

tween two fairly large quantities. Consequently, values of the heat of mixing calculated from constants of the pure liquids are not in very good agreement with the experimental values. The extent of the deviation is evident from Figs. 1 and 2 and from the values in col. 5 of Table II. However, in a free energy calculation (vapor pressure or solubility) the heat of mixing appears only as a correction term to a value calculated by Raoult's law. For this reason relatively rough values for the heat of mixing determined by equation (3) are sufficiently accurate to permit calculation, in conjunction with Raoult's law, of fairly accurate values for the free energy of regular solutions.

Acknowledgment.—The author wishes to express his gratitude to Professor Joel H. Hildebrand for suggesting this research and for his kind advice and help during the course of the work. He also wishes to thank Dr. M. J. Young and Mr. Melvin Arighi who assisted with some of the calculations and experimental measurements.

Summary

A calorimeter has been devised which is suitable for the measurement of heat capacities and of heats of mixing of corrosive liquids which must be

kept in a closed system to avoid decomposition. The experimental data obtained include heat capacities and heats of formation of solutions of carbon tetrachloride and silicon tetrachloride, carbon tetrachloride and benzene, carbon tetrachloride and *n*-heptane, benzene and *n*-heptane, and heat capacities of solutions of stannic chloride and carbon tetrachloride and of all the pure liquids, all at 25°.

The heats of mixing have been used to test the validity of the equation:

$$\Delta H = \frac{N_1 V_1 N_2 V_2}{N_1 V_1 + N_2 V_2} \left[\left(\frac{E_1^0}{V_1} \right)^{1/2} - \left(\frac{E_2^0}{V_2} \right)^{1/2} \right]^2 = \frac{N_1 V_1 N_2 V_2}{N_1 V_1 + N_2 V_2} D_{12}^2$$

It is concluded that (1) the equation can be used to calculate satisfactory values of the heat of mixing over the whole concentration range if one experimental value is available from which to determine the parameter D_{12}^2 empirically, and (2) the equation gives encouraging results for the heat of formation of carbon tetrachloride-silicon tetrachloride solutions when the parameter D_{12}^2 is determined from E^0/V values. These substances satisfy most closely the assumptions made in deriving the equation.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

The Compressions of Solutions of Certain Salts in Water, Glycol and Methanol

BY R. E. GIBSON

During the last few years papers from this Laboratory have reported the results of measurements of the compressions up to 1000 bars of a number of aqueous solutions mostly of salts.¹ It was found that the volume changes of aqueous solutions may be well represented as functions of the pressure by equations of the type

$$-\Delta P \bar{v}/x_1 + x_2/x_1 \Delta P \bar{v}_s = C \log \frac{B + P_e + P}{B + P_e}$$

and, as B and C are obtained from measurements on pure water ($x_1 = 1$ and $P_e = 0$), one compression measurement is sufficient to determine P_e , the effective pressure of the solution. Thus from measurements of compressions between 1 and 1000 bars it was possible to obtain close estimates

of the compressibilities of the solutions at any pressure.

In the course of these investigations several questions concerning the specific effects of different salts on the thermodynamic properties of water arose. A comparison of the effects of equivalent amounts of salts on the compressibility of water showed that in general a lyotropic series of anions and of cations was discernible, that is to say, the larger the ion or the smaller its charge the less was its effect in lowering the compressibility of water and consequently the less was the effective pressure of the solution. Ions with high values of the charge to radius ratio such as Li^+ , Be^{++} or Mg^{++} , however, lowered the compressibility of water much less than a simple picture of the forces between the ions and the

(1) (a) R. E. Gibson, *THIS JOURNAL*, **56**, 4 (1934); (b) *ibid.*, **56**, 865 (1934); (c) *ibid.*, **57**, 284 (1935); (d) *ibid.*, **57**, 1551 (1935).

solvent would lead one to expect. Furthermore, recent measurements² and an examination of the values in the literature demonstrated that the thermal expansibility of water in an aqueous salt solution is by no means that of pure water under a pressure equal to the effective pressure of the solution. To throw light on these questions, and to extend the empirical search for those properties of the pure components which are of significance in the prediction of the behavior of a solution under changes of pressure and temperature, the compressions of a number of salts in glycol and methanol were determined and will be discussed in this paper. These two solvents differ markedly in compressibility, glycol being less compressible and methanol more compressible than water, and they dissolve large amounts of a number of salts.

