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# THESIS

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

*Subject* \_\_\_\_\_

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

A THESIS

Submitted to the Faculty of The  
Graduate School of the University  
of Minnesota,

In partial fulfillment of the  
requirements for  
The degree of Master of Science.

By

Victor Yngve

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REPORT  
of  
COMMITTEE ON THESIS

THE undersigned, acting as a committee of  
the Graduate School, have read the accompanying  
thesis submitted by Mr. Victor Yngve  
for the degree of Master of Science  
They approve it as a thesis meeting the require-  
ments of the Graduate School of the University of  
Minnesota, and recommend that it be accepted in  
partial fulfillment of the requirements for the  
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### Review of Previous Work.

Many methods have been employed in measuring the vapor pressures of crystalline hydrates and their saturated solutions. All these methods may be classified under two heads, static and dynamic. Of the static methods the following are the most important.

(a) Methods depending upon the depression of the barometric column.<sup>1</sup> This method has been modified in various ways to insure complete removal of residual air.

(b) Tensimetric methods.<sup>2</sup> These methods depend upon the use of a manometer partially filled with mercury or other liquids depending on the sensitiveness and range required. The hydrate is placed in a bulb connected to one side of the manometer and a bulb on the other side contains concentrated sulphuric acid.

1. Debray, Compt. rend., 64, 603, (1867). Wiedemann, Pogg. Ann., Jubelband, 474, (1873). Pareau, Wied. Ann., 1, 55, (1877). Lescoeur, Ann. chim. phys. (6), 16, 378, (1889)

2. Frowein Z. phy. chem. 1, 5, 362 (1887)

All air is removed from the apparatus and the difference in the levels of the liquid in the manometer gives the vapor pressure. Sometimes a liquid whose vapor pressure is known is put into the second bulb and the method then becomes a differential one.

(c) Methods depending upon mist formation.<sup>1</sup> These methods depend upon the fact that the water content of the air in equilibrium with a hydrate or solution can be accurately determined by means of the dew point and hygrometric tables.

(d) The constant weight method of Müller-Erzbach.<sup>2</sup> In this method the hydrate is placed in a closed vessel with sulphuric acid of such a strength that it neither gains nor loses weight. The vapor pressure of the hydrate is then equal to that of the sulphuric acid used.

(e) The method of Foote and Scholes.<sup>3</sup> In this method

1. Helmholtz, Wied. Ann., 27, 508. Lescoeur loc. cit.

2. Ber., 14, 1093, (1881), Z. phy. chem., 2, 113, (1888).

3. Foote and Scholes, J. Am. Chem. Soc., 33, 1309, (1911).

the two hydrates are allowed to stand in contact with alcohol-water mixtures until equilibrium is established. The partial pressure of the water vapor of the alcohol-water mixture gives the vapor pressure of the hydrates.

Among dynamic methods the following are of importance.

(a) Diffusion method of Müller-Erzbach.<sup>1</sup> In this method the rate of evaporation of water from the substance, placed in a tube, was compared with the rate of evaporation of pure water placed in a similar tube. The rates of evaporation were assumed to be proportional to the vapor pressures. This method has not given satisfactory results.

(b) The transpiration method.<sup>2</sup> In this method a known volume of dry air is passed over the hydrate and the vapor pressures are calculated from the amount of aqueous vapor carried away.

1. Müller-Erzbach, Ber., 14, 1093, (1891).

2. Partington, J. Chem. Soc., 1, 99 (1), 466.

Tamman, Wied. Ann., 53, 322, (1888).

Tamman<sup>and</sup> Foote and Scholes (loc. cit.) claim that this method does not give reliable results, while Partington claims to have obtained satisfactory agreement in his measurements. Baxter and Warren<sup>1</sup> obtained good results by passing moist air over hydrates with low vapor pressures.

(c) Linebarger's method.<sup>2</sup> In this method Linebarger calculates the vapor pressures from the change in the boiling points of moist ether when the hydrates are in equilibrium with it.

(d) The boiling point method. In this method, which is usually applied to pure liquids or saturated solutions, the boiling points under reduced pressures are determined.

None of these methods seemed to combine accuracy, simplicity and ease of manipulation as well as the static method of Smith and Menzies.<sup>3</sup>

1. J. Am. Chem. Soc. 33, 340, (1911).
2. Linebarger, Zeit. phy chem., 13, 500 (1894).
3. J. Am. Chem. Soc., 32, 1412, (1910).

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 definite degree of accuracy will be given.

