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Pressure–Volume–Temperature Relations in Solutions. VI. The Apparent and Partial Volumes of Sodium Bromide Dissolved in Glycol and the Energy–Volume Coefficients of the Solutions at Various Pressures and Temperatures

BY R. E. GIBSON AND O. H. LOEFFLER

In aqueous solutions of electrolytes the volume changes on mixing, which may be expressed conveniently in terms of the apparent volumes of the solutes, are the results of several effects which are of coördinate importance. It has been suggested[1] that a study of the effect of temperature on the apparent volumes of substances in solution when the total volume of the solution is kept constant may facilitate the separation of the volume changes on mixing that arise from longer-range forces, *e. g.*, ion–ion, ion–dipole interactions, from those arising from short-range forces, *e. g.*, repulsive forces or those forces that cause the molecules to pack together in a structure of low coördination number in water and ice. Results obtained in this Laboratory show the apparent volumes of salts dissolved in water increase quite rapidly with temperature at constant volume, indicating that a considerable fraction of the volume change on mixing arises from short-range interactions, characteristic of the solvent. In order to obtain experimental confirmation of the hypothesis that the changes with temperature at constant volume in the apparent volumes of salts dissolved in water arise from the peculiar nature of water itself, we have examined the behavior of sodium bromide–glycol solutions, since we have already shown from thermodynamic data that the peculiar behavior observed in water is very much less pronounced in glycol[2,3] and its solutions. Indeed, we have already emphasized the value of glycol solutions as models in the consideration of aqueous solutions.[2,3]

In this paper we shall give the results of determinations of the specific volumes of a series of solutions of sodium bromide in glycol at 25°, the thermal expansions of the solutions from 25° to various temperatures up to 105°, and the compressions of the solutions to different pressures up to 1000 bars at 25, 45, 65, 85, and 105°. From these data various thermodynamic properties of the solutions, including those mentioned in the title, have been computed and will be discussed.

Experimental Results

Sodium bromide[1] and glycol[4] were purified by methods already described, and each solution was made up independently from weighed amounts of the components. We have already published accounts of the technique for measuring the specific volumes at 25°,[1] the thermal expansions,[5] and the compressions.[3] The same apparatus and procedure were used in this work, the only new feature being the fact that the highest temperature reached was 105° instead of

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[1] R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **63**, 443 (1941).

[2] R. E. Gibson and O. H. Loeffler, *ibid.*, **63**, 898 (1941).

[3] R. E. Gibson, *ibid.*, **59**, 1521 (1937).

[4] R. E. Gibson and John F. Kincaid, *ibid.*, **59**, 579 (1937).

[5] R. E. Gibson and O. H. Loeffler, *ibid.*, **61**, 2515 (1939).

85°. As before, all the results for the specific volumes and the thermal expansions at 1 bar are based on the specific volumes of water[6] and mercury[7] given in the "International Critical Tables." The compression results are also based on the same constants as those we have already published.[2]

Specific Volumes and Thermal Expansions at Atmospheric Pressure.—Table I gives the coefficients in equation (1) which represents quite adequately the specific volumes of the different solutions as functions of temperature at atmospheric pressure.

TABLE I

COEFFICIENTS IN EQUATION (1) EXPRESSING THE SPECIFIC VOLUMES OF SOLUTIONS OF SODIUM BROMIDE IN GLYCOL AS FUNCTIONS OF TEMPERATURE

$100\ x_2$	v_{65}	$10^4\ a_1$	$10^7\ b_1$	$10^9\ c_1$
0.000	0.92484_8	6.279_6	9.24_4	3.05_7
4.987	$.89223_5$	5.783_5	7.18_6	2.29_5
10.018	$.86012_8$	5.350_9	5.53_4	1.92_3
14.951	$.82912_7$	4.9707	4.16_1	1.63_4
20.117	$.79704_6$	4.605_2	2.98_6	1.46_0

$$v = v_{65} + a_1(t - 65) + b_1(t - 65)^2 + c_1(t - 65)^3 \quad (1)$$

Curves showing the differences between the observed specific volumes and those computed by equation (1) are given in Fig. 1.

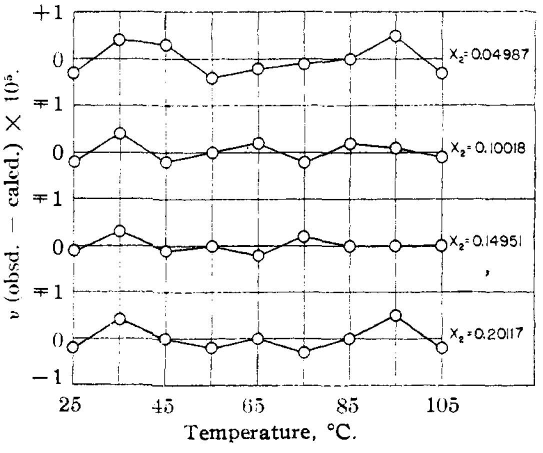

Fig. 1.—Differences between the specific volumes of sodium bromide–glycol solutions as observed at different temperatures and as computed from the expansion equation (1).

