estimated probable error in the volumes is 0.24%.

3. An equation of state has been fitted to these volumes with a root mean square error of 0.14%.

4. Bridgman's freezing curve for nitrogen has been checked and represented by a quadratic equation.

5. Various consequences of the equation of state have been discussed and some derived thermal data have been obtained from it. Of these the velocity of sound should prove useful as a check on the $P-V-T$ data.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Transition Temperature of Gypsum to Anhydrite

BY ARTHUR E. HILL

The temperature of the transition of gypsum to anhydrite, $CaSO_4 \cdot 2H_2O \rightleftarrows CaSO_4 + 2H_2O$, was set at 63.5° by van't Hoff[1] and his co-workers, in the course of their epoch-making researches upon the Stassfurt salt deposits. The temperature was arrived at by indirect vapor tension measurements and the application of thermodynamic reasoning; as pointed out by D'Ans,[2] the determination was accompanied by great difficulties because of the marked slowness of the system in coming to equilibrium. The given temperature has been quite generally accepted and quoted, and has of course considerable significance geologically. Partridge and White,[3] who determined the solubility of anhydrite at temperatures of 100° and upward, pointed out that their curve, if extrapolated below 100° to meet a solubility figure for anhydrite at 33° by Haddon and Brown[4] (the only figure then extant for a temperature below 100°), indicated a transition temperature as low as 38–39° for the two salts. A later figure by Roller[5] was also found to fit in with this hypothesis. Hara[6] and his co-workers obtained figures for four temperatures between 40 and 100°, using natural anhydrite and approaching equilibrium from undersaturation, which indicate a transition temperature with gypsum at about 37.5°. In the study of the system $CaSO_4$–K_2SO_4–H_2O in this Laboratory,[7] anhydrite was found by solubility measurements to be stable with respect to gypsum at 60° at all concentrations of potassium sulfate about 1%; in an investigation as yet unpublished we have found the same to be true at 50° in the presence of sodium sulfate, which would prove that the transition temperature is lower than van't Hoff thought, if it could be demonstrated that the anhydrite still remained the stable form as the concentration of the added salt approached zero. Quite recently D'Ans and Hoefer[8] have found that the transition temperature gypsum–anhydrite is lowered to 25° by a concentration of phosphoric acid of 83 g. per 100 g. of water, while at 83° anhydrite is stable with respect to gypsum at all concentrations of phosphoric acid; by use of analogies as to depression of transition points by a third component they argue that their results are in accord with van't Hoff's belief that the transition is at 63.5°.

That none of the investigations cited above carries complete conviction, from van't Hoff's publication down to the latest, is because in no one of the measurements, either of vapor tension or of solubility, has any evidence been adduced that the system studied was at equilibrium or anywhere near it, other than that a considerable time was allowed to elapse before measurements were made; since it is known that anhydrite–water systems at lower temperatures may remain undersaturated or supersaturated for months one has no criterion for deciding which if any of the experiments cited is correct. It has been my endeavor to conduct a few solubility experiments in which equilibrium was reached from two directions and which could therefore place the solubility curve of anhydrite definitely either above or below that of gypsum in the temperature range 66–40° and thereby fix the transition tempera-

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(1) Van't Hoff, *et al.*, *Z. physik. Chem.*, **45**, 257 (1903); also, van't Hoff, "Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen," Leipzig, 1912, p. 183, where the temperature is given as 66°.

(2) D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Verlagsgesellschaft für Ackerbau, Berlin, 1933, p. 5.

(3) Partridge and White, THIS JOURNAL, **51**, 360 (1929).

(4) Haddon and Brown, *J. Soc. Chem. Ind.*, **43**, 11 (1924).

(5) Roller, *J. Phys. Chem.*, **35**, 1132 (1931).

(6) Hara, *et al.*, *J. Soc. Chem. Ind. Japan*, **34**, suppl. binding 284 (1931); *J. Chem. Soc. Japan*, **55**, 1051 (1934).

(7) Hill, THIS JOURNAL, **56**, 1071 (1934).

(8) D'Ans and Hoefer, *Angew. Chem.*, **50**, 101 (1937).

