The Nernst Memorial Lecture.

HERMANN WALTHER NERNST.

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ABOUT twenty miles north-east of Torun (Thorn), the birthplace of Copernicus, is a small town, once in West Prussia and called Briesen, now in Poland and renamed Wabrezno. It was there, on June 25th, 1864, that Hermann Walther Nernst was born. His father, Gustav Nernst, who had married Ottilie Nerger, was posted at Briesen as a Prussian civil servant, but the Nernst family had lived for several generations in the town of Prenzlau, about fifty miles north of Berlin. One of them, early in the century, was a Lutheran pastor; another later farmed a large estate. Walther attended the Gymnasium at Graudenz, near Briesen, a large town now in Poland and renamed Grudziadz. He showed great ability in literature, poetry, and the classics, especially Latin composition, and later passed out as head boy of the school. His teacher in chemistry had aroused his interest in that science, and he made experiments in a small home laboratory. He then studied science in the Universities of Zürich, Würzburg, and Graz. In Graz he worked with Professor Albert von Ettinghausen, with whom he published in 1886—87 researches on the Ettinghausen–Nernst effect, which is a potential difference established across the sides of a metal plate down which heat is flowing in a temperature gradient, when a magnetic field is applied perpendicular to the flow of heat. This effect forms part of the experimental foundation of the modern electronic theory of metals, according to which both thermal and electrical conduction are due to the motion of electrons. Those moving from the hotter part of the metal have higher velocities and are, in consequence, more deflected in the magnetic field than the slower electrons from the cooler part of the metal. Nernst dedicated his book, " Theoretical Chemistry," to von Ettinghausen, " in treuer Erinnerung an seine Lehr- und Wanderjahre." In Graz he also met Boltzmann and Arrhenius. He took his degree of Ph.D. in 1887 at Würzburg under Friedrich Kohlrausch, famous for his work on the electrical conductivities of salt solutions.

Nernst thus started as a physicist, and in his later work his approach to physical chemistry was through physics. He rarely used organic compounds in his work, one exception being in his investigations with Hohmann (1893) on the equilibrium between amylene (pentene) and trichloroacetic acid :

$$CCl_3{\cdot}CO_2H + C_5H_{10} \rightleftharpoons CCl_3{\cdot}CO_2C_5H_{11}$$

which, they showed, obeyed the law of mass action. Nernst's transition from physics to physical chemistry was mainly due to the influence of Ostwald, whom he joined as assistant in Leipzig in 1887. Ostwald was actively developing and expounding the new physical chemistry, founded on the gaseous theory of solutions stated by van't Hoff in 1886, and the theory of electrolytic dissociation proposed by Arrhenius in 1887. These, and the study of chemical statics and dynamics, formed a rapidly extending field of investigation, which Nernst entered with enthusiasm and effect. From the first he was a warm supporter of the ionic theory, and he and Ostwald described an experiment to demonstrate the existence of free ions by their motion in an electrostatic field.

Ostwald was becoming increasingly interested in the significance of energy in physico-chemical processes, which he developed along the lines of what he called (following Rankine) " energetics," and he emphasised the importance to chemistry of both laws of thermodynamics. Nernst had a very sound knowledge of thermodynamics, derived mainly from Helmholtz. He differed from Ostwald in emphasising the importance of the atomic and molecular theories, and the title of his text-book, " Theoretical Chemistry, from the Standpoint of Avogadro's Rule and Thermodynamics " (first published in 1893), expressed his attitude towards the two main foundations of the science. This book in its several editions and translations was widely used for many years. It is not an easy book, but any student who could make a way through its thirty chapters would emerge well equipped to begin research. Although he gave a good account of the phase rule in the book, Nernst thought its importance had been exaggerated, saying that " the molecular theory, the thermodynamics of incomplete equilibria, and above all

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the law of mass action, are points of view of immensely greater importance and much deeper content than the schemes of the phase rule, however useful and necessary this may sometimes be in chemical research "; and he quotes van't Hoff [1] to the same effect.

Nernst had a sound mathematical competence. In the second half of the nineteenth century, even the elements of the calculus were generally regarded by chemists as superfluous. This may be true in some branches of chemistry, but in physical chemistry the spirit and methods of mathematics are indispensable. In collaboration with Schoenflies, the mathematical crystallographer, Nernst published in 1895 a small book, "Einführung in die mathematische Behandlung der Naturwissenschaften," which reached an eleventh edition in 1931. He disliked unnecessarily complicated or lengthy mathematics, and in his text-book of theoretical chemistry many intermediate steps must be supplied by the reader. His concise style enabled him to cover a large field in the book and it shows a wide knowledge of the literature. It mentions Waterston's paper on the kinetic theory of gases, read to the Royal Society in 1845 but first published, at the instance of Lord Rayleigh, in 1892; and it summarises the memoir of Jellett, of Dublin, on the optical investigation of mass action, published in 1873, work which Nernst said was conducted with great experimental skill and led to important theoretical results. Jellett's memoir was edited by Nernst for Ostwald's *Klassiker.*

In 1890 Nernst went as assistant to Riecke, professor of physics in Göttingen, and he became assistant professor of physics in 1891. In 1892 he married Emma Lohmeyer, daughter of an eminent surgeon. Those who met Frau Nernst can testify to her sincerity and charm. He owed much to her steadfastness and devotion, and many of his students must remember with gratitude her kindness, and her understanding of the difficulties of young people transplanted into a strange environment.

Although he was invited to succeed Boltzmann in Munich, Nernst was faithful to Göttingen, where in 1894 he became the first professor of physical chemistry and was provided with an Institute, in which he soon built up an active school of research, especially in electrochemistry and chemical thermodynamics. Many of his students in Göttingen, who came from all parts, were afterwards leaders in physical chemistry. He became Geheimrat in 1904, but in that year he was called to succeed Hans Landolt as professor of physical chemistry in Berlin. In the Autumn of 1905 he took up his duties in the second Chemical Laboratory, which was renamed the Physico-Chemical Laboratory, in the Bunsenstrasse. Emil Fischer was in Berlin, and was perhaps the most outstanding and brilliant chemist of the time, yet the fame of Nernst drew to his laboratory a good share of research students, and his school maintained its place alongside that of the great master of organic chemistry.

It was in Berlin, in 1911—13, that I had the good fortune to work in Nernst's laboratory. The arrangements were rather primitive, and although the Steward, Woicke, was helpful, practically everything, even corks, had to be bought outside. Nernst came round and spoke to everybody daily, asking for details of progress, if any. He was a man rather under middle height, at that time inclined to plumpness, wearing *pince nez* and formal morning dress, looking like a banker or a high business executive, and with a quiet voice and manner.* The assistants, von Wartenberg, Eucken, von Siemens, and Koref, were highly skilled experimenters, and helpful with advice and suggestions. The students were cheerful and friendly, and there was an atmosphere of optimism and comradeship which helped to tide over the difficulties inseparable from research in physical chemistry. The Professor was a most skilful and resourceful experimenter, with a profound distrust of large, complicated, and expensive apparatus. Electrical conductivities were measured at room temperature, not in a thermostat, and temperature-coefficient corrections applied. Wire resistances were replaced by Magnanini liquid resistances. One had first to accept some old apparatus and make it work, then new apparatus was either provided or allowed to be made. Even the simplest apparatus had to perform accurately the task allotted to it. My apparatus was necessarily rather large, and when Nernst saw it set up he refused to speak to me for a day or two. When he saw that its size was unavoidable, he relented, and provided me with his own post-office box and a new string galvanometer.

The Institute in 1911 was supplied with liquid hydrogen by an apparatus of Nernst's invention, which was made and sold by the mechanic, Hoenow, for £20. Nernst was then trying, with the assistance of Dr. F. A. Lindemann (now Lord Cherwell) and his brother, C. Lindemann, to make liquid helium. One morning the precious stock of helium (obtained from pitchblende) was under compression when the apparatus burst. I saw Nernst spreading

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[1] See also *Naturwiss.*, 1939, **27**, 393.

* The portrait reproduced facing p. 2853 is from a photograph taken in 1904.

the sides of his coat over the compressor in a vain attempt to catch the escaping gas, and saying pitifully : " Das Helium ! Das Helium ! "

Nernst's lectures on physical chemistry, delivered from 3 to 5 o'clock in the afternoon, with a short break at 4, mostly followed his book, and were enlivened by good experiments, personal anecdotes, and interesting criticisms. I remember his saying that, although Thomsen read his thermometers through telescopes, Berthelot obtained better results by avoiding large errors and sparing unnecessary refinements. Nernst himself, in an early research, had corrected Thomsen's values for the heats of formation of mercury compounds by using as a calorimeter a beaker with the rim cut off, standing on corks inside another beaker, and a very accurate and carefully calibrated thermometer. The results removed an apparent discrepancy with the Helmholtz equation for the electromotive force of a galvanic cell. A course of popular lectures on modern atomistics which Nernst gave in my time were well attended and much appreciated by non-specialists.

Nernst was mechanically minded. He was one of the first to run a motor car in Göttingen. On the outbreak of war in 1914 he left for active service in his small car, and accompanied the German army through Belgium to the Marne. His two sons also left for the front, and neither returned. He was awarded the Iron Cross of the first and of the second class for bravery in face of the enemy, and also the Pour le Mérite, the highest civil award. It is said that Nernst had some share in the early stages of gas warfare, but the Memorial Lecture on Haber fixes the main responsibility for this beyond doubt.

Nernst was mainly instrumental, through his personal influence with Ernest Solvay, in the foundation of the Solvay Conferences, in which he participated with considerable effect. He was also largely responsible for the creation of the Kaiser Wilhelm Institutes, which played an important part in the development of German science and industry after the first World War.

Nernst remained at the Institute in the Bunsenstrasse until 1922, when he succeeded Warburg as President of the Physikalisch-Technisches Reichsanstalt. Here he probably felt less at home than in academic surroundings, and his stay was short. Nernst was a great admirer of Shakespeare, and it is said that in a conference concerned with naming units after appropriate persons, he proposed that the unit of rate of liquid flow should be called the falstaff. He left the Reichsanstalt in 1924 to succeed Rubens as professor of physics and Director of the Physical Laboratory, which post he held until his retirement in 1933. The rest of his life was spent on his country estate, Zibelle, in Muskau, Lausitz, now on the border of Silesia and Poland. There he followed his interests in agriculture, fishing, and shooting, and there he died on November 18th, 1941. His remains were afterwards reinterred in Göttingen.