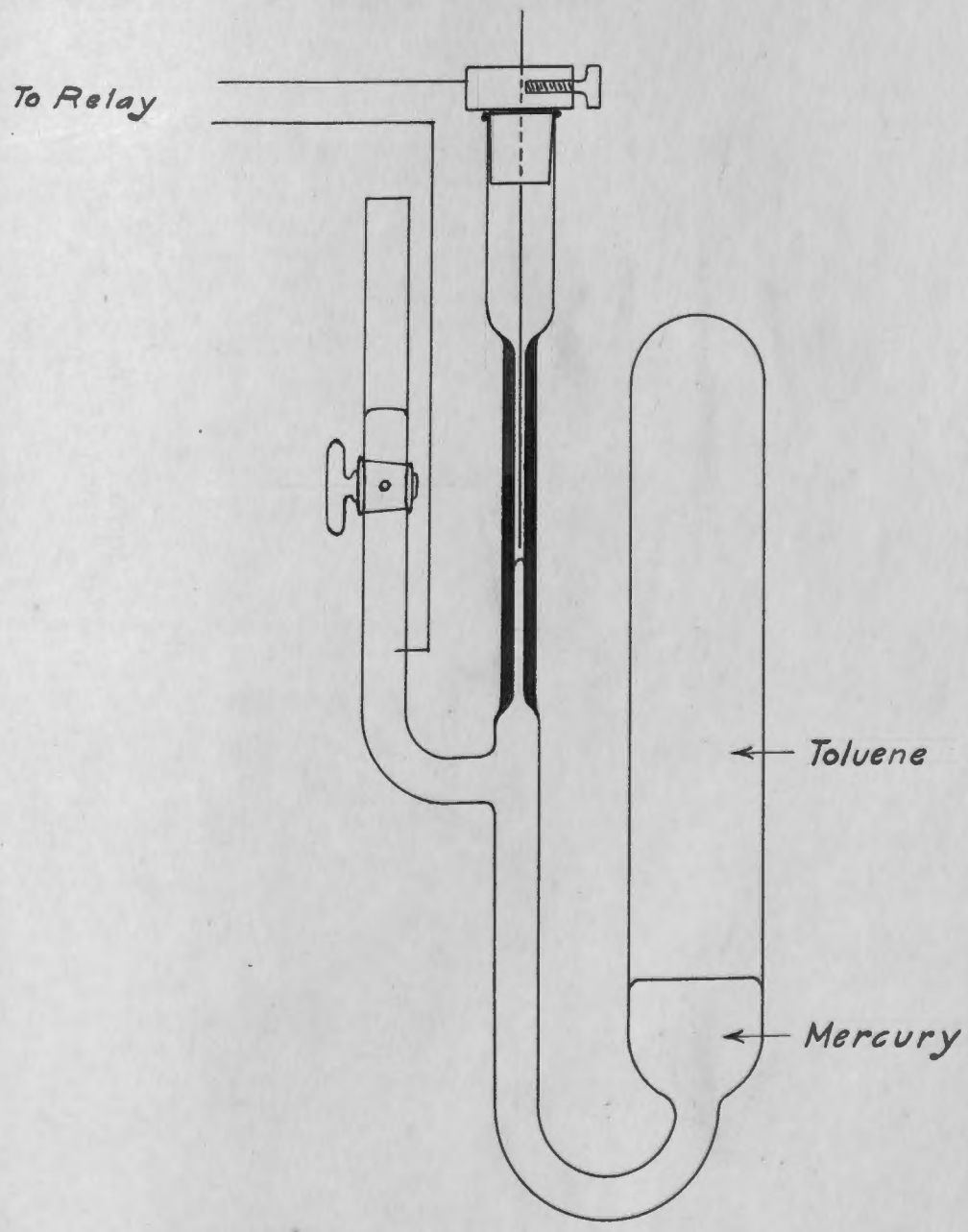


Fig I

### Details of Apparatus.

At the lower temperatures, up to 75 degrees C, the isoteniscope was immersed in a thermostat heated by the method of Derby and Marden.<sup>1</sup> A specially constructed toluene-mercury regulator, shown in Fig. 1, was used in order to easily change the temperature of the thermostat over a range of about 60 degrees. In all cases the regulation was within .05 of a degree.

For the higher temperatures vapor baths of alcohol-water and toluene-xylene mixtures were used. These baths when fitted with a reflux condenser gave excellent results and remained constant within .1 of a degree.

The manometer tube was 1 cm. in inside diameter and was mounted upon a support of thoroughly seasoned wood which bore a paper scale, covered with Bake<sup>lite</sup> varnish. The scale was carefully calibrated by means of an accurate cathetometer and during its use showed no variations due to atmospheric changes. Readings were made by means of a cathetometer to avoid parallax and to give a scale magnification.

1. J. Am. Chem. Soc., 35, 1767, (1913).

The readings are to estimated tenths of a millimeter.

The manometer mercury was purified by dropping it through dilute nitric acid and distilling in vacuo.

