracy in this way.

Fig. 2.

Examples of Condensed Systems

In condensed systems, also, Berthelot's principle sometimes fails completely; in particular, at the melting point and at the transformation point the affinity equals zero because the two phases in question are here in equilibrium, while the heat formed (heat of

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fusion or, respectively, heat of transformation) can even have considerable values. The application of the new heat law thus leads in this instance to especially characteristic consequences, the influence of the specific heats, which had formerly not been sufficiently recognized, proving decisive for the position of the melting or transformation point. As an example, let us look at the transformation of sulphur.

Transformation of Sulphur

Different authors have measured the heat of transformation of rhombic into monosymmetric sulphur, the maximum work to be obtained in this and the specific heats for both modifications; in addition, the temperature of the transformation point is known exactly.[4] It turned out that, with the aid of the simple formulas

$$U = 1.57 + 1.15.10^{-5}T^2$$
$$A = 1.57 - 1.15.10^{-5}T^2,$$

all observations can be reproduced almost within the accuracy of the errors of observation.
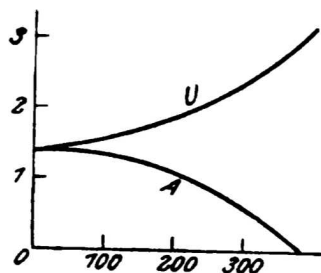

Fig. 3.

The accompanying curve (Figure 3) gives a picture that approaches reality still more closely; here, the U curve is drawn from the available thermal measurements and the A curve is determined graphically as described above. The latter is in agreement with the available measurements to the extent allowed by the accuracy of the available thermal measurements; since the very small difference of the specific heats of the two modifications of sulphur determines the course of the U curve, it can, of course, be indicated only within a certain accuracy. But it can probably

be considered definite, and it is this alone that we are concerned with, that the two curves are tangent to each other, in agreement with the new heat law.

Combination of Water of Crystallization

In recent times,[5] the reaction

$$CuSO^4 + H_2O = CuSO_4,H_2O$$
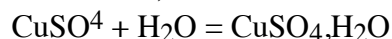
has been investigated very intensively. The quantities measured were the heat of hydration with liquid water, the dissociation potentials at higher temperatures, and the specific heats of the two salts and of ice down to very low temperatures (Figure 4).
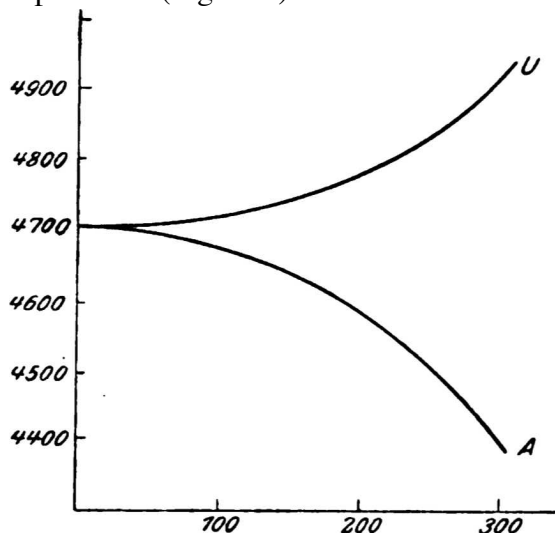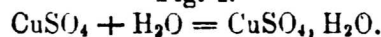

Fig. 4.
$$CuSO_4 + H_2O = CuSO_4, H_2O.$$

With the aid of the second heat law, it was then possible to calculate the dissociation potential π also for the ordinary zero temperature point; if p is the vapor pressure of ice at this temperature, it is found that

$$A = RT \ln \frac{p}{\pi} = 4,415 \text{ cal}.$$

On the other hand, with the aid of the new heat law, using the heat formed in this reaction at the same temperature (4,910 cal) and using the specific heats, the result was:

$$A = 4,475 \text{ cal},$$

in satisfactory agreement with the value above. Finally, for absolute zero, it was calculated that

$$A_0 = U_0 = 4{,}680 \text{ cal,}$$

and it can be seen (as seems to be most frequently the case) that U increases with temperature while A decreases; but the latter quantity would cross the temperature axis only at such high temperatures that the ice would have long ceased to exist and that, in practice, a point of transformation is therefore not present.

Such a process will always occur if the molecular heat of the water of crystallization is smaller than that of ice; potassium ferrocyanide, which crystallizes with three moles of water, is an example of the reverse case. The accompanying diagram (Figure 5)[6] shows the energy relationships, which are very peculiar here; one sees that U becomes 0 at $T = 160$, and that U becomes negative at higher temperatures, while A remains positive and even increases.
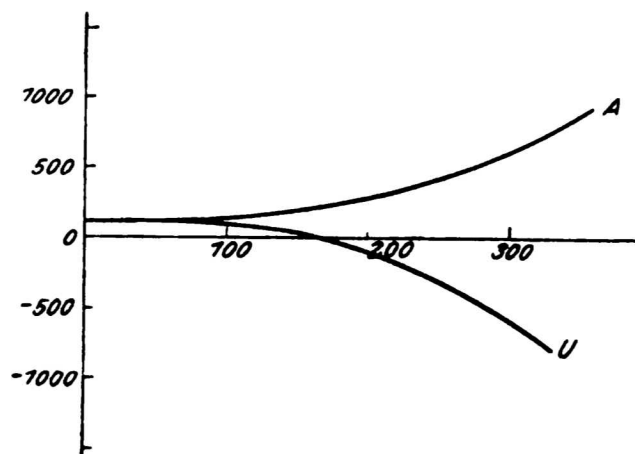
Thus, we may probably say in summary that it has been possible to test the new heat law on a very extensive and varied group of facts, numerous chemical equilibriums having been calculated from thermal data or from the combination of thermal data and vapor-pressure measurements.

Independent of this, it may also be derived, as I was unable to do in detail here, from a fact established by very many measurements done in recent times according to which the specific heats of solid and liquid substances assume vanishingly small values at very low temperatures.

Third, as Mr. Planck recently explained here, it is closely related to the theory of energy quanta, and thus even the phenomena of heat radiation, strange as this may sound at first, give support to our law from an entirely different direction.

Fig. 5.
$$K_4Fe(CN)_6 + 3\,H_2O = K_4Fe(CN)_6,\ 3\,H_2O$$

[1][Copied from Eduard Farber, Ed., *Milestones of Modern Chemistry*, Basic Books, New York, 1966, pp 186-202. Translation by Elisabeth F. Lanzl. —CJG]

[2]Undoubtedly it is more practical to define chemical affinity by the so called "thermodynamic potential," but in our considerations this does not make any noticeable difference.

[3]*Les équilibres chimiques* (Paris, 1888), p. 184.

[4]For details cf. Nernst, *Theoretische Chemie*, 7. Aufl. (1913), pp. 736-737.

[5]A. Siggel, *Zeitschrift für Elektrochemie*, Vol. 19 (1913), p. 341.

[6]Schottky, *Zeitschrift für physikalische Chemie*, Vol. 64 (1908), p. 441; W. Nernst, *Berichte der Berliner Akademie* (1910), p. 277.