

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

NEW HYDRATES OF MAGNESIUM PERCHLORATE. THEIR
STRUCTURAL RELATION TO KNOWN FORMS OF THE
HYDRATED PERCHLORIC ACIDS AND PROPERTIES
AS INTENSIVE DEHYDRATING REAGENTS

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Introduction

The oxonium structure of the crystalline form of perchloric acid having the melting point 49.90° ² has been previously shown by Volmer.³ The oxonium structure of all known hydrates of perchloric acid was indicated by the studies of Smith and Goehler.⁴ Previously known hydrates of magnesium perchlorate are the hexahydrate and trihydrate. The latter material (trade name, Dehydrite) and anhydrous magnesium perchlorate (trade name, Anhydron) are widely employed in the intensive drying of gases. The object of the present paper is to report new hydrates of magnesium perchlorate, to show their direct analogy to known forms of hydrated perchloric acid and to extend conclusions concerning the structural relations brought out by the perchloric acids and analogous magnesium salts.

Known Forms of Perchloric Acid and Analogous Magnesium Salts.—The data of Table I are used to show the analogy existing between various known forms of perchloric acid and the entire list of hydrated magnesium perchlorates. The diaquo- and tetraquo-magnesium perchlorates are prepared and described for the first time in connection with the work reported in this paper.

Discussion of Data in Table I.—In a previous paper⁴ the oxonium structure of the hydrated perchloric acids resulted in a somewhat different formulation being applied to the hydrous perchloric acids. For example, considering the perchloric acid associated with two molecules of water, the formulas assigned to this modification were the following: $\text{OH}_3\text{ClO}_4 \cdot \text{H}_2\text{O}$ (oxonium perchlorate monohydrate) for the stable form, m. p. -17.8° , and $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ (perchloric acid dihydrate) for the less stable form, m. p. less than -19.0° . While this former interpretation is somewhat at variance with the data of Table I, it is based upon the assumption that the anion in the one case is more extensively hydrated than in the other. The newly modified interpretation seems to be somewhat preferable from

¹ Presented by O. W. Rees in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

² Smith and Goehler, *Ind. Eng. Chem., Anal. Ed.*, **3**, 8-61 (1931).

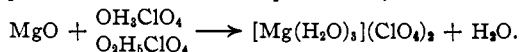
³ Volmer, *Ann.*, **440**, 200 (1924).

⁴ Ref. 2, p. 58.

TABLE I

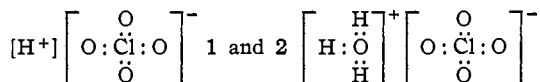
Perchloric acid hydrate		Mg salt—Werner formulation ^a
1	HClO ₄ (m. p. app. -112°) anhydrous perchloric acid ⁵	[Mg](ClO ₄) ₂ anhydrous magnesium perchlorate ⁸
2	OH ₂ ClO ₄ (m. p. 49.90°) oxonium perchlorate ⁴	[Mg(H ₂ O) ₂](ClO ₄) ₂ diaquo-magnesium perchlorate ⁷
3	O ₂ H ₃ ClO ₄ (m. p. -17.8°) dioxonium perchlorate ^{6,8}	[Mg(H ₂ O) ₄](ClO ₄) ₂ tetraquo-magnesium perchlorate ⁷
4	OH ₂ ClO ₄ ·H ₂ O (m. p. < -19°) oxonium perchlorate monohydrate ⁴	
5	O ₂ H ₃ ClO ₄ > H ₂ O (m. p. -29.8°) ⁸	
6	O ₂ H ₇ ClO ₄ (m. p. -37°) ⁸ trioxonium perchlorate	[Mg(H ₂ O) ₃](ClO ₄) ₂ hexaquo-magnesium perchlorate ^{6,8}
7	O ₂ H ₃ ClO ₄ ·H ₂ O (m. p. -43.2°) ⁸ dioxonium perchlorate monohydrate	
8	O ₂ H ₇ ClO ₄ > H ₂ O (m. p. -41.4°) ⁸	