The apparent volumes, computed from the relation[8]

$$x_2\phi_2 = v - x_1v_1^0 \quad (2)$$

were represented as functions of concentration by equation (3) with the coefficients given in Table II.

$$\phi_2 = a + bx_2^{1/2} + cx_2^{3/2} \quad (3)$$

TABLE II

COEFFICIENTS IN EQUATION (3) EXPRESSING THE APPARENT VOLUMES OF SODIUM BROMIDE IN GLYCOL AS FUNCTIONS OF THE CONCENTRATION EXPRESSED AS WEIGHT FRACTION OF SALT. THE LAST COLUMN GIVES THE APPARENT MOLAL VOLUME IN INFINITE DILUTION

t	a	b	c	Φ_2^*
25	0.26733	0.06218	−0.007	27.5_1
45	.26080	.07393	− .013	26.8_4
65	.25119	.08904	− .017	25.8_5
85	.23831	.10777	− .023	24.5_3
105	.22164	.12962	− .024	22.8_1

At 25° this equation fits our data, and the data obtained some years ago[4] as well as the equation we published at that time, and gives a much better fit at the higher temperatures. Indeed, from 0 to 20% the deviations are within the experimental error, but at 25% a deviation of 5 × 10^{-5} is found. The specific volumes of sodium bromide–glycol solutions given here agree with our previous results within 3 in the fifth decimal place. The partial volumes were computed from these data by the equation given in a previous paper.[9]

The compressions at different temperatures were measured from atmospheric pressure to 500 and 1000 bars, in a few cases to 250 and to 750 bars, and the corrections described in our last paper[2] were applied. The results were expressed by the Tait equation (eq. 4)

$$k = C \log [(B' + P)/(B' + P_0)] \quad (4)$$

with the coefficients[10] given in Table III. Deviations are plotted in Fig. 2. The constant C was taken as independent of temperature and of the concentration of the solution, and with this assumption the constant B' was computed for each solution at each temperature. This procedure differs somewhat from that which we have fol-

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(6) "International Critical Tables," Vol. III, p. 24.

(7) *Ibid.*, Vol. II, p. 548.

(8) The symbols used in this paper are as follows. The subscripts 1 and 2 refer to glycol and salt, respectively, in the solution, the superscript 0 indicates the pure component in the stable state under the experimental conditions. The weight and mole fractions are given by x and X, respectively; v and V are specific and molal volumes in milliliters, without subscripts they refer to the solution, with subscripts they denote partial quantities. The apparent volume and the apparent molal volume are denoted by ϕ and Φ, respectively. m is the concentration in moles per 1000 g. of solvent, t is the centigrade and T the absolute temperature. Δp means the increase with pressure of the quantity to which it is prefixed. $k = -\Delta_P v/v_{P=0}$. The superscript * refers to a property of the solute in an infinitely dilute solution. P is the pressure in bars. E is the total energy $r_2 = x_2/x_1$.

(9) Ref. 1, eq. 11.

(10) To avoid ambiguity the constant B will be called B' when it refers to a solution and B_0 when it refers to the pure solvent.

TABLE III

CONSTANTS IN THE TAIT EQUATION (EQUATION 4) FOR SOLUTIONS OF SODIUM BROMIDE IN GLYCOL. $C = 0.21763$

B' in kilobars

t	$100\,x_2 = 0.00$ $100\,X_2 = 0.00$	4.987 3.068	10.018 6.290	14.951 9.582	20.117 13.182
25	2.544	2.652	2.759	2.861	2.977
45	2.363	2.472	2.578	2.682	2.798
65	2.186	2.298	2.402	2.508	2.624
85	2.011	2.123	2.232	2.339	2.456
105	1.840	1.954	2.066	2.175	2.293

lowed with aqueous solutions.[11] From the compressions we computed the apparent compressions $\Delta_P\phi_2$ for sodium bromide in the different solutions under different conditions by equations analogous to equation (2). For the pressure intervals 1 to 500 bars and 1 to 1000 bars, $\Delta_P\phi_2$ was expressed as a function of concentration by equation (5)

$$10^3\Delta_P\phi_2 = a_2 + b_2x_2^{1/2} \qquad (5)$$

the coefficients being given in Table IV. The deviations were negligible. From this equation $\Delta_P v_2$ could be computed by well-known methods. It may be noted that $\Delta_P\phi_2$ and $\Delta_P v_2$ are always positive.

TABLE IV

CONSTANTS IN EQUATION (5) FOR EXPRESSING THE APPARENT COMPRESSIONS OF SODIUM BROMIDE IN GLYCOL AT 500 AND 1000 BARS AS FUNCTIONS OF CONCENTRATION

	500 bars		1000 bars	
t	a_2	$-b_2$	a_2	$-b_2$
25	8.5	10.3	14.3	18.5
45	10.7	13.1	17.4	21.6
65	13.5	16.4	21.7	26.5
85	17.1	20.5	27.5	33.1
105	22.0	26.2	35.5	43.1

By means of equations (1), (3), (4), and (5) it was possible to compute tables of the specific volumes of the solutions and the apparent volumes and partial volumes of the components at any temperature, pressure and concentration within our experimental range, and by equations derived from equations (1) and (4) the thermal expansibilities and the compressibilities were also calculated. The expansion coefficients $(\partial v/\partial T)_P$ at pressures above atmospheric were computed from $(\partial v/\partial T)_P$ at atmospheric pressure, and the constants in the Tait equation by a relation we have already published.[5] Use of this relation required a knowledge of $(\mathrm{d}B'/\mathrm{d}T)$ which was obtained from equations of the form

$$B' = B'_{25} + a_3(t - 25) + b_3(t - 25)^2 \qquad (6)$$

The coefficients in this equation are given in Table V. The thermodynamic coefficients $(\partial P/\partial T)_V$, $(\partial E/\partial V)_T$, $(C_P - C_V)$ were then computed by means of well-known relations.[12]

