[Contribution from the Geophysical Laboratory, Carnegie Institution of Washington]

Pressure–Volume–Temperature Relations in Solutions. IV. The Apparent Volumes and Thermal Expansibilities of Sodium Chloride and Sodium Bromide in Aqueous Solutions between 25 and 95°

By R. E. Gibson and O. H. Loeffler

We have indicated in earlier papers of this series[1] that interesting information about liquids and liquid solutions may be obtained from an analysis of the effect of temperature changes at constant volume on certain thermodynamic properties of the liquids, notably the coefficient $(\partial E/\partial V)_T$. In order to apply this type of investigation to aqueous solutions we found it necessary to measure the specific volumes of a number of solutions at different temperatures because reliable data, especially above 50°, were not available. The results in themselves have considerable bearing on the theory of aqueous solutions, and in this paper we shall present the data and discuss some deductions that may be drawn from them.

Experimental

The solutions of *sodium chloride* and *sodium bromide* were made up from weighed amounts of boiled distilled water and J. T. Baker c. p. Analyzed chemicals. Large amounts of the solutions (approx. 1 liter) were needed for the expansion and compression experiments, and the weighings were made on a rough balance. The specific volumes of the stock solutions were measured in U-tube pycnometers at 25°, and from known specific volume–concentration relations the exact concentrations were computed. For the sodium chloride solutions the density–concentration equation given by Hall was used.[2]

The establishment of a specific volume–concentration relation for the sodium bromide solutions was more difficult because the values found in the literature[3] did not agree with each other very well. Accordingly we made measurements of the specific volumes at 25° of two series of sodium bromide solutions prepared from accurately weighed amounts of salt and water. Series 1, studied in 1938, gave specific volumes that were consistently lower than did series 2, examined in 1940, and the discrepancy became larger in the more concentrated solutions, reaching a value of 1×10^{-4} in the 45% solutions. Entirely different samples of salt were used for each series. The presence of small amounts of chloride (approximately the amounts indicated on the labels by the manufacturers) appeared to be the cause of this discrepancy and led us to believe that specific volumes of both series were too high. This impurity may not be removed by ordinary recrystallization. The solid phase, either hydrated or anhydrous, which separates from a solution containing large amounts of sodium bromide and small amounts of sodium chloride is richer in chloride than the solution.[4] Indeed, we found that the specific volume of a 45% aqueous solution of sodium bromide always increased with continued recrystallization of the salt (approximately 3×10^{-4} after four recrystallizations) from water. Fractional crystallization of the salt from anhydrous methanol[5] did not improve matters. By evaporating solutions of either Baker c. p. Analyzed or Merck Reagent sodium bromide to dryness with large excess of hydrobromic acid three times, we obtained a sample of salt which remained unchanged by repeated recrystallizations from water. The specific volumes of 45% solutions of various samples of sodium bromide prepared in this way were constant within $\pm 1 \times 10^{-5}$, and were taken as standard. By comparison of the specific volumes of the most concentrated solutions of series 1 and 2 with these standard values, we were able to apply corrections for the impurity of the salt. The results are represented by equation (4), with the coefficients given in the first row of Table IV, and a deviation curve shown in Fig. 1, which shows that the agreement between the corrected results for the two series is satisfactory. The deviations between the specific volumes at 25° given by the other investigators[3] and those computed from equation (4) are given for comparison in Fig. 1. The concentrations of the stock solutions of sodium bromide were computed from their specific volumes with the help of this equation and the smoothed deviation curve.

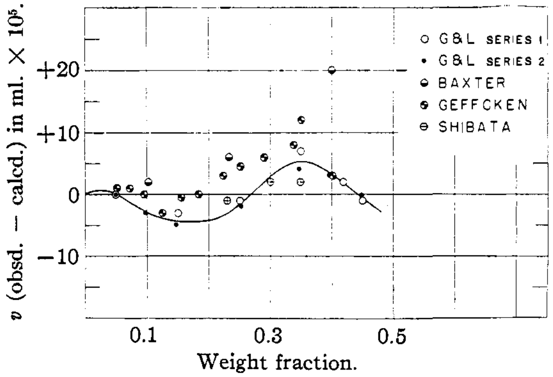

Fig. 1.—Differences between the observed specific volumes of sodium bromide solutions at 25° and those computed from equation (4).

