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

The Calculation of the Solubility of Certain Salts in Water at High Pressures from Data Obtained at Low Pressures

BY R. E. GIBSON

It has been shown[1] that at 25° the compression of water may be very well represented as a function of pressure up to 12,000 atmospheres by equation (1) which was originally proposed by Tait.[2]

$$-\Delta_P v = 0.3071 \log (2.923 + P) - 0.1430 \qquad (1)$$

$$-\Delta_P v = 0.2925 \log (2.7 + P) - 0.1262 \qquad (1')$$

Equation (1) is especially good at low pressures while equation (1′) holds better than equation (1) at the higher pressures. Furthermore, it was shown that if Tammann's hypothesis, that water in an aqueous solution behaves as pure water under a definite hydrostatic pressure, be invoked, the specific compression of any solution may be expressed as a function of the pressure by equation (2), it being also assumed that the compression of the salt is not altered by the process of entering into solution.

$$-\Delta_P v/x_1 + r_2 \Delta_P v_s = 0.3071 \log \frac{2.923 + P_e + P}{2.923 + P_e} \qquad (2)$$

A similar equation with the numerical coefficients from equation (1′) fits the experimental data better at the high pressures. The quantity P_e may be treated as the effective pressure which the salt exerts on the water and may be computed from density measurements at room pressure, but in this article P_e will be treated simply as an empirical constant to be computed from compression data at 1 kilobar.

It will readily be seen that

$$P_e = (P/(Q - 1)) - 2.923 \qquad (3)$$

$$\text{where } Q = \text{antilog} \frac{\Delta_P v/x_1 - r_2 \Delta_P v_s}{0.3071} \qquad (4)$$

In this paper it will be shown that equation (2) in conjunction with values of P_e computed from data at 1 kilobar may be used to calculate with useful accuracy the effect of high pressure on the solubility in water of those salts for which solubility data at high pressures are known. The method will also be applied to the computation of the solubility curve of potassium iodide under pressure.

The change of solubility with pressure may conveniently be calculated from thermodynamic data by taking account of the fact that at the equilibrium concentration, x_2, for any pressure P,[3]

$$(\mu_2 - \mu_{\text{satd.}})_{P=0} = -P(v_2 - v_s)_{P=0} - \int_0^P (\Delta_P v_2 - \Delta_P v_s)\mathrm{d}P \qquad (5)$$

where $(\mu_2 - \mu_{\text{satd.}})_{P=0}$ is the difference between the chemical potential of the salt in any solution and the chemical potential of the salt in the saturated solution at room pressure. It is only necessary to find the value of concentration for which this equation is satisfied at any pressure P. The first and second terms of equation (5) refer to quantities measured at room pressure and have already been discussed in detail. The term under the integral sign is the only one which involves measurements under pressure and it is to the evaluation of this term that equation (2) will be applied.

If equation (2), written with the coefficients better adapted to the high pressure results, be differentiated with respect to r_2, the pressure being kept constant, it will be seen that

$$-(\Delta_P v_2 - \Delta_P v_s) = 0.2925 \times 0.4343 \left[\frac{1}{2.7 + P_e + P} - \frac{1}{2.7 + P_e}\right] \frac{\mathrm{d}P_e}{\mathrm{d}r_2} \qquad (6)$$

$$\text{Hence } -\int_0^P (\Delta_P v_2 - \Delta_P v_s)\mathrm{d}P = 0.1270 \frac{\mathrm{d}P_e}{\mathrm{d}r_2} \left[2.303 \log \left(1 + \frac{P}{2.7 + P_e}\right) - \frac{P}{2.7 + P_e}\right] \qquad (7)$$

If, therefore, $\mathrm{d}P_e/\mathrm{d}r_2$, the variation of P_e with the weight ratio of salt to water be known, the third term in equation (5) may readily be calculated for any value of the pressure, it being assumed that extrapolation by equation (2) is justified.

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(1) Gibson, THIS JOURNAL, **56**, 4-14 (1934).

