

bility of a separation by diffusion must be considered when a mixture of gases of widely different densities is handled at low pressures.

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RECEIVED FEBRUARY 9, 1933

PUBLISHED JULY 6, 1933

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

## Changes of Chemical Potential in Concentrated Solutions of Certain Salts<sup>1</sup>

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The chemical potential of a component in a homogeneous mass or phase was defined by Willard Gibbs<sup>2</sup> by the following equation

$$\mu_1 = \left( \frac{dE}{dm_1} \right)_{S, V, m_2, m_3, \dots} \quad (1)$$

where  $\mu_1$  is the chemical potential of component 1,  $E$  is the total intrinsic energy,  $S$  the total entropy, and  $V$  the total volume of that mass of the phase which contains  $m_1, m_2, m_3, \dots$ , grams of the various components. From the two laws of thermodynamics Gibbs showed that necessary and sufficient conditions for the coexistence in equilibrium of two or more phases in contact with each other were that the pressure and the temperature should be the same throughout all the phases and that the chemical potential of each component substance, as defined above, must have the same value in all the phases of which it is an actual component.<sup>3</sup> Furthermore, it may be demonstrated rigorously that in any phase the chemical potential of a component is a function of the pressure, the temperature and the composition of the phase and of these variables only.<sup>4</sup>

In a phase of two components such as an aqueous salt solution one independent variable, *e. g.*, the weight fraction,  $x$ , of one or other component is sufficient to determine the composition so that

$$\begin{aligned} \mu_1 &= F_1(P, T, x_1) \\ \text{or } \mu_2 &= F_2(P, T, x_2) \end{aligned} \quad (2)$$

An outstanding practical problem in inorganic chemistry, namely, a determination, as complete as possible, of all the conditions under which a given set of phases in any particular system will coexist at equilibrium, resolves itself into the empirical determination of the chemical potentials of the components in each of the phases as functions of the temperature, the pressure and the composition. When this knowledge is at hand, it is a relatively simple matter to find the combinations of pressure, temperature

(1) Read before the Washington Section, American Chemical Society, April 14, 1932.

(2) J. Willard Gibbs, "Collected Works," Longmans, Green and Co., 1928, Vol. 1, p. 63.

(3) Gibbs, Ref. 2, p. 65.

(4) It is assumed that conditions are so chosen that effects due to capillarity, gravitational or electrostatic forces are negligibly small.

and composition which make the chemical potential of a given component equal in all the phases.

Thus, from measurements on single phases of the effect of pressure, temperature, and concentration on the chemical potentials of the components, and from a knowledge of one set of conditions under which these phases exist together in stable equilibrium, it is possible to calculate all the changes of  $P$ ,  $T$ ,  $x$  which leave the equilibrium undisturbed.

In this Laboratory attention has been directed to the effect of pressure on the solubility of the components in binary solutions at constant temperature. Methods have been devised for making accurate estimations of the compressibilities of solutions<sup>5</sup> and from these data the changes of the chemical potentials of the components with pressure can be calculated. A search of the literature showed, however, that although copious and excellent data for the calculation of the variation with concentration of chemical potentials in dilute solutions are available, adequate data for concentrated solutions are few and far between.<sup>6</sup> The experiments described here were undertaken to provide such data with an accuracy of 0.2 to 1% and at such concentration intervals that the slopes of the chemical potential *vs.* concentration curves might be known with confidence, especially in the region of saturation. The results have also some intrinsic interest, which will be discussed here from an empirical standpoint.

### Experimental

Of all the methods available for the measurement of the variation with concentration of the chemical potential of a given component, the determination of the vapor pressure lowering of the solvent is the simplest and most generally applicable to aqueous salt solutions. Unlike the freezing point depression method it may be applied directly at any desired temperature, and unlike those methods that depend on electromotive force measurements, it is independent of complex ion formation or the necessity of suitable reversible electrodes.

**Static Method.**—Most of our measurements of the vapor pressure lowerings were made by a static method in which the difference between the vapor pressure of a solution and that of pure water was determined by a differential manometer. This method has been used by many investigators,<sup>7</sup> notably Dieterici,<sup>8</sup> W. R. and C. E. Bousfield,<sup>9</sup> Frazer and Lovelace,<sup>10</sup> and by Fricke.<sup>11</sup> The actual apparatus used is shown diagrammatically in Fig. 1. While the general form is conventional, three features designed for accuracy and convenience may be noted.

(5) L. H. Adams, *THIS JOURNAL*, **53**, 3769–3813 (1931).

(6) Since this work was undertaken valuable results from J. N. Pearce and his school have appeared. J. N. Pearce and A. F. Nelson, *ibid.*, **54**, 3544 (1932).

(7) A summary of the literature is to be found in K. Jellinek, "Lehrbuch der physikalischen Chemie," Ferd. Enke, Stuttgart, 1928, Vol. II, pp. 704 ff.

(8) C. Dieterici, *Ann. Physik*, [3] **50**, 47 (1893); **62**, 616 (1897); **67**, 859 (1899).

(9) W. R. Bousfield and C. E. Bousfield, *Proc. Roy. Soc. (London)*, **A103**, 429–443 (1923).

(10) J. C. W. Frazer and B. F. Lovelace, *THIS JOURNAL*, **36**, 2439 (1914).

(11) R. Fricke and L. Havestadt, *Z. Elektrochem.*, **33**, 441 (1927); R. Fricke, *ibid.*, **35**, 631–640 (1929).

(1) The manometer liquid was *n*-butyl phthalate, a mobile liquid of density 1.0418 at 25°, whose vapor pressure at room temperature is a small fraction of that of mercury.<sup>12</sup> The difference between the levels of liquid in the manometer could be read with an accuracy of  $\pm 0.1$  mm., which corresponds to an accuracy of  $\pm 0.01$  mm. of mercury.

It was found, however, that reproducible results could not be obtained unless the commercial butyl phthalate was distilled directly into the manometer under a high vacuum and never allowed to remain in contact with air at atmospheric pressure for more than a few minutes at a time.

