involved. The decrease is most rapid at 0° and progressively becomes slower up to 25°, for all the solutions containing a high proportion of monovalent ions. Solutions containing only magnesium sulfate and water exhibit the reverse behavior. The decrease is slowest for the most dilute solutions (potassium chloride only) and progressively becomes more rapid to those of higher concentration (sodium chloride). These effects are best observed by plotting coefficients against concentrations.

Effects of Temperature.—The temperature coefficients of equivalent conductance considered decrease by about 1.5 to 2.0% of their values for each degree increase in temperature. The fact that they decrease is consistent with measurements showing coefficients to be negative at much higher temperatures. This decrease is most rapid for water and becomes less rapid the more concentrated the solution, except for solutions containing only magnesium sulfate and water. This difference and also the one mentioned in the preceding paragraph are likely due to the fact that magnesium sulfate is a different type of electrolyte in that it yields divalent ions.

Effects of Adding a Second Salt.—The addition of a salt that forms solutions with temperature coefficients higher or lower than those of sodium chloride solutions to the latter, produces solutions with coefficients of intermediate value. The magnitude of the intermediate value depends upon the concentration, and the temperature, even though the mole ratios are kept constant. The effect of adding a salt is either in opposition to or in addition to the effect of increasing the concentration, depending upon whether the coefficients of solutions of the added salt are higher or lower, respectively, than those of solutions containing only sodium chloride and water. For example, the addition of magnesium sulfate to sodium chloride solutions increases the temperature coefficients of the latter. Thus, two opposing factors are in operation, the effect of adding a salt with a larger temperature coefficient outweighing the effect of increasing the concentration.

When temperature coefficient is considered as a function of concentration, there is a pronounced maximum in the temperature coefficient at concentration no. 3 for magnesium sulfate solutions at 0°. Slight maxima occur also at the same concentration for this salt at 25° and for potassium chloride solutions at 0°. These maxima are reflected in the corresponding sodium chloride solutions to which the salts mentioned have been added. The maxima, particularly for the magnesium sulfate solutions at 0°, are larger than could be attributed to experimental errors, and as yet we can offer no explanation for them. It is a noteworthy fact that they occur mainly at 0°.

Summary

1. An equation is recommended for calculating the equivalent conductances of solutions as a function of centigrade temperature. The maximum deviation of the calculated from the experimental equivalent conductance was 0.02%, and the average deviation was only 0.006%.
2. By use of the differentiated form of the equation the temperature coefficients of equivalent conductance of twenty different solutions have been calculated with five-place accuracy at 0, 5, 10, 15, 20 and 25°. Also temperature coefficients of specific conductance have been calculated at 0, 5, 10, 15, 18, 20 and 25° for the conductivity water used and for 0.01 demal and 0.1 demal standard potassium chloride solutions.
3. Variations of temperature coefficients of electrical conductance of the salt solutions, due to concentration changes, temperature changes and the addition of a second salt have been determined.

COLLEGE STATION, TEXAS RECEIVED AUGUST 31, 1943

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Osmotic Pressures for Mixed Solvents[1]

BY FREDERICK T. WALL

During recent years osmotic pressure measurements have assumed increased importance as a means of determining molecular weights of high polymeric substances.[2a,b] Although the theory of osmotic pressures for simple systems has been well formulated, little attention has been devoted to the theoretical aspects of osmotic pressures for systems with mixed solvents. Since G. Gee[2] has carried out measurements under such conditions, it appears desirable to consider thermodynamically the significance of osmotic pressures for mixed solvents and to find out just what it is that one measures experimentally.

For an ordinary solution consisting of a solvent (A) and a solute (S), the osmotic pressure is a definite thermodynamic property of the solution. It is defined simply as the excess pressure which must be applied to the solution to increase the partial pressure of the solvent up to the vapor pressure of the pure solvent at the same tempera-

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[1] Original manuscript received July 12, 1943.

[2] (a) G. V. Schulz, *Z. physik. Chem.*, **176**, 317 (1936); R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943); P. J. Flory, THIS JOURNAL, **65**, 372 (1943). See also H. Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York, N. Y., 1940, p. 228, for a general discussion. (b) G. Gee *Trans. Faraday Soc.*, **36**, 1171 (1940)

ture. If p_A^0 is the vapor pressure of pure A and p_A the partial pressure of A for the solution, then the osmotic pressure is given by[3]

$$P = \frac{RT}{\overline{V}_A} \ln \frac{p_A^0}{p_A} \tag{1}$$

where $\overline{V}_A$ is the partial molar volume of A in the solution. Although one usually thinks of a semipermeable membrane in connection with osmotic pressure, it will be recognized that such a membrane need not exist to give equation (1) a definite meaning. Of course, if pure A is separated from a solution of S in A by a membrane impermeable to S, then P is just the excess pressure that must be applied to the solution to prevent solvent from passing through the membrane.