### Scale Calibration.

The scale was calibrated in the laboratory of the Dept. of Physics of the University of Minn., by means of an accurate cathetometer, for variation in graduation. Readings were made every five centimeters. Two concordant sets were taken. The manometer was then permanently placed in position and adjusted to a truly vertical position. The length of the region of the scale which was used was now determined in situ by means of a cathetometer. Six closely agreeing readings were averaged. From these observations a scale correction curve was constructed.

### Corrections.

The following corrections were made on all readings. The scale corrections were read off from the calibration curve. The mercury column was then corrected to zero degrees by means of the table in Ostwald-Luther (3), 153. The barometer was read to .1 mm. and was corrected for temperature. The barometer used was compared with a standard instrument and the readings were found to be correct.

The thermometer used below 100 degrees was compared with one recently standardized by the Bureau of Standards and had no scale correction.

The thermometer used above 100 degrees was corrected at 100 degrees by taking the boiling point of water in the usual way. It was then compared with a thermometer certified to .2 of a degree by the Reichsanstalt. This thermometer had no scale correction from 100 degrees to 200 degrees and the scale reading was therefore assumed to be uniform. In all cases where it was appreciable a correction was made for exposed thread.

Preliminary Determination of the  
Vapor Pressures of Water.

In order to test the accuracy of the method, trial determinations of the vapor pressures of water at several temperatures were made. Readings were taken at four temperatures and are given below together with the values by Scheel and Heuse taken from the tables of Landolt-Börnstein (4) 360.

Vapor Pressures of Water.

No. of obs.	Temp.	V. P. D. & Y.	V. P. S. & H.
2	25.09	24.00	25.89
2	34.15	40.30	40.25
2	43.41	66.40	66.22
3	54.64	115.80	116.08

### Purification of Materials.

The magnesium chloride used was Kahlbaum's zur analysis. It was recrystallized once from distilled water, washed and dried in a centrifuge fitted with a porcelain basket.

The mean of six determinations of the vapor pressure of the saturated solution of the uncrystallized salt at 23.15 degrees was 6.9 mm, while the value at the same temperature for the saturated solution of the recrystallized salt taken from the curve was 6.8 mm. The values are in good agreement.

The cobalt chloride used was Merck's "Highest Purity". It was recrystallized in the manner referred to above. Careful testing with dimethyl glyoxime failed to reveal any trace of nickel.

The nickel chloride used was Merck's "Highest Purity", and was not recrystallized.

The Vapor Pressure Relationships of  
Magnesium Chloride.

The following  $\text{MgCl}_2\text{--H}_2\text{O}$  systems were studied.

1. Saturated solutions of  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ .
2.  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  --  $\text{MgCl}_2 \cdot 4 \text{H}_2\text{O}$ .
3. Saturated solutions of  $\text{MgCl}_2 \cdot 4 \text{H}_2\text{O}$ .

1. Measurements of the vapor pressures of saturated solutions of  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  were made from 10.14 degrees to 117.2 degrees. In all these measurements, as well as those which follow, care was taken to bubble vapor out of the bulb in order to insure complete removal of air and, in the case of solutions, to insure saturation. The observations, which are in mm. of mercury, follow.

Table 1.

Number of observations	Temperature	Vapor Pressure
5	10.14	3.4
3	18.05	5.2
3	25.53	7.7
4	31.65	11.2
2	41.92	18.5
3	44.46	21.4
5	50.96	29.0
3	55.18	35.4
5	64.99	54.1
3	77.50	86.5
2	99.23	162.7
7	99.43	163.6
4	109.9	195.3
1	110.2	198.6
1	110.9	197.6
1	112.9	198.3
1	113.1	197.4
1	113.6	198.0
1	114.9	193.7
1	116.0	191.5
2	116.8	184.0
1	117.2	169.1

These values were plotted and a smooth curve drawn through them. Pressure values could then be read at any temperature. In the following table in column I the temperatures are given. Column II contains the pressure values taken from the curve. In column III are given the pressures calculated thermodynamically, from the one measurement at 25 degrees, by van't Hoff<sup>1</sup> and Speranski<sup>2</sup>. The values below 25 degrees are by the former, those above 25 degrees by the latter. It will be seen that both sets of values are divergent. In column IV is the data given by Lescoeur<sup>3</sup>.

1. van't Hoff et Al, Z. S. phys. Chem., 45, 288, 1903.
2. Speranski, Z. S. phys. Chem., 70, 519, 1910.
3. Lescoeur, Ann. chim. phy. (7), 2, 85.

Table II.

I.	II.	III.	IV.
*0.0	2.0	1.34	
*5.0	2.4	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		
35.0	13.4		
37.5	15.3		18.0
40.0	17.3	18.98	
45.0	21.8		
50.0	27.6		
55.0	35.2		
60.0	43.8	54.11	
64.5	53.0		53.0
65.0	54.1		
70.0	65.5		
75.0	79.0		
77.5	86.4		88.0
80.0	93.4	134.57	
85.0	109.		
90.0	127.		
95.0	146		
100.0	166.		159.0

\* extrapolated.

