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THE DISSOCIATION TENSIONS OF CERTAIN HYDRATED CHLORIDES AND THE VAPOR PRESSURES OF THEIR SATURATED SOLUTIONS.[1]

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A knowledge of the vapor-pressure relationships of certain hydrated chlorides was required in connection with a problem which is being studied in this laboratory. Since the required data could not be found in the literature, the measurements which follow were made to supply this deficiency. Partington[2] and Foote and Scholes[3] have classified and critically discussed the methods which have been employed for the measurement of the vapor pressures of hydrates. None of the methods they mention seem to combine accuracy, simplicity and ease of manipulation as well as the static method of Smith and Menzies.[4] Since this method is described at length in the exhaustive study cited, only essential details of the apparatus and the precautions taken to secure data of the desired degree of accuracy 0.1 to 2 mm. will be given.

[1] Presented at the meeting of the American Chemical Society, Urbana, Ill., April, 1916.

[2] Partington, *J. Chem. Soc.*, 99, I, 466 (——).

[3] Foote and Scholes, THIS JOURNAL, 33, 1309 (1911).

[4] Smith and Menzies, THIS JOURNAL, 32, 1412 (1910).

The Apparatus.

The *isoteniscope* was of the ordinary static type. The confining liquid in all these measurements was a heavy paraffin oil.

Temperature regulation was obtained at the various temperatures below 75°, by immersing the isoteniscope in a 10 l. cylindrical glass thermostat heated by the method of Derby and Marden.[1]

The especially designed toluene-mercury regulator used allowed of convenient adjustment of temperature of the thermostat at any point within a range of about sixty degrees. At temperatures from above 50° up to 75° the water in the thermostat was covered with a layer of low melting paraffin. In all cases the regulation was constant within 0.05°. For the higher temperatures above 75° a benzene-toluene-xylene vapor bath was used. This bath when fitted with a reflux condenser remained constant within 0.1°.

The manometer was of the open-end type. The tube of 1 cm. inside diameter was mounted upon a support of thoroughly seasoned wood which bore a paper scale covered with Bakelite varnish. The scale was carefully calibrated by means of a standard cathetometer and during its use showed no variation due to atmospheric changes. After the manometer was permanently placed and adjusted to a truly vertical position, the length of the scale was determined *in situ* by means of a cathetometer. From these observations a scale correction curve was constructed. Scale readings were made by means of a cathetometer to avoid parallax and to give a scale magnification and were estimated to tenths of a millimeter. The barometer, which was read to the nearest tenth of a millimeter, was compared with a standard instrument and the readings were found to be correct. All manometer and barometer readings were corrected to 0°. The manometer mercury was purified by dropping it through dilute nitric acid and distilling *in vacuo.*

The *thermometer* used below 100° was compared with one recently standardized by the Bureau of Standards and had no scale correction. The thermometer used above 100° was corrected at 100° by taking the boiling point of water in the usual way. It was then compared with a thermometer certified to 0.2° by the Reichsanstalt. In all cases where it was appreciable a correction was made for exposed thread.

Preliminary Measurements.—In order to test the accuracy of the method and the applicability of paraffin oil as a confining liquid in the isoteniscope, trial measurements of the vapor pressures of water at four temperatures were made. In Table I, under I, are given the number of observations made at each temperature, under t are given the corrected temperatures, under p_1 are given the vapor pressures found, and under p are given the values of Scheel and Heuse at the same temperatures taken from the

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[1] Derby and Marden, THIS JOURNAL, 35, 1767 (1913).

tables of Landolt–Börnstein. The pressures are given in mm. of mercury.

Table I.—Vapor Pressures of Water.

I.	t.	p_1.	p.	Difference.
2	25.09	24.0	23.89	+0.1 mm.
2	34.15	40.3	40.25	+0.0 mm.
2	43.41	66.4	66.22	+0.2 mm.
3	54.64	115.8	116.08	—0.3 mm.

It will be seen that the observed values are in good agreement with the true values. Paraffin oil then could safely be employed at least to 55° and above this temperature the errors must be well within a millimeter even at 70–80°. Larger errors due to the vapor pressure of the oil above this temperature would not obscure the relative relationships although leaving the true values somewhat in doubt.

The Vapor-pressure Relationships of Magnesium Chloride–Water.

