Jacobus Henricus van 't Hoff

A Short Biographical Sketch

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J H van 't Hoff is considered as one of the greatest chemists of all time. He started his career as an organic chemist. He solved the vexing problem of optical isomerism by proposing an asymmetric tetrahedral carbon bonded to form different groups. He extended this to include geometric isomerism, and to compounds with heteroatoms in place of asymmetric carbon. Thus he established the 'chemistry in space' or stereochemistry. He moved on to work on reaction kinetics, equilibria, thermodynamic properties of dilute solutions and related areas. He laid the foundation for physical chemistry through these discoveries and was awarded the first Nobel Prize in Chemistry in 1901. van 't Hoff died of tuberculosis at a relatively early age of 59.

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Four Groups – Two Arrangements

Weeks before submitting his doctoral thesis, "Contribution to the knowledge of cyanoacetic acid and malonic acid" in 1874, Jacobus Henricus van 't Hoff printed and distributed at his own cost, a pamphlet, "The Chemistry in Space". It contained twelve pages of text and one page of diagrams. It explained the necessity of tetrahedral structure of carbon that has four different groups to account for the isomerism of compounds with the same constitutional structure but of opposite optical rotation. The idea was published in a Dutch journal in September 1874. A similar concept was published independently by Joseph Achille Le Bel in a French journal in November 1874. van 't Hoff published an enlarged version in French, 'Chemistry in Space', the next year. It caught the attention of a larger scientific community only when its German version, translated by F Hermann in 1877, was available, and was recommended enthusiastically by an established scientist, Johannes Wislicenus.

Keywords
van 't Hoff – biography, chemistry in space, stereochemistry, chemical dynamics, Stassfurt salt deposits, osmotic pressure–theory, Le Bel.

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The proposal met with serious criticism by some senior scientists (Ladenburg, Kolbe, Mach), because it suggested that molecules possessed real three dimensional forms, with the atoms suitably located and that structure was not merely a concept. van 't Hoff was just 22 years of age and Le Bel five years older, both too young and inexperienced to be taken seriously, in the view of senior scientists. The existence of molecules as an assembly of atoms depicted in their structural formulas was still not clearly accepted at that time because the atomic hypothesis itself did not enjoy full support yet. The success of van 't Hoff's work on stereochemistry and osmotic pressure and Albert Einstein's paper on Brownian motion in 1905 (*Resonance*, December 2005, pp.106–124) finally convinced the scientific world about the physical reality of atoms and molecules. The evidence accumulated by van 't Hoff in favour of his hypothesis was too strong and the proof too compelling to ignore it.

When van 't Hoff published a vastly enlarged second edition, *The Arrangement of Atoms in Space*, in 1894, he got Wislicenus to write the preface for this also. But, by that time, van 't Hoff's reputation had reached such heights that Wislicenus had changed the tenor of his preface to respect from a mere condescension. He writes, "*… then I had to address to German chemists a letter of recommendation in favour of the little-known hypothesis of a very young colleague; now the name of the author has a renown so high, based on such an extraordinary series of important and far-reaching researches, that my recommendations would be altogether superfluous for his book, even if the theory here set forth had not acquired for itself the position in chemistry which in fact it possesses…*"

The idea of chemistry in space or stereochemistry was not a singular, sudden occurrence to van 't Hoff's mind. Many chemists before him, starting with Pasteur, had some concept of three dimensional molecular structures and the tetrahedral nature of carbon. Pasteur, based on his work on optically active compounds, suggested the presence of asymmetry at the molecular level (*Resonance*, January and March, 2007). However, it was van 't Hoff and Le Bel who clearly recognised that tetrahedral carbon bonded to four different groups at the four corners alone can be asymmetric and non-superimposable on its mirror-image molecule with attendant opposite optical rotation. van 't Hoff went a step further to propose a planar structure for ethylene and its derivatives. In this he scored over Le Bel in explaining the isomerism in ethylene derivatives and their optical inactivity due to the presence of a symmetry plane along the molecular plane comprising two carbons and four substituents.

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The experimental evidence was so much in favour of the hypothesis that the initial resistance died down soon and it achieved spectacular success in due course, prompting Wislicenus to make the following remarks in the preface referred to earlier.