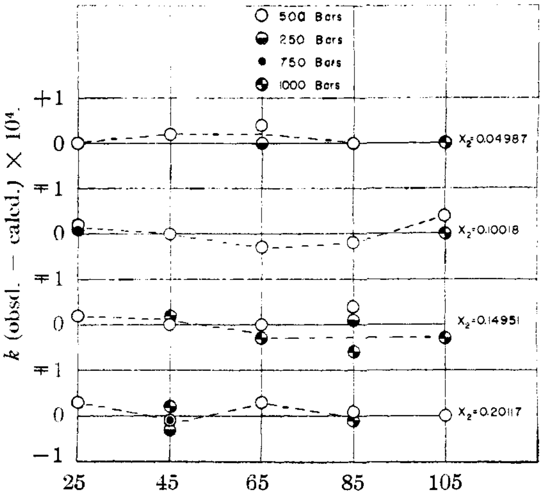

Fig. 2.—Deviation curves giving the fit of equation (4) for the compressions of the solutions at different temperatures. The 1000 bar observations used for the determination of B at each temperature are not shown on the diagram.

TABLE V

COEFFICIENTS IN EQUATION 6 EXPRESSING B' AS A FUNCTION OF TEMPERATURE FOR VARIOUS SOLUTIONS

$100\,x_2$	B'_{25}	$-10^3\,a_3$	$10^6\,b_3$
4.987	2.652	9.09	4.6
10.018	2.759	9.18	6.7
14.951	2.861	9.05	5.9
20.117	2.977	9.11	7.1

In Fig. 5 $(\partial E/\partial V)_T$ is shown as a function of concentration at different pressures and temperatures, and in Fig. 6 as a function of the volume.

Discussion of Results

Compressibility of the Solutions and the Term $(B' + P)$ in the Tait Equation.—In former discussions[13] we have applied Tammann's hypothesis that a dissolved salt acts on water in aqueous solutions in the same way as the application of a given external pressure, called the effective pressure, with considerable success to the calculation of the compressibilities of the solutions at 25° from a knowledge of the behavior of water at

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(11) R. E. Gibson, THIS JOURNAL, **56**, 865 (1934).

(12) The numerical results of these computations will not be published here, but tables giving the specific volumes, apparent volumes, compressions, compressibilities, thermal expansibilities, pressure–temperature coefficients, energy–volume coefficients, $(C_P - C_V)$, may be obtained from the American Documentation Institute, 2101 Constitution Avenue, Washington, D. C., in forms described under the Notice to Authors of Papers at the beginning of this issue of the Journal.

(13) R. E. Gibson, THIS JOURNAL, **56**, 4, 865 (1934); **57**, 284 (1935).

that temperature. We were, however, well aware of the limitations of this treatment and have pointed out that the hypothesis breaks down entirely when an attempt is made to estimate the thermal expansibilities from a knowledge of the effective pressures of the solutions and the influence of pressure on the thermal expansions of water.[14] In this paper we treat each glycol solution as a separate liquid in a series for which C is constant and calculate $(B' + P)$ for each solution by equation (4). This procedure differs from that used for water solutions but is quite as logical and avoids troublesome assumptions concerning the compressibility of the salt in the solution. It is based on the observation that in all the liquids that we have studied, except water, the constant C is very close to 0.215 and is the same in closely related liquids such as a series of benzene derivatives, even though the values of B' may vary by a factor of two, *cf.* benzene and aniline.[15] If B_0 is the value of B' for pure glycol, then at any temperature $B' - B_0$ corresponds to the effective pressure P_e in our earlier papers.[16] It will be seen from Table III that $B' - B_0$ for any concentration is very nearly independent of temperature, and, indeed, the compressibilities of the solutions at any temperature may be computed with good approximation from B_0 at that temperature, C, which is constant and $(B' - B_0)$ at 25°. However, the slight change in $(B' - B_0)$ with temperature may be real, and we have computed $(B' - B_0)$ as a function of r_2 by the relation

$$(B' - B_0) = a'r_2 + b'r_2^{3/2} \qquad (7)$$

The coefficients of this equation are given in Table VI.

TABLE VI

COEFFICIENTS IN EQUATION (7) EXPRESSING $(B' - B_0)$ AS A FUNCTION OF THE WEIGHT RATIO OF SALT AT DIFFERENT TEMPERATURES

t	a'	$-b'$
25	2.328	1.212
45	2.336	1.212
65	2.338	1.194
85	2.417	1.296
105	2.488	1.374

The Thermal Expansibilities and the Term $(B' + P)$ in the Tait Equation

The coefficients of thermal expansion of glycol at different pressures and temperatures may be expressed as linear functions of $1/(B_0 + P)$ over the whole range that we have studied. For example, the relation $(\partial \ln v/\partial T)_P = 2.86 + [8.63/(B_0 + P)]$ represents the data for $(\partial \ln v/\partial T)_P$ within experimental error except at 25° where the departures do not exceed 2% of $(\partial \ln v/\partial T)_P$. This relation is convenient for interpolation purposes but must be regarded as fortuitous, because in "normal" liquids such as carbon tetrachloride[2] or benzene and its derivatives[5] $(\partial \ln v/\partial T)_P$ varies linearly with $1/(B_0 + P)$ as the pressure changes at any one temperature, but the lines for the different temperatures do not coincide as they do in glycol.

