

Arrhenius Memorial Lecture.

DELIVERED ON MAY 10TH, 1928.

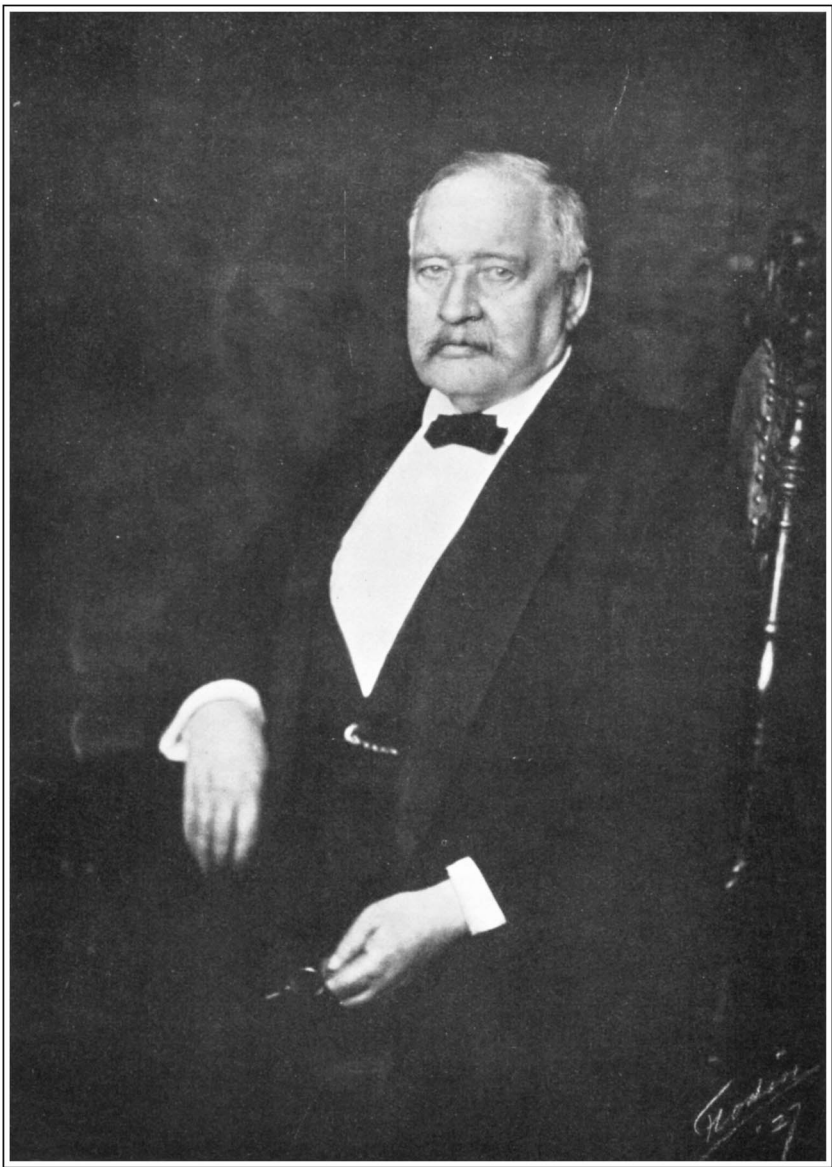
By SIR JAMES WALKER, F.R.S.

A LITTLE over forty years ago the conjunction of the ideas of osmotic pressure and of electrolytic dissociation ushered in a new era in the development of the physical chemistry of solutions—an era of unexampled fertility. Van 't Hoff and Arrhenius, the originators of these new ideas, have now both passed away. It is sixteen years since I was charged by the Society to deliver the van 't Hoff memorial lecture. To-day it is my task to discharge a similar duty in honour of Arrhenius. My relations to these men were altogether different; Arrhenius was a close friend, van 't Hoff a remote immortal. The sketch of the life and work of Arrhenius which I present is therefore not that of a completely detached historian, but is shaped by personal reminiscence and tinged with personal affection.*

I well remember when I first encountered his name. It was in the autumn of 1887 in the small departmental library of Baeyer's laboratory in Munich. On a shelf there lay the loose numbers of the first volume of the *Zeitschrift für physikalische Chemie*, newly founded by Ostwald. Turning over the pages of this interesting new journal, I saw what seemed to me the very odd name of Svante Arrhenius as author of a paper on the influence of neutral salts on the velocity of saponification of ethyl acetate. I did not find this paper of more than moderate interest, but later in the year there was published another by the same author on the dissociation of substances dissolved in water. This was plainly a novel and striking conception, and although I was not altogether convinced by the arguments it contained, I marked it for closer study at a later time.

In the spring of the following year I left Munich for Leipzig and was caught in the wave of Ostwald's enthusiasm for the new doctrines of osmotic pressure and electrolytic dissociation. In Ostwald's laboratory I used to work in a small room with Wilhelm Meyerhoffer, who afterwards collaborated with van 't Hoff in his phase-rule investigations. One day Meyerhoffer burst into the room, and pointing excitedly along the corridor, said: "Arrhenius is

* I take this opportunity of thanking the many friends both Swedish and English to whom I am indebted for information regarding Arrhenius. A bibliography of his work up to 1908 is to be found in *Z. physikal. Chem.*, vol. 69, and up to 1918 in *Medd. K. Vetenskapsakad. Nobel-institut*, vol. 5.



SVANTE AUGUST ARRHENIUS.

[To face p. 1380.]

there." I peered out and saw a stoutish fair young man talking to Ostwald near the entrance hall. It was Arrhenius. We were made acquainted by Ostwald, but at that time I saw little more of him. Next year he came to work in Leipzig, and I had the opportunity of meeting him daily. He was one of the simplest and least assuming of men. He gave himself no airs and treated us young fellows as if we were his scientific equals, although at that time he was being recognised in Germany as a leading spirit in physical chemistry. In his own country he was still unregarded.

