Macmillan Encyclopedia of Chemistry

Biographic Articles on
Ostwald, van't Hoff, Arrhenius, Nernst, Haber, Le Bel

(23 September 2002)

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Ostwald, Friedrich Wilhelm (1853-1932)

Ostwald (born September 2, 1853, Riga, Latvia, Russia; died April 4, 1932, at his private estate near Leipzig, Germany) almost single-handedly established physical chemistry as an acknowledged academic discipline. In 1909, he was awarded the Nobel Prize in chemistry for his work on catalysis, chemical equilibria, and reaction velocities.

Ostwald was graduated in chemistry at the University of Dorpat (now Tartu, Estonia) and appointed professor of chemistry in Riga in 1881, before he moved from Russia to Germany on the chair in physical chemistry at the University of Leipzig in 1887. For about twenty years he made Leipzig an international center of physical chemistry: by establishing an instruction and research laboratory that attracted virtually the whole next generation of physical chemists; by editing the first journal of the field (*Zeitschrift für physikalische Chemie*); and by writing numerous textbooks. In 1906, he retired from university and devoted the rest of his life to various topics, including the history and philosophy of science, color theory, painting, the writing of textbooks and popular books about science, the international organization of science, and the formation of an artificial language for the international exchange of ideas.

Since his master degree thesis in 1876, Ostwald followed the general approach of applying physical measurement and mathematical reasoning to chemical issues. One of his major research topics was the chemical affinity of acids and bases. To that end, he studied the point of equilibrium in reactions systems where two acids in aqueous solution compete with each other for reaction with one base and vice versa. Because chemical analysis would have changed the equilibria, he skillfully adapted the measurement of physical properties to that problem, such as volume, refractive index, and electrical conductivity. From his extensive data he derived for each acid and base a characteristic affinity coefficient independent of the particular acid-base reactions.

To understand the different chemical affinities, Ostwald drew on a new, but then hardly accepted and not yet fully developed, theory advanced by Svante Arrhenius. According to this theory of electrolytic dissociation, electrolytes like acids, bases, and salts dissociate in solution into oppositely charged ions to a certain degree, such that at infinite solution dissociation is complete. Ostwald recognized that if all acids contain the same active ion, their specific chemical affinities must correspond to the number of these active ions in solution, which depend on their specific degree of dissociation at each concentration, and which could be measured through electric conductivity studies. Applying the law of mass action to the dissociation reaction, a simple mathematical relation was derived between the degree of dissociation ($\underline{\alpha}$), the concentration of the acid ($\underline{c}$), and an equilibrium constant specific for each acid ($\underline{K}$):

$$\underline{\alpha}^2/(1-\underline{\alpha})\underline{c} = \underline{K}$$

This is Ostwald’s famous dilution law from 1888, which he proved by measuring electric conductivities of over 200 organic acids at various concentrations. He substantiated the dissociation theory not only to explain the different activity of acids, but also as a general theory of electrolytes in solution. The theory gained further support by Jacobus Henricus van’t Hoff who, at the same time, put it on a general thermodynamic basis to explain his law of osmotic pressure of solutions as well as Raoult’s laws of vapor pressure lowering and freezing point depression. Thereby, the new physical chemistry grew to a comprehensive theory of solutions, based both on thermodynamics and dissociation theory.

Ostwald was particularly successful in systematizing and propagating the new ideas, applying them to other fields, and organizing a school of physical chemistry. Many chemists rejected the dissociation theory because it predicted wrong values at high concentrations and for strong electrolytes. Notwithstanding concessions about its restricted validity, Ostwald provided numerous proofs of its broad usefulness in his textbooks on general, inorganic, and, particularly, analytical chemistry.

Originally, and wrongly, Ostwald studied reaction velocities as a measure of chemical affinity. Later, he broadly investigated temporal aspects of chemical reactions and provided a systematics for the field of chemical kinetics. He first recognized catalysis as the change of reaction velocity by a foreign compound, which allowed him to measure catalytic activities. He distinguished catalysis from triggering and from autocatalysis that he considered essential to biological systems. His most famous contribution to applied chemistry was on catalytic oxidation of ammonia to nitric acid, which became employed in the industrial production of fertilizers.

