

# The Preparation of High-purity Anhydrous Magnesium Chloride<sup>1</sup>

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## Introduction

A current research program on the measurement of densities and surface tensions of molten salt mixtures requires the preparation of pure, anhydrous magnesium chloride in pound quantities. Though many have worked on this problem in the past, the methods described in the literature are those pertaining either to industrial processes which yield a low-purity product or to methods which are difficult to carry out on any but a very small scale. Since the material required for our work must not attack platinum at 1000°C., it must be scrupulously free from carbon and other elements to which platinum is so sensitive at high temperatures.

Though magnesium chloride may be crystallized as the hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) in a very pure form, the problem involved in its use is one of removing the water from the hydrated material without permitting decomposition of the chloride through hydrolysis. The stepwise dehydration of the hydrate is shown in Table I.

TABLE I

### Dehydration Reactions for Magnesium Chloride Hydrates

- (a)  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$
- (b)  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O}$
- (c)  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$
- (d)  $\text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O}$

Reactions (a) and (b) in the above table can be carried out without appreciable hydrolysis by heating in a stream of air below 180°C. The removal of further water according to reactions (c) and (d) requires higher temperatures at which the following reactions set in:

- (e)  $\text{MgCl}_2 + \text{H}_2\text{O} \rightarrow \text{MgOHCl} + \text{HCl}$
- (f)  $\text{MgCl}_2 + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HCl}$

At lower temperatures reaction (e) takes place, but at high temperatures reaction (f) predominates. Many attempts have been made to restrain these hydrolysis reactions by using an atmosphere of dry hydrogen chloride but without complete success.

Another approach to the problem is to eliminate contact with water by reactions such as shown in Table II.

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TABLE II

- (g)  $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$   
 (h)  $\text{Mg} + 2\text{HCl}(g) \rightarrow \text{MgCl}_2 + \text{H}_2$   
 (i)  $2\text{Mg} + \text{TiCl}_4 \rightarrow 2\text{MgCl}_2 + \text{Ti}$   
 (j)  $2\text{Mg} + \text{ZrCl}_4 \rightarrow 2\text{MgCl}_2 + \text{Zr}$   
 (k)  $\text{Mg} + \text{S}_2\text{Cl}_2 \rightarrow \text{MgCl}_2 + \text{S}$  (and  $\text{MgS}$ )  
 (l)  $6\text{Mg} + 2\text{QCl}_3 \rightarrow 3\text{MgCl}_2 + \text{Mg}_3\text{Q}_2$   
     (Q = Group V element)  
 (m)  $\text{MgO} + \text{C} + \text{Cl}_2 \rightarrow \text{MgCl}_2 + \text{CO}$   
 (n)  $\text{MgO} + \text{CCl}_4 \rightarrow \text{MgCl}_2 + \text{COCl}_2$

All of these reactions suffer from the disadvantage of requiring very high temperatures and from the impossibility of avoiding contamination of the magnesium chloride product. Though the energy relations strongly favor reaction (g) ( $\Delta F^\circ_{298^\circ\text{K}} = -141,589$  calories), both this reaction and reaction (h) are prevented from going to completion due to the fact that magnesium chloride crystallizes in a layer lattice ( $\text{CdCl}_2$ -type) which causes it to form a stifling film which protects the magnesium from further attack by chlorine or by hydrogen chloride below the melting point of magnesium chloride ( $712^\circ\text{C}$ ). The danger of impurities in the form of reaction by-products or unused reactants prevents the remainder of the reactions listed in Table II from being suitable for making magnesium chloride of high purity.

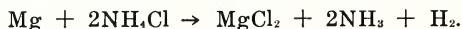
Another approach employed with considerable success by Richards (3) and later by Biltz and Huttig (1) is based upon the fact that ammonium carnallite ( $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) gives up its water of crystallization with less tendency toward hydrolysis than does hydrated magnesium chloride. Though it is necessary to use a stream of dry hydrogen chloride to suppress hydrolysis, Biltz and Huttig were able to obtain a product reported to be 99.85% magnesium chloride.

