

### Summary

The solubilities of potassium perchlorate and potassium nitrate have been measured in the presence of several added salts in pure glacial acetic acid.

The observed solubilities agree with those predicted by the interionic attraction theory if a sufficiently large ion diameter is assumed.

An empirical relationship from which the value of the activity coefficient may be calculated has been pointed out.

A somewhat better agreement is obtained with the extended theory of Gronwall, La Mer and Sandved than with the original Debye-Hückel development.

It is concluded that explanation of the properties of salt solutions requires that other properties of the solvent in addition to its dielectric constant must be considered.

CAMBRIDGE, MASSACHUSETTS

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

## THE VAPOR PRESSURES OF SATURATED AQUEOUS SOLUTIONS OF CERTAIN SALTS

BY H. W. FOOTE, BLAIR SAXTON AND J. K. DIXON

RECEIVED OCTOBER 7, 1931

PUBLISHED FEBRUARY 5, 1932

The literature of this subject has been summarized by Johnston and Leopold,<sup>1</sup> who pointed out, as have others, the difficulties of the usual static methods. One of the chief difficulties is in completely removing air from the saturated solution and another is in obtaining a solution for measurement which is neither supersaturated nor undersaturated. The above-mentioned writers found that equilibrium was established very slowly in their apparatus after removal of air by pumping, due presumably to difficulty in reaching complete saturation.

An apparatus which has been developed for another purpose has been found to avoid the difficulties mentioned above and to be suitable for determining the vapor pressure of saturated solutions from about 0° to somewhat above room temperature with an accuracy of approximately  $\pm 0.05$  mm. The apparatus eliminates the error caused by air dissolved in the solution by forming the solution in the absence of air, and as the conditions are such that a saturated solution is formed very rapidly, equilibrium is established in a very short period of time.

### Apparatus, Procedure and Materials

A diagram of the apparatus, not drawn to scale, is shown in Fig. 1. In its essentials, it consists of a bulb A, for holding the salt and solution, connected to the bulb B con-

---

<sup>1</sup> Johnston and Leopold, *THIS JOURNAL*, 49, 1974 (1927).

taining air-free water, to a mercury manometer (diameter of the tube 6 mm.), and to a mercury vapor pump attached at C which was backed by an oil pump. The pressure could be reduced to approximately  $10^{-4}$  mm. A McLeod gage, which however was not essential, was connected at D. The bulb for salt and saturated solution was connected by means of a ground-glass joint E containing a mercury seal, so that it could be disconnected and weighed as desired. The water in the bulb B had been boiled under diminished pressure at intervals over a period of several weeks before use, evaporating a considerable proportion of the water originally present and insuring the absence of dissolved air. The necessary stopcocks had been ground with great care and offered no difficulty from leakage.

For the determinations, the salt in weighed amount was introduced into its bulb and heated by means of a small electric oven for about eight hours at a temperature near  $200^{\circ}$  in the vacuum produced by the continuous action of the pumps. The bulb was then cooled and immersed in a two-liter Dewar flask containing water which was kept stirred and in which the temperature could be maintained very nearly constant during a determination. Below  $10^{\circ}$ , the variation in temperature was not more than  $\pm 0.04^{\circ}$ , and above this temperature, the variation was about  $\pm 0.02^{\circ}$ . The thermometer was checked against two standard thermometers.

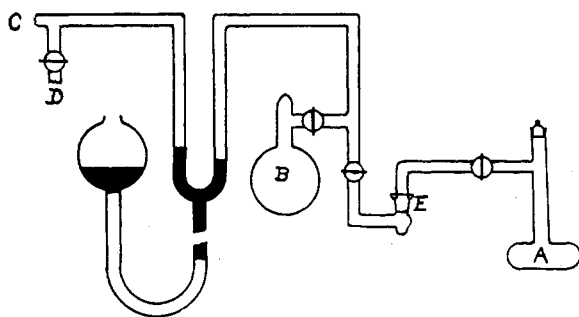


Fig. 1.