The following $MgCl_2$–H_2O systems were studied: Saturated solution of $MgCl_2.6H_2O$, saturated solution of $MgCl_2.4H_2O$, and the system $MgCl_2.6H_2O$–$MgCl_2.4H_2O$. Pure magnesium chloride was recrystallized once from distilled water, washed and dried in a centrifuge fitted with a porcelain basket. Six determinations of the vapor pressure of the saturated solution of the uncrystallized salt at 23.16° gave a mean value of 6.9 mm., while the value at the same temperature for the vapor pressure of the saturated solution of the recrystallized salt was 6.8 mm. The difference is within the limit of error of the method.

In almost all cases where two systems were being studied over the same range of temperature two isoteniscopes were used simultaneously in parallel and so arranged that, by means of suitable stopcocks, either one or both could be connected with the manometer. In this way, as the transition temperature was approached, the method became a differential one and the transition temperature could be determined as exactly as by means of the more cumbersome Frowein tensimeter.

In all these measurements, as well as those which follow, care was taken to bubble vapor out of the bulb in order to secure complete removal of air and, in the case of solutions, to insure saturation. Since the isoteniscopes were connected to the manometer by means of thick-walled rubber tubing, the apparatus was flexible enough to allow the bulbs to be shaken. This, and the small amounts of material needed, insured saturation in the shortest possible time.

In the tabulations for the various systems studied the following abbreviations are used to designate the phases which enter into the equilibrium: Stl. = saturated solution. V. = vapor. $6\,H_2O$, $4\,H_2O$, etc., designates the degree of hydration of the salt in the solid phase. For example, $6\,H_2O$–Stl.–V. signifies that the phases in equilibrium are for magnesium chloride and water, $MgCl_2.6H_2O$–saturated solution–vapor.

Under the phases is placed the temperature range over which the relationship was studied. The curves are also designated by the phases in equilibrium.

In Table II, under I, are given the number of observations at each temperature, under *t* are given the temperatures, under *p* are given the vapor pressures of the saturated magnesium chloride solutions. Below 117.2° the solid phase is $MgCl_2.6H_2O$, while above that temperature the solid phase is $MgCl_2.4H_2O$. Under p_6 are given the dissociation tensions of the system $MgCl_2.6H_2O–MgCl_2.4H_2O$.

TABLE II.—VAPOR PRESSURES OF $MgCl_2–H_2O$ SYSTEMS.

I.	*t*.	$6\ H_2O$–Stl.–V. 10.14°–117.2°. $4\ H_2O$–Stl.–V. 117.2°–138.3°. *p*.	$6\ H_2O$–$4\ H_2O$–V. p_6.
5.....	10.14	3.4	....
3.....	18.05	5.2	....
3.....	25.53	7.7	....
1.....	31.60	....	1.6
4.....	31.65	11.2	....
2.....	41.92	18.5	....
1.....	42.10	....	2.7
3.....	44.46	21.4	....
5.....	50.96	29.0	....
3.....	55.19	35.4	....
1.....	58.31	....	7.8
1.....	64.10	....	11.3
5.....	64.99	54.1	....
1.....	68.27	....	13.2
1.....	69.38	....	14.6
1.....	74.27	....	21.3
1.....	76.53	....	21.9
1.....	88.85	124.2	41.5
1.....	96.96	154.1	63.1
2.....	99.23	162.7	....
7.....	99.43	163.6	....
1.....	104.7	189.9	98.5
1.....	108.2	.....	116.8
1.....	109.9	195.3	.....
1.....	110.2	198.6	.....
1.....	110.9	197.6	.....
1.....	112.9	198.3	.....
1.....	113.1	197.4	146.1
1.....	113.6	196.0	.....
1.....	114.9	193.7	.....
1.....	115.6	.....	165.4
1.....	116.0	191.6	.....
2.....	116.6	184.0	.....
1.....	117.2	169.1	.....
1.....	117.7	170.8	.....
1.....	118.0	173.7	.....
1.....	119.2	181.5	.....
1.....	121.2	193.1	.....
1.....	122.6	205.0	.....
2.....	125.5	225.3	.....
1.....	128.9	247.9	.....
1.....	138.3	307.1	.....

The values in Table II were plotted and smooth curves drawn through them. Pressure values could then be read at any temperature. In Table III, under *t*, are given the temperatures, under *p* are given the vapor pressures of the saturated magnesium chloride solutions as read from the curve and under *p*(*v*H–S) are given the pressures according to van't Hoff[1] and Speranski.[2] From his one experimental value at 25°, van't Hoff has calculated thermodynamically the values below 25°, while Speranski from this data has calculated the values above that temperature. Under *p*(L) are given the values by Lescoeur.[3] Under p_6

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[1] Van't Hoff, *et al.*, *Z. physik. Chem.*, **45**, 288 (1903).

