

Percentage saturation =

$$\frac{100\gamma'}{4\gamma'} \left( 4 - \left( \frac{G'_1}{G'_1 + [\text{O}_2]} + \frac{G'_2}{G'_2 + [\text{O}_2]} + \frac{G'_3}{G'_3 + [\text{O}_2]} + \frac{G'_4}{G'_4 + [\text{O}_2]} \right) \right) \quad (9a)$$

and the new constants are related to the old constants by the four equations

$$\frac{1}{K'_4} = \Sigma G'_i = G'_1 + G'_2 + G'_3 + G'_4 \quad (9b)$$

$$\frac{1}{K'_4 K'_3} = \Sigma G'_i G'_j = G'_1 G'_2 + G'_1 G'_3 + G'_1 G'_4 + G'_2 G'_3 + G'_2 G'_4 + G'_3 G'_4$$

$$\frac{1}{K'_4 K'_3 K'_2} = \Sigma G'_1 G'_2 G'_3 = G'_1 G'_2 G'_3 + G'_1 G'_2 G'_4 + G'_2 G'_3 G'_4 + G'_1 G'_3 G'_4$$

$$\frac{1}{K'_4 K'_3 K'_2 K'_1} = \Sigma G'_1 G'_2 G'_3 G'_4 = G'_1 G'_2 G'_3 G'_4$$

Expressing results in terms of classical constants necessitates the use of Equation 5, which is rather complicated. No substantial advantage is gained in doing this. It therefore appears advisable to express results directly in terms of titration constants and to abolish the classical constants altogether.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## THE ETHERATES OF MAGNESIUM BROMIDE

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RECEIVED APRIL 28, 1930

PUBLISHED SEPTEMBER 5, 1930

The fact that the halides of magnesium are capable of uniting with ether to form compounds similar to hydrates has been known since the beginning of this century. Menschutkin<sup>2</sup> was the first to study them and gave them the name "etherates." He investigated their solubility in ether at various temperatures and found that as the solution became more concentrated, a heavy, oily, immiscible layer separated. He discovered that this heavy layer could be greatly supercooled and that when it did crystallize the magnesium halide was obtained in the form of the di-etherate. Later, Meisenheimer<sup>3</sup> and his co-workers discussed some of the properties of this oily liquid and of the crystalline magnesium halide etherates.

From a review of the literature, it is apparent that very little is known concerning the formulas of these etherates. Some claim that they contain one molecule of ether;<sup>4</sup> others, that they contain two molecules,<sup>5</sup> while some

<sup>1</sup> University Fellow, 1927-1928.

<sup>2</sup> Menschutkin, *J. Russ. Phys.-Chem. Soc.*, **35**, 610 (1903).

<sup>3</sup> Jakob Meisenheimer and Johannes Casper, *Ber.*, **54B**, 1655 (1921); Jakob Meisenheimer, Erich Piper and Hans Lange, *Z. anorg. allgem. Chem.*, **147**, 331 (1925).

<sup>4</sup> Tissier and Grignard, *Compt. rend.*, **132**, 835 (1901); Grignard, *ibid.*, **136**, 1262 (1903).

<sup>5</sup> (a) N. Zelinsky, *Chem. Zentr.*, II, 277 (1903); (b) W. Tschelinzeff, *Ber.*, **39**, 773 (1906).

even claim that they contain three and four molecules<sup>5a,b</sup> of ether per molecule of magnesium halide. On the other hand, Ahrens and Stapler<sup>6</sup> claim that they obtained non-etherated magnesium halides precipitated from ether solution. It is also quite evident that little is known of the properties of these compounds.

Because of these conflicting statements, it was decided to make a study of the above-mentioned compounds using magnesium bromide as a typical magnesium halide.

