

Solutions under Pressure*

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A method is given which permits the calculation of the volumes of aqueous solutions of salts at higher pressures solely from the volumes of these solutions at atmospheric pressure and the compressibility data of the pure substances involved. The volumes of aqueous solutions of sodium chloride, ammonium nitrate, and potassium sulfate are computed to 10 000 bars pressure and these agree with the observed values to within a fraction of one percent. Tammann's hypothesis, to the effect that water in solution is compressed by an ionized solute, is used; but, the extension of this hypothesis permits the calculation of the volumes of the solute and the water in solution and the effect of pressure on these volumes. The interpolation formulas derived also appear to be applicable to nonaqueous solutions of salts; and some tentative results are also given for mixtures of liquids (ethyl alcohol in water).

An equation is introduced, which like Tait's equation, represents the variation of volumes with pressure. This equation is fundamental to the development of the interpolation equations for solutions which are given in this article. It is found that an analogous equation reproduces refractive index and dielectric constant data for liquids and gases at high pressures. This leads to an equation, previously proposed, which is considered more useful in representing experimental data analytically than the corresponding formulas of Lorenz-Lorentz and Mossotti-Clausius.

INTRODUCTION

THE volumes of mixtures at higher pressures can be approximated, as we will show, from the volumes of these solutions at atmospheric pressure and the compressibility data of the pure components involved. Though applied only to solutions of salts in water, the method can be extended also to other solutions. Experimentally, it is possible to observe only the resultant contractions and expansions during solution, so that the volumes of the components in solution must be computed, and these computed volumes depend on the theories assumed. We use a modification of Tammann's hypothesis (which, briefly, states that in the presence of an ionized solute the water in solution behaves as though it were compressed); but, our extension of this hypothesis permits us also to calculate the effect of pressure on both the volumes of the solute and the water in solution.

The Tait equation

$$v^{(P_0)} - v^{(P)} = A \log[(P+B)/(P_0+B)], \quad (1)$$

where $v^{(P_0)}$ and $v^{(P)}$ are the specific volumes at the pressures P_0 and P and where A and B are constants, has been widely used to represent the variation of volume with pressure.¹

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¹ This equation was proposed in 1888 by Tait and was re-introduced later and applied more extensively, especially, by Gibson. For the literature on this equation see (a) J. R. Partington, *An Advanced Treatise on Physical Chemistry* (Longmans, Green and Company, London, 1949-1953), Vol. II, p. 66 ff.; (b) H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Corporation, New York, 1950), p. 270 ff.

If we interchange the variables v and P in Eq. (1) and introduce the new constants a and b , we get the equation

$$P_0 - P = a \log[(v^{(P)} - b)/(v^{(P_0)} - b)] \quad (2)$$

which, like Tait's equation, represents volume-pressure relations. In Table I are shown the parameters A , B , and a , b of Eqs. (1) and (2) fitted by the method of least squares to the volumes and pressures of some liquids, solids and a gas.²

Generally, the Tait equation is more adaptable to compressibility data for liquids over large pressure ranges than is Eq. (2). This may be seen in Table I, and especially in Table II, where the parameters of Eqs. (1) and (2) for water at different pressures are shown.³ Nevertheless, Eq. (2), which we introduce,⁴ is of particular significance in the development of the interpolation equation for solutions which is given below, though the inconstancy of the parameter b for water is a troublesome factor.

VOLUMES OF SOLUTIONS UNDER PRESSURE

We start with the equation

$$P_0 - P = a \log[(v_w^{(P)} - b)/(v_w^{(P_0)} - b)], \quad (3)$$

which represents the volume-pressure relation for

² For the constants of the Tait equation for other substances see (a) J. S. Rosen, *J. Chem. Phys.* **17**, 1192 (1949); (b) Harned and Owen, reference 1(b), p. 272, gives a number of the constants found by Gibson.

³ It is of some interest to note that for water (and presumably for other liquids) $1/a$ and b , the parameters of Eq. (2), are linear in v . For solids the parameters of Eqs. (1) and (2) are less variable.

⁴ L. H. Adams and E. D. Williamson [*J. Wash. Acad. Sci.* **9**, 30 (1919)] used an analogous equation for mustard gas.

TABLE I. The parameters A , B , a , and b of Eqs. (1) and (2) fitted by the method of least squares^a to the volumes and pressures. The last two columns give the average and maximum percent deviations between the observed and calculated values of v . The pressures and volumes are in the units of the original data.

Substance	$t^{\circ}\text{C}$	P_{max}	A	B^b	a	b	(%) _{Av}	(%) _{max}
Benzene ^c	25	868 ⁿ	0.25013	985.8	0.0043	0.0077
Benzene	25	868	3128.7	0.9996	0.0089	0.0162
Benzene ^c	35	1030 ⁿ	0.24961	896.8	0.0005	0.0010
Benzene	35	3119.3	1.0034	0.0166	0.0410
Benzene ^c	45	1188 ⁿ	0.25360	830.9	0.0008	0.0023
Benzene	45	3096.8	1.0066	0.0253	0.0620
Sodium chloride ^d	25	1000 ⁿ	87 019.	0.39	0.00	0.00
Sodium chloride	25	...	0.23185	51 970. ^p
Ammonium nitrate ^{e, f}	25	1000 ⁿ	39 389.	0.5128	0.00	0.00
Potassium sulfate ^{f, g}	25	1000 ⁿ	30 582.7	0.3592	0.000	0.000
Ammonia ^h	100	55 ^o	1.2085	-14.05	0.675	1.167
Ammonia	100	55 ^o	41.274	0.2126	1.48	2.17
Carbon bisulfide ⁱ	30	12 000 ^o	0.2005	1129	0.074	0.211
Carbon bisulfide	30	12 000	9637.6	0.5865	0.75	1.11
Glycol ^j	25	1000 ⁿ	6917.2	0.8016	0.00	0.00
Methanol ^k	25	1000 ⁿ	2886.6	1.08606	0.00	0.00
Ethyl alcohol ^l	25	1500 ^o	3432.0	1.0833	0.027	0.061
Water ^d	25	1500 ⁿ	0.24781	2269	0.010	0.16
Water	25	3000 ⁿ	0.30807	2907	0.009	0.013
Water	25	1000 ⁿ	7189.2	0.8590	0.00	0.00
Water	25	2000 ⁿ	8934.5	0.8289	0.013	0.027
Copper ^m	20	12 000	0.424	255 490.
Copper	20	12 000	597 000.	0.8131

