

Century of Nobel Prizes

1903 Chemistry Award: Svante August Arrhenius (1859-1927)

Shridhar R Gadre

Svante August Arrhenius was born at Wijk, near lake Mälär, in Sweden on February 19, 1859. His parents were Svante Gustav Arrhenius (a town land surveyor) and Carolina Christina Thunberg. The family name 'Arrhenius' is believed to have been changed to 'Arrhenius' by the Svante's uncle, Johan Arrhenius, a Professor of botany. The family moved to Uppsala for better prospects in 1860. It is recorded that he learnt to read at the age of three. Reports also say that this rather precocious and plump boy used to help his father in casting his laborious accounts. Svante attended the cathedral school of Uppsala and graduated in 1876 with a good record in mathematics and physics. He joined the University of Uppsala to study chemistry under Professor Clévé, who was apparently an uninspiring teacher and also one who neglected the theoretical aspects of chemistry. In 1881, Svante turned to physics and joined Professor Thalén, who unfortunately did not encourage independent research. Ultimately, he joined the Swedish Academy Professor Eric Edlund in Stockholm. With Edlund's enthusiastic support, he submitted his first research paper in 1883. This research work dealt with the decay of galvanic polarization with time.

At this time the conducting properties of electrolytic solutions were being studied vigorously. Pure water was known to be poor conductor of electricity. However, on addition of a drop of an acid or a pinch of salt, water was observed to conduct electricity. It was believed that the electric current is attached to the molecules of dissolved substances, which were split into carriers of positive and negative electricity. Between the years 1832 to 1834, Michael Faraday worked on the theory of this electrochemical phenomenon. He coined with William Whewell, many new words such as electrolyte, electrode, anode and cath-

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Keywords

Arrhenius, activation energy, ionic solutions.



S A Arrhenius

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ode. He called the charge carriers in electrolytic solution as 'ions' (*ion* (Greek): *I move*). Berzelius had earlier pointed out that there is a connection between electricity and chemical affinity. However, the origin of this affinity was completely unknown. With the advances in thermodynamics, it was believed that the chemical processes could be generally explained on the basis of heat phenomena. Thus, it was the most opportune time to consolidate the foundations of physical chemistry (called as 'general chemistry' by Ostwald). This process took place much later (between 1920 to 1930) in organic chemistry and inorganic chemistry (from 1940 to 1950).

Arrhenius realized the central importance of the problem of electrolytic conduction of solutions. Renowned scientists such as van't Hoff, Raoult and Kohlrausch were also actively engaged in studying this area. Arrhenius measured the electrolytic conductance of a large number of acids, bases and salts. The results were tabulated to show the dilution that was needed to double the conductivity of the solutions. This factor turned out to be nearly 2, for simple salts as shown earlier by Kohlrausch. Svante Arrhenius published this work in the form of two research articles in the *Swedish Academy Journal* in 1885. The second paper dealt with the theory of electrolytic dissociation. He considered the case of hydrochloric acid, a non-conductor in anhydrous state that turns into conductor if water is added to it. Here, Arrhenius proposed a distinction of the dissolved molecules into 'active' and 'inactive' (Box 1). He did not give a detailed and precise account of the 'active' and 'inactive' parts in his paper. He also proposed in these papers the notion of coefficient of activity. This was defined as a ratio of the number of ions contained in a solution to the number it would contain if the electrolyte was completely transformed into simple electrolytic molecules. Nowhere in these papers has the word 'dissociation' been mentioned although the concept is implicit. However, he does mention that the coefficient of activity would be large in very dilute solutions. Earlier, a German experimental physicist, Friedrich Kohlrausch had found in 1868 that the

Box 1.

"In what respect these two (active and inactive) parts differ remains to be elucidated. Probably the active part is a compound of the inactive part and the solvent..."

Svante Arrhenius on the nature of electrolytic solution.

conductivity of electrolytic solutions increased with dilution to a limiting value. In 1875, Arrhenius showed that this limiting conductivity at constant temperature is a sum of the conductivities of the corresponding cation and anion.

Arrhenius found considerable resistance to his theory in the initial years. Sodium metal was known to react violently with water to liberate hydrogen gas. Chlorine was also known to be a gas with pungent odour. It was asked how sodium and chlorine atoms could together produce a stable, odourless solution. The dissociation of the salt into the positive and negative ions became much clearer after the discovery of the electron (as a unit of electrical charge) by J J Thomson in 1897. However, like van't Hoff¹, Arrhenius continued to get attacked for relying too much on imagination and mathematics in chemical thinking (see *Box 2*).