### Experimental Work

**Preparation of Crystals.**—Pure magnesium turnings were put into an Erlenmeyer flask and 100–200 cc. of dry ether added. All reasonable precautions were taken to eliminate air and moisture. Liquid bromine was then added, a few drops at a time, allowing the solution to clear considerably before the next addition was made. It was frequently advisable to cool the flask to keep the heat of reaction from boiling away the ether. Above a certain concentration (about 3%  $MgBr_2$  at room temperature) two layers appeared, the upper one clear, colorless and of about the same density as ether, the bottom one a clear, heavy, oily liquid which usually ranged from very faint yellow to a reddish-brown. Only the faintly yellow layers crystallized but they gave beautiful crystals that seemed very pure. The crystals were prepared in two ways: (I) by separating the heavy bottom layer without contact with air or moisture and with a gentle suction removing part of the ether, leaving a supersaturated solution. Large crystals of magnesium bromide etherate were precipitated from the two layer system after standing for about one month. (II) By cooling the filtered two phase system below  $10^\circ$ , the heavy layer solidified forming white crystals. The clear liquid was decanted and the crystals drained. These crystals were much smaller than those prepared from the supersaturated solution but were easier to make and gave larger yields.

TABLE I  
ANALYSIS OF CRYSTALS

Analysis	Method of prepn.	Method of analysis	Mg	Br	$(C_2H_5)_2O$
1	I	Loss of weight on heating in vacuum at room temp.	1	2	1.10
2	I	Same as No. 1	1	2	2.00
3	I	Loss of weight by vacuum	1	2	1.04
4	II	Same as No. 1	1	2	2.15
5	II	Same as No. 1	1	2	2.13
6	II	Same as No. 1	1	2	2.30
7	I	Loss of weight in vacuum	1	2	0.97
8	I	Same as No. 1	1	2	1.97
9	II	$Mg_2P_2O_7$ for Mg; AgBr for Br	1	1.95	2.68
10	II	AgBr for bromine	1	1.95	2.85
11	II	Same as No. 10	1	2	3.00
12	II	Same as No. 10	1	2	3.10
13	II	Same as No. 10	1	2	3.00

In analysis No. 1 the crystals were made at room temperature, dried in an atmosphere of ether, placed in a weighed test-tube fitted with a one-holed stopper carrying a

<sup>6</sup> Felix B. Ahrens and Adolf Stapler, *Ber.*, **38**, 3264 (1905).

short piece of glass tubing and weighed. The tube was then evacuated under 50-mm. pressure for twelve hours. It was then reweighed and the loss in ether recorded.

In analysis No. 2 the tube from analysis No. 1 was heated while being evacuated to constant weight. By comparing the last weight with the original weight, it was possible to determine the total weight of ether lost. It is seen that approximately one molecule of ether was lost quite easily by the first evacuation, while the total loss was two molecules, indicating that the crystals investigated contained two molecules of ether originally.

In analysis No. 3 the tube was left for forty hours at room temperature under a pressure of 50 mm. Since these crystals had been exposed for quite a time no effort was made to determine the total amount of ether lost but simply the amount left after the first evacuation.

In analyses Nos. 4, 5 and 6 the crystals were prepared by cooling the heavy layer and then drying the resulting crystals in a stream of carbon dioxide. Since there was no time limit to the passing of carbon dioxide over the crystals and since the tri-etherate has a very high vapor pressure, it is not surprising that these results vary and that they show values too high for a di-etherate and too low for a tri-etherate.

In analyses Nos. 7 and 8 large crystals were formed slowly at room temperature and broken up and the central portion was taken for analysis; hence these values should be quite accurate.

In analyses Nos. 9 and 10 the crystals were made at 0° and transferred to a weighed flask. The weighed crystals were dissolved in water, diluted and an aliquot part taken and analyzed. The results are low but indicate an etherate higher than the di-etherate.

In analyses Nos. 11, 12 and 13 the crystals were prepared at 0° but in a weighed flask. They were drained for one-half hour below 10°, weighed and analyzed. There was little chance for loss of ether due to exposure in these analyses.