The saturated solution of the salt was produced by allowing vapor from the water bulb B to enter the salt bulb, where it condensed. By keeping the salt always in large excess, the liquid formed a saturated solution promptly. The pressure could then be determined by direct reading of the manometer, the readings being taken with a cathetometer. It is evident that air could be effectively eliminated by this method, but the question of whether a saturated solution could be formed promptly by the procedure required demonstration. There was also the possibility, if too little water was condensed on the finely divided crystals, that adsorption would take place, giving too low a value of vapor pressure. The fact that vapor pressures did not vary when the amount of vapor condensed varied rather widely, showed that the results were not influenced by adsorption. This does not mean that adsorption may not affect the vapor pressure if the liquid condensed is very small in amount, but it means that enough water was present to overcome this effect. To show that solutions were saturated, conditions were varied to promote undersaturation or the reverse by suitably varying the amount of condensed vapor and by temporary variation in temperature. It was found by these means that the pressures readjusted themselves to constant values rather rapidly. Ordinarily, equilibrium was established in about ten minutes, but readings were taken at ten-minute intervals for a period of an hour. In one case (that of potassium sulfate at  $0^{\circ}$ ), it was demonstrated that the pressure obtained at the end of ten minutes was identical with

that obtained at the end of twenty-four hours. At least two series of determinations were made, one on rising and the other on falling temperature, varying also the amount of condensed vapor, without any effect being evident from the different conditions greater than the error in reading pressure. The weight of salt taken varied between 3.5 and 9 g. and of water, between 0.08 and 0.85 g.

Except for cesium chloride, all salts were purified by usual methods and it is quite certain that errors introduced by impurities are less than the error in reading the manometer. The sample of cesium chloride was obtained from Dr. O. E. Schupp of this Laboratory, who had purified it by special methods applicable to cesium salts.

The corrections applied to measured pressures to reduce to pressures in millimeters of mercury at 0° were taken from the "International Critical Tables."

### Vapor Pressures

The thermodynamic equation giving the change in equilibrium pressure with temperature for any univariant system has been given by Gibbs.<sup>2</sup> For the three phase system here considered, this becomes

$$\frac{dP}{dT} = \frac{S' + S'' - S'''}{V' + V'' - V'''} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \quad (1)$$

where  $S$  and  $V$  represent the total entropy and total volume of a phase and the single accent refers to the vapor, the double to the liquid, and the triple to the crystalline phase. Using molal and partial molal values, this becomes

$$\frac{dP}{dT} = \frac{n_1\bar{H}'_1 + n_2\bar{H}''_2 - n_1\bar{H}''_1 - n_2\bar{H}''_2}{T(n_1\bar{V}'_1 + n_2\bar{V}''_2 - n_1\bar{V}''_1 - n_2\bar{V}''_2)} = \frac{n_1\Delta H_v - n_2\Delta H_s}{T(n_1\Delta V_v - n_2\Delta V_s)} \quad (2)$$

where  $\Delta H_v$  is the molal heat of vaporization of pure water,  $\Delta H_s$  is the molal heat of solution of the salt to give a saturated solution,  $\Delta V_v$  is the volume increase on vaporizing a mole of pure water,  $\Delta V_s$  is the volume increase on the solution of one molal of salt to give a saturated solution, and  $n_1$  and  $n_2$  are the number of moles of water and salt, respectively, in the saturated solution.

Neglecting the volumes of the condensed phases, assuming the validity of the ideal gas law for water vapor, expressing the composition of the solution on the molality basis, and the heats in calories, we have

$$253.96 \frac{d \log P}{d(1/T)} = -(55.51 \Delta H_v - n_2 \Delta H_s) = -\Delta H' \quad (3)$$

which is one form of the equation of van't Hoff.<sup>3</sup>

Equation 3 can be evaluated, thus getting the slope of the  $\log P - (1/T)$  curve, or it can be integrated and  $\log P$  expressed as a function of  $T$ , if  $\Delta H'$  is a known function of  $T$ . It is obvious that

$$\frac{d \Delta H'}{dT} = 55.51 c'_{p1} + m_2 c''_{p2} - C + \left( \bar{H}_2''' - \frac{\partial H}{\partial m_2} \right) \frac{\partial m_2}{\partial T} \quad (4)$$

<sup>2</sup> Gibbs, Equation (129), "On the Equilibrium of Heterogeneous Substances," *Trans. Connecticut Acad.*, 3, 108 (1876); "The Collected Works of J. Willard Gibbs," Longmans, Green and Co., New York, 1928, Vol. I, p. 55.