We were able to avoid all troubles arising from the evolution of air at the higher temperatures by storing the

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[1] R. E. Gibson and O. H. Loeffler, This Journal, **61**, (a) 2515, (b) 2877 (1939).

[2] R. E. Hall, *J. Wash. Acad. Sci.*, **14**, 172 (1924).

[3] W. Geffcken, A. Kruis and L. Solana, *Z. physik. Chem.*, **B35**, 347 (1937); G. P. Baxter and C. C. Wallace, This Journal, **38**, 70 (1916); Z. Shibata and P. Holeman, *Z. physik. Chem.*, **B13**, 347 (1931).

[4] H. E. Boeke, *Z. Krist.*, **45**, 360 (1908).

[5] A. V. Rakovskii and V. V. Polyanskii, *Trans. Inst. Pure Chem. Reagents* (U. S. S. R.), **6**, 5 (1927).

solutions in evacuated flasks and by warming them to 60–70° immediately before use.

The specific volumes of the solutions were determined at 10° intervals between 25 and 95° in a weight dilatometer made of vitreous silica. This apparatus, together with the auxiliary equipment and technique, has been described in the second paper of this series.[1a] The main readings were made with rising temperature, but one or two check readings were always made while the temperature was being lowered from the highest value to 25°. These checks showed that the results were not vitiated by leakage, by the formation of air bubbles, or by hysteresis in the vitreous silica. In each experiment the mass of solution in the dilatometer was determined carefully. After each run the temperature was brought to 25.00 ± 0.01° and the mercury in the dilatometer was removed and weighed. From these data the specific volume of the solution at 25° was computed and this determination always checked the original measurement in the U-tube pycnometer within 1 in the fifth decimal place.

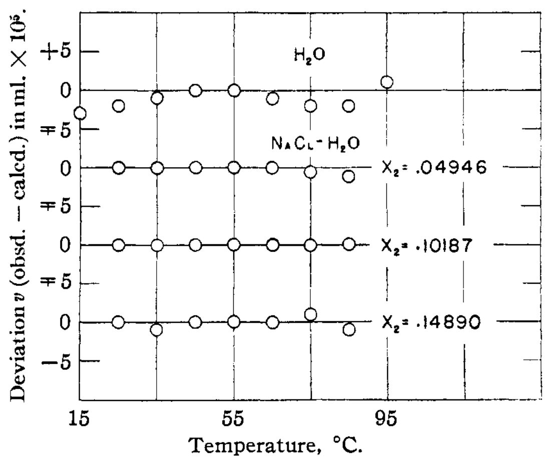

Fig. 2.—Differences between the specific volumes of water and sodium chloride solutions as observed at different temperatures and as computed from the expansion equations (1) and (2).

Results

Specific Volumes as Functions of Temperature.—We used the values of the specific volumes of water at different temperatures given in the "International Critical Tables"[6] in calibrating our dilatometer, and we must emphasize that all the results for solutions given in this and in succeeding papers are based on these specific volumes of water. By a simple recalculation our results may be made to conform with other specific volume data for water such as those of Smith and Keyes,[7] but we do not consider that sufficient new experimental data have been obtained to warrant a departure from the older values. The computations of Tilton and Taylor[8] show the consistency of the older data and indicate that more refined interpolations change the values in the "Critical Tables" by only two or three in the sixth decimal place in the range 0 to 40°, whereas the data of Smith and Keyes differ from the "Critical Tables" by as much as two hundred and thirty in the sixth decimal place in the same temperature interval.

In order to express the volumes of water and dilute aqueous solutions as functions of the temperature, we have used an equation proposed by Ipatov,[9] which fits the data over the range 15–95° more closely and is slightly simpler in form than the equations used by Thiesen and others.[8] Ipatov's equation[10] for water is

$$\log v = \frac{(t - 3.98)^2}{244{,}860 + 15{,}040(t - 3.98)^{0.62}} \qquad (1)$$

and it reproduces the specific volumes of water as given in the "Critical Tables" within the small errors indicated by the deviation curve in Fig. 2. For a number of the sodium chloride solutions we used equation (2), a form of Ipatov's equation modified to facilitate the computations. The coefficients appropriate to the various solutions are presented in Table I

$$\log 10v = \frac{t^2 + C'}{A' + B't^n} \qquad (2)$$

and the residuals are given by the deviation curves in Fig. 2. For most of the solutions, however, simple cubic equations of the form

$$v = v_{55} + A(t - 55) + B(t - 55)^2 + C(t - 55)^3 \qquad (3)$$

when fitted to the data by the method of least squares gave a representation which was quite satisfactory for interpolation purposes. Indeed in all the solutions containing more than 20% salt these equations could be used for the computation of expansion coefficients without undue loss of precision. The coefficients of equation (3) for the different solutions are recorded in Table II, and the residuals are plotted in Fig. 3. The dilute solutions of sodium bromide presented

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(6) "International Critical Tables," Vol. 3, p. 24.