From the results it seems clear that there are three definite etherates of magnesium bromide: (1) the tri-etherate which is readily decomposed, (2) the di-etherate which is more common, and (3) the mono-etherate. If the etherate is made at a temperature of about 0° and dried at this temperature and carefully analyzed, we obtain the tri-etherate. If the crystals are at all exposed, owing to their high vapor pressure we have a mixture of the di- and tri-etherates. If the crystals are made at room temperature we get the di-etherate, and if a tube containing the di-etherate is evacuated at room temperature under a pressure of 50 mm., we obtain the mono-etherate.

**Analysis of Liquid Layers.**—Menschutkin<sup>2</sup> made the statement that the concentration of the di-etherate in the two liquid layers varied with the temperature; therefore, it was decided to verify this. The two-layer systems were made in the usual manner and filtered through glass wool. The mixtures were then placed in flasks surrounded by water at a known temperature. Some of the bottom layer was then drawn into a dry pipet, allowed to run into a tared tube and weighed. The ether was then driven off by suction and heating until the weight of the residue was constant. Considering the residue as anhydrous magnesium bromide and the loss in weight as due to the ether, it was possible to calculate the ratio of ether in the bottom layer to the magnesium bromide.

TABLE II

ANALYSIS OF HEAVY LAYER				
Analysis	Temp., °C.	Method of analysis	MgBr <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
1	11.2	Vacuum + heat	1	3.32
2	12	Vacuum + heat	1	3.48
3	14	Vacuum + heat	1	3.58
4	17	Vacuum + heat	1	3.40
5	17.5	Bromine as AgBr	1	3.46
6	19	Vacuum + heat	1	3.41
7	20	Vacuum + heat	1	3.59
8	20	Vacuum + heat	1	3.74
9	22.5	Vacuum + heat	1	3.51
10	22.5	Vacuum + heat	1	3.57
11	24	Mg by Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ; Br by AgBr	1	3.48
12	24	Vacuum + heat	1	3.45
Average			1	3.50

Table II shows but slight change in concentration of the heavy oily layer with temperature. The irregularity of these results is due, no doubt, to the very slowly attained equilibria here involved. There is, however, a definite trend showing more ether in the solution at the higher temperature.

Table III shows a definite increase in magnesium bromide with temperature. The clear upper layer at room temperature always became cloudy and precipitated the heavy oily layer on cooling to a lower temperature. The amount of magnesium bromide in the upper layer at room temperature averaged about 3-3.5% and in the lower layer about 41%.

As to the composition of the top layer, there was very little work done. However, a few determinations were made by withdrawing five cubic centimeters with a pipet, putting it into a weighed crucible and treating with concentrated sulfuric acid. The ether was then burned off, the excess acid evaporated and the residue weighed as magnesium sulfate. From this, it was possible to determine the amount of magnesium bromide per 5 cc. of solution.

TABLE III

ANALYSIS OF TOP LAYER			
Analysis	Temp., °C.	Method of analysis	Grams of MgBr <sub>2</sub> /5 cc.
1	5	Mg as MgSO <sub>4</sub>	0.0979
2	12	Same as No. 1	.1002
3	14	Same as No. 1	.1002
4	17	Same as No. 1	.1009
5	19.5	Same as No. 1	.1124
6	24	Same as No. 1	.1239
7	28	Same as No. 1	.1223
8	31	Same as No. 1	.1315

**General Properties.**—Some of the properties of the etherates mentioned in the literature were verified. The fact that the etherates were rather

unstable and decomposed on contact with air and moisture, was brought out quite clearly by the analyses.

**Action on Water.**—The etherates are decomposed by water and ether is given off. Some experiments in which the volume of ether liberated from the di-etherate was measured indicated that one molecule of ether was displaced very readily but that the mono-etherate is more stable and requires a longer time for complete decomposition. This coincides with the work of Meisenheimer and Casper.<sup>3</sup>

**Action of Absolute Alcohol.**—When absolute alcohol was added to the crystals, ether was evolved as with water but not so vigorously.