[2] Speranski, *Ibid.*, **70**, 519 (1910).

[3] Lescoeur, *Ann. chim. phys.*, [7] **2**, 85.

are given the pressure values for the system $MgCl_2.6H_2O–MgCl_2.4H_2O$ as read from the curve.

TABLE III.—VAPOR PRESSURES OF $MgCl_2–H_2O$ SYSTEMS AT ROUNDED TEMPERATURES.

	6 H_2O–Stl.–V. 0.0°–117.2°. 4 H_2O–Stl.–V. 117.2°–140°.			6 H_2O–4 H_2O–V. 35.0°–117.2°.
t.	p.	p(vH–S).	p(L).	p_e.
0.0	2.0[1]	1.34	...	...
5.0	2.4[1]	1.96	...	...
10.0	3.2	2.82	...	...
15.0	4.4	4.00.	4.4	...
20.0	5.8	5.6	5.75	...
25.0	7.5	7.70	7.5	...
30.0	10.1	....	...	1.5[1]
35.0	13.4	....	...	1.9
37.5	15.3	....	18.0	...
40.0	17.3	18.98	...	2.5
45.0	21.8	....	...	3.3
50.0	27.6	....	...	4.5
55.0	35.2	....	...	6.2
60.0	43.8	54.11	...	8.3
64.5	53.0	....	53.0	...
65.0	54.1	....	...	11.3
70.0	65.5	....	...	15.1
75.0	79.0	....	...	20.0
77.5	86.4	....	88.0	...
80.0	93.4	134.57	...	26.2
85.0	109.0	....	...	34.0
90.0	127.0	....	...	43.7
95.0	146.0	....	...	56.5
100.0	166.5	....	159.0	75.0
105.0	190.0	....	...	99.5
107.5	194.9	....	...	...
110.0	197.7	....	...	127.5
112.5	197.7	....	...	...
115.0	194.0	....	...	160.0
116.0	190.5	....	...	...
117.0	175.0	....	...	...
117.2	169.1	....	...	169.1
120.0	186.7	....	...	...
125.0	220.0	....	...	...
130.0	255.0	....	...	...
135.0	287.6	....	...	...
140.0	321.5[1]	....	...	...

The vapor-pressure curves of the $MgCl_2–H_2O$ systems studied are shown in Fig. 1. A T is the vapor-pressure curve of the saturated solutions of the hexahydrate. It will be noted that the curve becomes retroflex near the transition temperature T. This is due to the large increase in solubility of the hydrate near its transition temperature. T C is the vapor-

[1] Extrapolated.

pressure curve of the saturated solutions of the tetrahydrate. D T is the vapor-pressure curve of the system $MgCl_2.6H_2O–MgCl_2.4H_2O$. It intersects the curve A T at T.

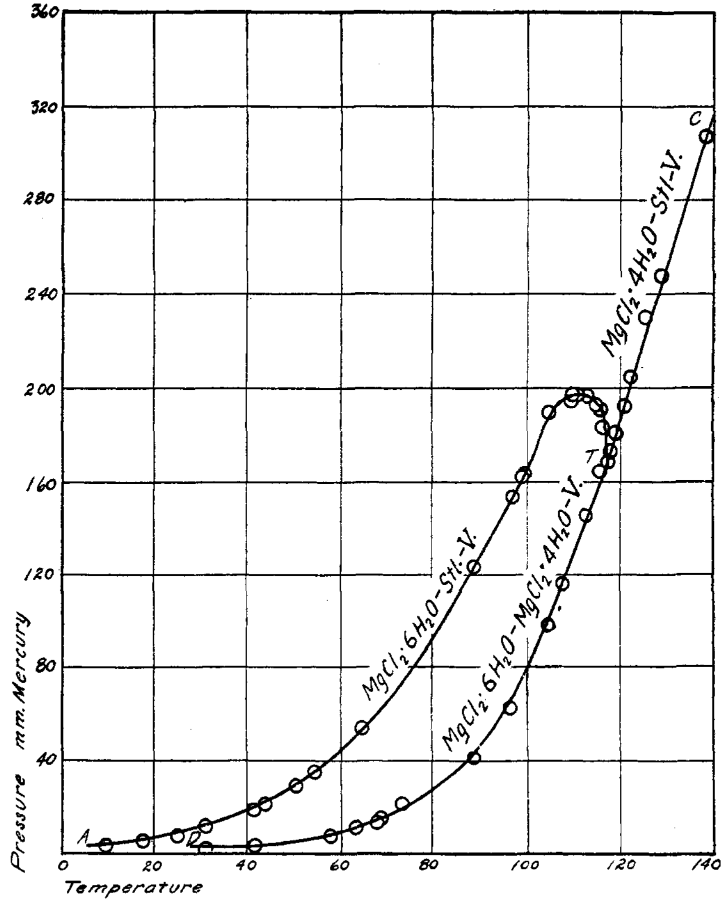

Fig. 1.

