WALTHER NERNST

Studies in chemical thermodynamics

Nobel Lecture, December 12, 1921

I should best fulfil my obligation to give a lecture relating to my prize-winning publications, if I discussed my heat theorem, which supplements the older thermodynamics, with special reference to its chemical applications, and described the experimental tests which it has undergone in numerous investigations in my laboratory.

But this has already been done, especially in recent years, by a number of different authors in textbooks and monographs. On this important occasion, a keen desire to avoid simply repeating what has been said earlier, prompts me to discuss the subject from the viewpoint of electrochemistry.

This of course really limits my task, but on the other hand it broadens it, because in this way I shall be able to describe more clearly the development of my work.

Thus, my lecture will take on a highly personal note, and generally speaking it is better, where possible in natural science, to study objects of research independently of the accidents of their historical development. But the fact that a prize is awarded to an individual who, as a child of his time and equipped with the logical and experimental methods of his time, is really only able, by climbing on the shoulders of his predecessors, perhaps to see a little further in some direction than anybody else before him - does not this fact lead to such strong individualization that his personality must obtrude more than usual into his grateful reply?

From the start of my scientific career the galvanic cell, the first form of which, the Volta pile, popularized physics in a single stroke and at the same time presented us with so many problems, appeared to me to merit especially further study.

The picture looked fairly hopeless to begin with. A law according to which the e.m.f. of a cell could be easily calculated on the basis of the equation:

$$E = \frac{U}{23,050} \text{ volts} \tag{1}$$

(here U is the heat evolution in gramcalories of the current-generating chemical process) had been originally created by no less a person than Helmholtz and was accepted as a generally reliable but sometimes quite misleading rule. Many other theories of the mechanism of current generation came and went, and when Helmholtz again, with a grasp of genius, developed the theory of the electrical double layer and, here unconsciously following the precedent of W. Gibbs, also replaced the above incorrect thermodynamic equation by the equation

$$E \cdot 23,050 - U = 23,050 \, T \frac{\mathrm{d}E}{\mathrm{d}T} \qquad (2)$$

we were still without any sure and more fundamental understanding of the galvanic cell. It was particularly disillusioning to find a man like Helmholtz returning repeatedly throughout his scientific career to his first love, the galvanic cell, which he had courted in his great youthful work "*Erhaltung der Kraft*" (The conservation of energy), without however succeeding in finding a satisfactory solution.

As often in natural science the picture changed quite suddenly. New fruitful concepts appeared, through the interplay and extension of which most of the darkness has been to a large extent dispelled in a single stroke. Such means were Van 't Hoff's theory of osmotic pressure, Arrhenius' theory of electrolytic dissociation, and finally many new approaches to the treatment of chemical equilibria, which, brilliantly presented, are to be found scattered throughout the first edition of Ostwald's "*Lehrbuch der Allgemeinen Chemie*" (Textbook of general chemistry). So there arose in 1889 the osmotic theory of galvanic current generation, which has not been seriously challenged since it was put forward more than thirty years ago and has undergone no appreciable elaboration since its acceptance, surely a clear sign that it has so far satisfied scientific needs.

I must exclude from this discussion my theory of liquid chains, in the mathematical and physical extension of which, as you will know, Professor Planck was of great assistance, the theory of electrolytic chains by means of which in at least some special cases I believe that I have solved in a visual manner and above all quantitatively the problem of thermoelectricity, the quantitative calculation of residual currents, and finally the study of the theory of concentration chains using dilute solutions, as well as the quantitative calculation of the absolute diffusion rate of electrolytes, which is closely

bound up with this. I would like, however, to deal briefly with my equation for the metal-electrolyte potential difference :

$$E = \frac{RT}{n} \ln \frac{C}{c}$$

(3)

(where R is the gas constant, n is the chemical valency of the ion concerned, C is a constant specific to the electrode, and c is the ion concentration), an equation which has been used successfully for a long time, and one might say daily, by numerous investigators in their electrochemical work.

I would like to discuss the field of application of Eq. (3) in electrochemical and also purely chemical problems, on the basis of a few simple tests. If we dip two silver electrodes into a U-tube filled with dilute potassium nitrate solution, we find that the e.m.f. fluctuates and is indeterminate; if approximately equal quantities of silver nitrate are added to the two electrodes, the e.m.f. of the cell becomes determinate, i.e. close to zero thus exactly as one would expect from Eq. (3). But if the silver concentrations in the vicinity of the two electrodes are noticeably different from each other, what is termed a "concentration chain" arises, the force of which can be found directly from the above equation. The equation shows, however, that these concentration currents are usually produced by small e.m.f.'s, and experience confirms this. The picture changes when we add potassium chloride to one of the silver electrodes, thus largely removing the silver ions from the solution; then the e.m.f of the chain produced in this way, in accordance with our equation, assumes truly substantial values, and since the extremely low concentrations of the silver ions can be calculated on the basis of the laws of the mutual influence in the solubility of salts, which I evolved and tested experimentally, it is possible to calculate the e.m.f. of such chains when the silver content at one electrode and the chlorine content at the other electrode is known; thus a not uninteresting way was found of further checking Eq. (3).

