

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

## EQUILIBRIUM IN BINARY SYSTEMS UNDER PRESSURE. II. THE SYSTEM, $K_2SO_4-H_2O$ , AT 25°

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In a previous paper<sup>1</sup> the results of an investigation of the system,  $NaCl-H_2O$ , under high pressures were presented. Measurements of the effect of hydrostatic pressure on the volumes of the several phases were made, and thence, by the application of a simple thermodynamic principle, the conditions of equilibrium between the various phases were calculated for pressures somewhat greater than 10,000 bars (metric atmospheres). The freezing-point and solubility curves thus delineated were confirmed by direct measurements, but the indirect, *i. e.*, thermodynamic, method was the one that was found to be the most convenient for the study of multi-component systems under high pressure.

In this paper are given results for the system,  $K_2SO_4-H_2O$ , at 25° and at pressures up to approximately 10,000 bars. The experimental and calculatory methods were essentially the same as those used in the previous investigation, and the nomenclature, except where the contrary is specifically noted, is the same as that of the former paper.

### Measurements of the Compression of the Solutions

**Low-Pressure Experiments.**—Since the high-pressure apparatus is not suitable for measurements at pressures below 1000 bars, the compression at this pressure was determined by means of the glass piezometer previously described.<sup>2</sup> The solutions were made up by weight from potassium sulfate that had been recrystallized from water and dried at about 800°. On account of the transition with large volume change, which potassium sulfate undergoes at 588°, heating the salt above this temperature not only insures thorough drying but also reduces the crystals to a convenient granular condition.

The most concentrated solution used contained 10% by weight, since the solubility of potassium sulfate at 25° and atmospheric pressure is only 10.76%. Table I shows the results for the compression,  $k$  (fractional diminution in volume), at 1000 bars for solutions of four different concentrations, and the previously determined value of  $k$  for pure water. The weight fraction of salt is denoted by  $x_2$ . In Table I are given also the values of the important compression-concentration gradient,  $\partial k/\partial x_2$ , and the values of  $\bar{v}_1$  and  $\bar{v}_2$ , the fictive volumes of water and potassium sulfate at 1000 bars, or rather the change in these quantities caused by the pressure

<sup>1</sup> L. H. Adams, *THIS JOURNAL*, **53**, 3769-3813 (1931).

<sup>2</sup> Adams, *Ref. 1*, p. 3774.

TABLE I

COMPRESSION,  $k$ , OF POTASSIUM SULFATE SOLUTIONS AT 1000 BARS AND 25°

$x_2$	$k$	$-\partial k/\partial x_2$	$\bar{v}_1 - (\bar{v}_1)_0$	$\bar{v}_2 - (\bar{v}_2)_0$
0.0	0.03930	0.0640	-0.0394	0.0568
.025	.03787	.0624	- .0393	.0513
.05	.03647	.0608	- .0392	.0470
.075	.03470	.0592	- .0389	.0429
.10	.03322	.0576	- .0385	.0391

mentioned. The values of  $\partial k/\partial x_2$  were obtained by differentiating the equation

$$k = 0.03930 - 0.0640 x_2 + 0.032 x_2^2 \quad (1)$$

which, over the limited concentration range obtainable with this salt, seemed to give a fair representation of the data except possibly at concentrations very close to zero. The values of  $\bar{v}_1$  and  $\bar{v}_2$  were obtained from the relations [equations (29) and (28), respectively, of the previous paper]

$$\bar{v}_1 - (\bar{v}_1)_0 = -(\bar{v}_1)_0 k + x_2 v_0 \frac{\partial k}{\partial x_2} \quad (2a)$$

and

$$\bar{v}_2 - (\bar{v}_2)_0 = -(\bar{v}_2)_0 k - x_1 v_0 \frac{\partial k}{\partial x_2} \quad (2b)$$

in which  $v$  is the specific volume of the solution, and the subscript zero refers to atmospheric pressure.

**High-Pressure Experiments.**—For pressures above 1000 bars the measurements of the compression,  $k$ , were made by the usual piston-displacement method. The directly determined quantity was the difference between the compression of the solution (reckoned from 2000 bars, the arbitrary "initial" pressure) and that of pure water, that is,  $\Delta k - \Delta k'$ , the superscript prime referring to  $P = 2000$ . The results are shown in Table II, which includes also the values of  $k$  itself for the various concentra-

TABLE II

COMPRESSION,  $k$ , OF POTASSIUM SULFATE SOLUTIONS AT HIGH PRESSURES

$P$ , bars	$-10^5$ $(\Delta k - \Delta k')$ $x_2 = 0$		$-10^5$ $(\Delta k - \Delta k')$ $x_2 = 0.025$		$-10^5$ $(\Delta k - \Delta k')$ $x_2 = 0.05$		$-10^5$ $(\Delta k - \Delta k')$ $x_2 = 0.075$		$-10^5$ $(\Delta k - \Delta k')$ $x_2 = 0.10$	
	0	$k$	0	$k$	0	$k$	0	$k$	0	$k$
1	0	0.0000	0	0.0000	0	0.0000	0	0.0000	0	0.0000
1000	0	.0393	- 85	.0378	-212	.0365	-276	.0347	- 380	.0332
2000	0	.0699	0	.0675	0	.0650	0	.0625	0	.0600
3000	0	.0945	73	.0914	128	.0883	177	.0854	250	.0821
4000	0	.1152	130	.1115	226	.1080	326	.1046	472	.1006
5000	0	.1330	184	.1288	311	.1250	425	.1214	618	.1169
6000	0	.1485	222	.1439	340	.1402	504	.1361	724	.1314
7000	0	.1622	191	.1579	366	.1536	543	.1494	811	.1442
8000	0	.1746	226	.1700	415	.1655	627	.1610	922	.1555
9000	0	.1858	215	.1813	425	.1766	632	.1721	934	.1666
10000	0	.1964	221	.1918	425	.1872	661	.1824	1003	.1765

tions and pressures, as obtained by combining<sup>3</sup> the results for  $\Delta k - \Delta k'$  with those for  $\Delta k$  at 1000 bars given in Table I and with the previously determined values for the compression of water. A comparison of the compression of solutions of potassium sulfate with the previous results for sodium chloride shows that the addition of a given *weight* of potassium sulfate reduces the compression of water (at any pressure) almost the same amount as the addition of the same weight of sodium chloride, although the latter salt produces a slightly greater effect.