Consider now a solution of solute (S) in a mixture of solvents (A and B). One could define an osmotic pressure for each of the solvents by means of equations of type (1). That, however, would in general give two different osmotic pressures, neither of which would correspond to a measured pressure if one used a membrane permeable to both A and B but impermeable to S. Accordingly, it seems desirable to define a new osmotic pressure, bearing in mind the experiment which might be used for the measurement.

Suppose that a solution of S in A and B is separated from a mixture of A and B by a membrane impermeable to S only (Fig. 1). In the following discussion the term "solution" will be applied to the phase containing S and the term "solvent" to the other phase. Let x_i, p_i and $\overline{V}_i$ represent, respectively, the mole fraction, partial pressure and partial molar volume of the i-th component in the solution, and let the same symbols with primes (x_i', p_i', $\overline{V}_i'$) represent the corresponding quantities for the solvent. Also let p_i^0 be the vapor pressure of the pure ith component at the temperature of the experiment. For the sake of simplicity, it will first be supposed that Raoult's law holds. Since for high polymeric substances[4] and for many pairs of solvents, Raoult's law does not hold, the treatment will then be followed by a consideration of the effect of deviations from Raoult's law.

System with Raoult's Law Valid.—If Raoult's law holds, then

$$p_i = x_i p_i^0$$

and

$$p_i' = x_i' p_i^0 \tag{2}$$

To prevent A from passing through the membrane, it is necessary to apply a pressure P_A on the solution, where

$$P_A = \frac{RT}{\overline{V}_A} \ln \frac{p_A'}{p_A} = \frac{RT}{\overline{V}_A} \ln \frac{x_A'}{x_A} \tag{3}$$

Likewise to prevent B from passing through the membrane, a pressure P_B must be applied, where

$$P_B = \frac{RT}{\overline{V}_B} \ln \frac{p_B'}{p_B} = \frac{RT}{\overline{V}_B} \ln \frac{x_B'}{x_B} \tag{4}$$

In general P_A will not equal P_B; to make them equal, it is necessary that

$$\frac{1}{\overline{V}_A} \ln \frac{x_A'}{x_A} = \frac{1}{\overline{V}_B} \ln \frac{x_B'}{x_B} \tag{5}$$

It is seen from equation (5) that if P_A equals P_B, the mole ratio of A to B on the two sides of the membrane will not be the same unless $\overline{V}_A = \overline{V}_B$.

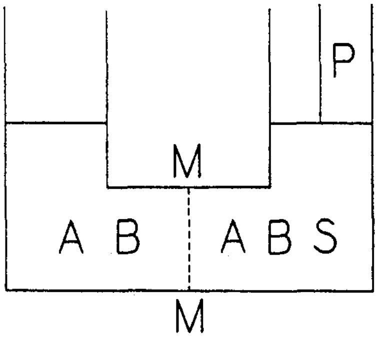

Fig. 1.—Solution (A,B,S,) separated from solvent (A,B) by membrane (M-M) which is impermeable to S.

Let us now investigate what will happen if the experiment illustrated in Fig. 1 is started with the same mole ratio of A to B on each side of the membrane. Then

$$\frac{x_B'}{x_B} = \frac{x_A'}{x_A} \tag{6}$$

and

$$P_A \overline{V}_A = P_B \overline{V}_B \tag{7}$$

Suppose $\overline{V}_A > \overline{V}_B$; then $P_A < P_B$. If a pressure P_A is applied to the solution, no A will pass through the membrane, but B will enter the solution, thus increasing the volume of the solution. On the other hand, if a pressure P_B is applied, no B will pass through the membrane, but some A will leave the solution, thereby decreasing its volume. Evidently there will be some intermediate pressure P (where $P_A < P < P_B$) such that the volume of the solution will remain stationary. This will occur when the ratio of the number of moles of A leaving the solution to the number of moles of B entering the solution is in the inverse ratio of their partial molar volumes. When this state is obtained, one might be inclined to call P the "osmotic pressure" of the solution. Actually (if one waits long enough), P will gradually change as diffusion takes place until equation (5) holds, and only then will true equilibrium be established. Accordingly this method of using mixed solvents will make osmotic pressure measurements time consuming, because diffusion must take place and equilibrium cannot be reached by the application of pressure alone. Moreover,

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[3] See, for example, MacDougall, "Physical Chemistry," rev. ed., The Macmillan Co., New York, N. Y., 1943, pp. 255–257.