**Action of Dry Ether.**—When ether was added to the di-etherate the crystals softened. When ether was added to the mono-etherate or the non-etherated magnesium bromide, there was a reaction and heat was given off, as was first noticed by Tschelinzeff.<sup>5b</sup>

**Transition Points.**—After it had been definitely shown that there are three distinct etherates, the next logical step was to determine the temperatures below which the various etherates are stable, that is, the points at which partial liquefaction takes place owing to the fact that ether is split off and the non-etherated or a lower etherated compound formed. Our work seemed to indicate that such points existed. The thermometric method failed; thus crystals prepared at 0° were heated slowly from 0 to 15° and the change in temperature plotted against time, but the curve showed no break. There did seem to be a change in the form of the crystals. The dilatometric method was also tried with no better result. This behavior can be explained on the ground that the equilibrium is very sluggishly attained and that the heat of formation of the etherate is rather low.

In spite of these negative results, experimental evidence strongly indicated a change in form of the crystals at about 13°. Crystals were prepared by cooling and then without decanting the excess liquid the crystals were maintained at some definite temperature for hours. By this method it was discovered that the crystals appeared to melt quite a bit below room temperature. Finally the value of 12.5° was reached, at which the crystals appeared stable. However, after about eight hours at this temperature (within 0.2°) the sharp outline of the crystals disappeared and a slow but nevertheless certain transformation of the crystals could be seen to be taking place.

Experiments were then conducted to approach the point from the other side. The two-layer mixtures were prepared and cooled to a definite constant temperature. They were then seeded with a crystal of the etherates. The temperature was raised each time until finally at 12.4° solidification took place very slowly. At 12.6° the heavy layer did not solidify when seeded. However, if this material stood for a month, crystals would grow in this layer as previously stated, but we considered them to be the di-etherate and not the tri-etherate.

**Vapor Pressure Curves of Crystals.**—If these etherates of magnesium bromide are definite compounds and have definite transition points, it should be possible to distinguish these points by means of their vapor pressures. It was decided that the static method of determination was best suited for this type of compound.

**Apparatus.**—Several types of apparatus were tried but due to the extreme ease with which the etherate crystals decomposed, it was found

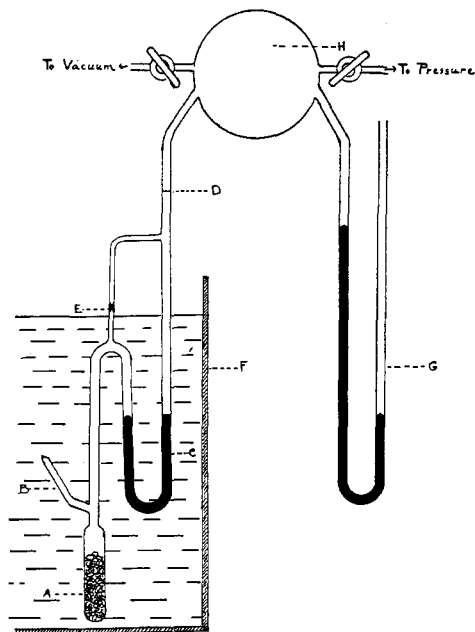


Fig. 1.—Apparatus for determining vapor pressure of crystals.

necessary to devise an apparatus in which the volume above the crystals was as small as possible. The apparatus in Fig. 1 was finally adopted as the most satisfactory. The entire apparatus with the exception of the bulb A was made from 8-mm. pyrex tubing. The bulb A and U-tube C were made separately for each determination and sealed to the permanent part at D. The bulb H was connected to the apparatus to give a larger volume and hence greater ease in regulating the height of the mercury in C. A commercial thermostat of standard make was used for all the determinations with this apparatus. The tenth of a degree thermometer used was compared to standard thermometers at frequent intervals.