Svante Arrhenius came of Swedish farmer folk, a remote ancestor being one Lasse Olofsson, who in 1620 moved to the village of Årena, from which the family derived its surname in the Latinised form of Arenius, the spelling being changed in the early part of the nineteenth century to Arrhenius by the uncle of Svante, Professor Johan Arrhenius, a botanist and secretary of the Academy of Agriculture. Johan and his younger brother, Svante Gustav Arrhenius (1813—1888), the father of our Svante, went as students to the University of Upsala, and the latter subsequently established himself in that town as a land surveyor. He was appointed collector to the University, but the emoluments of the post were so meagre that he was forced to undertake in addition the management of the estate of Wijk, on Lake Mälär, which belonged to Count von Essen. He married in 1855 Caroline Thunberg, and at Wijk there was born on 19 February, 1859, a son whom they called Svante August Arrhenius. Owing to improved prospects the family moved to Upsala in the beginning of 1860. Young Svante was educated at the Cathedral School of Upsala, and was fortunate in the fact that the Rector of the school was a good teacher of physics. He left at the age of seventeen with a good record in mathematics and physics to enter the University of Upsala, where he soon passed the candidate's examination, admitting to study for the doctorate. It seems to have been his original intention to take chemistry as his main subject under Cleve, well known for his investigations on the rare earths and on complex ammoniacal compounds. Cleve, however, was apparently an uninspiring teacher and neglected the theoretical side of chemistry. Arrhenius records that he never heard any mention from the rostrum of the periodic law, although it was already ten years old, nor when he came to write his thesis had he any knowledge of the existence of the law of Guldberg and Waage, which was even older. In 1881 he definitely turned to physics, although the conditions for its study in Upsala were far from ideal. Thalén was at that time Professor of Physics there. His reverence for his master and predecessor Ångström was so great that, beyond the apparatus

for elementary students, there was little else in the department but instruments for exact measurements of wave-lengths, a subject for which Arrhenius had no liking. Thalén did not encourage independent work in his laboratory, and Arrhenius was forced to look about for some other opportunity to begin physical research. He, with a fellow student, repaired in September 1881 to Stockholm with the intention of working in the laboratory of Erik Edlund, Professor of Physics to the Swedish Academy. Edlund gave them a hearty welcome, and they began by assisting him in his work on electromotive forces in the spark discharge. In the spring of the following year Arrhenius started his first independent research on the decay of galvanic polarisation with time, an account of which was published in the *Bihang* of the Swedish Academy in 1883. From this he passed to the measurement of the conducting power of electrolytic solutions.

It is of interest to enquire into the reasons which induced Arrhenius to take up this line of work. The pursuit of science, like other human activities, is not exempt from the prevalence of fashions. At the period under consideration the study of the properties of solutions was in the air. Van 't Hoff was busy tracing the analogy between dilute solutions and gases, Raoult was developing empirical methods for the determination of the molecular weights of dissolved substances, Kohlrausch had just perfected his telephone method for determining electrolytic conductivities, Ostwald was working at reaction velocities and the affinities of acids and bases in aqueous solution. Arrhenius yielded to the same influence, but curiously enough what led him to the investigation of electrolytic solutions was not directly concerned with the conducting substances themselves. He tells us that Cleve in his lectures had emphasised the impossibility of ascertaining the molecular weights of substances, such as sugar, which could not be volatilised without decomposition. Arrhenius rightly recognised that this was a great drawback, by the removal of which a considerable advance in chemistry would be rendered possible. He was unaware of Raoult's work, and thought that some light might be thrown on the molecular weight of dissolved substances by measurements of electrolytic conductivity. He knew that when some of the water of a conducting solution was replaced by more complex non-conducting substances, such as alcohol, the conductivity was lowered, and he thought it might be feasible to deduce the molecular weight of this added substance from its effect on the conductivity. He had not proceeded far with his measurements, however, when he recognised that the state of the conducting salt was the matter of primary importance.

The theory of electrolysis and electrolytic solutions was also decidedly in the air at the same period. The chains of Grotthus, the hypothesis of Clausius on continual momentary separation of ions, Hittorf's work on migration, Helmholtz's conception of the atomic nature of electricity, the work of Kohlrausch on conductivity, were all leading up to some definite comprehensive theory which in the end was furnished by Arrhenius.

Arrhenius completed his experimental work in the spring of 1883 and wrote the theoretical part at his home in the summer of the same year. The memoir containing the results of his conductivity experiments and the conclusions he deduced from them was submitted to the Swedish Academy of Sciences in June 1883, and published in the following year (*Bihang*, vol. 8, Nos. 13 and 14). It is in French and is entitled "Investigations on the galvanic conductivity of electrolytes. Part I. Determination of the conductivity of extremely dilute solutions by means of the depolariser. Part II. Chemical theory of electrolytes." Arrhenius undertook the experimental investigation of dilute solutions himself, for although Kohlrausch had made similar measurements and had quoted some numerical data, the final publication of his results was delayed till 1885. The depolariser which Arrhenius used was an apparatus devised by Edlund in 1875, and corresponds roughly to a hand-driven rotating commutator. It is of interest to note that the conductivity cell which bears Arrhenius's name is described in this paper.

Arrhenius measured the resistance of a considerable number of salts, acids and bases at various dilutions, sometimes as high as $v = 10,000$. Unfortunately the actual dilutions are not given, so that it is difficult to correlate the data of Arrhenius with those of other authors. He tabulated his results so as to show in what ratio the resistance of an electrolyte is increased when the dilution is doubled. This ratio, as Kohlrausch had found earlier, is nearly equal to 2 for most salts, *i.e.*, specific conductivity is nearly proportional to concentration. Departure from this ideal value he took as a basis for classification of the dissolved electrolytes, and showed that chemically similar substances fell into the same category when classified according to dilution-ratios. A discussion of the data led Arrhenius to the conclusion that "if on dilution of a solution the conductivity does not change proportionally to the amount of electrolyte, then a chemical change has occurred on addition of the solvent." He exemplifies this by the consideration of potassium cyanide with the abnormally high dilution ratio of 2.14, which he attributes to the partial splitting of the salt into acid and base on dilution with water. The abnormal values

obtained for soluble hydroxides and dilute solutions of acids he attributes to the presence of small quantities of ammonium carbonate in the solvent water.

The importance of this paper, however, does not lie in the experimental measurements or in the detailed deductions, but in the general ideas which Arrhenius developed in the second part. Instigated and encouraged by Otto Pettersson, then Professor of Chemistry in Stockholm, Arrhenius greatly expanded this theoretical section, which contains the germ of the later theory of electrolytic dissociation. He bases his theoretical treatment on the hypothesis of Williamson and Clausius. How this hypothesis presented itself to a clear and critical contemporary mind, unacquainted with the work of Arrhenius, may best be gathered from the admirable report on electrolysis presented by Oliver Lodge to the British Association in 1885.

