3. Carbon produced by the explosion of graphitic acid showed a density of 2.215, and is, therefore, probably graphite.
4. Samples of the graphites originally showed no "drift" or increase in weight with time after immersion in the liquid. The natural graphites, however, after being swelled, or increased in volume by treatment with fuming nitric acid and heat, displayed remarkable drifts. Pressure was used to hasten completion of the drift.
5. The tendency to drift was largely destroyed by a severe compression of the swelled material previous to the density determination.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 398]

THE VAPOR PRESSURES OF CERTAIN HYDRATED METAL SULFATES

BY CLIFFORD D. CARPENTER AND ERIC R. JETTE

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A review of the literature not only reveals a striking incompleteness in the experimental data on the vapor pressure of hydrates, but considerable discrepancy in much of the corresponding data given.

Soon after Vogel[1] observed that blue vitriol effloresces rapidly over sulfuric acid Watson[2] made what appears to be the first attempt to measure the vapor pressure of a hydrate. Since that time many investigators have made such measurements, but as Wilson[3] has recently pointed out, the work "prior to 1875 had little scientific value owing chiefly to the hazy notions which prevailed as to the nature of the phenomenon." Although Gibbs[4] formulated the phase rule in 1877, it does not seem that investigators in this field realized its merits until about 15 years later. It is interesting to note that Andreae,[5] apparently unfamiliar with the phase rule 14 years after its proposal, interpreted the results of some vapor-pressure measurements of hydrates in accordance with the requirements of those of the phase rule. It is also evident that some of the other investigators of this period understood the general nature of the requirements for defining the point of equilibrium between the various phases.

Although much of the earlier data is unsatisfactory, considerable progress was made in developing methods for the measurement of vapor pressures. It will not be necessary, however, to discuss these methods in detail, for extensive bibliographies and discussions of the more important investigations have been given by Johnston[6] on hydroxides and carbonates, by Smith and Menzies[7] on general methods as applied to all phases of the subject, by Menzies[8] on "Apparent Anomalies Outstanding in the Results of

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[1] Vogel, *Schweigger's J.*, **22**, 160 (1818).

[2] Watson, *J. prakt. Chem.*, **14**, 112 (1838).

[3] Wilson, THIS JOURNAL, **43**, 704 (1921).

[4] Willard Gibbs, *Trans. Connecticut Acad.*, **1874–1878**.

[5] Andreae, *Z. physik. Chem.*, **7**, 241 (1891).

[6] Johnston, *ibid.*, **62**, 330 (1908).

[7] Smith and Menzies, THIS JOURNAL, **32**, 898, 907, 1412, 1434, 1449, 1541 (1910).

[8] Menzies, *ibid.*, **42**, 1951 (1920).

Measurements of Dissociation Pressures," and by Wilson[8] on "Some New Methods for the Determination of the Vapor Pressure of Salt Hydrates."

After a careful consideration of the previous work on vapor pressures of salt hydrates it was thought that a more extensive study of each system under consideration would be desirable, for with few exceptions vapor pressure measurements on a single hydrate have been made for only one or two temperatures. Some measurements, however, were made by Wiedmann[9] up to 98.5°, by Schotty[10] at 90° and by Derby and Yngve[11] from 10° to 140°, but most measurements have been made near 25°.

Since this investigation involved the measurement of vapor pressures of each hydrate studied over a considerable range of temperature, it was necessary to design a thermostat which would operate with sufficient accuracy at the higher temperatures. As preliminary experiments demonstrated that in many cases equilibrium is reached slowly, it was thought true equilibrium could be best obtained by approaching it from both sides. The static method was therefore selected as being the most suitable, and a modification of the Bremer-Frowein[12] tensimeter with mercury as the enclosing liquid and pure water as the comparison substance was employed. The temperatures were measured by mercury in glass thermometers.

Apparatus

Thermostats.—Four thermostats were used. Two were of commercial types, one working at 25° and one from 30° to 50°. For temperatures from 50° to 65° a Pyrex jar 24 × 38 cm. was insulated with a magnesia heat insulator 37 mm. thick and regulated by means of a commercial regulator. A narrow window was provided in the insulation so that readings could be made. For temperatures from 65° up, and during the later experiments down to 60°, a special thermostat was assembled (Fig. 1).

A Pyrex jar **a**, referred to above, insulated with magnesia **b** was surrounded by a asbestos box 38 × 38 × 38 cm. **c** in which an electric bulb **f** of appropriate capacity could be suspended to keep the temperature very near that at which the termostat was set. This box had a small removable door **h** in front of the window **i** in the magnesia insulation, which could be opened when readings were to be taken. Water was put into the jar and covered with a 12mm. layer of paraffin. The thermostat, stirrer and other attachments were inclosed in a space surrounded and covered by a large wool blanket supported by 4 tall posts. This acted as a second chamber in which electric bulbs could be suspended to keep a constant temperature. The thermostat was thus kept in a double "constant temperature room."