(2) The symbols used in this paper, which are the same as those used in the preceding papers of this series, may be summarized as follows

x_1 = weight fraction of water in solution
x_2 = weight fraction of salt
r_2 = x_2/x_1
c_2 = concentration of salt in grams per cc. of solution
P = pressure in kilobars (10^9 dynes per sq. cm.)
k = change in volume per unit volume
$-\Delta_P v$ = specific compression of any phase for a given
$-\Delta_P v_w$ = specific compression of pure water increase of
$-\Delta_P v_s$ = specific compression of solid salt pressure
$-\Delta_P v_2$ = partial compression of salt in solution
v = specific volume of solution
v_2 = partial volume of salt in solution
ρ_s = specific volume of solid salt
ρ = density of a phase
v_w = density of water

(3) Adams and Gibson, THIS JOURNAL, **54**, 4528 (1932).

The Pressure–Solubility Curves of Sodium Chloride, Potassium Sulfate and Ammonium Nitrate at 25°.—The influence of pressure on the solubility in water of sodium chloride, potassium sulfate and ammonium nitrate has been determined by exact thermodynamics from measurements made over the whole range of pressure from atmospheric to ten kilobars.[3,4] In order that an estimate of the usefulness of equation (7) in computing the third term of equation (5) might be made, the solubilities of these three salts at various pressures were calculated by the extrapolation equations and compared with the values determined by experiment. The calculations were made as follows. The equivalent pressures P_e for the different solutions were obtained from the observed compressions of the solutions at 1 kilobar by means of equation (3), and the slopes, dP_e/dr_2, were determined graphically. For sodium chloride solutions P_e was found to be a linear function of r_2, for potassium sulfate solutions also the results, although somewhat erratic, could only be represented as a straight line, but for solutions of ammonium nitrate a curve with a maximum for P_e was found to represent the data most adequately. From the values of dP_e/dr_2 the third term in equation (5) was immediately computed by equation (7). The remaining data required by equation (5) were taken from the articles which have just been mentioned. Values of $(\mu_2 - \mu_{\text{satd.}})$ are not explicitly given in the papers on the sodium chloride–water or the potassium sulfate–water systems under pressure, but the chemical potential–concentration relations used in these papers lead to the following values of $(\mu_2 - \mu_{\text{satd.}})$ at 25°. For sodium chloride $(\mu_2 - \mu_{\text{satd.}})$ is -9.2, -45.6, -86.2, -131.0 joules at $x_2 = 0.25$, 0.20, 0.15 and 0.10, respectively, and for potassium sulfate -2.0, -11.4 and -22.9 joules at $x_2 = 0.10$, 0.075 and 0.05, respectively.[5]

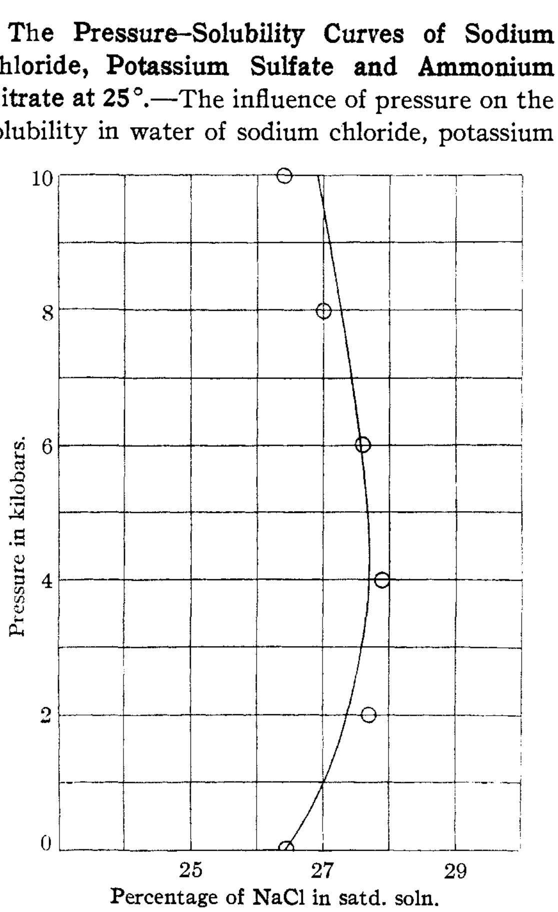

Fig. 1.—An illustration of the agreement between the values of the solubility of sodium chloride at different pressures as computed by means of the extrapolation equations (circles), and as found by experiment over the whole pressure range (curve).