^a For convenience in fitting Eq. (2) $\Sigma(P_{\text{obs}} - P_{\text{calc}})^2$ is minimized. $P_0=1$, except where indicated otherwise.

^b B is in the same units as the pressure.

^c R. E. Gibson and J. F. Kincaid, *J. Am. Chem. Soc.* **60**, 511 (1938).

^d L. H. Adams, *J. Am. Chem. Soc.* **53**, 3780 (1931).

^e L. H. Adams and R. E. Gibson, *J. Am. Chem. Soc.* **54**, 4530 (1932).

^f L. H. Adams and R. E. Gibson, *J. Wash. Acad. Sci.* **21**, 388 (1931).

^g L. H. Adams, *J. Am. Chem. Soc.* **54**, 2240 (1932).

^h F. G. Keyes and J. G. Kirkwood, *Phys. Rev.* **36**, 1572 (1930). The initial pressure P_0 is 20 atmos.

ⁱ W. E. Danforth, *Phys. Rev.* **38**, 1224 (1931).

^j R. E. Gibson, *J. Am. Chem. Soc.* **59**, 1523 (1937).

^k R. E. Gibson, *J. Am. Chem. Soc.* **57**, 1552 (1935).

^l A. L. T. Moesveld, *Z. physik. Chem.* **105**, 450 (1923); see also J. S. Rosen, *J. Opt. Soc. Am.* **37**, 932 (1947). The volumes of solutions at atmospheric pressure were taken from *International Critical Tables*, Vol. III, p. 117.

^m T. W. Richards, *J. Am. Chem. Soc.* **46**, 1422 (1924).

ⁿ Pressure in bars.

^o Pressure in atmospheres.

^p The values given by R. E. Gibson, *Am. J. Sci.* **235A**, 57 (1938).

water. $v_w^{(P)}$ and $v_w^{(P_0)}$ are the specific volumes of pure water at the pressures P and P_0 [P_0 is the initial pressure and if taken at atmospheric pressure is indicated by the superscript (0)].

The choice of this equation⁵ is of particular significance in the development of the interpolation

⁵ Tait's equation, and its extension to solutions of electrolytes, has been used by Gibson and by Brander. R. E. Gibson, *J. Am. Chem. Soc.* **56**, 11 (1934); **57**, 384 (1935). Harned and Owen, reference 1(b), p. 271 ff. outlines Gibson's work in some detail. See also E. Brander, *Soc. Sci. Fennica Commentationes Phys. Math.* **8**, 17 (1935); **9**, 1 (1936). For the literature on solutions see, Partington, Vol. II, p. 31 ff.; P. W. Bridgman, *Revs. Modern Phys.* **18**, 17 (1946).

equations given here. Tamman's hypothesis, which we will use, states that a given amount of water in solution behaves as the same amount of pure water under an additional constant pressure P_t . When applied to Eq. (3), the pressure P_t is added to both P and P_0 and is canceled, so that it does not explicitly appear in the equation for water modified by the presence of a solute. The consequence of the elimination of this P_t is important; this elimination subsequently frees us from troublesome logarithmic equations and permits the expression of our interpolation equations in a more amenable algebraic form. It is for this reason that Eq.

TABLE II. The parameters of Eqs. (1) and (2) for water^a at 25°C at different pressures P . The constants shown were obtained by adapting these equations^b to the volumes of water at the two pressures shown in the first column; P , the average of these pressures, is taken to correspond to the values of the parameters found in this way.

Pressures, in kilobars	P	a^c	b^d	A	B	v
1-1	0.75	7 189.2	0.8590			0.9722
1-2	1.5	9 169.7	0.8253			0.9473
2-3	2.5	10 013.4	0.8127	0.301413	2821	0.9199
3-4						
4-5	4.5	12 498.8	0.7813	0.299235	2790	0.8781
5-6	5.5					
6-7	6.5	14 516.6	0.7603	0.288696	2630	0.8469
7-8	7.5	15 745.2	0.7490			0.8339
8-9	8.5	16 767.0	0.7403	0.286981	2600	0.8221
9-10						

^a The data of L. H. Adams, J. Am. Chem. Soc. 53, 3780 (1931).

^b We have set $P_0=1$ in both Eqs. (1) and (2).

^c $1/a$ is linear in v for pressures $P>1500$.

^d b is linear in v for pressures $P>2500$.

(3), rather than Tait's equation, is more useful for the extension to solutions under pressure.⁶

Thus, by applying Tammann's hypothesis to water modified by the presence of a solute, Eq. (3) becomes

$$(P_0 + P_t) - (P + P_t) = a \log \left[\frac{(v_w^{(P+P_t)} - b)}{(v_w^{(P_0+P_t)} - b)} \right]; \quad (4)$$

or,

$$P_0 - P = a \log \left[\frac{(\psi_1^{(P)} - b)}{(\psi_1^{(P_0)} - b)} \right]; \quad (5)$$

where we have $v_w^{(P+P_t)}$, the volume of pure water under the additional pressure P_t , equal to $\psi_1^{(P)}$. $\psi_1^{(P)}$ and $\psi_1^{(P_0)}$ are, therefore, the specific volumes of water in solution when the solutions are at the external pressures P and P_0 . The constants a and b in Eqs. (3) and (5) are assumed to be the same in both equations and may be determined from the compressibility data of pure water.