Arrhenius submitted this work to the University of Uppsala as his doctoral dissertation. It is interesting to note that, it was awarded a fourth class (non sine laude approbatur) and his defence was rated as third class (cum laude approbatur). However, he received extremely encouraging response from van't Hoff, Clausius, Lothar Meyer and in particular from Wilhem Ostwald and Oliver Lodge to whom he had sent copies of his work (*Box 3*). In August 1884, thoroughly impressed by his work, Ostwald went to meet him in Uppsala and discuss the meaning of these findings (*Box 4*). He offered Arrhenius the position of a docent in Riga. However, due to the illness and eventual death of his father, Arrhenius could not join the position. In the next five years, he was supported by the Swedish Academy of Science to visit various reputed laboratories. During this period, he worked with Ostwald (Riga), Kohlrausch (Wüszberg), Boltzmann (Graz) and van't Hoff (Amsterdam). He finally visited Ostwald again, who had now moved to Leipzig.

Arrhenius published two articles on acids and bases, one each in 1894 and 1899. He defined an acid (base) as a substance that delivers a hydrogen (hydroxide) ion to the solution. The most

Box 2.

"The fact is, there has been a split of chemistry into two schools since the intrusion of the Arrhenic faith, rather it should be said, the addition of a new class of workers into our profession-people without knowledge of the laboratory arts and with sufficient mathematics at their command to be led astray by curvilinear agreements.... It is essential to cast out from our midst, root and branch, this physical element and return to our laboratories."

H Armstrong (1936).

See *Resonance*, Vol. 6, No. 12, p.36, 2001.

Box 3.

"These celebrated men with whom the Uppsala professors were not to be compared, treated me as a colleague and not as a stupid schoolboy..."

Arrhenius on Clausius, Lothar Meyer, Ostwald and van't Hoff



Box 4.

In the words of Wilhelm Ostwald, who, as one of the ionists, spread the doctrines of Arrhenius:

The scene in the laboratory of Uppsala is still fresh in my mind where the chief (Arrhenius) was pointing to a beaker containing an aqueous solution. He asked me "And do you believe that the sodium atoms are just swimming around in this?" When I said "yes", he threw a glance at me that expressed an honest disbelief in my chemical sensibility.

important thermodynamic consequence of this definition was the constancy of the heat of neutralization, i.e. for the reaction $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$. This constancy had been experimentally observed.

In the article on van't Hoff¹, the 1901 Nobel Laureate in Chemistry, the osmotic pressure of ionic solutions has been discussed. When Arrhenius received the reprint of van't Hoff's paper in February 1887, he noticed that the osmotic pressure, π , of many solutions obeyed the equation $\pi = icRT$. Here c is the solution concentration and i , an empirical correction factor, later termed as the van't Hoff factor. Arrhenius immediately made a connection between the factor i and his theory of electrolytic dissociation and wrote van't Hoff a letter explaining the same in March 1887. His explanation was enthusiastically accepted by van't Hoff who published a paper in *Zeitschrift für Physikalische Chemie* explaining the factor i in terms of dissociation of electrolytes into ions. Arrhenius compared the value of the factor i calculated from the measurements of conductivity, osmotic pressure and freezing point depression for a variety of substances. He found a very good agreement between these values (see Box 5).

As seen in the earlier article¹, van't Hoff had, in 1884, described the dependence of the equilibrium constant K on the temperature, T . This is expressed by the relation

$$d(\ln K)/dT = Q / RT^2,$$

where Q is the heat of the reaction. Arrhenius was working

Box 5. Comparison of the Empirical Factor i made by Arrhenius

Substance	From freezing point depression	From conductivity measurements
Ba(OH) ₂	2.69	2.67
NaOH	1.96	1.88
CH ₃ NH ₂	1.00	1.03
(NH ₄) ₂ SO ₄	2.00	2.17
CH ₃ OH	0.94	1.00

between the years 1887 to 1889 on the velocity of hydrolysis of ethyl acetate and the inversion of cane sugar. He found that the reaction velocity is enhanced by about 10 to 15 percent for rise of one degree in the reaction temperature. This warranted an explanation.

Arrhenius in 1889, using $K = k / k'$ in the above expression (where k and k' are the rates of the forward and backward reactions, respectively) derived an important relation between the reaction rate and temperature. This equation is now called the Arrhenius equation.

$$d(\ln k)/dT = E_a / RT^2$$

The integrated form of this equation turns out to be

$$\ln k = -E_a / RT + \text{constant.}$$

Here, E_a is called the activation energy. A qualitative plot of the energy changes as a reaction proceeds is shown in *Figure 1*. The 'hump' that the reactants have to overcome is called the activation energy for the forward reaction. The Arrhenius equation is found to be applicable to many homogeneous and heterogeneous reactions.

