# ETHERATES OF MAGNESIUM PERCHLORATE

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Magnesium perchlorate was first prepared by Serrullas (1) along with the perchlorates of the alkali metals and the other alkaline earth metals. Rowley, during a study of the three component system, water-diethyl ether-magnesium bromide, tried determining the amount of water in a sample of ether solution by the use of anhydrous magnesium perchlorate. It was noted that the magnesium perchlorate appeared to retain considerable ether even when heated. Since other magnesium compounds form etherates, especially the halides, it was not a surprising phenomenon. The ethyl etherates of the magnesium halides were first investigated in detail by Menschutkin (2). Later, Meisenheimer (3) (4) and his co-workers discussed some of the properties of the magnesium halide etherates. More recently, Evans and Rowley (5) studied the properties of the etherates of magnesium bromide and determined their vapor pressures. This work on the magnesium halide etherates as a background led to this study. It was decided to study the solubility of magnesium perchlorate in diethyl ether in hopes of proving the existence of any crystalline etherates and possible transition points.

**Experimental.**—Commercial Dehydrite, prepared by G. Frederick Smith and Co., was used as a starting material. The samples used in this investigation were freshly dehydrated before use by heating to 250° C in an electric furnace for a few hours while being connected to a Cenco Hy-Vac oil pump. The anhydrous magnesium perchlorate was free from chlorides and when analyzed for magnesium, by the standard pyrophosphate method, showed a purity of above 99.9 per cent. The anhydrous ether was prepared by drying reagent ether over sodium, distilling from sodium on to freshly cut sodium. Only the middle fraction of the distillate was used, and the ether was always kept over sodium.

The apparatus (fig. 1) for conducting the experiment was designed to hold a relatively large volume of ether, exclude moisture, permit good stirring, and to

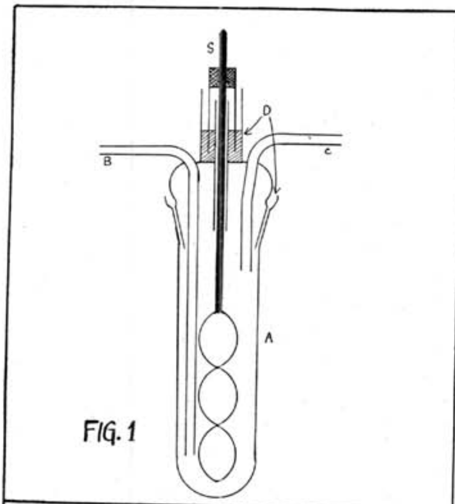

FIG. 1

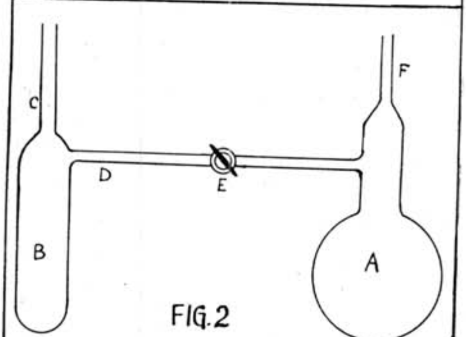

FIG. 2

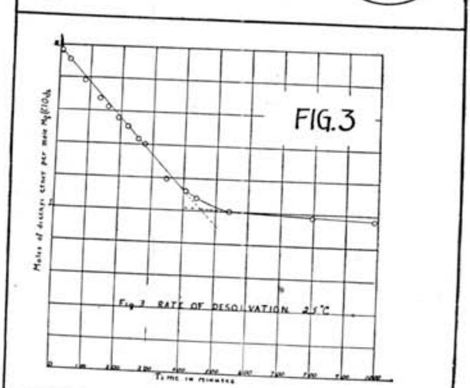

FIG. 3

allow for easy removal of the liquid without contamination.

Willard and Smith (6) reported the solubility as .2908 grams of magnesium perchlorate per 100 grams of diethyl ether at 25° C. The first results obtained during this study were higher than this and it was impossible to obtain check results. However by using the same solid for a series of determinations it was noticed that decreasing values were obtained. One typical series of analyses at 25° C is given in table I to show the trend. Rowley (7) had found that small amounts of water in ether increased the solubility of magnesium bromide. A study of the effect of water on the solubility of magnesium perchlorate in ether gave results as shown in table II. Consequently a new method of carrying out the experiments was necessary.

Several sets of apparatus, as illustrated in fig. 2, were made of pyrex glass. Ether in flask (A) was dried by means of sodium wire. Gentle suction was then applied and the flask sealed off at (F). The dehydrated magnesium perchlorate was then dropped in tube (B) and the lower end of the tube surrounded by an electric furnace at 250° C. After heating for several hours, while the tube was exhausted through the outlet tube with a vacuum pump, the outlet was sealed off at (C). When cooled, ether was distilled over and tube (B) was sealed off at (D). This method enables one to prepare both the anhydrous ether and the anhydrous magnesium perchlorate, and to bring them together, without any exposure whatever. These tubes were then placed in a constant temperature bath and turned end over end for at least 24

TABLE I.—SOLUBILITY OF MAGNESIUM PERCHLORATE IN DIETHYL ETHER, SHOWING THE TREND OF VALUES USING SAME SOLID FOR A SERIES OF DETERMINATIONS AT 25°C

| Sample | G/1000 $Et_2O$ |
|---|---|
| #54 | .3354<br>.3354 |
| #55 | .1963<br>.2010 |
| #56 | .1326<br>.1334 |
| #57 | .1181<br>.1238 |