The Vapor-pressure Relationships of Cupric Chloride Water.

Saturated solutions of $CuCl_2.2H_2O$ and the system $CuCl_2.2H_2O–CuCl_2.H_2O$ were studied. The cupric chloride was made from the sulfate by precipitation with sodium carbonate and solution in hydrochloric acid. The twice crystallized salt still showed the presence of small amounts of sulfate. The results should not be affected by this impurity since the sulfate hydrate has a lower vapor pressure than the chloride hydrate.

In Table IV, under I, are given the number of observations at each temperature, under *t* are given the temperatures, under *p* are given the vapor pressures of the saturated cupric chloride solutions and under p_2 are given the dissociation tensions of the system $CuCl_2.2H_2O$–$CuCl_2.H_2O$.

TABLE IV.—VAPOR PRESSURES OF $CuCl_2$–H_2O SYSTEMS.

I.	t.	2 H_2O-Stl.-V. 17.90°-64.45°. p.	2 H_2O-H_2O-V. 17.90°-64.18°. p_2.
1	17.90	...	3.7
1	26.60	23.3	8.7
2	31.40	30.9	11.7
1	39.88	49.5	18.8
1	53.54	94.3	54.3
1	64.18	...	105.6
1	64.45	150.6	...

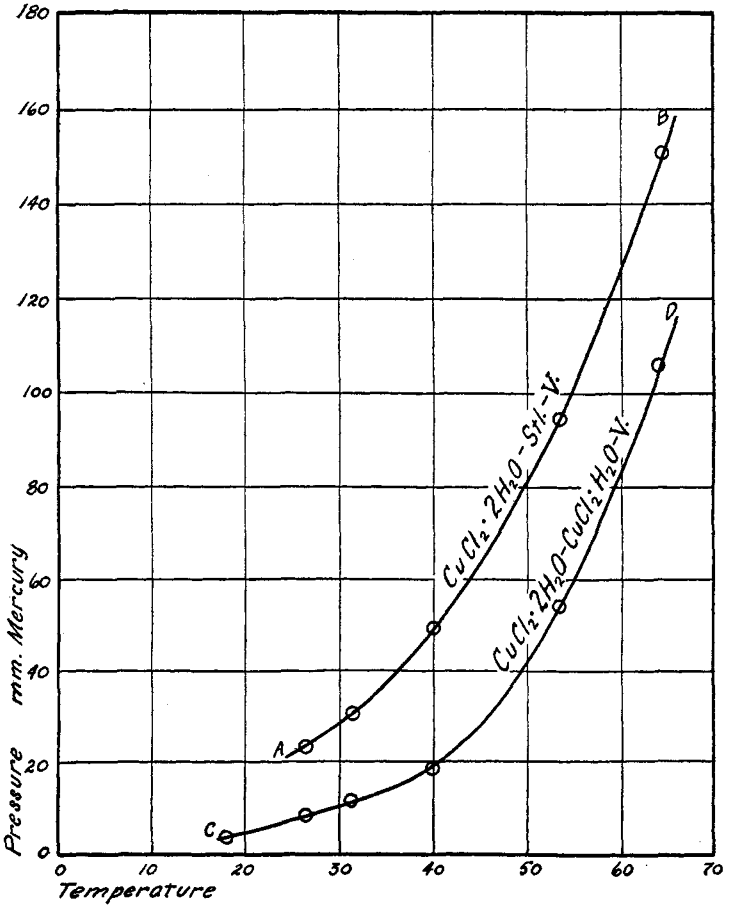

Fig. 2.

The values for every 5°, taken from the curve, are given in Table V.