Lodge writes: "No polarisation exists inside a homogeneous electrolyte; *there is no chemical cling of the atoms there, but only a frictional rub.* Such a fact as this, if well established, renders necessary *some form* of dissociation hypothesis. The form of dissociation hypothesis suggested by Clausius and Williamson is well known. It supposes that the vast majority of molecules in an electrolyte are quite unsusceptible to the influence of electrodes, but that a few of them (the number being increased by complexity of composition and rise of temperature) are, by collision or otherwise, dissociated and exist in the free atomic state, each atom with its appropriate charge. These alone feel the influence of the electrodes. . . . Individual atoms, although permitted to combine as soon as they like, on this theory, are commonly thought of as existing in the dissociated state for a finite time. If there are chemical or other objections to such a view, it need not be held; all that the facts of electrolysis require is the most momentary dissolution of partnership—temporary but quite perfect freedom. . . . Provided a sufficient supply of such temporary severances occurs throughout the liquid, no individual atom need remain uncombined for a thousandth of a second, so far as the phenomena of electrolysis are concerned."

Arrhenius derives from the hypothesis the notion of closed circular currents in the electrolytic solution in its normal state (*i.e.*, when not undergoing electrolysis) which are due to the separation of the ions and their recombination with other than their original partners. This notion he uses in dealing with the equilibrium between electrolytes in aqueous solutions. But by far the most important original idea, on which he bases his further treatment, is that of the distinction of the dissolved molecules into

active and inactive. He arrives at it in the following way. A solution of ammonia exhibits a feeble molecular conductivity which increases with dilution. This Arrhenius attributes to the progressive conversion of the non-electrolytic NH_3 into the electrolytic NH_4OH as dilution is increased. He proceeds: "It has been shown that pure anhydrous hydrochloric acid is a non-conductor, that is, a non-electrolyte. If water is added to it, it is converted into an electrolyte, naturally in a progressive manner. It is impossible to deny the complete analogy of this phenomenon with that occurring on the dilution of ammonia or acetic acid, although it takes place much more rapidly." He sums up in the following statement: "The aqueous solution of any hydrate [*i.e.*, acid or base] is composed, in addition to the water, of two parts, one active (electrolytic), the other inactive (non-electrolytic). These three substances (*viz.*, water, active hydrate, and inactive hydrate) are in chemical equilibrium, so that on dilution the active part increases and the inactive part diminishes."

Arrhenius gives nowhere in this memoir a precise account of the nature of the active and inactive portions. He indicates and illustrates what they might be, but that is all; he does not define. The most important special feature of the paragraph is the statement that the active part increases on dilution. He continues: "In what respect these two parts differ remains to be elucidated. Probably the active part (as with ammonia) is a compound of the inactive part and the solvent. Or possibly inactivity may be caused by the formation of molecular complexes. Or again the difference between the active and inactive parts may be purely physical. The same statement applies to bases, and we may also speak of the inactivity of dissolved salts, in which case the notions of inactivity and complexity completely coincide."

With regard to solutions of normal salts he makes the following statements: (1) "Aqueous solutions of all electrolytes contain the dissolved electrolyte at least in part in the form of molecular complexes. (2) If the attenuation of the solution of a normal salt is continued, the complexity approaches asymptotically an inferior limit. (3) The limit to which the complexity of a normal salt at extreme dilution tends to approach is of the same degree for all normal salts. Probably this limit will not be attained before all the salts are split up into simple molecules, represented by the chemical molecular formula."

"To fix our ideas, I have introduced the notion of coefficient of activity defined as follows:—The coefficient of activity of an electrolyte is the number expressing the ratio of the number of ions actually contained in the electrolyte to the number of ions it

would contain if the electrolyte were completely transformed into simple electrolytic molecules."

"Before going on we shall describe more precisely the notion of coefficient of activity by the aid of the hypothesis of Williamson and Clausius. According to § 2 this coefficient is defined by the number of ions present in a solution. But to each pair of ions there corresponds an electrolytic molecule which can take part in the production of a circular current; that is to say, its ions are endowed with the movement assumed by the hypothesis. If now an electrolyte is constituted in such a manner that only a certain fraction $1/n$ can at the same time take part in such a movement, it is evident that its coefficient of activity is $1/n$. It is not necessary, however, that a chemical difference should exist between the active and inactive parts. For greater clearness we choose an ammoniacal solution as example. In this solution there are two different parts, one active NH_4OH , the other inactive NH_3 . If the latter is transformed into the former, the sum of the molecules of the two species is not augmented. Thus if m and n are the numbers of molecules of NH_4OH and NH_3 , the first factor of the coefficient of activity will be $\frac{m}{m+n}$. Now several of the NH_4OH molecules may be associated with each other, so that the number of physical molecules of NH_4OH is p , of $(\text{NH}_4\text{OH})_2$ q , of $(\text{NH}_4\text{OH})_3$ r , etc., where evidently $p + 2q + 3r + \dots = m$. Again of the molecules NH_4OH only a fraction $1/\lambda$ presents a simultaneous movement of ions. The corresponding numbers for $(\text{NH}_4\text{OH})_2$ and $(\text{NH}_4\text{OH})_3$ are $1/\mu$ and $1/\nu$. In this case the coefficient of activity of the ammonia will be equal to

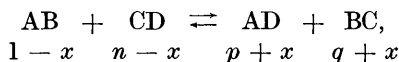
$$\frac{m}{m+n} \left(\frac{p}{m\lambda} + \frac{q}{m\mu} + \frac{r}{m\nu} + \dots \right) = \frac{1}{m+n} \left(\frac{p}{\lambda} + \frac{q}{\mu} + \frac{r}{\nu} + \dots \right).$$

It is interesting to compare with this coefficient of activity the "dissociation ratio" of Lodge, which is defined in the report from which I have already quoted. Lodge writes: " mn^3 is the number of grammes of the electrolysed or dissociated substance in a unit cube, and this we may write $N\mu$ where N stands for the number of monad gramme-equivalents of the really electrolysed substance per c.c. and μ is its molecular weight compared with hydrogen." Considering the case of two electrolytes dissolved in the same solution, he proceeds: "there will be N_1 and N_2 to represent the amount of dissociated substance present, reckoned in gramme-equivalents per cubic centimetre of solution. We come to the conclusion that we do not know the absolute velocity of any ion, and cannot know it without further information regarding the

dissociation ratio (that is N_1/N' or N_2/N') of each substance present, where N' is the total number of monad gramme-equivalents of the dissolved substance in a cubic centimetre of solution."