**Loading and Manipulation of Tensimeter.**—The apparatus was washed with alcohol, then with ether, finally connected to the vacuum pump and heated with a blowtorch. The bulb A was then surrounded with ice and the crystals introduced through the side arm B, which was then sealed off. Mercury was placed in the U-tube C and the piece sealed to the rest of the apparatus at D. There was no water in the thermostat, the bulb A being surrounded with carbon dioxide snow. The apparatus was then connected to a vacuum oil pump which gave a vacuum of less than 1 mm. and the entire apparatus evacuated until the mercury ceased to rise in the manometer G. At the same time that the pressure became negligible (about one to two minutes), the connecting tube was sealed tight at E where a constriction had already been made. In this way the volume above the crystals was very small and at exactly the same temperature as

the crystals themselves. Cold water was then run into the thermostat and as the vapor pressure of the crystals increased, air was let into the apparatus to equalize the levels of the mercury in the U-tube. If the vapor pressure decreased, air was drawn out.

**Results.**—After much experimenting at different temperatures, it was discovered that the temperature of the crystals at the time of evacuation was a very important factor. If the crystals were at  $0^{\circ}$  or even at  $-10^{\circ}$  the force of the pump was sufficient to decompose the tri-etherate

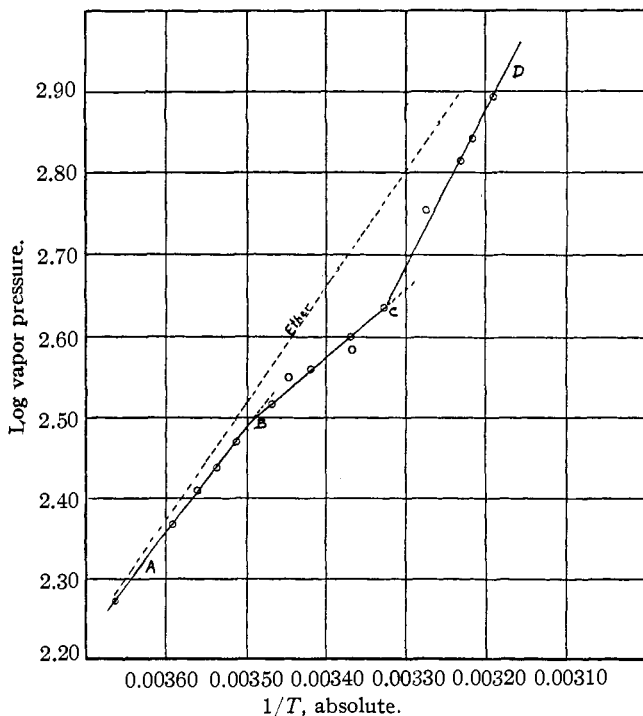


Fig. 2.—Vapor pressure curve starting with magnesium bromide tri-etherate at  $5^{\circ}$  and raising to  $40^{\circ}$ .

and give lower values and inconsistent results. On the other hand, if the crystals were at the temperature of carbon dioxide snow, it was found that at this temperature the vapor pressure was only about 4 or 5 mm. and the crystals were not completely decomposed during the short time that the pump was in operation. On warming to a temperature of about  $5^{\circ}$ , the vapor pressure reached a value of about 233 mm., which is very close to the value for the vapor pressure of pure ether. The value, however, was a little low and reference to Fig. 2 will show how the variation increases with rise in temperature.

On raising the temperature of the crystals above  $13^{\circ}$ , they seemed to

become soft with the appearance of some liquid. Above 30° they underwent a marked change with the formation of a large amount of liquid and a fine white precipitate. These changes were evident when the vapor pressure curves were drawn (Fig. 2).

