[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Vapor Pressures of Saturated Solutions

BY WARREN W. EWING

In a recent article Roehl,[1] in discussing the vapor pressure–temperature relations of saturated aqueous salt solutions, states: "A search of the literature was made and all the data possible to locate for saturated aqueous solutions plotted as log P against $1/T$. It was found that all the curves were straight lines and all parallel to the water curve."

Hirschler[2] explains these results by means of thermodynamic equations and various assumptions and concludes: "We may thus state a working rule that the vapor pressures of saturated aqueous salt solutions plotted as log P *vs.* $1/T$ will be parallel to the curve of pure water. In the absence of data a determination of the vapor pressure of the saturated solution at any one temperature will enable the entire curve to be drawn with a good degree of approximation."

The purpose of the present contribution is to show that this is not a safe rule to follow. In a few cases, it may give roughly approximate results, but in others may lead to ridiculous conclusions.

It is well recognized that the equation obtained on integration of the Clapeyron–Clausius equation is only approximate, due to the variation in the latent heat of evaporation of the liquid. Thus even a rough plotting of this curve based on the data for water shows that the curve deviates from a straight line above 60° (Curve AB, Fig. 1). A comparison of the data for saturated aqueous solutions of potassium chloride at a series of temperatures shows, moreover, that the curve for this substance is by no means parallel with that of water. Thus using the most recent data[3,4] the value of log P_0 − log P, which should be a constant on the basis of Roehl's rule, is, at −10.69, 39.31 and 107.4°, 0.0451, 0.0864 and 0.1122, respectively. If the values at 39.31° were taken as a basis for calculating the vapor pressure of the potassium chloride solutions at −10.69 and 107.4°, deviations of about 50 and 6%, respectively, would result. This latter deviation would be equivalent to an error of nearly 10° in the calculated cryohydric temperature.

Saturated solutions of salts which form hydrates with water show still greater deviations from the rule. To illustrate this, the data for saturated solutions of calcium nitrate are shown in Fig. 1 over the temperature range 0 to 100°. CDE is the curve for the saturated solutions of the tetrahydrate; FG for the trihydrate; HI for the dihydrate; KL for the anhydride. A glance suffices to show that these curves are not straight lines and that they are not parallel to the water curve. The tetrahydrate in the region CD might be expected to obey the rule, but the deviation is obvious. The curve for the anhydride somewhat approximates the rule, probably because the solubility of the anhydride does not vary much with temperature.[5] However, even in this case, the behavior is far from satisfactory. Magnesium nitrate,[6] zinc nitrate[7] and cadmium nitrate[8] deviate in much the same manner as does calcium nitrate.

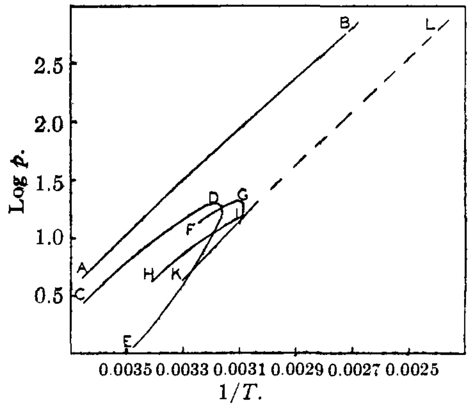

Fig. 1.—Vapor pressures of saturated calcium nitrate solutions.

Summary

The conclusion that a straight line is obtained when the logarithm of the vapor pressure of a saturated aqueous solution is plotted against the reciprocal of the absolute temperature, which is

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[1] Roehl, THIS JOURNAL, **58**, 1291 (1936).

[2] Hirschler, *ibid.*, **58**, 2472 (1936).

[3] For vapor pressure of water, see "I. C. T.," Vol. III, pp. 211, 212 and 233.

[4] For data on potassium chloride solutions, see Berkeley, *Trans. Roy. Soc.* (London), **203A**, 189 (1904); Leopold and Johnston, THIS JOURNAL, **49**, 1974 (1927), and "I. C. T." Vol. IV, p. 259.