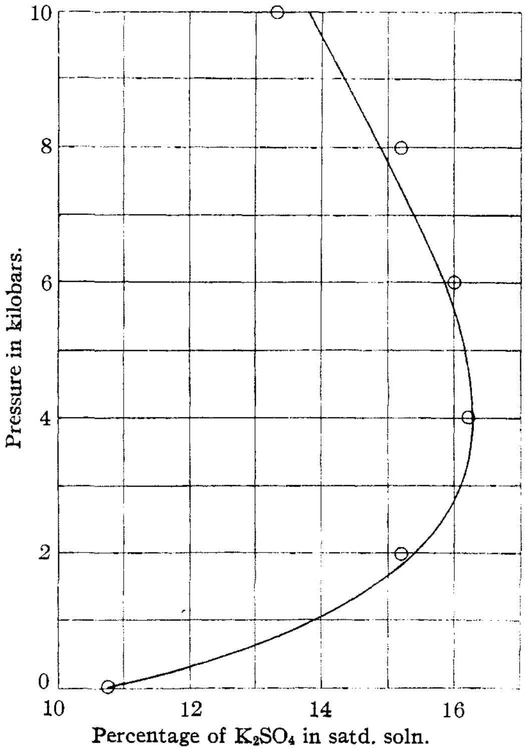

Fig. 2.—An illustration of the agreement between the values of the solubility of potassium sulfate at different pressures as computed by means of the extrapolation equations (circles), and as found by direct experiment over the whole pressure range (curve).

The results are illustrated in Figs. 1, 2 and 3. The curves give the solubilities of the different salts at various pressures as determined from direct measurements over the whole pressure

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(4) (a) Adams, This Journal, **53**, 3769–3813 (1931); (b) Adams, *ibid.*, **54**, 2229–2243 (1932).

(5) These figures were kindly supplied to me by Mr. Adams from his notebooks.

range, the circles represent the values obtained for the solubilities at different pressures when the third term in equation (5) is computed from measurements made at 1 kilobar by means of the extrapolation equation (7). The agreement between the circles and the curves is very satisfactory and indicates that one may use equation (7) to extrapolate from data at 1 kb. to 10 kb. with a degree of approximation which is quite adequate for many purposes. It should be noted that the third term in equation (5) is by no means insignificant. For example, if this term were entirely neglected in the case of potassium sulfate solutions the computed value of the solubility at 4 kb. would be greater than 0.2 g. of salt per gram of solution.

The Pressure–Solubility Curve of Potassium Iodide.—The data for the three terms in equation (5) necessary for a determination of the effect of pressure on the solubility of potassium iodide in water were obtained as follows.

The partial volumes of potassium iodide in aqueous solutions were computed from density data by a method recently published.[6] As the best values of the densities of potassium iodide solutions, *viz.*, those of Shibata and Holemann[7] and of Baxter and Wallace[8] differ significantly in concentrated solutions, it was considered necessary to repeat the experimental determinations at suitable intervals over the whole range of concentration.

Merck Reagent potassium iodide was dissolved in air-free distilled water, and crystallized by evaporation of the filtered solution in a vacuum desiccator. The solution discolored slightly during the process. The crystalline product was dried by suction and by heating for several days at 250°. During the heating the salt was crushed several times in an agate mortar. After such treatment, density results reproducible to less than 1 part in 100,000 could be obtained for the concentrated solutions, when different samples of solid salt were used. If, however, the salt were only dried for about six hours at 250°, even when thoroughly powdered, the densities of 50% solutions were uncertain by as much as 1 part in 10,000. The solutions were all made directly from weighed amounts of salt and water and their densities were determined in a pycnometer which has been used many times.[9] The experimental results are given in Table I. In the fourth column of this table the differences between the observed value of the density and that computed by equation (8), an interpolation equation, are given.