<sup>3</sup> Van't Hoff, "Vorlesungen über theoretische und physikalische Chemie," Friedrich Vieweg und Sohn, Braunschweig, 1898, Vol. I, p. 33.

where  $C$  is the total heat capacity,  $H$  the total heat content of a quantity of saturated solution containing 1000 grams of water and  $c'_{p_1}$  and  $c''_{p_2}$  are the molal heat capacities of water vapor and crystalline salt, respectively. Then

$$\Delta H'_{(T)} = \Delta H'_{(T_0)} + \int_{T_0}^T \Delta C_p \, dT + \int_{T_0}^T \left( L_2''' - \frac{\partial L}{\partial m_2} \right) \frac{\partial m_2}{\partial T} \, dT \quad (5)$$

where  $\Delta C_p = 55.51 c'_{p_1} + m_2 c''_{p_2} - C$ ;  $L_2'''$  is the relative molal heat content of the crystalline salt; and  $L = m_2 (\Delta H_s + L_2''')$  is the relative heat content of a saturated solution containing 1000 g. of water. Hence

$$253.96 \frac{d \log P}{d(1/T)} = -\Delta H'_{(T_0)} - \int_{T_0}^T \left[ \Delta C_p + \left( L_2''' - \frac{\partial L}{\partial m_2} \right) \frac{\partial m_2}{\partial T} \right] \, dT \quad (6)$$

and

$$253.96 \log P = -\frac{\Delta H'_{(T_0)}}{T} - \frac{1}{T} \int_{T_0}^T \left[ \Delta C_p + \left( L_2''' - \frac{\partial L}{\partial m_2} \right) \frac{\partial m_2}{\partial T} \right] \, dT + \int \frac{\Delta C_p + \left( L_2''' - \frac{\partial L}{\partial m_2} \right) \frac{\partial m_2}{\partial T}}{T} \, dT + i \quad (7)$$

Of the systems studied in this paper, there are sufficiently accurate thermal data in the literature in only two cases, sodium and potassium chlorides, to justify the use of equations (6) and (7). These data are given in Table I.

TABLE I

Substance	$T_0$	$\Delta H_v(T_0)$	$m_2$	$\Delta H_s(T_0)$
NaCl	298.1	10,484 <sup>a</sup>	6.145 <sup>b</sup>	466 <sup>d</sup>
KCl	298.1	10,484 <sup>a</sup>	-7.71 + 0.042 $T^b$	3692 <sup>d</sup>
	$c'_{p_1}$	$c''_{p_2}$	$C$	$\Delta C_p$
NaCl	8.44 <sup>e</sup>	12.15 <sup>g</sup>	1063 <sup>f</sup>	-520
KCl	8.44 <sup>e</sup>	12.38 <sup>g</sup>	968 <sup>c</sup>	-595 + 0.52 $T$
	$L_2'''$	$L$		
NaCl				
KCl	-4285	1534-910 $m_2$		

<sup>a</sup> "International Critical Tables," Vol. V, p. 138. <sup>b</sup> *Ibid.*, Vol. IV, pp. 235, 239. <sup>c</sup> *Ibid.*, Vol. V, p. 115. <sup>d</sup> Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925). <sup>e</sup> Lewis and Randall, "Thermodynamics," p. 80. <sup>f</sup> *Ibid.*, p. 85. <sup>g</sup> Russell, *Physik. Z.*, **13**, 59 (1912).

From these data and the measured vapor pressures, the following equations were derived

$$(\text{NaCl}) \quad \log P = -\frac{2890.7}{T} - 4.715 \log T + 22.612 \quad (8)$$

$$(\text{KCl}) \quad \log P = -\frac{2995.5}{T} - 6.680 \log T + 0.001024 T + 27.569 \quad (9)$$

In the remaining cases,  $\Delta H'$  was assumed to be constant in the temperature interval used and the best empirical constants were determined for an equation of the type

$$\log P = -\frac{A}{T} + B \quad (10)$$

Thus the vapor pressures of the other three saturated solutions are given by the equations

$$(\text{CsCl}) \quad \log P = -\frac{2198.5}{T} + 8.5621 \quad (11)$$

$$(\text{K}_2\text{SO}_4) \quad \log P = -\frac{2332.5}{T} + 9.1881 \quad (12)$$

$$(\text{Na}_2\text{SO}_4) \quad \log P = -\frac{2696.6}{T} + 10.3630 \quad (13)$$

The differences between the vapor pressures calculated by Equations 8-13 and those measured are shown in the diagram, Fig. 2. The average