(2) By means of the three-way stopcocks A and B it was possible to measure directly (a) the vapor pressure of the solvent, (b) the difference between the vapor pressure of the solution and that of the solvent, (c) as a check, the vapor pressure of the solution. In this way it was unnecessary for the determination of the vapor pressure lowering to know very accurately either the temperature of the thermostat or the density of the manometer liquid; an important source of uncertainty was therefore avoided. It was essential to have the thermostat well stirred and to be sure that the temperature of the manometer liquid did not change rapidly. A summary of the procedure will illustrate these points.

(3) Dissolved gases were removed from the solvent and the solution by one of two methods: (a) solidification and melting, repeated at least twice under a high vacuum, (b) vacuum sublimation of the solvent onto a surface cooled in liquid air by the method described by Hibben.<sup>13</sup> Either method was adequate to prevent disturbance of the results by evolution of gases other than water vapor from the solution.

The thermostat was maintained at 20° by a simple system of two coils and a circulating pump. One coil was immersed in a mixture of water and ice; the other was in the thermostat, and the pump circulated a light oil through the system. A toluene regulator and relay system started the pump when the temperature of the bath became too high and stopped it when it fell too low. The air of the room, being always above 25°, did the heating. A tube and propeller stirrer kept the contents of the thermostat thoroughly mixed. In such a bath the average fluctuation of the temperature from the mean value was 0.02°, or two microvolts on a two-*junction* copper-constantan thermoelement.

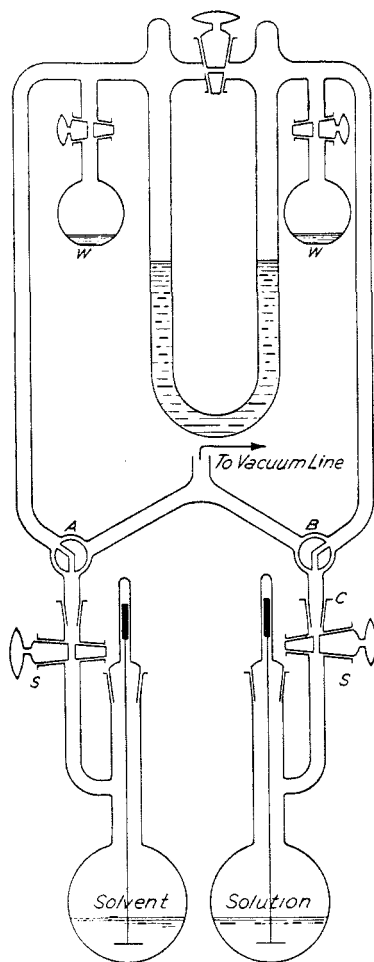


Fig. 1.—Diagrammatic sketch of apparatus for the determination of the vapor pressure lowerings of concentrated solutions by static method.

(12) K. C. D. Hickman, *J. Phys. Chem.*, **34**, 627 (1930).

(13) J. H. Hibben, *Bur. Standards J. Research*, **3**, 97 (1929).

The experimental procedure was as follows. A solution slightly more dilute than desired was put in the flask labeled "Solution" in Fig. 1, and attached to a vacuum line, interchangeable ground-glass joints being used for all temporary connections. The flask was evacuated and at the same time cooled in a mixture of chloroform and solid carbon dioxide. The solution boiled vigorously and gradually solidified. It was left for ten to fifteen minutes with the pressure less than  $10^{-3}$  mm. The stopcock S was then closed and the solid allowed to melt, after which the process was repeated at least once. Finally the flask was completely evacuated, the stopcock closed and the whole attached to C (Fig. 1). The solvent was treated in a similar way once for all and left permanently connected to the vapor pressure apparatus.

The solution was well stirred and left overnight in the thermostat at  $20^{\circ}$ . Next morning both solution and solvent were momentarily connected to the vacuum line, left for thirty minutes, and then the solvent was connected to one limb of the manometer, the other limb being connected to the pumps. The difference in the levels of the manometer liquid indicated the vapor pressure of the water at the temperature of the thermostat in mm. of *n*-butyl phthalate.

Stopcock B was then turned so that the solution was connected to the manometer. The differential pressure, now registered, represented the difference between the vapor pressure of the solvent and that of the solution. The volume of the manometer was appreciable in comparison to that of the apparatus as a whole, hence when stopcock B was opened water vapor was removed from the solution container. The drift of the differential pressure was downward at the beginning; equilibrium was reached by evaporation of water vapor from the solution under these conditions. By opening the stopcock momentarily and allowing water vapor from the evacuated flask W to enter the solution side of the system we were able to reach the equilibrium also by condensation of water vapor on the solution. This was done in every case.

Finally a second determination of the vapor pressure (in mm. of *n*-butyl phthalate) of the water at the temperature of the thermostat gave a correction for any changes which had occurred during the experiment. The vapor pressure of the water,  $p_0$ , as given in the table of results, was obtained by averaging the first and second determinations.

**Vapor Pressures of Salt Solutions by a Dynamic Method.**—The method of drawing the same air over the solution and the solvent in series, both being immersed in the same thermostat, was first used by Walker.<sup>14</sup> It was refined by Berkeley, Hartley and Burton,<sup>14a</sup> who determined the loss in weight of the solvent and solute after a given amount of air had been passed carefully over both.

Washburn and Heuse<sup>15</sup> enlarged the saturators and determined by absorption the amount of water removed from the solution and the solvent when the same air was drawn slowly over them. Equilibrium was approached from both sides.

Pearce and Snow<sup>16</sup> designed an apparatus for dynamic measurements of the vapor pressure of liquids wherein a known volume of "Detonating gas" generated electrolytically could be passed over the liquid, and the vapor content of the emerging gas estimated by analysis. In this way the volume of gas passed over the liquid was known with considerable accuracy.

The apparatus used here was a modification of that used by Washburn and Heuse, much smaller and with vertical saturators, consisting of five limbs, 40 cm. long, of tubing 1.5 cm. in diameter. The saturators were connected in series and the same air was

(14) J. Walker, *Z. physik. Chem.*, **2**, 602 (1888).

(14a) Earl of Berkeley, E. G. J. Hartley and C. V. Burton, *Phil. Trans.*, **A209**, 177 (1909); **A218**, 295 (1919).

(15) E. W. Washburn and E. O. Heuse, *THIS JOURNAL*, **37**, 309 (1915).