Although associated with some of the outstanding theories in physical chemistry, Nernst was highly practical and inventive, and was much interested in the applications of science in industry and daily life. In 1897 he realised that the highest temperature attainable in the carbon-filament electric lamp was too low for efficiency, and he replaced the carbon by a rod of a mixture of zirconia and rare earths. This is non-conducting at room temperature and requires preliminary heating by a spiral of platinum wire enclosed in porcelain. When the glower lights up, the heater is cut out by an automatic switch. Another difficulty now enters, *viz.*, the progressive fall in resistance of the glower with rise of temperature, which would lead to excessive current. This was corrected by having in series with the glower a spiral of fine iron wire enclosed in a bulb of hydrogen at low pressure. Iron shows an abnormal rise of resistance at a dull red-heat, and keeps the overall resistance constant. The conductivity of the glower is electrolytic, the metals which tend to be liberated being reoxidised by the surrounding air. The lamp had an efficiency of about 1½ watts per candle power, compared with 4 watts for the carbon lamp. The Nernst lamp later gave way to the metal-filament lamp, with an efficiency of ½ watt per candle power, but fortunately he was able to derive a substantial benefit from his invention, selling his patents outright to the A.E.G. for the sum of a million marks. The firm had a high opinion of Nernst's business ability as well as of his scientific eminence, and he was offered a directorship.

Nernst was a joint inventor with Dolezalek of an improved quadrant electrometer; he invented and demonstrated an electrolytic phonograph, and described some experiments which threw doubt on the value of the process of drying peat by electroendosmosis.

The Neo-Bechstein piano, invented by Nernst about 1922, depended on the electronic amplification of the sound produced by a small instrument so as to give the effect of a grand piano. The idea is very characteristic of him, but the instrument was not then a commercial success.

Nernst was fond of travel and became personally acquanted with many of the scientists of Europe and the two Americas. He gave the Silliman Lectures at Yale University in 1906, the special University Lectures in London in 1913, and a course at La Plata. All these lectures were published. His last visit to England, to receive the honorary Doctor of Science of Oxford, was in 1937. He became an Honorary Member of the Royal Institution in 1899, Honorary Fellow of the Chemical Society in 1911, and Foreign Member of the Royal Society in 1932. He received the 1920 Nobel Prize for chemistry in 1921, and was Rector of the University of Berlin in 1921—22.

Nernst's outstanding characteristics were his directness of approach, his versatility, and his great receptivity for new ideas. Although his mind worked rapidly, he was most painstaking and patient, and would spend much time and effort in numerical calculations. His approach to theory was largely through numerical data, in which he took a great interest: he would arrange and classify them until they gave up some general law. His mental quickness could be disconcerting. In an informal lecture he might break in with questions, suggestions, and criticisms, which could put a less nimble wit out of its stride. He was never, in my experience, knowingly unkind in such cases, although he could be rather dogmatic. In taking up new theories, he liked to reshape them in his own way, leaving out the unessential parts and simplifying the rest.

I must now attempt to give some account of the main features of Nernst's scientific work. This covered many fields, but the main parts can be put under five heads: (1) electrochemistry; (2) the theory of solutions; (3) thermodynamics and chemical equilibria; (4) the solid state; (5) photochemistry. It should be realised that many publications by his students in their names alone embody some important ideas suggested by Nernst.

ELECTROCHEMISTRY

The theory of electrolytic dissociation, proposed by Arrhenius in 1887, when taken in conjunction with the earlier measurements by Hittorf and Kohlrausch of the mobilites of ions, gave a convincing picture of the mechanism of electrolytic conduction, but a large and important branch of electrochemistry still awaited theoretical explanation. This concerned the electromotive forces of galvanic cells. From the time of Volta, two apparently conflicting theories had divided the allegiance of electrochemists. Volta, Davy, and Berzelius supported the contact theory, which located the seat of the electromotive force at the contact of two different metals. The chemical theory, advocated by Faraday and by Auguste de la Rive, sought the origin of the electric current in the chemical reaction in the cell. About 1850, Helmholtz and Lord Kelvin recognised that the energy of the current is mainly supplied by the chemical energy of the reaction, but the exact way in which the potential difference comes into being was not clear, and experiments had shown that potential differences can arise between solutions of electrolytes of different concentrations or different compositions, when no metallic contacts or chemical action can intervene.

The solution of the problems was given by Nernst in publications[2] in 1888—89 on "the electromotive activity of ions" and, although his theories have been modified and extended, the daily work of practical electrochemists is still based on equations first obtained by him. Every pH measurement rests on them, and the determination of pH by indicators and the use of buffer solutions were developed at his suggestion in 1903.[3]

He began by applying Fick's general theory of diffusion to an electrolyte. In solutions of different concentrations in contact, the driving force on each ion was assumed to be proportional to the osmotic pressure gradient, $-\mathrm{d}p/\mathrm{d}x$. The moving ion experiences a large frictional resistance, which may be taken as the force required to move a g.-ion with unit velocity, the mobility U or V of the cation or anion being the reciprocal of this force, or the velocity per unit force. The diffusate in unit time is equal to the number of ions multiplied by the force on each and the speed with which it moves. For univalent ions of concentration c, the force per mole is $(1/c)(\mathrm{d}p/\mathrm{d}x)$, and the diffusates through a cross-section q due to the osmotic pressure gradient, in a time $\mathrm{d}t$, are:

$$-Uq(\mathrm{d}p/\mathrm{d}x)\mathrm{d}t \text{ and } -Vq(\mathrm{d}p/\mathrm{d}x)\mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The ions moving with different velocities for a very short time set up electrostatic forces which equalise the velocities, and if ϕ is the potential and $-\mathrm{d}\phi/\mathrm{d}x$ the potential gradient, the diffusates due to the electrostatic forces are:

$$-Ucq(\mathrm{d}\phi/\mathrm{d}x)\mathrm{d}t \text{ and } +Vcq(\mathrm{d}\phi/\mathrm{d}x)\mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[2] *Z. physikal. Chem.*, 1888, **2**, 613; 1889, **4**, 129.

[3] Salessky, *Z. Elektrochem.*, 1904, **10**, 204; Fels, *ibid.*, p. 208. The phosphate buffer was simultaneously used by Szily (see Friedenthal, *ibid.*, p. 113; Salm, *ibid.*, p. 341). The name pH for $-\log [\mathrm{H}^+]$ was proposed by Sörensen in 1909.

Since the ions now move with the same speed, the joint action of the osmotic pressure and potential gradients gives a diffusate :

$$\mathrm{d}S = -Uq\mathrm{d}t[\mathrm{d}p/\mathrm{d}x + c(\mathrm{d}\phi/\mathrm{d}x)] = -Vq\mathrm{d}t[(\mathrm{d}p/\mathrm{d}x) - c(\mathrm{d}\phi/\mathrm{d}x)] \quad . \quad . \quad . \quad (3)$$

By comparing this with Fick's law, containing the diffusion coefficient D :

$$\mathrm{d}S = -Dq(\mathrm{d}c/\mathrm{d}x)\mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

putting $p = c\boldsymbol{R}T$, and eliminating $\mathrm{d}\phi/\mathrm{d}x$, it follows that :

$$D = \boldsymbol{R}T \,.\, 2UV/(V + U) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By solving (3) for $\mathrm{d}\phi/\mathrm{d}x$:

$$\mathrm{d}\phi/\mathrm{d}x = (V - U)/(V + U) \,.\, (1/c)(\mathrm{d}p/\mathrm{d}x) = \boldsymbol{R}T(V - U)/(V + U) \,.\, (\mathrm{d}\ln c/\mathrm{d}x) \quad (6)$$

and by integration :

$$\phi_2 - \phi_1 = e = (V - U)/(V + U) \,.\, \boldsymbol{R}T \ln (c_2/c_1) \quad . \quad . \quad . \quad . \quad (7)$$

where e is the potential difference between the solutions ($c_2 > c_1$), the sign giving the charge on the concentrated solution. A simple thermodynamic deduction of (7) was also given by Nernst.

The case of solutions of different electrolytes was not worked out (it was treated later by Planck), but Nernst proposed a "principle of superposition," according to which the potential difference between two solutions depends only on the ratio of the concentrations, that between 0·01N-potassium chloride and 0·01N-hydrochloric acid being the same as that between 0·1N-potassium chloride and 0·1N-hydrochloric acid. All these results were confirmed by experiments. Nernst [4] pointed out that liquid contact potentials give an experimental proof of the existence of free ions in solutions.

Nernst later suggested [5] that a liquid contact potential could be eliminated by adding an indifferent electrolyte (potassium nitrate or acetate) at the same concentration on both sides, but Tower's method of the salt bridge [6] is the one now mostly used.

Nernst's theory of the production of galvanic current was developed as follows. Metals go into solution only as positive ions. The tendency of a metal to go into solution may be pictured as a "solution pressure," which is opposed by the osmotic pressure of its ions in the solution, tending to deposit them on the metal electrode. The solution acquires a positive and the metal a negative charge, and the equilibrium of the solution pressure and osmotic pressure corresponds with a potential difference e between the electrode and the solution. If the metal has a very small solution pressure, ions will be deposited on it from solution, giving the electrode a positive charge and leaving the solution negatively charged. If the solution pressure and osmotic pressure are equal, there is no tendency for metal to pass into solution or for ions to be deposited on the metal, and the potential difference e is zero.

Let A be the work gained when 1 electrochemical equivalent of electrode metal passes isothermally and reversibly into a solution of its ions of osmotic pressure p. The electrical work is :

$$A = e$$

If p becomes $p + \mathrm{d}p$, A becomes $A + \mathrm{d}A$, and e becomes $e + \mathrm{d}e$, and $\mathrm{d}A$ is the work done in bringing 1 electrochemical equivalent of ion from the pressure $p + \mathrm{d}p$ to the pressure p. This is $p\mathrm{d}v$, where $\mathrm{d}v$ is the increase in volume of the solution when $p + \mathrm{d}p$ changes to p. Hence :

$$\mathrm{d}e = p\mathrm{d}v = -(RT/p)\mathrm{d}p,$$

where $pv = RT$, R being the gas constant per electrochemical equivalent. By integration :

$$e = RT \ln (P/p) = RT \ln (C/c)$$

where $c = p/RT$ is the concentration, and P and C are integration constants. Since $e = 0$ when $p = P$, this is the solution pressure. If e_0 is the potential difference in a solution of unit concentration :

$$e = e_0 - RT \ln c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and if e_1 is the potential of a standard electrode and e' the contact potential between the two solutions, the electrode potential referred to the standard electrode is :

$$e = e_0 - (e_1 + e') - RT \ln c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Put $e_1 = 0$, then if e' is eliminated, the equation (8) is recovered. Nernst [7] in 1900 proposed to

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[4] *Chem. Zentr.*, 1890, **60**, 145.