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Word Count: 716

Author: Joachim Schummer

Van't Hoff, Jacobus Hendricus (1852-1911)

Van't Hoff (born August 30, 1852, Rotterdam, Netherlands, died March 1, 1911, Berlin, Germany) was in his youth, with Le Bel, the founder of modern stereochemistry and then became one of the fathers of modern physical chemistry. In 1901, he was awarded the first Nobel Prize in chemistry for his work on chemical dynamics and the osmotic pressure in solutions.

As with many creative minds, van't Hoff's career was initially blocked by the ignorance of the scientific establishment. Unemployed for two years, the doctor in chemistry eventually took a teaching job in physics at the veterinary school in Utrecht. Success only came in 1877 when the newly founded University of Amsterdam offered him a lectureship and, in 1878, a professorship in chemistry. Although his international reputation allowed him to bargain for a new chemical laboratory, which was completed in 1891, he finally moved to Berlin in 1896 as both university professor and member of the Prussian Academy of Science.

Shortly before he submitted an only average doctoral thesis in synthetic organic chemistry to the University of Utrecht, twenty-two-year old van't Hoff printed and distributed a twelve-page pamphlet at his own expense that, although ignored for some years, should lay the foundation of modern stereochemistry. Inspired by previous ideas of Johannes Wislicenus to extend chemical structure theory from constitutional formulas to representations in three-dimensional space, van't Hoff suggested a structural distinction between optical isomers which were hitherto represented by the same formula. By screening the then known substances with optical activity (i.e. rotation of the plane of polarized light), he found that all their constitutional formulas contained at least one carbon atom that combined with four different atomic groups. If the latter were placed at the corners of a tetrahedron in three-dimensional space, with the carbon atom at its center, there were exactly two possible tetrahedra with asymmetric carbon atoms, each being the mirror image of the other, that could account for the pairs of optical isomers. Further support of the structural theory came from his observation that for every known chemical transformation where the optical activity of a reactant disappeared, there was no more asymmetric carbon atom in the structural representation of the reaction product. Independently and virtually simultaneously, Joseph Le Bel arrived at the same theory in Paris.

Due to his early interest in philosophy, particularly that of Auguste Comte, van't Hoff's chemical research strove for general and theoretical insight in chemistry and, thus, gradually shifted from organic to physical chemistry. In 1884 he published his *Études de dynamique chimique* (Studies in Chemical Dynamics) with many pioneering ideas for chemical kinetics and thermodynamics. Based on numerous measurements of organic reaction rates he classified chemical reactions according to different orders and molecularities, and formulated the temperature dependence of reaction rates, now known as "Arrhenius equation." Following up earlier ideas, he interpreted chemical equilibria as being dynamic states where back and forth reaction rates just equal, which he represented by the double arrow. He further formulated the temperature dependence of the equilibrium constant, know as "van't Hoff isochore," and suggested what came to be known as "Le Chatelier's principle." Most importantly, he laid the foundation of chemical thermodynamics by expressing the relation between what is now called the free energy of a reaction and its equilibrium constant.

During the late 1880s, van't Hoff turned the seemingly exotic phenomenon of osmotic pressure into a crucial part of the new physical chemistry of solutions. He discovered that the osmotic pressure, π, increased with the concentration of the solute, $c = n/V$, and the absolute temperature, T, according to the equation

$$\pi = nRT/V$$

which is formally equivalent to the ideal gas law

$$p = nRT/V$$

with R being the gas constant in both cases. The surprising correspondence suggested that the osmotic pressure depended only on the number of solute molecules and not on their chemical nature, like other so-called colligative properties such as vapor pressure lowering and freezing point depression. Van't Hoff not only put all these phenomena on a common thermodynamic ground; he also successfully explained apparent anomalies with Arrhenius new theory of electrolytic dissociation.

In his later years, van't Hoff applied chemical thermodynamics to the formation of marine salt deposits which made him also one of the pioneers of the science of petrology.

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Word Count: 711

Author: Joachim Schummer

Arrhenius, Svante August (1859-1927)

Arrhenius (born February 19, 1859, Vik, Schweden; died October 2, 1927, Stockholm, Sweden) was a co-founder of modern physical chemistry through his theory of electrolytic dissociation for which he received the third Nobel Prize in chemistry in 1903. He also made important contribution to chemical kinetics and many other branches of science.