(7) L. B. Smith and F. G. Keyes, *Proc. Am. Acad. Arts Sci.*, **69**, 285 (1934).

(8) L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. Standards*, **18**, 205 (1937).

(9) I. V. Ipatov, *J. Phys. Chem.* (U. S. S. R.), **5**, 1230 (1934); *cf. C. A.*, **29**, 5718 (1935).

(10) The symbols used in this paper are as follows. The subscripts 1 and 2 refer to water and salt in the solution, respectively, the superscript 0 indicates the pure component in the state stable under the conditions of the experiment. The weight and mole fractions are given by x and X, respectively, and v and V are specific and molal volumes, 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. C_2 is the concentration in moles per liter, t is the centigrade and T the absolute temperature.

quite a problem. Equation (2) was not at all satisfactory, and it is obvious from the residuals in Fig. 3 that the cubic equations were under a strain. For interpolation, however, these cubic equations and the deviation curves are adequate, the fifth decimal place being easily obtained, but in the range 0–25% sodium bromide the equations must be used with care if expansion coefficients are to be computed. It should be noted that the 95° point was never used in fitting the equations to the data.

Specific Volumes as Functions of Concentration.—In order to facilitate the interpolation of our data along the concentration axis and to expedite the computation of partial volumes, we fitted equation (4) to our results at the different temperatures. In the sodium chloride series the

$$v = v_1^0 + a'x_2 + bx_2^{3/2} + cx_2^{5/2} \qquad (4)$$

equations were passed through the points at x_2 = 0.0496, 0.1489 and 0.2493. Table III gives the coefficients for this series and, in the last column, the deviations at x_2 = 0.1019 and 0.1996 under the headings 1 and 2, respectively. The coefficients of equation (4) for the sodium bromide solutions are given in Table IV. In this series the deviations were zero at x_2 = 0.0491, 0.2500 and 0.4434 (except at 25°, see Fig. 1), and had the values given in Table IV at x_2 = 0.1500 and 0.3455. We have dispensed with the deviation curves in this paper, as the reader may easily reconstruct them from the data given in the tables. It will be noted that the fit of the equations becomes progressively better as the temperature rises.

The Apparent Volumes and Apparent Expansibilities.—The apparent volumes of the salts in solutions of various concentrations were computed at the different temperatures by the relation which defines the apparent volume, *viz.*

$$v = x_2\phi_2 + x_1v_1^0 \qquad (5)$$

or from the equation

$$\phi_2 = a + bx_2^{1/2} + cx_2^{3/2} \qquad (6)$$

where b and c are the same as in equation (4), and $a = (v + a')$ is the apparent volume of the salt at zero concentration. Values of a are listed in Tables III and IV and illustrate the well-known fact that the apparent volumes of electrolytes in water pass through a maximum as the temperature is raised.[11]

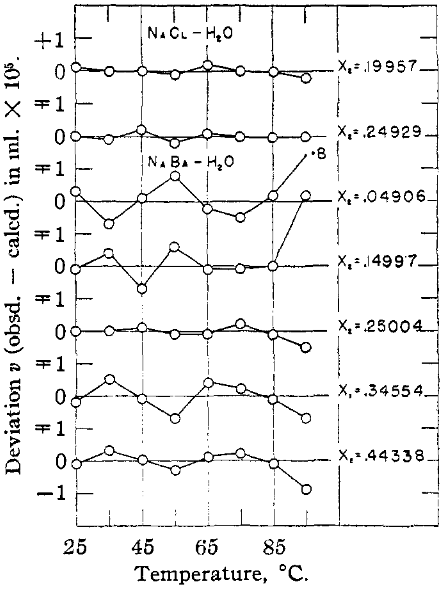

Fig. 3.—Differences between the specific volumes of sodium chloride and sodium bromide solutions as observed at different temperatures and as computed by equation (3) with the coefficients in Table II.