[5] Bugarsky, *Z. anorg. Chem.*, 1897, **14**, 145.

[6] Tower, *Z. physikal. Chem.*, 1895, **18**, 17; 1896, **20**, 198; cf. Negbaur, *Ann. Physik*, 1894, **44**, 737.

[7] *Z. Elektrochem.*, 1900, **7**, 253.

take the hydrogen electrode as the standard electrode. With small adjustments by means of activities, these equations are still in use.

Others of Nernst's researches on electrochemistry are on decomposition potentials, the residual current, a theory of contact potentials, the theory of the lead accumulator, the determination of the ionic product of water by the acid–alkali cell, the electromotive activity and deposition of alloys, and the diffusion of electrolytically deposited hydrogen through platinum and palladium, and the proof that a palladium electrode becomes charged with hydrogen in a solution of a reducing agent, so behaving as a hydrogen electrode. He devised a simple apparatus for demonstrating the migration of a coloured ion in electrolysis by the moving-boundary method, and an apparatus for measuring transport numbers by the Hittorf method. He proposed [8] a method for measuring the hydration of ions from transport measurements in solutions containing an indifferent solute. A Wheatstone bridge with condensers in the ratio arms was used to measure the internal resistance of a cell.

Nernst's theory of the dropping mercury electrode was based on that of a concentration cell, and Palmaer proved experimentally that the mercury drops cause changes of concentration of mercury ions in solution. In a solution containing only a very small concentration of mercury ions, corresponding with the solution pressure, the dropping and the stationary mercury should have the same potential, and, by combining the stationary electrode with a calomel electrode, the potential of the latter could be found. Palmaer prepared such a solution, and found $+0{\cdot}52$ v for the absolute potential of the normal calomel electrode.

Nernst,[9] who was always receptive of new ideas and discoveries, used the atomistic theory of electricity, calling the unit charges positive and negative electrons, $\oplus$ and $\ominus$, which combine with atoms or radicals to form ions. The negative electron might exist momentarily free in solutions during such reversible changes as $Cl + Br^- \rightleftharpoons Cl^- + Br$. The positive electron would be isolated with difficulty, because of its great affinity for material particles. Nernst and Moers (1920) first recognised the existence of the negative hydrogen ion, H^-, and showed that hydrogen tends to move to the anode in the electrolysis of fused lithium hydride, Li^+H^-.

Nernst and Riesenfeld (1901) investigated the electrolytic phenomena at the boundary of two solvents, and Nernst (1908) proposed a quantitative theory of nerve stimulation. The electrical stimulus was assumed to depend on changes of concentration of an electrolyte at the boundary between protoplasm and the cell liquid, in which the ions have different mobilities. With alternating currents of high frequency and small intensity, the concentration changes are compensated by diffusion from the solution, and no physiological effect results. High-frequency currents are painless. With lower frequency and higher intensity, the concentration changes are appreciable and there is nerve stimulation. The equations were confirmed by experiments with frog muscle, the oldest detector of galvanic phenomena.

The Nernst method (1894) for measuring the dielectric constants of liquids by a Wheatstone bridge circuit with condensers in the bridge arms, the conductivity of the liquid being compensated, is a good example of his skill in devising apparatus, and has been largely used. He was the first to show,[10] in detail, that solvents of high dielectric constant should promote ionisation, this being independently but briefly stated soon afterwards by J. J. Thomson.[11] Nernst pointed out that solvents with great ionising power show a tendency to association, and emphasised that the dielectric constant is not the only property promoting ionisation, since there are specific influences, particularly the association of the ions with the solvent molecules, since ions have a great tendency to form co-ordination compounds. Nernst and Drude showed that an ionised solute causes a contraction of the solvent by electrostriction due to the charged ions, if the dielectric constant of the solvent increases with pressure.

THEORY OF SOLUTIONS

In his theoretical consideration of dilute solutions Nernst followed van't Hoff in starting with the osmotic pressure, pointing out that, although the thermodynamical investigations are all based on the calculation of the maximum work obtained by the addition of the solvent to a solution in various ways, the generalisation of Avogadro's rule by the analogy between gaseous and osmotic pressure provides a simple theoretical explanation of the properties of dilute solutions. His treatment of diffusion was based on osmotic pressure. He described a simple

[8] *Göttingen Nachr.*, 1900, 68, and papers following this.

[9] " Theoretische Chemie," 4th edn., 1903. The ideas are similar to those later proposed by Ramsay, *J.*, 1908, **93**, 774.

[10] *Göttingen Nachr.*, 1893, 491 (July); *Z. physikal. Chem.*, 1894, **13**, 531.

[11] *Phil. Mag.*, 1893, **36**, 313 (October).

apparatus for demonstrating osmotic pressure and worked out equations for the osmotic pressure in mixed solvents. With Abegg (1894) and with Hausrath (1905) he carried out precision measurements of the freezing points of solutions, the theory of the errors being developed. He pointed out that the method of producing constant temperatures by freezing salt solutions, published by T. W. Richards in 1903, had been published from Nernst's laboratory by Roloff in 1892. He developed the theory of the elevation of boiling point for a volatile solute, considered the determination of molecular weights in dilute solid solutions, and generalised the equations for hydrolysis.

Nernst was responsible for the theory of solubility product[12] (1889), which Ostwald showed in detail could provide a rational foundation for qualitative and quantitative analysis, and in 1891 he generalised the distribution law,[13] which Berthelot and Jungfleisch had found, in 1872, to apply to some solutes but not to others. Nernst showed that the discrepancies are due to the circumstance that the solute has different molecular weights in the two solvents. The results with benzoic acid agreed with the law if it was assumed to exist as double molecules in benzene but single molecules in water. He also took account of the depolymerisation equilibrium by applying the law of mass action. Roloff, at Nernst's suggestion, used the distribution law to demonstrate the presence of the ion Br_3^- in solutions of bromine in potassium bromide solution. Nernst showed that the molecular weight of a solute may be found from its effect in reducing the partial miscibility of ether and water, which may be followed by the freezing point.

The theory of the velocity of heterogeneous reactions developed by Nernst[14] (1904) assumed that equilibrium is practically instantaneously established at the boundary of two phases, and that the measured velocity is determined almost entirely by the rate at which the reactant diffuses to the interface. If the liquid is vigorously stirred, the solution has a constant composition outside a layer of thickness δ adhering to the solid. If a is the original concentration in the solution, the diffusate to the interface of area O in time $\mathrm{d}t$ is:

$$OD(a - x)\mathrm{d}t/\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where D is the diffusion coefficient. Boguski had found for the solution of marble in acid that the velocity is proportional to the concentration and surface:

$$\mathrm{d}x/\mathrm{dt} = kO(a - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and from (10) and (11):

$$k = D/\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Brunner found that the velocity of solution of magnesia is greater in acetic acid, which diffuses more rapidly, than in the stronger benzoic acid, and the phenomenon is essentially physical; it depends on the diffusion coefficient D, and the velocity cannot give an order of reaction. Although Nernst's theory does not hold for all heterogeneous reactions, it does seem to apply to the solution of metals in iodine solution and, whereas the results for the velocity of crystallisation from solutions were thought to be in disagreement with the theory, the latest experiments seem to support it.

Nernst attempted[15] (1901) to give a thermodynamic explanation of the failure of Ostwald's dilution law for strong electrolytes, but this difficult problem was solved only later, on the basis of the theory of interionic attraction. He was never convinced of the complete ionisation of electrolytes and some of his last work (1926—28), with Orthmann, on the heats of dilution of very dilute solutions of electrolytes, was interpreted as showing that there is a very small, practically negligible, un-ionised fraction in equilibrium with the ions according to the law of mass action.

Nernst emphasised that colloidal solutions resemble true solutions more than mechanical suspensions, since they have small but measurable diffusivities and freezing-point lowerings, and appreciable osmotic pressures, all methods giving high molecular weights of the same order. He took the side of Ehrlich in his controversy with Arrhenius, who had applied the law of mass action to the combination of toxins and antitoxins, which he regarded as reversible. Nernst considered (1904) that Arrhenius had mistaken very slow changes for equilibrium states. This led to some coolness between the two old friends, which seems to have been put right later. Although it belongs to a rather different field, Nernst's explanation[16] (1910) of the sharp clearing points of liquid crystals on the basis of an extension of Bose's swarm theory, makes use of the

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[12] *Z. physikal. Chem.*, 1889, **4**, 372.

[13] *Ibid.*, 1891, **8**, 110.

[14] *Ibid.*, 1904, **47**, 52.

[15] *Ibid.*, 1901, **38**, 487.

[16] *Z. Elektrochem.*, 1910, **16**, 702.

abnormal increase of vapour pressure of very small drops, and hence belongs to surface chemistry. This interesting contribution seems to be imperfectly known and is rarely mentioned.

THERMODYNAMICS

Nernst's approach to thermodynamics was a simplification of that of Helmholtz. Every spontaneous process when suitably performed can yield work, which is a maximum when the process is conducted reversibly. The second law shows that the maximum work of an isothermal process depends only on the initial and the final state. The work done in a reversible Carnot's cyclic process absorbing a finite amount of heat Q at an absolute temperature T is :

$$\mathrm{d}A = Q(\mathrm{d}T/T) \qquad (13)$$

where $T - \mathrm{d}T$ is the lower temperature in the cycle and Q is the latent heat absorbed in the change along the upper isotherm. Let the state of the system be defined by T and any number of variables x, such as volume, surface area, or quantity of electricity, such that if T changes but the x's are held constant no work is done; whilst if T is held constant and x changes by $\mathrm{d}x$ the work $\mathrm{d}A = X\mathrm{d}x$ is done, where X is a generalised force such as pressure, surface tension, or electromotive force. Clapeyron had shown (1834) that the area of a small Carnot cycle, representing the work done, is equal to the area of a cycle formed of the two isothermals and the verticals through x, the initial state, and $x + \mathrm{d}x$, the final state. Since the finite process involving the change of x by Δx and the absorption of Q is the sum of the upper isotherms of the infinitesimal cycles, equation (13) follows by summation, and applies to each species of x. This proof is strict, and is the most direct approach to the formulation.