^a Triaquo-magnesium perchlorate^{6,9} may be considered as the salt formed by the action of oxonium perchlorate and dioxonium perchlorate, thus:



an extended study of new hydrated magnesium salt analogs of the acids under discussion predicted by a study of Table I. The two new hydrated magnesium perchlorates [Mg(H₂O)₂](ClO₄)₂ and [Mg(H₂O)₄](ClO₄)₂ were, as a result, studied for the first time. The present interpretation was also suggested by the paper of Latimer and Rodebush,¹⁰ in which they present a plausible explanation for the association of water molecules to form dihydrol and trihydrol or more extensively associated water molecules. The present interpretation is also made more plausible by the study of the perchlorate amines of the alkaline earth metals and magnesium to be reported at a later date. Finally, the new interpretation as applied to the structure of the hydrated perchloric acids naturally follows from a study of the physical constants of the magnesium perchlorate hydrates following the rules of coordination in their Werner formulations.

The Structure of the Hydrated Perchloric Acids.—The electronic structure of the hydrated perchloric acids numbering 1–8 in Table I are given as follows, each individual form identified by number



Structure 1 is readily accepted. Structure 2, oxonium perchlorate, is the only one possible in accordance with the findings of Volmer follow-

⁵ Van Wyk, *Z. anorg. Chem.*, **48**, 1 (1906).

⁶ Willard and Smith, *THIS JOURNAL*, **44**, 2254 (1922).

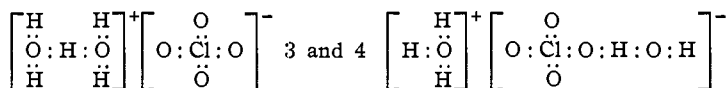
⁷ Smith, Rees and Hardy, this paper.

⁸ Weinland and Ensgraber, *Z. anorg. Chem.*, **84**, 372 (1914).

⁹ Smith, Brown and Ross, *Ind. Eng. Chem.*, **16**, 20 (1924).

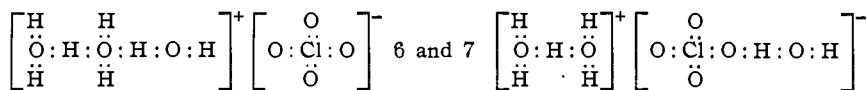
¹⁰ Latimer and Rodebush, *THIS JOURNAL*, **42**, 1419 (1920).

ing x-ray studies. The hydration of the anion resulting in the structure $[H]^+ \left[\begin{array}{c} O \\ | \\ O : \ddot{Cl} : O : H : O : H \\ | \\ O \end{array} \right]^-$ is not possible since two crystalline forms of this acid are not known as shown by Smith and Goehler.² The structure shown in the above hydrated anion is excluded because of the well-known great increase in stability of oxonium perchlorate as compared to anhydrous perchloric acid. This is not observed in the comparison of higher hydrates in which hydration of the anion is postulated. The melting point of oxonium perchlorate is comparatively high (49.90°), which is associated with hydration of the cation. Therefore for the pairs of known modifications of the higher hydrated perchloric acids, that having the higher melting point must be considered to have the total hydration associated with the cation.



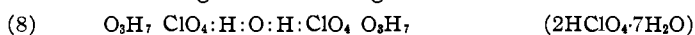
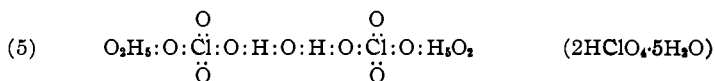
In the case of structure 3 and structure 4, two forms of this acid were shown to exist by Smith and Goehler.⁴ The unstable form, 4, having the lower melting point, is so readily transformed to form 3 that the existence of this modification was not indicated by van Wyk,⁵ although two forms of the next higher hydrate were shown in the same investigation, probably because of an increased difference in melting points in the latter case. That the stable form is that indicated in formula 3 is proved by the previously demonstrated dissociation of the material to form successively oxonium perchlorate, formula 2, and finally anhydrous perchloric acid.¹¹ These dissociations would not be possible were the stable forms to correspond to those having hydrated anions.