An even more striking empirical relation is shown in Fig. 3 where the expansion coefficient $(\partial v/\partial T)_P$ for glycol is plotted against $1/(B_0 + P)$, which is equal to $(x_1v_1^0/v)[1/(B + P_e + P)]$. The points for all temperatures and pressures lie approximately on the same straight line, the maximum discrepancy being less than 2% of $(\partial v/\partial T)_P$. On the same diagram $(1/x_1)(\partial v/\partial T)_P - (x_2/x_1)(\partial v_2^0/\partial T)$, which represents the thermal expansion of the amount of solution containing 1 g. of glycol minus a contribution due to the salt in this mass of solution, is plotted against $1/(B' + P)$ for the solution. For sodium bromide $(\partial v_2^0/\partial T)$ was taken arbitrarily as 0.56×10^{-4} cc. per gram per degree, which is somewhat higher than the coefficient of expansion of crystalline sodium bromide, *viz.*, 0.3×10^{-4}. The points for all the solutions fall on the straight line for pure glycol except for the higher concentrations at 25 and 45°. Even at these temperatures, however, the greatest discrepancy does not exceed 5% of $(1/x_1)(\partial v/\partial T)_P - (x_2/x_1)(\partial v_2^0/\partial T)_P$. Figure 3 shows that the thermal expansion coefficient of glycol either in the pure state or in solution with sodium bromide may be com-

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(14) R. E. Gibson, THIS JOURNAL, **59**, 1521 (1937); *Sci. Monthly*, **46**, 103 (1938).

(15) R. E. Gibson and O. H. Loeffler, *J. Phys. Chem.*, **43**, 207 (1939).

(16) The equation used for computing $(B + P_e)$ may be written in the form

$$k = C\frac{x_1v_1^0}{v}\log\frac{B + P_e + P}{B + P_e} - \frac{x_2}{v}\Delta_P v_2^0$$

Comparison of the derivatives of this equation with those of equation (4) shows that

$$(B' + P) = \frac{v}{x_1v_1^0}(B + P_e + P)$$

if the small correction term $(x_2/v)\Delta_P v_2^0$ is neglected. The equation using $(B + P_e)$ tacitly assumes that the specific compressions of the components are additive in ideal solutions, whereas the equation using B' does not. This assumption may not be strictly true, but it is a sufficiently good approximation to warrant its application to the consideration of the properties of the solvent in solutions of electrolytes.

It should be remarked that the equation with $(B + P_e)$ and the equation with B' both represent the compression data for the solutions equally well, and no choice between them can be made on empirical grounds.