Comparing Eqs. (3) and (5), we may write

$$\psi_1 - b = c(v_w - b); \quad (6)$$

and from this we have also

$$\psi_1^{(0)} - \psi_1^{(P)} = c(v_w^{(0)} - v_w^{(P)}), \quad (6')$$

where c is a constant (corresponding to a given concentration of solute whose weight fraction is x_2^*). Equation (6') (which is especially interesting in that it does not involve the parameter b) states that with a change of pressure the increase in the specific volume of pure water is proportional to the increase in specific volume of water in solution. Thus, the application of

⁶ As we shall see, our results also apply to nonaqueous solutions; in this case, we adjust Eq. (3) to the volumes of the solvent.

Tammann's hypothesis gives us the simple linear relation of Eq. (6'); and this relation between pure water in solution is of primary importance in our subsequent development.

For other concentrations, we replace Eq. (6') by

$$\psi_1 - b = c^\alpha (v_w - b), \quad (7)$$

where

$$\alpha = x_2/x_2^* \quad (7')$$

or

$$\alpha = (x_2/v_s^{(0)}) / (x_2/v_s^{(0)*}), \quad (7'')$$

where the asterisk designates some arbitrary concentration⁷ and where $v_s^{(0)}$ is the specific volume of the solution at atmospheric pressure. Hence, α indicates the relative concentration of the solute and is the ratio of either the weight fraction of salt x_2 or of the volume concentration $x_2/v_s^{(0)}$.⁸

The foregoing generalization may be justified by the reiteration of Tammann's hypothesis, and with some simplifying assumptions on the effect of adding more solute to the water in solution.

We now introduce the equations

$$v_s^{(0)} = x_1\psi_1^{(0)} + x_2\psi_2^{(0)}, \quad (8)$$

$$v_s^{(P)} = x_1\psi_1^{(P)} + x_2\psi_2^{(P)}, \quad (8')$$

where ψ_1 and ψ_2 are the corresponding specific volumes of the water in solution and the solid in solution (the

⁷ So that α is 1 for the solution whose volume is $(v_s^{(0)})^*$ and which contains $(x_2)^*$ g solute. In practice, it is convenient to so designate the lowest concentration of the data examined.

⁸ It may be noted that other expressions for the concentration in α might be used (e.g., x_2/x_1 , to correspond to molal concentration); but only those defined by Eqs. (7') and 7'') are used here.

volume of the solute as a liquid) and where x_1 and x_2 are the weight fractions of water and solute. ψ_1 varies with concentration of the solution and with pressure, while ψ_2 is assumed to remain the same for all concentrations of the salt, but to vary with pressure.

Replacing ψ_1 in Eq. (8') by its value in Eq. (7), we finally derive the equation

$$v_s^{(P)} = x_1 c^\alpha (v_w^{(P)} - b) + b x_1 + x_2 \psi_2^{(P)}. \quad (9)$$

In particular, at atmospheric pressure, Eq. (9) becomes

$$v_s^{(0)} = x_1 c^\alpha (v_w^{(0)} - b) + b x_1 + x_2 \psi_2^{(0)}. \quad (9')$$

Only c and $\psi_2^{(0)}$ are unknown; and these may be found by writing Eq. (9') for each concentration and determining by the method of least squares their best values. We then use Eq. (9), after making some appropriate assumption about $\psi_2^{(P)}$, to determine $v_s^{(P)}$, the volume of the solution at pressure P .⁹

VOLUME OF SOLUTE IN SOLUTION

The variation of v_s , the volume of the crystalline salt, with pressure may also be represented by the equation

$$P_0 - P = a_2 \log[(v_s^{(P)} - b_2)/(v_s^{(P_0)} - b_2)]. \quad (10)$$

We assume that the volumes of the salt in solution, ψ_2 , are given by

$$P_0 - P = a_2 \log[(\psi_2^{(P)} - b_2)/(\psi_2^{(P_0)} - b_2)], \quad (10')$$

where the constants a_2 and b_2 are the same as for the crystalline salt. This would follow from the hypothesis that the salt in solution is compressed (or dilated) by the addition of water; this view being somewhat analogous to Tammann's hypothesis that the addition of salt to water compresses the water.

Comparing Eqs. (10) and (10'), we may write

$$\psi_2 - b_2 = c_2 (v_s - b_2). \quad (11)$$

From this we have

$$\psi_2^{(0)} - \psi_2^{(P)} = c_2 (v_s^{(0)} - v_s^{(P)}), \quad (11')$$

where c_2 is a constant.¹⁰ These equations are similar to

⁹ We assume c and α [if defined by Eq. (7'')] to be the same for all pressures.

¹⁰ R. E. Gibson [J. Am. Chem. Soc. **56**, 4, 865 (1934)] assumes that on the application of pressure the dissolved solute is compressed the same amount as the solid salt. As we shall see, this is hardly adequate in most cases; in fact, Gibson [Am. J. Sci. (5) **35A**, 49 (1938)] subsequently concludes that if ψ_2 is to be independent of the concentration, it is necessary to assume that the compressibility of the solute in solution is three times as great as in the solid state.

Eqs. (6) and (6') for the solvent, except that we assume here that c_2 is the same for all concentrations of the salt.