TABLE IV  
VAPOR PRESSURES STARTING WITH  $\text{MgBr}_2 \cdot 3(\text{C}_2\text{H}_5)_2\text{O}$  AT 5° AND RAISING THE TEMPERATURE TO 40°

Temp. of bath, °C.	Barometer, mm.	Manometer, mm.	Vapor press., mm.	Log. V. P.	1/T (abs.)
0.0	728.4	541	187.4	2.2728	0.003665
5.5	746	513	233	2.3674	.003590
7.9	751.5	494	257.5	2.4108	.003560
9.8	741	467	274	2.4378	.003536
11.8	747	452.5	294.5	2.4691	.003511
15.4	746	417.5	328.5	2.5165	.003468
17.3	742.5	387	355.5	2.5508	.003445
19.7	742	378.5	363.5	2.5605	.003416
23.9	737	353.5	383.5	2.5838	.003368
24.1	735.5	332.5	403	2.6053	.003366
27.2	735.5	308.5	427	2.6304	.003331
32.3	748	180	568	2.7544	.003275
36.3	746.5	93	653.5	2.8153	.003233
38.0	739	43	696	2.8426	.003215
40.4	738	+23.5	761.5	2.8817	.003191

In plotting the log of the vapor pressures against the inverse temperature (absolute), a straight line graph was produced (Fig. 2). This graph shows three distinct lines intersecting at two points (B and C). The first break in the curve occurs at 13.5°. The second break occurs at about 28°. Thus, the vapor pressure curves bear out the fact that three etherates of magnesium bromide exist: the tri-etherate,  $\text{MgBr}_2 \cdot 3(\text{C}_2\text{H}_5)_2\text{O}$ , stable below 13°; the di-etherate,  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ , stable below 28°; and the mono-etherate,  $\text{MgBr}_2(\text{C}_2\text{H}_5)_2\text{O}$ , formed above 28°.

In reference to Fig. 2, it must be remembered that the lower curve AB is the vapor pressure curve for the system  $\text{MgBr}_2 \cdot 3(\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ , and ether vapor and at the transition point B we have the system  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{MgBr}_2 \cdot 3(\text{C}_2\text{H}_5)_2\text{O}$ , solution and ether vapor. Thus, the next curve BC is the vapor pressure curve for  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ , solution and ether vapor. In other words, it is the vapor pressure curve for a saturated solution of  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  in ether and not the curve for  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{MgBr}_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  and ether vapor. At C,  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{MgBr}_2(\text{C}_2\text{H}_5)_2\text{O}$ , solution and ether vapor are in equilibrium and the curve CD represented the system  $\text{MgBr}_2(\text{C}_2\text{H}_5)_2\text{O}$ , solution and ether vapor.

Since we have discovered that these systems reach equilibrium very slowly, it is only natural that if the temperature is raised suddenly, the



solubility of  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  in ether will increase, but if the solid dissolves very slowly to reach its equilibrium, the vapor pressure recorded will be the vapor pressure of an ether solution that is unsaturated with  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  and since the vapor pressure decreases with concentration, this vapor pressure will be too high. On the other hand, if the temperature is lowered suddenly from an equilibrium at high temperature, we will have a solution supersaturated with respect to  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  and hence a lower vapor pressure than we should have at this temperature. This would explain some of the difficulties encountered with the curves BC and CD in Fig. 2.

TABLE V

Temp. of bath, °C.	VAPOR PRESSURE OF $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ SYSTEM				
	Barometer, mm.	Manometer, mm.	Vapor press., mm.	Log. V. P.	1/T (abs.)
0.0	735.6	689	46.5	1.6674	0.003665
5.0	742.5	669	73.5	1.8662	.003600
7.5	747.5	656	91.5	1.9614	.003565
8.5	751.5	650	101.5	2.0063	.003550
13.5	762	611	151	2.1790	.003490
18.5	760	536	224	2.3503	.003430
26.0	759	349	410	2.6128	.003344
28.0	742	284	458	2.6609	.003322
30.0	743	251	492	2.6919	.003300
31.0	743	229	514	2.7109	.003289

TABLE VI

Temp. of bath, °C.	VAPOR PRESSURE OF $\text{MgBr}_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ SYSTEM				
	Barometer, mm.	Manometer, mm.	Vapor press., mm.	Log. V. P.	1/T (abs.)
0.0	742	733	9	0.9542	0.003665
15.1	741	699.5	41.5	1.6180	.003471
22.1	742.5	670	72.5	1.8603	.003389
27.5	742.5	630.5	112	2.0492	.003328
34.1	739	566	173	2.2380	.003256

