

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE PREPARATION AND PROPERTIES OF MAGNESIUM PERCHLORATE AND ITS USE AS A DRYING AGENT¹

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This paper deals with the preparation of anhydrous magnesium perchlorate and its hydrates $Mg(ClO_4)_2 \cdot 6H_2O$ and $Mg(ClO_4)_2 \cdot 3H_2O$, a study of their properties and a comparison of the anhydrous perchlorate and the trihydrate with phosphorus pentoxide as dehydrating agents.

Historical

Magnesium perchlorate was first prepared by Serullas.² A more detailed study of this substance was made by Weinland and Ensgraber,³ who prepared the hydrate, $Mg(ClO_4)_2 \cdot 6H_2O$, by drying the sample in a vacuum over phosphorus pentoxide. They failed to note that this treatment yields finally the lower hydrate, $Mg(ClO_4)_2 \cdot 3H_2O$, because the dehydration is rather slow even in its early stages. No mention of this second hydrate was found in the literature.

Preparation of Magnesium Perchlorate Hexahydrate

The purest imported magnesium oxide was treated with a slight excess of pure dil. perchloric acid, which was prepared by the method of Willard.⁴ The solution thus formed was evaporated until crystallization began at the surface and fumes of perchloric acid were being given off. The mixture was then allowed to cool to room temperature with the addition of sufficient water to keep the crystal mass semifluid. After centrifugal drainage the product, containing but a slight amount of perchloric acid, was redissolved, recrystallized, and again centrifuged. The needle-like crystals thus obtained were shown by spectroscopic examination to contain no calcium or barium in spite of the fact that the oxide employed in their preparation was similarly shown to contain traces of these impurities.

Analysis of the Hexahydrate for Water of Crystallization

The salt prepared as above described could not be freed from its slight excess of water by drying at 110° , since after 24 hours of such treatment a sample lost 30% of its crystal water. A few grams of the material was dried by storing for 4 weeks over anhydrous magnesium perchlorate in a desiccator at room temperature.

A weighed portion of the material in a platinum crucible was dissolved

¹ From a dissertation submitted by G. F. Smith to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Serullas, *Ann. chim. phys.*, **46**, 2, 297 (1831).

³ Weinland and Ensgraber, *Z. anorg. allgem. Chem.*, **84**, 372 (1914).

⁴ Willard, *THIS JOURNAL*, **34**, 1480 (1912).

in water and a slight excess of sulfuric acid added. The solution was then evaporated and heated until the excess of the sulfuric acid was evaporated, using a ring burner, and the last traces were removed by igniting the crucible for 10 minutes in an electric crucible furnace at 650° . From the weight of the magnesium sulfate the weight of magnesium perchlorate was calculated and the weight of crystal water lost in the process thus obtained. The mean of two closely agreeing duplicates gave 32.76% water of crystallization while the theoretical value for the hexahydrate is 32.62%. The remainder of the material when analyzed after being kept for 3 months longer over anhydrous magnesium perchlorate, gave by a single determination 32.40% of water of crystallization; this leads to the conclusion that the hexahydrate of magnesium perchlorate is not further dehydrated in contact with the anhydrous reagent.

The hexahydrate thus obtained melted between 145° and 147° and its density as determined by immersion in carbon tetrachloride, in which it is insoluble, was found to be 1.970 at $25^{\circ}/4^{\circ}$, corrected to a vacuum. In this determination the usual precautions were observed, such as pulverizing the sample and evacuating after immersion, to remove trapped air. Although this salt as crystallized from water solutions does not deliquesce in air, the fused material does so in a pronounced manner.