**Density of Potassium Sulfate Solutions.**—Before use can be made of these measurements for determining the equilibrium in the system,  $K_2SO_4-H_2O$ , it is necessary to have reliable data on the densities of the solutions at atmospheric pressure. These densities should be known to about one unit in the fifth place after the decimal point in order to obtain the desired accuracy in the fictive volumes of the two components. Unfortunately, there are only a few salts for which the densities of their aqueous solutions have been measured with reasonable accuracy—despite the fact that the determination of density is one of the simplest and the most fundamental of measurements. The best values for potassium sulfate solutions (as shown in the "International Critical Tables") are given only to the fourth figure after the decimal, and, as has now been found, there are errors as great as eight units in this place. It was necessary, therefore, to make a series of measurements on the densities of the solutions at 25°. This was done, with the recrystallized and carefully dried salt, according to the same method and by the use of the same pycnometer as that described in connection with earlier density determinations at this Laboratory.<sup>4</sup> The temperature of the thermostat was  $25^\circ \pm 0.003$  and the volume of the pycnometer at 25° was 55.0373 ml. This volume agreed well with the previous determinations, *viz.*, 55.0384 (Hall, 1920), 55.0365 (Gibson, 1927), and 55.0371 (Gibson, 1930).

The results are shown in Table III, and the "densities,"  $d$ , in ml./g. and the "specific volumes,"  $v$ , in g./ml. at round concentrations are given in Table IV. It was noted that for potassium sulfate, and also for other salts,  $\Delta v / \Delta x_2$  when plotted against  $x_2$  gave a line which curved notably at the origin but with increasing concentration rapidly approached a straight line. This at once suggested that the data might be represented well by an equation of the form

$$v = A + Bx_2 + Cx_2^2 + D(1 - e^{-Ex_2}) \quad (3)$$

in which  $A$ ,  $B$ ,  $C$ ,  $D$  and  $E$  are constants,  $A$  being the specific volume of pure water (1.002932 at 25°). It was found that with  $B = 0.79032$ ,  $C = 0.297$ ,  $D = 2.40 \times 10^{-4}$  and  $E = 100$ , this equation represented the

<sup>3</sup> Adams, Ref. 1, p. 3782.

<sup>4</sup> R. E. Hall, *J. Wash. Acad. Sci.*, **14**, 167-173 (1924); R. E. Gibson, *J. Phys. Chem.*, **31**, 496-510 (1927); *ibid.*, **35**, 690-699 (1931).

TABLE III  
DENSITIES AND SPECIFIC VOLUMES OF POTASSIUM SULFATE SOLUTIONS AT 25°

$x_2$	$d$ , g./ml.	$v_{\text{obs.}}$ , ml./g.	$v_{\text{calcd.}}$	Diff. $\times 10^4$ (obs. - calcd.)
0.0000	0.997077	1.002932	1.002932	0
.4995	1.001101	.998890	0.998897	3
.5001	1.001112	.998889	.998892	-3
2.5012	1.017154	.983135	.983131	4
4.9939	1.037375	.963972	.963967	5
5.0011	1.037426	.963924	.963913	11
7.5033	1.058132	.945062	.945064	-2
9.8655	1.078029	.927619	.927613	6
10.0038	1.079214	.926600	.926602	-2

TABLE IV  
SPECIFIC VOLUMES OF POTASSIUM SULFATE SOLUTIONS AT ROUND CONCENTRATIONS,  
AND THE FICTIVE VOLUMES OF THE TWO COMPONENTS. TEMPERATURE, 25°

$x_2$	$v$ , ml./g.	$d$ , g./ml.	$\bar{v}_1$	$\bar{v}_2$
0.000	1.002932	0.997077	1.00293	0.183
.025	.983140	1.017149	1.00258	.2252
.050	.963921	1.037430	1.00196	.2411
.075	.945089	1.058102	1.00102	.2553
.100	.926630	1.079179	0.99972	.2688

data with gratifying accuracy. As indicated by the last column of Table III, the average deviation (without regard to sign) between the observed values of  $v$  and those calculated from equation (3) was only  $4 \times 10^{-6}$ , which was no greater than the error of measurement.

The fictive volumes,  $\bar{v}_1$  and  $\bar{v}_2$ , of water and potassium sulfate in solution were calculated from the equations

$$\bar{v}_1 = v - x_2 \frac{dv}{dx_2} \quad (4a)$$

and

$$\bar{v}_2 = v + x_1 \frac{dv}{dx_2} \quad (4b)$$

the values of  $dv/dx_2$  being obtained by differentiating equation (3); except that, because there was good reason for believing that equation (3), despite the satisfactory way in which it fits the data, does not give precisely the right slope at zero concentration, the value of  $\bar{v}_2$  at  $x_2 = 0$  was determined by plotting the values of  $\bar{v}_2$  against  $\sqrt{x_1/x_2}$  and extrapolating the (nearly linear) curve back to zero. The results for  $\bar{v}_1$  and  $\bar{v}_2$  are shown in Table IV.