(16) J. N. Pearce and R. D. Snow, *J. Phys. Chem.*, **31**, 231 (1927).

drawn first over the solution and then over the water—no bubbling took place. As the air left each saturator it passed into absorption tubes filled with "Anhydrone," which absorbed the water vapor from the air. "Anhydrone" proved to be a very efficient drying agent; indeed, at the rate of flow used, one inch of dry "Anhydrone" removed all weighable amounts of water from the air. The moisture content of the air entering the solution saturator was controlled so that equilibrium could be reached from both sides. After each experiment the solution in the last limb of the saturator was compared against the original solution in a Rayleigh-Zeiss interferometer; in no case was any change in concentration observed.

The drop in pressure over the whole apparatus was between 2 and 3 mm. of water. If  $m_0$  and  $m_1$  are the gains in weight of the tubes absorbing water from the air leaving the water saturator and the solution saturator, respectively, if  $B_0$  and  $B_1$  are the total pressures over the solvent and the solution, respectively, and  $p_0$  and  $p_1$  the vapor pressures of the solvent and the solution, it may be shown that<sup>15</sup>

$$\frac{p_0 - p_1}{p_1} = \frac{m_0(B_0 - p_0) - m_1(B_1 - p_0)}{B_1 m_1} \quad (3)$$

As no appreciable error was introduced by assuming that  $B_0$  was equal to  $B_1$ , this equation becomes

$$\frac{p_0 - p_1}{p_1} = \frac{m_0 - m_1}{m_1} \times \frac{B - p_0}{B} = A \quad (4)$$

Hence

$$\frac{\Delta p}{p_0} = \frac{p_0 - p_1}{p_0} = \frac{A}{1 + A} \quad (5)$$

By these formulas  $\Delta p/p_0$  was immediately computed<sup>17</sup> from the measured quantities,  $m_0$ ,  $m_1$  and  $B$ .

**Materials. Sodium Chloride.**—J. T. Baker c. p. Analyzed sodium chloride was recrystallized twice from solution by the addition of hydrochloric acid gas, filtered, dried and ignited. The solutions were made by direct weighing of the appropriate amounts of salt and water in a stoppered flask.

**Sodium sulfate** was purified by recrystallization as the decahydrate from J. T. Baker c. p. Analyzed sodium sulfate. The hydrate was dried in a vacuum desiccator over sodium hydroxide and ignited. Each solution was made directly from the salt and water.

**Ammonium nitrate** solutions were prepared by dissolving the salt which had been recrystallized from J. T. Baker c. p. Analyzed ammonium nitrate and subsequently dried in a vacuum desiccator and heated several times to 130°. The solutions were analyzed after each vapor pressure experiment by comparison with a freshly prepared standard in a Rayleigh-Zeiss interferometer.

**Potassium thiocyanate** solutions were made by dissolving Merck Reagent potassium thiocyanate in water. The composition of the solution, whose vapor pressure had been measured, was estimated from its density, determined in a pycnometer at 25°.

**Lithium chloride** solutions were prepared by neutralizing pure concentrated hydrochloric acid with Merck lithium carbonate. Lithium chloride trihydrate was crystallized from the solution at about -50° and dried by vacuum filtration. The salt was allowed to melt at room temperature, forming a stock solution containing about 40% LiCl. The other solutions were made from this one by dilution with distilled water.

(17) This formula takes no account of the departures from Dalton's law of mixtures of air and water vapor. H. T. Gerry and L. J. Gillespie [*Phys. Rev.*, **40**, 269 (1932)] have shown that in some cases the vapor pressure calculated on the assumption of Dalton's law shows significant departures from that calculated from a study of the properties of real gases. Such an effect is minimized in the differential method and, as the data for such computations are not at hand, no such correction has been made.

In every case the composition of the solution was determined from the density at 25° with the aid of Baxter and Wallace's<sup>18</sup> accurate values of the densities of solutions of lithium chloride.

**Experimental Results.**—The experimental results are given in Tables I and II, which are self-explanatory, and are plotted in Fig. 2.

TABLE I  
EXPERIMENTAL RESULTS BY THE STATIC METHOD

Solution number	Specific volume ( $v$ )	Wt. fraction of salt ( $x_2$ )	Vapor pressure of solvent ( $p_0$ )	Vapor pressure lowering $\Delta p$	$\frac{\Delta p}{p_0}$
Lithium Chloride at 20.28°					
7	0.7809	0.4385	233.65	203.6	0.8714
1	.7976	.4049	233.7	192.65	.8243
2	.8204	.3584	233.5	173.0	.7409
8	.8206	.3582	234.75	173.65	.7397
3	.8396	.3194	233.7	151.55	.6485
4	.8680	.2614	233.9	113.65	.4859
5	.9015	.1932	233.55	69.4	.2972
6	.9236	.1486	233.7	45.4	.1943
Potassium Thiocyanate at 20.28°					
1	0.7269	0.6274	234.9	103.1	0.4389
6	.7418	.5900	234.0	92.2	.3940
5	.7589	.5475	233.8	80.95	.3462
4	.7714	.5168	233.9	73.3	.3136
3	.8020	.4425	233.2	55.4	.2418
2	.8190	.4017	233.75	48.6	.2079
7	.8576	.3084	233.1	33.35	.1431
Ammonium Nitrate at 20.28°					
1		0.6052 <sup>a</sup>	230.05	71.6	0.3113
2		.6047	233.65	72.8	.3116
3		.5610	233.8	64.4	.2754
4		.5007	233.75	54.45	.2329
5		.4601	229.4	47.5	.2071
6		.2948	233.65	28.25	.1209
7		.2228	233.85	20.9	.0894
8		.1597	233.45	14.6	.0625
Sodium Chloride at 20.28°					
1		0.2634 <sup>b</sup>	233.5	57.35	0.2456
2		.2634	233.2	57.15	.2451

<sup>a</sup> Concentrations measured with interferometer. <sup>b</sup> Saturated solution at 20.28°.

A comparison of the values of  $\Delta p/p_0$  for sodium chloride solutions as obtained by the dynamic method with that of previous investigators showed that the results obtained with this apparatus were very reliable. For instance, the value of 0.1615 for  $\Delta p/p_0$  of a 20% solution of sodium chloride

(18) G. P. Baxter and C. C. Wallace, THIS JOURNAL, **38**, 70 and 259 (1916).

