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.

WASHINGTON, D. C. RECEIVED OCTOBER 21, 1940

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[20] T. J. Webb, THIS JOURNAL, **48**, 2589 (1926); J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 540 (1933); A. Voet, *Trans. Faraday Soc.*, **32**, 1301 (1936).

[21] W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

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

BY AARON E. MARKHAM AND KENNETH A. KOBE

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.

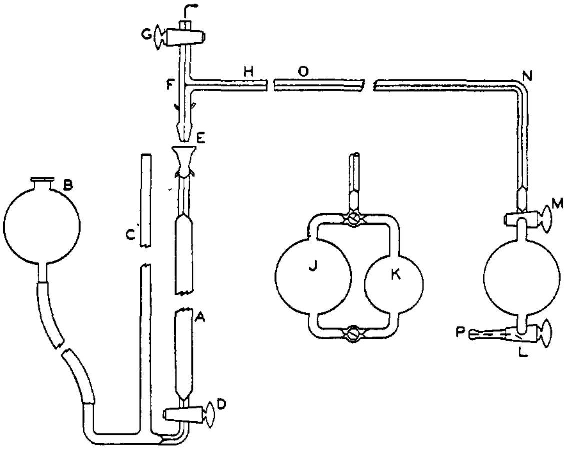

Fig. 1.—The gas solubility apparatus.

The absorption flask consists of two bulbs, J and K, one having about twice the volume of the other. They are connected at the bottom through the three-way cock L, and at the top through the three-way cock M. A capillary tube leads from M to O. Immediately above M is a small enlargement of the capillary, to trap liquid that might otherwise be forced up to the capillary when filling with gas.

During a run, the absorption flask is in a thermostat, whose water level comes nearly up to N. The buret and manometer tube C are jacketed in a large glass tube through which water flows from the thermostat, being returned to the thermostat by an air-lift. A still larger glass tube surrounds this one, providing an air space to reduce heat interchange. The tube from E to H is capillary, so only a very small volume of gas is outside the thermostat. At 0.2° the variation in temperature was occasionally as much as 0.1°, and at the other temperatures never more than 0.03°.

A framework of metal supports the absorption flask. It connects to a motor which oscillates the flask through an arc of about 10°, with O-N as an axis, at 160 oscillations a minute.

The buret and the bulbs of the absorption flask are calibrated by filling with mercury. A cathetometer is used for the buret readings.

Manipulation.—The solution is boiled under reflux at atmospheric pressure to free it from dissolved gas. Experiment has shown that such boiling, over the forty-five minute period used, results in no appreciable loss of water. Two tubes lead from the refluxing flask. One tube, for withdrawing solution, dips to the bottom of the flask. The other is connected to the reflux condenser by a short rubber tube, which can be sealed with a clamp. While still boiling, the rubber connection to the condenser is sealed and the solution cooled under vacuum to the temperature of the thermostat. Connection is then made to the absorption flask at P. Cocks L and M are so arranged that there is passage through one bulb from P to O, but the other bulb is isolated. Suction is then applied at O, and the bulb filled with the solution.

After one bulb is filled with liquid, the cocks are turned to give free passage through the other bulb from P to O, isolating the full bulb. Several drops of solvent are then drawn into the empty bulb, and the refluxing flask and vacuum disconnected. The operations up to this point are carried out outside the thermostat, but with the bulbs immersed in water at thermostat temperature. The buret is now filled with mercury by raising the leveling bulb, and the cock D closed. The absorption flask is put into the thermostat, connected to the gas supply at P, and O and H, which meet end to end, are connected by a short stub of rubber tube, wired on and sealed with wax. The gas, from the cylinder, goes first through a saturator[1] in the thermostat, and is filled with a solution like that in which the solubility is being measured. The gas entering the absorption bulb is saturated with vapor from such a solution. The several drops previously drawn into the bulb ensure such saturation. With the gas and suction connected at P and G, respectively, the bulb is alternately evacuated and filled with gas by manipulation of the cocks L and G. The suction used is an aspirator capable of giving pressures down to about fifteen millimeters. Four such evacuations and fillings are made, after which the cock D is opened, the leveling bulb lowered, and the buret filled with gas. The cock L is then shut and the gas supply disconnected. The leveling bulb is adjusted to such a level that the partial pressure of the gas is exactly 760 mm., allowance being made for the density of the mercury, capillarity effects, barometric pressure, and the vapor pressure of the solution. The buret level at this time is recorded.