**Fictive Volumes under Pressure.**—The change of the fictive volumes under pressure is determined by the compression,  $k$ , of the solutions. The most convenient method of carrying out the calculation depends on the ease with which  $k$  can be represented as a function of  $x_2$  (at constant  $P$ ) or of  $P$  (at constant  $x_2$ ). With potassium sulfate solutions, just as was

found previously for sodium chloride solutions, the compression reckoned from 2000 bars (that is,  $k-k'$ ) seems to vary linearly with the concentration at constant pressure. Hence it was advantageous to deal directly with  $k-k'$  and to calculate the increase in  $\bar{v}_1$  and  $\bar{v}_2$ , respectively, due to an increase of pressure from 2000 to  $P$ , by the relations

$$\bar{v}_1 - \bar{v}_1' = -(\bar{v}_1)_0(k - k') + x_2 v_0 \frac{\partial(k - k')}{\partial x_2} \quad (5a)$$

and

$$v_2 - \bar{v}_2' = - (v_2)_0(k - k') - x_1 v_0 \frac{\partial(k - k')}{\partial x_2} \quad (5b)$$

The first step consisted in finding  $\partial(k-k')/\partial x_2$  at each pressure. This was done by representing  $k-k'$  as a linear function of  $x_2$  using the method of least squares. Next, the values of this compression-concentration gradient were smoothed by means of the equation

$$-10^5 \frac{\partial(k - k')}{\partial x_2} = 0.304(P - P') + 8000(1 - e^{-3.4 \times 10^{-4}(P - P')}) \quad (6)$$

which fitted the results for the gradient with an average deviation (regardless of sign) of 0.0014. Then,  $\bar{v}_1 - \bar{v}_1'$  and  $\bar{v}_2 - \bar{v}_2'$  at each pressure from 1000 to 10,000 bars were computed by means of equations (5a) and (5b); and finally, by use of the change in  $\bar{v}_1$  and in  $\bar{v}_2$  from 1 to 1000 bars, as shown in Table I, the values of  $\bar{v}_1$  and  $\bar{v}_2$  at the various pressures were obtained.

The fictive volumes under pressure were calculated also by another method, suggested by the recent discovery<sup>5</sup> that the "apparent molal volume" of electrolytes is a linear function of the square root of the concentration per unit volume for dilute solutions, and is very approximately so for concentrated solutions. The approximate linear relation holds also if the mole ratio or the mass ratio is substituted for the volume concentration. If  $\varphi$  be defined<sup>6</sup> by the relation,  $\varphi = v/x_2 - x_1 v_w/x_2$ , in which  $v_w$  is the specific volume of pure water, and if  $\varphi$  is a linear function of  $\sqrt{x_2/x_1}$  not only at atmospheric pressure but also at all other pressures, then it follows that

$$\Delta_P \varphi \equiv \frac{\Delta_P v - x_1 \Delta_P v_w}{x_2} = a + b \left( \frac{x_2}{x_1} \right)^{1/2} \quad (7)$$

in which  $a$  and  $b$  are constants (for a given salt and at a given temperature and pressure). Furthermore, from equation (7) in combination with

<sup>5</sup> D. O. Masson, *Phil. Mag.*, [7] 8, 218-235 (1931); A. F. Scott, *J. Phys. Chem.*, 35, 2315-2319 (1931); W. Geffcken, *Z. physik. Chem.*, 155A, 1-28 (1931). See also the accurate measurements by A. B. Lamb and R. E. Lee [THIS JOURNAL, 35, 1666-1693 (1913)] on the densities of very dilute aqueous salt solutions. From a study of these results it may be seen that the square root plot for moderate concentration may be extrapolated with safety to zero, or at least to extremely small concentrations.

<sup>6</sup> It should be noted that here  $\varphi$  is not the "apparent molal volume" (as usually defined); it is that quantity divided by the formula weight of the salt, and might be called the "apparent specific volume" of the salt in solution.

equations [similar to (4a) and (4b)] for the fictive volumes under pressure in terms of  $\Delta v$ , it may readily be shown that

$$\Delta_P \bar{v}_1 \equiv \bar{v}_1 - (\bar{v}_1)_0 = \Delta_P v_w - \frac{b}{2} \left( \frac{x_2}{x_1} \right)^{3/2} \quad (8a)$$

and

$$\Delta_P \bar{v}_2 \equiv \bar{v}_2 - (\bar{v}_2)_0 = a + \frac{3b}{2} \left( \frac{x_2}{x_1} \right)^{1/2} \quad (8b)$$

The supposition that (7) would give a faithful representation of the compression results was confirmed by applying the equation to the previously obtained data for sodium chloride solutions.

In order to calculate  $\bar{v}_1$  and  $\bar{v}_2$  under pressure by these equations, the values of  $k$  for the potassium sulfate solutions, as given in Table II, were converted to  $\Delta v$ 's by the relation,  $\Delta_P v = -v_0 k$ , then  $\Delta_P \varphi$  was calculated, and  $a$  and  $b$  at each pressure determined graphically by plotting  $\Delta_P \varphi$  against  $\sqrt{x_2/x_1}$ . These values of  $a$  and  $b$  were then used in equations (8a) and (8b) to calculate  $\bar{v}_1$  and  $\bar{v}_2$  at the various pressures. The fictive volumes thus calculated agreed well with those calculated by the previous method,

TABLE V

FICTIVE VOLUME OF WATER IN POTASSIUM SULFATE SOLUTIONS UNDER PRESSURE

Pressure in bars	$\bar{v}_1$ $x_2 = 0$	$10^4 \Delta_P \bar{v}_1$	$\bar{v}_1$ $x_2 = 0.025$	$10^4 \Delta_P \bar{v}_1$	$\bar{v}_1$ $x_2 = 0.05$	$10^4 \Delta_P \bar{v}_1$	$\bar{v}_1$ $x_2 = 0.075$	$10^4 \Delta_P \bar{v}_1$	$\bar{v}_1$ $x_2 = 0.10$	$10^4 \Delta_P \bar{v}_1$
1	1.0029	0	1.0026	-3	1.0020	-9	1.0010	-19	0.9997	-32
1000	0.9635	0	0.9633	-2	0.9628	-7	0.9621	-14	.9612	-23
2000	.9328	0	.9327	-1	.9322	-6	.9317	-11	.9309	-19
3000	.9081	0	.9080	-1	.9076	-5	.9072	-9	.9065	-16
4000	.8874	0	.8873	-1	.8869	-5	.8865	-9	.8860	-14
5000	.8695	0	.8694	-1	.8691	-4	.8687	-8	.8682	-13
6000	.8540	0	.8539	-1	.8534	-4	.8533	-7	.8529	-11
7000	.8402	0	.8402	0	.8398	-4	.8396	-6	.8392	-10
8000	.8278	0	.8278	0	.8275	-3	.8273	-5	.8269	-9
9000	.8166	0	.8166	0	.8163	-3	.8161	-5	.8157	-9
10000	.8059	0	.8059	0	.8057	-2	.8055	-4	.8051	-8