From Eq. (11) for atmospheric pressure,

$$\psi_2^{(0)} - b_2 = c_2 (v_s^{(0)} - b_2), \quad (11'')$$

we can find c_2 , since $\psi_2^{(0)}$ has already been found by adapting Eq. (9') to the volumes of the solution at atmospheric pressure, and b_2 determined by adjusting Eq. (10) to the volumes of the solid salt.¹¹ Equation (11) or (11') may then be used to determine ψ_2 , the volume of the solute at any pressure P .

Except for the most incompressible solids, the value of b_2 in Eq. (10) would depend on the pressure range to which this equation is adjusted. But the value of b_2 is sometimes critical, as may be seen when we solve for c_2 by Eq. (11''), if $(v_s^{(0)} - b_2)$ is very small (e.g., potassium sulfate considered in the following). It is essential, therefore, to determine the appropriate value of b_2 , and the following considerations may resolve some of the questions as to how this may best be done. Equation (11), for determining ψ_2 , is equivalent to an extrapolation (when $c_2 > 1$) from the curve of the solid salt. The value of b_2 around $P=0$ in Eq. (10) therefore, would appear to be the most appropriate value to use in continuing the v_s vs P curve into the region from which we extrapolate the ψ_2 values. For this reason, we have determined b_2 for the salts considered in this article, by adjusting Eq. (10) to the volumes of the salt at the lowest available pressures (1, 500, and 1000 bars in our case).

In formulating Eq. (9), we have modified Tammann's idea which assumes that in solution the water behaves approximately as the same volume of water at a higher pressure. Equation (3), instead, indicates that only a portion of the water is compressed, and that b is the relatively incompressible part of the water. Unfortunately, the parameter b for water in Eq. (3) does not remain sufficiently constant over our pressure range (to 10 000 bars), as may be seen from Table II where we have computed the values of b over short intervals for the entire range. This would imply that the relatively incompressible part of water, b , varies with the external pressure; so that, to compute v_s by Eq. (9), we must use the value of b appropriate to the external pressure P (Table II).

In Tables III to V are shown the results of computing

¹¹ b_2 may sometimes be found less laboriously, depending upon how the compressibility of the crystalline salt is reported in the literature. Thus, P. W. Bridgman [The Physics of High Pressure (Bell and Sons, London, 1949), p. 160] gives the compressibilities of solids as a quadratic function of pressure, from which two quantities κ and ϕ [the compressibility and change of compressibility, $(-1/v)(dv/dP)$ and $(-1/\kappa)(d\kappa/dP)$, respectively] may readily be computed. Then $b_2 = v^{(0)}(1 - \kappa_0/\phi_0)$ (the subscripts indicating that κ and ϕ are evaluated at $P=0$). J. Slater [Phys. Rev. **23**, 488 (1924)] reports his measurements for the compressibilities of the alkali halides directly with the values of κ_0 and ϕ_0 .

TABLE III. The constants^a of the equations for the calculation of the specific volumes at high pressures of aqueous solutions of sodium chloride^b at 25°C. The volumes at the higher pressures were computed by Eq. (9); and the results are shown in the last two columns where δ_{Av} and δ_{max} are, respectively, the average and maximum differences between the observed^c and computed volumes.

b	$\psi_2^{(0)}$	c^d	Conc. ^e	c_2	P , in kilobars	$10^4 \delta_{Av}$	$10^4 \delta_{max}$
0.7750	0.5340	0.95131 ^f	$(x_2/v_s^{(0)})$	1.986	0	1.7	-3.8
					1	14.	20.
					4	13.	17.
					5*	5.	9.
					6	2.	9.
					8		
0.7325	0.5567	0.95398 ^f	$(x_2/v_s^{(0)})$	2.30	0	1.8	-2.5
					8	6	9.
					9*	5	-14.
0.7125	0.5572	0.95731 ^f	$(x_2/v_s^{(0)})$	2.306	0	1.7	-3.1
					9	10.	17.
					10*	8.	11.
0.8450	0.5180	0.93415 ^f	$(x_2/v_s^{(0)})$	1.766	0	1.6	-2.4
					1*	2.	-6.
					2	-10.	-20.
0.8591	0.4746	0.94254*	x_2	1.167	0	0.8	1.1
					1*	9.	12.
					2	8.	11.

^a The constants are derived as follows: b is the parameter in Eq. (2) appropriately chosen (see Table II) to correspond to the external pressure P used in Eq. (9). This pressure is marked with an asterisk; results for other pressures are shown for comparison. c and $\psi_2^{(0)}$ are the constants of Eq. (9') obtained by adapting to this equation the volumes of the solution at atmospheric pressure. $b_2=0.39$ and is the constant in Eq. (10) obtained by adapting the volumes of solid NaCl at the pressures 1, 500, and 1000 bars. c_2 is obtained from Eq. (11) with $P=0$. With this value for c_2 , $\psi_2^{(P)}$, the volumes of the solute in solution at pressure P , were calculated by Eq. (11').

^b The maximum concentration is 25% (by weight); data for five concentrations are used.

^c The data of L. H. Adams, J. Am. Chem. Soc. 53, 3783 (1931). The compressibility data used for the solid NaCl are from Adams, *ibid.*, pp. 3780 and 3806. The volumes of NaCl solutions at atmospheric pressure were taken from *International Critical Tables*, Vol. III, p. 79.

^d This is the value of c which corresponds to $x_2=0.05$.

^e α in Eqs. (9) and (9') involves a ratio of the concentrations of the solutions. These concentrations have been taken either as x_2 or $x_2/v_s^{(0)}$; which of these has been used is indicated in this column.

^f $\alpha = (x_2/v_s^{(0)})/0.051623$. The denominator is the value of the numerator when $x_2=0.05$.

* $\alpha = x_2/0.05$.