Similarly two forms of the next higher hydrate of perchloric acid are known as follows



Here again the form 6 having the higher melting point is given the structure in which the cation is most highly hydrated.

As the ratio of acid to water molecules decreases, even before reaching the ratio $HClO_4:3H_2O$, there appears a tendency for polymerization through the medium of the ClO_4^- anion. Thus



¹¹ Ref. 2, p. 55.

Here, an implied polymerization through the union of the two molecules of forms 3 and 6 due to a bonding of both anions in each case by one water molecule might be explained by a similar union linking the two cations. The latter alternative is not plausible for a number of reasons. Corresponding hydrated magnesium perchlorates are not known. Two forms of the acids, 5 and 8, are not known. The rate of change in viscosity for solutions of perchloric acid in water with increase in acid concentration is greatest⁵ over the range corresponding to formulas 5 to 8, inclusive. More extensively hydrated forms of perchloric acid than that of formula 8 are not probable since a dilute solution of perchloric acid in water, when concentrated by boiling, begins to develop acid in the vapor phase at a concentration approximately represented by formula 8 for the liquid phase.

Acids of formulas 5 to 8 inclusive are easily dissociated to form dioxonium perchlorate (formula 3). Constant boiling perchloric acid (b. p. 203° at 1 atmosphere) corresponds most closely to the latter form (72.5% HClO_4). By distillation at reduced pressure it is impossible to exceed the concentration (73.60%) indicated by formula 3. Repeated and continuous distillation at pressures much less than one millimeter do not result in more than a minute increase in acid concentration (less than 0.3%) which must be attributed to the phenomena of superheating.¹² At the same time modifications 1, 2, 3, 4, 6 and 7 were shown to exist in the vapor phase upon distillation at reduced pressures from 7 to 18 millimeters and their separation in the vapor phase accomplished. The dissociations were then made possible by the effect of 50–60° of superheating. Dioxonium perchlorate is dehydrated to oxonium perchlorate by the use of concentrated sulfuric acid. Oxonium perchlorate is dehydrated to form anhydrous perchloric acid by contact with phosphorus pentoxide, which finally forms Cl_2O_7 .¹³

Conclusions relative to the precise structure of the hydrated perchloric acids necessarily are associated with intuitive speculation in a great measure. Following such lines of speculation it is interesting to express the relationship existing between values for the ratio of acid to water at which the hydrated perchloric acids exist and the melting point of the numbered forms previously discussed in connection with Table I. This is done graphically in Fig. 1. Here melting points are plotted on the vertical and acid–water molecular ratios on the horizontal axis. The stable forms 1, 2, 3 and 6 are shown on the solid black line AAA. The forms 4 and 7 which convert readily to forms 3 and 6, respectively, fall on the branch AC (dashed line). The polymerized forms 5 and 8 fall between these values on the part of AAA indicated by AB.

New Hydrates of Magnesium Perchlorate.—Since the more stable

¹² Smith and Koch, *Ind. Eng. Chem., Anal. Ed.*, **3**, 52 (1931).