TABLE VI

FICTIVE VOLUME OF POTASSIUM SULFATE IN AQUEOUS SOLUTIONS UNDER PRESSURE

Pressure in bars	$\bar{v}_2$ $x_2 = 0$	$10^3 \Delta_P \bar{v}_2$	$\bar{v}_2$ $x_2 = 0.025$	$10^3 \Delta_P \bar{v}_2$	$\bar{v}_2$ $x_2 = 0.05$	$10^3 \Delta_P \bar{v}_2$	$\bar{v}_2$ $x_2 = 0.075$	$10^3 \Delta_P \bar{v}_2$	$\bar{v}_2$ $x_2 = 0.10$	$10^3 \Delta_P \bar{v}_2$
1	0.183	0	0.225	42	0.241	58	0.255	72	0.269	86
1000	.243	0	.277	34	.288	45	.298	55	.308	65
2000	.279	0	.306	27	.316	37	.324	45	.332	53
3000	.302	0	.326	24	.334	32	.341	39	.348	46
4000	.318	0	.340	22	.347	29	.354	36	.360	42
5000	.329	0	.350	21	.357	28	.362	33	.367	38
6000	.338	0	.358	20	.364	26	.368	30	.373	35
7000	.345	0	.363	18	.369	24	.373	28	.377	32
8000	.350	0	.367	17	.372	22	.376	26	.380	30
9000	.354	0	.371	17	.375	21	.379	25	.382	28
10000	.357	0	.373	16	.377	20	.380	23	.384	27

except for  $\bar{v}_2$  at  $x_2 = 0$ . It seems probable that equation (7) takes account of the peculiar relations in very dilute solutions of electrolytes much better than the previous method; therefore, for  $\bar{v}_2$  at  $x_2 = 0$  only the values obtained from (8b) are here recorded. The final results are given in Tables V and VI, which include also the values of  $\Delta_x \bar{v}_1$  (the change with concentration, of  $\bar{v}_1$  at a given constant pressure), and of  $\Delta_x \bar{v}_2$ .

Figure 1 is a graphical representation of the way in which pressure affects the fictive volume,  $\bar{v}_2$ , of potassium sulfate in aqueous solution. With increasing pressure,  $\bar{v}_2$  for each concentration *increases*. In other words, the fictive compressibility is negative. This is similar to what was previously observed for sodium chloride in water. In the present case, however, no maximum is seen when  $\bar{v}_2$  is plotted against  $P$ . This is probably because a maximum is more readily attained only at high concentrations, and the solubility of potassium sulfate is not large enough for the maximum to appear unless the pressure were appreciably higher than 10,000 bars, in which event (at 25°) the solution would freeze.

A plot of  $\bar{v}_2$  or  $\bar{v}_1$  against  $x_2$  (at constant  $P$ ) would again demonstrate the striking fact that under high pressure, solutions tend to become more simple in nature, that is, more nearly "normal." At atmospheric pressure the change of  $\bar{v}_1$  or  $\bar{v}_2$  with varying concentration is large for salts such as potassium sulfate, but at 10,000 bars both  $\bar{v}_1$  and  $\bar{v}_2$  are much less affected by changes in concentration, and the solutions thus behave more nearly like ideal solutions.<sup>7</sup>

<sup>7</sup> Cf. Adams, Ref. 1, p. 3795.

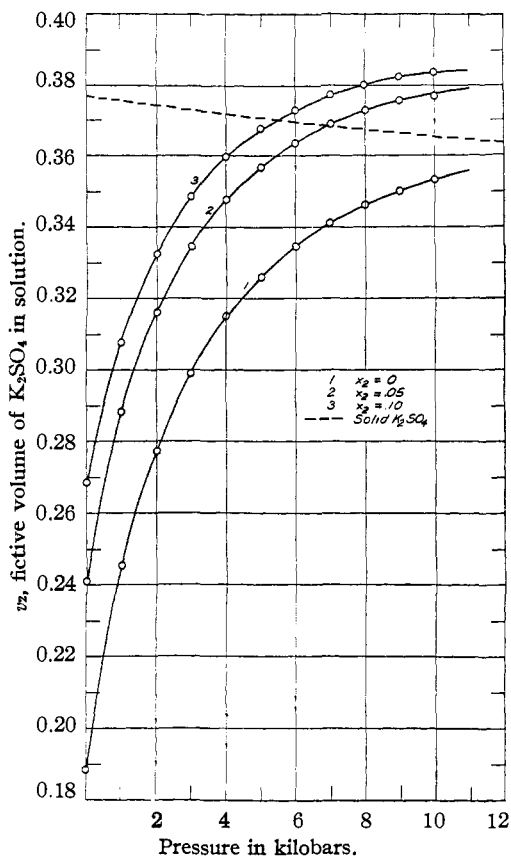


Fig. 1.—The effect of pressure on the fictive volume,  $\bar{v}_2$ , of potassium sulfate in aqueous solutions. Pressure produces a notable increase in  $\bar{v}_2$ , especially in dilute solutions. The dotted line shows the volume of solid  $K_2SO_4$  at various pressures.

### Determination of Equilibrium by the Thermodynamic Method

**Calculation of  $\mu_1$  and  $\mu_2$ .**—Equilibrium between the various phases in a system is always in accord with the principle, enunciated by Gibbs, that for any actual component its chemical potential,  $\mu$ , shall have at equilibrium the same value in all of the phases. The  $\mu$ 's may be readily calculated from the fictive volumes when these are known. As previously explained,<sup>8</sup> the most convenient method, in actual practice, is to use the equation

$$(x_1 \text{ constant}) \quad \Delta_x \mu_1 \equiv \mu_1 - (\mu_1)_w = \Delta_x(\mu_1)_0 + \int_1^P \Delta_x \bar{v}_1 dP \quad (9)$$

for  $\mu_1$ , and the similar equation for  $\mu_2$ . As before, the subscript zero refers to atmospheric pressure and the subscript  $w$  to pure water (zero concentration).

