

# Classics of Science:

## Electrolytic Dissociation



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Arrhenius' theory of electrolytic dissociation solved several baffling puzzles of electro-chemistry and provided a mechanism for explaining the curious fact that dissolved salts obey the long-known gas laws. The following extracts from the fifth and sixth Stillman lectures for 1912 give Arrhenius' own outline of the history of the science he did so much to develop.

*THEORIES OF SOLUTIONS,*  
by Svante Arrhenius, Yale University Press, 1912.

### Theories of Physical Chemistry

It is well known to all of us that the present great advance in physical chemistry is due chiefly to the introduction of two theories, the one expressing the far-reaching analogy existing between the gaseous and the dissolved states of matter, with which follows the thermodynamic treatment of chemical equilibria in solutions, and the other indicating that salts (acids and bases are regarded as hydrogen salts and as hydrates respectively) are in solution partially dissociated into their ions. As a rule it is said that this new development came abruptly and many people believe that for this reason the merit of these theories is greatly increased. I am of quite an opposite opinion. The ideas mentioned may be found in a less fully developed state in older speculations regarding the chemical behavior of solutions and we ought to lay great stress upon this fact, for it is the most convincing proof of their soundness that they should have developed quite continuously and organically from all the results of chemical experience. Of course when they at first took form, the ideas were

deduced from a rather small number of observations, so that their usefulness was not very evident and on the other hand, the conservative majority of scientists were opposed to the introduction of new notions which seemingly complicated their conception of Nature. The new points of view therefore lived a latent life, being again and again indicated, until there had been collected together a quantity of experimental material sufficient to demand the explanation which they were capable of giving. At such a stage in the evolution of new ideas, a rapid propagation of them takes place under sharp opposition from the teachers of the old conceptions and in the end they receive an overwhelming support simply because of the great importance of the phenomena which they alone are able to explain.

This normal course of evolution may easily be traced for the modern theory of physical chemistry. The chief progress in it is due to the discovery that the molecules of dissolved substances behave in a manner very similar to that of gases. The laws governing the properties of gases are well known and simple; by their application to the much greater and more important group of solutions we have won an extremely valuable knowledge of the nature of solutions which play by far the foremost role in chemistry. At the same time the far-reaching use of the laws of thermodynamic in this new chapter gave it its strength and high value.

### Newton's Observations

It is here in place to recall the interesting statement of Newton that the dissolved molecules in a solution tend to get away from each other so that they finally become distributed uniformly in the solvent.

In reality this idea gives a neat explanation of the phenomena of diffusion, which are so closely related to the force of osmotic pressure. Newton regarded this tendency of dissolved molecules as due to reciprocal repulsion of the dissolved molecules, just as the diffusion of gas-molecules may be regarded as effected by the mutual repulsion of those molecules. One might well say that the modern views regarding the analogy between gaseous and dissolved substances

might well have been developed from this conception of Newton. But the time was not then ripe. The experimental knowledge of chemical phenomena was too scarce for the formulating of laws regarding them. In the year 1839 Gay-Lussac expressed opinions which possess a startling suggestion of modernity. "As the effects of affinity do not change with temperature (he would better have said change but slowly with temperature), whereas dissolution (solubility) is in a high degree dependent upon it, it is very difficult to avoid the assumption that in dissolution as well as in evaporation the product is essentially limited, at a given temperature, by the number of molecules which are able to exist in a certain volume of the solvent. They are separated from this, just as gaseous molecules are precipitated by a lowering of temperature. . . . Dissolution is therefore in a high degree connected with evaporation, namely in this respect that both of them depend on the temperature and are subject to its variations. Hence they ought to show if not a complete identity in their effects at least a great analogy." The objection that in some cases, *e. g.*, with sulphate or selenate of sodium, the solubility-curve shows a break and sometimes a fall with increasing temperature, whereas this is not the case with the vapor-tension, is refuted by means of the assertion that at the temperature where the break occurs, the substance undergoing solution is subject to a transformation.

There is, however, a difference between a gas and a dissolved substance. "The molecules of the gas do not need a solvent to hold them in suspension in a certain volume; their mutual repulsion is enough for that purpose. On the other hand, when a solid or liquid substance is dissolved, its molecules would not remain in the limited volume if they were not united by their affinity to the molecules of the solvent."

### Osmotic Pressure in Plant Cells

Van't Hoff's fundamental discovery in 1885 was directly due to the investigations of De Vries and Pfeffer on the osmotic pressure of certain plant cells. They investigated a property well-known to cell-physiologists, namely that if cells are placed in aqueous solutions they take water from the solution, if this is weak, and give up water to it, if it is strong. With a certain concentration of the solution equilibrium is obtained. De

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Vries found that solutions of glycerol or of cane sugar, which contain the same number of molecules per liter, are in equilibrium with the same cells. Also equimolecular solutions of KCl, NaCl, KNO<sub>3</sub> and NaNO<sub>3</sub> are found to be in equilibrium with the same cells. But these salt solutions are only 0.6 times as concentrated as the corresponding solutions of glycerol or cane sugar which are in equilibrium with the same cells.