TABLE II.—EFFECT OF WATER ON THE SOLUBILITY OF MAGNESIUM PERCHLORATE IN ETHER AT 15° AND 25°C

| Mol $H_2O$/1 $Et_2O$ | G $Mg(ClO_4)_2$/100g $Et_2O$ | |
|---|---|---|
| | 25°C | 15°C |
| .016 | .519<br>.516 | .381<br>.379 |
| .115 | 1.401<br>1.393 | |

TABLE III.—SOLUBILITY OF ANHYDROUS MAGNESIUM PERCHLORATE IN ANHYDROUS DIETHYL ETHER GRAMS /100G ETHER

| Sample | 25°C | 15°C | 0°C |
|---|---|---|---|
| #74<br>#77<br>#78 | .0591<br>.0674<br>.0663 | | |
| #80 | | .0588 | |
| #82<br>#83 | | | .0438<br>.0436 |
| Mean | .0643 | .0588 | .0437 |

TABLE IV.—ANALYSIS OF SOLIDS IN EQUILIBRIUM WITH ETHER SOLUTIONS AT VARIOUS TEMPERATURES

| Sample | Temp. (Degrees C) | % $Mg(ClO_4)_2$ | Mole ratio $Et_2O/Mg(ClO_4)_2$ | Theoretical requirement |
|---|---|---|---|---|
| #74 Approx. | 25 | 63.7 | 1.75 | 60 .2% for $Mg(ClO_4)_2$ 2 $Et_2O$ |
| #78 Approx. | 25 | 64.7 | 1.65 | " " " |
| #80 | 25 | 62.82 | 1.79 | " " " |
| #81 | 25 | 58.4 | 2.15 | 50.2% for $Mg(ClO_4)_2$ 3 $Et_2O$ |
| #1 | 0 | 50.2 | 2.99 | " " " |
| #2 | 0 | 45.4 | 3.64 | |

hours. The results of the analyses of the solutions at 25°C, 15°C, and at 0°C are given in table III. It will be noticed that the solubility is much less than has been previously reported.

Other experimental work was done to find, if possible, what etherates existed in the solid phase in equilibrium with the solution. Various samples of magnesium perchlorate, that had been in contact with ether for a long time at constant temperature, were analyzed and table IV indicates the results of such analyses. It will be noted that apparently the dietherate is the solid phase in equilibrium at 25°C. These analyses were made by gently pumping off the ether until the white solid remaining just began to appear dry around the edges. Analysis of the solid, either by magnesium determination or by complete desolvation at 250°C, gave the same results.

The stability of the etherates was determined by pumping off the ether with an aspirator through a phosphorus pentoxide tube. At definite intervals the pumping was stopped and the loss in weight recorded. Figure 3 indicates the mole ratio of ether to magnesium perchlorate against the actual time of desolvation at 25°C. The graph, representing the rate at which the etherate decomposes, shows a change of slope when the mole ratio is one. This indicates that the dietherate has a relatively high vapor pressure at 25°C and one of the ether molecules is readily lost, leaving the monoetherate of magnesium perchlorate. This monoetherate is relatively stable at 25°C and loses its ether very slowly as indicated by the slope of the curve. As a matter of fact, the monoetherate is so stable that at 100°C it loses ether very slowly under reduced pressure. Complete desolvation requires several hours of continual evacuation and heating.

At 0°C there is apparently a trietherate of magnesium perchlorate. Sample #1 (table IV) was allowed to stand at 0°C in an ice bath with frequent shaking. After a day or two the aspirator was attached until the solid remaining began to show dryness around the edges. It was weighed and again subjected to evacuation. The trietherate loses ether quite readily, several hours being sufficient to reduce it to the dietherate. However, the dietherate is quite stable at 0°C. Continual evacuation for several days results in but a small loss of ether, there being 1.93 moles of ether per mole of magnesium perchlorate after three days of such treatment.

Sample #2 (table IV) was also allowed to stand in contact with ether for a day or two. The excess ether was then carefully pumped off as in the previous case and then weighed. The weight of the ether amounted to over three moles per one mole of magnesium perchlorate, probably due to the fact that the sample was still a little wet with ether.

Considerable heat is liberated when ether is brought in contact with the anhydrous magnesium perchlorate.

**Discussion.**—Although a better method of studying the various etherates would be to measure their vapor pressures, enough work was done to show the existence of three etherates of magnesium perchlorate. The monoetherate which is quite stable, a dietherate which loses one molecule of ether under reduced pressure at 25°C but slowly at 0°C, and a trietherate which easily decomposes with reduced pressure at 0°C.

## Summary

**1.** The solubility of anhydrous magnesium perchlorate in diethyl ether was measured at 0°C, 15°C and 25°C. The value at 25°C was found to be much lower than had been previously reported in the literature.

**2.** A mono-, di-, and trietherate of magnesium perchlorate were found to exist. The trietherate is formed at 0°C and possibly at 25°C. The dietherate is fairly stable at 25°C and very stable at 0°C. The monoetherate is fairly stable up to and above 100°C.

**3.** The heat of solvation of magnesium perchlorate in ether seems to be fairly high.

**4.** The presence of water greatly affects the solubility of magnesium perchlorate in ether, giving rise to high values.

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