To illustrate the advantages of germinating *Oenothera* seeds under experimental conditions over the old practice of sowing upon earth I will give the results for a problem as attacked under the old and new method. In 1914 I germinated on earth seeds from an F_1 hybrid plant, 13.35ac, of the cross *O. franciscana* $\times$ *O. biennis*. A sowing of 819 seed-like structures produced a culture of 402 seedlings, a germination of about 50%. The culture was grown partly to test the inheritance of a character (red coloration of the papillae on the stems and ovaries) present in *franciscana* and absent in *biennis*. This character was fully dominant in the F_1 of this cross and in its reciprocal. It seemed reasonable to expect that a proportion of the plants in the F_2 generation would present the clear green stems and ovaries (recessive) of *biennis*, but I found no plants of this type in the culture of 1914. This winter (1915) I germinated in Petri dishes seeds from the same F_1 hybrid plant, 13.35ac, and obtained 761 seedlings from about 921 seed-like structures,—a germination close to 82%. The new method had raised the proportion of germination more than 30%. Of the 761 seedlings I was able to bring 748 to rosettes, the 13 which died probably belonging to a small group of etiolated dwarfs difficult to grow. It becomes a matter of interest to see whether or not in this culture of 1915 a group of green-stemmed plants will appear.

[1] Renner, O., Befruchtung und Embryobildung bei *Oenothera Lamarckiana* und einigen verwandten Arten. *Flora, Jena*, 107, 115 (1914).

[2] De Vries Hugo, The Coefficient of Mutation in *Oenothera biennis* L. *Bot. Gaz., Chicago*, 59, 169 (1915).

THE OSMOTIC PRESSURE OF THE IONS AND OF THE UNDISSOCIATED MOLECULES OF SALTS IN AQUEOUS SOLUTION

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The concentration of the ions (C_i) and that of the undissociated molecules (C_u) are involved in the equation, $C_i^2 / C_u = K$, expressing the application of the law of mass-action to solutions of electrolytes. Hence the large divergence from this law which strong electrolytes exhibit may be due to the behavior of the ions, to that of the undissociated molecules, or to that of both. This so called anomalous behavior may be simply expressed by saying that for one or for both of these molecular species van't Hoff's law, $\Pi = CRT$, where Π is the osmotic pressure, C is the concentration in mols per unit-volume, R is the gas-

constant, and T is the absolute temperature, does not hold; for, if all of the molecular species entering into an equilibrium obey this law, the law of mass-action is a thermodynamic necessity.[1]

In this paper is outlined and applied a method for determining the extent to which the ions and the undissociated molecules deviate from van't Hoff's law, that is, for determining the relation between the osmotic pressure of the ions or of the undissociated molecules and their concentration. The significance of the results, particularly as applied to the calculation of the degree of ionization and to the validity of the law of mass-action, is discussed.

Besides the laws of thermodynamics, the assumptions involved in these calculations are that (1) in a dilute solution of a di-ionic electrolyte the osmotic pressure due to each of the two ions is the same, and that (2) the degree of ionization (γ) is given by the conductance-viscosity ratio $(\lambda\eta/\lambda_0\eta_0)$, the concentration of each ion then being $C\gamma$ and that of the undissociated molecules $C(1-\gamma)$. These assumptions are generally accepted; they are, however, briefly discussed below.

The total osmotic pressure (Π) of a solution is due in part to that of each of the two ions and in part to that of the undissociated molecules. Since by the first assumption above stated, the osmotic pressure of one ion is equal to that of the other, the relation $\Pi = 2\Pi_i + \Pi_u$ follows. The principles of thermodynamics, together with the same assumption, lead for equilibrium in a solution of di-ionic electrolyte, to the relation[1]

$$2d\,\Pi_i/C_i - d\Pi_u/C_u = 0 \qquad (1)$$

If now C_i and C_u are calculated from conductance data, and if the total osmotic pressure of the solution be known (from direct measurements or from freezing-point determinations, etc.), there remain in these two equations but two unknown quantities Π_i and Π_u.

The solution of these two equations gives for the rate of change of the osmotic pressure of the ions with their concentration the relation:

$$\frac{d\Pi_i}{dC_i} = \frac{1}{2}\left[\frac{\Pi}{C} + \frac{\gamma}{2\cdot303}\,\frac{d\,(\Pi/C_i)}{d\log C_i}\right] \qquad (2)$$

The first term Π/C may be calculated directly from the data. The second term, which is small in comparison with the other, may be conveniently evaluated by the graphic method of plotting values of Π/C_i against those of $\log C_i$ and determining the tangents. Having calculated $d\Pi_i/dC_i$ for a series of concentrations, values of Π_i/C_i may be determined by integration, either graphic or algebraic.