Preparation and Analysis of Magnesium Perchlorate Trihydrate

About 50 g. of the hexahydrate, as above described, was stored in an efficient vacuum desiccator over a generous portion of phosphorus pentoxide, changed at frequent intervals, and the desiccator was frequently pumped out so that a high vacuum was maintained continuously. When the temperature was kept at 0° or less, no loss of crystal water on the part of the hexahydrate was apparent, the weight of a sample remaining constant. When the temperature was allowed to rise to $20-25^{\circ}$, other conditions being equal, the salt began slowly to give up a part of its crystal water. The drying was continued during 4 months and the salt was analyzed at intervals of 1 month by the method previously described, with the following results: the original water content was 32.6% (hexahydrate); after 1 month it was reduced to 24.0%; after 2 months, 22.0%; after 3 months, 20.5%; and after 4 months, 19.75%. The percentage of water calculated for the trihydrate formula is 19.50. Thus the total water removed during these intervals of time was approximately 66.0%, 15.5%, 11.5% and 6.0%, respectively. The graph of the percentage of water removed plotted against the time interval involved showed the curve to be asymptotic to the time axis, and it became apparent that after sufficient time the theoretical value for the trihydrate would eventually have been reached. Further treatment was not given, however, and the properties of the material thus obtained were studied.

When either the trihydrate or the hexahydrate was completely melted

and allowed to cool slowly, it solidified at 145–147°. Perhaps this is the eutectic point of these 2 hydrates. The density of the trihydrate was found by displacement of carbon tetrachloride to be 2.044 at 25°/4°, corrected to a vacuum.

Preparation of Anhydrous Magnesium Perchlorate

Portions of about 100 g. of the hexahydrate, prepared as already described, were heated in large porcelain crucibles to a temperature slightly above the melting point. The crucibles were supported on trays contained within a Pyrex tube 8 cm. in diameter and 90 cm. long. The tube was electrically heated and a stream of air dried by phosphorus pentoxide passed through the tube continuously. A temperature of 170° served to drive off the greater portion of the crystal water, but at the end of the process the temperature was raised to 250°. The fused material, as it loses water, becomes heavily encrusted and must be stirred at frequent intervals. At the end the mass became pasty, and finally when all the water was removed a dry, white material remained which was taken from the crucibles while still hot and ground to a powder. It was then returned to the drying train, kept at 230–250° and samples were taken while hot to insure absence of moisture.

Water solutions of magnesium perchlorate so prepared were neutral and free from chloride. It was thus shown that anhydrous magnesium perchlorate is completely stable at 250°. At a slightly higher temperature slow decomposition begins, oxide and chloride being formed.

When anhydrous magnesium perchlorate was gradually elevated in temperature from 250° to about 400° it decomposed quietly without fusing, leaving a residue consisting principally of magnesium oxide. In this way the residual moisture in the salt was determined. Weighed portions of the salt were completely decomposed at 400° and the moisture evolved with the gas was absorbed in a phosphorus pentoxide tube. A blank correction was applied and the air was carefully purified. The samples were taken hot to avoid absorption of atmospheric moisture and glass stoppered sampling tubes were used for weighing. By this direct measurement the moisture found was less than 0.1%. In view of the extreme affinity of anhydrous magnesium perchlorate for water, even this value may not be as low as that in the original material prior to sampling.

Anhydrous magnesium perchlorate has a density of 2.60 at 25°/4° corrected to a vacuum as determined by displacement of carbon tetrachloride in the manner already described. When water is added to it a hissing sound is produced very similar to that produced by the addition of water to phosphorus pentoxide.