TABLE V.—VAPOR PRESSURES OF $CuCl_2$–H_2O SYSTEMS AT ROUNDED TEMPERATURES.

t.	2 H_2O–Stl.–V. 15.0°,–65.0°. p.	2 H_2O–H_2O–V. 15.0°–65.0°. p_2.	t.	2 H_2O–Stl.–V. 15.0°–65.0°. p.	2 H_2O–H_2O–V. 15.0°–65.0°. p_2.
15.0	..	2.6[1]	45.0	63.5	27.6
20.0	14.7[1]	5.0	50.0	79.8	41.5
25.0	21.2[1]	7.8	55.0	100.5	61.2
30.0	28.5	10.7	60.0	125.6	83.5
35.0	37.7	14.1	65.0	154.0[1]	110.5[1]
40.0	49.8	19.0			

The vapor-pressure curves of the $CuCl_2$–H_2O systems studied are shown in Fig. 2. A B is the vapor-pressure curve of the solution in equilibrium with $CuCl_2.2H_2O$, while C D is the vapor-pressure curve of the system $CuCl_2.2H_2O$–$CuCl_2.H_2O$.

The Vapor-pressure Relationship of Cobalt Chloride Water.

The following $CoCl_2$–H_2O systems were studied: Saturated solutions of $CoCl_2.6H_2O$, saturated solutions of $CoCl_2.2H_2O$, and the system $CoCl_2.6H_2O$–$CoCl_2.2H_2O$. Pure cobalt chloride was recrystallized from distilled water, washed and dried in a centrifuge fitted with a porcelain basket. Careful testing with dimethyl glyoxime failed to reveal any trace of nickel.

In Table VI, under I, are given the number of observations at each temperature, under t are given the temperatures, under p are given the vapor pressures of the saturated cobalt chloride solutions. Below 52.25° the solid phase was the hexahydrate while above that it was the dihydrate. Under p_6 are given the dissociation tensions of the system $CoCl_2.6H_2O$–$CoCl_2.2H_2O$.

TABLE VI.—VAPOR PRESSURES OF $CoCl_2$–H_2O SYSTEMS.

I.	t.	6 H_2O–Stl.–V. 23.4°–52.25°. 2 H_2O–Stl.–V. 52.25°–78.87°. p.	6 H_2O–2 H_2O–V. 23.05°–52.25°. p_6.	I.	t.	6 H_2O–Stl.–V. 23 4°–52.25°. 2 H_2O–Stl.–V. 52.25°–78.87°. p.	6 H_2O–2 H_2O–V. 23.05°–52.25°. p_6.
1.......	23.05	..	6.4	1.....	46.84	41.3	33.3
1.......	23.40	13.9	..	1.....	48.60	...	38.4
1.......	24.19	14.7	6.8	1.....	49.23	44.8	39.7
2.......	28.0	..	9.0	1.....	50.02	...	42.0
1.......	28.68	18.4	9.6	1.....	51.15	47.2	46.0
1.......	31.9	..	12.1	1.....	51.58	48.0	46.6
1.......	32.65	22.4	12.4	1.....	52.13	...	47.7
1.......	35.98	26.6	16.5	1.....	52.25	48.6	48.6
1.......	39.47	30.5	20.5	1.....	56.44	58.7	..
2.......	39.87	31.1	21.0	1.....	62.12	79.0	..
1.......	39.96	..	21.5	1.....	68.26	105.1	..
1.......	43.92	36.8	27.8	1.....	78.87	170.9	..

The vapor-pressure values at intervals of 5°, taken from the curve, are given in Table VII.

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[1] Extrapolated.

TABLE VII.—VAPOR PRESSURES OF $CoCl_2$–H_2O SYSTEMS AT ROUNDED TEMPERATURES.

	6 H_2O–Stl.-V. 20.22°–52.25°. 2 H_2O–Stl.-V. 52.25°–80.0°.	6 H_2O–2 H_2O–V. 20.0°–52.25°.		6 H_2O–Stl.-V. 20.0°–52.25°. 2 H_2O–Stl.-V. 52.25°–80.0°.	6 H_2O–2 H_2O–V. 20.0°–52.25°.
t.	p.	p_B.	t.	p.	p_B.
20.0[1]	11.8	5.4	52.25	48.6	48.6
25.0	15.3	7.2	55.0	54.7	....
30.0	19.7	10.2	60.0	60.2	....
35.0	25.1	14.9	65.0	91.0	....
40.0	31.3	21.2	70.0	114.2	....
45.0	38.7	29.6	75.0	144.8	....
50.0	45.9	41.9	80.0[1]	178.5	....