TABLE II  
 EXPERIMENTAL RESULTS BY THE DYNAMIC METHOD

Wt. fraction of salt ( $x_2$ )	Wt. of H <sub>2</sub> O removed from solution ( $m_1$ )	Wt. of H <sub>2</sub> O removed from solvent ( $m_0$ )	$m_0 - m_1$	$\frac{\Delta p}{p_0}$
Sodium Chloride at 25°				
0.2598	1.7927	2.3792	0.5865	0.2406
.2598	1.0273	1.3634	.3361	.2406
.2396	1.6678	2.1340	.4662	.2130
.2189	1.7368	2.1443	.4075	.1852
.1999	1.8238	2.1878	.3640	.1617
.1999	1.7049	2.0432	.3383	.1612
Sodium Sulfate at 27.5°				
0.2399	2.2923	2.4802	0.1879	0.0735 <sub>7</sub>
.2199	2.3212	2.4885	.1673	.0652 <sub>5</sub>
.1999	2.5427	2.7040	.1613	.0578 <sub>8</sub>
.1799	2.7358	2.8878	.1520	.0510 <sub>7</sub>
.1597	2.5762	2.7011	.1249	.0448 <sub>5</sub>
.1200	2.9220	3.0257	.1037	.0332 <sub>4</sub>
Control Experiments. Water in Both Saturators				
	1.3461	1.3464	0.0003	
	1.3928	1.3916	-.0012	
	1.7698	1.7711	.0013	
	1.6214	1.6215	.0001	

compares favorably with 0.1613 as obtained by Bousfield and Bousfield at 18°<sup>19</sup> and 0.1610 from Frazer's school.<sup>20</sup>

Solutions of sodium chloride saturated at 20.28° were also used to check the absolute values of the results given by the static method. For the relative vapor pressure lowering,  $\Delta p/p_0$  of a 26.34% solution, Bousfield and Bousfield's results gave 0.2460 at 18°, Frazer's, 0.2448 at 25°, and ours, 0.2453.

**Representation of Results.**—As the object of the work was to obtain  $\mu_1$  and  $\mu_2$  as functions of the concentration, it was desirable for us to find empirical equations that would express our data as accurately and as simply as possible. In this we were only partially successful, but most of our equations will be given, if only as a warning of their limitations.

For purposes of discussion we propose to express the concentration of the solution in terms of a modified mole fraction which is calculated on the assumption that the solute is completely dissociated and that each ion acts as a solute molecule. Thus if the solute is capable of dissociating into  $\nu$  ions we define the modified molecular weight of the solute as  $M_2' = M_2/\nu$  where  $M_2$  is the conventional formula weight.

Hence  $X_2'$ , the modified mole fraction, is defined as

$$X_2' = \frac{m_2}{M_2'} / \left( \frac{m_2}{M_2'} + \frac{m_1}{M_1} \right) \quad (6)$$

(19) Ref. 9, p. 441.

(20) "International Critical Tables," Vol. III, p. 297.

where  $m_2$  is the number of grams of solute in  $m_1$  grams of solvent and  $M_1$  is the formula weight of the solvent. The corresponding modified mole fraction of the solvent is given by  $X'_1 = (1 - X'_2)$ .

An ideal solution of a completely dissociated electrolyte may thus be defined as one for which the following relation, where  $\mu_1^i$  represents the chemical potential of water in the ideal solution and  $\mu_1^0$  that of pure water, holds

$$M_1(\mu_1^i - \mu_1^0) = RT \ln X'_1 \quad (7)$$

For an actual solution, however

$$M_1(\mu_1 - \mu_1^0) = RT \ln \frac{p_1}{p_0} = RT \ln a_1 \quad (8)$$

if, as is the case with aqueous solutions at room temperature, the vapor may

be treated as an ideal gas without significant error. From equations (7) and (8) it follows that

$$\frac{M_1}{2.303 RT} (\mu_1 - \mu_1^i) = \log \frac{a_1}{X'_1} \quad (9)$$

The quantity  $a_1/X'_1$  is an activity coefficient of the solvent analogous to  $\gamma$  as defined by Lewis and Randall,<sup>21</sup> the familiar activity coefficient of a solute.<sup>22</sup>

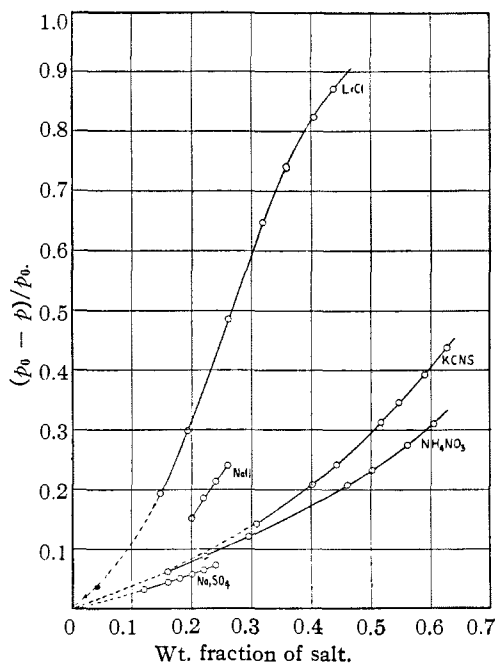
In this paper  $a_1/X'_1$  is preferred to  $\gamma$  (a) because it is more readily computed from the data not only of vapor pressure but also of freezing point and boiling point experiments, and (b) because the mole fraction is a more useful quantity for expressing concentration over the whole range than is the molality.

Fig. 2.—The relative vapor pressure lowerings of different solutions as functions of the weight fractions of solute.

It will be seen that the quantity  $\log (a_1/X'_1)$  is directly proportional to the difference between the partial molal free energy, or the chemical potential per mole of water in the actual

(21) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 328.

(22) It should be emphasized that the assignment of properties in a solution either to the solvent or the solute is a purely arbitrary matter. The experimental observations are made on the solution as a whole and the partial quantities are calculated by mechanical means. Thus, for instance, any information about the physical state of the solute obtained from the activity coefficient of the solute,  $\gamma$ , is also inherent in an activity coefficient or similar function of the solvent, and these latter are sometimes more readily computed from the data.





solution and the value which it would have if the solution were ideal. For ideal solutions the graph of  $\log (a_1/X'_1)$  as a function of  $X'_2$  is the  $X'_2$  axis. For all actual solutions  $\log (a_1/X'_1)$  is zero when  $X'_2 = 0$  and for all solutions whether electrolytic or not the initial slope of the curve of  $\log (a_1/X'_1)$  vs.  $X'_2$  is also zero. Thus we have a common starting point for the study of the behavior of all solutions including those of electrolytes.