The Efficiency of Anhydrous Magnesium Perchlorate as a Drying Agent

Two ground glass-stoppered U-tubes were filled with phosphorus

pentoxide and asbestos in alternate layers, one tube being used as a counterpoise. A third U-tube of identical proportions was filled with anhydrous magnesium perchlorate and cotton wool in alternate layers. The weight of magnesium perchlorate in the tube was 9.06 g. The total length of the column of drying agent in each tube was about 13 cm. All weighings were made by counterpoise. The tubes were always allowed to stand in the balance case for a considerable length of time in order to insure equilibrium conditions and the stopcocks were always opened for a moment just before a weighing. The train of apparatus and air flow was as follows. Air under pressure was passed through a calibrated flow-meter and then saturated with moisture by passing through a potash bulb containing water. From the potash bulb saturator the air passed successively through the magnesium perchlorate tube, the phosphorus pentoxide tube and finally a protection tube filled with phosphorus pentoxide to prevent backward diffusion of moisture. Small plugs of cotton wool were placed between all connections to prevent passage of spray or dust particles from one unit to another. All weighed parts of the train as well as the saturator bulb were immersed up to the horizontal cross connections in a thermostat accurately maintained at 25°.

The rate of flow of the moist air was varied from 1.5 to 3.5 liters per hour. The magnesium perchlorate and phosphorus pentoxide tubes were weighed 14 times during more than 8 hours of continuous test. At no time during the test had a weighable amount of water vapor escaped absorption in the magnesium perchlorate tube. Thus, after the 9.06 g. of magnesium perchlorate had taken up 5.23 g. of water the phosphorus pentoxide tube directly following weighed exactly the same as it did before the experiment. At the completion of the test about 1 g. of magnesium perchlorate was still unchanged. It was thus found that the magnesium perchlorate had absorbed nearly 60% of its own weight of moisture while the residual water vapor in over 210 liters of air used in the experiment was unweighable.

With the 10cm. U-tubes described above, the maximum rate of flow which would insure complete removal of water from air saturated at 25° was found to be 5.0 liters per hour. Thus with columns of equal length the rate of absorption is seen to be quite limited in comparison with that of phosphorus pentoxide. This is to be expected, since the mechanism of the absorption in the case of phosphorus pentoxide is that of true chemical combination rather than formation of water of crystallization, as in the case of magnesium perchlorate.

Efficiency of the Trihydrate as a Dehydrating Agent

The fact that phosphorus pentoxide was found to be incapable at a temperature of 0° and less, of drying magnesium perchlorate below the hexahydrate stage, while at ordinary temperatures the trihydrate was

thus formed indicated that this salt also possessed great dehydrating power. Accordingly, experiments were run duplicating conditions as above described for anhydrous magnesium perchlorate, the rate of flow and the temperature of the absorbent being varied. The results of these determinations are given in the following table.

Temperature °C.	Rate of gas flow L./hr.	H ₂ O unabsorbed by Mg(ClO ₄) ₂ ·3H ₂ O G.	Duration of experiment Hrs.
0	5.2	0.0000	11
25	5.0	0.0049	17
0	10.0	0.0024	2

At 0° and at rates of flow up to 5 liters per hour the trihydrate is as effective as phosphorus pentoxide and anhydrous magnesium perchlorate. At rates of flow up to 10 liters per hour the efficiency, while still high, falls off rapidly.

Among the advantages possessed by magnesium perchlorate as a drying agent in comparison with phosphorus pentoxide are the following.

1. The weight of water absorbed per unit weight of desiccating agent is several times greater with anhydrous magnesium perchlorate than with phosphorus pentoxide.
2. Anhydrous magnesium perchlorate does not become sticky upon handling, does not form channels through use and contracts in volume upon absorbing moisture.
3. It can be recovered and reactivated repeatedly.
4. Being a neutral drying agent it offers many possibilities as a dehydrating agent for materials for which phosphorus pentoxide and conc. sulfuric acid are not permissible. Work upon this phase of the subject will be taken up at a future date.

Summary

1. The preparation and some physical properties of anhydrous magnesium perchlorate, the hexahydrate and the trihydrate are described.
2. When the gas flow is not over 5 liters per hour anhydrous magnesium perchlorate is as efficient a drying agent as phosphorus pentoxide. The trihydrate compares favorably with the anhydrous salt at 0° and at equal rates of gas flow, but at higher temperatures it is less efficient. The advantages of anhydrous magnesium perchlorate as a drying agent are pointed out.

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