If $-U$ is the increase of energy in the change along the isotherm T, the first law gives :

$$Q = A - U \qquad (14)$$

and (13) and (14) give :

$$A - U = T\,\mathrm{d}A/\mathrm{d}T \qquad (15)$$

Equation (15) was extensively used by Nernst. It was first deduced in 1855 by Lord Kelvin,[17] and was used in chemical investigations by Horstmann in 1872. It was derived again by Helmholtz in 1882, who denoted A by F and called it free energy. As far as I know, it was never stated or used by Gibbs, although it is sometimes misnamed "the Gibbs–Helmholtz equation." Nernst attached importance, with stated reasons, to the symbols and signs in his equations; he was familiar with thermodynamic methods using entropy and chemical potentials, and often restated the results in terms of these functions, at the same time very properly pointing out that they bring nothing fundamentally new into the calculations. Beginners may find it easier to work with the symbol Δ for finite increments, but Nernst was more in sympathy with the practical electricians, who use Ohm's law in the form $C = E/R$, never symbolise E as a potential difference, and acquire facility in adapting this simple equation to complicated special cases. It will be seen presently that Nernst's formulation leads very directly to his new Heat Theorem.

Lord Kelvin in 1852 had pointed out that every spontaneous change decreases the free energy of a system, and Lord Rayleigh in 1875, and Helmholtz in 1882, applied this principle to chemical reactions. Since a chemical reaction proceeds in the direction of the affinity, the maximum work or decrease of free energy A may be taken as a measure of the affinity.

Helmholtz in 1847, and Lord Kelvin in 1850, had equated the electrical work of a galvanic cell to the heat of reaction, which amounts to equating A to U, and Julius Thomsen in 1853, and Berthelot in 1864, had proposed that the heat of reaction should be taken as a measure of the affinity in a chemical change. Thomsen said :

> "Every simple or complex action of a purely chemical nature is accompanied by an evolution of heat,"

and Berthelot that :

> "Every chemical reaction capable of accomplishment without the intervention of preliminary work, and apart from the intervention of energy foreign to the bodies present in the system, is necessarily produced if it evolves heat."

In a later statement of this *principe du travail maximum*,[18] Berthelot limited its application to reactions between solids, in which case it is approximately correct, and said that it would be

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[17] *Quart. J. Math.*, 1857, **1**, 57 (dated 1855); *Proc. Roy. Soc. Edin.*, 1898, **22**, 126 (deduction without the use of entropy).

[18] "Thermochimie," Paris, 1897, Vol. I, p. 10 *et seq.* At that time the position had been clarified by the publications of Helmholtz.

more exact at low temperatures. Since he defines " chemical heat," to which the principle applies, as that transformable into work, it is really free energy, and the name *travail maximum* was also significant.

Equation (15) shows that the equation :

$$A = U \qquad (16)$$

which is equivalent to the Thomsen–Berthelot principle, can, if dA/dT remains finite, be symbolically true only at the absolute zero, $T = 0°$, and Ostwald emphasised that the Thomsen–Berthelot principle cannot be a general law. In the early editions of his text-book Nernst had pointed out that, however true this algebra may be, in many cases the direction of reaction does coincide with evolution of heat, and that a law which holds in many cases, but fails in a few cases, is likely to contain some undiscovered truth. In 1907 he said :[19]

> " A long study of this relation in the past has led me to the hypothesis that *we are dealing with a law more or less approximate at ordinary temperatures, but true in the neighbourhood of the absolute zero.*"

He observed that equation (16) follows from (15) also if $dA/dT = 0$ whilst T is finite. In 1894 he had found this relation to hold very nearly for the maximum work of dilution of concentrated solutions of sulphuric acid, whilst with dilute solutions A and U are very different. The generalisation of this result, read to the Göttingen Academy on December 23rd, 1905, and published in 1906, is Nernst's new Heat Theorem, sometimes called (and by Nernst himself) the Third Law of Thermodynamics. It states that for reactions between pure solids or liquids, *i.e.*, in condensed systems :

$$\text{Lim}\ (dA/dT) = 0 \text{ as } T \longrightarrow 0 \qquad (17)$$

He first stated this in the form :

$$\text{Lim}\ (dA/dT) = \text{Lim}\ (dU/dT) = 0 \text{ as } T \longrightarrow 0 \qquad (18)$$

so that the curves representing A and U as functions of T approach and coalesce to a horizontal line from some finite temperature above the absolute zero, the distance from the absolute zero varying for different systems. It is easy to show that (18) is a necessary consequence of (17). From (14) and (15) :

$$dA/dT = Q/T = \Delta S \qquad (19)$$

where ΔS is the increase of entropy, hence (17) may be formulated :

$$\text{Lim}\ \Delta S = 0 \text{ as } T \longrightarrow 0 \qquad (20)$$

Kirchhoff in 1858 had shown that :

$$dU/dT = H_v - h_v \qquad (21)$$

where H_v and h_v are the heat capacities at constant volume of the initial and final systems, and hence (21) implies that Joule's extension of the law of Dulong and Petit (that the molecular heat of a solid compound is the sum of the atomic heats) is exactly true at the absolute zero. Planck in 1911 pointed out that (20) is identically true if :

$$\text{Lim}\ S = 0 \text{ as } T \longrightarrow 0 \qquad (22)$$

for each reacting solid separately, and since from thermodynamics :

$$T(dS/dT)_v = c_v \qquad (23)$$

c_v being the specific heat at constant volume, then :

$$\text{Lim}\ c_v = 0 \text{ as } T \longrightarrow 0 \qquad (24)$$

This remarkable result was first verified experimentally by Nernst with diamond, as is mentioned later.

In 1912 Nernst showed that the third law can be deduced from the assumption that a body cannot be cooled to the absolute zero by any finite process, but since Einstein was at first unable to accept this deduction it would seem preferable to retain the usual forms (17) or (18).

In his first publication of the Heat Theorem, Nernst expressed U in the form :

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \cdots \qquad (25)$$

pointing out that, however common it is for mathematicians to use such power series, this may not be the correct form. From 18 and (21) it follows that $\alpha = 0$, and :

$$U = U_0 + \beta T^2 + \gamma T^3 \qquad (26)$$

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[19] " Experimental and Theoretical Applications of Thermodynamics to Chemistry," 1907, 45 (italics in original).

If (15) is written in the form :

$$d(A/T)/dT = -U/T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

and U substituted from (26), it follows that :

$$d(A/T)/dT = -U_0/T^2 - \beta - \gamma T$$

and by integration :

$$A = U_0 - \beta T^2 - \tfrac{1}{2}\gamma T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

the integration constant, from (17), being zero. The two equations (26) and (28) express the consequences of the Heat Theorem for condensed reactions on the basis of equation (25). The integral of the general equation (27) may be written :

$$A = T\int(U/T^2)dT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

with no integration constant, and any suitable temperature function can replace (25), as was later done when specific heats were represented by the quantum theory. Nothing fundamentally new from the point of view of the Heat Theorem results from this procedure.

Nernst pointed out that Bodländer, following his suggestion, had calculated the solubilities of salts from the heats of formation and the electrolytic decomposition potentials of compounds (*e.g.*, silver iodide) giving solid products. Equation (28) was applied to the calculation of the transition point of sulphur, the dissociation pressures of hydrates, and the electromotive forces of some cells. At the time when it was proposed there was very little quantitative information which could be used as a test of the validity of the Heat Theorem. In the case of the Clark cell, operating at the cryohydric point (when the cell reaction occurs between pure substances), the A and U curves merge into a horizontal line at 150° K, and the Heat Theorem was shown to apply at such quite high temperatures in other condensed reactions. The approximate validity of the Thomsen–Berthelot principle was thus explained. It should not be supposed, however, that (28) is equivalent to (16), since for the reaction :

$$K_4Fe(CN)_6,3H_2O = K_4Fe(CN)_6 + 3H_2O(\text{ice})$$

the A curve rises steadily from 0° K, whilst the U curve sinks, cuts the temperature axis at about 160° K, and then changes in sign, thus contradicting (16).

The equations so far obtained do not apply to gas reactions or reactions in solutions, for which A and U are often widely different. Nernst in 1905 showed, however, that the Heat Theorem can be applied to gas reactions if these are supposed to take place between the vapours of the reacting substances in the solid state at low temperatures, the final equation for the gas reaction being true at any temperature. The deduction was based on equations (26) and (28) and, although it is easily generalised,* I will give it in the original form.

Consider the gas reaction :

$$CO + H_2O = CO_2 + H_2$$

Let C_{CO} etc. be the actual concentrations of the reacting gases, c_{CO} etc. their equilibrium concentrations, $K = c_{CO_2} \times c_{H_2}/c_{CO} \times c_{H_2O}$ the equilibrium constant, U the heat of reaction (evolved), and A the maximum work. Van't Hoff had shown that :

$$A = \boldsymbol{R}T \ln \frac{C_{CO} \times C_{H_2O}}{C_{CO_2} \times C_{H_2}} + \boldsymbol{R}T \ln K \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

an equation often called the reaction isotherm. Differentiation of (30) and substitution in (15) gives :

$$-U = \boldsymbol{R}T^2 \frac{d \ln K}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

an equation also found by van't Hoff, and often called the reaction isochore. With U from (25)—for a gas reaction α is not zero—(31) gives on integration :

$$\ln K = \frac{U_0}{\boldsymbol{R}T} - \frac{\alpha}{\boldsymbol{R}} \ln T - \frac{\beta}{\boldsymbol{R}} T - \frac{\gamma}{2\boldsymbol{R}} T^2 + I \quad . \quad . \quad . \quad . \quad . \quad (32)$$

If the integration constant I were known, K, and hence from (30) A, could be calculated, but I cannot be found from the two laws of classical thermodynamics. It can be found from the Nernst Heat Theorem as follows. If all the reacting substances are present as pure solids the Clapeyron–Clausius equation gives for the pressure of the saturated vapour (assumed to be an ideal gas) :

$$d \ln p/dT = \lambda/\boldsymbol{R}T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

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* See, *e.g.*, Partington, " A Text-Book of Thermodynamics," Constable, London, 1913, p. 491, using chemical potentials and equation (29).