[4] M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); P. J. Flory, *J. Chem. Phys.*, **10**, 15 (1942).

the final pressure will not be the osmotic pressure of the original solution but will be defined as that of the equilibrated solution.

To get the osmotic pressure of the original solution and to avoid diffusion, it would be necessary in principle to start with solvent and solution already satisfying equation (5). Under such circumstances an osmotic equilibrium can be established simply by the application of pressure. In practice this would be almost impossible to realize (especially if Raoult's law does not hold), since it presupposes more knowledge than is generally available.

It will now be shown that van't Hoff's equation holds for dilute solutions even with mixed solvents, providing the osmotic pressure is taken as the above-defined equilibrium pressure and providing Raoult's law applies. If a true equilibrium has been obtained, then $P_A = P_B = P$, and

$$\begin{aligned} \overline{V}_A P &= RT \ln (x'_A/x_A) \\ \overline{V}_B P &= RT \ln (x'_B/x_B) \end{aligned} \tag{8}$$

In equations (8) the x's apply to the equilibrated solution and solvent and not necessarily to the original ones. But if x_s is very small, then $(x'_A - x_A)/x_A \ll 1$ and $(x'_B - x_B)/x_B \ll 1$. Then approximately

$$\overline{V}_A P = RT \left(\frac{x'_A - x_A}{x_A} \right)$$

and

$$\overline{V}_B P = RT \left(\frac{x'_B - x_B}{x_B} \right) \tag{9}$$

But from equations (9) it can be shown that

$$(x_A \overline{V}_A + x_B \overline{V}_B) P = x_S RT \tag{10}$$

Let N_A, N_B and N_S be the total number of moles of A, B and S in a volume V of solution. Then

$$(N_A \overline{V}_A + N_B \overline{V}_B) P = N_S RT$$

or

$$(V - N_S \overline{V}_S) P = N_S RT \tag{11}$$

Neglecting $N_S \overline{V}_S$ as compared to V, there is obtained van't Hoff's equation

$$PV = N_S RT \tag{12}$$

If c equals the concentration of S in grams per unit volume, then

$$P/c = RT/M \tag{13}$$

where M is the molecular weight of the solute.

System not Subject to Raoult's Law.—If Raoult's law does not apply, then the thermodynamic treatment of osmotic pressures for mixed solvents becomes more involved. The equations become complicated because cognizance must be taken of solvent non-idealities even when the system is infinitely dilute with respect to solute. Because of this persisting non-ideality, it is not obvious that van't Hoff's equation will apply at infinite dilution.

However, if one assumes that Henry's law applies to the solute, it can be shown that van't Hoff's equation should be valid at infinite dilution regardless of the nature of the solvents as long as their vapors obey the perfect gas laws. The proof of this proposition rests upon the use of the three-component counterpart of the Duhem-Margules equation, but the details of the calculation will not be supplied here.

Discussion

The first point to be noted in connection with the use of mixed solvents is that the composition of solvent will not be the same on each side of the membrane after osmotic equilibrium is established. Starting with the same solvent ratio on both sides of the membrane, the apparent osmotic pressure (corresponding to a stationary volume) will not in general be the same as the equilibrium pressure. If the difference is appreciable, then the use of a dynamic method of measurement may lead to erroneous results. However, if the mole fraction of solute is small, the apparent osmotic pressure will be practically the same as the final pressure and the solvent composition will be substantially the same on the two sides of the membrane.

If Raoult's law holds, extrapolation of the osmotic pressure equations to infinite dilution will give van't Hoff's equation. In this event, correct molecular weights for solutes can be obtained by the usual simple means. On the other hand, if Raoult's law does not hold for the mixed solvents, extrapolation to infinite dilution of solute will not yield van't Hoff's equation unless the solute obeys Henry's law, which assumption is reasonable. Accordingly, van't Hoff's equation can always be used in practice for extrapolation purposes.

Although the use of mixed solvents introduces some doubtful points, correct results can be obtained but the measurements may be time consuming because of the necessity for diffusion taking place. Gee[2] reports no complications in connection with the use of mixed solvents; in fact he reports certain advantages. It appears that the magnitudes of the new effects discussed in this paper are small for dilute solutions. What the effect will be on the slope of a curve in which P/c is plotted against c cannot be predicted simply.