To Lodge the "dissociation ratio" is in all probability small. Arrhenius, on the other hand, contemplates the variability of the "coefficient of activity" with dilution and the likelihood of its being large in very dilute solutions.

So far the considerations are purely theoretical; now comes an important step, their union with experimental data. Kohlrausch had shown that the molecular conductivity of an electrolyte was additively composed of two terms, one depending on the positive radical and the other on the negative radical. But in extremely dilute solutions of salts the value for negative radicals was nearly the same; therefore, according to Arrhenius, "the molecular conductivity of the active part of an acid (in dilute solution) is constant and independent of the nature of the acid," and as a corollary from this "the better the (dilute) solution of an acid conducts electricity, the greater is its active part." For want of precise data for calculating the absolute value of the coefficient of activity, Arrhenius takes it as proportional to the molecular conductivity. Thus he is enabled to compare the activities of acids amongst themselves, and of bases amongst themselves. He finds at once that the activities of acids as thus determined from their conductivities agree well with our general notions regarding their strengths, and is led to the statement that "for acids and bases galvanic activity is accompanied by chemical activity." He proceeds to discuss double decomposition in electrolytic solutions, on somewhat hypothetical grounds, and arrives at a formula (containing coefficients of activity) which he applies practically to many important reactions. If in the general equation of double decomposition



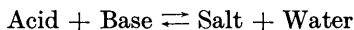
are the molecular proportions at equilibrium, and

α δ β γ are the coefficients

of activity of the various substances, then at equilibrium

$$(1-x)(n-x)\alpha\delta = (p+x)(q+x)\beta\gamma.$$

If the action considered is



the product of the coefficients of activity on the left is, when acid and base are strong, enormously greater than the product of those on the right, and salt-formation is, therefore, practically complete.

If acid or base is weak, the two products are comparable, and in consequence, entire neutralisation will not take place, notable quantities of acid and base remaining free. If the activity coefficient of one of the substances (say alcohol regarded as acid) is smaller than that of water, only traces of the salt are formed. Here we find a definite treatment of salt-hydrolysis based on the following principle: "What is common to all these cases is the necessity of regarding water as an acid (or as a base) which competes with other acids (or bases) present in the equilibrium." Arrhenius states further the proposition, which requires some restriction, that "at a dilution not excessively great the quantity of salt decomposed is approximately proportional to the square root of the quantity of the solvent water."

The theory is then applied to the displacement of one acid by another, to the influence of acid salts, and to equilibrium in heterogeneous systems. The consequences of the variation of the coefficient of activity in homogeneous and in heterogeneous systems are considered, and sections are devoted to the behaviour of molten electrolytes and to thermochemistry. He deduces the following important principle: "The heat of neutralisation evolved by the transformation of a base and an acid, both perfectly active, into water and a simple salt, is nothing but the heat of activation of water."

After a review of anterior theories Arrhenius summarises his work thus: "We have first shown the probability that electrolytes can assume two different forms, one active, the other inactive, such that the active part is always, in the same external circumstances (temperature and dilution), a certain fraction of the total quantity of the electrolyte. The active part conducts electricity, and is thus in reality electrolytic; not so the inactive part. Moreover we have proved that the necessary consequence of the hypothesis of Clausius and Williamson is that there exist continuous circular currents, in which the active parts alone participate. The molecules participating in such currents are necessarily decomposed according to the scheme of double decomposition, new electrolytes being thereby formed. On this basis we have founded a chemical theory of electrolytes, which, being deduced from very probable sources, possesses also a high degree of probability. This theory leads to formulæ valid for chemical processes, formulæ very conformable to those proposed by Guldberg and Waage, which have been verified in a great number of instances. . . . As a provisional approximation we have assumed the coefficient of activity to be equal to the molecular conductivity. The numbers calculated on this hypothesis and the reactions thus foreseen, agree very well

with experimental facts. . . . These propositions and these laws are taken from the most different parts of chemical science; but as the theory agrees so well with reality on these different points, it seems probable that it ought to do so also in intermediate regions. . . . The theory is completely free from any hypothesis of an affinity different from physical forces, and in this respect is preferable to all prior theories. . . . True, it may be objected that the theory is only valid for electrolytes, while previous theories have embraced all substances. Against this we remark that chemical knowledge is mainly based on the reaction of electrolytes. . . . Reactions in general seem to manifest a considerable analogy to those of electrolytes, so that one could perhaps in the future enlarge the theory until it becomes, with some modification, applicable to all substances.”

Nowhere does Arrhenius mention the word dissociation, although, as we have seen, the word is currently used by Lodge. The idea is, of course, there, but there is no identification of the “ active part ” of the electrolyte with free ions acting as separate molecules. The theory of electrolytic dissociation is as it were in solution in this memoir; it has yet to be crystallised out.

This comprehensive paper, which runs to 150 printed pages, was presented to the University of Upsala as a dissertation for the doctorate of the University. Its somewhat strange form is no doubt due to the use thus made of it. At the ends of sections and paragraphs there are numbered and italicised propositions, of widely different degrees of probability, and deduced by arguments of very different degrees of cogency. The paper then on a cursory inspection might convey an unfavourable impression if only the italicised portions were attended to. These propositions were probably the theses which were to be defended by the candidate in public debate with an opponent appointed by the University. The disputation passed off successfully and it must have been a bitter disappointment to Arrhenius when his dissertation was awarded a fourth class (*non sine laude approbatur*) and his defence a third (*cum laude approbatur*). After every allowance has been made for the novel and unusual character of the dissertation, it is difficult to see how the University of Upsala, the University of Bergman and Berzelius, should have condemned a brilliant thesis on the very subjects of affinity and electrochemistry associated with these names. For the award amounted to a condemnation; in view of it Arrhenius could not normally become a docent in the University of Upsala.