$$\rho = \rho_w + 0.72825\, c_2 - 0.02403\, c_2^{3/2} \qquad (8)$$

The solutions were made up as closely as possible

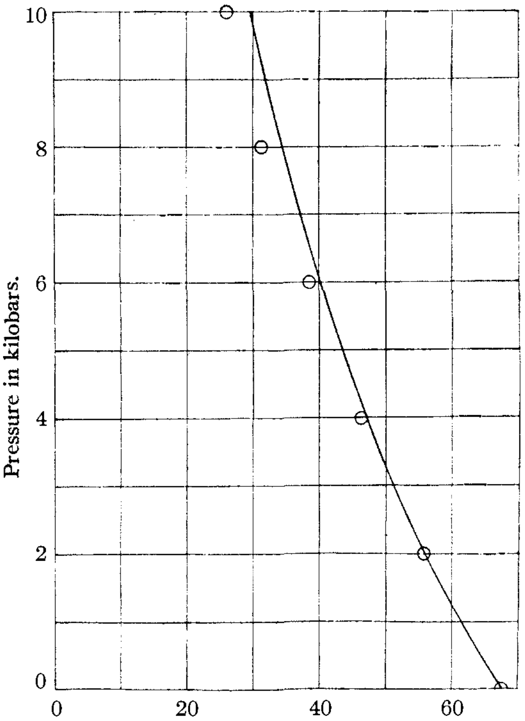

Fig. 3.—An illustration of the agreement between the values of the solubility of ammonium nitrate at different pressures as computed by means of the extrapolation equations (circles), and as found by direct experiment over the whole pressure range (curve).

TABLE I

EXPERIMENTAL RESULTS FOR DENSITIES OF AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AT 25.00°

x_2	c_2	ρ	$(\rho_{\text{obs.}} - \rho_{\text{calcd.}}) \times 10^5$
0.00000	0.00000	0.99708	0
.08366	.08877	1.06109	0
.14420	.16040	1.11236	2
.21293	.25052	1.17656	5
.28712	.36010	1.25420	7
.36086	.48414	1.34164	8
.44309	.64415	1.45377	2
.51528	.80785	1.56778	−17
.51617	.81002	1.56928	−17
.52732	.83759	1.58840	−23
.56629	.93940	1.65885	−46
.57027	.95028	1.66637	−49

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(6) Gibson, *J. Phys. Chem.*, **38**, 319 (1934).

(7) Shibata and Holemann, *Z. physik. Chem.*, **13B**, 352 (1931).

(8) Baxter and Wallace, THIS JOURNAL, **38**, 70 (1916). See also reference 6. The least square residuals in Table IV show distinct discrepancies between the results of the two sets of observers.

(9) Adams, Ref. 4b, p. 2231.

to even intervals of the square root of the volume concentration.

Approximate values of the fictive density[6] of water in the various solutions were computed directly from equation (8) and corrected from the slope of the deviation curve, obtained when the figures in column 4, Table I, were plotted against the concentration or against the square root of the concentration. From these corrected values of the fictive density of water, the partial volumes of potassium iodide in the various solutions were calculated. The results are recorded in Table II. The value of v_s, the specific volume of solid potassium iodide at 25°, was taken as 0.3202.[8]

TABLE II

DENSITIES AND PARTIAL VOLUMES IN SOLUTIONS OF POTASSIUM IODIDE AT EVEN INTERVALS OF THE VOLUME CONCENTRATION AT 25°

c_2	x_2	ρ	v_1	v_2	ψ_2
0.0	0.00	0.99708	1.00293	..	..
.01	.00996	1.00434	1.00292	0.276	..
.04	.03899	1.02601	1.00284	.280	..
.09	.08475	1.06197	1.00261	.283$_3$	0.305
.16	.14388	1.11208	1.00216	.2866	.311
.25	.21255	1.17619	1.00144	.2899	.318
.36	.28705	1.25414	1.00036	.2932	.317
.49	.36410	1.34576	0.99879	.2965	.316
.64	.44111	1.45087	.99651	.3000	.316
.81	.51616	1.56927	.99275	.3040	.316
.9025	.55255	1.63335	.99093	.3056	..
.9500	.57017	1.66617	.98994	.3064	.315

The Compressions of Solutions of Potassium Iodide at 1000 Bars.—With the pressure apparatus and piezometers already described[1] the compressions of solutions of potassium iodide resulting from a rise in pressure from 1 to 1000 bars were measured. The results are given in Table III, together with the corresponding values of the specific compressions.