The regulation of the temperature was accomplished by a thermoregulator **d**, of the usual form using mercury. In order that the regulator should register small temperature changes in all parts of the bath, it was constructed of 16 mm. Pyrex tubing having 8 fingers **d** as shown in Fig. 1. The electric circuit was attached to a controlling

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[9] Wiedmann, *Wied. Ann.*, **17**, 561 (1882).

[10] Schotty, *Z. physik. Chem.*, **64**, 415 (1908).

[11] Derby and Yngve, This Journal, **38**, 1439 (1916).

[12] Bremer, *Z. physik. Chem.*, **1**, 5 (1887).

device, designed by D. and J. Beaver,[13] which opened or closed the intermittent electric heaters. These heaters e were made by sealing a coil of Nichrome wire in an evacuated Pyrex glass tube 38 cm. long by 16 mm. in diameter. One was used as a continuous heater and one or two, as needed, intermittently.

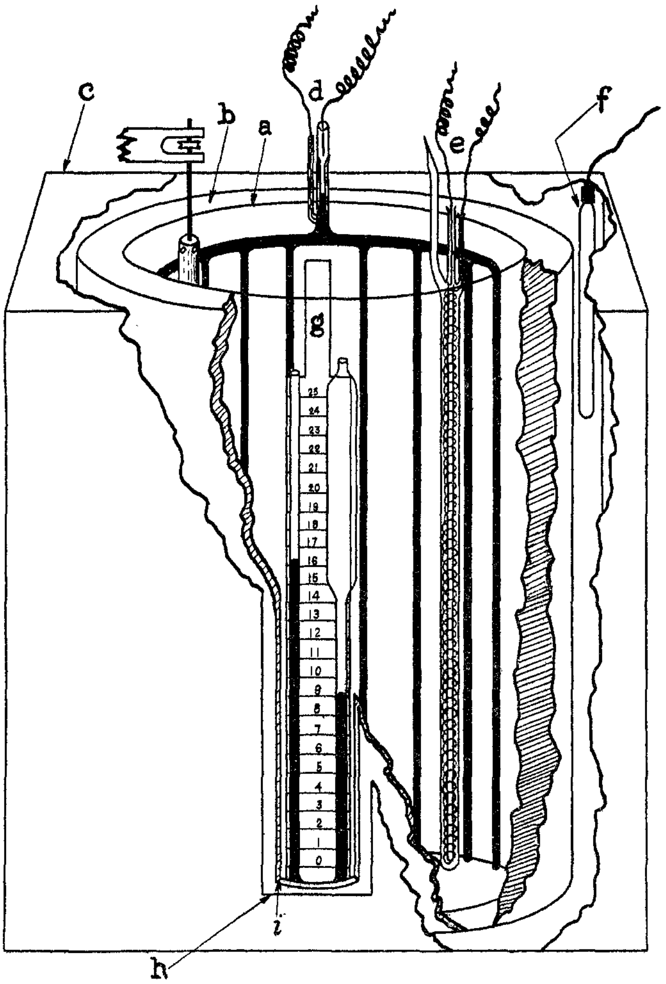

Fig. 1.

The stirring was accomplished by a turbine propeller in a tube 22 cm. × 38 mm. and mounted as described by Carpenter.[14] This produced a rapid circulation of the water in the bath.

Tensimeter.—The main features of the tensimeter are shown in Fig. 2A and its mounting in Fig. 2B and Fig. 1 (g).

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[13] Unpublished.

[14] Carpenter, *Chem. Met. Eng.*, **24**, 569 (1921).

It was of Pyrex tubing, 30 cm. over all and, except for the bulbs, of heavy wall 4 mm. tubing. The scale was a strip of milk glass 270 mm. long and 25 mm. wide and calibrated from 0 at 10 mm. from the lower end, to 250 mm. near the upper.