Arrhenius sent copies of his paper to Clausius, Lothar Meyer, Ostwald and van 't Hoff. “ These celebrated men,” he says, “ with whom the Upsala professors were not to be compared,

treated me as a colleague and not as a stupid schoolboy." Ostwald was eminently friendly. He himself in his work on chemical dynamics was being drawn to the conclusion that velocities of reactions in which acids participate are connected with the electric conductivities of the acids. He writes (*J. pr. Chem.*, 1884, **30**, 93) "To test the idea I have during the past six months made preliminary experiments, which however have often been interrupted by other work. Meanwhile Svante Arrhenius, working in another range of ideas, undertook similar experiments and has published them in two memoirs, which also contain a very notable theory of chemical affinity developed from them. To the author of these memoirs, which belong to the most important ever published on the subject of affinity, there must be accorded not only priority of publication but priority of the idea."

Oliver Lodge was impressed by the paper and wrote for the Reports of the British Association in 1886 an abstract and critical analysis of it extending to 30 closely printed pages. "The paper seems to me a distinct step towards a mathematical theory of chemistry. The title affixed to it is 'The Chemical Theory of Electrolytes,' but it is a bigger thing than this: it really is an attempt at an *electrolytic theory of chemistry*."

In August, 1884, Ostwald visited Arrhenius in Upsala, and his visit had a marked effect on Arrhenius's future. Ostwald undertook to get Arrhenius appointed as a docent in Riga, and the offer no doubt led to the favourable reception of an application by Arrhenius for a similar post in physical chemistry at Upsala. The two men had, while together, projected a scheme of research on physical chemistry to be undertaken in Ostwald's laboratory in Riga, but the illness and subsequent death of Arrhenius's father kept him in Upsala. Through Edlund's influence he received in December, 1885, a valuable travelling scholarship from the Academy of Sciences which enabled him to work in continental laboratories at discretion. The next five years were *Wanderjahre*. In 1886 he was with Ostwald in Riga, and Kohlrausch in Würzburg, during 1887 with Boltzmann in Graz, during 1888 with van 't Hoff in Amsterdam and again with Ostwald, now in Leipzig. In 1889 and 1890 he worked in the laboratories of Ostwald and Boltzmann. When in Sweden he lectured on physical chemistry in Upsala or worked in Edlund's laboratory in Stockholm. It was during this journeyman's period of his life that the theory of electrolytic dissociation was finally developed.

His original papers left the nature of the difference between the active and the inactive portions of the electrolyte unsettled, and the absolute value of the dissociation vague. As I have said, the

theory was still in solution. The nucleus which determined its crystallisation came through van 't Hoff's theoretical work on osmotic pressure and his interpretation of Raoult's experimental results.

Van 't Hoff, in a memoir presented to the Swedish Academy on 14 October, 1885, showed that it was possible to write for solutions an equation $PV = R'T$, analogous to the gas equation, where P , however, is the osmotic pressure instead of the gaseous pressure. The constant R' was in many cases equal to the gas-constant, but in many others differed from it. Van 't Hoff then wrote the general equation for dissolved substances in the form $PV = iRT$, where R is the gas-constant and i a coefficient sometimes equal to unity, but sometimes assuming values much greater, in particular for aqueous salt-solutions when the results are calculated from Raoult's experiments. For example, i is 1.98 for hydrochloric acid, 1.82 for sodium nitrate, and 1.78 for potassium chlorate. Van 't Hoff contented himself with these empirical values and made no attempt at an explanation. His paper was published in 1886, but Arrhenius did not receive a copy until March, 1887. On the 30th of that month he wrote to van 't Hoff from Würzburg: "Your paper has cleared up for me to a remarkable degree the constitution of solutions. If, for example, sodium chloride were normal in its behaviour, *i.e.*, if it consisted of simple molecules, its coefficient i would be equal to unity. But since i is much greater than unity, the natural explanation is to say that NaCl is partially dissociated, just as we say that at high temperatures I_2 is dissociated. Now this assumption might be deemed very rash, were it not that on other grounds we are led to look upon electrolytes as partially dissociated, for we assume that they decompose into their ions. But as these ions are charged with very great quantities of electricity of opposite sign, conditions are such that we cannot in all cases treat a solution of NaCl as if it simply consisted of Na and Cl. The pressure on the walls cannot, however, be appreciably affected, so that in this case the solution acts as if Na and Cl were free. And when we consider which substances (according to Raoult's experiments) are abnormal, it is not the inorganic (*e.g.*, not $HgCl_2$, CO_2 , H_2S , etc.), but the electrolytic substances (*i.e.*, substances which are conductors of the same order as salts) even when they are organic, *e.g.*, oxalic acid. Trichloroacetic acid and sulphonic acids must show this still more clearly when they come to be investigated. Since according to the above assumption electrolytes decompose into their ions, the coefficient i must lie between unity and the number of the ions. This in reality holds good: for example, the coefficient nearly reaches 2 for NaCl, KCl, KNO_3 , NaOH, etc., which have two ions;

for $\text{Ba}(\text{OH})_2$, CaCl_2 , K_2SO_4 , etc., which have three ions, it almost approaches 3, and so on. . . . From the above assumption we can even calculate the value of i from the conductivity, and this I shall probably soon carry out; till now time has failed me. What I called in my paper 'Sur la conductibilité' active molecules, are thus the same as dissociated molecules. One of the propositions which I then put forward would now be written:—In all probability all electrolytes are completely dissociated at the most extreme dilution." Here we have the first appearance of the theory of electrolytic dissociation. If we cannot fix its birthday, at least we can fix its birth-month. It is clear, definite, and concise, and all Arrhenius's previous theoretical treatment can easily be translated into terms of it. Van 't Hoff accorded the new idea a favourable reception. He replied on April 7: "Your statement that the number of ions roughly keeps pace with the values of i , and that the conductivity also increases with i , agrees with most of the cases known to me." . . . He remarks that he had always thought of the dissociation into ions as being confined to an extremely small portion of the salt, but confesses that he sees no grave difficulty in assuming a greater dissociation. Arrhenius in a letter dated 13 April is pleased to learn that this is van 't Hoff's view, and states that Emil Fischer, with whom he had discussed the matter in Würzburg, although he was friendly to the idea, was of opinion that most chemists would be opposed to such far-reaching dissociation. Arrhenius continues: "It is true that Clausius had only assumed that a minute quantity of a dissolved electrolyte is dissociated, and that all other physicists and chemists had followed him; but the only reason for this assumption, as far as I can understand, is a strong feeling of aversion to a dissociation at so low a temperature, without any actual facts against it being brought forward. In my paper on the conductivity of electrolytes I was led to the conclusion that at the most extreme dilutions all salts would consist of simple conducting molecules. But the conducting molecules are, according to the hypothesis of Clausius and Williamson, dissociated; hence at extreme dilutions all salt molecules are completely dissociated. The degree of dissociation can be simply found on this assumption by taking the ratio of the molecular conductivity of the solution in question to the molecular conductivity at the most extreme dilution." These two short excerpts give the gist of the complete theory.