If we add to the potassium-chloride solution in succession potassium iodide, potassium cyanide, and ammonium sulphide, then, on the basis of well-known laws of chemical equilibrium the concentration of the silver ions is, in the same succession, depressed far more strongly than was the case when the silver was precipitated with potassium chloride, and the e.m.f. rises accordingly. (Experiments.)

If we build in a U-tube-which contains effectively some cotton-wool in the bottom part to prevent convection currents - a Daniell cell, formed by

the electrolyte, a zinc bar, and a copper bar, then Eq. (3) has of course to be used in various ways with two different C-values, one of which relates to zinc and the other to copper, and it is possible to predict the total behaviour of the Daniell cell using dilute solutions. The situation is very interesting, as Hittorf found but could not explain, when by the addition of potassium cyanide in the neighbourhood of the copper electrode the copper ions are largely eliminated, while a solution of zinc sulphate is present in the neighbourhood of the zinc electrode, as in the ordinary Daniell cell. Then, according to Eq. (3), the current in the cell does not flow from the zinc to the copper, as in the ordinary Daniell cell, but in the reverse direction, and under these conditions copper goes into solution and zinc is precipitated. (Experiments.)

We can nowadays conclude, from a purely chemical point of view, that copper in potassium-cyanide solutions must be a hydrogen-evolving metal. But, if we dip a copper bar into concentrated potassium cyanide solution, at first no hydrogen is generated because here certain passive resistances that can be measured with accuracy are set up, which I have termed "the over-voltage phenomenon". These passive resistances must disappear when we wrap platinum wire round the copper bar, because hydrogen is liberated on platinum with almost no overvoltage. Indeed, a copper bar wrapped round with platinum wire, when present in a potassium-cyanide solution of sufficiently high concentration, immediately evolves hydrogen at a violent rate. (Experiment.)

In particular, it has also been possible to determine the behaviour of lead accumulator, in quite a detailed manner, qualitatively and quantitatively by means of Eq. (3). The high overvoltage occurring on the lead when hydrogen is liberated proved particularly significant for understanding the lead accumulator.

The osmotic theory of current generation stipulates moreover that when a metal ion concentration is higher than consistent with the solution tension of the particular metal, on immersion of the metal, ions of the relevant metal electrode must go into solution, while conversely they must settle on the electrode when the reverse is the case. In both cases, since the metal ions are positively charged, electric double layers occur, the charge of which in many cases immediately inhibits the precipitation or dissolution of the metal involved. By his fine and well-known experiments, Prof. Palmaer was able to demonstrate on dripping mercury that these deductions based on my theory are also correct.

The osmotic theory of the galvanic generation of current does not permit calculation of the actual value of the solution tension, but of its relative value; in individual cases such as with silver and mercury, the solution tensions are found to be very small, in others such as with zinc or even sodium they are tremendously large. From time to time criticism has been made with regard to the enormous size of these solution tensions, though as can be readily demonstrated, without justification. For, in the case of normal, i.e. non-electrolyte, dissolution, pressures are attained which, too, are enormous under certain circumstances. Let us for example consider the process when ice and sulphur trioxide dissolve in dilute sulphuric acid. During this process 38,000 calories are generated which, if electromotively active, would yield a galvanic cell with an e.m.f. of approximately

$$E = \frac{38,000}{23,050} = 1.65 \text{ volts}$$

that means a galvanic cell with an e.m.f. not much less than that obtained when, for example, a zinc rod and a chlorine-charged platinum plate are immersed in a zinc chloride solution. The two processes are exactly analogous; in the first case ice and sulphur trioxide dissolve to form sulphuric acid in dilute aqueous solution, in the second case zinc and chlorine in solid solution dissolve to form zinc chloride in aqueous solution. Admittedly, powerful chemical processes occur during the dissolution of the sulphur trioxide in water, but that can also be the case during the dissolution of metals since, in order to form positive ions (quite apart from possible hydration), the metal atoms necessarily give off negative electrons, and hence must alter chemically.

It has long been known that the e.m.f. of a galvanic cell is a measure of the affinity of the current-generating chemical process, and Helmholtz and others have previously pointed out that, conversely, electromotive forces can be calculated thermodynamically from a chemical equilibrium. To extend my electrochemical research I therefore set out together with my pupils to determine chemical equilibria in gaseous systems at high temperatures; we dealt particularly with the dissociation of water vapour and of carbon dioxide. Our first measurements for example enabled von Wartenberg and myself to determine thermodynamically the e.m.f of the oxyhydrogen gas cell. Not without surprise we found that in this case the value measured directly by electrochemical means was much too low.