Cock L is opened between the two bulbs, and cock M is opened between the bulbs and to the buret. The solution runs from the full bulb into the empty one, until both are filled to the same level. The motor is started, keeping the contents of each bulb in continual agitation and causing some of the solution to surge through the tube between bulbs at the end of each stroke. The leveling bulb is raised as solution proceeds. Solution is usually complete in about twenty minutes. Shaking is continued for at least ten minutes after there is no perceptible change in buret level. The leveling bulb is adjusted as before, and the final buret reading is recorded. In order to be sure equilibrium is established, the pressure is raised several millimeters, and shaking continued for several minutes. The buret level is then returned to its value before the pressure was raised. More gas dissolved while the pressure was higher, but in the course of about ten minutes the mercury level in the buret sinks nearly to its former value, usually within 0.1 or 0.2 mm.

The volume dissolved is found by difference and, with the known volume of solvent, the solubility is readily calculated. Two burets are available, and either bulb can be filled with solvent, in order to give satisfactory accuracy over a large range of solubility.

Materials.—The solutions were made by weighing the proper amount of analytical grade salt and dissolving in a weighed amount of freshly boiled distilled water. In the case of hydrated salts, analysis of the crystals or of a concentrated solution was necessary in making the solution. The concentration of each solution was verified by measuring the density, and comparing with values from the literature. Vapor pressures were found in the literature.

The gases were from commercial cylinders. Analysis

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(1) Markham, *Ind. Eng. Chem., Anal. Ed.*, **12**, 112 (1940).

showed the carbon dioxide to be 99.8% pure, and the nitrous oxide to be 99.7% pure. The nitrous oxide was analyzed by the method of Chaney and Lombard.[2]

Experimental Results

Methods of Expression.—Gas solubility can be expressed in many ways. The Bunsen coefficient is most commonly used. This coefficient, designated by α, expresses the volume of gas dissolved, at the specified temperature and partial pressure of 760 mm., by one volume of solvent, the gas volume being corrected by the ideal gas laws to zero degrees centigrade and 760 millimeters of mercury partial gas pressure.[3] Cooper and Maass[4] found that, based on the ideal gas law, the apparent molecular weight of carbon dioxide was 44.295 at 0°, 44.216 at 25°, and 44.182 at 40°. This deviation, amounting to nearly 0.2%, must be considered when comparison of solubility data from volume absorbed is made with data found by other methods, *e. g.*, titration. All solubilities determined in this work are expressed first in terms of α. Temperature corrections have been based on the ideal gas law, since the definition is purely arbitrary.

In expressing the data found in this work, another coefficient has been found convenient. It is designated by S, and refers to the volume of gas, reduced to standard conditions as in the calculation of α, which is dissolved by the quantity of solution of molality m containing one gram of water. Thus it is calculated by dividing α by the product of the weight fraction of water in the solution and its density at the temperature in question. S is proportional to gas molality.

TABLE I

SOLUBILITY OF CARBON DIOXIDE AND NITROUS OXIDE IN WATER

Temp., °C.	α	S	Detns.	Av. dev., ± × 1000
		Carbon Dioxide		
0.2	1.7023	1.7025	8	2.0
25	0.7565	0.7587	12	0.5
40	0.5133	0.5173	5	0.7
		Nitrous Oxide		
0.2	1.2970	1.2971	3	0.1
25	0.5392	0.5408	11	1.2
40	0.3579	0.3607	7	1.0