Van 't Hoff and Arrhenius now made their ideas available to a wider public by publishing them in the first volume of the *Zeitschrift für physikalische Chemie* in the latter half of 1887. Van 't Hoff accepts Arrhenius's theory for electrolytes and adds finally

Avogadro's Law to those of Boyle and Charles as being applicable to dilute solutions. Arrhenius gives the relationship between van 't Hoff's constant i and the degree of dissociation α in the form

$$i = 1 + (k - 1)\alpha$$

where k is the number of ions into which the molecule of the electrolyte dissociates, *e.g.*, 2 for KCl, 3 for K_2SO_4 . He compares the values of i calculated from Raoult's freezing-point data on the one hand, and from the molecular conductivity on the other, for some 80 different substances, and finds a very satisfactory accordance. In the second part of his paper he discusses the properties of electrolytes in aqueous solutions from the point of view of their additive character, which he attributes to the independence of their ions.

The theories of osmotic pressure and of electrolytic dissociation were now fairly launched, and, propelled by the driving-power of Ostwald through the waters of scientific opinion, they soon attained a world-wide recognition, though often meeting very heavy weather. That their reception was so favourable is indeed somewhat surprising, for it must be remembered that in those days the marvels of X-rays, of radioactivity, of wireless transmission, had not prepared the way for that loosening and abandonment of fixed physical ideas to which we are to-day accustomed, if not altogether reconciled. Their general acceptance was largely due to their comparative simplicity. They could be easily tested practically, and little mathematics was required in their development, so that experimental work, centred originally in Ostwald's laboratory, but gradually spreading to others in Germany and abroad, was in the next decade assiduously carried out by a new generation of physical chemists. Their application by Nernst (1889) to electromotive force was an advance of the first order. Arrhenius himself played a principal part in the development. Amongst his important contributions to the subject published in Ostwald's *Zeitschrift* may be mentioned the theory of isohydric solutions (1888), the heat of dissociation of electrolytes and the influence of temperature on the degree of dissociation (1889), the conditions of equilibrium between electrolytes (1890), the determination of electrolytic dissociation of salts from solubility experiments (1893), the hydrolysis of salts of weak acids and weak bases (1894), the alteration of the strength of weak bases by the addition of salts (1899).

At this point it may be well to refer to Arrhenius's position with regard to the problem of the abnormality of strong electrolytes, which, unlike the weak electrolytes, do not conform to Ostwald's dilution-law. Naturally this puzzling exception to the theory he

had put forward constantly claimed his attention. Although he did not succeed in accounting for it, he had arrived at a clear conception of the lines along which a solution might be sought, as may be seen from his book, "Theories of Solution," published in 1912 from the Silliman Lectures delivered at Yale in 1911. He groups the theories which might be brought forward to explain the anomaly under four headings :

1. Change of ionic friction with dilution.
2. Electric attraction of the charges of the ions.
3. Influence of foreign substances on the osmotic pressure (so-called salt-action).
4. Hydration of the ions.

The second of these, with its effect on the first and third, is now recognised as the chief cause of the abnormality. Arrhenius's original theory is sometimes spoken of as entirely obsolete. But it is well to remember that if the younger men of to-day see a little further into the nature of electrolytic solutions than Arrhenius, they do so by standing on Arrhenius's shoulders.

During these years Arrhenius also worked on other physico-chemical subjects, for example, on viscosity of pure liquids and solutions, on conduction in hot gases and flames, on diffusion in aqueous solution, on the velocity of hydrolysis of ethyl acetate and on the inversion of cane-sugar in acid solutions. In a paper on the last subject (1889) Arrhenius makes another theoretical contribution of great significance. He is discussing the effect of temperature on reaction velocity which amounts at the ordinary temperature to an increase of 10 to 15 per cent. for one degree rise. This is much too great to be accounted for by increase of molecular velocity or diminution of viscosity. Besides, the nature of the increase is altogether different from that exhibited in the temperature coefficient of ordinary physical properties. For equal increments of temperature the increase is not approximately arithmetical, but geometrical. This circumstance indicates that the increase in reaction velocity with temperature is not due to change in physical properties of the reacting substances. A similar very rapid change in reaction velocity is observed when ammonium salts are added to ammonia which is saponifying ethyl acetate. Here the explanation is that the ammonium salts greatly reduce the concentration of the free hydroxide ions which really determine the reaction. May we not then surmise that in the inversion of cane-sugar the amount of the really active substances is increased by temperature? The amount of hydrogen-ion, one of the active substances, is little affected by temperature. We must therefore

assume that the other really active substance is not cane-sugar, as this is not changed in amount by temperature, but another hypothetical substance, which is produced from cane-sugar as fast as it is removed by inversion. Arrhenius here reverts to his old distinction between "active" and "inactive" molecules. The hypothetical substance is "active cane-sugar" formed from the inactive substance. It is present at all available temperatures in very minute amount, and the quantity of it in equilibrium with the inactive cane-sugar increases about 12 per cent. per degree. We are therefore dealing principally with the effect of temperature on an *equilibrium*, namely, that between the active and the inactive substance, and can apply van 't Hoff's equilibrium equation

$$d \log_e k/dT = q/2T^2,$$

where k is the equilibrium constant and q is the heat of activation. For a small range of temperature this leads to

$$\log k = C - A/RT,$$

i.e., a straight line should be obtained on Arrhenius's assumption if we plot the logarithm of the velocity coefficient against the reciprocal of the absolute temperature, the slope of the line measuring the heat of activation. Arrhenius's equation actually applies to many homogeneous and heterogeneous reactions, and although there is much that is arbitrary in its derivation, it is in its general character quite in accordance with modern ideas.

