

Century of Nobel Prizes

1901 Chemistry Award: Jacobus Henricus van't Hoff (1852-1911)

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Shridhar R Gadre is a professor of physical chemistry at the Department of Chemistry, University of Pune. He has been actively working in the area of theoretical and computational chemistry. He feels that the history of the development of a concept should be inextricably woven into the teaching of a topic. Similarly, the subject could be made more lively by incorporating brief biographical sketches as well as anecdotes of the pioneers who developed the discipline. History of science, chess and trekking are his hobbies.

The first Nobel Prize in Chemistry was awarded to the Dutch physical chemist, Jacobus Henricus van't Hoff for his contributions to the discovery of *the laws of chemical kinetics and the osmotic pressure of solutions*. He received the Prize on December 10, 1901. This was the first year, the Nobel Prizes were awarded by the Nobel Foundation established by the will of the famous Swedish chemist Alfred Nobel. The other awardees of the year were Henri Dunant and Passy Frédéric (peace), Emil von Behring (physiology/medicine), Wilhem Conrad Röntgen (physics) and Sully Prudhomme (literature). Apart from his prize-winning work on chemical kinetics and osmotic pressure of solutions, van't Hoff pioneered research in organic stereochemistry with his postulate of tetrahedral carbon atom. His work has percolated into all branches of chemistry, although he is regarded as a founder of physical chemistry along with Wilhem Ostwald, Svante Arrhenius and J Willard Gibbs.

Henry (as he was called) was born (the third of seven children) in Rotterdam on August 30, 1852 in a Dutch family. His father was

Box 1.

Emil von Behring (physiology/medicine) – for his contribution to the area of serum therapy and its application to diphtheria.

Henri Dunant (peace) – for the formation (establishment) of the international red cross society.

Frédéric Passy (peace) – one of the founders of the peace movement and the interparliamentary union.

Willhelm Conrad Röntgen (physics) – for the discovery of the electromagnetic X-rays (also known by his name).

Sully Prudhomme (literature) – For high idealism, artistic accomplishment, and a rare reunion of heart and intellect-stimulating work.

Jacobus van't Hoff (chemistry) for his contribution to the discovery of laws of chemical reaction kinetics and osmotic pressure of solutions.



a practising physician and mother, the daughter of a wine dealer. Henry received liberal education in a private school. He excelled in mathematics as well as natural sciences and enjoyed singing, pianoforte playing and long country walks. At the age of 15, Henry entered a 'Hoogere Burgerschool' and chose to experiment with hazardous chemicals. These adventures in school came to a halt after they were discovered by the school authorities. However, he continued these experiments at home and is reported to have charged small fees from his spectators! His later education was at the polytechnic at Delft and University of Leiden. During this time, he was deeply influenced by Byron's poetry. Attracted by the fame of Kekulé, he moved to Bonn and found the teachings of the master on the constitution of organic substances interesting. However, personally he found Kekulé rather unsympathetic. After clearing his pre-doctoral qualifying examination at the University of Utrecht, he spent some time at Ecolé de Medicine, Paris with Professor Adolphe Wurtz. Here, he got acquainted with Joseph Achille Le Bel (with whom he later shared the credit of inventing the tetrahedral carbon atom). He submitted his PhD dissertation of a routine character on cyanuric and malonic acids in October 1874. However, a month before that he published a pamphlet in Dutch on his famous space formulas.



The monument to van't Hoff in Rotterdam. Reproduced with permission from the *Journal of Chemical Education*, Vol.29, p.377, 1952. Copyright © 1952, Division of Chemical Education, Inc.

Pasteur had earlier shown that the crystals of sodium tritrate were of two types. One kind rotated the plane of polarized light clockwise, the other did so counterclockwise. This property also persisted in solution and led to a stipulation that the molecules

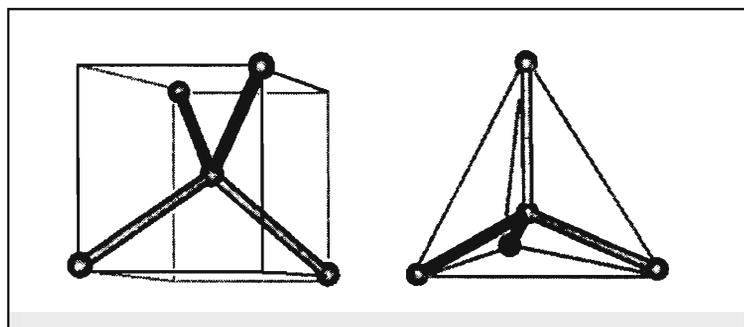


Figure 1. A simple way to visualize a tetrahedron and a cube.

was clarified by him in an extensive monograph in French, *La Chimie dans l'espace* (*The Chemistry of Space*) in 1875. These ideas were not received well by many of the organic chemists of repute who made discouraging and sarcastic comments about the suggestion of the three-dimensional nature of organic molecules. These included Kolbe as well as Ladenburg. However, with strong support from established chemists such as Wislicenus (seventeen years senior to van't Hoff) and further scientific evidence, the van't Hoff–Le Bel model gained acceptability. A great success of this model was its ability to predict the number of optically active isomers of an organic molecule containing several asymmetric centers. Between 1877 and 1881, van't Hoff wrote a 554 page book, in two volumes, entitled *Ansichten über die Organische Chemie* (*Views about Organic Chemistry*). However, it has been commented that the book is a large collection of data and gives no real insights, in contrast with his masterpiece, *Études de dynamique chimique* (*Study of Dynamics in Chemistry*) written three years later.

