HERMANN WALTHER NERNST

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Hermann Walther Nernst was born in Briesen* (Western Prussia) on the 25th June, 1864 (1,2).

He studied Physics at the Universities of Zurich, Berlin, Graz and Würzburg, from 1883 to 1887.

Fig.1 - Hermann Walther Nernst
(1864-1941)

At Graz he met Boltzman and following his suggestion he worked with von Ettinghausen. This collaboration led to the discovery that a difference of potential is produced in a metallic conductor when a magnetic field is applied perpendicularly to a temperature gradient (Von Ettinghausen-Nernst effect) (3,4).

* Now called Wabrzezno, in Poland

In 1887, having worked under the supervision of Kohlrausch, he received his Ph.D. degree from the University of Würzburg (5).

In the same year, while visiting Boltzman (at Graz), he met Ostwald. At the end of 1887 the latter scientist accepted the position of Professor at the University of Leipzig and Nernst that of his assistant.

Owing to Ostwald's influence, Nernst centered his lifelong scientific activity on the application of the principles of Physics to the solution of chemical problems.

He started by studying electrolyte diffusion (6) and, as a sequel to this work, suggested a theory on the electrochemical processes. He thus considered (2) the metallic electrodes as a reservoir of ions tending to an electrolytic dissolution, expressed by the value P, "electrolytic solution pressure". With a basis on this assumption, Nernst deduced, in his famous article (7).

"Die elektromotorische Wirksamkeit der Ionen",

Die elektromotorische Wirksamkeit der Ionen.

Von

Walther Nernst.

(Mit 3 Holzschnitten.)

Übersicht: 1. Die Fundamentalhypothesen. 2. Über ein allgemeines Prinzip für die in Elektrolyten wirksamen Kräfte. 3. Potentialdifferenz zwischen zwei verschieden konzentrierten Lösungen desselben Elektrolyten. 4. Flüssigkeitsketten. 5. Über die an der Grenzfläche umkehrbarer Elektroden auftretenden elektromotorischen Kräfte. 6. Über den Vorgang der Auflösung fester Körper. 7. Theorie der Konzentrationsketten. 8. Messungen. 9. Vergleich mit der v. Helmholtzschen Theorie der Konzentrationsketten. 10. Potentialdifferenz an der Grenzfläche zweier Elektrolyte. 11. Elektrolytische Thermoketten; Theorie und Messungen. 12. Über galvanische Elemente. [Kapitel 3, 5, 6, 7 im Auszuge bereits mitgeteilt: Berl. Sitzungsber. S. 83—95. 1889.]

1. Die Fundamentalhypothesen.

Richtung und Grösse elektromotorischer Kräfte aus anderweitigen, der Messung zugänglichen Erscheinungen zu berechnen, war bisher nur in vereinzelten Fällen möglich; es gelang dies zum ersten Male Herrn v. Helmholtz im Jahre 1847 für die elektromotorische Kraft der Induktionsströme, welche sich, eins der glänzendsten Ergebnisse des Gesetzes von der Erhaltung der Kraft, aus der elektrodynamischen Wechselwirkung zwischen Leitern und Magneten ableiten liess.

Bedeutend später, im Jahre 1879, glückte wiederum Herrn v. Helmholtz der Nachweis, dass die elektromotorische Kraft der Ströme, welche man beobachtet, wenn zwei aus demselben Metall gebildete Elektroden in zwei miteinander kommunizierende Lösungen verschiedener Konzentration eines aus diesem Metall gebildeten Salzes eintauchen, sich aus den Dampfspannungen und den Hittorfschen Überführungszahlen dieser Lösungen berechnen lässt. Später dehnte Herr v. Helmholtz seine Rechnungen auch auf diejenigen Ströme aus, welche bei der paarweisen Gegeneinanderschaltung umkehrbarer galvanischer Elemente, wie z. B. des *Zn-Hg*-Calomel-Elementes, entstehen, wenn dieselben mit verschieden konzentrierter Lösung gefüllt sind. Bei diesen Konzentrationsströmen vereinfachen sich die Rechnungen sogar noch insofern, als dabei die Überführungszahlen herausfallen.

Auch die Theorie dieser elektromotorischen Kräfte ist aus den Prinzipien der mechanischen Wärmetheorie hergeleitet, und zwar hier mit

Zeitschrift f. physik. Chemie. IV. (1889) 9

Fig.2 - Front page of the "Die elektromo torische Wirksamkeit der Ionen"

published in 1889, an equation of the type

$$E= \frac{RT}{nF} \ln \frac{P}{p} \qquad (1)$$

where E is the electrode potential*. In this expression** p stands for the "osmotic pressure".