The author is indebted to Dr. R. H. Ewart of the United States Rubber Company for helpful discussion and suggestions.

Summary

The problem of osmotic pressures for solutions with mixed solvents is considered thermodynamically. It is shown that in general the measured osmotic pressure has definite significance only if the solvent compositions are different on the two sides of the membrane and subject to certain relationships. However, it is shown that van't Hoff's equation can be expected to hold for in-

finitely dilute solutions. For concentrated solutions certain complications can be expected in the experimental determination of osmotic pressures using mixed solvents, especially if a dynamic approach is employed.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Concentration Distribution in Two-Salt Moving Boundaries

BY L. G. LONGSWORTH

Introduction.—The development of the schlieren scanning technique[1] for studying the electrophoresis of proteins has, somewhat unexpectedly, provided a tool with which to investigate in detail the moving boundaries that have been used for the measurement of the transference numbers of strong electrolytes. Such boundaries, it will be recalled, are formed between two solutions of binary salts having a common ion, the salt present in the region into which the boundary moves on passage of the electric current being called the "leading" electrolyte whereas that behind the boundary is termed the "indicator" electrolyte. Boundaries of this type will be called "two-salt" boundaries in order to distinguish them from other types of moving boundaries such as protein boundaries[2] and concentration boundaries.[3]

According to the theory developed by Weber[4] the mixing effect of inter-diffusion at a two-salt boundary is balanced by a separating effect due to ion migration[5] if the mobility, u_i, of the indicator ion constituent is less than the mobility, u_l, of the leading ion constituent and if the current is passed in the appropriate direction. Under these conditions the concentration distribution in the boundary for a given current density I is independent of the time and the boundary velocity is given by the relation

$$v = IT_l/FC_l \qquad (1)$$

in which F is the faraday, T_l the transference number of the leading ion constituent and C_l is the concentration, in equivalents per milliliter, in the body of the leading solution. Whereas the concentrations of the salt solutions forming the boundary initially may be selected independently of each other, the concentration, C_i, of the column of indicator electrolyte that is formed by the advancing boundary is not independent of C_l but is given by the relation

$$C_i = C_lT_i/T_l \qquad (2)$$

in which T_i is the transference number of the indicator ion at the concentration C_i. If the boundary is formed initially between the leading solution and the indicator solution at a concentration C_i' which is different from that, C_i, required by equation (2), then, as will be demonstrated later in this paper, a concentration boundary between the indicator salt at the two concentrations C_i and C_i' remains near the initial boundary position as the two-salt boundary advances.

In addition to the requirement that $u_i < u_l$ there is the restriction that the boundary system be stable gravitationally. This means that if the indicator solution is less dense than the leading solution the latter must be underneath and the boundary must descend. If the indicator solution is more dense than the leading solution the latter must be on top and the boundary must rise. Moreover, since the densities of most salt solutions increase with increasing concentration, gravitational stability also requires that the initial indicator concentration, C_i', be equal to or greater than that, C_i, of the adjusted indicator solution for a rising boundary whereas for a descending boundary $C_i' \leq C_i$.

Under the conditions prevailing in previous work with two-salt boundaries the transition from one solution to the other occurs within less than a millimeter. Such a sharp boundary can be located accurately with the aid of relatively simple optical arrangements, advantage being taken of the difference of refractive index at the boundary, and this is sufficient for a determination of the boundary displacement and hence the transference number T_l. The optical devices previously employed have not, however, given information concerning the magnitude and distribution of the gradients in the boundary and the manner in which these vary with the current. This information can now be obtained with the aid of the schlieren scanning camera. It is the purpose of this paper to report measurements of the gradients in typical boundaries and to show that they are in agreement with Weber's theory.[4]

Experimental Results.—The patterns of Fig. 1, recorded during the electrolysis at 0.5°, of 0.1 N potassium iodate:0.1 N potassium chloride at a current density of 0.00655 amp./sq. cm., are typical of the results obtained in this research. The time interval between all of the patterns after the second was one hour. In order to avoid overlapping of the concentration boundary peak, each successive pattern has been displaced a fixed distance vertically. The line h_0 in each pattern

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(1) Longsworth, THIS JOURNAL, **61**, 529 (1939).

(2) Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

(3) Longsworth, THIS JOURNAL, **65**, 1755 (1943).

(4) H. Weber, "Die partiellen Differential-Gleichungen der mathematischen Physik," Braunschweig, 1910, 5th edition, chapter 24.

(5) MacInnes and Cowperthwaite, *Proc. Natl. Acad. Sci.*, **15**, 18 (1929).