In order to determine the similar ratios for the undissociated molecules, the equation corresponding to (2) might be employed. In practice, however, it is more convenient to use a different method. By eliminating K, C_i and C_u from Storch's equation, $[C_i^n/C_u = K]$, from the differential equation obtained from this and from equation (1), the relation

$$d\Pi_u/dC_u = \frac{2}{n} d\Pi_i/dC_i$$

is obtained. That is, having calculated values of $d\Pi_i/dC_i$ and of n at any given concentration, by the methods which have been previously developed,[2] over a concentration-range, values of $d\Pi_u/dC_u$ may be determined, and hence by integration the osmotic pressure of the undissociated molecules may be calculated.

The results of such calculations for a few representative di-ionic electrolytes for whose solutions reliable freezing-point data[3] are available are given in the table. They are given as ratios of the form $\frac{d\Pi}{dC}/RT$. The deviations of these from unity show the degree of deviation from van't Hoff's law at the different concentrations. For most purposes the ratio $d\Pi/dC$ here considered is more useful than the integral ratio Π/C; for it is the former ratio which is introduced into thermodynamic relations in order to derive the mass-action law, the electromotive-force equation, etc. Further, the differential ratio gives information of a more definite character regarding the properties of the solution at any given concentration than does the integral ratio. The value of the former depends only upon the properties of the solution of the concentration in question, while that of the latter is influenced by, and to a great extent depends upon, the properties of the solutions of all concentrations from the infinitely dilute solution up to that in question.

Values of the Ratio $\dfrac{d\Pi_i}{dC_i}\Big/ RT$ *for the Ions*

Equivalents per liter	LiCl	NaCl	KCl	KNO₃	CuSO₄
0.001	.....	0.996	0.987	.....	0.927
0.002	.....	0.993	0.983	.....	0.919
0.005	.....	0.990	0.983	0.990	0.899
0.01	0.985	0.986	0.979	0.983	0.867
0.02	0.993	0.983	0.977	0.972	0.824
0.05	0.986	0.980	0.970	0.946	0.756
0.1	1.000	0.973	0.967	0.926	0.734
0.2	1.015	0.963	0.960	0.888	.....
0.3	1.046	0.965	0.958	0.850	.....
0.5	1.110	0.967	0.956	.....	.....

Values o the Ratio $\dfrac{d\Pi_u}{dC_u}\bigg/ RT$ for the Undissociated Molecules

Equivalents per liter	LiCl	NaCl	KCl	KNO₃	CuSO₄
0.001	.....	1.263	1.249	.....	1.090
0.002	.....	1.280	1.262	.....	1.091
0.005	.....	1.305	1.289	1.279	1.085
0.01	1.334	1.323	1.305	1.281	1.067
0.02	1.366	1.343	1.325	1.275	1.046
0.05	1.390	1.375	1.350	1.246	1.025
0.1	1.439	1.394	1.375	1.217	1.055
0.2	1.500	1.413	1.396	1.159	.....
0.3	1.577	1.446	1.412	1.100	.....
0.5	1.728	1.488	1.432	.....	.....

The results in the table show that, even in solutions as dilute as 0.001 normal, neither the ions nor the undissociated molecules obey van't Hoff's law, though with decreasing concentration both become more nearly normal.

The osmotic pressure of the ions is less than that calculated from this law. This is true in every case except for solutions of lithium chloride at 0.1 normal and above; hydration is doubtless the cause of this exception.

It can be shown, moreover, that the behavior of the ions may be represented within the error of the freezing-point determinations by an equation of the form

$$\frac{d\Pi_i}{dC_i} = RT\,(1 + kC_i^m)$$

The results seem to justify the assumption that the osmotic pressures of the two ions in a solution of a di-ionic electrolyte are the same up to moderate concentrations. For example, the behavior of the chloride ion is within the experimental error the same whether calculated from the data for sodium chloride or from that for potassium chloride.

The undissociated molecules have an osmotic pressure considerably greater than that calculated from van't Hoff's law. At moderate concentrations the various salts do not behave similarly. In the case of the chlorides the deviations continue to increase with the concentration, but in that of the nitrates a maximum is reached about 0.02 normal. This somewhat surprising result, that the behavior of the least hydrated is the most complex, is connected with the fact that the exponent n is for these salts a minimum at about 0.02 normal.

