error only), (3) the presence of ammonium sulfate and (4) the presence of citric acid. The first two can be avoided; while the error caused by sulfate is negligible in any but the most accurate work.

The general impression of great difficulty and inaccuracy that has surrounded the determination of magnesium and phosphoric anhydride as magnesium pyrophosphate, is largely the effect of the mass of conflicting publications on the subject. The standard procedures here recommended have been found to give accurate results with reasonable care and the data presented should answer many questions as to the value of recommendations to be found in the literature on the subject.

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THE EQUILIBRIUM PRESSURE OVER COEXISTING SALT HYDRATES AT TEMPERATURES BELOW 0°

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The phase relations for salt hydrates have been worked out fairly completely but there remain one or two minor points which appear not to have been specifically discussed. One of these is the question as to whether the vapor pressure curve of a system composed of two adjacent hydrates and vapor intersects the ice-vapor curve in the low temperature region.

The principle involved will be evident from a consideration of the P-T diagram as given in Fig. 1. The hydrates are denoted by S_1, S_2, S_3, etc.; the saturated solution by L, other solutions by L^{I}, L^{II}, etc.; ice by I and the vapor by V. The vapor pressure of all unsaturated solutions of the salt ranges between the water line and the line representing the vapor pressure of the system S_1-L-V; that of the system S_1-S_2-V is another line below the S_1-L-V line. Similarly, if other hydrates exist, there is a corresponding curve, for example, S_2-S_3-V for each pair of adjacent hydrates. Now the line for the unsaturated solution intersects the ice curve at the ordinary freezing temperature of the particular solution, the phases then present being I-L^{I}-V; that for the saturated solution S_1-L-V intersects the ice curve at the eutectic temperature, the four coëxisting phases being S_1-I-L-V. The question now arises as to whether the curve for systems composed of two hydrates and vapor will meet the ice-vapor curve if the temperature is sufficiently low; this point must, according to Blasdale, be considered.[1] Such an intersection would imply

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[1] Blasdale, "Equilibria in Saturated Salt Solutions," Chemical Catalog Company, New York, **1927**, p. 39.

a curious non-variant point at which I-S_1-S_2-V would be in equilibrium; or, in other words, that on cooling the system to a low enough temperature, solid water should split out from the higher hydrate provided the rate of reaction is appreciable. It is the purpose of this paper to consider such data as are available in order to ascertain the course of the vapor pressure curve for this type of system at low temperature.

From general theoretical considerations alone, the reality of such a point seems doubtful. In order that a hydrate may form, the tendency of the H_2O molecules to unite with the salt or salt hydrate molecule must be greater than the tendency to unite with one another. Hence, it seems likely that the escaping tendency of the H_2O molecules from a hydrate will always be less than from ice or, in other words, the vapor pressure curve of the hydrate pair system must always be below the ice-vapor curve.

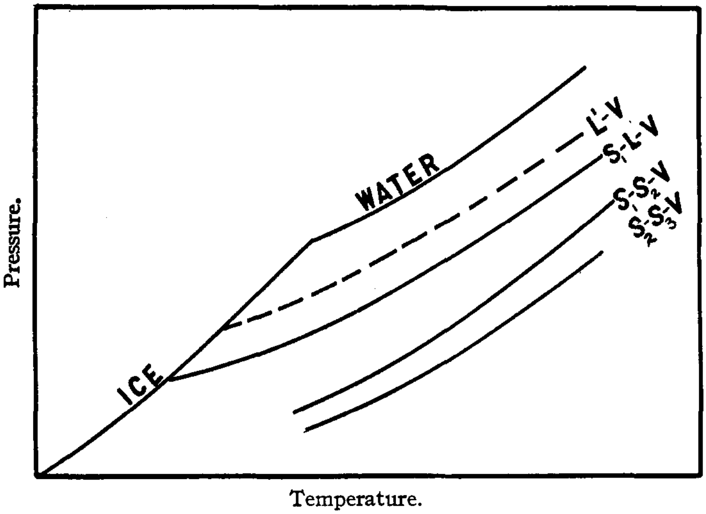

Fig. 1.—The equilibrium pressure over coexisting salt hydrates below 0 °C.

Furthermore, Norton and Johnston[2] have shown that the equilibrium pressure over two adjacent hydrates may be determined by adding to a solution in equilibrium with both solid hydrates, a third soluble component, and then measuring the vapor pressure at the new transition temperature, which by regulation of the added solute can be made to have a range of values. Under such circumstances the vapor pressure of this system is equal to the equilibrium pressure of the two crystalline hydrates at the particular temperature, provided always that both hydrates are present as solid phases. Hence, if the hydrate curve is to cut the ice curve, the vapor pressure of the system S_1-S_2-L''-V (where L'' is the equilibrium solution containing also the third component) must at some

[2] Norton and Johnston, *Am. J. Sci.*, **12**, 467 (1926).

temperature be equal to that of the system I-L''-V, a coincidence which would appear to be exceedingly improbable as a general rule.