The use of empirical equations such as equation (6) for the computation of apparent volumes at zero concentration is open to question. In a recent paper Redlich[12] has again brought forward theoretical and experimental reasons for the necessity of retaining the theoretical slope (coefficient of $C_2^{1/2}$) of the apparent volume–concentration curve at or near zero concentration, and he has proposed an equation for the apparent volume as a function of the concentration which covers the whole range and at the same time preserves this important condition. We have not used the Redlich equation because (a) the weight fraction is a more convenient unit than the volume concentration and is independent of pressure and temperature, (b) data for computing the theoretical limiting slope at different temperatures are not available, and (c) the values of the apparent molal volume at zero concentration computed by (6) agree very well with those given by Redlich, which were computed from the most reliable observations on very dilute solutions *viz.*, 23.48 ml./mole for sodium bromide and 16.61 ml./mole for sodium chloride. Our extrapolated value of Φ_2^0 for sodium chloride differs somewhat from that given by Redlich but gives a value of the difference between the apparent molal volumes of sodium chloride and sodium bromide at infinite dilution which agrees better with the same dif-

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[11] See R. E. Gibson, *Am. J. Sci.*, **35A** (Day Volume), 66 (1938) for discussion and references.

[12] O. Redlich, *J. Phys. Chem.*, **44**, 619 (1940).

ference for the potassium salts than does Redlich's value.

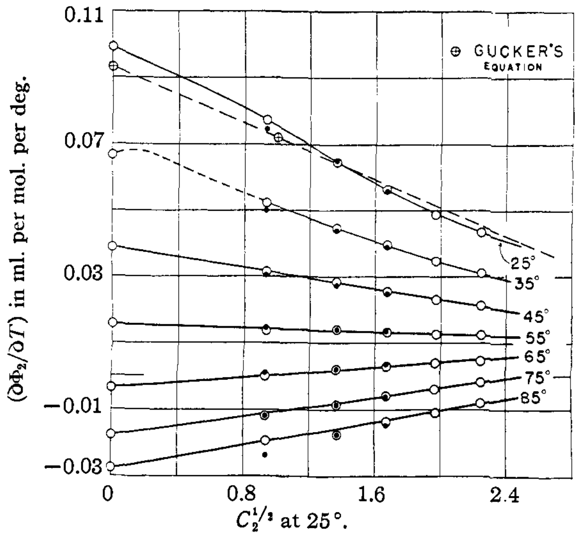

Fig. 4.—The apparent molal expansibilities $(\partial\Phi_2/\partial T)_P$ of sodium chloride in aqueous solutions as functions of concentration at different temperatures.

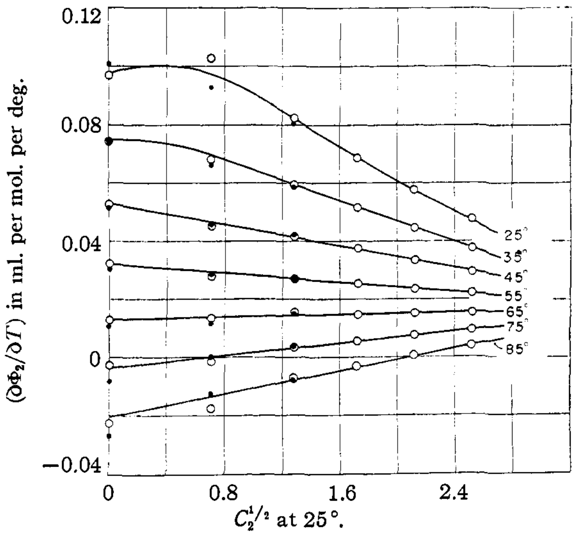

Fig. 5.—The apparent molal expansibilities $(\partial\Phi_2/\partial T)_P$ of sodium bromide in aqueous solutions as functions of concentration at different temperatures.