where λ is the molar heat of sublimation, which may be expressed in the form:

$$\lambda = \lambda_0 + \alpha_0 T + \beta_0 T^2 + \gamma_0 T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

From (33) and (34), by integration:

$$\ln p = -\frac{\lambda_0}{\boldsymbol{R}T} + \frac{\alpha_0}{\boldsymbol{R}} \ln T + \frac{\beta_0}{\boldsymbol{R}} T + \frac{\gamma_0}{2\boldsymbol{R}} T^2 + i' \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where i' is the integration constant. If C is the concentration, $p = C\boldsymbol{R}T$, and:

$$\ln C = -\frac{\lambda_0}{\boldsymbol{R}T} + \left(\frac{\alpha_0}{\boldsymbol{R}} - 1\right) \ln T + \frac{\beta_0}{\boldsymbol{R}} T + \frac{\gamma_0}{2\boldsymbol{R}} T^2 + i \quad . \quad . \quad . \quad . \quad (36)$$

where $i = i' - \ln \boldsymbol{R}$ is a constant depending only on the chemical composition of the substance, and called by Nernst the *chemical constant.* The value of C given by (36) and that of K given by (32) are substituted in (30) and, since the reaction is ultimately one between pure solids, (28) shows that the coefficient of T in the resulting equation is zero. This gives:

$$I = \Sigma n_1 i_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where n_1 is the number of molecules of a reacting substance, and hence the value of I in (32) is known. The case of a heterogeneous reaction follows as usual, the values of c and i vanishing for every solid phase, but the heat of reaction U being that of the complete reaction.

In 1907 Nernst[20] drew attention to some earlier publications of interest. Le Chatelier[21] in 1888, in considering equation (32), had said:

> "It is very probable that the constant of integration [*i.e.*, I], like the coefficients of the differential equation [*i.e.* (31)] is a definite function of certain physical properties of the reacting substances. The determination of the nature of this function would lead to a complete knowledge of the laws of equilibrium. It would make it possible to determine *a priori*, independently of any new experimental data, the complete conditions of equilibrium corresponding with any given chemical reaction. The exact nature of this constant has, up to the present, not been determined."

Le Chatelier drew attention to the importance of specific heats and vapour pressures in relation to the equilibrium constant, but added that he had not discovered the relation in question.

T. W. Richards,[22] in what Nernst calls "a very interesting paper" of 1902 on "the relation of changing heat capacity to change of free energy, heat of reaction, change of volume and chemical affinity," drew attention to the relation between the sign and value of $A - U$ and the change of heat capacity ($H_v - h_v$) in a chemical reaction, giving some diagrams for galvanic cells showing the coalescence of the curves of A and U as functions of temperature into horizontal lines below −200° c (the very low temperature is noteworthy). He says, however, that this is "a necessary consequence of the equation of Helmholtz" (*i.e.*, Kelvin's equation 15), in which $A = U$ when $T = 0$. He does not give anything equivalent to equation (18), saying that:

> "On the basis of the present data it is impossible to attempt to calculate the mathematical relation of $\partial U/\partial T$ to $\partial A/\partial T$, or to probe further into the mechanism of the change. When more exact data have been obtained, it may be possible to arrive at more definite conclusions."

Richards at that time reached the conclusion that:

> "In a reaction from which concentration effects have been eliminated, when the total heat capacity remains constant during the reaction, the change of free energy and the heat evolved are constant."

Equation (21) shows that this is equivalent to $\mathrm{d}U/\mathrm{d}T = 0$, but Richards does not draw attention to this and his paper is quite difficult to follow. A study of it by van't Hoff[23] in 1904 led to a result very different from (18). Eight years after Nernst's publication of the Heat Theorem, Richards[24] claimed that it had been anticipated in his paper of 1902, saying that:

> "All these ideas were afterwards (1906) adopted unchanged by Nernst in his development of the 'Wärmetheorem' usually named after him."

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[20] "Experimental and Theoretical Applications of Thermodynamics to Chemistry," New York, 1907, p. 54.

[21] Recherches expérimentales et théoriques sur les équilibres chimiques, *Ann. Mines*, 1888, **13**, 336, 356.

[22] *Proc. Amer. Acad.*, 1902, **38**, 293.

[23] Boltzmann Festschrift, 1904, 232.

[24] *J. Amer. Chem. Soc.*, 1914, **36**, 2433.

Nernst,[25] who drew attention to his reference to Richards in 1907, which he thought would "avoid superfluous polemics," now felt obliged to "refute the claim made by Richards to my Heat Theorem," which he did in an objective and decisive way; he showed that the results given by Richards would not hold if the U curve has a maximum or a minimum, which in many cases it has. G. N. Lewis,[26] perhaps the most brilliant pupil of Richards, later said very fairly and correctly that :

> "The curves presented by Richards very nearly imply the generalizations which were later embodied in the third law of thermodynamics."

Nernst had also, in 1907, referred to what he calls "the remarkable book" by Haber, pointing out that Haber's equations differ from his. In the English translation of his book,[27] Haber supplied a clear account of the Nernst Heat Theorem, said the conclusions he had drawn from Richards's paper were incompatible with it, and made no claim to have anticipated it. I believe that no valid doubt exists of Nernst's originality and priority in the statement of the new thermodynamic principle.

The values of the chemical constants i may be calculated by means of equations (35) and (36) from the vapour pressure curves, suitably corrected for deviations from the ideal gas state. Since data were mostly lacking at the time, Nernst used some ingenious empirical results. He assumed that : (i) for a gas containing m atoms in the molecule the molar heat C_p near the absolute zero is $3{\cdot}5 + 1{\cdot}5m$; (ii) the atomic heat of a solid element at absolute zero is much lower than the Dulong and Petit value, and may be taken as 1·5, but may be zero; (iii) for evaporation, Young's results give the empirical equation :

$$p(v_g - v_l) = \boldsymbol{R}T(1 - p/p_c),$$

where v_g and v_l are the molar volumes of the vapour and liquid and p_c the critical pressure; (iv) the heat of evaporation is expressible in the form :

$$\lambda = (\lambda_0 + 3{\cdot}5T - \varepsilon T^2)(1 - p/p_c)$$

where ε is a constant. The Clapeyron–Clausius equation (33) then gives :

$$\ln p = -\frac{\lambda_0}{\boldsymbol{R}T} + \frac{3{\cdot}5}{\boldsymbol{R}}\ln T - \frac{\varepsilon}{\boldsymbol{R}}T + i'$$

Therefore,

$$(i + \ln \boldsymbol{R})/2{\cdot}3023 = \lambda_0/4{\cdot}571T - 1{\cdot}75\log T + (\varepsilon/4{\cdot}571)T + \log p = C$$

where C is a "conventional chemical constant." For all substances except hydrogen and helium, C may be taken as approximately 3, for hydrogen and helium it is approximately 1·5. For a gas reaction, if ν is the excess of the number of molecules of the reacting species over the number of molecules of the products, then :

$$n_1\mathrm{A}_1 + n_2\mathrm{A}_2 + \cdots = n_1'\mathrm{A}_1' + \cdots; \ (n_1 + n_2 + \cdots) - (n_1' + \cdots) = \nu,$$

and if an equilibrium constant is expressed in terms of partial pressures :

$$K' = p_1^{n_1}p_2^{n_2}\cdots/p_1'^{n_1'}\cdots = (\boldsymbol{R}T)^{\nu}/K$$

where K is the equilibrium constant defined as in (30), then :

$$\ln K' = -Q_0/4{\cdot}571T + 1{\cdot}75\nu\log T + (\beta/4{\cdot}571)T + \Sigma n_1C_1$$

where

$$Q = Q_0 + 3{\cdot}5\nu T + \beta T^2$$

is the heat of reaction (evolved) at constant pressure. This equation was used in many interesting calculations. In many cases the term $(\beta/4{\cdot}571)T$ may be neglected and results of significance can then be obtained when full experimental data are unknown. Nernst found some empirical equations for C, *viz.* :

$$C = 1{\cdot}1a = 0{\cdot}14(\lambda/T_b),$$

where a is the constant of the van der Waals vapour-pressure equation :

$$\log(p/p_c) = a(T_c/T - 1)$$

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[25] "The New Heat Theorem," 1926, p. 228.

[26] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," New York, 1923, p. 437.

[27] "Thermodynamics of Technical Gas Reactions," transl. by A. B. Lamb (from the German edition of 1905), 1908; in "The New Heat Theorem," 1923, p. 227, Nernst calls this an "excellent book."

and λ/T_b is the Trouton coefficient. He showed that the Trouton coefficient is not a true constant, but for substances of low and high boiling point is given by:

$$\lambda/T_b = 9{\cdot}5 \log T_b - 0{\cdot}007T_b$$

Over a restricted range of temperature a similar relation applies to reactions of dissociation in condensed systems, where if T_1 is the temperature at which the dissociation pressure is atmospheric:

$$Q_p/T_1 = \text{const.} = 34$$

a result found empirically by Matignon (1899).

A number of interesting calculations showed that the above equations could give very useful information in many regions, and when experimental data were available, quite good agreement was found with the calculations. Many of the data needed, such as the specific heats of gases and of solids at high and low temperatures, vapour pressures at low temperatures, equilibrium constants of homogeneous and heterogeneous reactions (especially at high temperatures), and electromotive forces, were then unknown.

While still in Göttingen Nernst had begun work on gaseous equilibria at high temperatures. This work was in a sense an outcome of the Nernst lamp. The proceeds from this, mentioned on p. 2855, enabled Nernst to become a pioneer motorist. This aroused his interest in the chemical reactions in the internal combustion engine. The early work of Ste. Claire Deville had shown that the reactions $2H_2 + O_2 \rightleftharpoons 2H_2O$ and $2CO + O_2 \rightleftharpoons 2CO_2$ are incomplete at high temperatures and reach equilibria. In 1903 Nernst had made use of a cylinder of nitrous oxide to enrich the explosive mixture in the engine cylinders and thence to obtain increased power on hill climbs, and very soon he took up in Göttingen the study of the steam and carbon dioxide equilibria at high temperatures, very ingenious experimental methods being applied in association with von Wartenberg. The results of this work and other investigations of equilibria at high temperatures made in Berlin were at the time very significant and valuable, and provided new data in chemical thermodynamics.