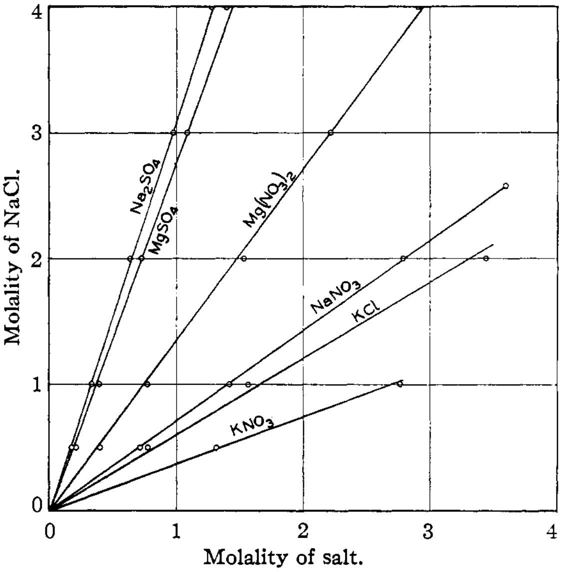

Fig. 2.—Duhring lines of equal gas solubility, using sodium chloride solution as reference.

Possible Sources of Error.—Cady, Elsey and Berger[5] objected to vigorous shaking because of the possibility of supersaturation resulting from the impact of liquid against gas bubbles. Morgan and Pyne[6] found that the accepted solubility for the carbon dioxide–water system at 25° was not in error from this source. In the present work, several experiments were performed to test the effect of shaking. When the absorption apparatus, filled as it is during an experiment, oscillates very slowly, the liquid flows slowly from one bulb to the other, without breaking the surface. Gas solution is slow. In several experiments conducted in this manner, results were obtained which checked those found in the usual way. Using one molal magnesium sulfate and carbon dioxide at 25°, enough gas dissolved in four hours of slow shaking to correspond to an α of 0.4142. Rapid shaking then dissolved enough more to bring α up to 0.4146. The results obtained by the usual method were 0.4140 and 0.4155. This, and other similar experiments, indicated that the rapid shaking used introduced no error.

The impurity of the gas, probably in each case consisting of relatively insoluble gases, introduces small errors. No correction has been made for such errors.

The hydrostatic head of the solution causes somewhat more gas to dissolve at the bottom of the vessel than at the top. This head is very small. No correction has been made for the error so introduced.

The solution expands when gas dissolves.

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[2] Chaney and Lombard, *Ind. Eng. Chem., Anal. Ed.*, **4**, 185–187 (1932).

[3] Bunsen, *Ann.*, **93**, 1–50 (1855).

[4] Cooper and Maass, *Can. J. Research*, **4**, 283–298 (1931).

[5] Cady, Elsey and Berger, THIS JOURNAL, **44**, 1456–1561 (1922).

[6] Morgan and Pyne, *J. Phys. Chem.*, **34**, 1578 (1930).

TABLE II

SOLUBILITIES OF CARBON DIOXIDE IN AQUEOUS SALT SOLUTIONS

		Potassium chloride		Sodium chloride		Potassium nitrate		Sodium nitrate		Magnesium nitrate		Magnesium sulfate		Sodium sulfate	
t	*m*	α	*S*	α	*S*	α	*S*	α	*S*	α	*S*	α	*S*	α	*S*
0.2	0.1	1.6611	1.6654			1.6680	1.6740								
	0.2	1.6268	1.6352	1.5996	1.6043	1.6470	1.6584	1.6167	1.6247						
	0.5	1.5285	1.5481			1.5733	1.6012	1.5040	1.5229	1.3928	1.4172	1.1988	1.1986		
	1	1.4020	1.4389	1.2778	1.2978	1.4610	1.5142			1.1439	1.1863	0.8441	0.8470		
	2	1.1982	1.2644	0.9877	1.0210					0.7849	0.8488	.4128	.4201		
	3	1.0460	1.1356	.7800	0.8218			0.8840	0.9589	.5612	.6326				
	4			.6286	.6755			[a] .4055	.5099						
25	0.1	0.7432	0.7475	.7379	.7413	0.7501	0.7552	.7415	.7458						
	0.2	.7307	.7369	.7197	.7243	.7421	.7500	.7289	.7352					[b]0.6335	0.6381
	0.5	.6937	.7055	.6687	.6767	.7182	.7345	.6946	.7069	.6476	.6627	.5580	.5606	.5330	.5399
	1	.6442	.6646	.5946	.6074	.6860	.7156	.6352	.6562	.5588	.5840	.4147	.4186	.3855	.3957
	2	.5646	.5998	.4816	.5017	.6296	.6834	.5406	.5758	.4200	.4587	.2250	.2306	[c] .2824	.2943
	3	.5030	.5503	.3917	.4164	.5818	.6568	.4659	.5109	.3225	.3683				
	4	.4563	.5141	.3288	.3568			[a] .2474	.3151						
														[b] .4394	.4450
40	0.5									.4460	.4590	.3814	.3852	.3735	.3804
	1	.4360	.4522	.4084	.4195	.4704	.4937			.3900	.4102	.2948	.2992	.2781	.2872
	2	.3853	.4168	.3328	.3487	.4370	.4776			.3015	.3316	.1658	.1708	[c] .2073	.2175
	3	.3520	.3874	.2767	.2960	.4083	.4642			.2375	.2736				