2. The vapor pressures of the system  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  --  $\text{MgCl}_2 \cdot 4 \text{H}_2\text{O}$  were studied between 31.60 degrees and 74.27 degrees. The observations follow.

Table III.

Number of observations	Temperature	Vapor Pressure
1	31.60	1.6
1	42.10	2.7
1	59.31	7.8
1	64.10	11.3
1	69.38	14.6
1	74.27	21.3

The values taken from the curve for every 5 degrees from 25 degrees to 75 degrees are given.

Table IV.

Temperature	Vapor Pressure
*25	.9
*30	1.5
35	2.0
40	2.5
45	3.2
50	4.4
55	6.3
60	8.7
65	11.6
70	15.3
*75	22.7

\* extrapolated.

3. Measurements of the vapor pressure of the saturated solutions of  $\text{MgCl}_2 \cdot 4 \text{H}_2\text{O}$  were made between 117.2 degrees and 138.3 degrees. The observations follow.

Table V.

Number of observations	Temperature	Vapor Pressure.
1	117.2	169.1
1	120.9	194.4
1	121.2	195.6
3	138.3	307.1

The smoothed values for every 5 degrees from 120 degrees to 140 degrees are given.

Table VI.

Temperature	Vapor Pressure
120	182
125	206
130	237
135	277
*140	321

\* extrapolated.