In 1884 Arrhenius obtained his Ph.D. from the University of Uppsala with a thesis on the conductivities of electrolytic solution. Although poorly rated by his examiners, his thesis opened him the door to the most distinguished physicists and physical chemists in Europe with whom he worked from 1886 to 1890. Based on his international reputation, the Technical High School at Stockholm offered him a post as lecturer, then as professor, and finally as rector, before he became director of the new physical chemistry institute of the Nobel foundation in 1905. At that time, his interests had already shifted toward other fields of science.

Nowadays chemist know Arrhenius mainly from the "Arrhenius equation" that describes the temperature dependence of chemical reaction rates

$$\underline{k} = \underline{A}\ \exp(-\underline{E}/\underline{RT})$$

with $\underline{k}$ being the reaction rate constant, $\underline{A}$ a pre-exponential factor, $\underline{E}$ the activation energy, $\underline{R}$ the gas constant, and $\underline{T}$ the absolute temperature. Yet, that equation was first formulated by Jacobus Hendricus van't Hoff in 1884. It was only five years later, however, that Arrhenius provided the interpretation of the equation still in use today. He suggested that the crucial step of a chemical reaction is the formation of activated molecules from the reactant molecules and that both states are in equilibrium separated from each other by the activation energy $\underline{E}$. Accordingly, he explained the temperature dependence of the reaction rate as a change of the equilibrium, such that with increasing temperature more activated molecules are formed to undergo reaction. Furthermore, plotting the empirical results of $\ln \underline{k}$ against $1/\underline{T}$ (Arrhenius plot) yields in many cases a straight line from the slope of which one can easily calculate the activation energy $\underline{E}$.

Arrhenius's most famous contribution, which made him with Wilhelm Ostwald and van't Hoff a co-founder of modern physical chemistry, was his theory of electrolytic dissociation. Electrolytes are substances like salts, acids, and bases that conduct electric currency in solution. Indicated already in his doctoral thesis and fully developed in 1887, Arrhenius suggested that every electrolyte, once dissolved in a solvent like water, dissociates into oppositely charged ions to a certain degree that depends on its nature and overall concentration. Before, chemists thought that electrolytes dissolved as uncharged molecules which could be separated only by strong electric forces such as in electrolysis. Although the forces for electrolytic dissociation remained unclear for some time, Arrhenius assumption could explain a wide range of phenomena and laws beyond electrochemistry. This included Raoult's laws of vapor pressure lowering and freezing point depression, Ostwald's dilution law, and van't Hoff's law of osmotic pressure of solutions. As Ostwald showed in his acid-base theory, it also provided a quantitative understanding of the chemical activities of electrolytes in solution.

In his later years, Arrhenius applied concepts of physical chemistry and physics to many other branches of science, including biochemistry, geo- and cosmic physics, and meteorology. In retrospect, his most remarkable contribution was his "Greenhouse Effect" model, according to which the temperature of the lower atmosphere is determined by the concentration of carbon dioxide. The earth surface, after being warmed up by sunlight, emits energy in the form of microwaves which cannot leave the atmosphere because particularly carbon dioxide again turns them into heat through absorption. At that time, the model was still used to explain the glacial periods, rather than today's climatic changes induced by the human production of carbon dioxide.

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Word Count: 612

Author: Joachim Schummer

Nernst, Hermann Walther (1864-1941)

Nernst (born June 25, 1964, Briesen, Prussia [now Wabrzezno, Poland]; died November 18, 1941, at his private estate near Bad Muskau, Germany) pioneered chemical thermodynamics in a wide range of topics. His most outstanding contributions were his laws of electrochemical cells and his heat theorem, also known as the Third Law of thermodynamics, for which he was awarded the Nobel Prize for chemistry in 1920.

Nernst first studied physics before he became assistant to Wilhelm Ostwald at the University of Leipzig in 1887, then the only institute for physical chemistry in Germany. In 1891 he was appointed associate professor in Göttingen and, three years later, convinced the officials there to create an institute for physical chemistry after the Leipzig model, which he directed until his move to Berlin in 1905, where he once more built up an institute. With Nernst the new physical chemistry not only spread over German universities, his extraordinary combination of theoretical and experimental skills as well as his textbooks set new standards for the field.