Thermometers.—The thermometers were all mercury in glass and were calibrated every 5° by a platinum resistance thermometer standardized as described by the Bureau of Standards.[15]

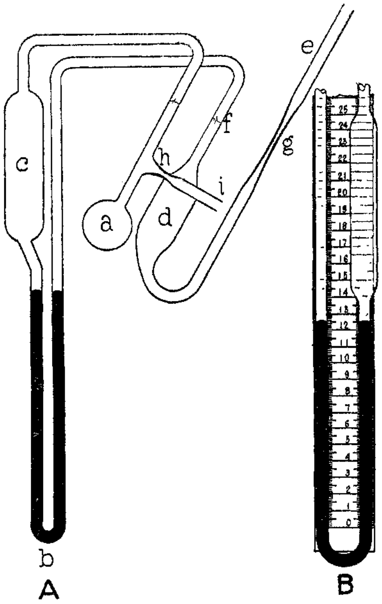

Fig. 2.

Preparation of Materials and Loading the Tensimeter

Preparation of the Hydrates.—Chemically pure hydrates were dissolved in pure water and recrystallized 5 or 6 times. After each crystallization the solid was drained from the mother liquor and washed. The final crystallization was always carried out by evaporation of the water at low temperatures. The lower hydrate was obtained by gently heating the higher until sufficient water had been driven off. The water content of the hydrates used was determined in all cases by weighing before and after dehydration.

Preparation of the Tensimeter.—The tensimeter was thoroughly washed with an alkaline solution, rinsed out and washed with sulfuric acid dichromate cleaning solution. It was then washed with pure water and finally steamed.

Preparation of Mercury.—The mercury used as enclosing liquid was washed with nitric acid as described by Hildebrand[16] and finally distilled under a partial vacuum with a slow stream of air bubbling through it.

Loading the Tensimeter.—After the mercury was introduced into the U (**b**), the side arm carrying bulb **a** was then sealed on. While this tube was in a vertical position conductivity water was distilled through i into **a**. After about 2 cc. had been collected it was sealed off at **h**. Bulb **a** was thus loaded with water essentially free from air. The hydrate was put into Bulb **d** and then sealed on at **f**.

The tensimeter was then placed in a horizontal position so that the mercury was in Bulb **c**, and attached at **e**, through pressure tubing, to a vacuum pump capable of producing a 1mm. vacuum. The pump was then started and a vacuum of 2 or 3 mm. maintained for from 1 to 2 hours. During this period the tensimeter was alternately heated and cooled. When it was gently warmed the mercury boiled. All parts of the instrument except the bulbs containing the mercury and water were heated very hot during evacuation. The instrument was gently tapped to aid in the removal of any gas trapped by the water, mercury or hydrate. During the evacuation 0.3 to 0.5 cc. of water distilled. Since 0.1 cc. of water vapor at 760 mm. pressure occupies about 160 cc., the tensimeter and surface of the hydrate were washed with a stream of 150 to 250 liters of water vapor at 2 to 3 mm. pressure.

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[15] *Bur. Standards Reprint*, **124**, THIS JOURNAL, **41**, 748 (1919).

[16] Hildebrand, *ibid.*, **31**, 933 (1909).

While the vacuum was maintained, the tensimeter was brought to a vertical position, and after the hydrate was gently warmed until slight evidence of dehydration took place, it was sealed off at **g**. From 2 to 4 tensimeters were loaded with the same hydrate. These were then mounted, as shown in Figs. 2B or 1 (**g**) so that they could be put into the thermostat or removed whenever desired. Some of these were used for months.

Experimental Part

Whenever measurements were to be made, 2 tensimeters were loaded with the same hydrate. One was then heated until the salt was partially dehydrated. After setting the thermostat, both tensimeters were introduced, one registering a lower pressure and one a higher pressure than they should at the point of equilibrium. This resulted in a slow increase in pressure in one case and a decrease in the other; thus equilibrium was approached from both a higher and a lower pressure at the same time.

TABLE I

$CuSO_4.5H_2O-3H_2O$ AT 35.17°

Pressure in millimeters (corr.)

Date April	From lower H_2O pressure	From higher H_2O pressure	Date April	From lower H_2O pressure	From higher H_2O pressure
1	Started	Started	9	16.4	16.9
3	15.7	17.8	10	16.4	16.5
4	15.9	17.5	12	16.5	16.5
5	16.1	17.3	14	16.5	16.6
6	16.1	16.9	..	..	..
8	16.3	16.8	..	Mean final value, 16.5	..

Data on the determination of one point at 35.17° for $CuSO_4.5H_2O-3H_2O$ are given in Table I and graphically expressed in Fig. 3.

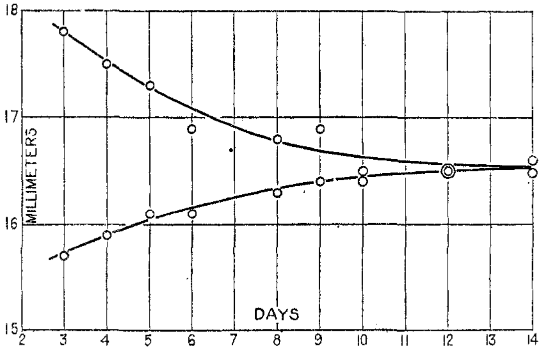

Fig. 3.