TABLE IV. The constants^a of the equations for the calculation of the specific volumes at high pressures of aqueous solutions of ammonium nitrate^b at 25°C. The volumes at the higher pressures were computed by Eq. (9); and the results are shown in the last two columns where δ_{Av} and δ_{max} are, respectively, the average and maximum differences between the observed^c and computed volumes.

b	$\psi_2^{(0)}$	c^d	Conc.	c_2	P , kilobars	max x_2	$10^4 \delta_{Av}$	$10^4 \delta_{max}$					
0.7750	0.6652	0.9602 ^e	$(x_2/v_s^{(0)})$	2.278	0	0.525	1.1	-2.3					
					1	0.525	3.	5.					
					3	0.525	5.	6.					
					5*	0.375	6.	10.					
					6	0.375	8.	10.					
					7	0.300	9.	9.					
					8	0.300	12.	12.					
					10	0.300	9.	9.					
					0.8591	0.6631	0.93917 ^e	$(x_2/v_s^{(0)})$	2.247	0	0.525	0.9	-2.0
										1*	0.525	-10.	-14.
5	0.375	-31.	-46.										
0.8591	0.6563	0.9463 ^f	x_2	2.145	0	0.525	0.2	-0.5					
					1*	0.525	-4.	-5.					
					5	0.375	-19.	-29.					

^a $b_2=0.5128$ is the constant in Eq. (10) and was obtained by adapting the volumes of solid ammonium nitrate at the pressures 1, 500, and 1000 bars. See the footnotes in Table III for the derivation of the other constants.

^b The maximum concentration is 52.5% (by weight); data for five concentrations were used at atmospheric pressure. Under pressure the solubility of ammonium nitrate is decreased.

^c The data of L. H. Adams and R. E. Gibson, J. Am. Chem. Soc. 54, 4524 (1932). The compressibility data for the solid ammonium nitrate were also taken from Adams and Gibson, *ibid.*, p. 4530.

^d This is the value of c which corresponds to $x_2=0.15$.

^e $\alpha = (x_2/v_s^{(0)})/0.15844$. The denominator is the value of the numerator when $x_2=0.15$.

^f $\alpha = x_2/0.15$.

TABLE V. The constants^a of the equations for the calculation of the specific volumes at high pressures of aqueous solutions of potassium sulfate^b at 25°C. The volumes at the higher pressures were computed by Eq. (9); and the results are shown in the last two columns where δ_{Av} and δ_{max} are, respectively, the average and maximum differences between the observed^c and computed volumes.

b	$\psi_2^{(0)}$	c^d	Conc.	c_2	P , in kilobars	10% δ_{Av}	10% δ_{max}
0.8591	0.4182	0.9636 ^e	x_2	3.4911	0	0.3	-0.7
					1*	1.5	2.9
					2	4.	4.
0.7750	0.5379	0.9637 ^f	$(x_2/v_s^{(0)})$	10.574	0	0.4	-1.0
					1	5.4	8.5
					6*	2.5	-3.1
					10	-8.6	-13.2
0.7750	0.4554	0.9727 ^e	x_2	5.6923	0	0.3	-0.5
					5*	14.	24.6
					6	12.	21.8

^a $b_2=0.3592$ is the constant in Eq. (10) and was obtained by adapting the volumes of solid potassium sulfate at the pressures 1, 500, and 1000 bars. See the footnotes in Table III for the derivation of the other constants.

^b The maximum concentration is 10% (by weight); data for four concentrations were used.

^c The data of L. H. Adams, J. Am. Chem. Soc. **54**, 2230 (1932). The compressibility data for the solid potassium sulfate are from Adams, *ibid.*, p. 2240; L. H. Adams and R. E. Gibson, J. Wash. Acad. Sci. **21**, 387 (1931).

^d This is the value of c which corresponds to $x_2=0.025$.

^e $\alpha=x_2/0.025$.

^f $\alpha=(x_2/v_s^{(0)})/0.02543$. The denominator is the value of the numerator when $x_2=0.025$.

TABLE VI. The specific volumes of aqueous solutions of sodium chloride to 10 000 bars^a computed from the volumes of the solutions at atmospheric pressure and the compressibility data^b of the solid salt. The constants of Eq. (9') and $\psi_1^{(0)}$, the specific volumes of water in solution (water under the pressure P_i), are given. The volumes of solution at the higher pressures were computed by Eq. (8'). The numbers shown in each column under the designated pressures are the differences between the observed and calculated volumes multiplied by 10⁴. $b=0.7750$. $b_2=0.39$. $c=0.95131$. $c_2=1.986$. $\psi_2^{(0)}=0.5340$.^d

x_2	$v_s^{(0)}$	α^f	$\psi_1^{(0)}$	P_i	$P=0$	$P=1000$	$P=5000$	$P=8000$	$P=10\ 000$
0	1.00293	0.0000	1.0029	0	0	0	0	0	0
0.05	0.96856	1.0000	0.9918	252	-3.8	0	0	0	3
0.10	0.93564	2.0704	0.9806	528	-2.6	0	0	-2	2
0.15	0.90386	3.2147	0.9691	836	-0.1	2	1	2	1
0.20	0.87311	4.4437	0.9576	1171	2.1	1	2	0	0
0.25	0.84310	5.7441	0.9461	1535	0.2	-1	1	0	0

^a The data of L. H. Adams, J. Am. Chem. Soc. **53**, 3783 (1931). The volumes of NaCl solutions at atmospheric pressure were taken from *International Critical Tables*, Vol. III, p. 79.

^b L. H. Adams, J. Am. Chem. Soc. **53**, 3780 and 3806 (1931).

^c The constant in Eq. (10) obtained by adapting the volumes of solid NaCl at the pressures 1, 500, and 1000 bars.