In September 1877, van't Hoff was appointed a lecturer in the town college, Amsterdam and promoted as ordinary professor of chemistry, mineralogy and geology later in June 1878. He married Johanna Mees in December 1878. In the following years, he investigated the concepts of reaction velocities, rate constants and chemical equilibrium and collected them in his famous treatise *Études de dynamique chimique*. Why did van't Hoff turn his attention from organic to physical chemistry? His main interest was to understand the transformation of organic molecules. The tools for gaining such an understanding were clearly reaction kinetics and thermodynamics. In the field of reaction kinetics, some significant work had been done by L Wilhelmy (1850), A V Harcourt and W Esson (1867) and by C M Guldberg and P Waage. However, the systematization and unification of these concepts needed the genius and analytical power of van't Hoff. He classified the reactions as unimolecular, bimolecular, etc. and showed how to determine the number of molecules participating in such chemical transformations. The

Box 4. Remarks by Ladenburg on the three dimensional space formulas

van't Hoff introduces into the formulas something that I and most chemists purposely keep out of them. viz., spatial representation. What I mean by a formula and want to be understood as such, has been expressed at different places, particularly in the article quoted by van't Hoff: A formula must give account of the composition, the molecular weight and the way the atoms are linked together.

Box 5.

The 'differential method' introduced by van't Hoff deals with reaction kinetics by measuring slopes of the graph of concentration vs time. If $v = kc^n$, then $\log v = \log k + n \log c$. Hence a double log plot of $\log v$ vs. $\log c$ yields both n and k .

terminology of 'order' of a reaction was Ostwald's clarification later in 1887. van't Hoff suggested the 'differential method' for obtaining the order of a reaction. The symbol \rightleftharpoons was introduced by him for denoting reversible reactions. It is still in use in chemistry. The investigation of phosphine and arsine decomposition on a glass surface was carried out by van't Hoff and Kooij in 1893. They found these reactions to be of first order. The shift in equilibrium caused by change in temperature was clearly stated by van't Hoff (a generalization of which is called the Le Chatelier principle). He also suggested the important equation

$$d(\ln K_p)/dT = (\Delta H/RT^2),$$

but did not present its proof. This is an important relation between the equilibrium constant (at constant pressure) for a reaction involving gases and the corresponding heat of reaction. It is called the van't Hoff equation (earlier called as the van't Hoff isochore, a clear misnomer). The integrated form of the van't Hoff equation is:

$$\log (K_2/K_1) = \Delta H^0 (T_2 - T_1) / \{4.576 T_1 T_2\}.$$

This allows the estimation of equilibrium ΔH^0 from the measured value of the equilibrium constants K_1 and K_2 at T_1 and T_2 , respectively. That the negative value of the free energy change implies spontaneity of the reaction was pointed out by van't Hoff in 1883. It may be noted that this was mentioned earlier implicitly by J W Gibbs in 1876 and H von Helmholtz in 1882.

It was first empirically found by Hood (1878) that the rate constant k of a chemical reaction varies with the absolute temperature T as

$$\log k = B - A/T,$$

where A, B are constants. Some theoretical significance to this law was given in 1884 by van't Hoff who argued on the basis of the effect of temperature on equilibrium constants. The idea was extended and successfully applied by Arrhenius in 1889 and



van't Hoff

Box 6.	c	π	π/c
Pfeffer's results (1877) of osmotic pressure of sucrose solutions at constant temperature. Concentration 'c' is expressed in g per 100g of solution, and the osmotic pressure (π) in mm of mercury.	1.0	535	535
	2.0	1016	508
	2.74	1518	554
	4.0	2082	521
	6.0	3075	513

the law is now known as the Arrhenius law. Since a catalyst is unchanged at the end of a reaction, it can have no influence on the position of equilibrium. Since this equilibrium constant K is a ratio of the rate constant k_1 and k_{-1} (in forward and reverse directions), a catalyst must influence the rates of forward and reverse reactions in the same proportion. This was verified experimentally by van't Hoff for several reactions.