The vapor pressures were obtained in this manner at several temperatures for the hydrates $CuSO_4.5H_2O-3H_2O$, $CuSO_4.3H_2O-1H_2O$, $MgSO_4.7H_2O-6H_2O$, $CoSO_4.7H_2O-6H_2O$, $CdSO_4.8/3H_2O-1H_2O$, $MnSO_4.5H_2O-1H_2O$ and for the saturated solutions of $MgSO_4.6H_2O$, $CoSO_4.6H_2O$, $MnSO_4.H_2O$. Table II gives in detail the actual readings and all calculations in obtaining the vapor pressures for the system $CuSO_4.5H_2O–3H_2O$, and Table III shows the values for all other systems without the detailed

TABLE II

THE VAPOR PRESSURE OF $CuSO_4.5H_2O–3H_2O$

Temp. °C.	Variation of thermostat ± °C.	Tensimeter No.	Diff. of Hg. levels corrected Mm.	Vapor press. H_2O Mm.	Variation in vapor press. of H_2O Thermostat ± Mm.	Vapor press. of hydrate Obs. Mm.	Mean Mm.
25.00	0.004	5-4-6*	15.87-15.87-16.03	23.76	0.00	7.9-7.9-7.7	7.8
30.17	0.01	5-6*	20.8-20.4	32.15	0.02	11.4-11.8	11.6
35.13	0.01	5-6*	26.1-26.0	42.49	0.02	16.4-16.5	16.5
36.65	0.04	5-4*	27.7-27.9	46.18	0.10	18.5-18.5	18.5
40.12	0.04	5-4*	32.6-32.5	55.69	0.12	23.1-23.2	23.2
45.07	0.03	5-4*	39.4-39.5	72.16	0.12	32.8-32.7	32.8
50.16	0.03	5-4*	47.9-48.2	93.38	0.15	45.5-45.2	45.4
55.29	0.05	5-4*	58.1-57.9	119.8	0.29	61.7-61.9	61.8
60.18	0.05	5-4*	67.2-66.7	150.7	0.35	83.5-84.0	83.8
60.46	0.01	6-5*	67.0-67.2	152.7	0.07	85.7-85.5	85.6
65.16	0.04	5-4*	76.3-76.4	188.9	0.34	112.6-112.5	112.6
70.16	0.02	8*	85.0	235.4	0.21	150.4	150.4
69.78	0.02	6-5*	84.4-83.9	231.5	0.21	147.1-147.6	147.4
80.13	0.03	6-5*	96.9-97.7	357.4	0.45	260.5-259.7	260.1
90.04	0.03	8-9-8*	94.3-94.1-93.9	526.8	0.60	432.5-432.7-432.9	432.7

TABLE III

CONDENSED TABLE OF VAPOR PRESSURES DETERMINED AS INDICATED IN TABLE II FOR

t °C.	p	t °C.	p	t °C.	p
$CuSO_4.3H_2O$		$CdSO_4.8/3H_2O$		$CoSO_4.7H_2O$	
25.00	5.6	25.00	17.8	25.00	17.0
35.13	11.8	24.99	17.6	32.50	28.7
45.17	22.1	30.17	25.5	36.65	38.0
50.23	30.9	35.17	35.0	40.18	48.1
65.11	77.7	40.12	47.8	40.22	48.4
80.08	183.1	40.25	48.7	45.07	66.0
80.05	183.5	45.07	63.8	45.17	66.5
$MgSO_4.7H_2O$		45.17	64.7	50.16	84.9
25.00	12.7	50.16	84.5	55.29	107.7
32.40	22.8	50.23	84.0	60.22	134.9
36.65	31.4	55.29	110.2	65.16	167.3
36.65	31.5	60.22	140.0	70.16	204.3
40.12	40.1	65.16	175.7	$MnSO_4.H_2O$	
40.19	40.6	70.16	218.6	25.00	19.8
40.22	40.6	75.87	279.3	24.99	20.1
45.07	57.2	80.03	334.3	30.17	27.1
45.21	58.0	80.03	334.6	32.47	31.1
50.16	78.6	90.04	500.3	35.17	37.0
50.29	79.0	...	...	36.65	40.4
55.26	99.3	...	...	40.17	49.1
55.33	99.6	...	...	40.19	49.3
60.18	123.5	...	...	45.14	64.4
65.15	153.0	...	...	60.29	138.7
65.11	153.9	...	...	65.16	174.7
69.74	185.7	...	...	...	...

readings and averaging as shown in Table II. The data of Tables II and III are expressed graphically in Fig. 4. Those marked with an asterisk are the tensimeters in which equilibrium was approached from the higher vapor pressure.