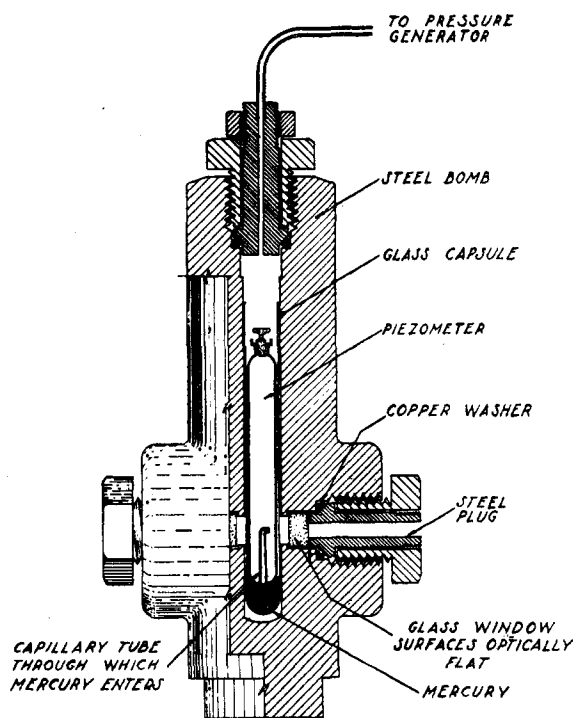


Fig. 1.—Diagrammatic sketch of apparatus permitting visual observation of piezometers under moderate pressures.

Experimental

Most of the compressions were determined with the apparatus described in the preceding papers,^{1a} but during the course of the work a new pressure bomb fitted with two glass windows was introduced and led to a material improvement in the precision of the results. The details of this bomb are illustrated in Fig. 1. The windows of port-hole glass were ground optically flat and so were the faces of the hardened stainless-steel plugs which hold them in

(2) R. E. Gibson and J. F. Kincaid, *THIS JOURNAL*, **59**, 25 (1937).

place. The flat adjacent surfaces of the windows and the steel plugs were washed with alcohol and pressed together, no adhesive being used. These windows, which have an aperture of $\frac{5}{16}$ inch (8 mm.) are of the general design proposed by Poulter³ and have proved to be very satisfactory. The apparatus supported pressures of 1500 bars at 60° for several hours on a number of occasions and pressures of 1000 bars for half an hour at least fifty times. There was never any sign of leakage.

In a compression experiment the piezometer was placed so that the end of the capillary through which the mercury entered was in line with the two windows. The capillary was illuminated through one window and observed with the help of a microscope through the other. A right-angled prism between the observation window and the microscope reduced wear on the nerves of the observer. In this apparatus it was possible to adjust the highest pressure so that the mercury was just flush with the tip of the capillary and all uncertainty as to the magnitude of the last drop was removed. It was observed that the size of the drops varied quite widely, being approximately 0.002–0.003 ml. when the piezometer contained water and 0.0015 ml. when it contained a 10% solution of lithium bromide. It may be remarked that with slight modification this apparatus may be used for determining the effect of pressure on interfacial tensions between mercury and other liquids.

In the course of a year six observations of the compression of water were made in one piezometer and the maximum departure from the mean was a part in a thousand, the precision of the pressure reading. In this work we also introduced a flat-topped piezometer made of vitreous silica. When the apparent compression of water to 1000 bars measured in this piezometer was corrected for the compressibility of vitreous silica as measured directly,⁴ the figure 0.03930 ± 0.00004 ml./ml. was obtained for the true compression of this liquid to 1000 bars at 25°. From measurements in the Pyrex glass piezometers we have the value 0.03935 ± 0.00005 ml./ml. The agreement between the values of the compression of water obtained in these piezometers of different materials gives us considerable confidence in the glass piezometer as a precision instrument despite statements to the contrary found in the literature.⁵

The purification of the glycol⁶ and methanol^{1d} and of all the salts except cadmium iodide has already been described. Three samples of cadmium iodide, Baker c. p. analyzed, with and without recrystallization, and Merck Reagent preparation were used. The specific volumes of aqueous solutions of these different samples were consistent to two or three in the fifth decimal place.

Results

We have already published the specific and apparent volumes of most of the solutions which form the subject of this paper, but there remain a few re-

(3) T. C. Poulter, *Phys. Rev.*, **40**, 860 (1932).

(4) L. H. Adams and R. E. Gibson, *J. Wash. Acad. Sci.*, **21**, 381 (1931); P. W. Bridgman, *Am. J. Sci.*, **10**, 363 (1925). The compression of vitreous silica between 1 and 1000 bars was taken as 0.00276 ml./ml.

(5) See, for example, P. W. Bridgman, "The Physics of High Pressure," G. Bell & Sons Ltd., London, 1931, p. 121.