TABLE III

SOLUTIONS OF POTASSIUM IODIDE AT 25°. EXPERIMENTAL RESULTS FOR COMPRESSIONS AT 1000 BARS

c_2	r_2	k	$\Delta_P v$	$\Delta_P v/x_1$	P_e (kb.)
0.0	0.0	0.0393$_0$	0.0394$_0$	0.0394$_0$	0.0
.09	.0926	.0377$_7$	.0355$_6$	.0388$_5$	.056
.16	.1681	.0366$_1$	.0329$_2$	.0384$_5$	.106
		.0366$_8$	.0329$_8$	.0385$_2$	
.25	.2699	.0349$_7$	.0297$_3$	.0377$_6$	.201
		.0350$_1$	.0297$_7$	.0378$_1$	.196
.36	.4026	.0333$_6$	.0266$_0$	.0373$_0$	.279
		.0333$_5$	.0265$_9$	.0373$_0$	.281
.49	.5726	.0317$_2$	.0235$_7$	.0370$_7$	.351
.64	.7893	.0296$_5$	.0204$_3$	.0365$_4$	.473
		.0296$_5$	.0204$_3$	.0365$_4$	.473
.81	1.0669	.0278$_1$	.0177$_2$	.0366$_2$	.554
		.0277$_1$	.0176$_6$	.0365$_0$	
		.0277$_5$	.0176$_8$	.0365$_4$	.556
.9503	1.3272	.0263$_1$	.0157$_9$	.0367$_5$	.614
		.0262$_5$	.0157$_5$	.0366$_5$	.626

The value of $\Delta_P v_s$, the specific compression of the solid salt, used in conjunction with $\Delta_P v/x_1$ in the calculation of P_e by equation (3) was taken from Slater's[10] measurements of the compressibility of solid potassium iodide. It was found that the values of P_e calculated for the solutions from compression data could be expressed within the error of experiment as a quadratic function of the weight ratio, r_2. When such an equation was fitted to the data by the method of least squares, equation (9) resulted.

$$P_e = 0.7725\, r_2 - 0.2312\, r_2^2 \qquad (9)$$

From this equation, $\mathrm{d}P_e/\mathrm{d}r_2$ was obtained directly. The values of $\int_0^P (\Delta_P v_2 - \Delta_P v_s)\mathrm{d}P$ and of $\int_0^P (v_2 - v_s)\mathrm{d}P$, the sum of the two terms on the right-hand side of equation (5), were then computed. The latter are given in Table IV.

TABLE IV

THE EFFECT OF PRESSURE ON THE CHEMICAL POTENTIAL DIFFERENCE BETWEEN POTASSIUM IODIDE IN VARIOUS SOLUTIONS AND SOLID POTASSIUM IODIDE AS COMPUTED FROM DATA AT 1 KB. BY EQUATION (7)

	$\int_0^P (v_2 - v_s)\mathrm{d}P$ in joules				
c_2	$P = 2$	$P = 4$	$P = 6$	$P = 8$	$P = 10$ kb.
0.64	3.31	5.77	7.82	9.61	11.24
.81	2.76	4.97	6.89	8.65	10.35
.9025	2.58	4.77	6.76	8.63	10.42
.9500	2.50	4.68	6.71	8.65	10.52

Pearce and Nelson[11] from vapor pressure measurements have computed the partial molal free energies of potassium iodide in solutions over the whole range of concentration. From their values ($\mu_2 - \mu_{\text{satd.}}$) the difference between the chemical potential (partial free energy per gram) of potassium iodide in any solution and its chemical potential in the saturated solution was readily computed.

Equation (5) was applied to these data, and, as a result, the curve in Fig. 4 is proposed as the probable pressure–solubility curve of potassium iodide in aqueous solutions. The curve is interesting, it being the first known case in which the solubility of a salt in water continues to increase with pressure up to 10 kilobars.

Direct Estimation of the Solubility of Potassium Iodide under Pressure.—Attempts were

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[10] Slater, *Proc. Am. Acad. Arts Sci.*, **61**, 135 (1926).