In the same way we may write for the solute

$$M'_2(\mu_2^i - \mu_2^0) = RT \ln X'_2 \quad (10)$$

where  $\mu_2^0$  is the chemical potential of 1 g. of liquefied solute at the pressure and temperature of the experiment, and

$$M'_2(\mu_2 - \mu_2^0) = RT \ln a_2 \quad (11)$$

which defines  $a_2$  for an actual solution. Hence

$$\log \frac{a_2}{X'_2} = \frac{M'_2}{2.303 RT} (\mu_2 - \mu_2^i) \quad (12)$$

Of all the relations between chemical potential and concentration which we examined those expressing  $\log (a_1/X'_1)$  as functions of  $X'_1$  or  $X'_2$  or of powers of  $X'_1$  and  $X'_2$  were the most promising. The values of  $\log (a_1/X'_1)$  calculated from the experimental results are given in Table III.

TABLE III  
EXPERIMENTAL VALUES OF  $\log (a_1/X'_1)$  FOR DIFFERENT SALTS

$x_2$	$m$	$X'_2$	$X'_1$	$a_1/X'_1$	$\log (a_1/X'_1)$
Lithium Chloride					
0.1486	4.117	0.1291	0.8709	0.9251	-0.0339
.1932	5.648	.1691	.8309	.8458	-.0727
.2614	8.348	.2312	.7688	.6687	-.1747
.3194	11.069	.2851	.7149	.4917	-.3083
.3583	13.176	.3219	.6781	.3821	-.4178
.4049	16.048	.3664	.6336	.2773	-.5570
.4385	18.420	.3989	.6011	.2139	-.6696
Potassium Thiocyanate					
0.3084	4.589	0.1419	0.8581	0.9986	-0.0006
.4017	6.909	.1993	.8007	.9893	-.0047
.4425	8.178	.2276	.7724	.9816	-.0080
.5168	11.007	.2840	.7160	.9586	-.0183
.5475	12.451	.3097	.6903	.9471	-.0237
.5900	14.809	.3479	.6521	.9293	-.0319
.6274	17.328	.3844	.6156	.9115	-.0403
Ammonium Nitrate					
0.1597	2.37	0.0787	0.9213	1.0176	0.00758
.2228	3.58	.1142	.8858	1.0282	.01208
.2948	5.22	.1583	.8417	1.0444	.01887
.4601	10.65	.2773	.7227	1.0971	.04025
.5007	12.53	.3110	.6890	1.1133	.04661
.5610	15.97	.3652	.6348	1.1415	.05748
.6052	19.15	.4083	.5917	1.1636	.06580

TABLE III (Concluded)

$x_2$	$m$	$X_2'$	$X_1'$	$a_1/X_1'$	$\text{Log } (a_1/X_1')$
Sodium Sulfate					
0.1200	0.960	0.04932	0.95068	1.0169	0.00728
.1600	1.341	.06623	.93377	1.0229	.00983
.1800	1.545	.07706	.92294	1.0282	.01208
.2000	1.760	.08685	.91315	1.0317	.01355
.2200	1.985	.09688	.90312	1.0350	.01494
.2400	2.223	.10720	.8928	1.0377	.01607

Under separate headings the behavior of each set of solutions will now be discussed.

**Lithium Chloride.**—The vapor pressure–concentration curve for lithium chloride solutions presented the most complicated case of all taken up here. Empirical relations between weight per cent. and relative vapor pressure lowering were practically worthless.

The curve of  $\log (a_1/X_1')$  vs. concentration is shown in Fig. 3. It represents, in addition to the data from Table I, the results at low concentrations obtained by Lovelace, Bahlke and Frazer.<sup>23</sup> It was found that equations of the type proposed by Margules<sup>24</sup> to represent vapor pressure–concentration relationships in binary mixtures of non-electrolytes expressed  $\log (a_1/X_1')$  as a function of the concentration with fair approximation. Equation (1') in which  $\log (a_1/X_1')$  is expressed in terms of  $\log X_1'$  and  $\varphi (= X_1'X_2')$  is the most successful one of this type that we have encountered.

$$\log (a_1/X_1') = 5.1657 \log X_1' + 2.2429 \varphi + 4.721 \varphi^2 - 24.615 \varphi^3 \quad (1')$$

The coefficients of  $\log X_1'$  and  $\varphi$  were so adjusted that the slope was zero at  $X_1' = 1$ . The degree of approximation is seen in the second column of Table IV, where the differences between the observed values of  $p$ , the vapor pressure of the solution, and those calculated by equation 1' are given in mm. of mercury. It was assumed that at 20° the vapor pressure of water was 17.54 mm.

TABLE IV

DIFFERENCES IN MM. OF MERCURY BETWEEN OBSERVED VALUES OF  $p$  AND THOSE CALCULATED BY THE EQUATIONS FOR SOLUTIONS OF LITHIUM CHLORIDE

$x_2$	Eq. 1'	Eq. 2'
0.4385	0.001	0.002
.4049	.000	.030
.3583	— .040	.012
.3194	.000	.005
.2614	.102	.004
.1932	.072	— .079
.1486	.000	— .005

(23) B. F. Lovelace, W. H. Bahlke and J. C. W. Frazer, THIS JOURNAL, **45**, 2930 (1923).

(24) M. Margules, *Sitzungsber. Wien Akad.*, [2] **104**, 1243 (1895).

Two other equations, one of the same type as equation (1'), in which the coefficients of  $\log X'_1$  and  $\varphi$  were so adjusted that the slope was positive at  $X'_1 = 1$ , and the other a four constant power series in  $\varphi$ , omitting the first power of  $\varphi$ , were found to be less adequate than equation (1') in representing the data for the lithium chloride solutions.