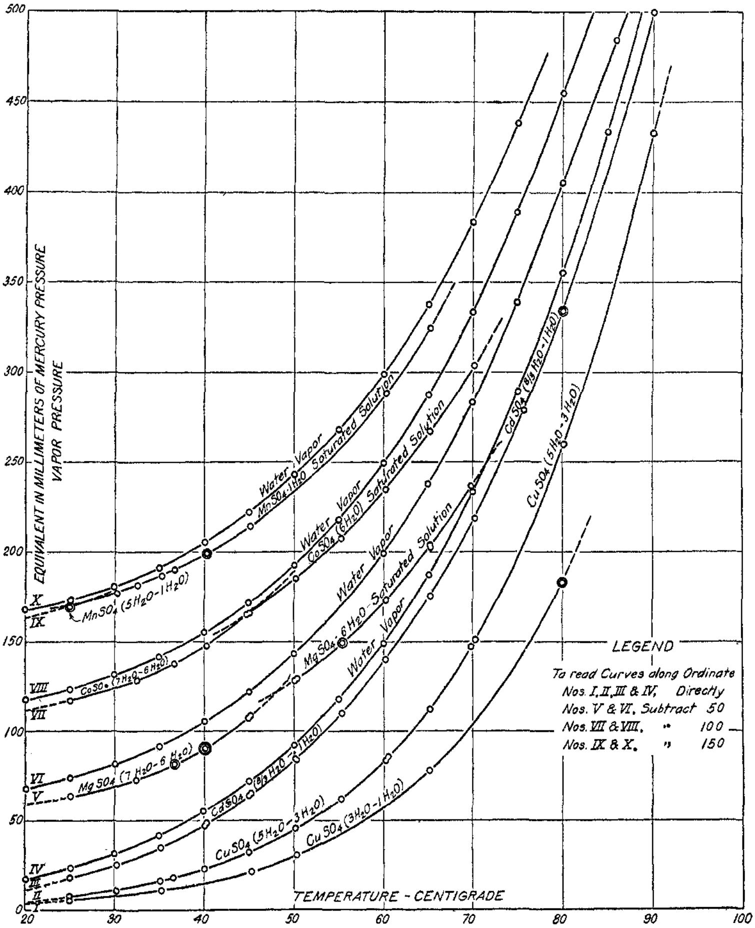

Fig. 4.

Discussion of the Accuracy of the Results

As this investigation was undertaken in order to obtain results with the greatest degree of accuracy, a brief review of the precautions taken in the experimental work and an estimation of the accuracy of the results obtained should be made. The preparation of pure hydrates and pure water have already been described. The necessity of knowing the exact temperatures was also recognized and a determination of them accomplished by standardizing the thermometers used, as described before. Enclosed "permanent gas," which is recognized as one of the chief difficulties, was removed by warming and washing the surface of all materials and apparatus with a stream of water vapor at low pressures as described previously. That it was eliminated is evident from the fact that instruments set up at different times and containing different amounts of water, hydrate, mercury, and exposed glass surface, gave satisfactory duplication in results. A further evidence is the fact that the same instrument used over a long period of time and at many different temperatures gave duplicate results when brought back to the temperatures used in the earlier experiments. In fact, new instruments when set up duplicated the results of others that had been prepared months before. A further possibility of error results in the reading of the mercury columns and the regulation of the thermostat. The reading of the heights of the mercury columns could readily be made with an error of not more than ±0.1 mm. and if this were +0.1 mm. in one reading and —0.1 mm. in the other, the error would be cumulative, or a total error of ±0.2 mm. The variation in the temperature also leads to some error, as a change of 0.69° at 25° causes a change of 1 mm. in the vapor pressure of water, and 0.049° causes the same change at 90°. At the lower temperatures the regulation was better than 0.005° and at the higher within 0.03°. The maximum error due to variations in temperature of the thermostat would therefore be less than 0.01 mm. at 25° and about 0.6 mm. at 90°.