The vapor-pressure curves of the $CoCl_2$–H_2O systems studied are shown in Fig. 3. The curve A T is the vapor-pressure curve of the solutions in equilibrium with $CoCl_2.6H_2O$. There is a slight tendency for the curve

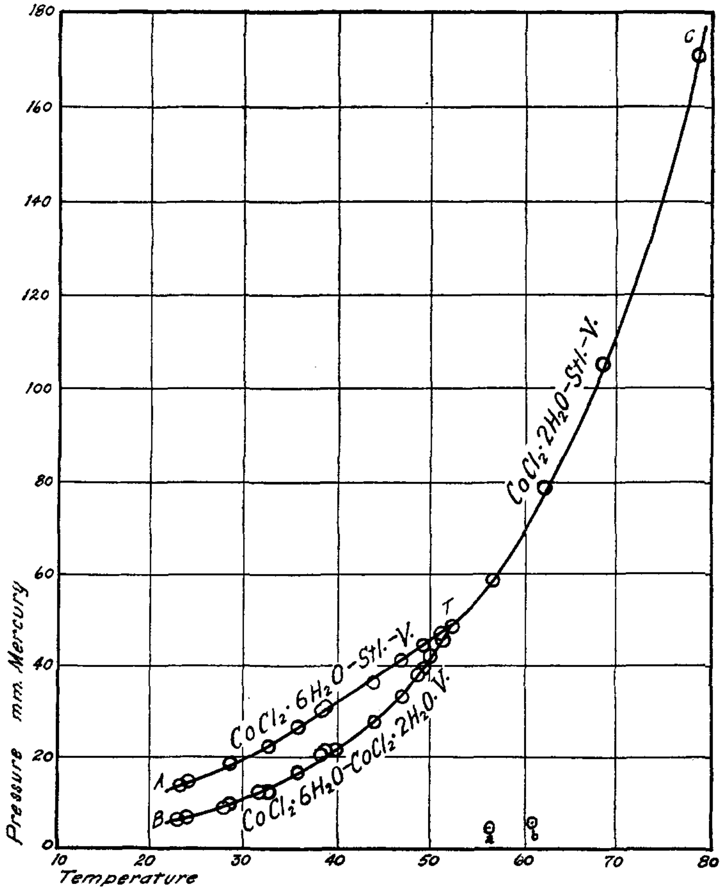

Fig. 3.

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[1] Extrapolated.

to flatten out as it approaches the transition point T. This is due to the increased solubility of the hydrate. The curve T C is the vapor-pressure curve of the solutions in equilibrium with $CoCl_2.2H_2O$. The curve B T is the vapor-pressure curve of the system $CoCl_2.6H_2O$–$CoCl_2.2H_2O$. It intersects the curve A T at T.

Water vapor was removed from the saturated cobalt chloride solution at a temperature above the transition point until a fall in the vapor pressure indicated the presence of a new phase. At 56.3° the pressure was 4.9 mm., and at 60.7° the pressure was 5.6 mm. (see points *a* and *b*, Fig. 3). The chloride content of the bulb was then determined by titration with 0.1 *N* $AgNO_3$ using K_2CrO_4 as an indicator. The degree of hydration was then calculated and the salt was found to contain 1.82 molecules of water. No evidence of the existence of the tetrahydrate was found.

The vapor-pressure measurements were not refined enough to show any indication of the polymorphic change of the red hexahydrate into the blue hexahydrate which occurs below the transition temperature.

The Vapor-pressure Relationship of Nickel Chloride Water.

Vapor-pressure measurements were made on the following $NiCl_2$–H_2O systems: Solutions in equilibrium with $NiCl_2.6H_2O$; solutions in equi-

TABLE VIII.—VAPOR PRESSURES OF $NiCl_2$–H_2O SYSTEMS.

I.	*t*.	6 H_2O-Stl.-V. 19.8°-45.22°. *p*.	4 H_2O-Stl.-V. 36.25°-54.1° *p'*.	6 H_2O-4 H_2O-V. 19.8°-36.25°. p_6.	4 H_2O-2 H_2O-V. 25.15°-79.06°. p_4.
5	19.8	9.6	..	7.3	...
1	20.6	..	..	7.8	...
2	24.1	12.0	..	10.1	...
1	24.6	..	..	10.4	...
1	25.95	..	..	..	6.0
1	26.00	..	..	..	6.1
4	30.3	..	..	15.2	...
1	30.7	..	..	15.2	...
4	31.0	17.5	..	16.1	...
1	32.31	..	..	..	8.9
2	35.05	21.5	..	20.9	...
2	36.25	22.5	22.5	22.5	...
1	38.20	..	..	..	14.2
1	39.80	26.6	..	..	...
1	40.57	..	28.9	..	...
2	45.22	33.3	36.7	..	...
1	47.69	..	..	..	26.4
1	48.34	..	42.6	..	...
1	54.1	..	56.4	..	...
1	54.50	..	..	..	40.4
1	54.63	..	..	..	40.7
3	59.63	..	..	..	56.3
2	66.34	..	..	..	84.1
1	79.06	..	..	..	108.1