Returning once more to his personal fortunes, we find that after 1887 he was recognised abroad as one of the chief figures of physical chemistry, but the death of Edlund in 1888 deprived him of his stoutest champion at home, and greatly reduced his chances of obtaining suitable academic employment in Sweden. Abortive negotiations to establish him in a chair of physics at Utrecht and of chemistry at Graz were succeeded by a definite call to the chair of chemistry at Giessen in 1891. Arrhenius, however, notwithstanding the *invidia inter suos* to which he had been subjected, was intensely patriotic and declined the offer on the chance of being appointed chief of the laboratory of physics in the Högskola (University College) at Stockholm, a post which at this time had become vacant. Arrhenius was successful in his candidature and obtained this lectureship, which was in 1895 converted into a professorship, although once more against formidable opposition, only overcome by the strong backing of German physicists. This chair Arrhenius held till 1905. During the years 1896—1902 he was Rector of the Högskola, and through his personality did much to stabilise and develop the struggling institution notwithstanding

that he had no fondness for administrative tasks. Although his laboratory was small and poorly equipped, the name of Arrhenius was sufficient to attract foreign workers, among whom may be mentioned Abegg, Bredig, Cohen and Euler, who afterwards succeeded him in the chair. Foreign distinctions also began to come his way. He was elected an honorary fellow of this Society in 1898, and was awarded the Davy Medal of the Royal Society in 1902. At last he received recognition, and that of the most handsome description, from his own countrymen by the award of the Nobel Prize for Chemistry in 1903.

His interest had meanwhile been diverted from the study of solutions to other fields of science, at first to cosmic and meteorological problems.

One of his very early papers (1883) dealt with an observation of globe lightning near Upsala, and his work on conducting gases had led him to study electrical phenomena in the earth's atmosphere. With his friend the meteorologist, Nils Ekholm, he investigated the influence of the moon on the electric state of the atmosphere, on the aurora and on thunder-storms. In a long memoir (1896) he attempted to account for the onset and passing of glacial periods by the variation in the amount of carbon dioxide in the atmosphere. This gas exerts a selective absorption, allowing the solar radiation freely to pass inwards, but to a great extent stopping the lower-temperature radiation from the earth outwards. Arrhenius calculated that from this green-house effect the temperature in the arctic regions might rise 8°C if the carbon dioxide content of the atmosphere increased to somewhat more than double its present value, and that in order to get the temperature of an ice-age between the 40th and 50th parallels, the value would have to sink to about half. The variation in the carbonic acid content he attributed chiefly to variation in volcanic activity. The problem of the Ice Ages is still a vexed question amongst geologists, but Arrhenius made a notable contribution to its discussion.

Another important paper on a geological subject was a theory of vulcanicity based on physico-chemical principles (1900). According to it the sea-floor acts as a kind of semipermeable membrane, permitting water molecules to pass but not silicate molecules. Water at no very great distance under the surface of the crust would be at a temperature above its critical point, and therefore a gas, and would be absorbed by the fluid magma under the great pressures existing. But by extrapolation from known data it may be shown that, although at room temperature water is a much weaker acid than silicic acid, yet at high temperatures the reverse is the case, water at 1000° being probably 80 times stronger than silicic acid.

In the magma, then, water will attack and decompose silicates, and thus be potentially stored up in the form of acid and base. When the magma on rising is cooled, the reverse process takes place; water is liberated and at a certain height will overcome the pressure of the column above it, eject the superincumbent fluid, and cause a volcanic eruption. A volcano thus acts in much the same way as a geyser. The theory aims at explaining the proximate cause of eruptions, and has met with wide acceptance.

In 1898 Arrhenius wrote a remarkable paper on the action of cosmic influences on physiological processes, and in 1903 he surprised his chemical friends by publishing his "Lehrbuch der kosmischen Physik," a work of extraordinary learning and scholarship. In it he passes under review an extensive collection of observational material and deals with it according to his own methods. The most striking novelty of treatment is the use he makes of radiation pressure, the existence of which had been predicted by Clerk Maxwell. It was applied by Arrhenius to various cosmic phenomena even before its experimental confirmation in the laboratory by Nichols and Hull and by Lebedev. Arrhenius calculated that at the surface of the sun the repulsive force of the radiation would balance the sun's gravitational attraction on black particles of diameter about 1.5μ , and specific gravity 1, and that smaller particles than these would be repelled. Schwarzschild made some necessary corrections and showed that the maximum repulsion would be for completely reflecting particles (sp. gr. 1) if their diameter was about 0.16μ , and it would then be 10 times the gravitational attraction. From the sun then we might expect streams of such minute particles to be shot out in all directions. Many of these particles would be electrically charged from the ionisation existing in the sun's gaseous atmosphere. Arrhenius shows how the phenomena of the solar corona, comets, the aurora, and the zodiacal light may be caused or influenced by these particles.

With the beginning of the present century Arrhenius's thoughts took a new turn. He became interested in serum therapy, and in the summer of 1902 he went to work in Ehrlich's laboratory in Frankfort. He collaborated with Thorvald Madsen and published jointly with him in the same year a memoir on the occasion of the opening of the Danish State Serum Institute, of which Madsen had been appointed director. It was entitled "Physical Chemistry applied to Toxins and Antitoxins." Madsen was responsible for the experimental methods, Arrhenius for the theoretical treatment. They maintained that the toxin-antitoxin combination (held by Ehrlich to be a firm chemical union) was in reality reversible, and governed by the ordinary mass-action law. The immunological

phenomenon of antitoxin action was likened to the interaction of a weak acid and a weak base, such as boric acid and ammonia, which only partly neutralise each other. The work constitutes a classical study among the early researches into the underlying nature of immunity phenomena, and contributed to laying the foundation of "immunochemistry," a term first applied by Arrhenius himself to a branch of biological research in which reactions of markedly specific character occur between biological principles of unknown chemical nature. Arrhenius pursued this type of research for a decade, and published two books dealing with it, "Immunochemistry" in 1908, and "Quantitative Laws in Biological Chemistry" in 1915.