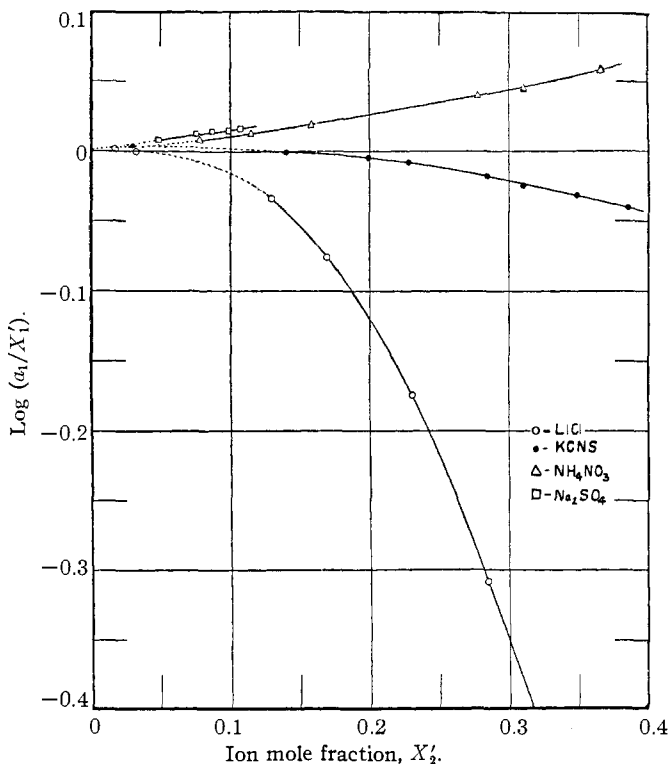


Fig. 3.— $\text{Log}(a_1/X'_1)$  as a function of the modified mole fraction of the solute. The ordinate is directly proportional to the difference between the chemical potential of water in the actual solutions and the chemical potential of water in ideal solutions of the same concentration. This quantity is always positive in very dilute solutions.

Although equation (1') does not express the data within the experimental error, it is noteworthy that an equation proposed for mixtures of non-electrolytes fits the data for aqueous solutions of lithium chloride over a range of concentrations from zero to forty per cent. as well as it does. Even at the dilute end the equation follows the data at least qualitatively, passing through a maximum in the neighborhood of 5% of lithium chloride.

By a simple transformation of the usual expression for the relation

between  $\gamma$  and the molality given by the simple interionic attraction theory,<sup>25</sup> it may be shown that in the neighborhood of  $X_1' = 1$

$$\log (a_1/X_1') = 0.879 X_2'^{3/2} \quad (13)$$

As was to be expected, this equation did not hold at any appreciable concentration but it was found that in the more concentrated solutions  $\log (a_1/X_1')$  was a relatively simple function of  $X_2'^{3/2}$ .

Equation (2'), a four constant power series in  $X_2'^{3/2}$ , fits the data very well over the range from 15 to 43% lithium chloride. The agreement is shown in the third column of Table IV. At low concentrations this equation ceases to give an adequate representation of the data and is entirely off at zero concentration.

$$\log (a_1/X_1') = -0.04935 + 2.9085 X_2'^{3/2} - 22.9814 X_2'^{3/2} - 23.8564 X_2'^{7/2} \quad (2')$$

Even a three constant power series in  $X_2'^{3/2}$  expressed the results almost within the error of experiment between 25 and 40% lithium chloride, but an equation which fits satisfactorily from zero concentration to saturation is still to be found.

**Ammonium Nitrate.**—The quantity  $\log (a_1/X_1')$  was positive for ammonium nitrate solutions over the whole range that we investigated (see Table III). It was possible to express  $\log (a_1/X_1')$  very accurately as a function of the concentration by equation (3'). The deviations of the calculated from the observed values never exceeded the experimental error and even the zero error was only 0.0009.

$$\log (a_1/X_1') = 0.0009 + 0.31317 X_2'^{3/2} - 1.5789 X_2'^{5/2} \quad (3')$$

Equation (4'), a form developed by van Laar<sup>26</sup> from theoretical considerations for mixtures of non-electrolytes, was also tried; the variable in this equation was  $r_1 = X_1'/X_2'$ .

$$\log \frac{a_1}{X_1'} = \frac{1.4027}{(1 + 0.3233 r_1)^2} \quad (4')$$

The equation did not fit the experimental results as well as equation (3') but the average deviation without regard to sign reduced to mm. of mercury was only 0.027 mm., a very fair performance for a two-constant equation over a concentration range of 60%.

**Potassium Thiocyanate.**—For solutions of this salt  $\log (a_1/X_1')$  first increases,<sup>27</sup> passes through a maximum, and finally decreases as the concentration is increased. Over the range from 40 to 63% of potassium thiocyanate,  $\log (a_1/X_1')$  is a linear function of  $X_2'^{3/2}$ , equation (5'). No attempt was made to express  $\log (a_1/X_1')$  as a function of concentration over the entire range.

$$\log (a_1/X_1') = 0.0190 - 0.2490 X_2'^{3/2} \quad (5')$$

(25) See, for example, J. N. Brønsted and V. K. La Mer, *THIS JOURNAL*, **46**, 555 (1924). The literature on this subject is summarized by H. S. Harned in Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1931, pp. 783-808.

(26) J. J. van Laar, *Z. physik. Chem.*, **72**, 723 (1910); **83**, 599 (1913).

(27) The values of  $\log (a_1/X_1')$  in very dilute solutions were calculated from the data of Biltz, *Z. physik. Chem.*, **40**, 201 (1902).

**Sodium Sulfate.**—We are at present studying the change in solubility of sodium sulfate and sodium sulfate decahydrate under pressure, and in order to be absolutely sure of the chemical potential changes in the very concentrated solutions, vapor pressure measurements were made at intervals of 2%.

The values of  $\log (a_1/X_1')$  are positive for this salt at all concentrations up to the saturation point. Over a large range of concentration  $\log (a_1/X_1')$  could be represented as a linear function of  $X_2'$  as shown in Fig. 4, which expresses the results of calculations with equation (6').

$$\log (a_1/X_1') = 0.15421 X_2' \quad (6')$$

The dotted curve in Fig. 4 gives the deviation in mm. of mercury between the observed value of the vapor pressure of the solutions of sodium sulfate and the vapor pressure as calculated from equation (6').