TABLE I

SOLUBILITY OF ANHYDRITE AT 65°

	From undersaturation, %	From supersaturation, %
Initial concn.	0.00	2.229
25 days	.136	0.173
4 months	.135	.152

SOLUBILITY OF ANHYDRITE AT 45°

Time, days	In pure water		Time	In 0.5% K_2SO_4		Time	In 0.1% K_2SO_4	
	Undersat.	Supersat.		Undersat.	Supersat.		Undersat.	Supersat.
0	0.00	0.211%	0	0.00	0.204	0	0.00	0.204%
28	.200	.210	32 days	.189	.204	5 mos.	.182	.188
88	.201	.211	5 mos.	.190	.194			

SOLUBILITY OF ANHYDRITE AT 35°

Time	In pure water		In 0.04% K_2SO_4		In 0.08% K_2SO_4		In 0.12% K_2SO_4	
	Undersat.	Supersat.	Undersat.	Supersat.	Undersat.	Supersat.	Undersat.	Supersat.
0	0.00	0.250%	0.00	0.236%	0.00	0.230%	0.00	0.225%
28 days	.242	.245	.228	.233	.218	.222	.207	.207
80 days	...	.242	.229	.232	.218	...	.208	.206
Gypsum	.212	...	.204	...	.195	...	.188	...

ture beyond doubt. It was not to be expected that complete attainment of equilibrium would be arrived at, but it has been possible to show that at 65° the solubility of anhydrite is markedly below that of gypsum by results obtained from supersaturation, that at 45° the solubility is still below that of gypsum and at 35° it is above that of gypsum; adding to these results, which seem not to be open to attack except as to insignificant errors, a number of what may be called non-equilibrium results, a consistent solubility curve for anhydrite can be drawn between 100 and 20°, giving a transition point to gypsum at 42°.

It was pointed out in an earlier research[7] that when anhydrite and water are in contact at 50°, the approach to equilibrium from undersaturation and supersaturation reaches a zero velocity after a few days, and that for a three-month period following there remains a difference of some 5% between the two with no measurable change. A similar fact with respect to calcite and aragonite was noted by Bäckstrom;[9] in view of the infrequency with which solubilities of moderately insoluble compounds have been measured from the two directions of approach, it is possible that this phenomenon is more general than has been suspected. For this reason there is, in the experiments at 65°, a resultant lack of agreement between the figures obtained, but nevertheless certainty that the true figure lies between the limits found; for the lower temperatures an entirely different method of approach was used.

Experimental Results.—The anhydrite was prepared by boiling a suspension of gypsum in 20% sulfuric acid for three days; the material thus obtained, after washing and drying, exists in crystals averaging 20–30 microns in length, which have been found to correspond in their properties with natural anhydrite.[7] About 10–20 g. of this salt in 250 cc. of solvent was used in each experiment and rotated in closed bottles in the thermostat for the times indicated; for analysis, 50-cc. samples were filtered by suction at the temperature of the experiment, precipitated with ammonium oxalate and the calcium weighed as calcium oxide after ignition at high temperature. The results at three temperatures are given in Table I.

The results at 65° represent approach toward equilibrium in aqueous solution from undersaturation and supersaturation. The results from undersaturation reach a static condition within a few days; those from supersaturation reach such a condition after a longer time, but fail to reach the same value as from undersaturation. The true figure must lie between these two values, and is decidedly lower than the solubility of gypsum at 65°, which is[10] 0.196%, indicating that the transition temperature is considerably below that given by van't Hoff. The solid residues from all the experiments were tested for possible hydration by washing with water, alcohol and ether and subjecting to air drying, under which treatment gypsum does not lose water of hydration; they were then heated in an oven at 100° for fifteen hours or longer. The losses in the various cases varied from 0.03 to 0.10%, which amount may reasonably be ascribed to adsorbed water and to indicate substantial absence of hydration.

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(9) Bäckstrom, *Z. physik. Chem.*, **97**, 179 (1921).

(10) "International Critical Tables," Vol. IV, p. 229.