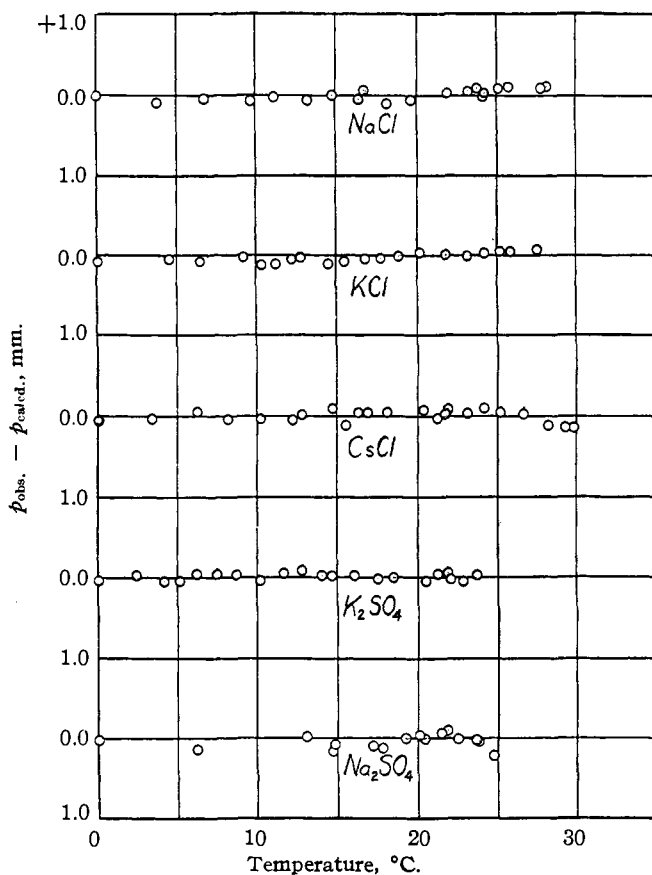


Fig. 2.— $p_{\text{obs.}} - p_{\text{calcd.}}$  as a function of temperature.

deviation between observed and calculated results is  $\pm 0.05$ , which is approximately the error of observation in reading pressures. It is probable that the values for sodium sulfate are the least accurate, as they were the first determined.

It is clear from Equation 3 that the heat of solution of a salt in forming a saturated solution can be calculated from the temperature coefficient of the vapor pressure of the saturated solution if this is of sufficient accuracy, but that, in general, the measurements must be carried out with greater precision than those in this investigation, which were not done with this end in view. However, we have made the attempt for the two cases (sodium and potassium chlorides) for which there are measured data.

From the slope of the  $\log P-(1/T)$  curve for potassium chloride, we obtained 3490 at  $25^\circ$ , which differs from the measured value by 5.4%. The result with sodium chloride was unsatisfactory. Finally, the  $A$  constant for sodium sulfate shows that the heat of solution is negative.

The system with sodium sulfate which we investigated is metastable below  $32^\circ$  and should have yielded a mixture of the anhydrous salt and decahydrate instead of the saturated solution of the anhydrous salt, but the metastable system always formed in preference to the other. After some difficulty, the transformation to the stable system was accomplished and the following vapor pressures were determined in the order given, first adding and then removing water.

SYSTEM $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}-\text{Na}_2\text{SO}_4$ -VAPOR						
$T, 24.75^\circ$ $\text{Na}_2\text{SO}_4, 5.7575 \text{ g.}$						
$P, \dots\dots\dots$	18.90	18.85	18.85	18.85	18.80	18.80
Wt. $\text{H}_2\text{O}, \text{g.}$	0.2459	0.3217	0.4149	1.2320	1.1765	1.0984

The results of Baxter and Lansing<sup>4</sup> give a value of 19.00 mm. when their interpolation formula is used.

### Summary

A modified static apparatus has been described for measuring the vapor pressures of saturated salt solutions. The vapor pressures of saturated solutions of sodium chloride, potassium chloride, cesium chloride, potassium sulfate and sodium sulfate—the last, a metastable system—have been measured from  $0^\circ$  over a range of temperature approximating  $25^\circ$ .

The temperature coefficients of the vapor pressures of saturated solutions of potassium chloride and sodium chloride have been calculated from thermal data, thus allowing a comparison between observed and calculated vapor pressures. The differences, shown in Fig. 2, average  $\approx 0.05$  mm.; which is approximately equal to the error of observation.

In the three other systems thermal data are lacking and vapor pressures have been calculated by the expression  $\log P = -(A/T) + B$ . The differences between observed and calculated values, also shown in Fig. 2, average  $\approx 0.06$  mm.

NEW HAVEN, CONNECTICUT

<sup>4</sup> Baxter and Lansing, THIS JOURNAL, 42, 149 (1920).