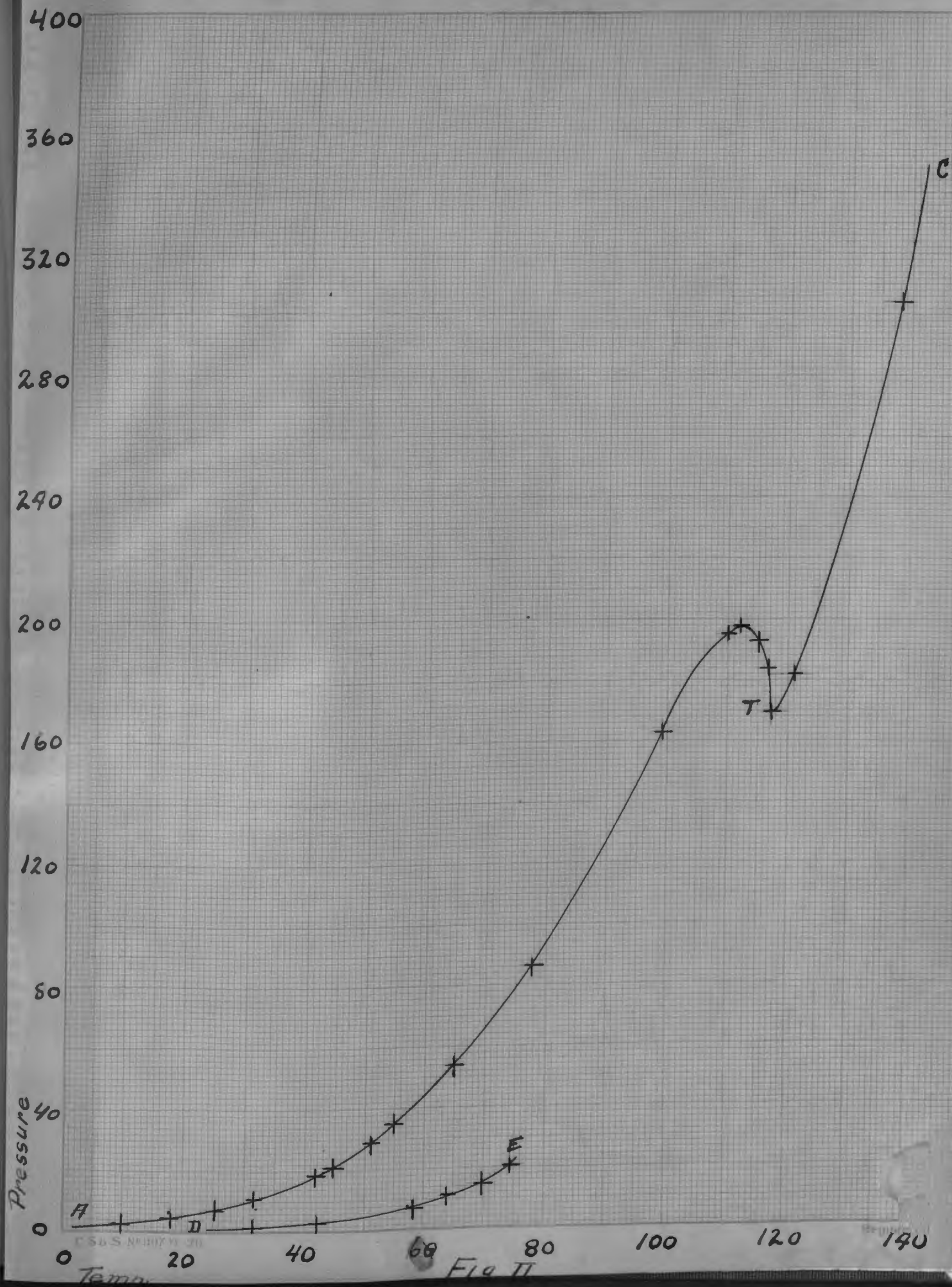


Fig. II

Discussion of the Vapor Pressure Curves of  
the system  $\text{MgCl}_2\text{--H}_2\text{O}$ .

The vapor pressure curves of the system  $\text{MgCl}_2\text{--H}_2\text{O}$  are shown in Fig. II. 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 point. This is due to the very large increase in the solubility of the hydrate near the transition temperature. T. C. is the vapor pressure curve of the saturated solutions of the tetra-hydrate. D E is the vapor pressure curve of the system  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O} \text{ -- } \text{MgCl}_2 \cdot 4 \text{H}_2\text{O}$ . It should intersect the curve A T at T.

The Vapor Pressure Relationships of  
Cobalt Chloride.

The following  $\text{CoCl}_2$ --  $\text{H}_2\text{O}$  systems were studied.

1. Saturated solutions of  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ .
2.  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$  --  $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ .
3. Saturated solutions of  $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ .

1. Vapor pressure measurements on the saturated solutions of  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$  were made between 23.40 degrees and 52.25 degrees. The observations follow.

Table VII

Number of observations	Temperature	Vapor Pressure
1	23.40	13.9
1	24.19	14.7
1	28.68	18.4
1	32.65	22.4
1	35.98	26.6
1	39.47	30.5
2	39.87	31.1
1	43.92	36.8
1	46.84	41.3
1	49.23	44.8
1	51.15	47.2
1	51.58	48.0
1	52.25	48.6

The smoothed values read from the curve at 5 degree intervals of temperature are given below

Table VIII

Temperature	Vapor Pressure
*20.0	11.8
25.0	15.3
30.0	19.7
35.0	25.1
40.0	31.3
45.0	38.7
50.0	45.9

\* extr<sup>a</sup>polated.

2. The vapor pressure measurements on the system  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O} \text{ -- } \text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$  were made between 23.05 degrees and 52.25 degrees. The observations follow.

Table IX

Number of observations	Temperature	Vapor Pressure
1	23.05	6.4
1	24.19	6.8
2	28.0	9.0
1	28.68	9.6
1	31.9	12.1
1	32.69	12.4
1	35.98	16.5
1	39.47	20.5
3	39.87	21.0
1	39.96	21.5
1	43.92	27.8
1	46.84	33.3
1	48.60	38.4
1	49.23	39.7
1	50.02	42.0
1	51.15	46.0
1	51.58	46.6
1	52.13	47.7
1	52.25	48.6

The smoothed values read from the curve at 5 degree intervals of temperature are also given.

Temperature	Vapor Pressure	Table X
*20.0	5.4	
25.0	7.2	
30.0	10.2	
35.0	14.9	
40.0	21.2	
45.0	29.6	
50.0	49.9	

\* extrapolated.

3. The measurements on the vapor pressures of the saturated solutions of  $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$  were made between 52.25 degrees and 78.87 degrees. The observations follow.