In Table VII are shown the results of the calculation concerning  $\mu_1$ . Under each concentration are two columns; the first gives  $\Delta_x/(\mu_1)_0 - \Delta_x \mu_1$ , that is, the negative of the definite integral in equation (7), and the second gives  $-\Delta_x \mu_1$ , obtained by subtracting the value of  $\Delta_x(\mu_1)_0$  (at that concentration) from the values in the first column.

TABLE VII

#### CHEMICAL POTENTIAL, $\mu_1$ , OF WATER IN POTASSIUM SULFATE SOLUTIONS UNDER PRESSURE

$\Delta_x \mu_1$  is the difference (in joules) between the value of  $\mu_1$  for the particular concentration and the value for pure water at the same pressure.

Pressure in bars	$(\Delta_x \mu_1)_0 - \Delta_x \mu_1$ $x_2 = 0$		$(\Delta_x \mu_1)_0 - \Delta_x \mu_1$ $x_2 = 0.025$		$(\Delta_x \mu_1)_0 - \Delta_x \mu_1$ $x_2 = 0.05$		$(\Delta_x \mu_1)_0 - \Delta_x \mu_1$ $x_2 = 0.075$		$(\Delta_x \mu_1)_0 - \Delta_x \mu_1$ $x_2 = 0.10$	
	1	0	0	0.00	0.82	0.00	1.59	0.00	2.40	0.00
1000	0	0	.03	.85	.08	1.67	.16	2.56	.26	3.49
2000	0	0	.05	.87	.15	1.74	.28	2.68	.47	3.70
3000	0	0	.06	.88	.21	1.80	.38	2.78	.64	3.87
4000	0	0	.07	.89	.26	1.85	.47	2.87	.79	4.02
5000	0	0	.08	.90	.30	1.89	.55	2.95	.93	4.16
6000	0	0	.09	.91	.34	1.93	.63	3.03	1.05	4.28
7000	0	0	.09	.91	.38	1.97	.70	3.10	1.15	4.38
8000	0	0	.09	.91	.41	2.00	.76	3.16	1.25	4.48
9000	0	0	.09	.91	.44	2.03	.81	3.21	1.34	4.57
10000	0	0	.09	.91	.46	2.05	.85	3.25	1.42	4.65

The values of  $\Delta_x(\mu_1)_0$ , that is,  $\mu_1 - (\mu_1)_w$  at atmospheric pressure, were obtained from data on the freezing points and vapor pressures of potassium sulfate solutions given in the "International Critical Tables" and from Åkerlöf's<sup>9</sup> measurements on the e. m. f. of cells containing potassium sulfate solutions, the method of calculation being the same as that described in the previous paper. The weighted mean of  $\Delta_x(\mu_1)_0$  computed from the various kinds of data is shown in the first row of Table VII opposite  $P = 1$ .

<sup>8</sup> Adams, Ref. 1, p. 3798.

<sup>9</sup> G. Åkerlöf, THIS JOURNAL, 48, 1160-1176 (1926).



Table VIII similarly gives the results of the calculation concerning the effect of pressure on  $\mu_2$ . In this instance only  $\Delta_x\mu_2 - \Delta_x(\mu_2)_0$  is shown, and

TABLE VIII  
EFFECT OF HIGH PRESSURE ON THE CHEMICAL POTENTIAL OF POTASSIUM SULFATE IN AQUEOUS SOLUTIONS

$\Delta_x\mu_2 - (\Delta_x\mu_2)_0$  is equivalent to  $\Delta_P\mu_2 - (\Delta_P\mu_2)_w$ . Here  $\Delta_x\mu_2$  is the difference between the value of  $\mu_2$  for the particular concentration and the value at zero concentration and the same pressure.

Pressure in bars	$\Delta_x\mu_2 - (\Delta_x\mu_2)_0$ in joules				
	$x_2 = 0$	$x_2 = 0.025$	$x_2 = 0.05$	$x_2 = 0.075$	$x_2 = 0.10$
1	0	0.0	0.0	0.0	0.0
1000	0	3.7	5.1	6.3	7.5
2000	0	6.8	9.2	11.3	13.4
3000	0	9.3	12.6	15.5	18.3
4000	0	11.5	15.7	19.2	22.7
5000	0	13.7	18.5	22.7	26.7
6000	0	15.7	21.2	25.8	30.4
7000	0	17.5	23.7	28.7	33.7
8000	0	19.3	26.0	31.4	36.8
9000	0	21.0	28.2	34.0	39.7
10000	0	22.6	30.2	36.4	42.5

here  $\Delta_x\mu_2$  means  $\mu_2 - (\mu_2)_w$ , not as in the first paper,  $\mu_2 - (\mu_2)_s$ , the subscript  $s$  referring to a fixed and arbitrary concentration. However, the values of  $\Delta_x\mu_2 - \Delta_x(\mu_2)_0$  given in Table VIII may by simple subtraction be transformed into the corresponding values on the former basis. It is important to remember that, although  $\Delta_x\mu_2$  as now defined is always negatively infinite, this does not prevent its change with pressure,  $\Delta_x\mu_2 - \Delta_x(\mu_2)_0$ , from having a finite value.<sup>10</sup>

**The Freezing Pressure Curve of Ice<sub>V<sub>I</sub></sub>.**—At 25° pure water freezes to ice<sub>V<sub>I</sub></sub> at 9630 bars, but upon the addition of potassium sulfate (or almost any other solute) the freezing pressure is raised, by an amount determined by the equality of the  $\mu$ 's of ice<sub>V<sub>I</sub></sub> and the water in solution at the given pressure. For convenience the consequent identity of  $\mu_1 - (\mu_1)_w$  (*i. e.*,  $\Delta_x\mu_1$ ) and  $\mu_{V<sub>I</sub>} - (\mu_1)_w$  is utilized in the calculation of the freezing pressure curve. The values of the latter quantity<sup>11</sup> were taken from the previous paper. In order to find the freezing pressures at several concentrations, the values of  $\Delta_x\mu_1$  for each concentration were plotted against pressure, and the intersections of these curves with the curve for  $\mu_{V<sub>I</sub>} - (\mu_1)_w$  were then the freezing pressures at the respective concentrations. The results are shown in Table IX, which also gives for comparison the lowering of freezing temperature (of ice<sub>T</sub>) at atmospheric pressure and at the same concentration. As in the case of sodium chloride and water, the freezing pressure curve shows a greater curvature than that of the freezing temperature.