Now Moritz Traube in 1867 had given a method of preparing artificial cells, which possess the properties of attracting water from or giving it up to surrounding aqueous solutions according to their concentrations, just like natural cells. In 1877 Pfeffer used Traube's cells for measuring the force with which distilled water was attracted into such a cell filled with a solution of, *e. g.*, 1 per cent. cane sugar. If the solution in the cell is subjected to a certain pressure the water is driven out from the sugar solution: the sugar itself does not pass through the cell walls, which latter consisted of a thin membrane of ferro-cyanide of copper, precipitated in the porous walls of an earthenware vessel. At a certain pressure, which was found to be 505 millimeters of mercury at 6.8° C., equilibrium was reached so that no water went into the cell from the surrounding distilled water and no water was pressed out from the solution of cane sugar through the cell walls. This pressure, the so-called osmotic pressure of a solution of 1 per cent. cane-sugar, increases with temperature. It is nearly proportional to the concentration of the sugar-solution when this is changed.

### Sugar in Solution Obeys Gas Laws

These results of Pfeffer's measurements were communicated to van't Hoff by his friend De Vries, who asked for a theoretical explanation. Van't Hoff made the following simple calculation: A gas containing one gram molecule in 22,400 c.c. at 0° C. possesses a pressure of just 1 atmosphere or 60 millimeters of mercury. At 6.8° C. the pressure is a little higher, namely, 779 millimeters, according to the law of Gay-Lussac. If this gas was expanded until it contained one molecule in 34,200 c.c., which is the concentration of a 1 per cent. solution of cane sugar—the molecular weight of cane sugar being 342—its pressure at 6.8° C. would according to Boyle's law be 508 millimeters. This figure agrees within 1 per cent.

and within the errors of observation in Pfeffer's experiments with that, 505 mm., found for the osmotic pressure of an equimolecular solution of cane sugar. In other words the osmotic pressure increases proportionally to the concentration (just as the gas pressure does according to Boyle's law) and within the errors of experiment as van't Hoff deduced from Pfeffer's figures, also to the absolute temperature (as in Gay-Lussac's law for gases), there exists a perfect analogy between the osmotic pressure of a solution (of cane sugar) and the pressure of a gas containing the same number of molecules in the same volume.

As soon as this fundamental fact was stated, van't Hoff applied all the laws which had been deduced from thermodynamics for the pressure of gases and for saturated vapors, which correspond to saturated solutions, to the osmotic pressures of dissolved substances. . . .

The whole investigation of van't Hoff (1885) was a triumphant march through the different domains of physical chemistry; only one difficulty, but a rather severe one, was found. The great majority of substances examined did not follow the law of Avogadro, as cane sugar did. This was already manifest from De Vries' investigations, according to which one molecule of sodium chloride exerts the same osmotic pressure as about 1.7 molecules of cane-sugar dissolved in the same quantity of water. To account for this difference, van't Hoff introduced a coefficient *i* (the isotonic coefficient) which was determined experimentally. . . .

This was a great inconvenience, for it really spoilt the analogy between the dilute and the gaseous states of matter, but it was very soon eliminated by the theory of electrolytic dissociation. . . .

### Conductivity and Dilution

In 1883 I investigated the conductivity of electrolytes as depending on their concentration and temperature and came to the conclusion (published 1884) that their solutions contain two different kinds of molecules, of which the one is a non-conductor, the other conducting electricity in consequence of properties attributed to it by the hypothesis of Gay-Lussac, Williamson and Clausius. These latter were simply called active molecules. The number of active molecules increases with dilution at the expense of the inactive ones and tends to a limit, which is probably first reached when all inactive molecules have been trans-

formed into active ones. At very high dilutions the additive property of the conductivity postulated by Kohlrausch is not only true within certain groups of electrolytes of similar composition but for all electrolytes of whatsoever composition. An acid is the stronger the greater its conductivity. At infinite dilution all acids have the same strength. These assertions were demonstrated to be in accord with the thermochemical measurements of Berthelot and Thomsen. Similar rules are valid for bases. Chemical activity therefore coincides with electrical activity.

**Svante August Arrhenius** was born February 19, 1859, at Wijk, near Upsala, Sweden, and died October 2, 1927 at Stockholm. He is the author of the theory of electrolytic dissociation of salts in solution, which was first announced in 1883 when he was 24 years old. It is one of the most important theories of physical chemistry, and for it he received the Nobel prize for Chemistry in 1903.

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### MEMORANDUM

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