Century of Nobel Prizes: 1909 Chemistry Laureate

Wilhelm Ostwald (1853-1932)

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The Nobel Prize in 1909 for Chemistry was awarded to Wilhelm Ostwald, for his pioneering work on catalysis, as well as fundamental studies on chemical equilibria and reaction rates. At the time of award, Ostwald had already retired as a Professor from Leipzig University. It is due to the efforts of Wilhelm Ostwald, more than any other scientist, that physical chemistry came to be recognized as a branch of chemistry in its own right. Apart from his pathbreaking researches, he founded *Zeitschrift für Physikalische Chemie* in 1887 and himself edited 100 volumes of it up to 1922. He also established the *Deutsche Electrochemische Gesellschaft* (German Electrochemical Society) in 1894. This was expanded in 1902 into the *Deutsche Bunsen-Gesellschaft für Angewandte Physikalische Chemie* (German Bunsen Society for Applied Physical Chemistry). Ostwald wrote several textbooks including *Lehrbuch der Allgemeine Chemie* (Textbook of General Chemistry), Gründriâ der Allgemeinen Chemie (Outline of General Chemistry) and *Hand- und Hilfsbuch Physikalisch-Chemischer Messungen* (Handbook and Manual for Physicochemical Measurements). These activities are an indication of Ostwald being a gifted author and organizer, apart from being a highly creative scientist.

Wilhelm Ostwald was born in Riga, Latvia on September 2, 1853. His parents were Gottfried Wilhelm Ostwald and Elisabeth Leuckel. He become interested in carrying out chemical experiments at an early age. It is reported that as an eleven-year old boy, he made his own fireworks. Wilhelm was educated at the *Realgymnasium* in Riga. Later he was admitted to Dorpat University in 1872, where he studied chemistry. Here, he read about Julius Thomsen's measurements of heats of chemical reactions. It occurred to him that other properties of solutions could as well be employed for monitoring chemical reactions. He started

Keywords
Catalysis, chemical equilibria, chemical reaction rates.

Box 1. 1909 Nobel Laureates and a Brief Description of their Work

Beernaert, Auguste Marie Francois (Belgium, Peace)	Diplomatic commitment for reduction in arms race as member of the international peace conference and the permanent international court in Haag.
Estournelles, Paul Baron de Constant De Rebecque d' (France, Peace)	Diplomatic representative of France at the peace conference of Haag in 1899 and 1907.
Braun, Karl Ferdinand (Germany, Physics)	Contribution in the development of wireless telegraphy, and amongst other things, invention of crystal detector.
Marconi, Guglielmo (Italy, Physics)	Contribution in the development of wireless telegraphy and invention of sending and receiving systems as technically integrated systems.
Kocher, Emil Theodor (Switzerland, Physiology or Medicine)	Pathbreaking work in physiology, pathology and surgery of the thyroid gland.
Lagerlöf, Selma (Sweden, Literature)	In acknowledgement of the high idealism, the lively imagination and spiritual presentation that show in her works.
Ostwald, Wilhelm (Germany, Chemistry)	In recognition of his work on catalysis and investigations into the fundamental principles governing chemical equilibria and rates of reactions.

a new discipline named as ***volume chemistry*** for this purpose. From detailed measurements of densities and refractive indices, he tabulated extensively the affinities of many acids. The title of his PhD thesis submitted to the Kaiserlichen University, Dorpat in 1878 was *Volumchemische und Optisch-chemische Studien*. He was trained at the physics institute by Professor Arthur von Öttingen and at the chemistry laboratory by Professor Karl Schmidt. Ostwald has acknowledged the guidance of these two teachers in his scientific training.

In 1877, Ostwald was admitted as an unpaid academic lecturer at Dorpat University. He was appointed as a full time professor of chemistry at Riga Polytechnicum in 1881. In 1887, he accepted the professorship of physical chemistry at Leipzig University. In the mean while, Ostwald was married to Helene von Reyher in 1880. They had two daughters and three sons. One of the sons, Karl Wilhelm Wolfgang Ostwald (known as Wo. Ostwald) be-came a lecturer at Leipzig University and was regarded as a leader in colloid chemistry.

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Ostwald worked on the problem of chemical affinity and rates of chemical reactions. In 1888, he derived the (now) so-called Ostwald dilution law. This work was published in Volume 2 of the newly established *Zeitschrift für Physikalische Chemie*. It dealt with the dissociation of an electrolyte MA as $MA = M^+ + A^-$ Here the corresponding equilibrium constant is given by

$$K = \{\alpha^2 c/(1-\alpha)\}. \{f_{M+}.f_{A-}/f_{MA}\} \qquad (1)$$

In this expression, α is the degree of dissociation of the acid, with initial concentration, c. The second term involves the activity coefficients of ions M^+, A^- and the undissociated acid, MA. In very dilute solution, these activity coefficients may be approximated to unity, leading to

$$k = \alpha^2 c/(1-\alpha). \qquad (2)$$

Note that k in (2) is different from the equilibrium constant K in (1) and is not exactly a constant (due to the neglect of activity coefficients). Ostwald suggested the use of conductivity of solutions for calculating α. If Λ_c and Λ_0 are the conductances of solutions with concentration of solutes, c and 0 (the case of infinite dilution), respectively, he proposed that the degree of dissociation, α may be estimated by the ratio, viz. $\alpha = \Lambda_c/\Lambda_0$. It was found that with this measure of α, the Ostwald dilution law fails for electrolytes such as KCl. However, it was found to apply reasonably well for the case of weak electrolytes, e.g. acetic acid. In 1891, Ostwald worked on the theory of coloured acid-base indicators. This work involved the use of the law of mass action. He incorporated his formulation in *Die wissenschaftlichten Grundlagen der analytischen Chemie* (the scientific foundations of analytical chemistry) published in 1894.

