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.

BETHLEHEM, PENNA. RECEIVED MARCH 13, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Vapor Pressures of Saturated Aqueous Solutions

BY WILLIAM A. WEST AND ALAN W. C. MENZIES

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-

---

(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).

braic sign, this equation is identical for anhydrous salts with that suggested by Hirschler[5]

$$\frac{\mathrm{d} \ln P}{\mathrm{d}T} = \frac{\Delta H - \Delta H_s/N_1}{RT^2}$$

where ΔH is the same as Roozeboom's q, ΔH_s the integral heat of solution for one mole of solution and N_1 the mole fraction of water in the solution. In order that this equation should be true for saturated aqueous solutions which are in equilibrium with a hydrated solid phase, it would be necessary to define N_1 as the mole fraction of water in a two-component liquid mixture of water and the hydrated salt. This does not correspond with the customary definition of N_1.

Hirschler points out that when the negative term $\Delta H_s/N_1$ in his equation is negligibly small in comparison with ΔH, then the equation becomes identical with that for the vapor pressure of pure water. He states that ΔH_s is usually much smaller than ΔH and that "for most aqueous salt solutions, N_1 is not far from unity." It is at this point that one is misled if one fails to remember how N_1 must be defined, as above noted, when the solid phase is hydrated.

Using therefore Roozeboom's form of the equation, writing it in the form

$$\frac{\mathrm{d} \log P}{\mathrm{d}(1/T)} = -\frac{q + Q_c^x/(x - c)}{4.6}$$

and plotting $1/T$ as abscissa increasing from right to left, one observes, upon considering the term $Q_c^x/(x - c)$: (A) when this term is very small in comparison with q, the slope of the curve under discussion will be similar to that of water; (B) when the term is smaller than q but of the same sign, the curve will be steeper than the curve for water; (C) when the term is smaller than q but of opposite sign, the curve will be less steep than that for water; (D) when this term is numerically equal to q but of opposite sign, the slope of the curve becomes zero; (E) when the term is larger than q and of opposite sign, the curve has negative slope; (F) when $x = c$ the term becomes infinite and the slope infinite; and (G) when $c > x$ the slope is again positive with the curve retroflex.

Most of these potentialities are realized in practice in the case of saturated solutions of lithium iodide trihydrate[6] but we prefer to utilize the interesting experimental results of Ewing and his collaborators upon the nitrates of calcium[7] and of magnesium[8] as examples for interpretation by means of Roozeboom's equation. Accordingly, we graph these results in Fig. 1, showing the logarithm of the vapor pressure of the saturated solutions plotted against reciprocal temperature. On the graph for magnesium nitrate hexahydrate we have indicated the type of slope by key letters corresponding to our analysis above. As an aid in clarification, we have added at the top of Fig. 1 a graph of the molal solubility[9] of this salt, numbered on the ordinate axis to the left of the diagram, against the identical temperature scale as abscissa. This graph makes it clear that, since the temperature maximum of the solubility curve occurs at the congruent melting point of the hydrate, it is at this temperature that $x - c = 0$, and the slope of the pressure curve, shown below it, is therefore infinite. It may be noted that Roozeboom in discussing the case of calcium chloride hexahydrate mentioned the possibility of a retroflex portion of the curve, although no actual case was known at that time.

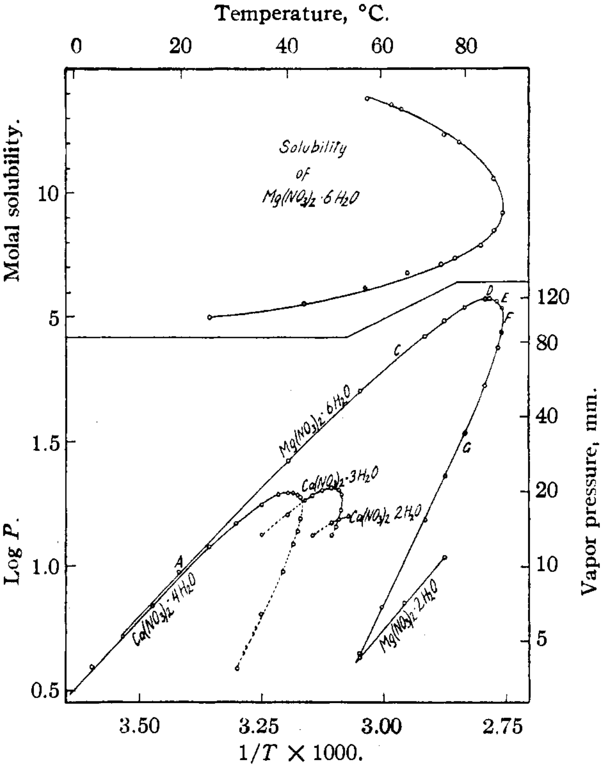

Fig. 1.—(Below) Aqueous pressures of saturated solutions of nitrates of calcium and of magnesium.