The physical chemist is at some disadvantage, compared with the organic chemist, since new compounds remain, but new measurements soon give way to newer, and sometimes better, ones. The pioneering investigations are soon forgotten, and results which in their time were highly important and significant are amplified and revised by later workers, who not infrequently reap the benefit of newer techniques which make their task much easier than that of the earlier pioneer experimenters, whose contributions to science tend to be overlooked. In fairness to Nernst and his associates, it should be emphasised that they enriched chemical thermodynamics with a substantial fund of new data of a kind then almost completely lacking. It will be possible only to mention some of this work in outline.

Vapour densitities were measured in a small iridium Victor Meyer apparatus heated in an iridium tube furnace to over 2000° c, quantities of about 0·001 mg. being weighed in an ingenious microbalance devised by Nernst. The principle of Deville's hot and cold tube was used to measure the dissociation of steam and carbon dioxide, and the velocity of formation and decomposition of nitric oxide. Dissociation was measured by heating a platinum wire in steam, and heating hydrogen sulphide in a platinum bulb, through which the hydrogen diffused. This work was done in collaboration with von Wartenberg, Löwenstein, Preuner, Jellinek, and Langmuir. The explosion-pressure method was used in a much improved form by Pier, Bjerrum, and Siegel to measure the dissociation and mean specific heats of gases at high temperatures. Nernst (1904) pointed out that the dissociation of a gas could be measured from the abnormal increase in thermal conductivity with temperature. Langmuir afterwards discovered atomic hydrogen by this method. From the results for the dissociation of steam, Nernst and von Wartenberg calculated the electromotive force of the Groves gas battery, in which hydrogen and oxygen are in contact with platinum electrodes in aqueous solutions, finding 1·232 v at 17°. The observed value is 1·15 v, but this is really the potential of an oxide of platinum. Brönsted measured the electromotive force of the cell $Pt,H_2/NaOH$ aq./HgO,Hg and by calculating the oxygen pressure by extrapolation of the dissociation pressures of mercuric oxide at higher temperatures, calculated the electromotive force at 17° for hydrogen and oxygen at atmospheric pressure as 1·234 v, in good agreement with that calculated by Nernst and von Wartenberg.

The high-temperature equilibrium work involved the use of optical pyrometry and the technique of this was carefully studied. By combining results from such measurements with those found from electromotive forces, many other equilibrium constants, such as that of the

Deacon process, could be calculated. Only one investigation, that of the synthetic-ammonia equilibrium, will be mentioned, on account of its historical interest.

In 1905 Haber and van Oordt had measured the yields of ammonia at atmospheric pressure, but these are so small that a good result could hardly be expected. Nernst found that they were not in agreement with those calculated from the Heat Theorem, and he began work on ammonia synthesis. To obtain higher yields and greater velocities, he worked under pressure, up to about 50 atm., using glass tubes. This work, by Nernst and his pupils Jellinek and Jost, was the first carried out for the reaction under pressure, and the first to give reasonably accurate results. The results differed appreciably from those found by Haber and van Oordt, and in 1906 Nernst, informing Haber of this, suggested that he should make experiments at higher pressures. For some reason, Haber was disinclined to accept this suggestion, and in 1907, in a discussion of Nernst's paper, he maintained this attitude, at the same time clearly if not openly implying that Nernst's method was faulty and that his results were inaccurate. Newer measurements with Le Rossignol had, he said, given results closer to Nernst's but still different from them. They were still based on work at atmospheric pressure, with indicators to detect the small traces of ammonia formed. The conclusion of the discussion by Nernst [28] is quite objective, even if rather sharply worded. He had a great admiration for Haber's work, which he more than once put on record, but he always reacted sharply to adverse criticism of the accuracy of his own, particularly if it was not supported by experiments made under the same conditions as he had used. It was not until 1908 that Le Rossignol, in Haber's laboratory, reported measurements made under pressure. The later history of ammonia synthesis does not concern us, but it may be mentioned that the earlier values of the heat of reaction and the specific heats were later found to be incorrect and, on the theoretical side, the then unknown existence of ortho- and para-hydrogen introduces a complication into calculations of equilibria involving hydrogen. Nernst gave a favourable report on Haber's patents concerned with the catalyst to the Badische Anilin A.-G. but he did not patent his own contribution of the use of high pressures, since he was assured by Duisberg that the use of such pressures was impossible in technical practice. The difficulties were, in fact, afterwards overcome by Bosch, and this unexpected development very naturally caused Nernst some annoyance.

In 1905 my teacher, Professor H. B. Dixon, read to the German Chemical Society an account of what Nernst called his " outstanding experimental researches " on the detonation wave. In a lecture in that year, and in a pamphlet on the internal combustion engine, Nernst gave a clear account of this work, suggesting, however, that Dixon's molecular theory could be replaced by one based on hydrodynamics. The theory of the detonation wave, involving discontinuities in the solution of the differential equations, had proved to be very difficult, but the notable theoretical investigations of D. L. Chapman,[29] undertaken at Dixon's suggestion, were later extended by R. Becker,[30] who gave a satisfactory account of the phenomena on the lines of hydrodynamics, as suggested by Nernst, pointing out, however, that Dixon's fundamental idea that the molecules on the hot side of the wave front shoot into the unburnt gas, and by their collision with cold molecules bring these immediately into chemical reaction, is essentially correct.

Nernst also initiated some experiments on the ignition points of gases by adiabatic compression, but the results found by Falk [31] in his laboratory were shown by Dixon and by Tizard to be vitiated by pre-flame combustion whilst the gases are being compressed, and the conclusion that the mixture $H_2 + O_2$ has the lowest ignition temperature is incorrect. This was later confirmed in Nernst's laboratory by Cassel.[32]

It remains to say something about the Nernst Heat Theorem (the third law of thermodynamics) in relation to the two older laws. Maxwell had pointed out that the first law of thermodynamics, the law of conservation of energy, seemed to hold without exception, whilst the second law would fail in principle if heat is resolved into molecular motion, since if individual molecules are considered, processes violating the second law are easily imagined. Nowadays, the measured change of mass with velocity of particles accelerated in the cyclotron suggests that the laws of conservation of mass and energy do not hold separately, but survive only in a combined form. The second law of thermodynamics, on the other hand, seems to have

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[28] *Z. Elektrochem.*, 1907, **13**, 521; " Theoretical Chemistry," 1923, 758; " The New Heat Theorem," 1926, 274.

[29] *Phil. Mag.*, 1899, **47**, 90.

[30] *Z. Physik*, 1922, **8**, 321.

[31] *J. Amer. Chem. Soc.*, 1906, **28**, 1517.

[32] *Ann. Physik*, 1916, **51**, 685; when Cassel began his work he was unaware of Dixon's results, which I mentioned to him.

maintained its integrity in all experimentally attainable conditions. The third law, like the second, rests on a statistical basis, applying to a large number of individuals, but cases in which it fails, small in number, are experimentally realisable.

In solid carbon monoxide and nitrous oxide near the absolute zero, the molecules are not all aligned in the same way and do not, in a reasonable time, take up a position of maximum order, all pointing in the same direction. The solids have, therefore, a positive residual entropy. Solid hydrogen, again, is a mixture of ortho- and para-hydrogen, the transition into para-hydrogen being incomplete. Some have thought that the third law should be limited to perfect crystals, but it seems that the only sure criterion of a perfect crystal is that it follows the third law, and Nernst always maintained that the law applies to liquids. According to Mayer and Mayer,[33] the most general statement of the third law (if such is possible) is of no great interest or value to an experimenter; if there is a zero-point entropy it is impossible to give general directions for its experimental determination; and whatever difficulties there may be in giving at the same time a strict and also experimentally useful statement of the third law, its value must not be underestimated.

Some experiments by Gibson and Giauque,[34] often quoted as indicating a failure of the Nernst Heat Theorem, are in reality indecisive. They were supposed to indicate a finite entropy for a glassy solid at the absolute zero, but this does not follow from them except by an inadmissible extrapolation, and the suggestion made by Simon [35] (who at that time was working in Nernst's former laboratory in Berlin), that specific-heat measurements made rapidly in an ordinary vacuum-calorimeter are vitiated by a very slow adjustment of the glass to an equilibrium state, has been shown to be correct.

The chemical constant i was calculated for a monatomic gas from statistical principles by Sackur (1911—13) and Tetrode (1912) by the equation :

$$i = \ln (2\pi \boldsymbol{m})^{3/2} \boldsymbol{k}^{5/2}/\boldsymbol{h}^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where $\boldsymbol{m}$ is the mass of the atom, $\boldsymbol{k}$ is Boltzmann's constant, and $\boldsymbol{h}$ is Planck's constant. Nernst found fairly good agreement of this equation with the values of i obtained from vapour-pressure measurements with mercury and argon, but in other cases there was disagreement. It is now known that the expression after the logarithm should be multiplied by a statistical weight g, which is unity for argon and mercury, and also zinc vapour, but 2 for sodium, potassium, and thallium vapours, and this was confirmed experimentally by Egerton. A supposed difference between chemical constants found from vapour pressures and those calculated from equilibrium measurements, suggested by Eucken, was afterwards shown to be due to experimental errors.

In modern thermodynamics little use is made of chemical constants. The entropy is calculated from heat capacities and other thermal data by well-known methods and, since it is related to the maximum work and heat of reaction by the equations (15) and (19), *viz.* :

$$A - U = T(\mathrm{d}A/\mathrm{d}T), \text{ and } \mathrm{d}A/\mathrm{d}T = Q/T = \Delta S$$

It follows that :

$$A = U + T\Delta S,$$

and, when A is known, the equilibrium constant can be calculated by van't Hoff's equation (30). Such calculations are superior to Nernst's method when experimental data are available, but they are, of course, only another way of using the Nernst Heat Theorem, and have no theoretical basis apart from it. They offer nothing fundamentally new but are, as it were, a praiseworthy improved method of book-keeping. They require experimentally determined specific heats at very low temperatures, and in this field Nernst was also a pioneer.

THE SOLID STATE

The experiments of Tilden and Dewar had shown that atomic heats fall notably below the Dulong and Petit value at the temperatures of liquid air and liquid hydrogen, but they gave only mean values over a large range of temperature. Nernst, Koref, and Lindemann (1910) * greatly improved the experimental method by introducing a new calorimeter, which consisted of a copper block inside a Dewar vessel. The block was provided with thermocouples and the substance, contained in a silver vessel and strongly cooled, was dropped into a cavity in the

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[33] " Statistical Mechanics," New York, 1940, p. 103. Older opinions, such as that of Fowler and Stern, *Rev. Mod. Phys.*, 1932, **4**, 707, must now be regarded as untenable.