In the course of these studies I established in the first place empirically dis-

tinct relationships between the state of the chemical equilibrium and the evo-
lution of heat in the particular reaction but only when comparing reactions
in which the change in the number of molecules during the reaction was the
same. This change is, for example, the same for the two reactions

$$Cl_2 + H_2 \rightleftharpoons 2\,HCl$$
$$2\,NO \rightleftharpoons N_2 + O_2$$
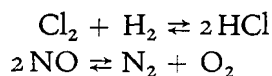
since in both cases the number of molecules remains unchanged during the
reaction. As it happens these reactions evolve practically the same heat and
hence the state of the equilibrium is, at least approximately, also the same.
These similarities disappear, however, when the above two reactions are
compared with chemical processes which proceed like, for example, the
reaction

$$2\,H_2 + O_2 \rightleftharpoons 2\,H_2O$$
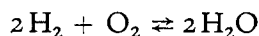
with a change in the number of molecules, and occur again when the disso-
ciation of water vapour is compared with the that of carbon dioxide. I am
not aware that attention had previously been paid to this orderliness, now
fully clarified through consideration of the specific heats and especially by
the introduction of the chemical constants.

In very lengthy, tedious calculations I then made a closer check on these
points which I believe to have clarified in principle soon afterwards by the
publication of my work *Über die Berechnung chemischer Gleichgewicht aus ther-
mischen Messungen* (The calculation of chemical equilibria from thermal
measurements) (1906). The simple principle at which I arrived at that time
may be stated as follows: that in all cases chemical affinity and evolution of
heat become identical at low temperatures. Not, and this is the essential
point, in the sense that they intersect at absolute zero, but rather in the sense
that they invariably become practically identical some distance before abso-
lute zero is reached; in other words the two curves become mutually tangen-
tial in the vicinity of absolute zero.

If we frame this principle in quite general terms, i.e. if we apply it not only
to chemical but to all processes, then we have the new heat theorem which
gives rise to a series of very far-reaching consequences:

I. The best working capacity attainable in the most favourable case during
a process can be computed from the heat evolution which must, however, be
known down to the lowest temperatures.

2. This can also be expressed by stating that the evolution of heat at an

arbitrary temperature, and the specific heats of the substances concerned must be known to very low temperatures.

3. The specific heats must be strictly additive at very low temperatures, or in other words the evolution of heat at very low temperatures must always be independent of the temperature.

Of course, the above principles, although applicable to all processes occurring in Nature, are particularly useful in connection with chemical ones. In this very context Berthelot, as we know, imagined that the chemical affinity could be equated with the evolution of heat, but this assumption, although correct in many cases, could not be upheld. We now appreciate clearly in which cases Berthelot's principle is correct; when very large a- mounts of heat are evolved, and restricting the scope to condensed systems, the influence of the specific heat becomes relatively small, and Berthelot's principle applies mostly with adequate approximation, provided the temper- atures are not too high. For processes in which little heat is evolved, e.g. fusion, it often breaks down completely.

Having drawn the above conclusions I had to devote myself to the task of verifying the consequences of my heat theorem as rigorously as possible by experimental means - a task which took me many years. And again I was only able to do so by working out methods, constantly aided and actively supported, of course, by my assistants and pupils, to determine the specific heats down to the lowest possible temperatures. I can truly say that at my Institute in more than 100 experimental studies an abundance of data were collected which confirmed the new theorem as accurately as allowed by the precision of what were at times very difficult experiments.

In particular I should like to mention the following. Quite in keeping with an assumption I made at an early stage it was found experimentally that in all cases the specific heats of solids become very small at low temper- atures. The quantum theory proved of assistance here. After Einstein's at- tempt to demonstrate the behaviour of specific heats more qualitatively in terms of the quantum theory, Debye showed on the basis of my findings that the specific heats of solids at very low temperatures must increase in propor- tion to the third power of the absolute temperature. And this in itself very convincing theoretical finding of Debye's could then be fully confirmed ex- perimentally, in the most exact way, in my laboratory on a multiplicity of substances. I would like especially to emphasize the fact that this enabled my heat theorem to be thoroughly tested in a large number of cases. When specific-heat measurements can be continued down to such low temperatures

as to come within the scope of the Debye law, the behaviour of the specific heats can quite safely be extrapolated to absolute zero.

These temperatures are, admittedly, sometimes very low, and with amorphous substances such as glass, etc., even at the temperature of hydrogen boiling under greatly reduced pressure, this state is still far off. Here it will be necessary to go down to helium temperatures and this will be made possible by the work of Kamerlingh Onnes.