Whether these apparent maximum errors are real is a pertinent question. At the lower temperatures, where equilibrium is reached slowly, an error of ±0.6 mm. due to thermostat regulation would become very serious, but no such difficulty exists. On the other hand, at the higher temperatures equilibrium is reached quickly and as the temperature of the thermostat is taken at each reading, the pressure at that temperature is probably close to the equilibrium pressure. Since the temperatures and pressures recorded at these higher points are averages of several readings, the error is far below the apparent error. If, however, we accept the individual maximum apparent errors on one tube as ±0.2 mm. at the lower temperatures and ±0.6 mm. at the higher, the shape of the vapor-pressure curve will be very near the true shape and any result obtained by reading the curve would be within the experimental error. An error of ±0.2 mm. on a single point at 25° on a value of 10 mm. represents a possible error of 4% while an error at 90° of ±0.6 mm. on a value of 250 mm. represents an error of less than 0.5%. Accepting the maximum apparent errors, the relative error at the higher vapor pressure becomes very small; but a 4% error at the lower pressure, if real, would seriously affect the absolute values. It must be borne in mind, however, that every tensimeter was read many times, and the average reading taken as the final, and that no point was determined by only 1 tube but by the average of at least 2.

In order to make this 4% relative error real, every reading would need to have a maximum error and always in the same direction, that is, it would always be necessary to read 1 tube consistently 0.2 mm. high and the other consistently 0.2 mm. low in order that each individual value should have a maximum error. That such an error could not be possible is better illustrated by considering the method of determining the point of equilibrium and the procedure in reading the value already shown in Table I and Fig. 2, which shows that the maximum ±0.2 mm. error exists for only 2 of the 18 points. It is evident, therefore, that the real error is much below the maximum possible error obtained when considering the extreme cases.

Interpretation of the Results

The most evident lessons from the results of this investigation can be learned by a study of the curves in Fig. 4. As shown in Fig. 4, Curves V, VII and IX, a transition takes place and in two cases is located by the intersection of two curves.

In the case of $MgSO_4.7H_2O–6H_2O$ (see Curve V) the hydrate is stable up to 48.4°. The upper segment is the vapor-pressure curve for a saturated solution of $MgSO_4.6H_2O$. This verifies the findings of Van der Heide[17] who showed by the dilatometer that the transition point is between 48° and 48.5°. The solubility data as collected by Seidell[18] give an indication of this point (see Fig. 5). Too much cannot be expected from these solubility data, as the 14 points are taken from 12 observers. The position of this point is only approximately located by solubility data.

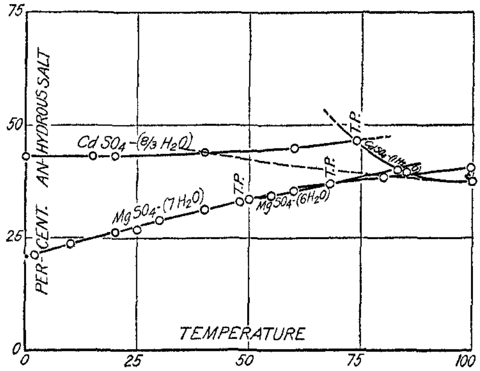

Fig. 5.

$CoSO_4.7H_2O–6H_2O$ is stable up to 45.1° (see Curve VII). No previous record of this point has been found. Marignac,[19] however, working with the dilatometer, found a transition point at 40.8° and by a thermometric method at 40.6°; our results show no indication of a transition of any kind around 40°.

The vapor-pressure curve for a saturated solution of $MnSO_4.H_2O$, and one point at 25° for the hydrate are given (see Curve IX). The hydrate is not stable above 27°. The transition point, therefore, cannot

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[17] Van der Heide, *Z. physik. Chem.*, **12**, 418 (1893).

[18] Seidell, "Solubilities of Inorganic and Organic Substances," 2nd ed., **1919**.

[19] Marignac, *Assn. Chem. Phar.*, 97, 247 (1856).

be located from our data by this method. The transition point has been found to be 27° by Cottrell.[20]

The vapor pressure of $CdSO_4.8/3H_2O$–$1H_2O$, determined over a wide range and plotted in Curve III, gives little evidence of any transition point. It must be noted, however, that the curve does not correspond with that of the water or with the other curves given. This might not be apparent at first, as it is "tangentially" parallel with the water curve but not parallel in the sense that a second curve is when measured by the distance along the ordinates. The peculiarity in vapor-pressure change seems to be paralleled by the peculiar change in solubility. Etard[21] found the greatest solubility to be at 68° while Mylias and Funk[22] found it to be between 73.5° and 74.5°, at which point the solubility commenced to drop very rapidly. If the solubility decreases as shown in the curve of Fig. 5, the solution grows rapidly more dilute above this point and thus results in causing the vapor pressure to increase more rapidly. It must be noted that the real change in solubility is small.