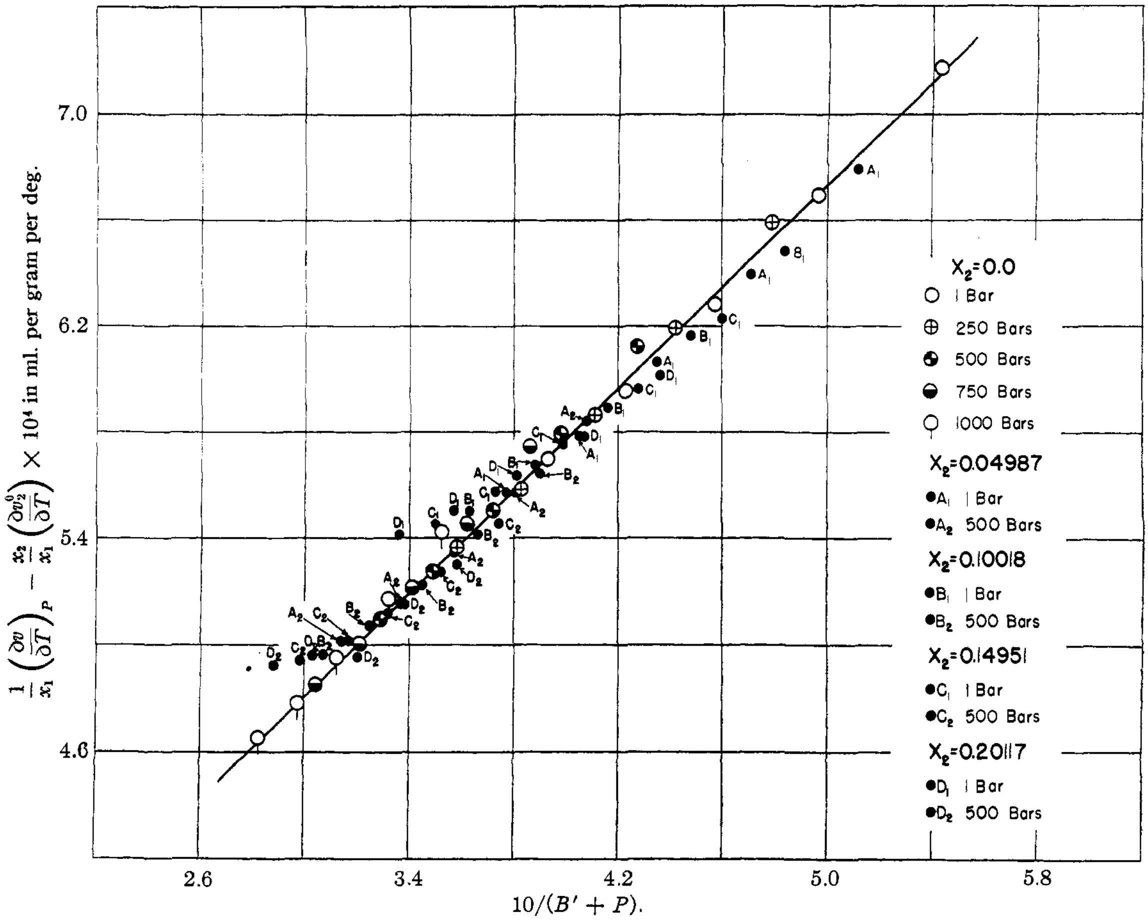

Fig. 3.—The thermal expansibilities of glycol and solutions of sodium bromide in glycol at different pressures and temperatures as functions of $1/(B' + P)$.

puted from a knowledge of $(B_0 + P)$ at any pressure or temperature in the range studied, but in view of the fact that the relation between $(\partial v/\partial T)_P$ and $(B_0 + P)$ is so much simpler than that found with liquids such as carbon tetrachloride, we consider it unwise at present to extend any conclusions from this observation beyond glycol solutions.

Apparent Volumes and Volume Changes on Mixing

The apparent volume ϕ_2 of sodium bromide in glycol solutions decreases with rise of temperature at constant pressure and increases with rise of pressure at constant temperature. When, however, both pressure and temperature are varied in such a way that the total volume of the solution is kept constant, ϕ_2 does not change significantly; in other words, ϕ_2 is independent of temperature at constant, volume, a feature in which the behavior of glycol solutions is much simpler than that of water solutions. This result is illustrated in Fig. 4, where the apparent volumes are plotted against the specific volumes of the solutions at different pressures and temperatures, and where it will be seen that all the points for any given solution fall on the same curve. A curve for the infinitely dilute solution where the partial and the apparent volumes are identical is included in this diagram. The contraction in volume which occurs when an amount of solution containing 1 g. of salt is formed from the solid salt and glycol is measured by $(v_2^0 - \phi_2)$. From the thermal expansibility[17] and the compressibility[18] of solid sodium bromide we computed $(v_2^0 - \phi_2)$ at different temperatures and pressures and found it also to be independent of temperature at constant volume. The partial volumes of sodium bromide in the different solutions at various pressures and temperatures were

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[17] G. P. Baxter and C. C. Wallace, THIS JOURNAL, **38**, 78 (1916).

[18] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **67**, 370 (1932).

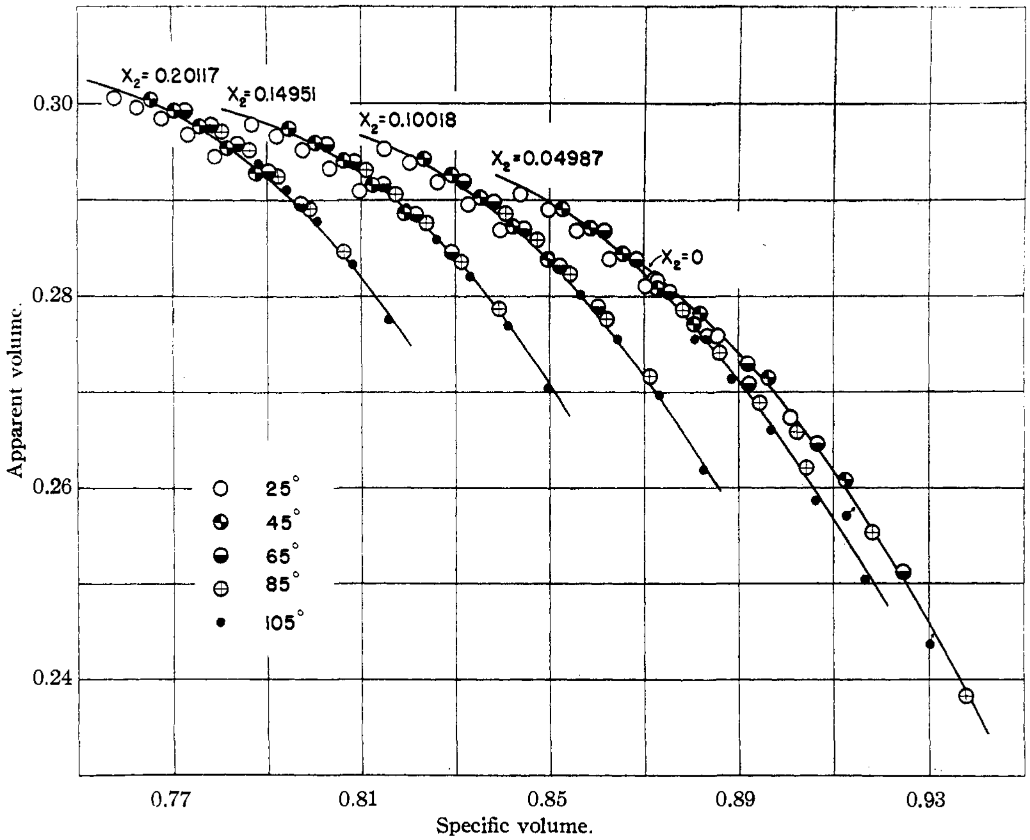

Fig. 4.—The apparent volumes of sodium bromide in glycol at different pressures and temperatures as functions of the specific volumes of the solutions. Note that all points for each solution lie essentially on one curve.