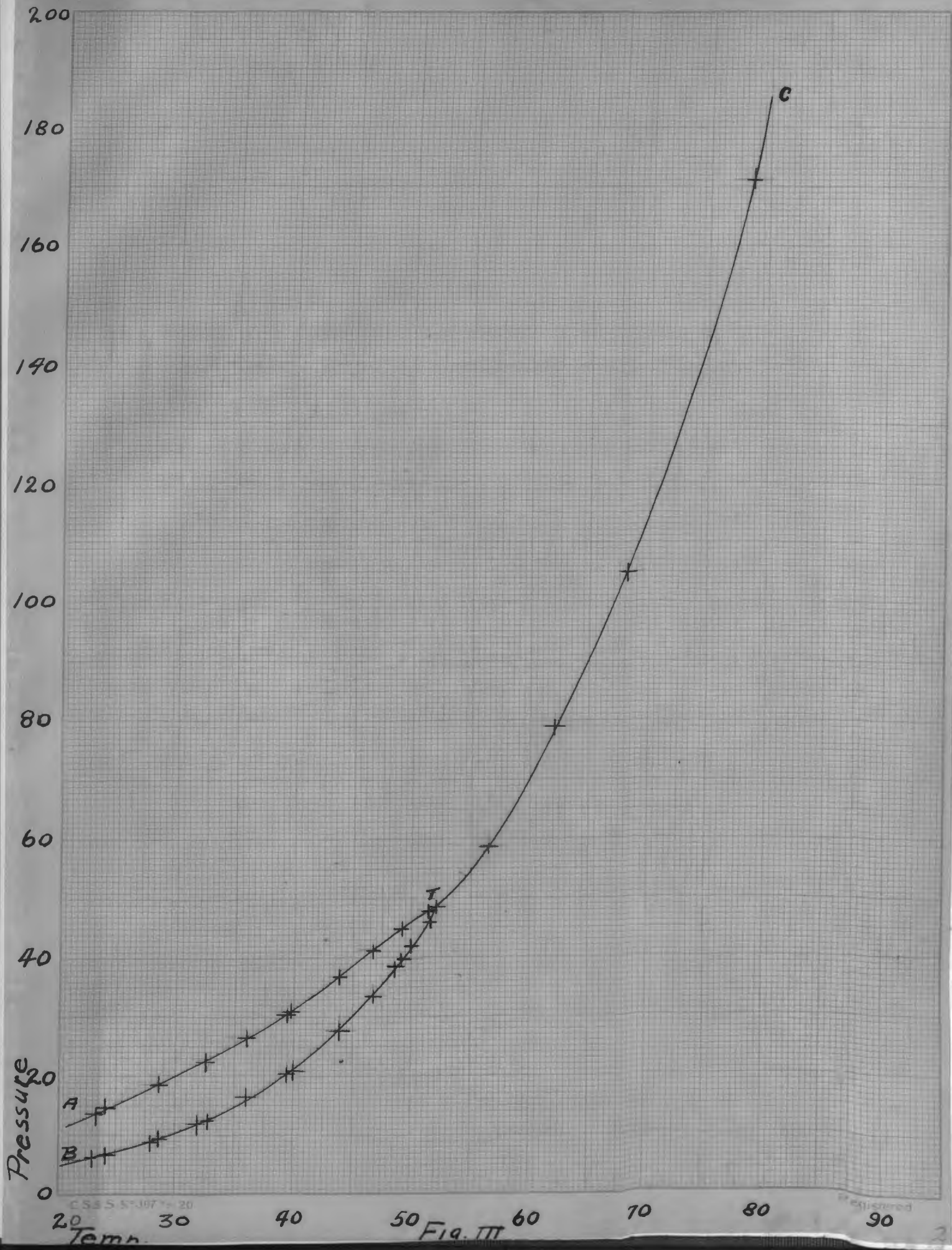
Table XI		
Number of observations	Temperature	Vapor Pressure
2	52.25	48.6
1	56.44	58.7
1	62.12	79.0
1	68.26	105.1
1	78.87	170.9

The smoothed values read from the curve at intervals of 5 degrees of temperature are also given.

Table *XII*

Temperature	Vapor Pressure
55	54.7
60	60.2
65	91.0
70	114.2
75	144.8
*80	178.5

\* extrapolated.



*Discussion of the*  
The Vapor Pressure Relationships of  
Cobalt Chloride.

The vapor pressure relationships of the hydrates and saturated solutions of cobalt chloride are shown in Fig. III. The curve A T is the vapor pressure curve of the solutions in equilibrium with  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ . There is a slight tendency for the curve to flatten out as it nears the transition point T. This is due to the increased solubility of the hydrate. The curve B T is the vapor pressure curve of the system  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O} \text{ -- } \text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ . It intersects the curve A T at T. The curve T C is the vapor pressure curve of the saturated solutions of  $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ .

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 temperatures.

## Vapor Pressure Relationships of Nickel Chloride.

Vapor pressure measurements were made on the following systems of  $\text{NiCl}_2\text{--H}_2\text{O}$ .

1. Saturated solutions of  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ .
2.  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$  ---  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$ .
3. Saturated solutions of  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$ .
4.  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$  ---  $\text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$ .

1. The measurements on saturated solutions of  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$  were made between 19.8 degrees and 45.22 degrees. The measurements above 36.25 degrees are in the unstable region above the transition temperature.

The observations follow:-

Table XVII

Number of observations	Temperature	Vapor Pressure.
6	19.8	9.6
3	24.1	12.0
4	31.0	17.5
1	35.05	21.5
2	36.25	22.5
1	39.80	26.6
2	45.22	33.3

The smoothed values as read from the curve at 5 degree intervals of temperature follow.

Table XIV

Temperature    Vapor Pressure.

*15.0	8.2
20.0	9.7
25.0	12.6
30.0	16.5
35.0	21.5
40.0	26.8
45.0	33.1
*50.0	39.7

\* extrapolated.

2. Measurements were made on the dissociation tensions of the system  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O} \text{ -- } \text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$  between 19.8 degrees and 36.25 degrees. The values are given below.