In 1890 Nernst became assistant lecturer in Physics at the University of Gottingen. In the next year he was associate professor for the same discipline. Finally, in 1894, he was appointed full professor of Physical Chemistry at the same University.

Nernst stayed in Gottingen until 1904, carrying out an important research work in the domain of Physical-Chemistry. Of this work, and standing out as particularly relevant in the field of Electrochemistry, we would mention the theory on the solubility product (8), the theory on lead accumulators (9), a work on electrocapillarity (10), the theory of polarization (12, 13) and the theory on the electric stimulus of nerves (14, 15).

In this branch of Physical-Chemistry he was also active as one of the founders of the "Deustche elektrochemische Gesellschaft"*** and as the editor, for years, of the "Zeitschrift für Elektrochemie". From 1895 he also collaborated in the edition of the "Jahrbuch für Elektrochemie".

The work developed by Nernst in the field of Electrochemistry led to the recognition of his merit by the scientific community. However, the climax of his career started on the 23rd December 1905

* The formula deduced was

$$E = 0.860\ T \ln \frac{P}{p} \times 10^{-4} \text{ volt,}$$

which appears on the reverse of the commemorative medal of the 5th anniversary of the "Sociedade Portuguesa de Electroquímica"

** In terms of concentration, this equation is now known in Physical Chemistry as the Nernst equation.

*** Later called "Deutsche Bunsengesellschaft" with the scientific communication entitled

"Uber die Berechnung chemischer Gleichgewichte aus thermischen Messungen",

which he presented at the University of Gottingen.

He went to Gottingen for the purpose, since in the same year he had left this city to become professor* of Physical-Chemistry at the University of Berlin.

This work, where his "Warme-Theorem"** is enunciated, was published in 1906 (16) and represented an essential contribution to the interpretation of chemical equilibrium***.

Ueber die Berechnung chemischer Gleichgewichte aus thermischen Messungen.

Von

W. Nernst.

Mit einer Figur.

Vorgelegt in der Sitzung am 23. Dezember 1905.

Für die Beziehungen zwischen chemischer Energie und Wärmeentwicklung bei chemischen Prozessen glaubte bekanntlich Berthelot eine sehr einfache Lösung gefunden zu haben, indem er beide Größen einander gleichsetzte.

Damit hängt aufs Engste die bereits früher aufgestellte sogenannte Thomsonsche Regel zusammen, wonach die von einem galvanischen Elemente gelieferte elektrische Arbeit der Wärmeentwicklung des stromliefernden Prozesses gleich sein sollte [1]).

Nachdem man aber zur Bestimmung der chemischen Energie, d. h. der maximalen Arbeit, die von einem chemischen Prozesse geleistet werden kann, zwei Wege aufgefunden hatte, indem man obige Größe einmal aus dem chemischen Gleichgewichte, sodann auch aus der elektromotorischen Kraft reversibler galvanischer Elemente abzuleiten gelernt hatte, da zeigte sich, daß keineswegs jene maximale Arbeit mit der thermochemisch bestimmten Wärmetönung zusammenfällt.

Besonders klar hat dies Helmholtz ausgesprochen, der übrigens bereits vor Berthelot zunächst die Vermutung aufgestellt hatte [2]), daß die elektromotorische Kraft durch die Wärmetönung gegeben sei (sogen. Regel von Thomson) und der dann später (1882)

1) Vergl. hierzu z. B. Nernst, Theoret. Chemie, vierte Aufl., S. 668 u. 691.
2) Gesetz von der Erhaltung der Kraft. 1847.

Kgl. Ges. d. Wiss. Nachrichten. Math.-phys. Klasse. 1906. Heft 1. 1

Fig. 3 - First page of the paper where Nernst enunciated his "Warme-Theorem"

The interest in this interpretation was closely associated with the experimental studies on chemical equilibrium carried out by Nernst at Gottingen. These studies involved the formation of nitric oxide at high temperatures (17,18,19) and the synthesis of ammonia (20).

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* Filling a vacancy left by the retirement of Landolt

** Heat Theorem

*** Calculation of the chemical equilibrium from measurements of reaction heats.

The validity test of the "Warme-Theorem" did represent a serious challenge from the experimental point of view, since it required measurements of physical properties, especially specific heats at very low temperatures (near absolute zero). Nernst, however, successfully met every difficulty thanks to his excellence as an experimentalist. Consequently, he is regarded today as one of the founders of a new domain of Experimental Physics: Cryogenics.