During his Leipzig period, Nernst performed a series of electrochemical studies from which he finally, at the age of 25, arrived at his famous Nernst equations. These equations describe the concentration dependence of the potential difference of galvanic cells, such as batteries, and are of both greatest theoretical and practical importance. Nernst started with investigating the diffusion of electrolytes in one solution. Then he turned to the diffusion at the boundary between two solutions with different electrolyte concentrations and recognized that the osmotic pressure difference would result in an electric potential difference or electromotive force (emf). Next he divided both solutions into two concentration half-cells, connected with each other by a liquid junction, and measured the emf via electrodes dipped into both solutions. The data supported his first equation according to which the emf is proportional to the logarithm of the concentration ratio. Finally, he investigated galvanic cells where a redox reaction (e.g., $Zn + 2Hg^{+} \rightarrow Zn^{2+} + 2Hg$) was divided such that oxidation ($Zn \rightarrow Zn^{2+} + 2e^{-}$) and reduction ($2Hg^{+} + 2e^{-} \rightarrow 2Hg$) occurred at the electrodes in two half-cells. By combining Helmholtz's law, which related thermodynamics to the emf of electrochemical cells, and van't Hoff's equation, which related chemical equilibria to thermodynamics, Nernst derived his second equation for such galvanic cells. Supported by many measurements, the equation described the emf of galvanic cells as a function of the concentration of all substances involved in the reaction.

Nernst's formulation of the Third Law of thermodynamics was originally an ingenious solution to a crucial practical problem in chemical thermodynamics, namely, the calculation of chemical equilibria and the course of chemical reactions from thermal data alone, such as reaction heats and heat capacities. Based on the first two laws of thermodynamics and van't Hoff's equation, chemical equilibria depended on the free reaction enthalpy $\Delta\underline{G}$, which is a function both of the reaction enthalpy, $\Delta\underline{H}$, and the reaction entropy, $\Delta\underline{S}$, according to the Gibbs-Helmholtz equation:

$$\Delta\underline{G} = \Delta\underline{H} - \underline{T}\Delta\underline{S}$$

The problem was that, while enthalpy values could be calculated from thermal measurements, entropy values required data at the absolute zero of temperature, which was practically inaccessible. Guided by some theoretical reasoning and then supported by a huge measurement program at very low temperatures, Nernst in 1906 suggested his heat theorem. According to a later formulation, it states that all entropy changes approaches zero at the absolute zero.

The theorem not only allowed calculating chemical equilibria, it was also soon recognized as an independent Third Law of general thermodynamics with many important consequences. One such consequence is that it is practically impossible to reach the absolute zero. Another consequence is that one can define a reference point for entropy functions, such that the entropy of all elements and all perfect crystalline compounds is taken as zero at the absolute zero. Furthermore, the heat theorem and Nernst's large experimental evidence provided early support for the new quantum mechanics.

Nernst made numerous other important contributions to physical chemistry. Next famous is perhaps his distribution law that describes the concentration distribution of a solute in two immiscible liquids and which allows calculating extraction processes. He formulated several theories, such as those of the electrostriction of ions, the diffusion layer at electrodes, and the solubility product. He also established new methods to measure dielectric constants and to synthesize ammonia, on which Fritz Haber should follow up.

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Word Count: 732

Author: Joachim Schummer

Haber, Fritz (1868-1934)

Haber (born December 9, 1868, Breslau, Prussia [now Wroclaw, Poland]; died January 29, 1934, Basel, Switzerland) successfully applied physical chemistry to technological problems. In 1918 he won the Nobel Prize in chemistry for his synthesis of ammonia from the elements as the crucial step in the production of fertilizers and explosives.

Haber, whose father was a larger natural dyestuff importer, was destined to enter the family business at a time when synthetic dyes began to dominate the market. After his study of organic chemistry and technology at various universities and some brief experience in chemical factories, he returned to his father's firm, though with little fortune and inclination. In 1894 he became assistant to Hans Bunte at the Technical University of Karlsruhe. Self-taught in physical and electrochemistry, he soon successfully applied the new theories to chemical technology, particularly to the combustion of hydrocarbons, the electrolysis of salts, and the fixation of nitrogen. Only in 1906, he was appointed professor in Karlsruhe which he left six years later to become director of the new Kaiser Wilhelm Institute for Physical Chemistry in Berlin. During WW II, that institute turned into Germany's headquarters of chemical weapon research and production with Haber as its head. After the war, he increasingly engaged in national science management and international relations. When the Nazis in 1933 began to dismiss all Jews from civil service, Haber, himself a Jew converted to Christianity, immediately resigned and emigrated to Great Britain. He was invited to head the physical chemistry section of the new Weizmann Institute in Palestine, but died shortly before its foundation.