Table XV

Number of observations    Temperature    Vapor Pressure.

4	19.8	7.3
1	20.6	7.8
2	24.1	10.1
1	24.6	10.4
4	30.3	15.2
1	30.7	15.2
4	31.0	16.1
2	35.05	20.9
2	36.25	22.5

The smoothed values as read from the curve at 5 degree intervals of temperature are also given.

Table ~~XVI~~

Temperature Vapor Pressure.

*15.0	6.5
20.0	7.6
25.0	10.5
30.0	14.9
35.0	20.9

\* extrapolated.

The chlorine content of the hydrate in the bulb was determined by titration with N/10  $\text{AgNO}_3$  using  $\text{K}_2\text{CrO}_4$  as an indicator. The degree of hydration of the salt was then calculated. The value 5.74 was found

3. The measurements on saturated solutions of  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$  were made between 36.25 degrees and 54.1 degrees. Attempts were made to super-cool the solution but all readings made below the transition temperature coincided with those made on the saturated  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$  solutions. The values follow.

Table ~~XVII~~

Number of observations	Temperature	Vapor Pressure
2	36.25	22.5
1	40.57	28.9
3	45.22	36.7
1	48.34	42.6
1	54.1	56.4

The smoothed values as read from the curve at 5 degree intervals of temperature are also given.

Table XVIII

Temperature	Vapor Pressure
40	28.1
45	36.3
50	46.5
55	58.9

4. The system  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O} \xrightarrow{\text{NiCl}_2} 2 \text{H}_2\text{O}$  was studied from 25.95 degrees to 79.06 degrees. The values of the dissociation tensions follow.

Table XIX

Number of observations	Temperature	Vapor Pressure
1	25.95	6.0
1	26.00	6.1
1	32.31	8.9
1	38.20	14.2
1	47.69	26.4
1	54.50	40.4
1	54.63	40.7
3	59.63	58.3
2	66.34	84.1
1	79.06	108.1

The smoothed values as read from the curve at 5 degree intervals of temperature are also given.

Table XX

Temperature	Vapor Pressure
*15.0	4.9
20.0	5.2
25.0	5.9
30.0	7.6
35.0	11.0
40.0	16.3
45.0	22.7
50.0	29.8
55.0	39.2
60.0	58.3
65.0	78.3

\* extrapolated.

The degree of hydration of the nickel chloride in the bulb was determined as before. It was found to contain 3.78 molecules of water.