[a] Salt molality is 8. [b] Salt molality is 0.25. [c] Salt molality is 1.5.

TABLE III

SOLUBILITY OF NITROUS OXIDE IN AQUEOUS SALT SOLUTIONS

		Potassium chloride		Sodium chloride		Potassium nitrate		Magnesium nitrate		Magnesium sulfate		Sodium sulfate	
t	*m*	α	*S*	α	*S*	α	*S*	α	*S*	α	*S*	α	*S*
0.2	0.2					1.2183	1.2267						
	0.5					1.1355	1.1556	1.0139	1.0316	0.8778	0.8777		
	1	0.9880	1.0140	0.9178	0.9327	1.0174	1.0545	0.7921	0.8215	.6019	.6039		
	2	.7784	0.8212	.6675	.6902			.5238	.5664	.2771	.2820		
	3	.6349	.6893	.5053	.5330			.3618	.4079				
25	0.5							.4488	.4593	.3840	.3858	0.3565	0.3612
	1	.4329	.4466	.4026	.4127	0.4552	0.4749	.3850	.4023	.2790	.2816	.2476	.2547
	2	.3580	.3803	.3166	.3299	.3961	.4299	.2785	.3042	.1442	.1478	[a] .1721	.1797
	3	.3030	.3315	.2502	.2662	.3524	.3978	.2104	.2403				
40	0.5							.3061	.3150	.2612	.2638	.2425	.2472
	1	.2885	.2993	.2719	.2797	.3100	.3254	.2620	.2756	.1945	.1969	.1722	.1791
	2	.2416	.2613	.2181	.2288	.2761	.3018	.1989	.2188	.1018	.1049	[a] .1226	.1297
	3	.2077	.2286	.1743	.1866	.2475	.2814	.1556	.1793				

[a] Salt molality is 1.5.

Such expansion affects the observed volume of gas dissolved. Measurements were made of the density of the solutions both before and after saturation with gas, to find the magnitude of the expansion. The effect to be observed is very small, but the results show that the solubilities as measured are low by several hundredths, possibly up to 0.1%. Thus solutions of nitrous oxide in three molal potassium chloride at 25° caused the density to change from 1.1185 to 1.1190, while the liquid volume increased by 0.007 ml. per 100 ml. of solution, or per 33 ml. of gas. The corresponding error in α is 0.02%.

The vapor pressure data were taken from the literature, interpolated between concentrations. Where necessary, the temperature correction was estimated from a plot of log *P* against 1/*T*. Error in the accepted value of the vapor pressure must be small and could have little effect. It does not affect the result if Henry's law holds over the range of the error, because the gas law correction to 760 mm. partial pressure is cancelled by the Henry's law correction for change in solubility. Data from the literature show that in salt solutions Henry's law holds well over a wide range of pressure.

Change in vapor pressure of the solution caused by solution of the gas could cause small errors, but at the low concentration of the gas in the liquid phase (0.075 molal is the maximum) the change in vapor pressure is probably too small to be perceptible.

Uncertainty in adjustment of pressure in the apparatus could lead to small errors in the buret level, possibly as much as 0.3 mm. The two burets have cross sections of about 0.8 and 0.48 sq. cm., respectively, and the volume of liquid could be either 43.2 or 87.6 cc., depending on the bulb used. Error in the buret level of 0.3 mm. then corresponds to error of 0.025 cc. in gas volume, or a maximum of 0.0006 in units of α. This error could be repeated at both readings of the volume. Usually the error, depending on the combined effects of several small ones, is much less than the maximum. Error in calibration of bulbs and buret was too small to be considered.