(6) R. E. Gibson and J. F. Kincaid, *THIS JOURNAL*, **59**, 579 (1937).

sults of specific volume determinations made with the same apparatus and procedure which are now given in Table I. Our observations of the compressions of pure glycol to different pressures are

TABLE I

SPECIFIC VOLUMES OF DIFFERENT SOLUTIONS AT 25.00°

100 x_2	v	ϕ_2	$(v_{obsd.} - v_{calcd.}) \times 10^3$
Sodium Bromide-Methanol $\phi_2 = 0.02630 + 0.2599 x_2^{1/2}$			
0.000	1.2713 ₈		
3.097	1.2342 ₄	0.0720	- 1
6.257	1.1975 ₄	.0913	- 1
9.480	1.1609 ₇	.1061	- 2
13.368	1.1176 ₅	.1214	1
Cadmium Iodide-Methanol $\phi_2 = 0.13765 + 0.02831 c_2$			
3.331	1.2337 ₂	0.1391	2
5.767	1.2061 ₅	.1403	7
11.661	1.1395 ₇	.1410	5
20.993	1.0345 ₉	.1434 ₃	1
29.999	0.9339 ₉	.1467 ₀	- 1
41.559	.8062 ₆	.1521 ₉	- 2
50.628	.7076 ₇	.1579 ₄	+ 2
59.332	.6147 ₀	.1645 ₇	-18
Cadmium Iodide-Water $\phi_2 = 0.16970 + 0.02548 x_2^{1/2}$			
0.000	1.00293		
2.838	0.9794 ₁	0.1743	- 9
4.990	.9617 ₇	.1782	- 5
5.625	.9565 ₈	.1789	- 3
7.530	.9409 ₉	.1803	- 1
9.847	.9220 ₆	.1816	1
15.446	.8763 ₃	.1834 ₃	2
19.993	.8393 ₁	.1845 ₆	- 1
24.574	.8020 ₆	.1855 ₂	- 3
29.523	.7618 ₉	.1865 ₀	- 5
39.396	.6820 ₇	.1884 ₇	4
40.324	.6745 ₅	.1885 ₇	2
Cadmium Iodide-Glycol $\phi_2 = 0.19687 + 0.00979 x_2$			
0.000	0.90101		
5.501	.86231	0.1974	0
10.102	.83000	.1980	1
17.567	.77762	.1985 ₅	- 1
29.650	.69306	.1996 ₃	- 4
38.461	.63160	.2005 ₇	- 3
49.836	.55260	.2018 ₃	7

TABLE II

THE COMPRESSIONS OF GLYCOL AT VARIOUS PRESSURES AT 25°

Pressure range in bars	k , ml./ml.	$-\Delta P v$, ml./g.	$-\Delta P v$, (obsd. - calcd.) $\times 10^4$
1-300	0.0104 ₀	0.00937 ₇	-0.2
1-500	.0168 ₃	.0152 ₀	.8
1-800	.0257 ₂	.0231 ₇	.6
1-1000	.0312 ₄	.0281 ₄	- .2
1-1250	.0376 ₉	.0339 ₆	.6

recorded in Table II. In Table III the compressions of the different solutions together with related quantities of interest are tabulated. At the head of each section is given a simple equation which represents the data adequately.

TABLE III

THE COMPRESSIONS TO 1000 BARS AND RELATED QUANTITIES FOR DIFFERENT SOLUTIONS AT 25°

100 x_2	$k \times 10^4$	$-\frac{\Delta P v}{x_1} \times 10^4$	$\frac{\Delta P \phi_2}{\times 10^4}$ (Mean)	$(v_{obsd.} - v_{calcd.}) \times 10^4$	P_0 (in kilobars)
Sodium Iodide-Methanol $10^4 \Delta P \phi_2 = 1027.8 - 889.4 c_2^{1/2}$					
0.000		1018.0			
7.287	744.8	954.1	806.1	0.4	0.081
	745.6	955.2		- .7	
14.520	692.4	896.8	709.1	- .2	.160
	693.6	898.3		1.3	
22.774	635.9	838.1	605.5	0.9	.255
	638.1	840.9		-1.9	
31.287	583.0	787.3	506.7	2.1	.356
38.209	539.9	748.7	435.9	1.5	.441
	539.5	748.2		1.0	
Lithium Bromide-Methanol $10^4 \Delta P \phi_2 = 1680.0 - 1535.6 x_2^{1/2}$					
4.033	753.3	960.3	137.3	0	0.071
7.187	719.5	920.0	126.5	-0.1	.125
15.833	630.8	816.7	107.0	.2	
	630.6	816.5		.4	.289
24.352	545.5	719.5	927	1.7	.487
30.123	489.8	657.1	837	0	.650
35.114	442.3	603.9	765	-2.6	.818
Sodium Bromide-Methanol $10^4 \Delta P \phi_2 = 1549.4 - 1674.2 x_2^{1/2}$					
3.097	767.2	977.3	1273	0.6	0.050
6.257	738.2	943.1	1122	- .6	.094
9.480	709.9	910.5	1026	- .8	.139
13.368	676.8	873.2	940	.3	.196
	676.3	872.5		1.0	
Cadmium Iodide-Methanol $10^4 \Delta P \phi_2 = 331.0 - 176.6 c_2$					
5.767	779.4	997.6	333	0.7	0.027
11.661	757.0	977.3	308	- .6	.052
20.993	717.0	938.9	297.7	.7	.104
29.999	674.9	900.5	274.2	- .1	.161
41.559	614.4	847.6	239.6	- .3	.251
50.628	563.3	808.1	204.7	0	.330
59.332	514.3	777.4	164.9	6.4	.406
	514.2	777.2	165.1	6.6	
Sodium Iodide-Water $10^4 \Delta P \phi_2 = 152.5 - 93.55 c_2^{1/2}$					
0.000		393.5	394.6		
10.016	370.1	381.2	120.4	0.1	0.118
19.740	346.1	368.0	108	.2	.272
34.424	306.1	347.2	90.3	- .3	.555
44.546	276.3	333.3	76.3	.1	.791
	276.7	333.8		- .4	
49.706	260.5	326.9	68.5	-1.0	.931
50.483	256.9	324.5	68.3	0.3	.971