librium with $NiCl_2.4H_2O$; the system $NiCl_2.6H_2O$–$NiCl_2.4H_2O$; and the system $NiCl_2.4H_2O$–$NiCl_2.2H_2O$. The degree of hydration of the last two systems was determined in the manner referred to above for cobalt and they were found to contain 5.74 and 3.78 molecules of water, respectively. The nickel chloride used was "Highest Purity" and was not recrystallized.

In Table VIII, under I, are given the number of observations at each temperature, under t are given the temperatures, under p are given the vapor pressures of the solutions in equilibrium with $NiCl_2.6H_2O$, under p' are given the vapor pressures of the solutions in equilibrium with $NiCl_2.4H_2O$, under p_6 are given the dissociation tensions of the system $NiCl_2.6H_2O$–$NiCl_2.4H_2O$, and under p_4 are given the dissociation tensions of the system $NiCl_2.4H_2O$–$NiCl_2.2H_2O$.

The vapor-pressure values at every 5°, taken from the curve, are given in Table IX.

TABLE IX.—VAPOR PRESSURES OF $NiCl_2$–H_2O SYSTEMS AT ROUNDED TEMPERATURES.

t.	6 H_2O-Stl.-V. 15.0°–50.0°. p.	4 H_2O-Stl.-V. 36.25°–55.0°. p'.	6 H_2O–4 H_2O-V. 15.0°–36.25°. p_6.	4 H_2O–2 H_2O-V. 15.0°–65.0°. p_4.
15.0	8.2[1]	....	6.5[1]	4.9[1]
20.0	9.7	....	7.6	5.2
25.0	12.6	....	10.5	5.9
30.0	16.5	....	14.9	7.6
35.0	21.5	....	20.9	11.0
36.25	22.5	22.5	22.5	....
40.0	26.8	28.1	....	16.3
45.0	33.1	36.3	....	22.7
50.0	39.7[1]	46.5	....	29.8
55.0	....	58.9	....	39.2
60.0	....	....	....	58.3
65.0	....	....	....	78.3

The vapor-pressure relationships of the $NiCl_2$–H_2O systems studied are shown in Fig. 4. The curve A T D is the vapor-pressure curve of the solution in equilibrium with $NiCl_2.6H_2O$. Here again there is a tendency for the curve to flatten out as it nears the transition point T. We have not noticed any reference in the literature to this increase in solubility of a hydrate near its transition temperature. It would seem to indicate that changes in the physical behavior of a hydrate precede its transformation into a lower hydrate. The curve extends into the unstable region above the transition temperature to D. Here the vapor pressure of the unstable system is lower than that of the stable system. Findley[2] has pointed out that this is due to the greater solubility of the unstable hydrate. The curve B T is the vapor-pressure curve of the system

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[1] Extrapolated.

[2] Findley, "The Phase Rule," p. 144.

$NiCl_2.6H_2O-NiCl_2.4H_2O$. It cuts the curve A T D at T. The curve T C is the vapor-pressure curve of the solutions in equilibrium with $NiCl_2.4H_2O$. It is practically a continuation of the curve B T. The curve