Figure 3 shows the vapor pressure curves of the three etherate crystals. Curve I is that of the tri-etherate,  $\text{MgBr}_2 \cdot 3(\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$  and ether vapor, showing the break at about  $13^\circ$ , where a solution of the di-etherate in ether is formed. Curve II is that of the di-etherate,  $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ , mono-etherate and ether vapor, showing the point at about  $28^\circ$  where another molecule of ether is given off and a solution of the mono-etherate in ether is formed. The lower curve, III, is that of the mono-etherate crystals,  $\text{MgBr}_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ ,  $\text{MgBr}_2$  and ether vapor.

If these ether compounds of magnesium bromide are definite crystalline substances, it should be possible to obtain a "step" curve showing the vapor pressures of the different compounds at a constant temperature. A sample of the magnesium bromide-ether compound prepared by cooling

the two-layer mixture, as previously described, was placed in a bulb connected to a manometer and fitted with a stopcock connected to a vacuum pump. The procedure consisted of drawing all the gas from the system

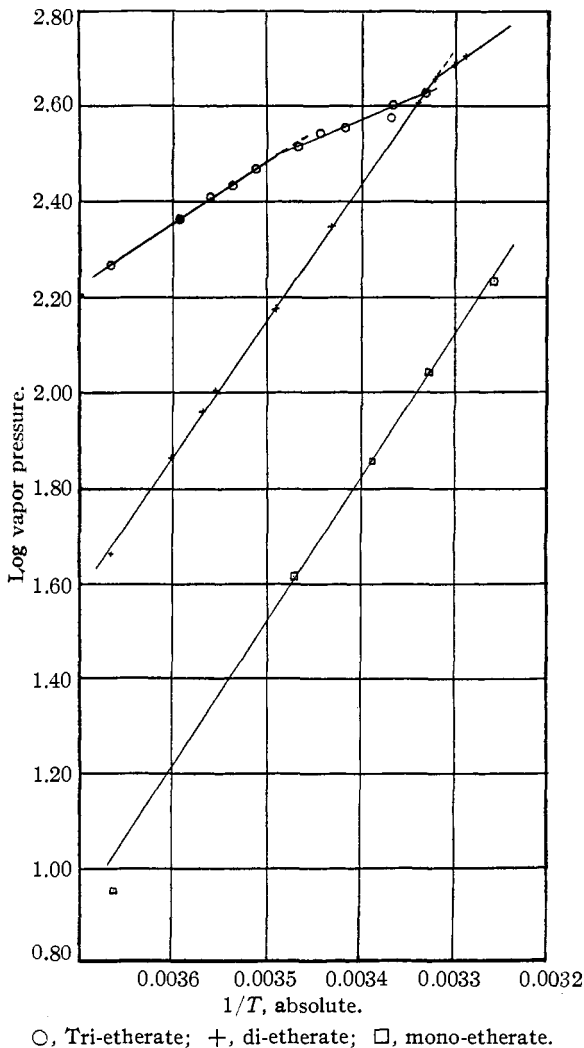


Fig. 3.—Vapor pressure curves of etherate crystals of  $MgBr_2$ .

with the pump, closing the stopcock and allowing the system to come to equilibrium. At first the bulb was immersed in a bath of solid carbon dioxide and acetone during the evacuation, which lasted for about one minute, in order to prevent the complete decomposition of the higher

etherate before measurement could be taken. After closing the stop-cock, this low temperature bath was replaced by ice and water, at which temperature the system was allowed to come to equilibrium. When all of the crystals had changed to the di-etherate, the time of evacuation was lengthened until some of the periods were for over an hour. During the latter part of the run the ice-bath was kept in place continually. Plotting vapor pressure of the crystals against the number of times evacuated, we