"*It has already effected to the full all that can be effected by any theory, for it has brought into organic connection with the fundamental theories of chemistry facts which were before incomprehensible and apparently isolated, and has enabled us to explain them from these theories in the simplest way. By propounding to us new problems the hypothesis has stimulated empirical investigation on all sides; it has caused a vast accumulation of facts, has led to the discovery of new methods of observation, has become amenable to the test of experiment, and has at the same time started in our science a movement full of significance, in a certain sense, indeed, a new epoch*".

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The story of stereochemistry is an ever growing one, as new vistas in the area keep opening up regularly. It is important not just in chemistry, but in biochemistry, biology, drug design, molecular self-assembly, and many other areas.

Despite the revolutionary changes it brought about and the new direction it gave in the area of structural chemistry, the Nobel Prize that van 't Hoff got was not for stereochemistry, but for his equally revolutionary discoveries in physical chemistry. It is a bit mystifying as to why the Nobel Committee left out this important achievement. Was it because there still was some lurking opposition to the physical reality of atoms in 1901?

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New Branch of Chemistry Launched

By early 1880's, van 't Hoff's interests changed from molecular structures to molecular transformation. He got deeply interested in reaction kinetics, equilibrium, dilute solutions, chemical affinity and thermodynamics. In 1884, he published a book, *Studies in Chemical Dynamics*. He explained the effect of temperature on the equilibrium of reactions. In 1885, Le Chatelier showed the general applicability of this relationship and it is now known as the van 't Hoff–Le Chatelier principle.

van 't Hoff developed a graphical method for obtaining the rate constant and order of a reaction, and proposed an equation, now known as van 't Hoff equation, that lays down the relationship between equilibrium constant and the heat of reaction. His ideas of the effect of temperature on equilibrium constants were further developed by Arrhenius (who had worked with van 't Hoff in 1888) in 1889 to what is now called the Arrhenius equation. He also collaborated with Ostwald in the area of kinetics.

During the same period of time (1885), van 't Hoff came to know about the findings of the botanist Wilhelm Pfeffer through his colleague, Hugo de Vries, a professor of botany, which showed dependence of osmotic pressure of a solution on its concentration and temperature. (Pfeffer had measured the variation of osmotic pressure with solution concentration earlier in 1877.) The sharp intellect of van 't Hoff immediately grasped the significance of this orderly relationship and his analytical mind quickly found its similarity with the gas laws. Based on this idea, he derived an equation for osmotic pressure and established that the thermodynamic laws applicable to gases are equally valid for dilute solutions. When this was extended to ionic substances by Arrhenius, it became necessary to propose dissociation of the electrolytes in solution in order for the osmotic pressure law to hold good in

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these cases, and this led to the electrolytic dissociation theory of Arrhenius (1884–87). The consequences of this law are extremely important in the realm of natural sciences, as for example, it explains the basis of many biological functions, and Francois-Marie Raoult's results on lowering of freezing point, dissociation of electrolytes, reverse osmosis and many other phenomena in chemistry.

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The genius of van 't Hoff is evident if one considers that all these discoveries of fundamental nature in physical chemistry were made by him during a period of just a few years between 1883 and 1889. He made these extraordinary achievements amidst a heavy load of teaching that he had to do as a professor. In fact, he used to complain that he was left with very little time for research and cites it as one of the reasons for leaving Amsterdam and moving to Berlin. However, it should be noted that he was essentially a theoretical chemist, and not so much of an experimental one. His greatness as a scientist lies in his uncanny ability to see a central principle in the vast amount of experimental observations made by others. This is evident from his explanation of optical activity by using almost all the related optical rotation data obtained from the published literature. Again, his Nobel Prize winning work on osmotic pressure depended mainly on the experimental results of W Pfeffer, H de Vries, and Eilhard Mitscherlich. In an obituary, Wilder Dwight Bancroft mentions van 't Hoff's admission of this. He (Bancroft) writes, "In his whole life he (van 't Hoff) never made what would be called a very accurate measurement and he never cared to. I remember his saying to me eighteen years ago, 'How fortunate it is that there are people who do that sort of work for us!' "But how can any one blame van 't Hoff for this, if the experimenter cannot see the theory hidden in his results. In fact, neither Pfeffer who made a lot of measurements on osmotic pressure, nor Clausius with whom Pfeffer discussed this problem was able to see its relationship with concentration and temperature. On the other hand, van 't Hoff was able to see the similarity of this relationship with the gas law the very moment he heard about Pfeffer's findings from de Vries.