[34] *J. Amer. Chem. Soc.*, 1923, **45**, 93.

[35] *Z. anorg. Chem.*, 1931, **203**, 219; Obald and Newton, *J. Amer. Chem. Soc.*, 1937, **59**, 2495.

* A summary of the work described in this section, with references to publications, is given in Nernst's book, " The New Heat Theorem," 1926.

block. This apparatus gave a mean specific heat over an interval of temperature. A new vacuum-calorimeter, developed by Nernst and Eucken, consisted of a metal cylinder, or a sealed metal canister, containing the substance with some air or hydrogen (a good conductor of heat) and wrapped with a spiral of platinum or lead wire to serve at the same time as a heater and as a resistance thermometer. The unit was suspended by fine leading wires inside a glass jacket containing hydrogen and immersed in liquid air or liquid hydrogen, which could be boiled under low pressure. When the block had cooled to the temperature of the bath, the hydrogen gas was pumped out so as to establish a good vacuum. A measured amount of electrical energy was supplied to the spiral of wire and the rise in temperature measured. This gave the true specific heat over a small interval of temperature. Nernst and Schwers also used a copper canister with a thermocouple having one junction in a block of lead, the temperature of which remained nearly constant. Much work was carried out on the methods of temperature measurement. The vacuum-calorimeter has been improved and is now extensively used in low-temperature work.

Nernst's results showed that with some solids, such as lead, the specific heat falls only slowly with temperature until very low temperatures are reached, whilst with others, such as copper and aluminium, the specific heat falls more rapidly. In the case of diamond, the atomic heat of which is notably below the Dulong and Petit value of 6 g.-cal. at room temperature, the atomic heat fell to zero at 50° K. Nernst, with F. A. Lindemann (now Lord Cherwell) and Koref, made many measurements of specific heats of solids at low temperatures, and these were the first to give serviceable results.

Einstein in 1907 had extended Planck's quantum theory of radiation to monatomic solids. The classical theory, given by Boltzmann, assumed that the atoms in a solid are vibrating with simple harmonic motion, and that their kinetic energy at any temperature is the same as that of atoms of a monatomic gas. The averate kinetic and potential energies of a harmonic oscillator are equal, and the sum is $3\boldsymbol{R}T$ per g.-atom, hence the atomic heat at constant volume is $3\boldsymbol{R}$ or 6 g.-cal. at all temperatures, which is the Dulong and Petit value. According to Einstein, however, the atoms in a solid cannot take up energy continuously but only in quanta, $\boldsymbol{h}\nu$, where $\boldsymbol{h}$ is Planck's constant and ν the characteristic frequency of vibration of the atom. The energy between two quanta taken up is missing, and the atomic heat is thus smaller than the classical value, which assumes continuous absorption. If the quantum is small, as with lead, the missing gaps are small and the value of the atomic heat is near 6 g.-cal.; with large quanta, as with aluminium, the gaps are large, and the atomic heat is much lower than this value. The quantitative value is easily found. I will give the calculation according to D. L. Chapman.[36] Suppose the linear oscillators of frequency ν are gas molecules A, the energy being quantised and having the values 0, $\boldsymbol{h}\nu$, $2\boldsymbol{h}\nu$, $3\boldsymbol{h}\nu \cdots$, $n\boldsymbol{h}\nu$. If the increase of energy is identified with a heat of reaction according to the equation :

$$\mathrm{A}_n = \mathrm{A}_0 + n\boldsymbol{h}\nu$$

and if $N_0, N_1, \cdots, N_E$ are the numbers of oscillators with energies $0, 1, \cdots, E = n\boldsymbol{h}\nu$, van't Hoff's equation (31) gives :

$$\mathrm{d} \ln (N_E/N_0) = n\boldsymbol{h}\nu/\boldsymbol{k}T^2,$$

where $\boldsymbol{k} = \boldsymbol{R}/\boldsymbol{N}$, is Boltzmann's constant, the equilibrium constant being $K = N_E/N_0$. If C is an integration constant and $\boldsymbol{h}\nu/\boldsymbol{k}T = x$, then :

$$N_E = CN_0\mathrm{e}^{-nx}$$

and the average energy of a linear oscillator, after dividing out CN_0, is :

$$(\boldsymbol{h}\nu \,.\, \mathrm{e}^{-x} + 2\boldsymbol{h}\nu \,.\, \mathrm{e}^{-2x} + 3\boldsymbol{h}\nu \,.\, \mathrm{e}^{-3x} + \cdots)/(1 + \mathrm{e}^{-x} + \mathrm{e}^{-2x} + \mathrm{e}^{-3x} + \cdots)$$
$$= \boldsymbol{h}\nu/(\mathrm{e}^x - 1) \quad . \quad . \quad (38)$$

the last step being an ordinary long division. The energy of an atom in the solid, Einstein assumed, is equal to that of three linear oscillators at right angles, or per g.-atom the energy is :

$$E = 3\boldsymbol{N}\boldsymbol{h}\nu/(\mathrm{e}^x - 1) = 3\boldsymbol{R}\beta\nu/(\mathrm{e}^{\beta\nu/T} - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where $\beta = \boldsymbol{h}/\boldsymbol{k}$. Differentiate with respect to T, and the atomic heat at constant volume becomes :

$$C_v = \mathrm{d}E/\mathrm{d}T = 3\boldsymbol{R}(\beta\nu/T)^2\mathrm{e}^{\beta\nu/T}/(\mathrm{e}^{\beta\nu/T} - 1)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

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[36] *Ann. Reports*, 1914, **11**, 3.

which is Einstein's equation.* Observed values of C_p may be converted into C_v by a formula given by Nernst and Lindemann :

$$C_p = C_v + 0{\cdot}0214 C_p^2 T/T_m$$

where T_m is the melting point. The experiments in Nernst's laboratory showed that the observed atomic heats fall off less rapidly at low temperatures than Einstein's formula requires; for example with copper :

T (°K)	88	33·4	22·5
C_v, obs.	3·38	0·538	0·223
C_v, calc.	3·31	0·234	0·023

Nernst and Lindemann (1911) found that the experimental value could be represented by a simple and elegant formula which consists of a sum of half the Einstein values with the frequencies ν and ν/2, so that only one frquency ν is still required :

$$C_v = \frac{3}{2}\boldsymbol{R}\left\{\left(\frac{\beta\nu}{T}\right)^2 \frac{e^{\beta\nu/T}}{(e^{\beta\nu/T}-1)^2} + \left(\frac{\beta\nu}{2T}\right)^2 \frac{e^{\beta\nu/2T}}{(e^{\beta\nu/2T}-1)^2}\right\} \quad . \quad . \quad . \quad . \quad (41)$$

Thus, for ½KCl, by using the value $\beta\nu = 218$ found experimentally by the optical method of residual rays :

T (°K)	331	86	52·8	30·1	22·8
C_v, obs.	6·16	4·36	2·80	0·98	0·58
C_v, N.L.	6·06	4·43	2·97	1·23	0·61
C_v, E.	5·90	3·54	1·70	0·235	0·039

A theoretical equation giving results as good as those from the Nernst–Lindemann equation was deduced by Debye (1912). He identified the heat content of a solid with the energy of short elastic waves of length still large compared with the distance between the atoms. There is now a spectrum of frequencies terminated by a frequency ν_m imposed by the atomic structure. The elastic solid containing $\boldsymbol{N}$ atoms was treated as a continuum and the ordinary theory of elasticity gives for the number of vibrations between frequencies ν and ν + dν :

$$(9\boldsymbol{N}\nu^2/\nu_m^3)d\nu$$

Each vibration is given the energy according to Einstein's equation (38). By integration :

$$E = \frac{9\boldsymbol{R}}{3}\int_0^{\nu_m} \frac{\beta\nu^3}{e^{\beta\nu/T}-1}\,d\nu = 9\boldsymbol{R}T\left(\frac{T}{\beta\nu}\right)^3 \int_0^{\beta\nu/T} \frac{y^3 dy}{e^y - 1} \quad . \quad . \quad . \quad . \quad (42)$$

where y is the variable in the definite integral. This may be integrated in series. At very low temperatures :

$$E = aT^4;\ C_v = 4aT^3;\ a = \tfrac{3}{5}\pi^4\boldsymbol{R}/(\beta\nu_m)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

where a is a constant. The Debye equation gives good results at low temperatures, as is seen from the results of Nernst and Schwers and of Onnes and Keesom :

Copper, $\beta\nu_m = 323{\cdot}5$			Lead, $\beta\nu_m = 88$		
T (°K)	C_v, obs.	C_v, calc.	T (°K)	C_v, obs.	C_v, calc.
15·24	0·0491	0·0486	15·98	1·87	1·87
18·03	0·0792	0·0804	22·4	3·00	3·06
19·58	0·1010	0·1030	30·24	4·06	4·03
21·50	0·1410	0·1365	47·6	5·07	5·04

In the case of compounds, Nernst suggested that C_v is the sum of a Debye function for the whole molecule and of Einstein functions for the separate atoms, each having a characteristic frequency, and this has a theoretical foundation. The extrapolation of specific heats to absolute zero from the lowest experimental temperature can be carried out by the Debye T^3-formula, which is now generally used in calculating the entropies, the region below the lowest experimental temperature being supplied by the formula.

The quantum theory of the specific heats of gases was opened out by Nernst [36] (1911). He assumed that the vibrational energy of gas molecules is represented by Einstein's formula (38), and that the rotational energy may be represented by the same equation with a frequency proportional to the square-root of the absolute temperature, as on the classical theory. He recognised that at low temperatures not only the vibrational energy, if present, but also the rotational energy, will approach zero, and he predicted that the rotational energy of hydrogen,

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* A zero-point energy $\tfrac{1}{2}\boldsymbol{h}\nu$ should be included in (38), but this disappears in the differentiation.

[36] *Z. Elektrochem.*, 1911, **17**, 265.

which has an abnormally low molecular heat even at room temperature, should vanish at the temperature of liquid hydrogen. The value of C_v for hydrogen should then become 3 g.-cal., the same as that of a monatomic gas. This was verified by Eucken with compressed hydrogen in a small steel vacuum-calorimeter. At low temperatures the heat capacity of the metal is small, and that of the gas can be measured with fair accuracy. The correct theory of the rotational energy of gas molecules was closely approached by Bjerrum (1912), who related it to the absorption in the long infra-red, but it was only after the development of wave mechanics that the accurate equation for the specific heat of hydrogen was obtained. It involves the two kinds of hydrogen molecules, ortho- and para-hydrogen.