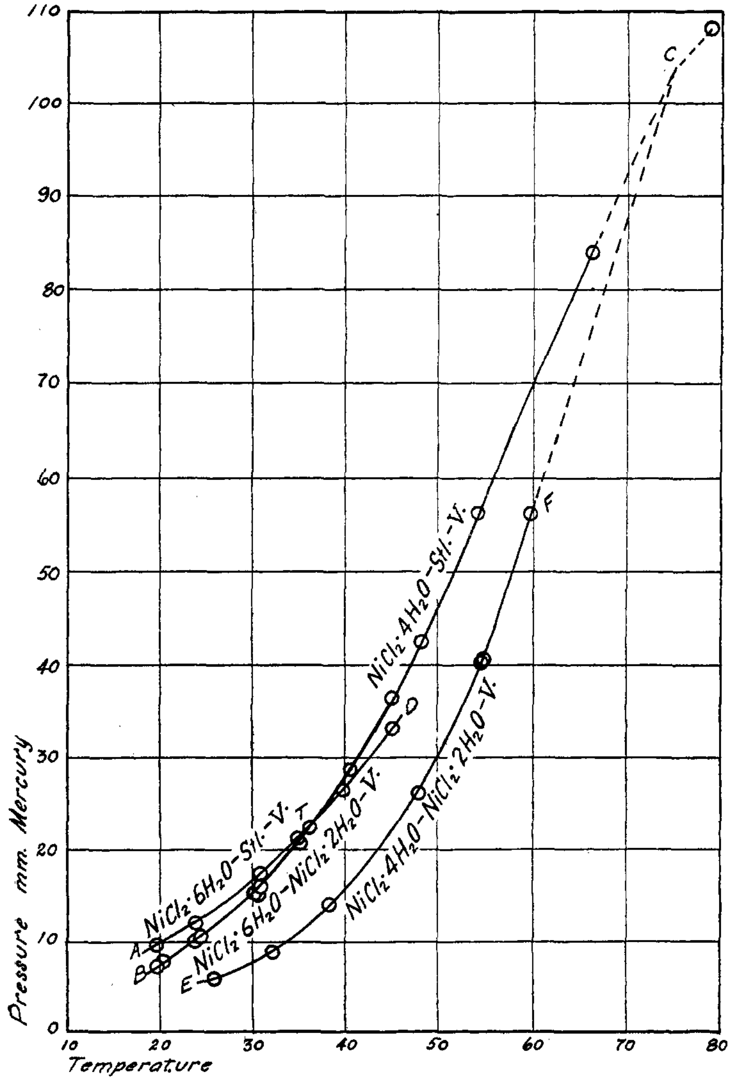

Fig. 4.

E F is the vapor-pressure curve of the system $NiCl_2.4H_2O-NiCl_2.2H_2O$. This should cut the curve T C approximately at 75°,[1] the transition temperature of the tetrahydrate into the dihydrate. The curves when

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[1] Etard, *Ann. chim. phys.*, [7] 2, 545 (1894).

extrapolated, as shown by the dotted lines, intersect at about this point. The transition of the hexahydrate into the tetrahydrate which takes place at 36.25° has never been noted before. Lescoeur[1] found no evidence of the tetrahydrate. The measurements given here seem to point clearly to its existence.

Summary.

The static method of Smith and Menzies has been employed in determining the dissociation tensions of hydrates and the vapor pressures of their saturated solutions. The method has been found convenient and the data given by it have been consistent and of the required degree of accuracy.

The following systems were studied over the indicated temperature range and transition temperatures were observed as listed:

Systems.	Temp. range.	Transition temp
Components $MgCl_2$–H_2O.		
$MgCl_2.6H_2O$–Stl.–V	10.14°–117.2°	....
$MgCl_2.4H_2O$–Stl.–V	117.2° –138.3°	....
$MgCl_2.6H_2O$–$MgCl_2.4H_2O$–V	31.6° –115.6°	117.2°
Components $CuCl_2$–H_2O.		
$CuCl_2.2H_2O$–Stl.–V	26.60°–64.45°	....
$CuCl_2.2H_2O$–$CuCl_2H_2O$–V	17.90°–64.18°	....
Components $CoCl_2$–H_2O.		
$CoCl_2.6H_2O$–Stl.–V	23.40°–52.25°	....
$CoCl_2.2H_2O$–Stl.–V	52.25°–78.87°	....
$CoCl_2.6H_2O$–$CoCl_2.2H_2O$–V	23.05°–52.25°	52.25°
Components $NiCl_2$–H_2O.		
$NiCl_2.6H_2O$–Stl.–V	19.80°–36.25°	....
$NiCl_2.4H_2O$–Stl.–V	36.25°–54.10°	....
$NiCl_2.6H_2O$–$NiCl_2.4H_2O$–V	19.80°–36.25°	36.25°
$NiCl_2.4H_2O$–$NiCl_2.2H_2O$–V	25.95°–79.06°	....

The existence of $NiCl_2.4H_2O$ hitherto in question has been definitely shown.

The tendency of p,t curves of saturated solutions of hydrated salts to become parallel to the t axis or even retroflex in close proximity to transition points has been noted in the systems studied. This change must result from a large increase in solubility as this point is reached. This relationship has been treated in detail by Roozeboom[2] from the thermodynamic standpoint.

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[1] Lescoeur, *Ann. chim. phys.*, [6] 19, 547 (1890).

[2] *Z. physik. Chem.*, 4, 31 (1889). Roozeboom's work was kindly called to our attention by the editors.