Gas Solubility Formulas

Additive Effect of Ions.—Data from the present work give an indication of the extent to which the reduction in solubility is an additive function of the ion concentrations. Thus in Table IV, column 2, data for the solubility of carbon dioxide at 25° in solutions of sodium chloride, potassium chloride, and potassium nitrate have been combined to predict the solubility in sodium nitrate solutions. The results so predicted can be compared with those found by experiment (column 3). Different methods of expressing solubility have been treated in the same manner, all giving approximately the same agreement. Only the comparison of α is given.

TABLE IV

SOLUBILITY OF CARBON DIOXIDE IN SODIUM NITRATE SOLUTIONS

m	α predicted	α experiment
0.1	0.7448	0.7415
0.2	.7311	.7289
0.5	.6932	.6946
1	.6364	.6352
2	.5466	.5406
3	.4705	.4659

Up to one molal, the deviation is within experimental error, considering the number of measurements involved in each comparison. In more concentrated solutions, the deviation becomes larger than experimental error, going up to about 1%.

A New Equation.—A new equation is proposed to represent the solubility of gases in aqueous salt solutions

$$\frac{S_m}{S_0} = am + \frac{1}{1 + bm} \qquad (1)$$

in which a and b are empirical constants dependent upon the particular solute present. It is seen that when no solute is present ($m = 0$), S_m equals S_0, as must be the case. The activity coefficient, as defined by Randall and Failey,[7] becomes

$$\gamma = \frac{S_0}{S_m} = \frac{1 + bm}{1 + am + abm^2} \qquad (2)$$

Using the experimental data, values of a and b have been found for each combination of gas, solute and temperature by the method of least squares. These values are given in Table V. Comparison of the calculated values of S with the observed values shows that in only a few cases is the difference greater than the probable experimental error (0.2%). The constants of the formula were found by the method of least squares and are given in Table V.

Differentiation of equation 2 shows that the slope of the curve of γ against m is

$$\frac{b - a - 2abm - ab^2m^2}{(1 + am + abm^2)^2}$$

At small values of m, this reduces to a slope of $b - a$. From the rather close agreement of equation 1 it is to be expected that this relation holds. The values in the tables show that γ is nearly a linear function of m up to concentrations of one molal for carbon dioxide in solutions of sodium and potassium chlorides and nitrates. Furthermore, the slope in each case is substantially equal to $b - a$. This relation merely confirms the agreement already noted between the observed and calculated values of S.

Randall and Failey[7] plotted log γ/μ against $\sqrt{\mu}$, finding that a horizontal straight line frequently resulted. Taking data from Table II, the ratio of log γ to m was found to have rather small variation:

(Carbon dioxide at 25°)

m	$\log_{10}\gamma/m$ NaCl	$\log_{10}\gamma/m$ KNO_3
0.1	0.0988	0.0217
0.2	.0997	.0259
0.5	.0992	.0282
1	.0966	.0253
2	.0897	.0226
3	.0868	.0209

Equation 2 indicates that at small concentrations the ratio of log γ to m should be nearly constant. The first term of the expansion of ln u is $(u - 1)/u$. Thus to a first approximation

$$\ln \gamma = m\,\frac{b - a - abm}{1 + bm}$$

and at small values of m

$$\frac{\ln \gamma}{m} = b - a$$

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(7) Randall and Failey, *Chem. Rev.*, **4**, 271–285 (1927).

Duhring Lines.—The solubility data for carbon dioxide in the various salt solutions have been represented as Duhring lines[8] by plotting molalities of equal gas solubility using sodium chloride as the reference salt solution. Straight lines can be drawn through the points, the deviation being slight in all cases except with potassium salts where there is some curvature. No improvement in fit of data points is secured by using other salts, or any hypothetical salt, as the reference salt. Similar lines are obtained with other gases and other temperatures. Such a method serves as an excellent approximation method where few data are available, as all lines start from a common origin and but one or two data points are necessary to give a satisfactory approximation.