The most abundant component of common air, elementary nitrogen stubbornly resists chemical reactions. However, certain bacteria can transform it to ammonia (the so-called fixation of nitrogen) as the essential supply to the protein production of plants. That was already known in the late 19th century when a rapidly growing population required a more efficient agriculture to be supported by fertilizers including "fixed nitrogen". Since at that time natural niter or guano from Chile was virtually the only nitrogen source for fertilizers, chemists were challenged to devise methods for the fixation of nitrogen from the air. In the early 1900s, several prominent physical chemists, including Le Chatelier, Ostwald, and Nernst, were experimentally and theoretically working on the issue from two different approaches to nitrogen: oxidation to nitrogen oxide and reduction with hydrogen to ammonia.

While most researchers soon dropped the topic because of little success, Haber from 1904 on continued investigating both approaches under contract with the BASF company who offered him money, apparatuses, and patent shares. The path to ammonia turned out to be more promising if the reaction rates were increased by catalysts at high temperature. Thermodynamics required low temperature, however, to move the equilibrium toward higher yields of ammonia. Since thermodynamics predicted the same effect at high pressure, Haber and his coworkers in Karlsruhe searched for temperature and pressure conditions which a reaction vessel could withstand and which brought acceptable yields. Success came only when they found more effective catalysts, first osmium and uranium. In addition, they pushed the equilibrium to the product side by continuously drawing off ammonia from the reaction mixture and continuously providing new reactants, resulting in 1909 in a steady flow reactor at about 100 atm and 500 °C with ammonia yields of some 10%.

Had Haber shown that the production of ammonia from the elements was feasible in the laboratory, it was up to Carl Bosch, a chemist and engineer at BASF, to transform the process into large-scale production. The industrial converter that he and his co-workers created was completely revised, including a cheaper and more effective catalyst based on extensive studies in high-pressure catalytic reactions. That should bring Bosch the chemistry Nobel Prize in 1931, and the world multi-million tons of fertilizer per year.

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Word Count: 635

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Le Bel, Joseph Achille (1847-1930): 400

Le Bel (born January 24, 1847, Pechelbronn, France; died August 6, 1930, Paris, France) was, with van't Hoff, the founder of modern stereochemistry by establishing the relation between optical activity and asymmetric carbon compounds.

Le Bel was the son of a wealthy family that controlled petroleum workings in Pechelbronn, Alsace. In 1865, he was sent to the École Polytechnique at Paris to obtain a chemical education for improving the extraction and refinery of petroleum. Yet, he should spend the greatest part of his life in Paris doing chemical research. After graduation, he worked with Antoine Balard and Adoph Wurtz, with intermediary periods of building up new plants at home. Finally in 1889, he sold his shares and established a private laboratory in Paris where he devoted himself to organic chemistry and, in his later years, to paleontology, botany, and philosophy. A freelancer who never held an academic appointment, Le Bel received general recognition as chemist and even became president of the French Chemical Society in 1892.

In 1874, at the age of 27, Le Bel presented a brief paper to the Paris Chemical Society that founded his scientific fame, although that should remain his only outstanding contribution to chemistry. By the late 1840s, Louis Pasteur had separated two sorts of tartrate crystals of the same composition, each crystal shape being the mirror image of the other. These crystals in solution not only rotated the plane of polarized light to a certain angle (optical activity), the two sorts also did that into opposite directions. Pasteur called such pairs of substances optical isomers, and because they showed no difference in chemical properties, they were represented by the same constitutional formula in the new chemical structure theory. Le Bel now extended the structure theory, from constitutional to configurational representations in three-dimensional space, to account for the difference of optical isomers. He argued that if a tetravalent carbon atom combines with four different groups, as in tartrate, the carbon must be asymmetric in three-dimensional space (i.e. without symmetry plane or center). Furthermore, for each such asymmetric carbon there are exactly two different structures (stereoisomers), each being the mirror image of the other, like the crystal shapes of Pasteur. Le Bel's structure theory could not explain optical activity, but it explained and predicted which compounds had stereoisomers and which not, an approach that he extended also to nitrogen compounds.

Strangely enough, van't Hoff, with whom Le Bel had worked together in Wurtz's laboratory shortly before, independently arrived at the same theory from a different starting point virtually at the same time.

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Word Count: 426

Author: Joachim Schummer