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From his own work and that of many of his contemporaries such as Wilhelm Ostwald and Svante Arrhenius, he realised that physical chemistry would stand on its own as a separate branch of chemistry. In association with Ostwald, he started *Zeitschrift für Physikalische Chemie* in 1887 which he co-edited until his death. With so much of extraordinary, pioneering contribution to physical chemistry, it is no wonder that he is called the Father of Physical Chemistry and is considered as one of the greatest chemists of all time along with Antoine Lavoisier, Louis Pasteur, and Friedrich Wöhler, and was selected to receive the inaugural Nobel Prize in Chemistry in 1901.

Family and Early Days

Indeed, it is a good fortune of chemistry that van 't Hoff did not heed the advice of his parents to take up medicine instead of chemistry, as they were quite apprehensive of his making a living as a chemist, while a medical doctor could lead a decent life. (It looks like the attitude of parents about the education of their wards was not much different in the late nineteenth century from what it is today.) van 't Hoff had developed an interest in chemistry at a very young age, probably because he was fascinated by the mixtures and medicines in his father's apothecary.

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Jacobus Henricus (also written as Hendricus) van 't Hoff was born in Rotterdam, The Netherlands, on August 30, 1852. His father's name was also Jacobus Henricus van 't Hoff, and mother's was Alida Jacoba Kolff. He had his early education in a private school and for two years in a 'Hoogere Burgerschool' (Higher Public School). By this time, he had already started experimenting with chemicals. He was good at mathematics too. To pursue his studies in the subject of his love, chemistry, he joined the Polytechnic School at Delft in 1869 and received a Technology Diploma in 1871. During this period, he did vacation work in a sugar factory as a technologist, which he found to be boring, and decided not to take a job of that kind, but to study science further. He studied mathematics for a year at the University of Leiden. In

Box 1. Summary of van 't Hoff's Achievements

Major Contributions

1874 – Provided explanation for optical activity in organic substances, by proposing asymmetry in carbon attached to form different groups positioned at the apexes of the tetrahedron – The dawn of stereochemistry.

1884 – Studies in chemical dynamics – Described a new graphical procedure (differential method) for determining the order of a reaction. Derived equations for rates and chemical equilibria. Applied thermodynamic laws. Introduced the concept of chemical affinity. (van't Hoff equation)

1885 – Theory of osmotic pressure. Demonstrated that gas laws are applicable to dilute solutions. (van't Hoff factor). This led to Arrhenius theory of dissociation of electrolytes.

1887 – Started *Zeitschift fur physikalische Chemie* in association with Wilhelm Ostwald.

Till 1895 – worked on Arrhenius theory of electrolytes.

1896–1905 – Studies of the salt deposits at Stassfurt. Helped development of Prussia's chemical industry.

Important Books/Publications

1874 – Proposal for the development of three-dimensional chemical structure formulae (in Dutch).

1875 – Chemistry in Space (in French). This was translated to German in 1877 with recommendation by Wislicenus. Its English translation (Arrangement of Atoms in Space) came in 1891. The second edition (in German) was published in 1894 (with a preface again by Wislicenus). It was translated into English in 1898.
Ten years in the history of a theory (in French) (About his stereochemistry theory).

1877-81 – Views about organic chemistry in two volumes (in German).

1884 – Studies in Dynamic Chemistry (in French).

1885 – Chemical equilibria in gaseous systems or strongly diluted solutions (in French).

1887 – Starts the journal *Zeitschift fur physikalische Chemie.*

1898-99 – Lectures on theoretical and physical chemistry in three parts. (in German).

1905-09 – On the formation of oceanic salt deposits in two volumes (in German).

Important Awards and Recognitions

1885 – Member of Royal Netherlands Academy of Sciences
1892 – Member of Royal Academy of Sciences, Goettingen
1893 – Davy Medal of Royal Society, London (along with Le Bel)
1894 – Appointed Chevalier de la Legion d'Honneur, Paris
1898 – Member of the Chemical Society, London
1898 – Member of the American Chemical Society
1901 – Nobel Prize
1901 – Honorary doctorates of Harvard and Yale Universities
1903 – Honorary doctorate of Victoria University, Manchester
1905 – Member of Academie des Sciences, Paris
1908 – Honorary doctorate, Heidelberg University
1911 – Helmholtz medal of the Royal Prussian Academy of Sciences
1911 – Senator der Kaiser-Wilhelm Gesellschaft

addition to his interest in science he had a great love for nature. He used to take part in botanical excursions and enjoyed long walks alone as well as in company as often as he could manage. His interests were not limited to science and nature, but extended to philosophy and poetry as well. In fact he tried his hand in writing poetry in his younger days. Lord Byron was his idol.