<sup>10</sup> It may be useful to note that  $\Delta_x\mu_2 - \Delta_x(\mu_2)_0$  is identical with  $\Delta_P\mu_2 - \Delta_P(\mu_2)_w$ .

<sup>11</sup> Adams, Ref. 1, last column of Table X, p 3802.

It is interesting to calculate the theoretical initial slope of the freezing pressure curve. In general, for the change of freezing pressure

$$\frac{dP}{dx_2} = \frac{\partial\mu_1/\partial x_2}{v_{VI} - \bar{v}_1} \quad (10)$$

by analogy with the equation for the change of solubility under pressure.<sup>12</sup> By substitution of the value of  $\partial\mu_1/\partial x_2$ , as given by Gibbs' approximation for dilute solutions,<sup>13</sup> there is obtained

$$\frac{dP}{dx_2} = \frac{RT}{x_1^2 M_2' (\bar{v}_1 - v_{VI})} \quad (11)$$

for the slope at high dilutions. Taking  $x_1 = 1$ ,  $\bar{v}_1 - v_{VI} = 0.071$ ,  $T = 298$ ,  $R = 83$  decijoules, and  $M_2' = 174.2/3 = 58.1$ , we find  $dP/dx_2$  at  $x_2 = 0$  to be 60 bars for 1% change in salt concentration, which is slightly greater than the average slope from 0 to 2.5% as shown in the third column of Table IX.

TABLE IX

FREEZING PRESSURES OF ICE<sub>VI</sub> IN CONTACT WITH POTASSIUM SULFATE SOLUTIONS AT 25°

$x_2$ , wt. fraction of K <sub>2</sub> SO <sub>4</sub>	$P$ in bars	$P - P_0$ (ice <sub>VI</sub> )	$t_0 - t$ (ice <sub>I</sub> )	$10^2 \frac{t_0 - t}{P - P_0}$
0.0	9630	0	0.000	..
.025	9770	140	0.615	0.44
.05	9930	300	1.168	.39
.075	10100	470	1.742	.37
.10	10290	660		

For the initial slope of the freezing temperature curve we have the relation, similar to equation (11)

$$\frac{dT}{dx_2} = - \frac{RT^2}{x_1^2 M_2' \Delta \bar{h}_1} \quad (12)$$

in which  $\Delta \bar{h}_1$  is approximately the heat of melting of ice<sub>I</sub> per gram. Combining equations (11) and (12) we obtain

$$\frac{(-dT/dx_2)_I}{(dP/dx_2)_{VI}} = \frac{T_I^2 (\bar{v}_1 - v_{VI})}{T_{VI} \Delta \bar{h}_1} \quad (13)$$

which is an important relation for determining the limiting ratio, in dilute solution, between the freezing temperature lowering and the freezing pressure elevation. (This equation closely resembles the Braun equation for the relation between the effect of pressure and of temperature on solubility.) This limiting ratio is independent of the nature of the solute, and

<sup>12</sup> Adams, Ref. 1, equation (45), p. 3804.

<sup>13</sup> This may be written  $\partial\mu_1/\partial x_2 = -RT/x_1^2 M_2'$ . See R. W. Goranson, "Thermodynamic Relations in Multi-component Systems," Carnegie Institution of Washington, Publ. No. 408, 1930, p. 320. In general  $M_2'$  is the effective molecular weight of the solute, *i. e.*, one-third of the formula weight for a tri-ionic salt such as potassium sulfate in very dilute solutions.

depends only on the solvent; for water (if  $T_{V1}$  is 298°) it is  $0.53 \times 10^{-2}$ , which is in accord with the trend of the ratio given in the last column of Table IX.

**The Solubility Curve of Potassium Sulfate.**—The solubility at various pressures was calculated by means of the equation, used in the former paper

$$x_2 = (x_2)_0 + \int_1^P \frac{v_2 - \bar{v}_2}{\partial\mu_2/\partial x_2} \cdot \quad (14)$$

The values of  $v_2$ , the specific volume of the solid salt under pressure, were taken from the measurements by Adams and Gibson;<sup>14</sup>  $\bar{v}_2$  is given in Table VI;  $(x_2)_0$ , the solubility at atmospheric pressure, was taken as 0.1076 according to the "International Critical Tables"; and  $\partial\mu_2/\partial x_2$  was calculated from the data used above for the calculation of  $\mu_1$ . From the e. m. f. data  $\partial\mu_2/\partial x_2$  at  $x_2 = 0.1076$  was found to be 273 joules. The coefficient was also computed, by the method described in the earlier paper, from the heat of solution of the salt and change of solubility with temperature. With  $\Delta\bar{h}_2 = 112$  joules and  $(dx_2/dt)_{\text{satn.}} = 0.00148$ ,  $\partial\mu_2/\partial x_2$  at  $x_2 = 0.1076$  was found to be 254. Probably more weight should be given to the first value, and we shall take  $\partial\mu_2/\partial x_2$  as 265 joules at atmospheric pressure and at  $x_2 = 0.1076$ . The e. m. f. data allow us to calculate the change of  $\partial\mu_2/\partial x_2$  with concentration. Thus at  $x_2 = 0.10$ ,  $\partial\mu_2/\partial x_2$  is 290, and at  $x_2 = 0.15$  (by extrapolation) is 185. At pressures other than atmospheric the magnitude of  $\partial\mu_2/\partial x_2$  was computed by numerical integration of the equation

$$\frac{\partial\mu_2}{\partial x_2} = \left(\frac{\partial\mu_2}{\partial x_2}\right)_0 + \int_1^P \frac{\partial v_2}{\partial x_2} dP \quad (15)$$

The variation under pressure of  $\partial\mu_2/\partial x_2$  for potassium sulfate at concentrations near saturation is considerably greater than for sodium chloride. In the present instance, an increase of pressure from 1 to 10,000 bars changes  $\partial\mu_2/\partial x_2$  at  $x_2 = 0.10$  to 502, and at  $x_2 = 0.15$  to 380.