^d These are the constants of Eq. (9') obtained by adapting to this equation the volumes of the solution at atmospheric pressure.

^e Obtained from Eq. (11) with $P=0$. With this value for c_2, ψ_2^P , the volumes of the solute in solution at pressure P , were calculated by Eq. (11').

^f $\alpha=(x_2/v_s^{(0)})/0.051623$. The denominator is the value of the numerator when $x_2=0.05$.

TABLE VII. The specific volumes of aqueous solutions of NH_4NO_3 to 10 000 bars^a computed from the volumes of the solutions at atmospheric pressure and the compressibility data^b of the solid salt. The constants of Eq. (9') and $\psi_1^{(0)}$, the specific volumes of water in solution (water under the pressure P_i), are given. The volumes of solution at the higher pressures were computed by Eq. (8'). The numbers shown in each column under the designated pressures are the differences between the observed and calculated volumes multiplied by 10⁴. $b=0.7750$. $b_2=0.5128$. $c=0.9602$. $c_2=2.278$. $\psi_2^{(0)}=0.6652$.

x_2	$v_s^{(0)}$	α^d	$\psi_1^{(0)}$	P_i	$P=0$	$P=1000$	$P=5000$	$P=7000$	$P=10\ 000$
0	1.00293	0.0000	1.0029	0	0	0	0	0	0
0.15	0.94433	1.0000	0.9938	205	-2.3	-3	4	8	15
0.30	0.88843	2.1258	0.9841	440	0.2	-2	5	10	22
0.375	0.86138	2.7408	0.9789	570	1.0	-5	-5	-9	...
0.450	0.83489	3.3932	0.9736	708	0.8	-3
0.525	0.80893	4.0858	0.9681	875	-1.5	-8

^a The data of L. H. Adams and R. E. Gibson, J. Am. Chem. Soc. **54**, 4524 (1932).

^b L. H. Adams and R. E. Gibson, J. Am. Chem. Soc. **54**, 4530 (1932).

^c The constant in Eq. (10) obtained by adapting the volumes of solid ammonium nitrate at the pressures 1, 500, and 1000 bars.

^d $\alpha=(x_2/v_s^{(0)})/0.15844$. The denominator is the value of the numerator when $x_2=0.15$.

TABLE VIII. The specific volumes of aqueous solutions of K_2SO_4 to 10 000 bars^a computed from the volumes of the solutions at atmospheric pressure and the compressibility data^b of the solid salt. The constants of Eq. (9') and $\psi_1^{(0)}$, the specific volumes of *water in solution* (water under the pressure P_t), are given. The volumes of solution at the higher pressures were computed by Eq. (8'). The numbers shown in each column under the designated pressures are the differences between the observed and calculated volumes multiplied by 10^4 . $b = 0.7750$. $b_2 = 0.3592$. $c = 0.9637$. $c_2 = 10.574$. $\psi_2^{(0)} = 0.5379$.

x_2	$v_s^{(0)}$	α^d	$\psi_1^{(0)}$	P_t	$P=0$	$P=1000$	$P=6000$	$P=8000$	$P=10\ 000$
0	1.00293	0.0000	1.0029	0	0.	0	0	0	0
0.025	0.98314	1.0000	0.9947	186	-1.0	-3	0	-3	0
0.050	0.96392	2.0399	0.9864	383	-0.3	-2	-4	0	4
0.075	0.94509	3.1208	0.9781	592	0.1	-5	-6	2	10
0.100	0.92663	4.2439	0.9698	817	-0.1	-6	0	15	26

^a The data of L. H. Adams, J. Am. Chem. Soc. **54**, 2230 (1932).

^b L. H. Adams, J. Am. Chem. Soc. **54**, 2240 (1932); L. H. Adams and R. E. Gibson, J. Wash. Acad. Sci. **21**, 387 (1931).

^c The constant in Eq. (10) obtained by adapting the volumes of solid potassium sulfate at the pressures 1, 500, and 1000 bars.

^d $\alpha = (x_2/v_s^{(0)})/0.02543$. The denominator is the value of the numerator when $x_2=0.02543$.

by Eq. (9) (and with different values of b) the volumes at higher pressures of aqueous solutions of sodium chloride, ammonium nitrate, and potassium sulfate. The volumes of solutions calculated for the higher pressures agree with the observed values to within a fraction of one percent; but it will be noted that, generally, where the value of b corresponds appropriately to the external pressure, the best results are obtained.

Though this procedure yields good results for volumes of solutions at higher pressures, it also suggests difficulties. The values of c and $\psi_2^{(0)}$ in Eq. (9') depend on the choice of b . This implies, both, that $\psi_2^{(0)}$, the volume of the salt in solution, and c which measures the effect of a given amount of salt on water, depend on the external pressure. Furthermore, the volume of the solute, $\psi_2^{(0)}$, depends upon the particular choice of α as well as b . Thus, it is apparent that Eq. (9'), which defines the volume of the solute in solution, has several inherent uncertainties which must be resolved before we can attribute to these volumes intrinsic meaning.¹²

We outline another approach by which Eq. (9) gives results for the volumes of solutions at higher pressures that are in excellent agreement with experimental data. We assume that $b=0.7750$ and that the exponent α is given by Eq. (7''). This value of b is taken because it corresponds to the external pressure of five kilobars (see Table II) which is half our pressure range. With b and α thus defined, we adjust Eq. (9') to the volumes of solution at atmospheric pressure in the usual way. This determines $\psi_2^{(0)}$, the volume of the solute in solution; and, by using Eq. (8) we obtain $\psi_1^{(0)}$, the volumes of the water in solution (which vary with concentration). The volumes of the solution at higher pressures, v_s , are then calculated by Eq. (8') from the following considerations. Since $\psi_1^{(0)}$ is considered to be a volume of pure water under a pressure, we can find this pressure P_t by Eq. (1) (or from the

volume-pressure curve of water); then, $\psi_1^{(P)}$, the corresponding volume of water in solution at pressure P , is the volume of *water* at pressure $P+P_t$. With this value of $\psi_1^{(P)}$, and the value of $\psi_2^{(P)}$ obtained as previously outlined, $v_s^{(P)}$ for higher pressures are given by Eq. (8').