In quest of further knowledge in chemistry, he went to Bonn to learn from Friedrich August Kekule (*Resonance*, May 2001) between the autumn of 1872 and spring of 1873. Here he seems to have heard about a possible three-dimensional disposition of carbon compounds suggested by Alexander Butterov in 1862. Kekule was using some kind of ball and stick model. (While in Bonn, van 't Hoff enjoyed his long walks in the beautiful mountains in the vicinity of Bonn). From Bonn, he went to Paris to work with Charles-Adolphe Wurtz, where he met Joseph Achelle Le Bel. However, according to van 't Hoff's own assertion, the two independent discoverers of tetrahedral carbon never exchanged views on this topic, though he realised here that optical activity could be explained if four different groups are attached to carbon and are situated at the corners of a tetrahedron.

In 1874 van 't Hoff obtained his doctorate degree from Utrecht University under the guidance of Prof E Mulder.

In 1876, he was appointed as a lecturer of chemistry and physics at the veterinary college in Utrecht. In September the next year, he secured a similar position at University of Amsterdam where, in June the very next year, he was appointed Professor of Chemistry, Mineralogy and Geology. He occupied this chair for the next eighteen years.

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He married Johanna Francina Mees in 1878, and had four children – Johanna Francina (b. 1880), Aleida Jacoba (b. 1882), Jacobus Henricus (b.1883), and Govert Jacob (b. 1889). It is striking and interesting to observe that van 't Hoff had the same name as his father's and again his son got it, and his two daughters were named after his wife and mother, respectively.

During 1884–89 came his major contribution to physical chemistry and his rise to fame was meteoric that caused his overshadowing important senior scientists like Johannes Diderik van der Waals.

Salt Deposits – Profitable Raw Materials

In 1896 he was invited to Berlin University as Honorary Professor, which came with membership of the Royal Prussian Academy of Sciences. He accepted it happily as he had to spend just one hour every week lecturing, unlike in Amsterdam, where he was overloaded with the task of giving elementary lectures and evaluating a large number of students including medical students, which left him very little time for research. He remained in this position at Berlin University till his death.

In Berlin, between 1896 and 1905, he worked on the problem of oceanic deposits, particularly the salt deposits of Stassfurt, assisted by W Meyerhoffer, an earlier co-worker at Amsterdam. These deposits contained, in addition to rock salt, considerable quantities of other salts, which helped to set up numerous chemical factories in Stassfurt and neighbouring villages. He published his findings on these deposits as scientific papers and in the form of books in two volumes – "Zur Bildung Ozeanischer Salzablagungen" (On the formation of oceanic salt deposits).

van 't Hoff was not only a marvellous researcher, but also a gifted writer. His fame rests on his publications. He published all his work as scientific papers and compiled much of it in the form of books as well. His zeal for writing extended to other spheres of activities, as for instance, he wrote a detailed account of his visit to the US in 1901 on the invitation from Chicago University to deliver lectures in physical chemistry.

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van 't Hoff valued the power of imagination; indeed, he delivered a lecture on this topic on accepting the professorship at Amsterdam University in 1878, particularly as a counter to the criticism of his ideas on stereochemistry. (See Classics pp.88–100 in this issue.)

The Last Days

It was unfortunate that van ’t Hoff succumbed to tuberculosis on March 1, 1911, in Stiglitz near Berlin. It seems he had contracted the disease by 1906 and was forced to stay in a sanatorium. But this did not hold back his zeal for research, and as if in mockery, he published a paper “Sanatoriums Betractung” (view of sanatorium) dealing with heat and work relationship in active life and while bedridden, in *Biochemische Zeitschrift*, 1908. In 1909–10 he published the work on the catalytic role of the enzyme emulsin in the formation and decomposition of glycosides, which is believed to be the beginning of enzyme chemistry. It was indeed a great loss to the scientific world that he died at an early and still productive age.

Suggested Reading

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