We consider that equation (6) has ample empirical justification but we do not wish to suggest in any way that it replaces the theoretically sounder but practically more cumbersome equation of Redlich. While we also recognize that the fact that equation (6) gives good values of the apparent volumes of the salts at zero concentration at 25° is no compelling reason for believing that the same will be true at all temperatures, we have attempted to find $(\partial\Phi_2/\partial T)_P$ at zero concentration by fitting cubic equations to our extrapolated apparent volumes (*a* in Tables III and IV) and by interpolation of the tabular differences. The results are plotted in Figs. 4 and 5 together with the apparent molal expansibilities of the salts, $(\partial\Phi_2/\partial T)$, in solutions of different concentrations, computed by the relation

$$x_2(\partial\phi_2/\partial T) = (\partial v/\partial T) - x_1(\partial v_1^0/\partial T) \qquad (7)$$

$(\partial v_1^0/\partial T)$ being computed from equation (8) and $(\partial v/\partial T)$ from equations (9) or (10) which were derived from equations (1), (2) and (3), respectively. The deviation curves were not used.

$$(\partial v_1^0/\partial T) = \frac{[1{,}127{,}825(t-3.98)+47{,}798(t-3.98)^{1.62}]}{[244{,}860+15{,}040(t-3.98)^{0.62}]^2}\,v_1^0 \qquad (8)$$

$$(\partial v/\partial T)/v = \frac{2.303\,B'C'}{(A'+B't^n)^2}\left[\frac{2A'}{B'C'}\,t+\frac{1}{C'}\,(2-n)t^{n+1}-nt^{(n-1)}\right] \qquad (9)$$

$$(\partial v/\partial T) = A + 2B(t-55) + 3C(t-55)^2 \qquad (10)$$

From Tables I and II it will be seen that equations (9) and (10) were both used only in the case of the most concentrated solution of sodium chloride. Values of $(\partial v/\partial T)$ computed by both equations agreed within 0.05% at all temperatures except 25° where the discrepancy amounted to 0.3%.

Table I

Coefficients in Equation (2) Expressing the Specific Volumes of Various Solutions as Functions of Temperature

Components	100 x_2	A'	B'	C'	n
NaCl–H_2O	4.946	2,643,458	− 52.061	2,601,088	1.45
NaCl–H_2O	10.187	1,847,901	−110.075	1,787,705	1.20
NaCl–H_2O	14.890	1,727,595	−211.949	1,645,716	1.05
NaCl–H_2O	24.929	2,575,740	−525.501	2,373,295	0.98

Table II

Coefficients in Equation (3) Expressing the Specific Volumes of Various Solutions as Functions of Temperature

Components	100 x_2	v_{55}	10^4A	10^7B	10^9C
NaCl–H_2O	19.957	0.88551_1	4.427_3	11.90_4	0.41_7
NaCl–H_2O	24.929	$.85552_2$	4.276_5	9.04_9	1.00_0
NaBr–H_2O	4.906	$.97729_1$	4.872_3	29.56_0	−6.11
NaBr–H_2O	14.997	$.90204_1$	4.630_4	19.85_0	−1.97
NaBr–H_2O	25.004	$.82854_5$	4.353_8	12.52_5	-0.08_3
NaBr–H_2O	34.554	$.75930_2$	4.053_9	7.66_1	0.97_2
NaBr–H_2O	44.338	$.68912_3$	3.726_3	4.46_1	1.06_0

In Figs. 4 and 5 the apparent molal expansibilities of the salts at various temperatures are plotted against the square root of the number of moles per liter at 25°. In the apparent molal expansibilities errors in $(\partial v/\partial T)_P$ are magnified by a factor $1/x_2$, and discrepancies in our expansion equations are shown up. At intermediate temperatures the uncertainty in the computed expansion coefficients, $(\partial v/\partial T)_P$, depends almost entirely on the experimental observations and does not exceed 0.2%. At the ends of the temperature range, however, factors connected with the problem of fitting empirical equations to the data cause the uncertainties in the slopes to increase.[13] At 25 and 85° an uncertainty of 1% in the computed expansion coefficients is possible, and it will be noticed that the apparent molal expansibilities are most erratic at these temperatures. By plotting the mean apparent expansibility $\Delta\Phi_2/\Delta T$ (computed from tabular differences) against the mean temperature, we were able to estimate $(\partial\Phi_2/\partial T)$ since the plot showed only a gradual curvature. In general these values of $(\partial\Phi_2/\partial T)$ agreed with those obtained from equation (7) within 0.5%. The larger discrepancies are shown by the dots representing the mean apparent molal expansibilities in Figs. 4 and 5. The broken curve in Fig. 4 represents the equation used by Gucker[14] to express as a function of concentration the best values of the apparent thermal expansibilities of sodium chloride available up to 1934.