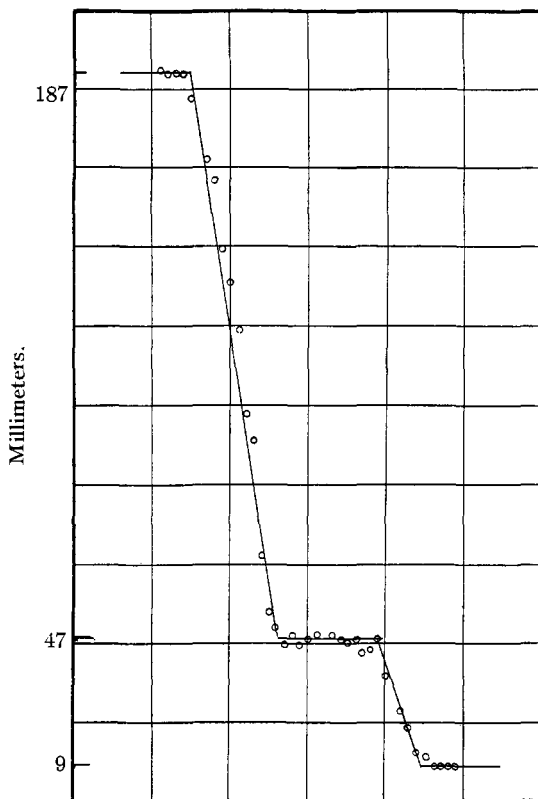


Fig. 4.—Vapor pressure of various etherates at 0°.

obtain a "step" curve as indicated in Fig. 4. The tri-etherate of magnesium bromide is shown with a pressure of 187 mm. at 0°. The pressure then drops to 47 mm., indicating a change to the di-etherate form. From this point it drops to 9 mm., which is the vapor pressure of the mono-etherate of magnesium bromide at 0°. This curve took about thirty days to complete due to slow equilibrium of the system.

#### Discussion

The most outstanding fact discovered in working with the etherate crystals of magnesium bromide is the slowness with which they change

form. This was evident in all the experiments carried out in this Laboratory and was the reason why negative results were obtained in trying to determine the transition point of the crystals by means of the thermometric and dilatometric methods, even though there is quite a noticeable heat change in the transformation. No doubt this fact was also responsible for Menschutkin's statement that the crystals of the di-etherate of magnesium bromide melted at  $22.8^{\circ}$ .<sup>2</sup> He evidently prepared the crystals by cooling and then tried to determine the melting point in the usual way by slowly raising the temperature. As has been shown above, it is very easy to raise the temperature of the crystals to room temperature before they start to change form. In such a case it is not surprising that he obtained a value of  $22.8^{\circ}$ ; a value, incidentally, which was not found in any of the work done in this Laboratory.

Because of the low transition point of the tri-etherate with extremely high vapor pressure and consequent instability, it is not surprising that most of the workers reported the di-etherate as the only form, with an occasional mention of the mono-etherate. The principal fact that led to the exact identification of the tri-etherate was the break in the vapor pressure curve at  $13^{\circ}$ . If this break was the transition point of the di-etherate, it was extremely difficult to explain how it was possible to obtain the di-etherate crystals above this temperature. Thus, experiments were started to prove the existence of the third form with the success shown by the analyses. After the completion of this work, Meisenheimer<sup>7</sup> independently published an article stating the existence and some of the properties of this tri-etherate of magnesium bromide.

### Summary

1. The existence of three distinct etherates of magnesium bromide has been shown.
2. Two transition points of the crystals were obtained, one where the tri-etherate changes to the di-etherate at  $13 \pm 0.5^{\circ}$ , and the other where the di-etherate changes to the mono-etherate at  $28 \pm 1.0^{\circ}$ .
3. Some of the properties of the etherates were studied with special reference to the slowness with which transition takes place.
4. The vapor pressures of the crystals were measured and the curves plotted.

EVANSTON, ILLINOIS

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<sup>7</sup> Jakob Meisenheimer, *Ber.*, **61B**, 708-20 (1928).