Ueno (4) has reported work on the preparation of anhydrous magnesium chloride by means of the following reaction:



By heating the reactants at  $200\text{-}300^\circ\text{C}$ . for magnesium oxide and at  $400\text{-}490^\circ\text{C}$ . for calcined magnesite, Ueno obtained anhydrous magnesium chloride contaminated with magnesium oxide. Gaskin (2) carried out the same reaction using magnesium hydroxide or magnesium basic chloride by heating them at  $300\text{-}450^\circ\text{C}$ . with ammonium chloride. He claimed a product containing 95% anhydrous magnesium chloride.

The experimental work reported herein consisted of a comparison of the most successful methods reported in the literature with another reaction investigated in this laboratory. The reaction not previously reported in the literature which shows considerable promise as a means of producing magnesium chloride of high purity in the completely anhydrous condition is the following:



The advantages inherent in this reaction are set forth in the following statements. 1. The reaction does not involve the elements of water, and no water can take part in the reaction or form any hydrates of magnesium chloride. 2. The reaction will proceed to completion within the temperature range of 200-400°C., thus avoiding contamination by reaction of hot magnesium chloride with the reaction container. 3. No non-volatile products are formed which might contaminate the product. 4. The reaction can be carried out in glass equipment of suitable design. 5. Magnesium of high purity (99.99%) is obtainable as a reagent. 6. Ammonium chloride can be recrystallized to remove impurities.

### Experimental

#### Reaction of Magnesium with Ammonium Chloride

Twice-recrystallized ammonium chloride which showed a negative test for iron with  $\alpha$ - $\alpha$ 'dipyridyl reagent was mixed with +35 mesh chips of magnesium purified by treating the melt with zirconium to settle out impurities. The weight ratio of ammonium chloride to magnesium was 3:1. The mixture was placed in the small chamber (or ampoule) of the 30 mm. Pyrex combustion tube shown in Figure 1.

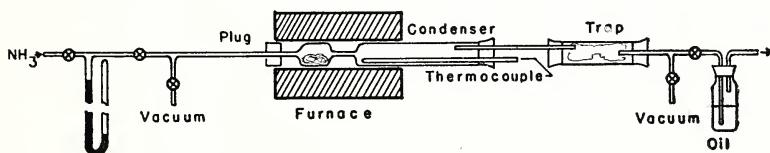


FIGURE 1

The tube was heated in an electric furnace commonly used for combustion analyses. The tube was connected, as shown in Figure 1, so that it could be evacuated or a stream of ammonia passed through it. The ammonia escaped through the oil trap which sealed the system against the atmosphere. Temperatures within the furnace were measured by means of a glass-enclosed thermocouple which projected into the larger portion of the combustion tube. The latter served as a condenser for excess ammonium chloride not consumed during the reaction. The air in the combustion tube was removed at the beginning of each experiment and was replaced by an atmosphere of ammonia which had been dried in the liquid state by means of sodium.

The sample was heated up slowly between 200 and 360°C. Two hours were allowed for completion of the reaction within this temperature range.

After completion of the reaction the excess ammonium chloride was distilled into the condenser. The ampoule (portion of the Pyrex tube containing the reaction mixture) was then sealed off under vacuum and separated from the remainder. When ready for analysis this sealed tube with the sample in it was broken under a known quantity of standard sulfuric acid solution. This was transferred to a volumetric flask with the washings of the beaker and glass fragments and diluted to a known

volume with distilled water. Aliquot portions of the sample were analyzed for magnesium ion, for chloride ion, and for total ammonia content. The ammonia present as ammoniate was calculated by back-titration of the excess of standard acid with standard base. The total ammonia content was determined by the Kjehldahl method. The magnesium ion was determined gravimetrically as the pyrophosphate. The chloride ion was determined gravimetrically as silver chloride.