(Above) Molal solubility of magnesium nitrate hexahydrate.

---

[5] Hirschler, THIS JOURNAL, **58**, 2472 (1936).

[6] "International Critical Tables," Vol. III, p. 369.

[7] Ewing, THIS JOURNAL, **49**, 1963 (1927).

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

[9] Ewing, Brandner, Schlichter and Griesinger, *ibid.*, **55**, 4827 (1933).

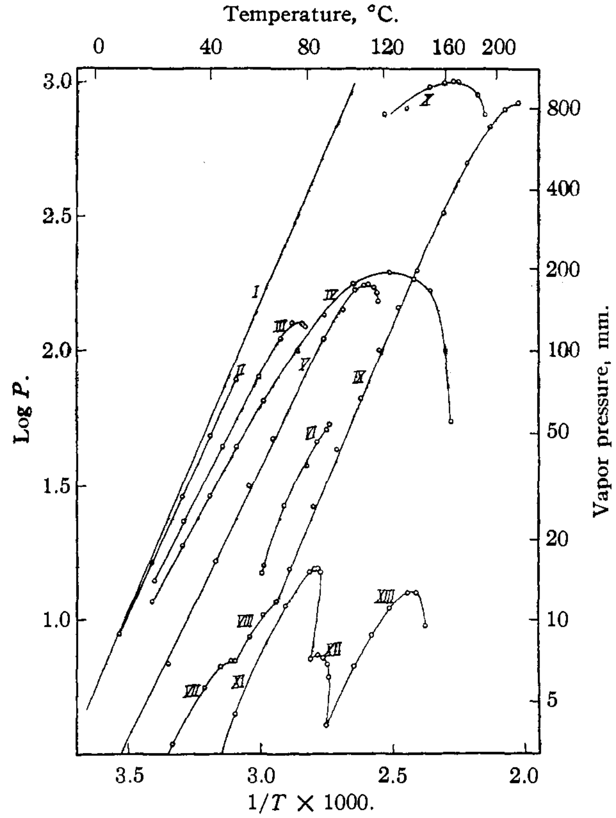

Fig. 2.—Aqueous pressures of certain saturated solutions. To avoid confusion, coördinates have been altered as follows: III, abscissa increased 0.5; VII, VIII, IX decreased 0.2; XI, XII, XIII decreased 0.1; V, ordinate decreased 0.05.

In discussing methods for smoothing and interpolation for vapor pressure data, Collins and Menzies[10] wrote: "For saturated solutions it is not usually possible to represent the facts by an equation of the type N'' (linear in the variables log P and $1/T$). They tabulated over a range of temperature the heats of vaporization per gram of water from saturated solutions of a number of salts, of which we select four for Table I, pointing out that the crystallization process also was here involved concomitantly with the process of vaporization. Since the heats are a measure of the slope of the curve under discussion, a glance at Table I is very informative, for the heats and thus the slopes may be compared for the four saturated solutions, and for water (shown in column two). In this table, the capital letter following the heat value designates the type of slope of the curve according to our classification above. From the fact that the lettering B or C is found at concentrations where $x - c$ is positive, it is clear that the quantity Q_c^x may have either algebraic sign. The numerical value of this quantity may be small, and is subordinate in importance to the value of $x - c$ when this grows small.

TABLE I

HEATS OF VAPORIZATION IN CALORIES PER GRAM OF WATER FROM CERTAIN SATURATED SOLUTIONS AND FROM PURE WATER

T, °C.	H_2O	$CuSO_4$, $5H_2O$	$SrCl_2$, $6H_2O$	$SrBr_2$, $6H_2O$	$CaCl_2$, $6H_2O$
25	583	557 C	521 C	486 C	249 C
28.5	581				0 D
30	580				−81 E
					$CaCl_2$, $2H_2O$
50	569	553 C	489 C	467 C	575 B
			$SrCl_2$, $2H_2O$		
75	555	540 C	546 C	397 C	571 B
82.3				0 D	
87				−261 E	
		$CuSO_4$, $3H_2O$		$SrBr_2$, H_2O	
100	540	507 C	540 A	548 B	570 B
		$CuSO_4$, H_2O			
125	523	515 C	453 C	614 B	515 C

Since the cases studied by Collins and Menzies were not selected by them for the purposes of the present discussion, it is fortuitous that they serve to demonstrate so many types of variation from the slope of the graph for water. Accordingly, we have drawn from the literature some additional data and show graphs in Fig. 2 of the vapor pressure of a number of saturated aqueous solutions, using the same coördinates as before. The numbers upon the several graphs refer to the following saturated solutions: II, potassium nitrate,[11] III, strontium bromide hexahydrate,[9] IV, ammonium nitrate,[12] V, magnesium chloride hexahydrate,[13] VI, lithium chloride monohydrate,[14] VII, calcium chloride hexahydrate,[3,9] VIII, calcium chloride alpha-tetrahydrate,[3,9] IX, calcium chloride dihydrate,[3,9] X, silver nitrate,[15] XI, lithium iodide trihydrate,[6] XII, lithium iodide dihydrate,[6] XIII, lithium iodide monohydrate.[6] We add the graph for water, numbered I, for comparison, and have included that for potassium nitrate (II) because it exhibits lack of parallelism but little curvature. In cases where marked curvature is shown, the value of the term $Q_c^x/(x - c)$ is (a) significantly large in relation to q, and (b) in process of changing significantly with

---

(10) Collins and Menzies, *J. Phys. Chem.*, **40**, 379 (1936).