[5] Ewing, Krey, Law and Lang, THIS JOURNAL, **49**, 1958 (1927), and Ewing, *ibid.*, **49**, 1963 (1927).

[6] Ewing, Klinger and Brandner, *ibid.*, **56**, 1053 (1934).

[7] Ewing and Fisher, *ibid.*, **59**, 1046 (1937).

[8] Unpublished data.

parallel to a corresponding straight line for water, is seriously in error in the case of such a favorable substance as potassium chloride, and is grossly in error for calcium nitrate and similar hydrated salts.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Vapor Pressures of Saturated Aqueous Solutions

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Experimental data on the vapor pressure of saturated aqueous solutions have become more numerous since the days of Roozeboom,[1] but the equation which he published in 1889 may still be used profitably to interpret the newer data. Its application in the present article may serve to correct some current misconceptions.

If the vapor pressure of pure water is plotted with coördinates log p and $1/T$, the graph so obtained does not diverge very strongly from a straight line. As opportunely pointed out by Ewing[2] some recent writers unfortunately have put forward the statement that the graphs for the vapor pressures of saturated solutions plotted in a similar manner are also all straight lines, parallel to the line for water. Ewing points out the failure of this generality to meet the experimental facts. The present article offers an interpretation of the great diversity of different slopes of this curve which are actually encountered in practice.

In the first place, one may consider in general what mole fractions of water are found in saturated solutions of salts. The broadest variety of such mole fractions is shown in the case of such a salt as ammonium nitrate[3] where the mole fraction of water, near unity at the cryohydric temperature, diminishes to zero at the melting point, 169°, of the salt. It is obvious that the graph whose form we are here discussing will be very similar to that of water while the solutions are sufficiently dilute; that a pressure maximum will be reached at some higher salt concentration; and that the value of the pressure of water vapor will fall to zero (and its logarithm to minus infinity) when the concentration of salt attains the mole fraction unity (and the solubility of the salt is infinite). In such cases, it is evident that the graph cannot be a straight line parallel to the corresponding graph for water (see Fig. 2, graph IV). Most salts melt much higher than ammonium nitrate, and the mole fractions of anhydrous salt in their saturated solutions as commonly studied do not approach unity. One might therefore be tempted to say that, insofar as all saturated salt solutions are rather dilute solutions, the "straight line rule" holds true. Unfortunately, the good promise of this modified statement is lessened when one learns, as shown below, that, in the plentiful cases where the solid phase is hydrated, one must state concentration in terms of moles of hydrated salt rather than of anhydrous salt when studying the slope of the graph in question. Stated in these terms, mole fractions of salt become much larger.

Insofar as non-aqueous solutions of non-ionic, lower-melting solutes are concerned the prospect of the mole fraction of "solute" running as high as unity is much greater.

If the finding of Leopold and Johnston[4] that Babo's law holds within the error of experiment, can be applied to the cases here concerned, then it may be stated, with utmost brevity, that the "straight line rule" can be true only to the degree that change of mole fraction of solvent is without significant influence in causing change in aqueous pressure.

The subject may be clarified most completely from the viewpoint of the equation of Roozeboom[1]

$$\frac{\mathrm{d} \ln P}{\mathrm{d}T} = \frac{q + Q_c^x/(x - c)}{2T^2}$$

where q is the molar heat of vaporization of water, Q_c^x the integral heat of solution for one formula weight of the solid phase in forming its saturated solution from pure water, x the total moles of water containing one mole of anhydrous solute, and c the moles of water of crystallization in one formula weight of the solid phase.

Apart from a difference in convention of alge-

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[1] Roozeboom, *Z. physik. Chem.*, **4**, 31 (1889).

[2] Ewing, THIS JOURNAL, **59**, 1293 (1937).

[3] *Cf.* "International Critical Tables," Vol. IV, 217.

[4] Leopold and Johnston, THIS JOURNAL, **49**, 1974 (1927).