THEORY OF ATTRACTION PRESSURE

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It was shown in the preceding paper[1] that the attraction pressure, which is not taken into consideration in the theory of van't Hoff and Arrhenius, is very different for different bodies and depends on the solvent as well as on the dissolved substances. When it is a question of aqueous solutions, the attraction pressure is nothing else but the water-attractive power of the dissolved body. Therefore we conclude that hydrates exist in solutions. This hypothesis, which formerly has been neglected or restricted too much by the adherents of the theories of van't Hoff and Arrhenius, is, as we know, at this time generally accepted. There exist two possibilities with regard to the hydrating effect of the attraction pressure.

1. If we suppose as van der Waals[2] does that the sphere of action (*Wirkungssphäre*) reaches only from molecule to molecule, we reach the conclusion that every dissolved molecule of a non-electrolyte or every ion of a salt is loosely connected only with *one* molecule of water with an intensity, which corresponds to the attraction pressure.

2. The sphere of action is more extended; the *molecules and ions of the dissolved body surround themselves, similarly to the condensation nuclei of the gases, with a water covering, which generally corresponds to the attraction pressure.* We will begin with the discussion of the first hypothesis:

If we suppose with Poynting[3] that one molecule or one ion of the dissolved body is connected with *one* molecule of water, and that this bound water cannot evaporate, and if the solution contains *n* molecules of the dissolved body to N molecules of the solvent, we get for the vapor pressures

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[1] Jour. Phys. Chem., 14, 452 (1910).

[2] Continuität des gasförmigen flüssigen Zustandes, Leipzig.

[3] Poynting: Phil. Mag., [5] 42, 289 (1896) and my Grundriss phys. Chem., Enke, Stuttgart, 1904, p. 195.

the solution and the solvent f_1 and f_0 respectively, the relation:

$$\frac{f_1}{f_0} = \frac{N - n}{N} \text{ also } \frac{f_0 - f_1}{f_0} = \frac{n}{N}.$$

This simple derivation of Raoult's law was the reason that Poynting's hypothesis formerly appealed to me very strongly, and some time ago I called attention to the papers of A. Werner,[1] who, though guided by quite other ideas, had developed a theory of *monohydrates* which was, in principle, identical with Poynting's theory.

In spite of all that, I do not hesitate to accept the second hypothesis. In the preceding paper I have referred briefly to a number of investigations, among others to the researches of Garrard and Oppermann, Washburn, etc., on the electrolytic transference of ions, to the well-known investigations of Jones on the freezing point, and to the experiments of Kohlrausch on the temperature coefficient of friction and electrical conductivity, all of these show that in general or in most cases the dissolved bodies are surrounded corresponding to their attraction pressure with a more or less extended covering of water. We think that there exist in a *dilute* solution *bound* and *not bound* (or influenced and not influenced) molecules of water, and we suppose a *limit of concentration*, for which the number of *unbound* molecules will be just equal to zero. We think that this limit of concentration is the same as that concentration, for which the *heat of dilution* becomes equal to zero. That concentration separates the *dilute* solutions[2] from the strong ones.

If we consider a *dilute* solution according to van't Hoff, we will understand, why in separating a part of the solvent from the dissolved body by *freezing* or evaporating, the *special nature* of the *dissolved body* either does not appear at all or becomes active in a *secondary* manner only, for it is clear

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[1] Werner: Ber. chem. Ges., Berlin, **40**, 4133, 1907 and especially Fortschritte der anorganischen Chemie Vieweg Braunschweig, **1909**, p. 218.

[2] It will moreover be an open question, whether the hypotheses 1 and 2 may not be joined together by a kinetic hypothesis, but we will not enter today more fully into these considerations.

that by the more or less extensive hydration the different effects of the ions on the existing surplus of solvent will be equalized, and as long as no bound water is present, the bodies are acting in relation to freezing and boiling point primarily only according to the number of particles.