TABLE III (Concluded)

100 x_2	$k \times 10^4$	$-\frac{\Delta P^0}{x_1} \times 10^4$	$\frac{\Delta P\phi_2}{\times 10^4}$ (Mean)	$\frac{(A_{obsd.} - A_{calcd.})}{\times 10^4}$	P_e (in kilobars)
Cadmium Iodide-Water					
0.000		394.0			
2.838	390.3	393.4	21		0.000
4.990	388.3	393.1	17		.005
5.625	387.1	392.4	27		.009
7.530	384.8	391.6	29		.019
15.446	374.1	387.7	34		.070
	374.0	387.6			
24.574	360.3	383.7	31.6		.122
40.324	334.7	378.3	23.2		.233
Sodium Iodide-Glycol					
$10^4 \Delta P\phi_2 = 92.4 - 153.1 x_2^{1/2}$					
0.000	312.3	281.4			
3.807	306.6	279.3	53	0.3	0.023
7.847	300.2	277.1	51	.1	.057
15.667	289.9	275.6	32	.1	.100
	289.7	275.3			
21.523	283.6	276.6	18	-1.0	.109
30.506	272.1	277.9	7.9	0.1	.130
34.879	267.2	280.1	1.9	.1	.127
39.869	261.2	283.1	-2.6	1.1	.120
Potassium Iodide-Glycol					
$10^4 \Delta P\phi_2 = 30.2 - 107 x_2$					
6.857	303.5	279.9	20	-0.2	0.028
13.469	294.3	278.6	18	.3	.070
20.924	285.0	279.2	8	.1	.097
28.526	275.8	281.4	0	.1	.115
Cadmium Iodide-Glycol					
$10^4 \Delta P\phi_2 = -4.0 - 45.0 x_2$					
5.501	308.4	281.4	0	0.4	
10.102	305.6	282.1	-6	.2	
17.567	300.9	283.3	-11.3	.1	
29.650	293.2	288.3	-17.6	-.1	
38.461	287.2	294.3	-21.4	-.1	
49.836	279.4	307.3	-26.6	-.2	
Lithium Bromide-Glycol					
$10^4 \Delta P\phi_2 = 188.4 - 217 x_2^{1/2}$					
4.069	302.1	275.6	137	-0.4	0.064
8.115	291.4	269.6	130	-.6	.141
	292.1	270.2		0	.134
12.360	282.4	265.6	112	0	.199
20.593	264.3	258.0	90.2	.1	.319
30.100	244.2	251.3	69.9	.2	.444
Sodium Bromide-Glycol					
$10^4 \Delta P\phi_2 = 152 - 202 x_2^{1/2}$					
4.647	302.1	276.3	105	-0.2	0.057
9.361	292.2	271.9	92.0	.2	.119
15.215	281.4	268.2	73.5	.1	.181
19.569	273.7	266.2	62.5	0	.220
24.983	264.4	264.4	51.0	0	.261
Sodium Bromide-Glycol (Compressions to 500 bars)					
$10^4 \Delta P\phi_2 = 78 - 82 x_2^{1/2}$					
4.647	162.3	148.6	72	0.6	
9.361	157.3	146.4	54	.1	
15.215	151.0	143.9	45	-.2	
19.569	146.0	142.0	41	-.1	
24.983	139.6	139.6	37	.1	

Discussion of Results

Apparent Volumes at Atmospheric Pressure.—

Cantelo and Phifer⁷ from an analysis of the density data in the "International Critical Tables" and from results of their own (not published) concluded that the partial molal volume and hence the apparent molal volume of cadmium iodide has the constant value of 67.16 ml./mole or 0.1634 ml./g. in aqueous solutions containing from 2 to 45% cadmium iodide. According to our results the apparent volume of cadmium iodide does vary with concentration, not very rapidly, however, in the more concentrated solutions. It is noteworthy that ϕ_2^s is by no means a linear function of $c_2^{1/2}$ even in the dilute solutions, indeed a linear function of $c_2^{1/2}$, which, as will be seen in Table I, fits quite well in the more concentrated solutions, breaks down in the dilute range, ϕ_2 for cadmium iodide diminishing more and more rapidly as the solution becomes very dilute. In this and other respects⁹ cadmium iodide acts as a moderately weak electrolyte like sulfuric or phosphoric acids whose behavior has been discussed by Geffcken and Price.¹⁰ McBain, van Rysselberghe and Squance^{9b} concluded that the conductance ratio, α , measures substantially the dissociation of cadmium iodide in aqueous solutions and the data of Jones^{9c} indicate that over a concentration range from 3 to 20% by weight α varies from 0.25 to 0.15. Following the treatment of Geffcken and Price we plotted