also found to be independent of temperature at constant volume. This experimental result, that the apparent volume of sodium bromide in glycol is solely a function of the volume of the solution, seems to be one of considerable significance and indicates that when an electrolyte dissolves in a liquid whose molecular distribution is not sensitive to changes in total volume, the contraction on mixing depends solely on the potentials of the average long-range forces which are fixed when the mean distance between the molecules is fixed.

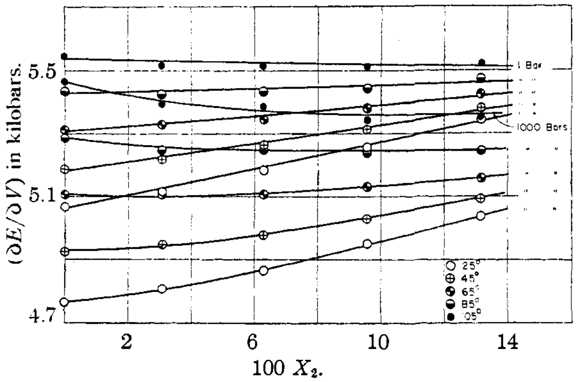

Fig. 5.—The energy–volume coefficients of solutions of sodium bromide in glycol at different temperatures and pressures as functions of the mole fraction of salt.

The Energy–Volume Coefficients of the Solutions

From the definition given in equation (2) we see that, if the apparent volume is independent of the temperature at constant specific volume, $(\partial P/\partial T)_V$ must be the same for the solution as for the pure solvent, in other words, $(\partial E/\partial V)_T$ must be independent of concentration at any given pressure and temperature. In Fig. 5 the energy–volume coefficients of different solutions of sodium bromide in glycol are plotted against the mole fraction of salt for various temperatures at 1 and 1000 bars. Above 45° $(\partial E/\partial V)_T$ is practically independent of concentration, and even at lower temperatures it varies only about 6% over the concentration range from pure glycol to 15 mole per cent. of sodium bromide.

The observed energy–volume coefficient $(\partial E/\partial V)_T$ may be regarded[2] as the sum of a re-

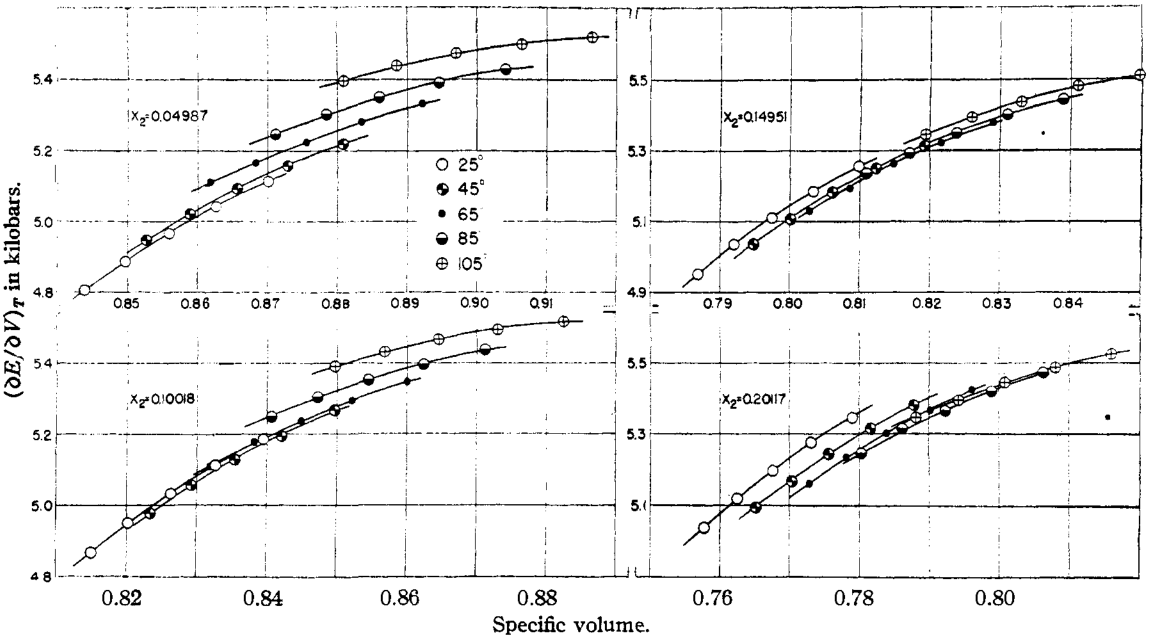

Fig. 6.—The energy–volume coefficients of solutions of sodium bromide in glycol as functions of the specific volumes Note the change in the relative positions of the curves for the various temperatures as the concentration of salt increases.