TABLE III

COEFFICIENTS IN EQUATION (4) FOR EXPRESSING THE SPECIFIC VOLUMES OF SODIUM CHLORIDE SOLUTIONS AS FUNCTIONS OF CONCENTRATION AT DIFFERENT TEMPERATURES. APPARENT MOLAL VOLUMES OF SODIUM CHLORIDE AT INFINITE DILUTION

t	$-a'$	b	c	a	Φ_2^0	v(obsd.-calcd.) $\times 10^5$ (1)	(2)
25	0.7216_4	0.1466_3	0.070_9	0.2812_9	16.4_4	−6	4
35	$.7105_6$	$.1304_4$	$.072_2$	$.2954_1$	17.2_7	−5	4
45	$.7052_0$	$.1208_7$	$.072_3$	$.3046_5$	17.8_1	−5	2
55	$.7058_4$	$.1193_9$	$.069_0$	$.3086_4$	18.0_4	−4	2
65	$.7096_3$	$.1191_0$	$.070_3$	$.3101_6$	18.1_3	−4	2
75	$.7176_4$	$.1243_2$	$.068_2$	$.3081_2$	18.0_1	−3	1
85	$.7282_2$	$.1287_6$	$.075_1$	$.3041_5$	17.7_8	−3	3
95	$.7426_4$	$.1393_6$	$.074_9$	$.2969_5$	17.3_6	−3	1

TABLE IV

COEFFICIENTS IN EQUATION (4) FOR EXPRESSING THE SPECIFIC VOLUMES OF SODIUM BROMIDE SOLUTIONS AS FUNCTIONS OF CONCENTRATION AT DIFFERENT TEMPERATURES. APPARENT MOLAL VOLUMES OF SODIUM BROMIDE AT INFINITE DILUTION

t	$-a'$	b	c	a	Φ_2^0	v(obsd.-calcd.) $\times 10^5$ (1)	(2)
25	0.7751_0	0.0540_4	0.023_7	0.2278_3	23.4_5		
35	$.7697_7$	$.0501_4$	$.018_0$	$.2362_2$	24.3_1	−2	6
45	$.7674_6$	$.0472_6$	$.014_6$	$.2423_9$	24.9_5	−3	3
55	$.7680_7$	$.0455_1$	$.013_4$	$.2464_1$	25.3_6	0	3
65	$.7713_8$	$.0457_8$	$.012_4$	$.2484_1$	25.5_6	0	3
75	$.7764_7$	$.0456_6$	$.013_8$	$.2492_9$	25.6_6	−1	3
85	$.7848_8$	$.0496_1$	$.013_1$	$.2474_9$	25.4_7	1	2

If the deviations are neglected, the partial volumes of sodium chloride and sodium bromide may be computed from the data in Tables III and IV, by means of the equation

$$v_2 = a + \frac{3}{2}bx_2^{1/2} + \left(\frac{5}{2}c - \frac{1}{2}b\right)x_2^{3/2} - \frac{3}{2}cx_2^{5/2} \quad (11)$$

Discussion of Results

Apparent Expansibilities as Functions of Concentration.—Closely related to the fact that the thermal expansibilities of liquids decrease with pressure is the fact that the apparent expansibilities of the solutes in moderately dilute solutions are generally negative when the solutions are formed with considerable contraction on mixing. Under such conditions the apparent expansibilities increase algebraically (become less negative) as the concentration rises. This behavior is observed in solutions of electrolytes in non-aqueous solvents; for example, the apparent expansibilities of electrolytes in methanol and in glycol are negative and increase with concentration.[15] Aqueous solutions, however, behave in an unusual manner at lower temperatures, the apparent expansibilities of the solutes being positive and the slopes of the apparent expansibility and concentration curves being negative.[16] Our results show quite clearly that both these anomalies characteristic of water solutions disappear as the temperature is raised. It also has been shown by Gucker that the Debye–Hückel limiting law for electrolytes and existing data on the temperature and pressure coefficients of the dielectric constant of water require the initial slopes of the curves of the apparent expansibility plotted against the square root of the volume concentration to be positive even at lower temperatures. In Fig. 5 our values of $(\partial\Phi_2/\partial T)$ at zero concentration for sodium bromide (obtained by an admittedly approximate method) tie up with the other points at 25 and 35° by curves which pass through maxima and are compatible with a positive initial slope. The same may be true of the apparent expansibilities of sodium chloride, as is indicated by the dotted curve for the 35° results in Fig. 4, but the question cannot really be settled without very precise data for dilute solutions. The sigmoid

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[13] See J. S. Burlew, THIS JOURNAL, **62**, 692 (1940).