For solutions more dilute than 0.01 normal and in some cases to a much higher concentration, an empirical equation of a form similar to that which holds for the ions expresses the relation between the osmotic

pressure of the undissociated molecules and their concentration. In the case of potassium chloride these relations, one for the ions and one for the undissociated molecules, express the results for solutions between 0.001 normal and 0.5 normal, so closely that the average difference between the total osmotic pressure of the solution calculated from them and that experimentally determined is but 0.10 percent.

The behavior of the undissociated molecules of copper sulphate is remarkable in two particulars. First they show an almost constant deviation from van't Hoff's law from 0.001 normal to 0.02 normal. In the second place, while the bivalent ions are considerably more abnormal than are the univalent ions, the undissociated molecules of this salt obey van't Hoff's law much more closely than do those of the uni-univalent salts.

H. Jahn[4] and recently G. N. Lewis[5] have considered it to be less reasonable to assume that (1) the concentration of the ions is proportional to the electrical conductivity of the solution, than it is to assume that (2) the concentration of the ions is proportional to their osmotic pressure or activity, that is, that the ions are normal or that they obey van't Hoff's law. Parallel to this latter assumption is the one that (3) the undissociated molecules are normal. The degree of ionization calculated upon any of these three assumptions is different from that calculated upon the other two. That is, the acceptance of one compels the rejection of the others.

It may be shown in another way that the experimental data are such that it is not possible for both the ions and the undissociated molecules of strong electrolytes to be normal. By combining the mass-action law relation, $C_i^2/C_u = K$, and the differential equation derived from this with the thermodynamic equation (1) above, it can be shown that the necessary and sufficient condition that the law of mass-action hold over a certain concentration range is that at all concentrations $d\Pi_i/dC_i = d\Pi_u/dC_u$; that is, that the rates of change of the osmotic pressures of the ions and of the undissociated molecules with their respective concentrations be the same. Since the mass-action law is not obeyed by solutions of strong electrolytes this relation does not hold, and the relation $\Pi = CRT$ cannot be true for both molecular species. The computation of the mol-number i from freezing-point data, and the calculation of the degree of ionization on this basis, assumes that both the ions and the undissociated molecules are normal. Since the resulting values do not obey the mass-action law, the method is inconsistent and theoretically incorrect. It has long been recognized that actual gases are not 'perfect' gases. Unfortunately the idea that in

general solutes may be treated as normal or 'perfect' solutes is much more persistent.

The magnitude of the deviation of the strong electrolyte from the normal behavior depends greatly upon the terms in which this deviation is expressed. The equilibrium expression C_i^2/C_u increases with the concentration. Thus for potassium chloride it increases from 0.026 at 0.001 normal to 0.55 at 0.1 normal, an increase of 21 fold. The results given in the table show that this behavior is accounted for by a deviation of 3.3% in the osmotic pressure of the ions and of 37% in that of the undissociated molecules. The percentage deviation when expressed as here in terms of osmotic pressure is smaller than when it is expressed, as Lewis[5] has done, in terms of activity; this follows from the logarithmic relation between the two.

A more thorough study of these topics is appearing in *The Journal of the American Chemical Society.*

[1] E. W. Washburn, *J. Amer. Chem. Soc.*, 32, 484–5 (1910).

[2] S. J. Bates, *J. Amer. Chem. Soc.*, 35, 519 (1913).

[3] The data have been taken in great measure from the compilation of A. A. Noyes and K. G. Falk, *J. Amer. Chem. Soc.*, 32, 1011 (1910). This has been supplemented by the recent measurements of F. Flügel, *Zs. physik. Chem.*, 79, 577 (1912), of W. A. Roth, *Ibid.*, 79, 599 (1912), of E. W. Washburn and D. A. McInnes, *J. Amer. Chem. Soc.*, 33, 1686 (1911) and of L. H. Adams, *Ibid.*, 37, 481 (1915).

[4] *Zs. physik. Chem.*, 33, 545 (1900).

[5] *J. Amer. Chem. Soc.*, 34, 1631 (1912).

THE EXTENSION OF THE SPECTRUM BEYOND THE SCHUMANN REGION

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The violet limit of the spectrum determined by direct eye observation lies in the neighborhood of 4000 angstrom units; with a glass prism and lenses the spectrum may be followed photographically to wave length 3000 or thereabout; with a quartz system or with a reflecting grating, the limit may be pushed to wave length 1850. Victor Schumann showed that the absorption of the air and of the gelatine of the photographic plate were responsible for the abrupt termination of the spectrum. By employing a vacuum spectroscope and a special photographic plate whose emulsion was very poor in gelatine, he was able to push his observations to wave length 1230. At this point he was stopped by the opacity of the fluorite of which his lenses were made.