Experimental results of specific heats, obtained in his laboratory, were compared with the predictions of Einstein's model, based on quantum mechanics, when he met this scientist in Zurich (March, 1910). To their satisfaction, the agreement was found to exist, except at very low temperatures. The experimental measurements of specific heats performed by Nernst, required to test his "Warme Theorem", thus played an important role in the acceptance of quantum theory.

This fact was expressed by Simon, one of his most brilliant students, who decisively contributed to the subsequent canonization of the "Warme-Theorem" as the 3rd law of Thermodynamics. In fact, in his "Guthrie Lecture" in 1956 (21), he stated:

"Also we must nor forget that the Third Law was an extremely strong stimulus to the development of quantum theory and it is perhaps not quite idle to consider how the development would have taken place had Nernst's deliberations started ten years earlier as they might well have done. Perhaps the quantum of action would have been discovered as a consequence of the disappearing specific heats rather than from the ultra-violet catastrophe of the radiations laws".

The experimental studies carried out by this scientist in the field of low temperatures in order to test Nernst's "Warme--Theorem" led him to express, in 1927, the 3rd law (22) in a form which is quite close to the present one:

"At absolute zero the entropy differences disappear between those states of a system between which reversible transitions are possible at least in principle".

But if Nernst's scientific genius was revealed in the studies already mentioned, his interests also extended to other areas. He carried out studies on the distribution of benzoic acid between water and benzene, which led to the formulation of the so-called Nernst distribution law (23,24). He also devoted his time to photochemical studies, namely the formation of HCl from H_2 and Cl_2 (25).

In 1922 Nernst left the University of Berlin to preside over the "Physikalisch-Technische Reichsanstald". However, owing to economic problems, his plans to re-organize this scientific institution were unsuccessful. He therefore went back to the same university in 1924, this time to hold the chair of Physics*.

Leaving to his collaborators, especially Simon**, the task of upholding and reformulating his "Warme-Theorem", he dedicated the last years of his scientific life to cosmological problems, namely in the branch of Astrophysics. Besides being concerned with the problem of interpreting the evolution of the Universe through the 2nd law of Thermodynamics, he also studied the chemical (26) and physical characteristics of the stars (27, 28, 29, 30).

Nernst retired in 1934 and spent the rest of his days in his country estate, Zibelle, near Muskau***.

The last years of Nernst's life were spent in total obscurity since he was, in fact, ostracized by the nazi regime owing to his independence, namely in opposing the anti-Einstein campaign carried out by anti-semite organizations.

He died in November 1941 of a heart attack. Thus was the world deprived of one of those men of genius who, together with Planck, Einstein, Schrodinger, Hertz and Polanyi, constituted a real pleiad of scientists who gained for the German School of Physics of the beginning of this century its world-wide reputation.

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* left vacant by the death of Rubens

** who would later become the director of the famous cryogenic laboratory at Oxford - "Clarendon Laboratory"

*** now at the German Democratic Republic near the border with Poland

On the whole, Nernst was a scientist of genius, especially gifted to make himself the instruments he needed for his studies. For the purpose he would always bear in mind the principle that such instruments should be as simple and inexpensive as possible. In this respect Simon (31) reports that when Nernst needed to carry out measurements in the neighbourhood of absolute zero

"He visited Kamerlingh Onnes in Leiden, but decided that the immense elaboration of his liquid hydrogen plant was quite beyond the financial and other resources of the Berlin laboratory. He, therefore, set about devising a simple liquefier. This liquefier, costing only about £ 20, enabled him to produce in some hours quite enough hydrogen for his purpose".

With a basis on this principle, he planned and made several instruments, such as an apparatus to carry out measurements of dielectric constants (32), another to determine molecular weights and the so-called Nernst lamp (33,34). In this lamp the usual

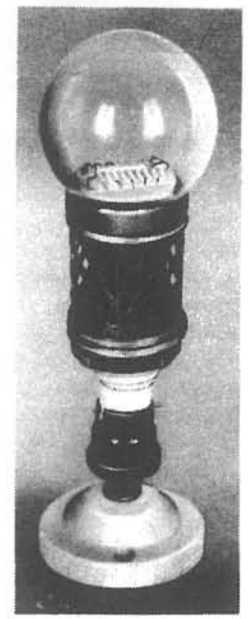


Fig. 4 - Nernst lamp

carbon filament was replaced by wires made of a rare earth oxides mixture. In this way a higher efficiency was achieved. This lamp also reflected his concern for the technological applications of

Chemistry and Physics.