[14] F. T. Gucker, Jr., *ibid.*, **56**, 1017 (1934).

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

[16] See F. T. Gucker, Jr., *ibid.*, **56**, 1017 (1934); F. T. Gucker, Jr., and C. E. Moser, *ibid.*, **61**, 1558 (1939) (urea in water).

character of the curves in Figs. 4 and 5 confirms our previous remarks on their probable shape.[17]

Comparison of the Apparent Volume—Temperature Relations for Sodium Chloride and Sodium Bromide.—The anomalies in the thermal expansions of aqueous solutions of electrolytes in water, together with certain differences between the behavior of sodium chloride and sodium bromide solutions, may be illuminated if account is taken of the following effects. (a) Attraction between the ions and the water dipoles. If undisturbed by structure changes as in glycol solutions, this effect causes contraction on mixing, lowers the apparent volume (electrostriction) and also *lowers* the expansion coefficients of water, making the apparent expansibility of the salt more negative. This effect predominates in water at higher temperatures. It is proportional to the polarizing power of the ions. (b) Interionic attraction, which lowers the effective concentration of ions but is only of secondary importance in a comparison of the behavior of different salts of the same type. (c) The effect of the ions on the molecular distribution in the solution. It is now well recognized that directed forces between water molecules cause them to pack together in a liquid arrangement whose coördination number is very low, being between 4 and 5 at ordinary temperatures.[18] A considerable fraction of the total volume of the liquid is, therefore, unavailable to the molecules at any instant, but, as the temperature rises and the coördination number increases, this fraction decreases. The consequent increase in the density of packing accounts for the relatively low thermal expansibility of water and its rapid rise with temperature. Addition of salt to water generally increases the coördination number of the liquid both by the interaction of the ions with the water molecules and by the packing of the ions into the volume unavailable to the water. This effect produces a further decrease in the apparent volume of the salt but *raises* the thermal expansibility of the solution.

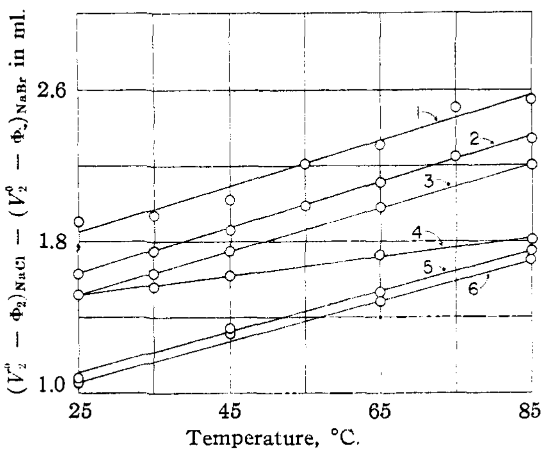

Fig. 6.—The differences between the volume changes on mixing in sodium chloride and in sodium bromide solutions. These differences are plotted as functions of temperature for various concentrations at constant pressure, 1 atmosphere (curves 1, 2 and 3), 1000 atmospheres (curves 5 and 6) and at constant volume (curve 4).