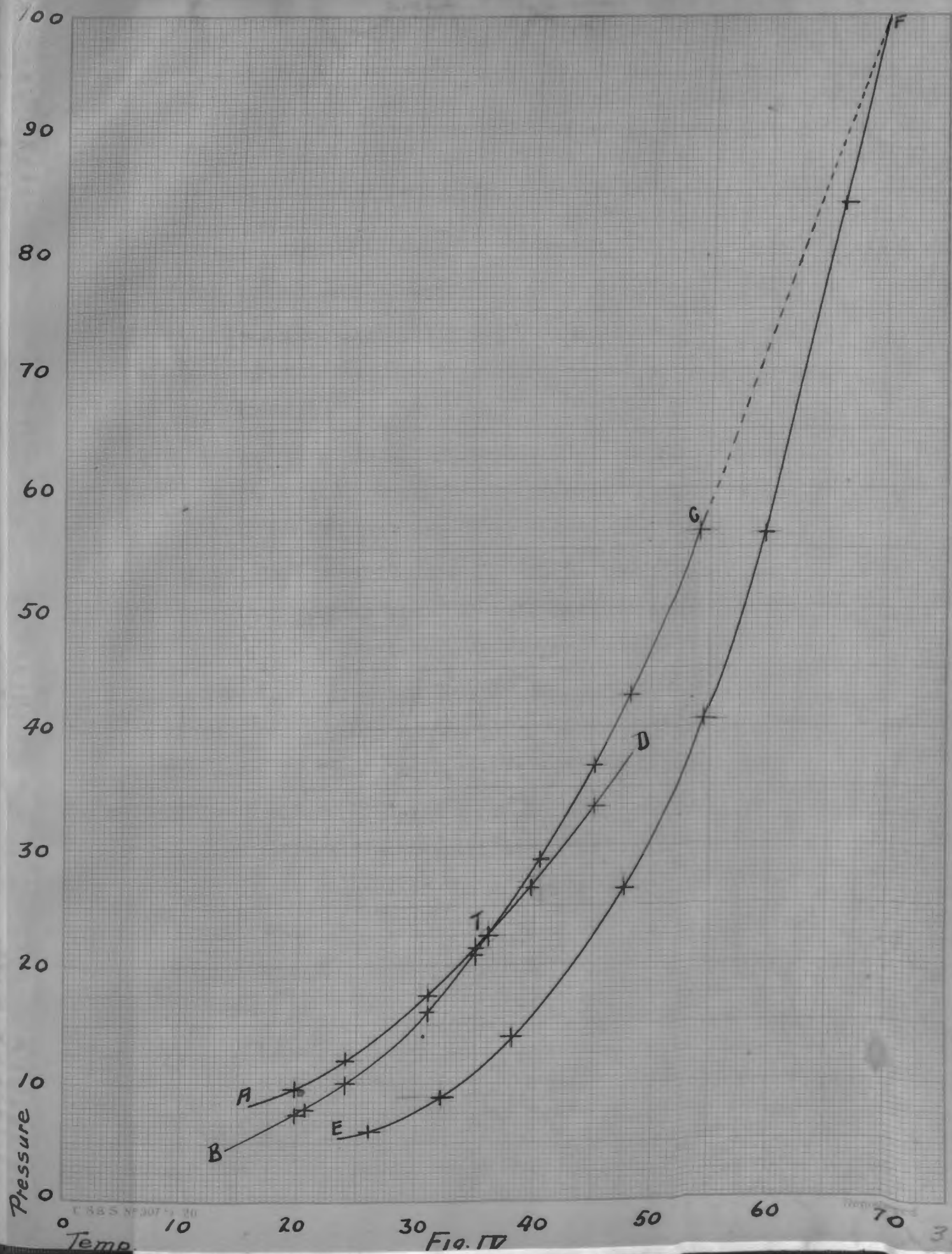


FIG. IV

Discussion of the Vapor Pressure Relationships  
of Nickel Chloride.

The vapor pressure relationships of the hydrates and solutions of nickel chloride are shown in Fig. 5. The curve A T D is the vapor pressure curve of the solution in equilibrium with  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ . It will be noticed that there is a tendency for the curve to flatten out as it nears the transition temperature T. This is due to the increased solubility of the hydrate. The curve extends to D into the unstable region above the transition temperature. It will be noted here that the vapor pressure of the unstable system is lower than that of the stable system. This is due, as Findley<sup>1</sup> has shown, to the greater solubility of the unstable hydrate. The curve B. T is the vapor pressure curve of the system  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O} \text{ -- } \text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$ , It cuts the curve A T D at T, the transition temperature. The curve T C is the vapor pressure curve of the solution in equilibrium with  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$ .

1. Findley, The Phase Rule, (3), 144.

It is practically a continuation of the curve B T.

The curve E F is the vapor pressure curve of the system  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O} \text{ -- } \text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$ . This should cut the curve T C approximately at 70 degrees<sup>1</sup>, the transition temperature of the tetra-hydrate into the di-hydrate. The curves when extrapolated, as shown by the dotted lines, intersect at about this point. The transition point of  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$  into  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$  which lies at 36.25 degrees, has never been noted before. Lescoeur<sup>2</sup> found no evidence of the tetra-hydrate. The measurements given here seem to point clearly to its existence.

1. Etard, Ann. chim. phy. (7) 2, 545; (1894).

2. Lescoeur, Ann. chim. Phys. (6), 19, 547; (1890).

### Summary.

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

Measurements have been made of the vapor pressures of the saturated solutions of  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  from 10.14 degrees to 117.2 degrees. The vapor pressure measurements of the saturated solutions of  $\text{MgCl}_2 \cdot 4 \text{H}_2\text{O}$  have been made from 117.2 degrees to 138.3 degrees. The dissociation tensions of the system  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  --  $\text{MgCl}_2 \cdot 4 \text{H}_2\text{O}$  have been determined from 31.60 degrees to 74.27 degrees.

The vapor pressures of the saturated solutions of  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$  have been determined from 23.40 degrees to 52.25 degrees. The vapor pressures of the saturated

solution of  $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$  have been measured from 52.25 degrees to 78.87 degrees. The dissociation tensions of the system  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O} \text{ -- } \text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$  have been determined from 23.05 degrees to 52.25 degrees. No evidence was found of the existence of the tetrahydrate of cobalt chloride. The value 52.25 degrees was found for the transition of the hexahydrate into the dihydrate.

The vapor pressures of the saturated solutions of  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$  have been determined from 19.8 degrees to 36.25 degrees. The vapor pressures of saturated solutions of  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$  were measured between 36.25 degrees and 54.1 degrees. The dissociation tensions of the system  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O} \text{ -- } \text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$  have been determined between 19.8 degrees and 36.25 degrees. Measurements have been made of the dissociation tensions of the system  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O} \text{ -- } \text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$  between 25.95 degrees and 79.06 degrees. The existence of the tetrahydrate of nickel chloride, hitherto in question, has been verified. The transition of the hexahydrate

of nickel into the tetrahydrate has been noted for the first time. A value of 36.25 degrees has been found for the transition temperature.

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