#### Reaction of Magnesium Oxide with Ammonium Chloride

The apparatus used for this reaction was substantially the same as that for the magnesium-ammonium chloride reaction. The condenser in this case was longer and extended farther beyond the furnace. At the cold end of the condenser some sodium hydroxide pellets were placed to absorb the water evolved by the reaction. An atmosphere of dry, gaseous ammonia was used throughout the run.

The ampoule containing a mixture of magnesium oxide with about three times its weight of ammonium chloride was heated slowly to 360°C. over a period of two and one-half hours. The temperature was kept at 360-370°C. for another forty-five minutes and finally raised to 400°C. for a short period to remove ammonium chloride. The subsequent treatment of the material in the ampoule was identical to that outlined for the above reaction.

#### Dehydration of Ammonium Carnallite

The apparatus used for this reaction was that shown in Figure 2.

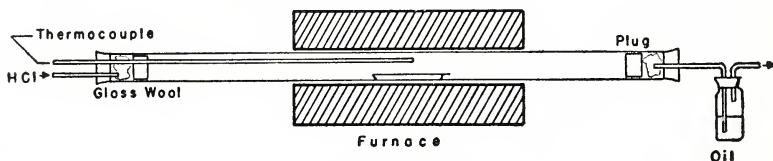


FIGURE 2

Equal weights of magnesium chloride hexahydrate crystals and of ammonium chloride were mixed in a clean evaporating dish. The mixture in the dish was then heated in air in an oven at 100°C. until it appeared to be dry, but it was not allowed to fuse. Some of the mixture was used to fill a glazed porcelain combustion boat which was then placed in a silica tube which could be heated by means of an electric furnace, as shown in the figure. The air was removed from the furnace tube and an atmosphere of dry hydrogen chloride passed through the silica tube during the heating operation. The tube was heated slowly to permit the temperature rise within the range of 200-360°C. to occur over a two-hour period to prevent hydrolysis. Over another period of four hours the temperature was raised to 750°C. to fuse the magnesium chloride formed. When cooled to 100°C. the boat containing the clear, fused salt was removed and then put into distilled water to dissolve the magnesium chloride. The quantities of magnesium and chloride ions were determined for the sample by the methods mentioned above.

## Results

The experimental results are summarized in Tables III, IV, and V.

TABLE III  
Reaction of Magnesium with Ammonium Chloride in  
Ammonia Atmosphere

NH <sub>4</sub> Cl Used, grams	Mg Used, grams	Moles NH <sub>4</sub> Cl Per Mole Mg Used	Mg Found, grams	Cl Found, grams
2.3064	0.3114	3.20	0.3125	1.0220
2.1388	0.2522	3.71	0.2525	0.7247
2.6004	0.3014	3.74	0.3010	0.9040
2.8701	0.3199	3.89	0.2842	0.9252
2.7027	0.5141	2.27	0.5155	1.5457
3.6814*	0.2986*	5.59*	0.2966*	0.8617*

Moles Cl : Mg	NH <sub>3</sub> Found, grams	Moles NH <sub>3</sub> : Mg	NH <sub>4</sub> Found, grams	Moles NH <sub>4</sub> Cl : Mg	% Purity MgCl <sub>2</sub>
2.020	0.3487	1.595	0.3934	0.204	99.01
1.969	0.4685	2.653	0.4663	None	98.45
2.006	0.3259	1.546	0.3372	0.053	99.70
1.985	0.3358	1.687	0.3850	0.247	99.25
2.002	0.4338	1.199	0.4533	0.054	99.90
1.992*	0.0025*	0.012*	0.0027*	None*	99.60*

\* Sample heated under vacuum to remove ammonia and ammonium chloride.