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in two different experiments, the starting concentrations are a_1 and a_2 with the corresponding times being t_1 and t_2, then it was proved by him that n, the order of the reaction is given by

$$n = 1 + \frac{\log (t_1/t_2)}{\log (a_2/a_1)}. \tag{3}$$

This may be compared to the differential method suggested by van't Hoff in 1884. He also proposed a method called the *isolation method* for more complicated reactions. Here, the orders with respect to the reactants A, B, C, etc. are determined in 'isolation' for example, by taking excess of all reactants but one.

Ostwald also contributed to the theory of transformation of a substance from a metastable to a stable state. He proposed a *law of successive reactions* for such cases. This law states that a system does not directly pass from a less stable condition into the most stable one. It traverses through intermediate states of progressively higher stability. This law is found to be true in a large number of cases.

Ostwald's name appears in all textbooks in physical chemistry in connection with an important property of fluids, viz. *viscosity*. For a smooth flow of a fluid through a tube, it was observed that the volume rate of flow ($V' = dV/dt$) is given by

$$V' = \pi P R^4/(8\ \eta l) \tag{4}$$

Here, P is the pressure drop along the tube of length l and radius R; and η is the coefficient at viscosity (see *Box* 2). This coefficient is measured in units called *poise*. Ostwald constructed a simple glassware for viscosity measurements, which is referred as the *Ostwald viscometer*. This (*Figure* 1) consists of a U tube with two bulbs A and B connected by a thin capillary, C. The time of fall of a liquid is measured between two marks x and y. Since the same tube is employed for measuring the viscosity of two liquids (1 and 2), the relative viscosity is given by $\eta_1/\eta_2 = \rho_1 t_1/\rho_2 t_2$. Here, η_1 stands for coefficient of viscosity of liquid 1 with density ρ_1 and the time of fall, t_1. Although many variants of it are available, the Ostwald viscometer is still popular due to its simplicity.

Box 2. Coefficients of Viscosity (η) of some Liquids at 20°C in Centipoise

Liquid	η
Acetone	0.329
Chlorobenzene	0.800
Water	1.008
Ethanol	1.200
Nitrobenzene	2.013
Glycerol	$\sim 10^3$

Ostwald's most recognized contribution is in the area of *catalysis* (Greek: loosen). This term was introduced by the famous Swedish chemist, Jöns J Berzelius in 1835. Several examples of catalysis were known by this time. These included transformation of starch into dextrin and sugar by acids (Kirchhoff,1811); decomposition of hydrogen peroxide in the presence of manganese dioxide, platinum, etc. (Thénard, 1818); transformation of alcohol to ether in presence of sulfuric acid (Mitscherlich, 1834), etc. Mitscherlich had termed this phenomenon as *chemical action by contact,* for which Berzelius later introduced the term *catalysis.* He stated that *The catalytic force actually appears to consist in the* ability *of substances to arouse the affinities dormant at this temperature by their mere presence and not by their affinity so as to result in a compound substance...*

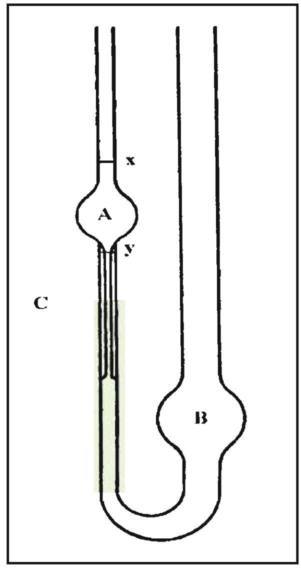


Figure 1. The Ostwald viscometer.

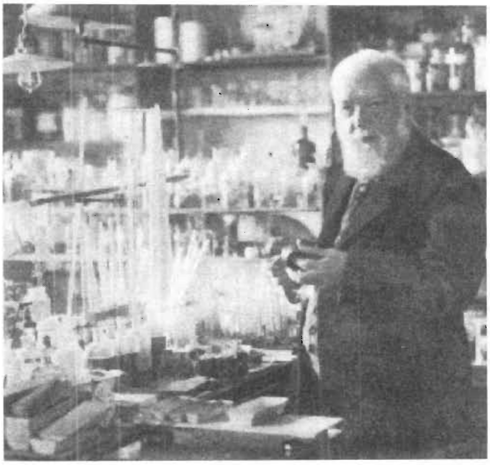
This discussion on understanding the nature of catalyst continued further. In that connection, there also arose a debate between Berzelius and Liebig on the subject. A clarification came through a definition of the rate of a chemical reaction which was still not known. Such a definition was proposed by L Wilhelmy in 1850 with reference to inversion of sucrose (incidentally, a reaction catalysed by acids). Ostwald studied, in 1883, the rise in acid titre in an aqueous solution of common acetic ester (as well as methyl acetate) to which hydrochloric acid was added. With several further studies, Ostwald concluded in 1887 that the nature of catalysis lies in acceleration of a reaction and *not in its inducement.* This viewpoint was published in 1888.