At 45 and at 35°, at which temperatures an approach to equilibrium from supersaturation in water could not definitely be depended upon, results were carried out in dilute potassium sulfate solution as well as in water, so that extrapolation of results to zero concentration could be made. The figures are shown graphically in Fig. 1, curves I and II; the results from undersaturation fall upon a straight line, and give values for the solubility in water which can be in error hardly more than one or two units in the third place.

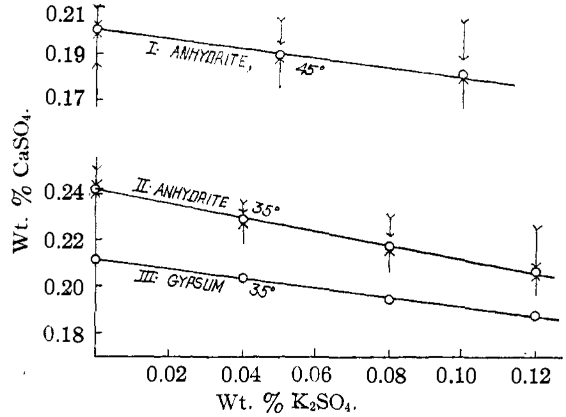

Fig. 1.—Solubilities of anhydrite and of gypsum: Curve I, anhydrite at 45°; II, anhydrite at 35°; III, gypsum at 35°.

The solubility at 25° has been measured from undersaturation only since anhydrite is unquestionably metastable at this temperature and cannot be exposed to water for long periods. In one week's time the sample had not hydrated measurably. It seems probable that the figure obtained is a little low on account of insufficient time.

TABLE II

SOLUBILITY OF ANHYDRITE AT 25°

Time	From undersaturation, %
0	0.00
1 hour	.234
1 day	.267
2 days	.271
7 days	.274

The Solubility Curve, 20 to 100°.—Above 100°, where equilibrium is reached in a moderately short time, the figures of Partridge and White[3] are available. With the figures at four temperatures here reported, a few others are available and in good accord, so that a fairly complete solubility curve can be drawn from 20 to 100°. The figures are assembled in Table III.

TABLE III

SOLUBILITY OF ANHYDRITE, 20 TO 100°

Reference	Temp., °C.	Wt. % anhydrite
Roller[5]	20	0.298
This paper	25	.274
This paper	35	.242
This paper	45	.201
This paper	65	.136
Hill and Yanick[11]	75	.114
Hill[7,11]	100	.067

The curve is shown in Fig. 2, together with the curve for gypsum as taken from the "International Critical Tables." The figures of Hara[6] and the figure of Haddon and Brown[4] are not included in the above table and curve since they are considerably lower than the results tabulated, and appear to represent incomplete attainment of equilibrium from the side of undersaturation.

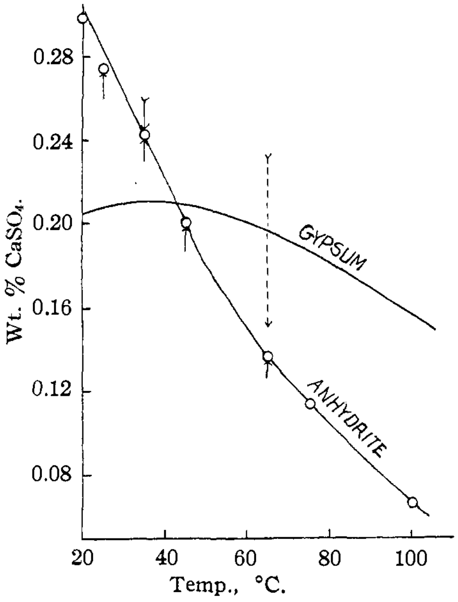

Fig. 2.—Solubility curves for gypsum and anhydrite, 20 to 100°.

Summary

The solubility of anhydrite in water has been determined at 65, 45 and 35°, with approach from both supersaturation and undersaturation. Using these data and previously existing data, a solubility curve can be drawn between the temperatures of 20 and 100°; the curve cuts the well authenticated curve for gypsum at 42°, placing the transition temperature some 20° lower than van't Hoff's figure of 63.5–66°.

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(11) Hill and Yanick, THIS JOURNAL, **57**, 645 (1935).