[11] Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932).

made to determine directly the effect of high pressure on the solubility of potassium iodide in water in order to confirm the results of the calculations just described. A glass vessel, illustrated in Fig. 5, contained a solution saturated with potassium iodide at 25° and 1 bar. The platinum gauze disk near the top of the vessel supported relatively large crystals of the fused salt. The bottom opening of the tube dipped into mercury contained in a steel capsule. The apparatus was enclosed in a steel bomb and subjected to a constant pressure between 5 and 10 kb. for one to two hours. Potassium iodide dissolved and equilibrium was obtained by convection. The process of solution was evidently rapid, since an increase in the time of the experiment from one and one-half to four hours made no significant difference in the result. After the experiment a thick layer of fine crystals was observed in the lower portion of the glass tube while most of the original crystals had dissolved. The platinum disk and the remnants of the original crystals were encrusted with new crystals of the salt. The upper portion of the solution was withdrawn to the level of the platinum gauze and the relative amounts of salt and water in the lower portion of the glass vessel were taken as the concentration of the saturated solution at the maximum pressure. It was assumed that while the pressure was being lowered the excess of salt in the solution below the disk was deposited as fine crystals which fell to the bottom and that the salt which crystallized on or above the disk came from the solution above the disk. The results of these direct determinations of the solubility of potassium iodide at high pressures are indicated by the circles in Fig. 4. Similar experiments were made in which the solution was contained in a cylindrical glass capsule plugged at the mouth with absorbent cotton, the solid salt being held near the upper end of the capsule in a platinum cage. The liquid used for transmitting the pressure in the bomb was in this case a saturated solution of potassium iodide. Here again the composition of the contents of the capsule below the bottom of the platinum cage was taken as a measure of the concentration of the saturated solution at the highest pressure. The results of these experiments are expressed as the points marked by crosses in Fig. 4. That the solubility of potassium iodide did not decrease with pressure was demonstrated by an experiment in which a saturated solution with a crystal of salt at the *bottom* of the containing vessel was kept for some time under high pressure. No significant amount of new crystals was found at the bottom of the capsule in this case. The results of the direct solubility measurements under pressure plotted in Fig. 4 give a very good confirmation of the calculated pressure–solubility curve. It will be noticed, however, that at the highest pressures the calculated solubility is less than the observed

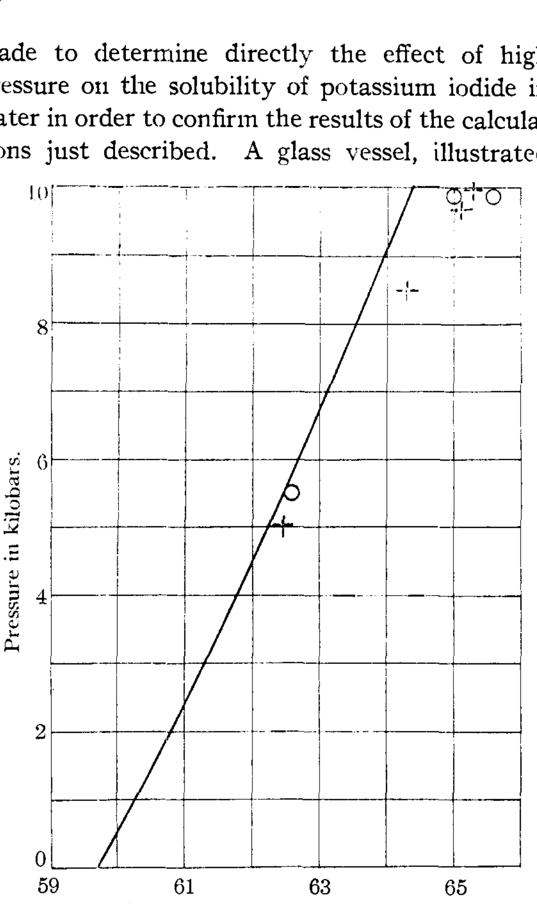

Fig. 4.—The pressure–solubility curve of potassium iodide in aqueous solutions computed by extrapolation from data at 1 kb. The circles give the direct determination made with the apparatus shown in Fig. 5. The crosses represent results of direct determinations made in an open tube.

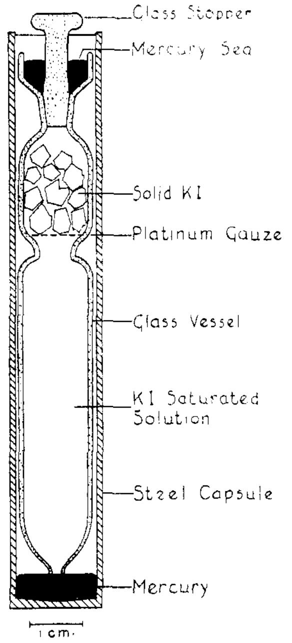

Fig. 5.—An apparatus for measuring the *increase* in the solubility of a solid in a liquid as a result of high hydrostatic pressures.

solubility in all the four cases studied here. Potassium iodide appears to offer no exception in this particular.