Tables VI, VII, and VIII show some of the results in computing the volumes of sodium chloride, ammonium nitrate, and potassium sulfate solutions to 10 000 bars with this interpretation of ψ_1 and ψ_2 .¹³ The volumes of the sodium chloride solution are reproduced almost exactly; and though, the results for ammonium nitrate and potassium sulfate do not agree as well as those for sodium chloride, the largest deviation from the experimental values are never more than a fraction of one percent.

REFRACTIVE INDEXES AND DIELECTRIC CONSTANTS OF LIQUIDS AND GASES UNDER PRESSURE

It has recently been shown¹⁴ that the equation

$$(1/f_P) - (1/f_P) = A' \log[(P+B)/(P_0+B)] \quad (12)$$

reproduces refractive index and dielectric constant data for liquids and gases at high pressures. f are the functions of the refractive indexes and dielectric constants which appear in the formulas of Lorenz-Lorentz, Mossotti-Clausius,¹⁵ Gladstone and Dale, the empirical Eykman formula, etc. In these functions, n^2 , the square of the refractive index at pressure P , may be replaced by ϵ , the dielectric constant at pressure P , to obtain the corresponding function involving dielectric constants.

¹³ In these tables $\psi_1^{(0)}$ and P_t are shown for each concentration; P_t/α is essentially constant.

¹⁴ See J. S. Rosen, J. Opt. Soc. Am. **37**, 932 (1947); J. S. Rosen, reference 2(a); B. B. Owen and S. R. Brinkley, Phys. Rev. **64**, 32 (1943).

¹⁵ Frequently referred to as the "Lorentz-Lorenz" and "Clausius-Mossotti" equations. These, according to Partington, Vol. IV, p. 8 and p. 538, do not correctly credit priority or properly spell Mossotti's name.

¹² For an interpretation of the solute volumes of the alkali halides in water obtained by this method, see J. S. Rosen, J. Phys. Chem. **60**, 7 (1956).

TABLE IX. The parameters A' , B' and a' , b' of Eqs. (12) and (14) for the indices of refraction of benzene and the dielectric constants of ammonia. The last two columns give the average and maximum percent deviations between the observed and calculated values of the refractive index (or dielectric constant).

Substance	$t^{\circ}\text{C}$	P_{max}	A'	B'^a	a'^a	b'	(%) _{av}	(%) _{max}
Benzene ^b	25	868 ^d	0.683243	1006.6	0.00016	0.00038
Benzene	25	868	3228.1	3.011	0.0032	0.00621
Benzene ^b	45	1188 ^d	0.699133	859.	0.0026	0.0051
Benzene	45	1188	3192.05	3.0308	0.00275	0.00476
Ammonia ^c	100	55 ^e	28.789	-14.12	0.163	0.314
Ammonia	100	55	41.585	4.796	0.239	0.351

^a Compare B' and a' with B and a for the same substance in Table I.

^b The data of R. E. Gibson and J. F. Kincaid, J. Am. Chem. Soc. **60**, 511 (1938).

^c The data of F. G. Keyes and J. G. Kirkwood, Phys. Rev. **36**, 1572 (1930).

^d Pressure in bars. $\lambda=589 \text{ m}\mu$.

^e The initial pressure is 20 atmos. Equations (12) and (14) are fitted with this value for P_0 and with the value of $1/f_{P_0}$ corresponding to this pressure.

Because of its theoretical value, the Lorenz-Lorentz function $f=(n^2-1)/(n^2+2)$ (or the Mossotti-Clausius function, when n^2 is replaced by ϵ) is of special interest. There is good evidence^{2(a)} that when this function is used, the parameter B' in Eq. (12) is the same as the B determined by the analogous Tait equation (1) for the compressions of the substance. If, then, we compare Eqs. (1) and (12), and assume the parameters B and B' to be equal, we get

$$1/f = sv + i, \quad (13)$$

where s and i are constants independent of the pressure. The analogous formulas of Lorenz-Lorentz and Mossotti-Clausius are $f\nu=C$, where C is the specific refractive or specific polarization "constant." Equation (13) has been shown to hold for existing data at high pressures for both refractive indexes and dielectric constants of liquids (polar, as well as nonpolar) and gases.¹⁶

If we interchange $1/f$ and P in Eq. (12), and introduce the new constants a' and b' , we get the equation

$$P_0 - P = a' \log \left(\frac{1/f_P - b'}{1/f_{P_0} - b'} \right), \quad (14)$$

which also reproduces the variations of the indexes of refraction and dielectric constants of liquids and gases with pressure. If we compare Eqs. (2) and (14), and assume that a and a' are equal, the Eq. (13) again follows. This assumption, that a and a' are equal, is compatible with our previous assumptions that the parameter B involved in Eq. (1) for the compression of the substance is the same as the B' in the analogous interpolation formula (12).

In Table IX are shown the parameters A' , B' and

a' , b' , of Eqs. (12) and (14), fitted by the method of least squares to the indices of refraction of benzene and the dielectric constants of ammonia at high pressures (see also Table I).