It need only be mentioned in passing that the study of specific heats at very low temperatures has at the same time stimulated research with regard to the theory of the solid, particularly the crystalline, states. One such instance is the interesting theory of the process of melting proposed by F. A. Lindemann, who was my colleague for many years.

So far we have tacitly restricted ourselves to solids, either in the crystalline or in the amorphous state; in the latter case one deals with liquids, super-cooled according to Tammann's well-known theory, which after sufficient cooling change to a glass-like state. Experience does, it is true, show that only relatively few liquids, such as molten quartz, for instance, can be transformed without difficult into the vitreous state (e.g. quartz glass) by sufficiently rapid cooling, but there can be no doubt that in principle every fluid can be brought down to absolute zero by continuous cooling, i.e. without abrupt changes. There are therefore no objections in principle to the application of my heat theorem in the case of fluids, even if the specific heats of the super-cooled liquids mostly elude direct determination owing to their great tendency to crystallization. I have adopted this point of view from the beginning and I still believe today that it is entirely incontestable.

The case is essentially different, however, with regard to gases. Here I pointed out in my first papers on the subject that my heat theorem, to begin with, does not appear to be applicable to gases, because we cannot continuously cool down to absolute zero a gas kept at a constant volume, or, more correctly, because we do not know how a gas would behave if such cooling were possible.

Here too, however, we have made considerable progress, and even if it has not been possible to reach a definite conclusion regarding the questions at issue, we have, I think, already come fairly close to solving the problem.

Here again it was the quantum theory which came to the rescue. First of all I was able to show that the specific heats of polyatomic gases, since their rotational movement must be lost when sufficiently cooled, must assume the value applicable to monatomic gases at a sufficiently low temperature. In the

case of hydrogen I was able to demonstrate the probability, from Regnault's measurements, that at room temperature hydrogen has already lost a part of its rotational energy; when Eucken subsequently, at my instigation, carried out measurements of the specific heat of hydrogen at very low temperatures it was shown that here indeed the specific heat of hydrogen fell to the value applicable to monatomic gases, which is certainly a remarkable result, but one which is easily explainable, qualitatively at least, by the quantum theory.

An important practical application of this now ensues immediately for the behaviour of vapour pressure at very low temperatures. The specific heat of the condensate is zero at this point. That of the vapour assumes the values applicable to monatomic gases and its exact value is therefore known, and Clausius-Clapeyron's formula accordingly gives, for the vapour pressure, the following formula:

$$\ln p = \frac{\lambda_0}{RT} + 2.5 \ln T + i \qquad (4)$$

which is, as can be seen, a simple and quite certainly a completely strict vapour-pressure formula, which of course is applicable only in the neighbourhood of absolute zero. (λ_0 is the heat of vaporization at absolute zero, R is the gas constant, T is the absolute temperature, and i the integration constant.)

I established this formula immediately after I had recognized that all gases must behave like monatomic gases at very low temperatures so far as specific heat is concerned.

From my heat theorem it easily follows that the integration constant i is dependent only upon the nature of the gas, i.e. that it must have the same value, quite irrespective of whether the gas concerned is obtained by the evaporation of a crystal or a liquid or indeed from any chemical process whatever.

It is now of considerable interest that the numerical value of i can be obtained from the quantum theory if the validity of my heat theorem is accepted. As I was now able to demonstrate several cases in which in fact that value can be verified from the quantum theory with tolerable certainty by various persons (Sackur, Stem, Tetrode), I could in this way arrive at a new and, I believe, particularly striking confirmation of the accuracy of my heat theorem.

In all this work we have only dealt so far with a confirmation of my heat theorem for solids or liquids; we have not, even in the case of formula (4, hereby dealt with a direct application of my heat theorem to gases.

I should now like to conclude my remarks, however, with this reference - that at present the point of view is held in many quarters, as also in several of my papers, that at very low temperatures gases as well reach a state in which their specific heat is zero and their pressure is therefore independent of temperature (the so-called "degenerate state of gases"). This would mean that my heat theorem is also directly applicable to gases as well. This result is not of immediate practical importance, for owing to the introduction of the so-called "chemical constants", the chemical equilibria have of course already become calculable in gases as well; from the theoretical point of view, however, this affects very important questions, the certain and exhaustive answer of which may be awaited with eager expectation. All those who have probed deeply into these questions will probably accept the fact that it is highly probable that my heat theorem is directly applicable to mixed crystals and similar matter, even though there is understandably no experimental proof as yet.

Finally, I should perhaps point out that recently my heat theorem has been successful in assisting Eggert, Saha and others in deciding astrophysical questions.