Nernst later extended the Heat Theorem to gases at low temperatures, but his equations involved an error pointed out by Bennewitz. The quantum theory of gases is a little more complicated than Nernst suspected, since it follows one of two newer types of statistics, but the result, that the specific heat should vanish at the absolute zero, comes out as Nernst supposed. Ordinary gases could not exist at a temperature low enough to show a deviation from Maxwell–Boltzmann statistics (which itself is only an approximation), but electrons, which obey Pauli–Fermi statistics, should, on account of their very small mass, have only very little energy even at room temperature; this explains why Dulong and Petit's law, applying as it does to the ponderable positive ions, is so nearly obeyed by metals, the electrons contributing practically nothing to the energy. At very low temperatures, where the heat content of the ponderable ions has sunk to a very low value, the small specific heat of the electrons becomes appreciable, since it is proportional to the absolute temperature T, not to T^3.

It should be mentioned that the frequency used in the specific heat equations may be determined, not only by the optical residual ray method (which can be used only with ionic salts), but also from the compressibility or, as Lindemann showed, from the melting point.

Some important consequences of the Heat Theorem, pointed out by Nernst,[37] follow very simply from equation (20), $\text{Lim}\ \Delta S = 0$ as $T \longrightarrow 0$. Clapeyron's equation for the latent heat of expansion is :

$$l_v = T(\mathrm{d}p/\mathrm{d}T)_v$$

hence :

$$\text{Lim}\ (l_v/T) = \text{Lim}\ (\mathrm{d}p/\mathrm{d}T)_v = 0 \text{ as } T \longrightarrow 0$$

Since $(\mathrm{d}p/\mathrm{d}T)_v = -(\mathrm{d}p/\mathrm{d}v)_T(\mathrm{d}v/\mathrm{d}T)_p$, if $(\mathrm{d}p/\mathrm{d}v)_T$ is finite :

$$\text{Lim}\ (\mathrm{d}v/\mathrm{d}T)_p = 0 \text{ as } T \longrightarrow 0$$

The latent heat of extension of a liquid film is :

$$l_A = -T(\mathrm{d}\sigma/\mathrm{d}T),$$

where σ is the surface tension ; hence :

$$\text{Lim}\ (-l_A/T) = \text{Lim}\ (\mathrm{d}\sigma/\mathrm{d}T) = 0 \text{ as } T \longrightarrow 0$$

The magnetisation of a paramagnetic substance follows an equation :

$$M = T(\mathrm{d}m/\mathrm{d}T)_p$$

where m is the magnetic moment per unit mass produced by unit field, and M the heat absorbed. The Heat Theorem gives :

$$\text{Lim}\ (M/T) = \text{Lim}\ (\mathrm{d}m/\mathrm{d}T)_p = 0 \text{ as } T \longrightarrow 0$$

The electromotive force of the Peltier effect is related to the Peltier heat by the equation :

$$Q = T(\mathrm{d}e/\mathrm{d}T)_p$$

and it is to be expected that :

$$\text{Lim}\ (Q/T) = \text{Lim}\ (\mathrm{d}e/\mathrm{d}T)_p = 0 \text{ as } T \longrightarrow 0.$$

All these equations agree with experimental results when these are available.

PHOTOCHEMISTRY

If light waves fall normally on a metallic mirror and are reflected, stationary waves are produced by interference, and Wiener (1890), by covering the mirror with a thin sensitive photographic film making a small angle with it, found that the antinodes of the electric waves appear as dark lines on the film. Drude and Nernst (1892) used a florescent film, which made the positions of the antinodes visible. These results were important in confirming that the vibration of the electric vector in light waves corresponds with Fresnel's vibration, and is perpendicular to the plane of polarisation.

[37] *J. Chim. phys.*, 1910, **8**, 228.

Modern photochemistry dates from Einstein's law of photochemical equivalence (1912), which states that a molecule undergoing photochemical change absorbs one energy quantum, $h\nu$, from the radiation in the primary photochemical process. The products of this primary reaction may then undergo secondary reactions not depending on illumination. Although Einstein's law was found to hold for many reactions, in the famous reaction on the study of which Bunsen and Roscoe founded photochemistry, the union of hydrogen and chlorine, $H_2 + Cl_2 = 2HCl$, at least a million molecules of HCl are formed per absorbed quantum, instead of two, as would be expected from the equation $Cl_2 + h\nu = 2Cl$. Nernst (1918)[38] explained this in a very simple and ingenious way. The absorbed quantum dissociates the chlorine molecule into atoms. A chlorine atom then reacts with a hydrogen molecule to form HCl and atomic hydrogen by a secondary process. The hydrogen atom in turn reacts with a chlorine molecule to form an atom of chlorine, which starts the process again :

$$\begin{gathered} Cl_2 + h\nu = 2Cl \\ Cl + H_2 = HCl + H \\ H + Cl_2 = HCl + Cl \end{gathered}$$

This atomic chain is propagated until the active atoms are removed by collision with the walls of the vessel or with other particles, such as oxygen molecules, and the reaction stops. There is little doubt that this theory is, in principle, correct. Nernst published two papers with Noddack on photochemistry, and his pupil Eggert has been very active in this field.

In his later years Nernst had seen great changes brought about in the field of physical theory by the quantum theory and the theory of relativity. Laws of Nature which had been supposed to be accurately true had been shown to be approximations, and he inclined to the view that it may never be possible for us to know the ultimate truth of phenomena. In his lectures in London in 1913 he had quoted Shakespeare :

> " But this eternal blason must not be
> To ears of flesh and blood "

In his address as Rector of Berlin University in 1922 he developed this thought. A natural law is only idealised experience (*Erfahrung*), a lucky combination of a number of results of observation. The conviction grows on us that we do not possess a single natural law in a final form. The simplest among possible representations is to be preferred, not only because it is the most convenient but also because it is likely to be the most probable. A law which has been revised in the light of new knowledge still retains its wide range, but the limits of its applicability have been more sharply defined; and scientific theories, far from dropping off like withered leaves in course of time, seem, with certain restrictions, to be endowed with eternal life. Every important theory will suffer restrictions, but it will always retain the essence of a sum of truths.

Great changes had been made in the picture of the universe. The ether, which had played an important part in the development of optical theories in the nineteenth century, had disappeared and in its place was left only a vacuum. Nernst was conservative in theory. He retained the ether, and he was solicitous of the fate of the universe. He could not contemplate either the old heat-death of the universe, when all its energy will have changed into heat at a uniform temperature, or the newer, more gruesome death, in which all matter will have passed into radiation. His latest publications are concerned with astrophysical theories, and the energy of the universe. They have not found a place in the modern structure of astrophysics but they are so typical of him that a passing mention of them cannot be omitted. He began, as usual, by collecting and tabulating numerical data. The temperature in the early life of a star at first rises rapidly and then slowly falls to about 2000° K. Nernst assumed that new stars are being formed as giant nebulæ, and their mass continually decreases. Three sources of energy were assumed : (i) radioactive decay in the early period, (ii) atomic disintegration in the long subsequent period, (iii) gravitational energy when white dwarfs are formed with increase of density, perhaps by the formation of neutrons. The essential part of the theory is that the loss of mass is non-relativistic, there being no simultaneous production of radiation, since experimental evidence for this he thought was lacking. Matter and energy, however, are interconvertible. The universe is in a stationary state, matter being in equilibrium with an immense store of zero-point energy in the ether. Owing to fluctuations in the thermodynamic equilibrium state, the energy of the ether is transformed into atoms rich in energy. These

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[38] *Z. Elektrochem.*, 1918, **24**, 335.

partly disintegrate, forming cosmic radiation, and partly coalesce to form fixed stars. The stationary state of the universe requires that matter must also pass back, non-relativistically, into the energy of the ether.

Although these speculations, the last fruits of his fertile imagination, are in themselves not without interest, they have had no influence on the rapid and fluctuating progress of modern cosmology. The same cannot be said of another contribution of Nernst in this field, which has played a very important part in the development of quantitative stellar theory.

In 1918 he pointed out that the chemical constant of the electron may be calculated by (37), and hence the thermal dissociation of an atom into a positive ion and an electron may be determined if the heat of dissociation is known. This could be found in some cases from the Bohr atom model. The detailed treatment of this phenomenon by Nernst's pupil Eggert in 1919, and independently by Saha in 1920, has proved to be of great importance in the calculation of temperatures and pressures in reversing layers of stellar atmospheres from observations on the intensities of absorption lines in the spectra. This is a particularly interesting and important application of the Heat Theorem, which was suggested by Nernst himself.

My duty in presenting a picture of Nernst and of his work is now ended. His contributions to Physical Chemistry are solid and I believe that they will endure. In physical chemistry, as in geology, time is a great leveller. Landscapes of theory dissolve and are replaced by newer formations overlying and concealing more primitive ones. Yet there are some hard and resisting primitive masses which appear, unconformably sometimes, projecting from the level of material derived from the comminution of old formations. In physical chemical theory such are, I think, the electrochemical and thermodynamic theories of Nernst. They offer themselves for our admiration.

In his time he was one of the great masters. To different individuals he would appear in various aspects. It was as a very young man, with little experience, that I spent a short time with him, and in my memory he remains a man of great intellectual power, but also something more. He took an interest in me which he showed in many ways. Soon after I arrived in Berlin, speaking German imperfectly, I was required to give a lecture to the Colloquium. This was carefully written out, but very soon he interrupted with criticisms and comments. The audience, knowing his ways, was quiet and attentive, and I finished without script. He saw that I lacked confidence and this was his treatment of the complaint. It was for my good and was meant kindly. My research was not easy, but even his presence, without words, was an incentive; one felt that he could do the work easily himself, and that perseverance would remove lack of skill, a fault which could be cured by application. If one visited his house, he might ask for an opinion of a picture, and I remember that he once asked my advice as to whether a tree in his garden should be removed. He would leave about publications by the visitor as if he wished it to be thought that he had read them. His true kindness is something I remember with gratitude, and I would like to leave you with such an idea of him. I feel that I am fortunate in having known him, and I value this opportunity to pay some tribute to his memory.