At this stage, van't Hoff embarked upon yet another significant venture. Hugo de Vries, the famous Dutch botanist and his colleague at Amsterdam had been interested in studying the phenomenon of osmosis [osmosis (Greek):push] in cells in order to understand plant nutrition. Consider a solvent and a solution that are separated by a semipermeable (an adjective suggested by van't Hoff) membrane. It was noticed that excess pressure must be applied to the solution to prevent the passage of the solvent into it. This excess pressure is termed as osmotic pressure. Through casual conversations with de Vries, van't Hoff became aware of the technical advances made by Pfeffer in measuring the osmotic pressure of solutions. He concluded, from Pfeffer's measurements on 1% aqueous sugar solution that osmotic pressure, π follows the equation $\pi = cRT$ which is identical in form to the ideal gas law. Here, c is the concentration of the solution in terms of moles of solvent per litre of the solution; T , the temperature and R , the gas constant. In the papers written in *Achieves Neerlandaises* (1885) and *Transactions of the Swedish Academy* (1886) van't Hoff showed complete analogy between gases and dilute solutions.

However, he noted that for some substances, the equation obeyed

had a form $\pi = icRT$, with an extra factor i (later termed as the van't Hoff factor). Two years later, Arrhenius offered an explanation for this behavior in terms of electrolytic dissociation. Considering $M_xA_y = xM^+ + yA^-$, in which an electrolyte M_xA_y dissociates into $v(=x+y)$ ions, Arrhenius derived the expression, $i = 1 - \alpha + v\alpha$. Here the van't Hoff factor, i is given in terms the degree of dissociation, α and the number of ions, v . The collaborations between van't Hoff and Arrhenius led to significant advances in this area.

An explanation of the physical origin of osmotic pressure was offered by van't Hoff in terms of molecular bombardments on the semipermeable membrane, analogous to the kinetic theory of gases. Osmosis is one of the colligative properties that provides a sensitive method for the determination of molecular weights of polymers. The rare combination of analytical thinking and powerful imagination are evident from van't Hoff's work on osmotic pressure.

In 1887, Ostwald, in association with van't Hoff founded the *Zeitschrift für Physikalische Chemie*. This remained a core journal in physical chemistry for several years. Van't Hoff continued as its co-editor till his death in 1911. The laboratory of van't Hoff in Amsterdam was expanded in 1891 allowing him to accommodate several foreign students who liked to visit him. However, in 1895, a position of Professor at the Berlin University and the membership of the Prussian Academy of Science was offered to him. Here, his teaching duties were minimal (1 lecture per week) and he undertook collaborative research with his former student, Meyerhoffer on the oceanic salt deposits in Strassfurt potash beds. This work was 'applied' in nature. In 1890, he introduced the novel concept of solid solutions. This work attained importance in the area of alloys.

It has been pointed out that van't Hoff was a quiet, dreamy and romantic man. He had simple personal habits, hated professional decorum and treated his pupils as friends. He would think deeply before answering a query of a colleague or a stu-

Box 7.

It must be said that van't Hoff's work is in many ways more French than German. Soundness and solidity he certainly values, but he is in love with the idea in its general form, and his proofs are directed more towards establishing his idea.... than to modelling and rounding it off...

– van Deventer,
the assistant of van't Hoff.

dent. However, an answer would always be forthcoming in a day or two.

The first Nobel Prize in Chemistry was announced in October 1901. In December 1901, he travelled to Stockholm in Sweden to receive it. However, his health began to fail in 1906 after the demise of Meyerhoffer. In 1909 and 1910 respectively, he reported his last significant scientific finding. Here, he showed that the enzyme emulsin plays the role of catalyst in the formation and decomposition of glycosides. It is believed that he laid the foundation stone of enzyme chemistry in these papers. However, his health slowly deteriorated and he died peacefully on March 1, 1911. His deep contemplation, strong imagination and ability to develop new and bold links between apparently unrelated phenomena distinguished him from his contemporary chemists. van't Hoff has earned a permanent place in chemistry not only for the areas mentioned in his Nobel citation but also for his pioneering contributions to stereochemistry.

Suggested Reading.

The general references on Nobel Laureates in Chemistry are:

- [1] I Asimov, *A Short History of Chemistry*, Doubleday, New York, 1965.
- [2] W H Brock, *The Fontana History of Chemistry*, Fontana Press, London, 1992.
- [3] L K James, Ed., *Nobel Laureates in Chemistry 1901-1992*, American Chemical Society, Washington DC, 1993.
- [4] *Harenberg Lexikon der Nobelpreisträger*, Harenberg Laxicon, Dortmund, 1998.

Suggested Reading on van't Hoff's biography and work

- (1) For biographical information on J H van't Hoff, cf, The van't Hoff Memorial Lecture delivered before the Chemical Society, J Walker, *J. Chem. Soc.*, Vol. 103, pp.1127-1143, 1913.
- (2) See S Glasstone, *Textbook of Physical Chemistry*, McMillan, India (1974) for details of van't Hoff's contributions to physical chemistry.
- (3) H S van Klooster, *J. Chem. Educ.*, Vol. 29, pp. 376-379, 1952.
- (4) A F Holleman, *J. Chem. Educ.*, Vol. 29, pp.379-382, 1952.

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