A comparison of the different contributions of effects (a) and (c) to the volume relations in sodium chloride and in sodium bromide solutions is available from the curves in Fig. 6. Curves 1, 2 and 3 show the difference between $(V_2^0 - \Phi_2)$ for sodium chloride and $(V_2^0 - \Phi_2)$ for sodium bromide in 0, 1 and 1.94 molal solutions, respectively, as functions of temperature at constant pressure. This difference takes into account the volumes of the ions themselves and gives a direct comparison of the contractive effects of the two salts on the water. It will be seen that $(V_2^0 - \Phi_2)$ is greater for sodium chloride than for sodium bromide at the lower temperatures and that the difference increases as the temperature rises. In curves 5 and 6 the same difference at 1000 bars pressure is plotted for 1 and 1.94 molal solutions.[19] The initial differences between $(V_2^0 - \Phi_2)$ for the two salts are less than at one atmosphere, but the temperature coefficient is practically the same. Curve 4 shows the difference between $(V_2^0 - \Phi_2)$ for the two salts in a 1.94 molal solution as a function of temperature when the *volume* of each solution is kept constant at its value at 25° and 1 atmosphere. Under such conditions it is assumed that the effects of the longer-range electrostatic forces are kept constant and that the temperature effect is due to changes in molecular distribution. The small positive slope of curve 4 suggests that effect (c) is slightly larger in sodium bromide than in sodium chloride solutions at 25° and the difference falls off at higher temperatures, as would be expected. The positive values of $(V_2^0 - \Phi_2)_{NaCl} - (V_2^0 - \Phi_2)_{NaBr}$ at 25° and the fact that the slope of the constant pressure curves is much greater than that of the constant volume curve indicate, however, that the differences between the volume relations for sodium chloride and sodium bromide

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(17) R. E. Gibson and J. F. Kincaid, This Journal, **59**, 25 (1937).

(18) J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938).

(19) Taken from unpublished data obtained in this Laboratory.

are due chiefly to the electrostrictive effect (a) of the chloride ion being significantly larger than that of the bromide ion. Experimental and theoretical studies of the energies[20] and free energies[21] of hydration of ions indicate that the interaction of the chloride ion is greater than that of the bromide ion. The fact that the bromide ion is larger than the chloride ion actually accounts for the relative contributions of both effects (a) and (c) to the solutions.

The conclusions drawn from Fig. 6 concerning the relative effects of the ions on water also account for other features of the apparent volume and expansibility results; for example, they explain the observation that $(\partial\Phi_2/\partial T)$ is greater for sodium bromide than for sodium chloride at infinite dilution or any other equivalent concentration and that the maxima on the apparent molal volume–temperature curves at constant pressure (points where $(\partial\Phi_2/\partial T) = 0$) are at higher temperatures with sodium bromide than with sodium chloride solutions, since, it will be recalled, the larger electrostrictive effect of the chloride ion produces the greater diminution in the expansibility of the solutions. These maxima on the Φ_2–T curves at constant pressure are due to the balance between the opposing effects (c) and (a) on the apparent molal expansibilities.

Summary

The specific volumes of aqueous solutions of sodium chloride and sodium bromide covering the whole range of concentration have been measured at 10° intervals between 25 and 95°. The results are given by equations expressing the specific volume as a function of the temperature and as a function of concentration. From these equations the thermal expansibilities, the apparent and partial volumes and expansibilities may be computed at different temperatures and concentrations. An analysis of the results in terms of the electrostrictive effects of the ions and their effects on molecular distribution in the solution gives an explanation of some interesting features of the results, especially the maxima in the apparent volume–temperature curves, and suggests that although the bromide ion has a slightly larger effect in breaking down the water structure than the chloride ion, the main differences between the two solutions are attributable to the larger polarizing power of the chloride ion.

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The Solubility of Carbon Dioxide and Nitrous Oxide in Aqueous Salt Solutions

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Data in the literature on the solubility of gases in solutions of electrolytes are scattered and of doubtful accuracy. The experimental apparatus and technique have frequently neglected important factors, as maintaining constant partial gas pressure. The range of salt concentrations studied often has been limited to dilute solutions. The few equations given which relate gas solubility and salt concentration indicate trends rather than express accurately the experimental data.

It is the object of this work to present new data on the solubility of carbon dioxide and nitrous oxide in various salt solutions over wide ranges of concentration and to express accurately these data by means of a new equation.

Experimental

The apparatus used in this investigation is shown in Fig. 1. The principle of the Ostwald method is that a measured volume of gas is brought in contact with a measured quantity of gas-free liquid, equilibrium is established by agitation, and the volume of gas remaining is measured. The change in volume gives the amount dissolved by the liquid. The apparatus used in this work differs from other modifications in the method of providing a gas–liquid interface, and in the provision for agitating the absorption flask.

The buret, A, is about 110 cm. long. It is connected at the bottom by a T-tube to the mercury leveling bulb B and the manometer tube C, open at the top. The cock D is between the buret and the manometer tube. At the top, the buret is connected by the ground glass joint E to the T-tube F. One branch of this T-tube connects to the vacuum through the stopcock G. The other ends in a straight tube at H.