$$\Phi_2 - 3.5 \left(\sum \frac{\alpha v_i z_i^2}{2} \right)^{1/2} C_2^{1/2} = \Phi_2^0$$

against $(1 - \alpha)$, it being impossible to compute the "true" degree of association by the method of Sherrill and Noyes,¹¹ as Geffcken and Price did. The points were substantially on a straight line which, although it covered only a very short

(7) R. C. Cantelo and H. E. Phifer, *THIS JOURNAL*, **55**, 1333 (1933).

(8) The symbols used here are as follows. The subscripts 1 and 2 refer to the liquid solvent and the salt in solution, respectively, the subscripts w and s stand for pure solvent and pure solid salt. ΔP indicates the increase with pressure of the quantity to which it is prefixed. The weight fraction is represented by x , the grams per ml. by c , the moles per liter by C , the moles per 1000 g. of solvent by m , the specific volume in ml. by v , the apparent volume by ϕ , the apparent molal volume by Φ , the partial volume of the solute by v_2 and the molecular weight by M . The relative volume change with pressure is represented by k . The number of ions of charge z into which a salt dissociates is given by ν . $A = (\Delta P^0/x_1 - \Delta P^0 v_0)$.

(9) (a) E. Doehlemann and H. Fromherz, *Z. physik. Chem.*, **171A**, 353 (1935); (b) J. W. McBain, P. J. van Rysselberghe and W. A. Squance, *J. Phys. Chem.*, **35**, 999 (1931); (c) F. H. Getman, *ibid.*, **32**, 940 (1928).

(10) W. Geffcken and D. Price, *Z. physik. Chem.*, **B26**, 91 (1934).

(11) M. S. Sherrill and A. A. Noyes, *THIS JOURNAL*, **48**, 1861 (1926).

range, $(1 - \alpha)$ varying from 0.75 to 0.85, was extrapolated in both directions and it was found that when $(1 - \alpha) = 0$, $\Phi_2^0 = 35$ ml. and when $(1 - \alpha) = 1$, $\Phi_2^0 = 73.4$ ml. This latter value lies between 64.6 ml., the molal volume of solid cadmium iodide and 74.8 ml., the partial molal volume of cadmium iodide in the most concentrated glycol solution, and seems reasonable if we assume that undissociated cadmium iodide dissolves in water with little or no contraction. The value of Φ_2^0 for the completely dissociated salt is small and indicates that in infinite dilution Cd^{++} and I^- cause a very large contraction on mixing with water, approximately 29.6 ml. per mole of cadmium iodide. Although this contraction is large it is not unreasonable. Conservative estimates of the contractions occurring when calcium chloride and barium chloride are mixed with water in infinite dilution are respectively 33.7 and 29.73 ml. per mole. The molal volumes of these solid salts were taken from the data of Gillespie and Gerry.¹² For barium chloride in solution Φ_2 at zero concentration was computed by the equation given by Gibson and Kincaid² (p. 30) and for calcium chloride in solution Φ_2 at zero concentration was obtained by graphical extrapolation of apparent volumes computed from Pesce's¹³ results.

The non-aqueous solutions of cadmium iodide behave quite differently from the aqueous solutions. Both in methanol and in glycol ϕ_2 is a linear function of the first power of the concentration over a very large range. The conductance and osmotic data available indicate that cadmium iodide is very much less dissociated (0.1 or less) in methanol than in water solutions. The same undoubtedly holds for the glycol solutions. This linear relation between ϕ_2 and c_2 suggests that the salt is behaving as practically a non-electrolyte in these solutions. It may be remarked that solutions in glycol containing up to 20% cadmium iodide did not turn yellow on exposure to air even after a year.

Compressions to 1000 Bars.—The apparent compressions to 1000 bars, $\Delta_P\phi_2$, are in general well represented as linear functions of the square root of the concentration. The weight fraction is used wherever adequate on account of its convenience. The apparent compressions of cadmium iodide in all three solvents do not, however, follow the square root law. In water $\Delta_P\phi_2$ is positive but

(12) L. J. Gillespie and H. T. Gerry. *THIS JOURNAL*, **53**, 3962 (1931).