pulsive component $(\partial E_R/\partial V)_T$ and an attractive component $(\partial E_A/\partial V)_T$, and $(\partial E_R/\partial V)_T$ has been tentatively identified[5] with $(B + P)$ which we have seen rises considerably with concentration at a given pressure and temperature. Since $(\partial E_R/\partial V)_T$ and $(\partial E_A/\partial V)_T$ have opposite signs, it will be seen that both components of $(\partial E/\partial V)_T$ change numerically by the same amount when salt is added to glycol at constant pressure and temperature. In other words, the solution assumes an equilibrium volume in which the changes in the attractive and repulsive components of $(\partial E/\partial V)_T$ just balance each other. The energy–volume coefficients of the different solutions are plotted against their specific volumes in Fig. 6. It will be noticed that there is a transition from the water type of diagram ($(\partial E/\partial V)_T$ increasing with temperature at constant volume) to the normal type of diagram ($(\partial E/\partial V)_T$ decreasing with temperature at constant volume) as the concentration of sodium bromide increases. We have used the specific volumes of the solutions as abscissas, but there is little significance in a comparison of $(\partial E/\partial V)_T$ for the various solutions at the same specific volume. Indeed, one of our difficulties in extending the treatment of pure liquids to solutions, where the composition may vary, arises from the lack of a logical volume basis for use in comparison of their properties.

Comparison of ϕ_2^* for Sodium Bromide in Glyco and in Water

In Fig. 7 we have plotted ϕ_2^* for sodium bromide in water and in glycol as functions of temperature at atmospheric pressure. It will be

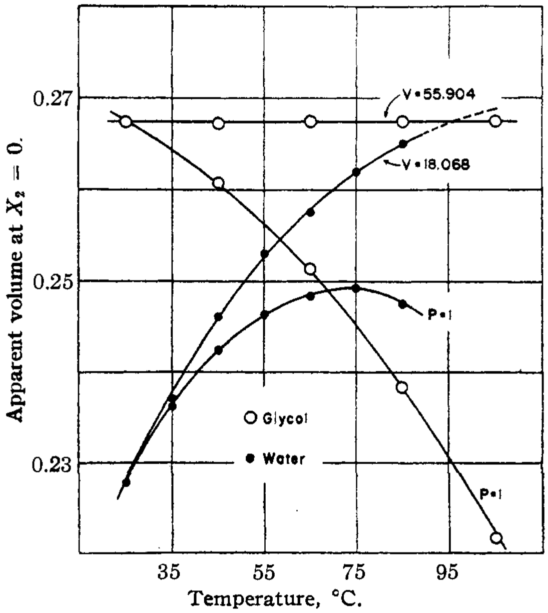

Fig. 7.—A comparison of the temperature variations of the apparent volumes of sodium bromide in infinite dilution in water and in glycol at constant pressure and at constant volume.

seen that ϕ_2^* (glycol) is much greater than ϕ_2^* (water) at 25°, but that the difference diminishes rapidly, and at 85° ϕ_2^* (water) is actually larger than ϕ_2^* (glycol). It is of interest to note that the compressibility of water is greater than that of glycol at 25° but less at 85°. On the same diagram we also give ϕ_2^* (water) and ϕ_2^* (glycol) as functions of the temperature at constant volume (the volumes of the pure liquids at 25° and 1 bar pressure). As we have already observed, ϕ_2^* (glycol) is practically independent of temperature at constant volume. ϕ_2^* (water), however, rises rapidly with temperature and appears to come to a constant value (or a maximum on the curve) which is slightly higher than ϕ_2^* (glycol). Since it is highly probable that the increase of ϕ_2^* (water) with temperature at constant volume is due to changes in molecular distribution in the water, it seems reasonable to conclude that when the disturbing effects of distribution changes are reduced by rise of temperature, sodium bromide has approximately the same apparent volume in water and in glycol and that, if anything, the electrostrictive effect is slightly larger in glycol than in water.

In Fig. 8 we have plotted the same type of diagram for 9.58 mole per cent. solutions of sodium bromide in water and in glycol. The results are essentially the same as in the infinitely dilute solutions and suggest that uncertainties introduced by the extrapolations to infinite dilution have not played an important part in the features of Fig. 7 that we have just discussed.

The apparent molal expansibilities $(\partial\Phi_2/\partial T)_P$ of sodium bromide in glycol are plotted against the square root of the molality in Fig. 9. This diagram may be compared with the similar one for sodium bromide in water.[19] In glycol the apparent molal expansibility of sodium bromide is always negative, becomes increasingly so as the temperature rises, and increases with concentration. At all temperatures and concentrations $(\partial\Phi_2/\partial T)_P$ for sodium bromide is less in glycol than in aqueous solutions.

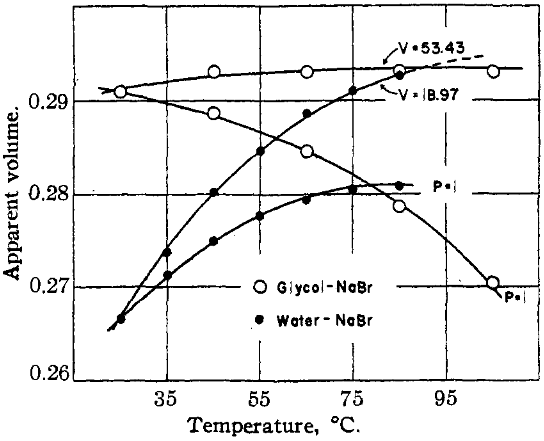

Fig. 8.—A comparison of the temperature variations of the apparent volumes of sodium bromide in 9.58 mole per cent. solutions in water and in glycol at constant pressure and at constant volume.