In the results for the vapor pressure of $CdSO_4.7H_2O$ given above, many points were duplicated several times and equilibrium was established very carefully. Although the shape of the curve gives little evidence of a transition point at 74°, it must be noted that it is peculiarly flat in this region. It will be shown below, however, that there are certain theoretical interpretations possible of its behavior.

Application of Results

Heat Reaction.—The heat reaction, which may in this case be considered as the latest heat of vaporization, has been calculated for each of the hydrates investigated except for that of manganese sulfate which was omitted for lack of data. In the reaction $AB.xH_2O + 1H_2O \rightleftarrows AB.(1 + x)H_2O + Qp$, Qp is given by the following relation: $Qp = RT^2 \frac{d\, ln\, p}{d\, T}$. Qp is therefore the heat of reaction per mole of water at constant pressure; p is the pressure of water vapor of the system at equilibrium at the absolute temperature T. Since the value Q is very sensitive to changes in p and T, the extreme values may easily diverge ±4% from the mean value of Q for the system considered. Q is determined for each system by substituting in the formula the experimental values recorded in Tables II and III.

The average value for $CuSO_4.3H_2O$ was 13,256; for $CuSO_4.5H_2O$, 13,268; for $CdSO_4.8/3H_2O$, 11,170; for $MgSO_4.7H_2O$, 14,035; for $MgSO_4.6H_2O$, saturated solution, 9,741; for $CoSO_4.7H_2O$, 12,795; and for $CoSO_4.6H_2O$, saturated solution, 9,760.

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[20] Cottrell, *J. Phys. Chem.*, **4**, 651 (1900).

[21] Etard, *Ann. chim. phys.*, [7] **2**, 536 (1894).

[22] Mylias and Funk, *Ber.*, **30**, 824 (1897).

It may be observed that the calculated values for Q for the systems $CuSO_4.5H_2O$–$3H_2O$ and $CuSO_4.3H_2O$–$1H_2O$ vary on both sides of the mean value but no steady increase or decrease of value is indicated. It is noteworthy that both systems show almost identical mean values for the calculated heat of vaporization over the same temperature range. In the case of $MgSO_4.7H_2O$–$6H_2O$, the calculated values of Q for the hydrate and the saturated solution are strikingly different. In fact this change is so evident that the approximate position of the transition point may be closely located. In order to appreciate this check on transition point, it must be borne in mind that the values used in the calculations were experimental.

In the case of $CoSO_4.7H_2O$–$6H_2O$, the same striking observations may be made as in the case of the $MgSO_4.7H_2O$–$6H_2O$ system.

In the case of $CdSO_4.8/3H_2O$–$1H_2O$, the calculated value of Q shows a fairly steady decrease up to about 70°, above which its value remains nearly constant.

Relation between Temperature and Pressure.—Very few attempts to find a mathematical expression for the variation of pressure with temperature in the case of hydrates have been reported in the literature. This is probably due to the short temperature ranges covered by previous investigators and, therefore, insufficient data on the subject. Pareau,[23] however, noted that his curves were, in general, similar to that of pure water. Baxter and Lansing[24] plotted the logarithm of the aqueous pressure against the reciprocal of the absolute temperature and obtained very nearly straight lines. These lines are represented very closely by an equation developed by Antoine[25] of the form $\log P = A + \frac{B}{T + C}$ where A, B and C are constants. The values for $\log p$ and $1/T$ have been calculated from the experimental values given in Tables II and III, and were then used in plotting lines, in the same manner as was done by Baxter and Lansing[24] for their vapor-pressure data. They are shown in Fig. 6. These points, both for the hydrates and saturated solutions, fall within the limits of experimental error on straight lines. This is not altogether unexpected for if the equation, $Q = RT^2 \frac{d\,ln\,p}{dT}$ is integrated, it reduces to the following form, $\frac{1}{T} = \frac{R}{Q}\,ln\,p + I$, where I is the integration constant. If, now, Q is constant, then R/Q is a constant and, therefore, the slope of a straight line.

The results shown on these lines are especially striking. The transition

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[23] Pareau, *Pogg. Ann.*, **1**, 39 (1877).

[24] Baxter and Lansing, This Journal, **42**, 419 (1920).

[25] Antoine, *Compt. rend.*, **110**, 632 (1890).

points are very definitely located by the intersection of the straight lines. They intersect, in the case of the $MgSO_4.7H_2O$–$6H_2O$, Line III, at a point corresponding to 48.1° and in the case of $CoSO_4.7H_2O$–$6H_2O$, Line II, at 45.9°. These points agree very closely with those indicated on the vapor pressure curves in Fig. 4.