But things will be quite different, as soon as the above-mentioned, limiting concentration has been exceeded, for then the work necessary to separate the solvent from the dissolved body will depend chiefly on the attraction pressure, and therefore we are not astonished that, according to Biltz, Jones, and others, the ascending of the freezing point curvatures with increasing concentration runs parallel with the attraction pressure. If the solutions become highly concentrated, we observe that bodies with a *great attraction pressure*, such as salts, freeze as *cryohydrates*, while cryohydrates do not exist for *non-electrolytes with a low attraction pressure.*

Further we may recall the well-known osmotic experiment by Pfeffer. In the osmometer a solution of sugar is separated from water by a semipermeable membrane. The water is evidently attracted by the sugar solution corresponding to the difference of pressure brought about by the attraction pressure of sugar. The *velocity* with which salts, sugar, and other bodies with large attraction pressure cause the entrance of water doubtless runs *parallel,* according to the results of the previous paper, with the *attraction pressures* of *molecules* and *ions.* But in proportion as the particles are gradually forming hydrates with increasing dilution, their *specific* influence will diminish by and by, and it may be possible, though it is *not certain,* according to the osmotic researches by Brown, Hoeber, de Vries (compare the previous paper) that the osmotic elevation is just the same after equilibrium is reached. Up to this point it seems that my theory will join very well to the theories of van't Hoff and Arrhenius. My theory would supplement those theories with regard to concentrated solutions. There we have a specific factor, because there is no unbound water, while in the *dilute* solutions we can disregard the specific influence of the hydrated ions. We can not deny that the two theories harmonize up to a certain point, but even in the case of dilute solutions we find *fundamental differences* in the point of view. When we consider simply the separation of the excess solvents from the dissolved body we can disregard the specific intensity factor of the solution energy, that is the attraction pressure, *but only in this case. If, however, there is a question of the separation of the dissolved body from the solvent, if therefore we consider the laws governing changes in solubility, then we are obliged to take account, even in dilute solutions of the specific influence of the attraction pressure.* Salts diminish the attraction pressure of non-electrolytes, of colloids, of red blood cells, and of bacteria (agglutination), and in the same way the non-electrolytes diminish the attraction pressure of salts. This whole inter-relation of the laws of solubility will now be understood, *while the osmotic theory has failed completely to bring this out.* We find quite the same for *osmosis* even in dilute solutions. It is not true that the cause of *semipermeability* is to be found only in the membranes themselves. The membranes which are semipermeable to salts, are not at all semipermeable to aqueous solution of non-electrolytes with a low attraction pressure. *There can never be an osmotic equilibrium between an aqueous solution of alcohol and cane sugar, even if the number of particles on both sides of the membrane is equal. Never do we have equilibrium between a solution of equal equivalents of sodium nitrate and sodium chloride, and even the osmotic equilibrium of molecular solutions of the same salts on both sides of a membrane will be disturbed at once, if a different decrease in the attraction pressure is caused by the addition of other bodies. The attraction pressure is the driving force of osmosis and not van't Hoff's osmotic pressure.*

At once we understand that these quite different views must especially enrich the *physiological* and *biological* sciences the more as just here van't Hoff's theory has failed completely in spite of all attempts to extenuate this fact. I refer once more to my publications, which will appear nearly simultaneously in the *Biochemische Zeitschrift* and especially in *Pflüger's*

Archiv der ges. Physiologie. These papers will bring many other proofs in favor of my theory.

And now to Arrhenius! Since attraction pressure and ionization nearly always run parallel, we may ask the question whether the hypothesis of ionization is necessary at all. I think that we cannot absolutely say no with regard to this question, but in this paper we will leave it aside.

Arrhenius has made, however, the same mistake in the calculation of the coefficients of dissociation, which an electrochemist would make who thought that the electrical energy of a current could only be increased by enlarging the electrical intensity and not the electromotive force of the current. *We must not forget that by increasing the attraction pressure we get the same effect as by augmenting the number of particles.* Therefore *many calculated dissociation factors*, especially those in non-aqueous solvents, *are surely very doubtful.* But the theory of Arrhenius is suffering from yet another fundamental fault. Though according to Faraday and Helmholtz the *electrostatic* and *chemical* forces of the ions are the same, Arrhenius makes them opposed to one another, for according to his views the ions are *electrostatically bound* in dilute solutions, but *chemically unbound.* Even if we assume that in dilute solutions the water-covering of the ions makes the re-association more difficult, we must acknowledge on the other hand that, in view of the powerful electrostatic forces, the re-association is not at all impossible. I think it very probable that the theory of the future will go back to the former idea of Clausius, that even in dilute solutions every dissociation is followed by an association, though the time in which the ions are joined may be very small in comparison with the time, during which they are separated. I think, however, that there are yet other ways of avoiding the difficulties of the Arrhenius theory.

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