It appears from the foregoing treatment that $1/f$, the reciprocal of the Lorenz-Lorentz or Mossotti-Clausius function, and not f , is more significant in representing the variations of n or ϵ with pressure. This view has subsequently been supported by the theoretical analysis of Brown¹⁷ who also derives Eq. (13) and shows that this equation, rather than the Lorenz-Lorentz or Mossotti-Clausius formulas, is more useful in representing experimental data analytically.

A conspicuous difference in the Lorenz-Lorentz and Mossotti-Clausius formulas and Eq. (13) is observed when we consider the dependence of the refractive index or dielectric constant on pressure and temperature; in this respect the older formulas are known to fail¹⁸ significantly. On differentiation, the Lorenz-Lorentz formula gives (with analogous formulas for ϵ)

$$\begin{aligned} dn/dt &= -[(n^2-1)(n^2+2)/6n]\alpha, \\ dn/dP &= [(n^2-1)(n^2+2)/6n]\beta; \end{aligned} \quad (15)$$

where α is the coefficient of thermal expansion and β is the compressibility. The corresponding equations when derived from Eq. (13) are multiplied by the factor svf —a factor which often differs considerably from one.

EQUATIONS FOR VOLUMES OF MIXTURES OF LIQUIDS UNDER PRESSURE

We have previously assumed that ψ_2 , the volume of the solid in solution, is constant for all concentrations at a given pressure P . For a mixture of liquids we cannot make this simplification, but must assume that the volume of each component in solution varies with the concentration.

¹⁶ The constants of Eq. (13) for a number of substances (for both indices of refraction and dielectric constants, and with some pressures up to 12 000 atmos) are given by J. S. Rosen, reference 2(a).

¹⁷ W. F. Brown, J. Chem. Phys. **18**, 1193-1206 (1950).

¹⁸ K. S. Krishnan, Proc. Roy. Soc. (London) **A126**, 155 (1929).

TABLE X. The specific volumes of aqueous solutions of ethyl alcohol to 1500 atmospheres^a computed from the volumes of these solutions at atmospheric pressure and the compressibilities of the pure components. The constants of Eqs. (16) and (2) are given; the volumes at higher pressure having been computed by Eq. (16). The numbers shown in each column under the designated pressure are the differences between the observed and calculated volumes multiplied by 10⁴. ^a $c_1=0.98642$. ^b $b_1=0.8307$. ^c $c_2=0.64777$. ^b $b_2=1.0833$. ^e

$100x_2^d$	α_1^e	α_2^f	$P=0$	$P=500$	$P=1000$	$P=1500$
0	0	2.0	0	0	0	0
10	1	1.8	24	35	38	36
20	2	1.6	5	27	34	35
30	3	1.4	-14	8	13	11
40	4	1.2	-13	5	2	-3
50	5	1.0	-1	7	-7	-12
60	6	0.8	9	7	-7	-29
70	7	0.6	10	6	-11	-40
80	8	0.4	0	-7	-10	-30
90	9	0.2	-14	-20	-7	-28
100	10	0.0	0	0	0	0

^a The data of A. L. T. Moesveld, *Z. physik. Chem.* **105**, 450 (1923); see also J. S. Rosen, *J. Opt. Soc. Am.* **37**, 932 (1947). The volumes of solutions at atmospheric pressure were taken from *International Critical Tables*, Vol. III, p. 117.

^b The constants of Eq. (16). The subscript 1 refers to water and 2 to alcohol.

^c The constant in Eq. (2) which represents the variations of the volumes of the pure component with pressure.

^d The percent (by weight) of alcohol.

^e $\alpha_1=x_2/0.1$.

^f $\alpha_2=x_1/0.5$.

Instead of Eq. (9), we introduce the equation

$$v_s = x_1 c_1^{\alpha_1} (v_1 - b_1) + b_1 x_1 + x_2 c_2^{\alpha_2} (v_2 - b_2) + b_2 x_2, \quad (16)$$

where v_1 and v_2 are the volumes of the pure components of the liquids, while b_1 and b_2 are the constants in Eq. (2) and may be determined by adapting the compressibility data of the pure components to this equation. As in Eq. (9), the exponents α_1 and α_2 indicate the relative concentrations. As before, α_1 is defined by Eq. (7') or (7''); but, we must replace x_2 by x_1 in these equations to define α_2 . c_1 and c_2 are found by writing Eq. (16) for each concentration at $P=0$ and determining by least squares their best values.

If we compare Eqs. (8') and (16), we get

$$\psi_1 = c_1^{\alpha_1} (v_1 - b_1) + b_1, \quad (17)$$

$$\psi_2 = c_2^{\alpha_2} (v_2 - b_2) + b_2, \quad (18)$$

which may be taken as the volumes of each of the components of the liquid in solution. For $c < 1$, the pure component is compressed in solution, and for $c > 1$ its volume expands in solution. When $\alpha_2=1$, we get Eq.

(9) which has been derived on the assumption that the volume of one component in solution is constant for all concentrations at a given pressure.

In Table X we give the parameters of Eq. (16) for mixtures of ethyl alcohol and water (0 to 100%), and the results of computing with these parameters the specific volumes at higher pressures. Though the computed volumes never depart by more than one half of one percent from the experimental values, Table X, undoubtedly, presents an oversimplified picture of the complex behavior of water and alcohol solutions. We can only tentatively indicate the more probable state: the effect of alcohol is to increase the volume of the water in solution at the lower and higher concentrations, and to compress the water in solution at intermediate concentrations. On the other hand, the effect of the water, it appears, is to compress the alcohol in solution at all concentrations. This conclusion has been reached by adapting the volumes of alcohol and water, extending over small ranges of concentration, to Eq. (9) instead of Eq. (16) and by assuming that ψ_2 , the volume of alcohol in solution, is practically constant at a given pressure over these small intervals of concentration.