(11) Adams and Merz, *J. Ind. Eng. Chem.*, **21**, 305 (1929).

(12) Jahnecke and Rohlfs, *Z. anorg. allgem. Chem.*, **192**, 237 (1930).

(13) Derby and Yngve, THIS JOURNAL, **38**, 1439 (1916).

(14) Applebey, Cranford and Gordon, *J. Chem. Soc.*, 1665 (1934).

(15) Meyerhoffer, in Mellor, "Inorganic and Theoretical Chemistry," Vol. III, 1923, p. 462.

temperature, chiefly by reason of the dominant influence of a small and changing denominator.

For anhydrous salts, since $c = 0$, a low value of $x - c$ means simply a high molal solubility. For potassium nitrate, the values of x at 10 and 50° are 26.7 and 6.6, respectively, and curvature is not yet evident. For ammonium nitrate, the values of x at 50 and 100° are 1.3 and 0.42, respectively, and curvature is marked. Marked curvature is likewise shown by silver nitrate (graph X), and would inevitably be shown by such salts as potassium thiocyanate,[16] whose saturated solutions reach a mole fraction of salt equal to unity, were the pressure data for these available.

In the case of salts forming hydrated solid phases, it is the solubility as stated in terms of moles of hydrate that is significant. This must obviously have large and quickly changing values near a congruent melting point, for there the solubility becomes infinite; while simultaneously $x - c$ is approaching and finally attaining the value zero. In Fig. 2, the maxima shown on graphs III, V, VII, XI, XII and XIII are each not far removed in temperature from a congruent melting point. The values of $x - c$ at these maxima are about 1.5, 1.0, 0.8, 0.24, 0.36 and 1.3, respectively.

Derby and Yngve[13] in discussing the decrement of aqueous vapor pressure with increasing temperature in the case of saturated solutions of magnesium chloride hexahydrate stated that this was "due to the large increase in solubility of the hydrate near its transition temperature." Rather the criterion for large increase in solubility is proximity to the congruent melting point, which in this instance is close at hand although "concealed." In numerous cases there is no marked increase of solubility near a transition temperature, because the (concealed) congruent melting point is too far distant.

Summary

The graph obtained on plotting the logarithms of the aqueous pressures of saturated solutions against reciprocal temperatures may show many types of slope, and extreme or even retroflex curvature. The slopes of such curves are interpreted by means of an equation suggested by Roozeboom, which is applied to experimental data which were lacking in his day.

PRINCETON, N. J. RECEIVED MARCH 22, 1937

---

[16] Kracek, *J. Wash. Acad. Sci.*, **26**, 307 (1936).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE RICE INSTITUTE]

The Nephelometric End-point of Atomic Weight Titrations

BY ARTHUR F. SCOTT AND FRANK H. HURLEY, JR.

The well-known Harvard method for determining atomic weights by the analysis of pure halogen compounds is essentially a titration process in which the halide ion in the analytical sample is precipitated by silver ion, the end-point being found by nephelometric tests. In making these tests of the relative amounts of silver and halide ions in the analytical solution, two equal, small samples of the solution are withdrawn; the halide content of one is precipitated as silver halide by the addition of silver ion, the silver content of the other is precipitated also as silver halide by the addition of an excess of halide ion. The small amounts of silver halide precipitated in these test samples remain in suspension for some time and their turbidities or opalescences are assumed to be proportional to the concentration of halide and silver ion, respectively. In accordance with this basic assumption equivalence of silver and halide in the titration process is assumed to have been attained when the corresponding opalescences of "excess Ag" and "excess X" test samples are equal. Recent discussions[1] of this "equal-opalescence" end-point for chloride analyses have cast doubt on its validity, and have indicated the need of further experimental study. Some new experiments bearing on this problem have been carried out and will be described in this report.

The conflicting evidence with regard to the validity of the chloride "equal-opalescence end-point" can be resolved in part by distinguishing between two different types of end-points as they have been developed in practice; first, the end-point established in the case of solutions which

---

[1] Johnson, *J. Phys. Chem.*, **35**, 540, 2237 (1931); **36**, 1942 (1932); **39**, 781 (1935); Johnson and Low, *ibid.*, **36**, 2390 (1932); Briscoe, Kikuchi and Peel, *Proc. Roy. Soc.* (London), **A133**, 440 (1931).