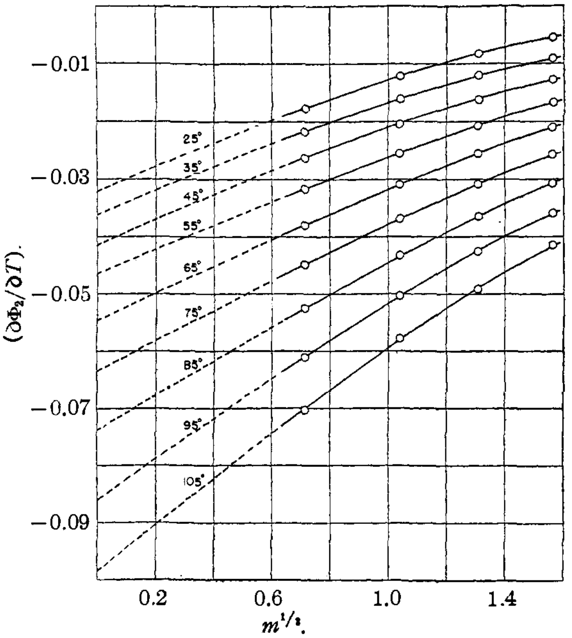

Fig. 9.—The apparent molal expansibilities $(\partial\Phi_2/\partial T)_P$ of sodium bromide in glycol solutions as functions of concentration at different temperatures.

Summary

From new measurements of the specific volumes at 25°, the thermal expansions and the compressions, we have compiled a table of volumes of a series of solutions of sodium bromide in ethylene glycol at different pressures, temperatures and concentrations. The ranges covered are 25 to 105°, 1 to 1000 bars and zero to 20% sodium bromide. With the aid of suitable empirical equations we have computed first and second derivatives from the above table and hence obtained the thermal expansibilities, the compressibilities, the pressure–temperature and the energy–volume coefficients and $(C_P - C_V)$ for the solutions and the apparent and partial volumes, compressibilities and thermal expansibilities of sodium bromide in the solutions.

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(19) Ref. 1, Fig. 5.

The energy–volume coefficients are approximately independent of concentration in the range of pressure and temperature we have studied. The apparent volumes of sodium bromide in glycol are independent of temperature at constant volume of the solution, and are compared with the corresponding quantities in aqueous solution.

The thermal expansibilities of ethylene glycol both in the pure state and in solution at different pressures and temperatures are representable by a single linear function of $1/(B + P)$, a quantity which is obtained directly from the compressibilities of the solutions.

WASHINGTON, D. C. RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE CLEVELAND CLINIC AND WESTERN RESERVE UNIVERSITY]

Electrometric and Conductometric Studies of the Neutralization Reactions of Phosphoric Acid. The Neutralization of Very Dilute Solutions of Phosphoric Acid with Sodium Hydroxide

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The first conductometric study of the titration reaction between phosphoric acid and sodium hydroxide was made by Daniel Berthelot,[1c] who recorded data obtained by constant volume titrations of 0.5, 0.1 and 0.01 molar phosphoric acid solutions. His method involved the addition of the desired amount of titer to a given volume of acid and the dilution of the resulting solution to a standard volume. The conductivity of the diluted solution was then measured.

In discussing his results, it is convenient arbitrarily to divide the titration curve into four parts. The portion of the curve which lies between the abscissa values of 0 and 1.0 equivalent of base added will be referred to as the first branch of the curve; the portion between 1.0 and 2.0 equivalents of base added, as the second portion of the curve; the section between 2.0 and 3.0 equivalents of base added, as the third branch of the curve; and the portion of the curve beyond this point, as the fourth branch of the curve.

Using this notation, we found that in the most concentrated solution which Berthelot used, the first branch of the curve was not investigated, the second was reported as being straight, the third as being curved and blending into the fourth. On increasing the dilution to 0.1 molar, Berthelot found that the third end-point could just be detected. On going to 0.01 molar he reported that both the first and the second branches were straight and that the third end-point had disappeared.

Further investigations by Kusters, Grüters and Geible,[2] by Schmidt,[3] by Thiele and Roemer,[4] and by Kolthoff,[5] clearly indicate the existence of a tendency of the various branches of the curve to approach linearity with increasing degrees of dilution.

More recently the literature has been reviewed by Lanzing and van der Wolk,[6] who at the same time presented data obtained from a series of eight titrations in an attempt to evaluate the results obtained by previous workers. By the use of their data, they confirmed the fact that neither the second nor the third stoichiometric point could be determined accurately by conductometric methods.

The first electrometric investigation of this neutralization reaction was carried out by Bovie[7] and hence involved the use of the direct reading potentiometer of his own design. Although it was indicated by this work that the first and second inflection points corresponded exactly to the first and second stoichiometric points, respectively, a later investigation by Davis, Oakes and Salisbury[8] showed that this was not quantitatively true when they titrated 0.0771 *M* phosphoric acid with 0.2 normal sodium hydroxide. However, they did show that in the titration of

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