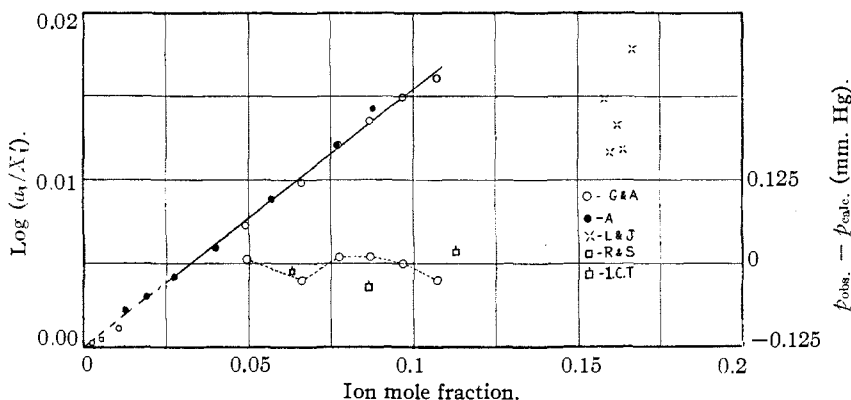


Fig. 4.— $\log (a_1/X_1')$  for sodium sulfate solutions (calculated from experimental data from various sources) as a function of the modified mole fraction. G and A refers to the results in this paper, A to the e. m. f. data of Åkerlöf, L and J to Leopold and Johnston's vapor pressure data at various temperatures, R and S to the freezing point measurements of Randall and Scott, and I. C. T. to the table of vapor pressures in the "International Critical Tables." The ordinate of the dotted curve is measured by the scale on the right-hand side of the diagram.

Activity coefficients ( $\gamma$ ) for sodium sulfate solutions have been calculated from electromotive force data in cells without transference.<sup>28</sup>

We calculated values of  $\log (a_1/X_1')$  from these values of  $\gamma$  and also values of  $\gamma$  from our vapor pressure measurements. Figure 4 shows the agreement between the values of  $\log (a_1/X_1')$  as calculated from vapor pressure and e. m. f. measurements. The initial points are taken from Randall and Scott's<sup>29</sup> accurate measurements of the freezing point lowering.

On the same diagram we have plotted the values of  $\log (a_1/X_1')$  as calcu-

(28) G. Åkerlöf, *THIS JOURNAL*, **48**, 1160 (1926); H. S. Harned and G. Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

(29) M. Randall and G. N. Scott, *THIS JOURNAL*, **49**, 647 (1927).

lated from the data in the "International Critical Tables"<sup>30</sup> which are evidently based on inaccurate data. Some uncertainty in our knowledge of the vapor pressures of solutions of sodium sulfate was introduced by the measurements of Leopold and Johnston<sup>31</sup> on the vapor pressures of saturated salt solutions at different temperatures. They estimated the concentrations of the solutions examined from the known solubility of the salt at the temperature of the experiment. Apparently they were mistaken as to the solid phase in contact with the solutions of sodium sulfate below 30°. They assumed it to be the decahydrate. Their vapor pressures show that it was the anhydrous salt, as the values of  $p/p_0$  which they give are entirely too low. Their assumption that the decahydrate was the solid phase and the consequent error in the concentration of the solution led to a curious diagram, Fig. 4 in their paper, a diagram which is very improbable. We have calculated  $\log(a_1/X'_1)$  from their corrected data and included the results in Fig. 4.

In this Laboratory a sample of sodium sulfate decahydrate which had melted in the bottle during the summer weather remained as anhydrous salt and saturated solution for nearly a year even though the average temperature of the room during that period was between 20 and 25°. It is, therefore, easy to see how the error crept into Leopold and Johnston's results.

**Calculation of the Chemical Potentials of the Water and Salt in Concentrated Solutions.**—When equation (8) or equation (9) is combined with one of the empirical equations expressing  $\log(a_1/X'_1)$  as a function of the concentration, the difference between the chemical potential of the water in the solution and that of pure water is obtained directly. In order to evaluate the chemical potential of the salt in the solution recourse must be had to Gibbs' equation 97 which, for a two-component system at constant pressure and temperature, may be written as

$$d\mu_2 = -\frac{x_1}{x_2} d\mu_1$$

or

$$\frac{d\mu_2}{dX'_2} = -\frac{M'_2 X_1}{M_1 X'_2} \frac{d\mu_1}{dX'_1} \quad (14)$$

Equation (3') has already been used in this way to calculate the values of  $\mu_1$  and  $\mu_2$  in solutions of ammonium nitrate.<sup>32</sup>

The general case may be illustrated by reference to equation (1') for solutions of lithium chloride which, when expressed in terms of natural logarithms, may be written as follows

$$\ln \frac{a_1}{X'_1} = a \ln X'_1 + a\varphi + c\varphi^2 + d\varphi^3 \quad (15)$$

(30) "International Critical Tables," Vol. III, p. 371.

(31) H. G. Leopold and J. Johnston, *THIS JOURNAL*, **49**, 1974 (1927).

(32) L. H. Adams and R. E. Gibson, *ibid.*, **54**, 4520 (1932).

In order that the first derivative shall be zero at the origin the coefficients of  $\ln X_1'$  and  $\varphi$  must be the same. From equations (8) and (15) we may write equation (16)

$$(\mu_1 - \mu_1^0) = \frac{RT}{M_1} \{(a + 1) \ln X_1' + a\varphi + c\varphi^2 + d\varphi^3\} \quad (16)$$

Hence

$$\frac{d\mu_1}{dX_1'} = \frac{RT}{M_1} \left\{ \frac{a+1}{X_1'} + a \frac{d\varphi}{dX_1'} + 2c\varphi \frac{d\varphi}{dX_1'} + 3d\varphi^2 \frac{d\varphi}{dX_1'} \right\} \quad (17)$$

On combining equations (14) and (17) we obtain the expression for the chemical potential of the solute  $\mu_2$

$$\mu_2 = \frac{RT}{M_2'} \int \left[ \frac{1}{X_2'} + (3a - 2c) + (8c - 2a - 3d)X_2' + (15d - 10c)X_2'^2 + (6c - 27d)X_2'^3 + 21dX_2'^4 - 6dX_2'^5 \right] dX_2' + \text{const.} \quad (18)$$

The constant of integration may be evaluated if  $\mu_2$  is made equal to zero at any concentration which it is desirable to consider as the reference

