

[Ostwald's dilution law]

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The researches of van 't Hoff, Planck, and Arrhenius on dilute solutions have in recent times led to the recognition of a complete analogy of these with gases. One of the most valuable advances of these studies is that the compounds usually spoken of as held together by the strongest affinities, such as, for example, potassium chloride, hydrogen chloride, or potassium hydroxide, must actually be regarded in dilute solutions as very largely dissociated.

Since this result is derived according to the laws of thermodynamics on the basis of a hypothesis which is at least very plausible, if not positive, it does not leave much to say against it, so much does it satisfy the usual views. But before deciding on such a change in viewpoint, we have the duty to apply the strongest tests possible for its verification.

One such test is to deduce the broadest possible consequences of the theory, to compare them with practice. The following lines attempt to develop such consequences, and this preliminary communication reports the results of the test.

If the electrolytes are dissociated in water solution and therefore obey laws which are analogous to the gas laws, then the dissociation laws which have been learned for gases will also find use for solutions. In the simplest case, where a molecule decomposes into two, the theory now leads to the following formula which is valid for gases (Ostwald, *Allg. Chem.*, **2**, 732):

$$R \log [p / (p_1 p_2)] = (\rho / T) + \text{const.},$$

which for a constant temperature and the case where no decomposition products are left over accords with the law

$$p / p_1^2 = C$$

where p is the pressure of the undecomposed part, p_1 of the decomposed part, and C is a constant.

Now, according to the work mentioned above, it is permissible to place the pressure in solution proportional to the actual masses u and u_1 of the substance and inversely proportional to the volume; the equation then becomes $p : p_1 = u/v : u_1/v$ and so $(u/u_1) v = C$. Further, the masses u and u_1 can be calculated from the electrical conductivity, as Arrhenius has shown. If we call the molecular conductivity of an electrolyte of volume v , μ_v , and the limit of conductivity of infinite dilution μ_o , then $u : u_1 = \mu_o - \mu_v : \mu_v$, since the conductivity μ_v is proportional to the dissociated mass of electrolyte u_1 . From this follows the dilution law, valid for all binary electrolytes:

$$(\mu_o - \mu_v) / \mu_v^2 = \text{const.}$$

The test of this conclusion can be performed with great assurance in the acids and bases, for which numerous measurements of electrical conductivity exist. Since I will publish future communications on this subject, I will content myself now with pointing out that the results of my calculations speak favorably for the theory. The formula expresses not only an altogether general law, which I have earlier found empirically for the influence of dilution on acids and bases, as well as over a hundred substances but it leads also to numerical results which in

part agree completely, in part show a variation whose size is of the same order of magnitude as has been established in gases.

[Reader's Note: the supporting experimental details are given in *Zeitschrift für physikalische Chemie*, volume 3, page 170, 241, (1889).]