TABLE IV  
Reaction of Magnesium Oxide with Ammonium Chloride in  
Ammonia Atmosphere

NH <sub>4</sub> Cl Used, grams	MgO Used, grams	Moles NH <sub>4</sub> Cl Per Mole MgO Used	Mg Found, grams	Cl Found, grams
1.7804	0.4135	3.24	0.1830	0.5131
2.3940	0.3732	4.85	0.1673	0.5121
2.1043	0.4566	3.50	0.2088	0.5850
2.2843	0.4930	3.50	0.2205	0.6858

Moles Cl : Mg	NH <sub>3</sub> Found, grams	Moles NH <sub>3</sub> : Mg	NH <sub>4</sub> Found, grams	Moles NH <sub>4</sub> Cl : Mg	% Purity MgCl <sub>2</sub>
1.934	0.3938	3.072	0.3928	None	98.15
1.983	0.5427	4.633	0.5557	0.116	99.15
1.915	0.2343	1.603	0.2352	0.006	95.75
2.055	0.5544	3.589	0.5664	0.078	97.32

TABLE V

Dehydration of Ammonium Carnallite in Hydrogen Chloride  
Atmosphere

Mg Found, grams	Cl Found, grams	Moles Cl : Mg	% Purity MgCl <sub>2</sub>
0.0714	0.2110	2.027	98.67
0.0414	0.1231	2.039	98.09
0.0725	0.2117	2.012	99.40

Note: Calculation of purity in above tables based on Cl : Mg ratio only.

### Discussion of Results

Reference to the data as presented above shows the highest degree of purity of the magnesium chloride based on the Cl : Mg atomic ratio was obtained from the magnesium-ammonium chloride reaction. Next highest purity was obtained by the dehydration of ammonium carnallite. The magnesium oxide-ammonium chloride reaction yielded the material of lowest purity. The justification for disregarding the ammonia and ammonium chloride present in the products of the reactions of ammonium chloride with magnesium and with magnesium oxide lies in the nature of the purpose to which the material is to be put, since it is to be fused when put to its ultimate use.

Choice between the methods described above as means of preparing quantities of anhydrous magnesium chloride of high purity depends upon the relative ease with which the larger-scale operations can be carried out. The data presented do not make a choice on this basis possible. Subsequent work must be done to serve as a basis for such a choice.

From the results it is obvious that anhydrous magnesium chloride tenaciously retains some ammonia and some ammonium chloride at temperatures up to 400°C. unless these are removed by heating under vacuum or by fusing the ammonium chloride product. This tenacity with which these substances are held shows the fairly strong tendency toward compound formation. Biltz and Huttig (1) studied the ammoniates of magnesium chloride and other magnesium halides and found the existence of several definite ammoniates. Some additional work performed by the authors but not reported in this paper shows the existence of a definite ammoniate,  $MgCl_2 \cdot NH_3$ , whose decomposition pressure was measured, but time did not allow completion of the system.

It is particularly interesting that the reaction between magnesium metal and ammonium chloride proceeds at a temperature so very much lower than that for the reaction of magnesium with either free chlorine or with hydrogen chloride. This is further pointed up by the fact that gaseous ammonium chloride has been shown by other investigators to be completely dissociated into ammonia and hydrogen chloride. Why does the reaction proceed readily at a low temperature in hydrogen chloride containing ammonia but not below the melting-point of magnesium chloride in its absence?

The authors believe that the answer lies in the existence of stable ammoniates of magnesium chloride. The CdCl<sub>2</sub>-type lattice of magnesium chloride mentioned above is of such a structure that it forms a protective film of the salt over the metal, effectively sealing the metal against further attack by chlorine or hydrogen chloride until the melting-point of the chloride is reached. This melting action destroys the ability of the chloride to protect the metal from attack. In the presence of ammonia one does not get pure magnesium chloride which would have a stifling action on the reaction. Instead one obtains certain ammoniates of magnesium chloride which have different crystal structures and which do not form protective films.

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