In Table X are shown the results for the solubility of potassium sulfate in water at pressures up to 12,000 bars, together with the most important steps in the calculation. The results above 10,000 bars were obtained by extrapolation of the data from which the solubility was determined. Since  $\bar{v}_2$  and  $\partial\mu_2/\partial x_2$  pertain to the saturation-concentration at each pressure, and since this concentration changes by a considerable amount under pressure, it was necessary to carry out the computation by a series of approximations. First,  $\bar{v}_2$  and  $\partial\mu_2/\partial x_2$  at  $x_2 = 0.1076$  were used in equation (14), and a first approximation thus obtained. Then, new values of  $\bar{v}_2$  and  $\partial\mu_2/\partial x_2$  were calculated at the approximated  $x_2$ 's, and the integration repeated. The third approximation differed very little from the second, and is the one shown in Table X.

<sup>14</sup> Adams and Gibson, *J. Wash. Acad. Sci.*, **21**, 387 (1931).

TABLE X  
SOLUBILITY OF POTASSIUM SULFATE IN WATER AT VARIOUS PRESSURES  
Temperature, 25°

Pressure in bars	$v_2$	$\bar{v}_2$ at satn.	$\bar{v}_2 - (\bar{v}_2)_{\text{satn.}}$	$\frac{\partial \mu_2}{\partial x_2}$ at $x_2 = 0.10$ (joules)	$\frac{\partial \mu_2}{\partial x_2}$ at satn. (joules)	$10^2 \Delta x_2$	$x_2$
1	0.3761	0.2722	0.1039	290	265	0.0	0.1076
1000	.3749	.3206	.0543	330	240	3.03	.138
2000	.3737	.3466	.0271	364	245	4.67	.154
3000	.3725	.3616	.0109	391	262	5.34	.161
4000	.3713	.3714	-.0001	414	281	5.55	.163
5000	.3702	.3779	-.0077	433	299	5.42	.162
6000	.3691	.3815	-.0124	449	318	5.09	.159
7000	.3681	.3842	-.0161	464	339	4.66	.154
8000	.3670	.3861	-.0191	478	360	4.16	.149
9000	.3660	.3872	-.0212	490	380	3.62	.144
10000	.3651	.3877	-.0226	502	400	3.05	.138
11000	.3641					(2.47)	(.132)

**The Equilibrium Diagram.**—The course of the freezing pressure curve for  $\text{ice}_{VI}$  and of the solubility curve of potassium sulfate is illustrated in Fig. 2. Initially the solubility rises rapidly with increase of pressure, but the rate of increase falls off, and attains a maximum at 3800 bars, at

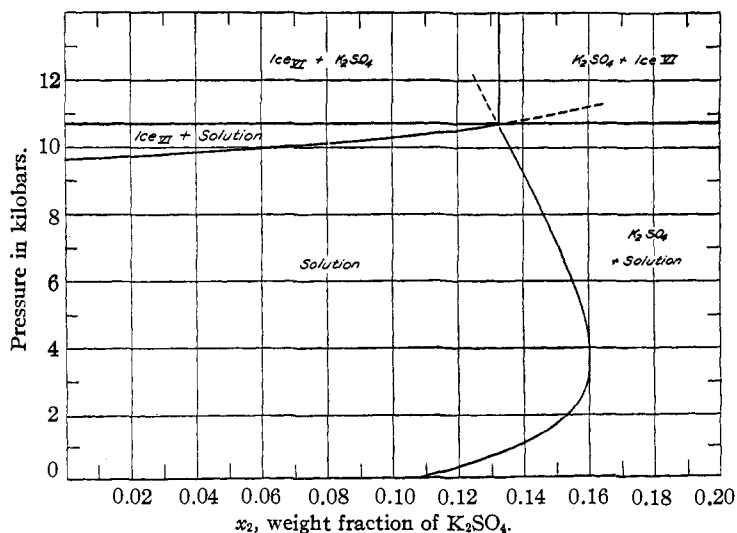


Fig. 2.—The equilibrium diagram for the system,  $\text{K}_2\text{SO}_4\text{-H}_2\text{O}$ , under pressure.

which point the solubility is 16.3%. At higher pressures the solubility diminishes steadily until the curve intersects the freezing pressure curve of  $\text{ice}_{VI}$  at  $P = 10,750$  and  $x_2 = 13.3$ , and subsequent increase of pressure would cause complete solidification to a mixture of  $\text{ice}_{VI}$  and solid salt.

This invariant point is analogous to an ordinary eutectic in a temperature-concentration diagram, and may be called a pressure-eutectic. A comparison with the diagram for  $\text{NaCl-H}_2\text{O}$  shows the following differences: (1) in general appearance the diagram is much more simple, mainly on account of the lack of formation of a solid hydrate, such as was observed in the former system; (2) the variation of solubility is much greater in the present case, although a maximum solubility is attained at nearly the same pressure; (3) the total increase of freezing pressure of  $\text{ice}_{\text{VI}}$  is much less than with  $\text{NaCl-H}_2\text{O}$  (partly due to the low solubility of potassium sulfate), so that the eutectic pressure is not far above the freezing pressure of pure water.

### Direct Determinations of Equilibrium

No direct measurements of the solubility of potassium sulfate under pressure were made, but a direct determination of the freezing pressure of a 10% solution was carried out by the method described in the previous paper.<sup>15</sup> The mean of two measurements, which differed by 19 bars, was 10,200 bars (rounded off to the nearest 10). The agreement with the indirect determination, 10,290 bars, is not quite as satisfactory as was expected. The discrepancy is probably mainly due to the uncertainty in the value of  $\mu_1$  at atmospheric pressure, especially in the concentrated solutions.