After the death of his staunch supporter, Professor Edlund, his chances of getting a suitable appointment in Sweden reduced considerably. He was offered the chair of chemistry in Giessen



S A Arrhenius

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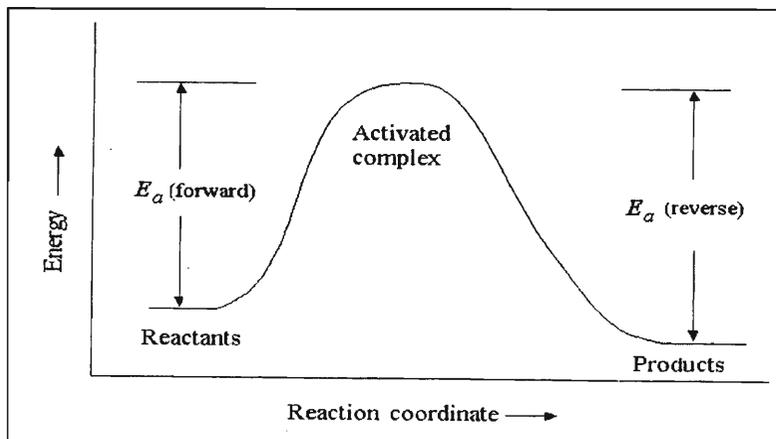


Figure 1. Diagrammatic representation of the energy change in a chemical reaction. Maximum energy (top of the curve) corresponds to the activated complex.

in 1891. However, he accepted the lectureship at the Högskola in Stockholm, which was converted to a Professorship in 1895. He was elected an honorary fellow of the Royal Society in 1898 and was awarded the Davy medal in 1902. Arrhenius was awarded the Nobel Prize in Chemistry in 1903 (for citations of the 1903 Nobel Prizes in all disciplines, see *Box 6*).

His interests were diverted to cosmic and meteorological problems after 1900. It is remarkable that about 100 years ago Svante Arrhenius asked a very important question “Is the mean temperature of the ground in any way likely to be influenced by the presence of the heat-absorbing gases in the atmosphere?” He went on to become the first person to investigate the effect that doubling atmospheric carbon dioxide would have on global climate. The question was debated throughout the early part of the twentieth century and remains a main concern of the earth scientists and environmentalists even today. This phenomenon is now known as the greenhouse effect. He believed that life on

Box 6. The 1903 Nobel Laureates in Various Disciplines

Discipline	Name, Country	Citation of the Nobel Prize
Chemistry	Arrhenius, Svante August Sweden	for his theory of electrolytic dissociation.
	Becquerel, Antonie Henri France	for his discovery of spontaneous radioactivity while experimenting with different uranium salts.
Physics	Curie, Marie Curie, Pierre France	for their invention of radioactive emissions.
Physiology or Medicine	Finsen, Niels Ryberg Denmark	for his scientific contribution to handling of various diseases, mostly of the skin tuberculosis.
Literature	Bjornson, Bjornstjerne Norway	in recognition of his literary work and also for his contributions to peace and smaller populations.
Peace	Cremer, William Randal Great Britain	one of the founders of the interparliamentary union for court of arbitration.



earth was brought here by spores carried through space from other planets by radiation. He believed that likewise these spores could have carried life to many planets resulting in life throughout the universe. In another biology-related problem, E A von Behring and Paul Ehrlich had worked on the action of toxins in the living organisms and the ability of the organisms to neutralize their effect by producing antitoxins. After 1902, Arrhenius joined Ehrlich in Frankfurt in this work on toxins and antitoxins. Ehrlich and Arrhenius together conjectured that the toxin-antitoxin interaction is also governed by the law of mass action.

Arrhenius authored several books. *Lärobok i teoretisk elektrochemi* (*Textbook of theoretical electrochemistry*) and *Theorien der chemie* (*Theories of Chemistry*) were published in 1900 and 1906. His book on *Immunochemistry* was also published in 1906. In 1903 he wrote *Lehrbuch der kosmischen Physik* (*Textbook of cosmic physics*).

Arrhenius was offered the directorship of the newly established Nobel Institute for Physical Chemistry. Certainly this was a well-deserved recognition for a scientist with such wide interests. The laboratory was inaugurated in 1909. Here, he pursued researches in physical chemistry, physiological and immune chemistry, meteorology, cosmic physics, etc. Dr. Hubert Alyea who worked in the laboratory of Arrhenius in 1925-26, recalls how Svante Arrhenius came into the laboratory at least twice every day. He would ask how the work was going and what was planned to be done that day. Often Arrhenius would offer suggestions, but did not insist on a specific research plan. Alyea characterized Arrhenius as a man who “spread joy in the lab”.

The health of Svante Arrhenius deteriorated slowly after the autumn of 1925. He died at Stockholm, after a week's illness, on October 2, 1927 and was buried in Uppsala. However, Arrhenius, along with his comrades, van't Hoff and Ostwald has earned a permanent place in the annals of physical chemistry.

Box 7.

Sir James Walker in the Arrhenius Memorial Lecture delivered on May 10, 1928.

There was a constant interplay between the speculative and the quantitative sides of his mind. I recollect that one day in the laboratory at Leipzig, Arrhenius downed his tools, saying “I have worked enough; now I must think”. He did not appear in the laboratory for a fortnight.

Suggested Reading

- [1] E Farber Abelard-Schuman, *Nobel Prize Winners in Chemistry 1901-1961*, London, 1963.
- [2] *Nobel Lectures: Chemistry 1901-1921*, Elsevier, Amsterdam, 1966.

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