In the year 1905 Arrhenius happened to be in Berlin and was asked by the University adviser of the Prussian Ministry of Education if he would be inclined to accept a position in the Prussian Academy, similar to that held by van 't Hoff. This was a very tempting proposal, but Arrhenius, with his usual patriotism, requested time to consider it, and asked and was granted permission to speak of it to the Minister of Education in Sweden. It had been the intention of the Academy of Sciences to found a Nobel Institute for Chemistry and one for Physics, but the wish having been expressed by King Oscar II that Arrhenius should not be allowed to leave Sweden, the Academy resolved to found forthwith, instead of the two proposed institutes, a Nobel Institute for Physical Chemistry, and of this new foundation Arrhenius was appointed director. It was housed at first in temporary quarters in Stockholm, but at Experimentalfältet, a pretty park in the neighbourhood of the town, a small laboratory was erected with an official residence attached. The laboratory was inaugurated in 1909. Here, with an assistant and a few research workers as guests, Arrhenius could work and write under ideal conditions on such problems of physical chemistry, physiological chemistry, immunochemistry, meteorology and cosmic physics as might please him.

The stormy period of Arrhenius's career was now definitely over, and from the time of his appointment to the Nobel Institute life went very smoothly with him. From being a scientific outcast in Sweden he became a scientific oracle, known and respected by all classes of the people.

He himself did little practical work in the new laboratory, but stimulated and encouraged others. One of his chief pleasures was to attend conferences in all countries for the purpose of meeting his scientific colleagues and discussing with them their special problems. He often visited England and was elected a foreign member of the Royal Society in 1911. In 1914 he gave the Faraday

Lecture to our own Society, and the Tyndall Lectures to the Royal Institution.

Arrhenius liked to acquire knowledge at first hand, and visited many laboratories for this purpose. He spent, for example, three weeks in Rutherford's laboratory in Manchester, working at a practical course in radioactivity under Geiger. At the end of a week he had started a research on the solubility of active deposits, and was with difficulty dragged away from his electroscope to witness some of Jacques Loeb's starfish experiments at the Marine Biological Station.

He devoted a large part of the later years of his life to popularising science. A firm believer in progress through enlightenment, he sought to bring a knowledge of scientific fact and method before the general public. His clear and easy style made his books attractive, though the matters dealt with were often in themselves difficult. The first of these books, "Världarnas Utveckling" (Worlds in the Making), which treats in a popular manner some of the subjects of his "Kosmische Physik," had an immediate and world-wide success, being translated into all the important European languages.

Happy in his work and happy in his family life, Arrhenius during his later years radiated contentment. He was twice married—in 1894 to Sofia Rudbeck, and in 1905 to Maria Johansson. By the first marriage he had one son, Olov Vilhelm Arrhenius, who is known for his work in soil science and agricultural botany, and by the second a son and two daughters.

His health remained good until the autumn of 1925, and although he recovered in a remarkable way from the first seizure, he retired from the Directorship of the Nobel Institute in February 1927, when he was granted a full pension and the right to remain in the official residence. On 2 October, 1927, he died after a week's illness, and was buried in Upsala on the eighth of that month after a solemn service in Stockholm on the previous day.

Arrhenius was of the old breed of natural philosophers, a true polyhistor, devoted to science at large. Being endowed with a memory both tenacious and accurate, he had a marvellous command of scientific fact. He was, however, no unimaginative empiric; his synthetic fancy played over the vast store of knowledge and sought relations between apparently isolated regions. In consequence, his original ideas were concerned with borderland sciences—physical chemistry, cosmic physics, geophysics, immunochemistry. The conjunction in him of two special faculties explains the character of much of his work—his aptitude for scientific speculation, and an extraordinary facility in dealing with figures. He loved

statistics and it is recorded of him that as a very small boy he delighted to sit beside his father and help him in casting his laborious accounts. Arrhenius might begin a new line of work by the consideration of tables of numerical data collected by himself or others. He would frame a formula to fit them—an exercise at which he was uncannily expert—and then evolve a physical hypothesis to account for the formula. Or he might start with a bold speculation as to how two entities were related, formulate this relation, and check the formula by means of data of observation or experiment. There was constant interplay between the speculative and the quantitative sides of his mind. I recollect that one day in the laboratory at Leipzig, after a long spell of very arduous experimental work, he downed tools, saying, "I have worked enough; now I must think," and did not reappear in the laboratory for a fortnight. Extreme experimental accuracy he never aimed at, considering it rather a disadvantage in the search for a general law, and he used to boast that he had never performed an exact experiment in his life. But this statement must be taken with a grain of salt. I know that his work at Leipzig was certainly more accurate than that of most of his fellow-workers in the laboratory, although carried out with the simplest possible apparatus.

Arrhenius had nothing academic about him save learning. In person he was stoutly built, blond, blue-eyed and rubicund, a true son of the Swedish countryside. His nature was frank, generous and expansive. He was full of robust vitality and primitive force. He had hearty likes and dislikes, and beneath his inborn geniality and good-humour was a latent combativeness, easily aroused in the cause of truth and freedom.

He was not politically active, but he was fond of discussing the large questions of world politics. He spoke very bitterly of Norway when she broke the union with Sweden, but later admitted that the separation had been best for both countries, and expressed to me the hope that Britain would give Ireland similar complete freedom. The World War he regarded as essentially a struggle between Germany and Britain, and although his greatest scientific friends belonged to the Central Powers, his sympathy was definitely with the Allies.

A word may be said about Arrhenius as a linguist. He held that to speak a foreign language what one wanted was, not so much knowledge, as courage. Being liberally endowed with this latter quality he spoke and wrote many languages with ease and confidence, if not with accuracy. Indeed he considered it a waste of time to acquire the niceties of a language, and was of opinion that there should be a universal language—he suggested a simplified

English. Any shortcomings of accent or idiom in his own English were amply compensated by a Shakespearean richness of vocabulary, which gave extraordinary pith to many of his sayings.

He paid little regard to literature or art, but keenly appreciated natural beauty, especially the gladdening phenomena of spring. His life-long interest in the lovely Northern Dancers and in comets that "brandish their crystal tresses in the sky" had most likely an æsthetic as well as a scientific basis.

Sweden can boast of many eminent names in science, of which two are by common consent of the first magnitude—Linnæus and Berzelius. Since the death of Berzelius she has had no name to rank with these save the name we commemorate to-day—Arrhenius. Yet withal Svante Arrhenius was so simple, so genuine, so human a personality, that those who had the privilege of his intimacy always forgot the great scientific master in the genial companion and the kindly, lovable friend.