Since the eutectic pressure is so comparatively low it was found possible to make a direct determination of this also. All that was required was to continue to increase the pressure on the solution until sufficient  $\text{ice}_{\text{VI}}$  had frozen out to bring the concentration of salt in the solution up to the saturation value, whereupon the pressure remained constant although the volume was further decreased—provided equilibrium was attained. Figure 3 illustrates the procedure in determining the eutectic pressure and also the freezing pressure of the solution. The latter was at the point marked A in the diagram. As increasing amounts of  $\text{ice}_{\text{VI}}$  froze out the equilibrium pressure followed along the line AB, and at B was saturated with respect to the salt. The solid salt did not immediately precipitate, however; some supersaturation was observed as shown by the dotted prolongation of AB. After the solution had been allowed to remain undisturbed for about one hour, salt had crystallized out and the pressure had fallen to practically the equilibrium value. Along the line BC the pressure remained substantially constant and at C the solution had entirely solidified to a mixture of  $\text{ice}_{\text{VI}}$  and solid potassium sulfate. The directly measured eutectic pressure was 10,880 bars, which is to be compared with 10,750 bars, the result of the indirect determination. The agreement is not so close as in the determination of the freezing pressure of the 10% solution by the two methods. It may be noted that the eutectic pressure (by the indirect

<sup>15</sup> Adams, Ref. 1, pp. 3811 *et seq.*

determination) is dependent on the course of the solubility curve, which in turn is considerably affected by any uncertainty in the value of  $\mu_2$  at atmospheric pressure. The principal difficulty here arises from the necessity for extrapolating  $\mu_2$  into a region of concentration far beyond that in which it has been measured. Indeed, the weakest link in the chain of data used for the determination of equilibrium in systems under pressure is probably the simple physical properties of the concentrated solutions at atmospheric pressure.

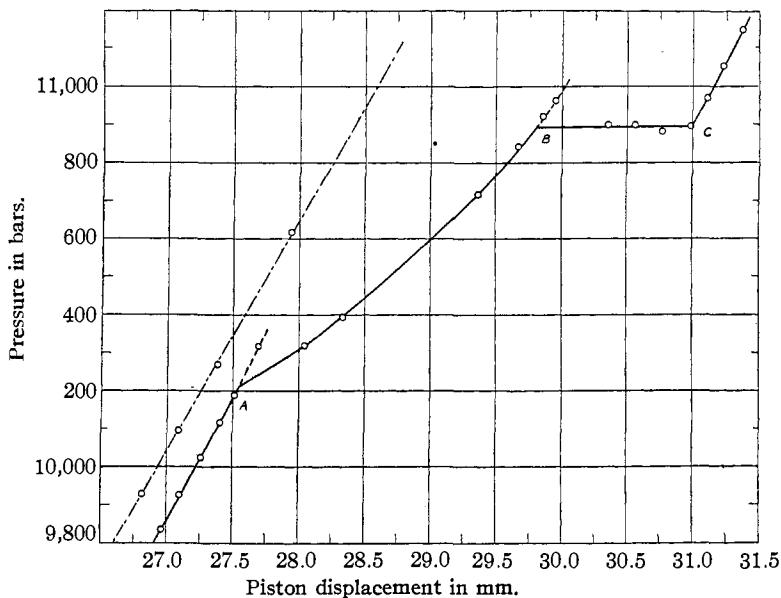


Fig. 3.—Diagram showing the method used in the direct determination of the freezing pressure of a 10%  $K_2SO_4$  solution and also the eutectic pressure. The point A indicates the beginning of freezing, B the eutectic pressure and C complete solidification.

### Summary

The compression of aqueous solutions of potassium sulfate was measured at pressures up to 10,000 bars, and from these measurements the fictive (partial) volumes and the chemical potentials of the two components were calculated according to the procedure described in a former communication.

Under pressure the fictive volume of the salt shows the same striking *increase* that was observed previously for sodium chloride. This phenomenon suggests that pressure causes solutions to become more nearly ideal.

From the values of the chemical potentials at various pressures the solubility curve of the salt and the freezing pressure curve of ice<sub>VI</sub> were calculated, and an equilibrium diagram for the system,  $K_2SO_4$ - $H_2O$ , under high-

pressure was constructed. Direct measurements of the eutectic pressure, and of the freezing pressure of a 10% solution, showed a fair agreement with the indirect determinations.

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## THE USE OF THE ANTIMONY ELECTRODE IN THE ELECTROMETRIC ESTIMATION OF MAGNESIUM<sup>1</sup>

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**Introduction.**—Extended work on "lime" in this Department demanded determination of magnesium at frequent intervals, especially in control work. The standard methods for such determinations were long and tedious. Their precision also has been a subject of controversy in recent years. The ordinary hydrogen electrode method suggested itself but was complicated and too highly sensitive to permit of ready handling without error. The convenience and simplicity of the antimony electrode made it desirable to investigate its application to the determination of magnesium. The present paper deals with this investigation.

**Literature.**—Hildebrand and Harned<sup>1a</sup> were the first to use the hydrogen electrode method for the determination of magnesium in the presence of calcium in dolomite and limestone. They considered their method as fairly rapid and accurate. H. S. Harned<sup>2</sup> applied the conductimetric method for the determination of magnesium in magnesium sulfate. According to him, the value "agreed with that from a gravimetric analysis." Later I. M. Kolthoff<sup>3</sup> confirmed the above work and stated that satisfactory results were obtained by precipitating the magnesium hydroxide with excess standard alkali, filtering and titrating back with standard acid. Gilbert A. Freak,<sup>4</sup> using the conductimetric method, studied the "effect of dilution in electro-titrimetric analysis." I. M. Kolthoff<sup>5</sup> confirmed Pinkhoff's result (Diss., Amsterdam, 1919) and made an extensive study of this magnesium reaction, using the hydrogen electrode. He declared that the method was of little practical use.

**The Use of the Antimony Electrode.**—The antimony electrode has found application in recent years in electrometric work. For the most

<sup>1</sup> Original manuscript received February 18, 1931.

<sup>1a</sup> Hildebrand and Harned, *Proc. 8th Intern. Congr. App. Chem.*, **1**, 217 (1912).

<sup>2</sup> Harned, *THIS JOURNAL*, **39**, 252-266 (1917).

<sup>3</sup> Kolthoff, *Z. anorg. allgem. Chem.*, **112**, 172 (1920).

<sup>4</sup> Freak, *J. Chem. Soc.*, **115**, 55-61 (1919).

<sup>5</sup> Kolthoff, *Rec. trav. chim.*, **41** (1922), and Kolthoff and Furman in "Potentiometric Titrations," John Wiley and Sons, Inc., New York, 1926.