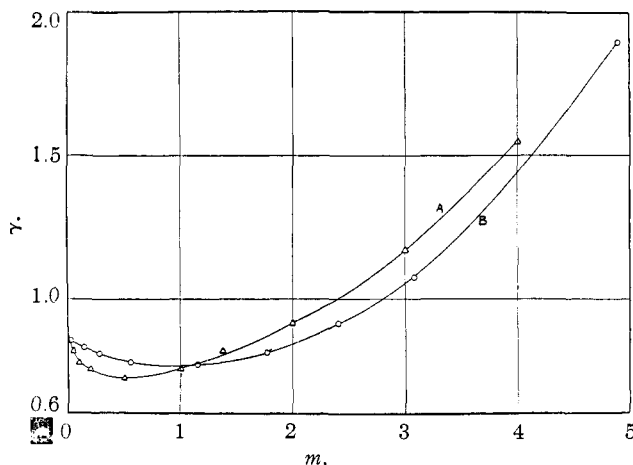


Fig. 5.—The activity coefficient  $\gamma$  for moderately dilute solutions of lithium chloride. Curve A is obtained from e. m. f. data and Curve B was calculated from observations on the vapor pressures of concentrated solutions.

concentration. The chemical potential of the lithium chloride in solutions of different concentrations was computed from equation (1') with the aid of equation (18) and hence the activity coefficient of the salt,  $\gamma$ , was calculated. In the calculation the mean activity of the solute,  $a_{\pm}$ , as defined by Lewis and Randall, was obtained from the formula  $a_{\pm} = \text{constant} \times e^{M_2'\mu_2/RT}$ , the constant being adjusted arbitrarily so that the resulting value of  $\gamma$  was equal to that obtained from e. m. f. data<sup>33</sup> at  $m = 0.0278$ . The results are given in Fig. 5, where  $\gamma$  as calculated from the vapor pres-

(33) See H. S. Taylor, "Treatise on Physical Chemistry," D. Van Nostrand, New York, 1931, p. 772.

sure results is plotted against  $m$ , the molality in curve B. The values of  $\gamma$  obtained from the e. m. f. data are shown by curve A. While the actual agreement is not good, the parallelism between the curves is striking, especially when it is remembered that equation (1') was obtained from results on the vapor pressure of *concentrated* solutions. Indeed, the most dilute solution used in the calculation of the coefficients of equation (1') contained 14.86 g. of lithium chloride per 100 g. of solution or 4.12 moles of lithium chloride per 1000 g. of water. Furthermore, it should be emphasized that the type of equation used to express the vapor pressure as a function of the concentration was developed primarily for solutions of non-electrolytes.

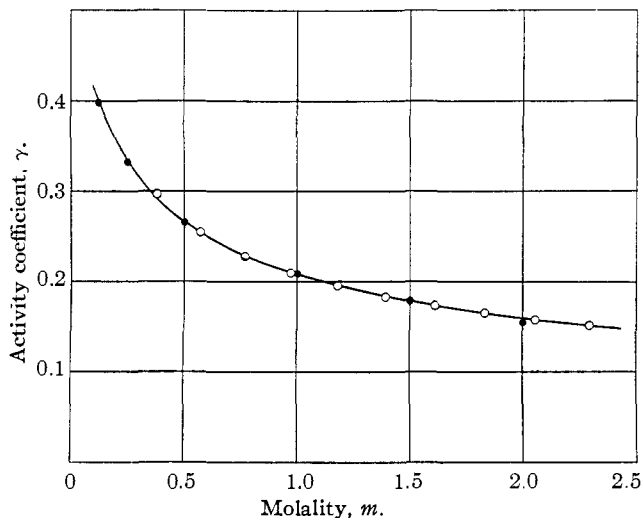


Fig. 6.—The activity coefficient of sodium sulfate in aqueous solutions,  $\gamma$  as a function of the molality. The open circles represent the results as calculated from equation (19) and the dots represent the results from e. m. f. data as measured and calculated by Åkerlöf.

The values of  $\log(a_1/X_1')$  for sodium sulfate solutions calculated from the e. m. f. data of Åkerlöf (see Fig. 4) were computed by graphical integration and, as the data furnished only four points in the range in which we are interested, the calculations cannot be regarded as very accurate. In order to compare our data more carefully with those of Åkerlöf we computed values of  $\gamma$  from equation (6'). When this equation was differentiated and combined with equation (14) we obtained

$$\mu_2 = \frac{2.303 RT}{M_2'} [0.64486 \log X_2' + 0.15421 X_2'] + \text{constant} \quad (19)$$

From the values of  $\mu_2$  for the sodium sulfate in solution we computed values of  $a_{\pm}$  and hence of  $\gamma$ . The comparison between the values of  $\gamma$  as given



by Åkerlöf and as calculated by us from the vapor pressure data via equation (6') is illustrated in Fig. 6. The constant in the equation

$$a_{\pm} = \text{constant} \times e^{M^{1/2}/RT}$$

was so adjusted that our values of  $\gamma$  were made equal to Åkerlöf's at  $m = 0.974$ . It will be seen that the agreement is very satisfactory and holds down to concentrations as low as 0.35 molal even though the experimental data were observed over the range from 1 to 2.2 molal. We may, therefore, conclude that the very simple equation (6') represents quite adequately the chemical potential-concentration relations in actual solutions of sodium sulfate.

### Summary

With the aid of a static apparatus of modified design the relative vapor pressure lowerings of concentrated solutions of lithium chloride, ammonium nitrate, potassium thiocyanate and sodium sulfate have been measured at room temperature. Various empirical equations expressing the relative vapor pressures of the solutions in terms of the concentration have been examined and it was found that for these salts equations expressing  $\log(a_1/X_1')$  as a function of  $X_2'^{1/2}$  were, on the whole, the simplest and fitted the data most closely. By means of these equations the difference between the chemical potential of either component in a solution of a given concentration and the chemical potential of the same component in a solution of any other concentration may be readily calculated. The convenience of the activity coefficient of the solvent,  $(a_1/X_1')$ , whose logarithm is directly proportional to the chemical potential difference between solvent in the solution and solvent in an ideal solution of the same concentration, both as to ease of computation and applicability over the whole range of concentration has been emphasized.

WASHINGTON, D. C.

RECEIVED FEBRUARY 15, 1933  
PUBLISHED JULY 6, 1933