(13) G. Pesce, *Z. physik. Chem.*, **160A**, 295 (1932).

very small and although there is considerable uncertainty in the figures given it must be concluded that $\Delta_P\phi_2$ at first increases with concentration and passes through a maximum. In methanol and glycol $\Delta_P\phi_2$ for cadmium iodide varies linearly with the first power of the concentration up to 50% solutions. The glycol-cadmium iodide solutions furnish our first example of negative values of $\Delta_P\phi_2$ over the whole range at low pressures in a salt solution. Evidently the cadmium iodide has only a very small effect in reducing the compressibility of glycol, probably because the dissociation of the salt is so small.

In order to calculate the effective pressures of these solutions, we fitted equations of the form of the Tait equation to our results for methanol¹⁴ and glycol. Equations (1) and (2) express quite adequately the specific compressions of methanol and glycol, respectively.

$$-\Delta_P v = 0.2807 \log(0.764 + P) - \log 0.765 \quad (1)$$

$$-\Delta_P v = 0.2054 \log(2.706 + P) - 0.08879 \quad (2)$$

In these equations P is in kilobars (10^9 dynes per cm^2).

Equation (2) may be used for extrapolation to high pressures and it agrees with Bridgman's data,¹⁴ but equation (1) could not be tested at higher pressures, there being no reliable data; furthermore the high compressibility of the liquid leads us to expect that any extrapolation exceeding 1500 bars will be dangerous. It should also be remarked that, although equation (1) fits the data within experimental error at 300 and 1000 bars, there are deviations of the order of 0.5% at 500 and 800 bars. The compressibility of methanol at 1 bar computed by equation (1) has the value 125.3×10^{-6} ml. per ml. per bar which is close to 125.6 interpolated from the data of Freyer, Hubbard and Andrews.¹⁵

By means of equations (1) and (2) and with the assumption that the compression of the solute is the same as in the pure solid state, we computed values of the effective pressure P_e for the different solutions. That P_e determines the compressibilities of the non-aqueous solutions at all pressures, as it does in the aqueous solutions we have studied, is still to be proved, but it was found that the compressions of sodium bromide-glycol solutions to 500 bars could be computed with an average error of less than 1% from the effective

(14) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **67**, 1 (1932).

(15) E. B. Freyer, J. C. Hubbard and D. H. Andrews, *THIS JOURNAL*, **51**, 759 (1929).

pressures calculated from the compressions at 1000 bars. The effective pressures given for sodium, potassium and cadmium iodide in glycol are only approximate. The quantity $\Delta p v_s / x_1$ changes very little with concentration in these solutions, and hence P_e depends too much on the correction for the compression of the solute. In glycol-cadmium iodide solutions any reasonable value of $\Delta p v_s$ gives negative values of P_e . In Fig. 2, P_e is plotted against the molality m for aqueous and glycol solutions of the different salts. It will be noticed that in glycol solutions the lithium salt no longer occupies the anomalous position it has in the aqueous solutions but that for equivalent solutions P_e increases in the order $KI < NaI < NaBr < LiBr$. The differences are large enough to be outside the uncertainties in the calculation of P_e that we have just emphasized. The relatively small values of P_e for lithium salts as compared with those of sodium or potassium salts in aqueous solutions seem, therefore, to depend on the water.

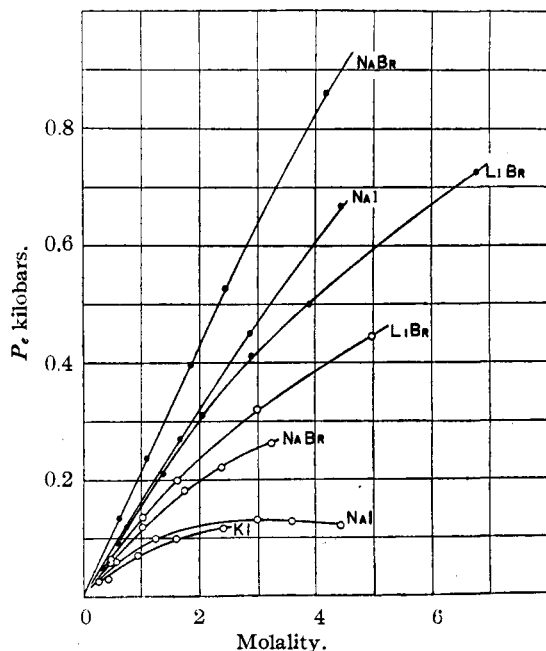


Fig. 2.—The effective pressures as functions of the molality for solutions of some salts in water and glycol. The open circles represent solutions in glycol, the dots solutions in water.

In the methanol solutions also, P_e for lithium bromide is certainly not less than P_e for the sodium salt (see Fig. 3), but in these solutions a rather unexpected feature was encountered, namely, that up to concentrations of 2 molal the

points of all the solutions lie on the same curve. This may be a coincidence but the similar effects of salts like sodium bromide and cadmium iodide which differ so widely in water and glycol solutions do call for explanation.