The experimental data available are in accord with these conclusions. Vapor pressures plotted on a P-T diagram are not satisfactory for this purpose because data at low temperatures are not always available and extrapolation with any certainty is impossible. The plot of log p versus $1/T$ is no better because in some cases the lines are so nearly parallel to the ice-vapor curve that again uncertainty exists. But this log plot may be used in another way. The lines on this plot may be represented by the equation

$$\log p = \frac{Q}{2.3RT} + B$$

where p is the vapor pressure of the system, Q is the heat effect, T is the absolute temperature and B is a constant, so that their slope is proportional to the quantity Q. Now Q is the sum of several factors; for ice these are the heat of fusion of ice and the heat of vaporization per mole of water; for the hydrate, the heat of hydration plus the heat of vaporization per mole of water. The heat of vaporization of water appears in both so that any difference in Q is due to a difference between the heat of fusion of ice and the heat of hydration of the salt (or salt hydrate) per mole of water. It is obvious that if the heat of hydration of the salt per mole of water is greater than the molal heat of fusion of ice, the curves will not intersect and that they will intersect only if the converse holds.

The heats of hydration per mole of water have been calculated from the tables of Landolt-Börnstein[3] for some 200 salt hydrates and of this number only 10 showed a value of less than 1.437 cal., the molal heat of fusion of ice.[4] About 70% of such values were between 2.0 and 4.0, the average for all being 3.6. These heat effects are not given for the temperatures under discussion but they are in general so much greater than 1.4 that it seems unlikely that their relative values will be altered very much by lowering the temperature.

The ten exceptions are: $KSH.{}^1/_4H_2O$, $K_2SO_3.H_2O$, $K_2S_2O_3.H_2O$, $KC_5H_7O_4.H_2O$ (pyrotartrate), $KC_4H_5O_5.H_2O$ (malate), $KC_4H_5O_4.H_2O$ (methyl malonate), $K(SbO)C_4H_4O_6.{}^1/_2H_2O$, $NaC_4H_7O_2.3H_2O$ (butyrate), $NaC_5H_9O_2.1{}^1/_2H_2O$ (valerate), $Sr(C_2H_3O_2)_2.{}^1/_2H_2O$.

A critical examination of the original sources shows that these ten values are open to criticism and suspicion. In the case of $KSH.{}^1/_4H_2O$, Sabatier's method[5] of preparation has since been shown to yield a product different from the above. The remaining values are due to Berthelot,[6]

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[3] Landolt-Börnstein-Roth-Scheel, "Physikalish-Chemische Tabellen," 5th Edition, 1923, p. 1570.

[4] Dickinson and Osborne, *Bull. Bur. of Stand.*, 12, 49 (1915).

[5] Sabatier, *Ann. chim. phys.*, [5] 22, 21 (1881).

[6] Berthelot, "Thermochemie," Gautier Villars and Sons, Paris, 1897, Vol. II.

Massol[7] and Guntz.[8] The data of Berthelot were taken before he developed his bomb calorimeter and are obtained by difference from other measurements at different temperatures. Furthermore, his calculations are based on O = 8. Massol's work and the paper by Guntz come under these last objections; moreover, in no case are there data from which the degree of purity of the materials used may be estimated. In addition, the paper by Guntz contains a number of obvious typographical errors which tend to lessen confidence in his results.

In view of the striking agreement in all cases except those in which the data seem not to be reliable, it may be safely concluded that the two vapor pressure curves do not intersect and that this non-variant point does not in fact exist. From this it follows that under all conditions the vapor pressure of water above a pair of adjacent hydrates is less than that above ice or water. This means that the heat of hydration of salts per mole of water must always be less than the molal heat of fusion of ice, which furnishes a valuable criterion for the critical examination of experimental data on vapor pressures of salt hydrate pairs and on heats of hydration.

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Summary

It is shown that at any temperature the vapor pressure of water over a system composed of two solid hydrates and vapor must always be less than the vapor pressure of ice. This furnishes a criterion of the accuracy of data on the heats of hydration of salts.

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[7] Massol, *Ann. chim. phys.*, [7] **1,** 145 (1894).

[8] Guntz, *ibid.*, [6] **13,** 388 (1888).