TABLE V

VALUES OF *a* AND *b* IN EQUATION 1

	Temp., °C.	CO_2		N_2O	
		a	*b*	*a*	*b*
NaCl	0.2	−0.0181	0.285	−0.0272	0.346
	25	− .0134	.229	− .0167	.280
	40	− .0113	.217	− .0138	.261
$NaNO_3$	0.2	− .0054	.240		
	25	− .0050	.150		
Na_2SO_4	25	− .0760	.666	− .0746	.834
	40	− .0838	.560	− .0685	.774
KCl	0.2	+ .0207	.216	− .0072	.270
	25	+ .0201	.168	+ .0001	.211
	40	+ .0380	.190	+ .0075	.210
KNO_3	0.2	+ .0350	.170	+ .0733	.350
	25	+ .0248	.088	+ .0243	.170
	40	+ .0343	.086	+ .0203	.130
$Mg(NO_3)_2$	0.2	− .0361	.366	− .0302	.496
	25	− .0268	.257	− .0252	.310
	40	− .0211	.230	− .0159	.280
$MgSO_4$	0.2	− .0852	.701	− .0844	.800
	25	− .0808	.575	− .0781	.665
	40	− .0736	.545	− .0848	.586

Summary

1. An apparatus for the measurement of gas solubility in liquids has been designed in which solubility measurements check within about 0.2 per cent.

2. The solubility of carbon dioxide and nitrous oxide in various aqueous salt solutions has been measured at 0.2, 25 and 40° over a wide range of salt concentrations.

3. It has been shown that the reduction in gas solubility is an additive function of the ion concentrations up to one molal.

4. A new equation is given to express gas solubility in salt solutions as a function of concentration. This equation in most cases fits the data within the experimental error.

SEATTLE, WASHINGTON RECEIVED JUNE 10, 1940

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[8] Perry and Smith, *Ind. Eng. Chem.*, **25**, 195–199 (1933).

[A JOINT CONTRIBUTION FROM HALL LABORATORIES, INC., PITTSBURGH, PA., AND FROM THE COÖPERATIVE X-RAY LABORATORY OF THE UNIVERSITY OF PITTSBURGH]

A Thermal, Microscopic and X-Ray Study of the System $NaPO_3$–$Na_4P_2O_7$[1]

BY EVERETT P. PARTRIDGE,[2] VICTOR HICKS[3] AND G. W. SMITH[2]

The discovery that solutions of sodium metaphosphate glass sequester calcium in a soluble complex corresponding to such a low concentration of calcium ion that addition of carbonate, oxalate, orthophosphate, or soap does not produce a precipitate has led, not only to rapid technical development of the use of this material in all fields of water conditioning, but also to renewed scientific and commercial interest in the meta- and pyrophosphates and in those less well-established compounds of intermediate composition collectively known as the polyphosphates.

The older literature has reference to compounds of empirical formulas $Na_{12}P_{10}O_{31}$, $Na_6P_4O_{13}$, $Na_9P_4O_{17}$ and $Na_5P_3O_{10}$. When Parravano and Calcagni[4] attempted to verify the existence of polyphosphates by studying the cooling curves of melts of sodium pyrophosphate and sodium metaphosphate, they could find no indication of any intermediate anhydrous compounds. More recently, however, the work of Huber[5] and of Andress and Wüst[6,7] has shown that sodium tripolyphosphate, $Na_5P_3O_{10}$, is a real compound. The

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[1] The portion of this investigation dealing with sodium metaphosphate and sodium pyrophosphate was presented at the Pittsburgh Meeting of the American Chemical Society, September 10, 1936, the remainder at the Cincinnati Meeting, April 9, 1940.

[2] Hall Laboratories, Inc., Pittsburgh, Pa.

[3] Coöperative X-Ray Laboratory, University of Pittsburgh. Present address: Westinghouse X-Ray Co., Inc., Long Island City, N. Y.

[4] Parravano and Calcagni, *Z. anorg. Chem.*, **65**, 1–9 (1910).

[5] Huber, *Z. angew. Chem.*, **50**, 323–326 (1937).

[6] Andress and Wüst, *Z. anorg. Chem.*, **237**, 113–131 (1938).

[7] Andress and Wüst, *ibid.*, **241**, 196–204 (1939).