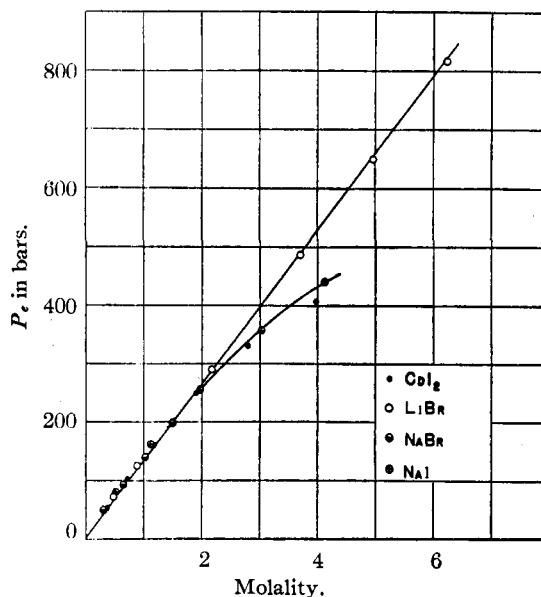


Fig. 3.—The effective pressures of methanol solutions of four salts as functions of the number of moles of salt per 1000 g. of alcohol.

It has already been noted that the effective pressures seem to play only an unimportant role in determining the thermal expansibilities of aqueous salt solutions. On the other hand, we observe a distinct parallelism between the effective pressures and the thermal expansibilities of glycol solutions. Both these features are illustrated in Fig. 4 where the differences between the specific thermal expansibility of the pure solvent and the solvent in different solutions (the specific thermal expansibility of the solute being assumed to be the same as in the pure solid state) are plotted against the effective pressures. It will be seen that the points for the different aqueous solutions scatter widely apart whereas those for the glycol solutions almost fall on one curve. From our results we cannot say definitely that P_e determines quantitatively the thermal expansibility of the solvent. The assumptions we have used, however, all tend to spread the curves apart and certainly the difference between the aqueous and the glycol solutions is very significant. If the P_e -expansibility curve for lithium bromide-glycol solutions were applied to compute the coef-

ficient of expansion of sodium bromide or sodium iodide-glycol solutions the maximum error in $(dv/dT)_P$ would be about 5%.

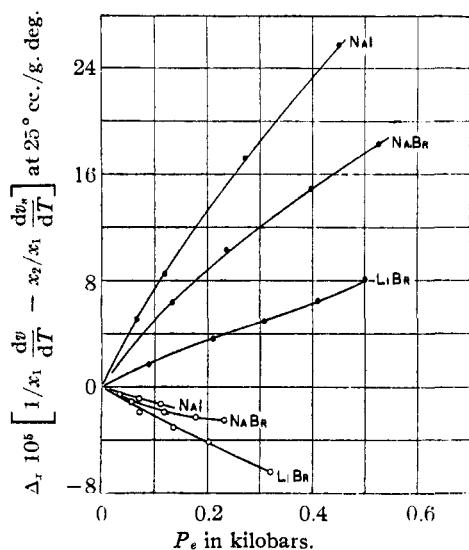


Fig. 4.—A comparison of the change in the apparent expansibility of the solvent as a function of the effective pressure for water and glycol solutions of different salts. The open circles represent the glycol solutions.

Partial Volumes at Different Pressures.—

From our data we have computed the partial volumes¹⁶ of the salts in different solvents and at different pressures. A sample of these results is given in Fig. 5. Generally speaking, in the non-aqueous as well as in the aqueous solutions the partial and the apparent volumes of the salts increase with pressure and the more compressible the solvent the larger is the initial value of $\Delta_P v_2$ and the steeper its diminution with concentration. The increase with pressure of the partial volumes of the salts in solution is not as mysterious a phenomenon as it is sometimes alleged to be. If contraction accompanies the formation of a solution and if the compressibility of the solvent decreases with pressure, it follows at once that $\Delta_P v_2$ must be positive at least in dilute solutions.

The quantity $(v_2 - v_s)$ depends on the difference between the compressibility of the solvent and the solute. The compressibilities of the solutes we have investigated are all small and we find that decrease in the compressibility of the solvent either by change of its nature (*i. e.*, change

from methanol to glycol) or by increase of the external pressure is accompanied by an algebraic increase in $(v_2 - v_s)$. It may also be noted that for different solutes $(v_2 - v_s)$ decreases algebraically as P_e increases. The curves in Fig. 5 show that at higher pressures $(v_2 - v_s)$ for a given solute depends less on the solvent than at low pressures. The more compressible a liquid is the more rapidly does its compressibility diminish with pressure and we may safely extrapolate our results to say that at very high pressures $(v_2 - v_s)$ for a given solute will become practically independent of the solvent and depend almost entirely on the volume change on fusion of the solute.