Box 3.

Key sections of industry are based on the action of catalysis. A factor of perhaps even greater weight is the growing realisation that enzymes, which are extremely important for the chemical processes within living organisms, act as catalysts and hence the theory of plant and animal metabolism falls essentially in the field of catalyst chemistry.

Wilhelm Ostwald, Nobel Lecture delivered on December 12, 1909.

Several interesting general characteristics of catalysis were experimentally known. These were summarized by Ostwald in 1888. For instance, the catalyst is unchanged chemically at the end of the reaction, although its physical state may change. Further, a very small amount of catalyst was generally found to be sufficient to effect a reaction. Although the role of catalyst in *accelerating* a reaction suggested by Ostwald was generally accepted, H E Armstrong (1885-1903) and later T M Lowry (1925-26) pointed out that there are certain reactions which occur only if a catalyst is present. With further evolution of the concept, the



Left. Ostwald at work in his country home* Villa Energie *near Leipzig.

Right. Wilhelm Ostwald and Svante Arrhenius.

definition prescribed in more recent textbooks is that a catalyst is a substance that lowers the energy (or free energy) of activation of a reaction.

Ostwald also contributed greatly to the chemical industry. He discovered a catalytic process (patented in 1902) to convert ammonia into nitric acid. Here, ammonia mixed with air, is heated and led over a catalyst, viz. platinum. This yields nitrous oxide, which on further oxidation and reaction with water forms nitric acid. This process, called the *Ostwald process*, was used by the Germans for producing explosive during World War 1. The process is still used in many countries. Many further developments of industrial importance have come from Ostwald's pupils such as Max Bodenstein and Alwin Mittasch.

Unfortunately, Ostwald's relations with the administrators and colleagues at the University of Leipzig slowly deteriorated. This

Box 4. Ostwald's Theory of Happiness

Ostwald suggested a theory of happiness in terms of the energy spent for various causes. He gave a formula for happiness in terms of *G (Glück)*, *A (Arbeit)*, the energy spent for doing useful work and *W (Wiederstand)*, energy required for overcoming resistance. His formula reads $G = k(A-W)(A+W)$, where k is a constant.

Box 5. The most General Problem of Science...

The general assumption of *coherence of the world,* which as we know from the basis of all science... The existence of this coherence, and thus the most general problem of science, can be expressed as the general function equation $F(a,b,c,d,....) = 0$.

Increasing specialization of the general equation yields the types of scientific discoveries being sought.

Wilhelm Ostwald, Nobel Lecture delivered on December 12, 1909.

Box 6. Wilhelm Ostwald and his Theory of Colours

From the year 1914, Wilhelm Ostwald worked on formulating a scientific and practically applicable theory of colors. He fractioned every colour in to its constituent components. In 1921, he put together an atlas with a total of 2500 colours. His theory of colours was applied for some time in textile industry and in porcelain painting. Ostwald's main works in this field include *Die Farbenfibel* (The colour manual), *Die Farbenlehre* (The theory of colours) and *Die Hormonie der Farben* (The harmony of colours).

led to his resignation from professorship in 1906, just three years before the award of the Nobel Prize to him.

In the earlier articles, we have seen how Wilhelm Ostwald encouraged Svante Arrhenius. There was also a close collaboration between Arrhenius and van't Hoff. It is this trio that laid the foundation of physical chemistry, with Ostwald being their visionary leader.

After 1906, Ostwald could devote considerable time for his studies and publications in philosophy (*Boxes* 4 and 5). Noteworthy among these are *Moderne Naturphilosophie* (Modern natural philosophy) and *Die Pyramide der Wissenschaften* (The pyramid of the sciences). He also continued his monistic (monism: an atheistic, science-based, quasi religion) writings with a view to fight the Church's claim to power in natural sciences. He also continued his hobby of painting and the allied interest in the theory of colors (see *Box* 6).

After such a long active and productive life, Ostwald died in his country home near Leipzig on April 4, 1932. However, he will be always remembered as the founder of physical chemistry as well as intellectually one of the most influential chemists of the twentieth century.

Box 7. Ostwald and Atomic Theory

Philosophically, Ostwald was a positivist. He denied the reality of atoms almost until the end of his life. He argued that chemists do not observe atoms but study the comprehensive laws regarding them in terms of weight and volume ratios. He believed that atoms were a hypothetical conception but was finally converted to atomism in 1908. Another eminent non-believer in atomic theory was Ernst Mach, who refused to accept it until his death in 1916 at the age of 78.

Suggested Reading

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