On the assumption that at one atmosphere external pressure, water in solution behaves as water under a pressure of P_e kilobars, it is possible to compute a quantity ψ_2 which may be regarded as the volume which one gram of solute occupies in solution. It has been shown[1] that for sulfates and sodium chloride ψ_2 is practically independent of the concentration, and of magnitude about 10% greater than that of the solid salt. For potassium iodide ψ_2 is also independent of the concentration, the values being given in the last column of Table II. They are, however, smaller than the volume of the solid—an observation which may throw some light on the continued increase of solubility with pressure. It is probable that on melting to form a solution, potassium iodide contracts slightly.

I am very much indebted to Mr. L. H. Adams of this Laboratory for the use of his new simplified high-pressure apparatus and for his help which made possible the direct determination of the solubility of potassium iodide at high pressures.

Summary

If it be assumed (a) that water in an aqueous solution behaves like water under a definite hydrostatic pressure (Tammann's hypothesis) and (b) that the specific compression of a salt in solution is the same as the specific compression of the solid salt, an equation expressing the properties of water as the function of the pressure may be adapted to give an extrapolation equation whereby the effect of pressures up to 10 kb. on the solubility of four salts in water may be computed with useful accuracy from measurements made at 1 kb. As the salts investigated differ quite widely, there is no reason to believe that the method is not generally applicable. In other words, if the compressions of a salt and a series of solutions at 1 kb. are known, it is possible to calculate the change with pressure up to 10 kb. of the difference between the chemical potential of the salt in any solution and that of the pure solid salt, *i. e.*, $(\mu_2-\mu_s)_P - (\mu_2 - \mu_s)_0$, which is equal to $\int_0^P (v_2 - v_s)\mathrm{d}P$, and, when this change of chemical potential with pressure is known, the influence of pressure on solubility and other equilibrium relations follows immediately.

New experimental data for the densities and compressions of solutions of potassium iodide are given and the extrapolated solubility curve is checked by approximate direct determinations of the solubility of this salt in water at pressures between five and ten thousand atmospheres.

WASHINGTON, D. C. RECEIVED JANUARY 8, 1934

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Equilibrium in Systems Composed of Sulfur Dioxide and Certain Organic Compounds

BY H. W. FOOTE AND JOSEPH FLEISCHER

The formation of solid addition compounds with sulfur dioxide has been reported in the literature for a number of organic compounds. The composition of such complexes formed with a series of amino compounds was investigated by Korezynski and Glebocka; similar studies were carried out with phenol by Holtzer and with pyridine by André; Baumé and Briner and Cardoso have investigated the system of sulfur dioxide and dimethyl ether; and Baumé and Pamfil the corresponding system with methyl alcohol. More recently, Hill has investigated the system formed by sulfur dioxide and aniline.[1]

Since vapor pressure measurements provide an excellent means of determining the composition of such molecular complexes and at the same time furnish knowledge of the existing equilibrium relations, this type of data was obtained in the present investigation of the systems formed by a number of organic substances with sulfur dioxide. The systems studied were chosen on the basis of existing data as likely to display the formation of solid addition compounds.

The apparatus and methods employed have been described previously.[2] The compounds used were either of Eastman C. P. grade or were purified by customary methods. The composition of all solid addition compounds was determined after

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(1) Korezynski and Glebocka, *Gazz. chim. ital.*, **50**, I, 378 (1920); Holtzer, *J. prakt. Chem.*, [2] **25**, 463 (1882); André, *Compt. rend.*, **130**, 1714 (1900); Baumé, *ibid.*, **148**, 1322 (1909); Briner and Cardoso, *J. chim. phys.*, **6**, 641 (1907); Baumé and Pamfil, *Compt. rend.*, **152**, 1095 (1911); A. E. Hill, THIS JOURNAL, **53**, 2598 (1931).

(2) Foote and Fleischer, *ibid.*, **53**, 1752 (1931).