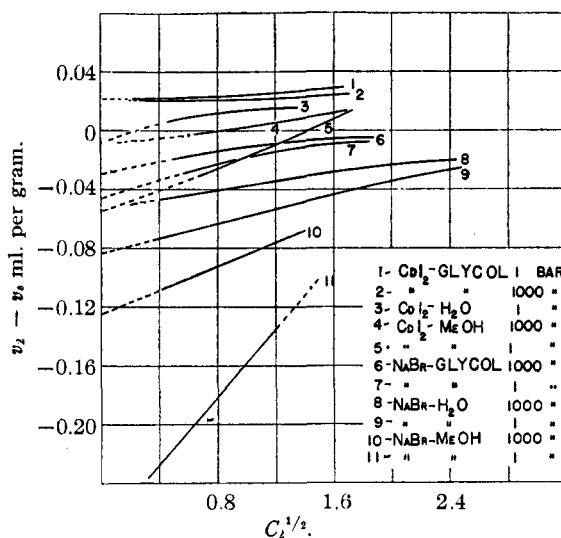


Fig. 5.—The expansions produced per gram of salt when sodium bromide and cadmium iodide are added to solutions in different solvents at different concentrations and pressures.

A necessary but not sufficient condition for an ideal solution according to the generally accepted definition¹⁷ is that the partial volumes of the components in the solution shall be equal to their volumes in the pure liquid state. At high pressures the solutions all approximate to this condition not because they become more ideal but merely because the attractive forces between solvent and solute produce less diminution in volume when the components become less compressible. When a liquid is compressed the repulsive forces increase much more rapidly than do the attractive forces. Likewise the contraction on formation of a solution in methanol is considerably greater than for the corresponding solution in

(16) For methods see L. H. Adams and R. E. Gibson, *THIS JOURNAL*, **54**, 4520 (1932), and F. T. Gucker, Jr., *J. Phys. Chem.*, **38**, 307 (1934).

(17) J. H. Hildebrand, "The Solubility of Non-electrolytes." Reinhold Publishing Corporation, New York, 1936, p. 59.

water although in general P_e is greater in the aqueous solution. The effective pressure is, therefore, a better criterion of ideality than the volume change on mixing.

As the chemical potential of a component in a phase must always be an increasing function of its concentration, it follows from well-known formulas¹⁸ that the solubility of a solid in a liquid will be raised or lowered by pressure according as $(v_2 - v'_s)$ is negative or positive, where v'_s is the specific volume of the solid phase whose solubility is under investigation (pure salt or addition compound). Thus for a given solute in different solvents we may expect an increase in solubility with pressure at low pressures in the more compressible solvents, particularly if P_e is large, and that this increase with pressure will diminish as the pressure is raised. In the less compressible solvents increase of pressure may lower the solubility even at atmospheric pressure. At high pressures the change in solubility of a solid with pressure will have a sign which is independent of the solvent and will in general be negative as it depends only on the sign of the volume change on melting of the solid.

(18) L. H. Adams, *THIS JOURNAL*, **53**, 3804 (1931).

Summary

The specific volumes and compressions of a number of solutions of salts in methanol, glycol and water have been determined, a new apparatus being used for the latter measurements. From these data apparent volumes and compressions and effective pressures have been computed. The apparent volumes of cadmium iodide in aqueous solution were found to vary with concentration in a manner different from that described in the literature.

The non-aqueous solutions behave under pressure in many ways like the aqueous solutions but they differ in three significant respects. The effective pressures of lithium bromide are greater than those of sodium bromide in glycol solutions, there is a marked correlation between the effective pressures and the apparent thermal expansibilities of glycol in different salt solutions, and up to 2 molal, methanol solutions of four salts whose aqueous solutions differ markedly all have the same effective pressures. The partial volumes of the salts in different solvents at different pressures have been examined and certain general conclusions about the course of pressure-solubility curves have been drawn.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Calorimetric Investigations of Organic Reactions. I. Apparatus and Method. The Inversion of Sucrose and the Decomposition of Diacetone Alcohol¹

BY JULIAN M. STURTEVANT

Introduction

Physical methods have been used frequently for the measurement of the velocities of homogeneous chemical reactions in solution. Such methods for making this fundamental chemical measurement are chiefly of importance in those cases to which analytical methods are inapplicable; such cases arise frequently in the organic field where analytical procedures are relatively few in number and inferior in accuracy.

Physical methods which have received most attention are based on changes in such properties as density, optical rotatory power, refractive index and electrical conductivity. Most of these methods are rather restricted in applicability. A method

based on following the evolution or absorption of heat during reaction should be much more widely applicable, since nearly all reactions proceed with an appreciable change in heat content. Aside from its general applicability, such a calorimetric method should have several advantages which will be discussed briefly.

Many physical methods require the use of relatively concentrated solutions in order that an appreciable change in the observed property be obtained. The great sensitivity attainable in calorimetric measurements would make it possible to work with dilute solutions even with reactions involving very small heat changes, and in many cases to obtain an accuracy not easily reached by other methods.

It is only necessary to determine the heat capac-

(1) Presented at the Chapel Hill meeting of the American Chemical Society, April, 1937.