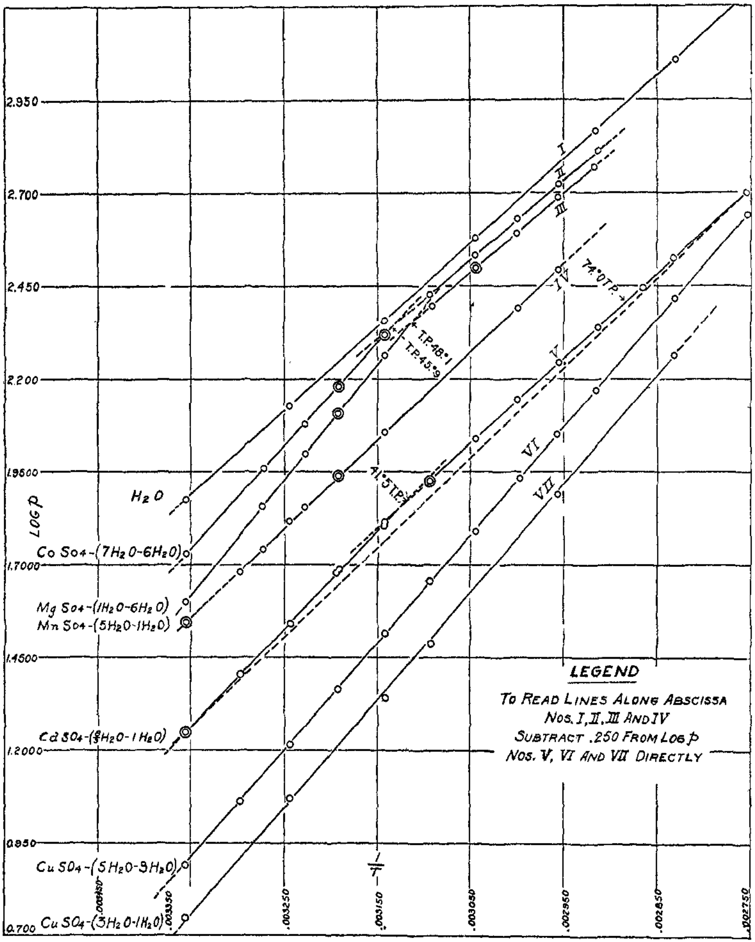

Fig. 6.

The case of $CdSO_4.8/3H_2O$–$1H_2O$, Line V, gives a very definite indication of a transition point at 41.5°. This seems quite likely for several reasons. If one refers to the vapor-pressure Curve III, Fig. 4, it will be noted that there is a peculiar flattening in its shape about this point. A reference to the solubility diagram Fig. 5, shows that the solubility begins to change more rapidly around this point. The change in Q is as great from 25° to 45° as from 45° to 90°. It is also a well-known fact that in preparing cadmium sulfate for the standard Clark and Weston cell the crystals must be prepared by slow evaporation at low temperatures. While little is known of the nature of the transition, it is possible that it is a molecular rearrangement resulting in a different crystal form.

The point at 74.0°, described by Mylias and Funk,[22] is not shown by any indication of an intersection of lines. It is possible that at the higher pressures, since a small change in log p represents a considerable change in pressure, the irregularity in the normal shape of a curve below and above the transition point, as shown around 74° in the vapor-pressure curve of cadmium sulfate, may not be given definitely by logarithmic expressions. In such a case the two straight lines above and below the transition point may be so nearly similar in direction that the possibility of a sharp intersection is eliminated.

Summary

A thermostat has been assembled for very accurate control of temperatures between 25° and 100°.

The static method has been employed for measuring vapor pressures of hydrates, and a Bremer-Frowein tensimeter, of special design, and manipulation to eliminate the usual errors, have been described.

Equilibrium has been reached from higher and lower pressures simultaneously for each point investigated.

The vapor pressures for $CuSO_4.5H_2O$, $CuSO_4.3H_2O$, $CdSO_4.8/3H_2O$, $CoSO_4.7H_2O$, $MgSO_4.7H_2O$, and $MnSO_4.5H_2O$ crystals, and for the saturated solutions of some of these at various temperatures between 25° and 90°, have been determined.

Certain new transition points have been located, for $CoSO_4.7H_2O$ at 45.1° and for $CdSO_4.8/3H_2O$ at 41.5°.

The transition point for $MgSO_4.7H_2O$–$6H_2O$, previously found by Van der Heide to lie between 48.0° and 48.5°, has been located at 48.4°.

It has been shown that the value of Q usually changes most abruptly at the transition point and that it is nearly constant so long as the same phases are present. On account of this fact most transition points are readily located by the intersection of the lines drawn through the points determined by the log p and $1/T$ relation.

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