In recognition of his scientific work in the domain of Thermochemistry he was awarded the Nobel prize for Chemistry in 1920.

Because he was a rich personality, with manifold aspects, he was also interested in the organization of several international conferences, amongst which the 1st of the "Solvay Conferences". These conferences played a major role on the development of Physics.

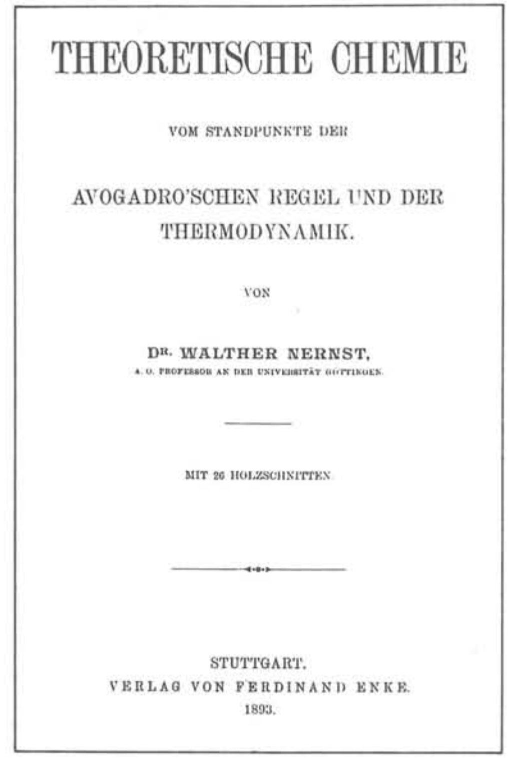
Fig. 5 - Participants of the 1st Solvay Conference held in 1911

From left to right, standing: O. Goldschmidt, M. Planck, H. Rubens, A. Sommerfeld, T. Lindermann, M. de Broglie, M. Knudsen, F. Hasenohrl, H. Hostelet, T. Herzen, J.Jeans, E.Rutherford, H. Kamerlingh Onnes, A. Einstein and P. Langevin.

From left to right, sitting: H.W. Nernst, M. Brillouin, E. Solvay, H. A. Lorenz, O. Warburg, J. Perrin, W. Wien, M. Curie and H. Poincaré.

Finally, Nernst developed an intense pedagogical activity as a university professor. Of the various books he wrote (31) we would cite "Theoretische Chemie", re-edited several times and

translated into many languages. For about 30 years this book was looked upon as the bible of Physical-Chemistry teaching.



THEORETISCHE CHEMIE

VOM STANDPUNKTE DER

AVOGADRO'SCHEN REGEL UND DER THERMODYNAMIK.

VON

DR. WALTHER NERNST,

A. O. PROFESSOR AN DER UNIVERSITÄT GÖTTINGEN.

MIT 26 HOLZSCHNITTEN

STUTTGART.
VERLAG VON FERDINAND ENKE.
1893.

Fig. 6 - Front page of the Theoretische Chemie published in 1893

Although his classes were not too stimulating for the students, Nernst enjoyed brightening them up with a certain sense of humour which he used to stress, with a hardly contained vanity, his scientific contributions. In fact, in his lessons (35):

"Nernst liked to refer to the first law of thermodynamics as having been discovered independently by three investigators (presumably Mayer, Joule and Helmholtz) and the second law by two independent investigators (Carnot and Clausius). Concerning

the third law of thermodynamics Nernst would say, "well, this I have just done by myself"*.

An eloquent analysis of Nernst's scientific personality is to be found in the following words Einstein wrote about him a few months after his death (36):

Although sometimes good naturedly smiling at his childlike vanity and self-complacency, we all had for him not only a sincere admiration, but also a personal affection. So long as his egocentric weakness did not enter the picture, he exhibited an objectivity very rarely found, an infalible sense for the essencial and a genuine passion for the knowledge of deep interrelations of nature. But for such a passion his singularly creative productivity and his important influence on the scientific life of the first third of this century would not have been possible."

The influence of Nernst's ideas can still be detected nowadays in the experimental research which has been carried out in Portugal at the "Laboratório de Termodinâmica Experimental", considering the academic link:

Nernst —> Eucken —> Clausius —> Staveley —> Calado —> myself.

As a member of this laboratory, headed by Prof. Calado, I feel particularly honoured with such an influence.

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* His students offer slightly different versions which, nevertheless, agree in essence. Sometimes Nernst would conclude that, considering the evolution of the number of investigators involved 3 → 2 → 1, there could exist no fourth law of Thermodynamics.

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