¹³ Michael and Conn, *Am. Chem. J.*, **23**, 444 (1900).

forms of perchloric acid show increasing melting points with decreasing hydration of the cation, and hydrated magnesium perchlorates other than the tri- and hexahydrated forms have not been previously shown, the di- and tetrahydrated magnesium perchlorates would be predicted from the existence of oxonium and dioxonium perchlorates. The two new forms of

hydrated magnesium perchlorate are indicated by the principles governing the formation of complex structures of the Werner type, namely: (a) oxygen shows a greater tendency to coordinate than does hydrogen. (b) The tendency of an ion to form a covalent link is greater the larger the charge, the less its size if a cation, and the greater its size if an anion. (c) The cation has a tendency to act as acceptor and the anion as donor. (d) Magnesium shows coordination numbers of 2, 3, 4 or 6 (its maximum). (Elements of the periodic table from sodium to bromine show a maximum coordination number of 6.) (e) Crystalline substances in which the two ions have different charges or where there is a great difference in their size are likely to show hydration.

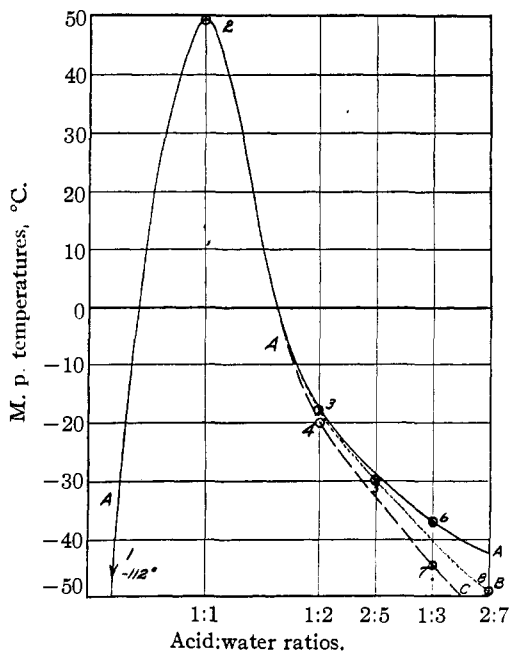


Fig. 1.

All the structures shown in Table I conform to these rules. With the possible exception of beryllium, magnesium represents the metal of lowest atomic weight suitable for study of the bivalent group. The already extended application of magnesium perchlorate as an intensive dehydrating agent increases the interest in this problem.

From an examination of Table II it will be seen that the vapor pressure of tetraquo-magnesium perchlorate lies between 3 and 10 millimeters at 50°. The vapor pressure of diaquo-magnesium perchlorate is less than 10 millimeters at 125°. (By separate determination it was easily shown that the vapor pressure of diaquo-magnesium perchlorate is zero at temperatures up to 135°.) The vapor pressure of diaquo-magnesium perchlorate becomes appreciable at 150° but its dissociation is very slow at this temperature. (Even at 200° the dissociation is slow and temperatures up to 250°

TABLE II

DEHYDRATION OF HEXAQUO-MAGNESIUM PERCHLORATE AT VARIOUS TEMPERATURES
(PRESSURE, 10-15 MM.)

Sample weights $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ from 2.5 to 3.75 g.

Temp., °C.	Percentage loss in weight						Mg. salt hydrate formed	Theoretical loss, %	
	Time in days								
	1	2	3	4	5	14	21		
50 ^a	0.20	0.50	...	3.79	...	10.79	10.70	$[\text{Mg}(\text{H}_2\text{O})_4](\text{ClO}_4)_2$	10.81
75	13.57	20.96	21.60	$[\text{Mg}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	21.62
100	21.66	21.66	$[\text{Mg}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	21.62
125	21.66	21.69	$[\text{Mg}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	21.62
150	20.98	...	28.49	..	31.89	$\text{Mg}(\text{ClO}_4)_2$	32.42

^a When the pressure was reduced to a value of 3-4 mm. after 29 additional days this sample was dissociated to form diaquo-magnesium perchlorate (loss found, 22.60%).

are preferable.) The preparation of diaquo-magnesium and anhydrous magnesium perchlorates on a large scale for commercial use has been described by Smith and Rees.¹⁴

TABLE III

DEHYDRATION OF HEXAQUO-MAGNESIUM PERCHLORATE IN CONTACT WITH VARIOUS
DEHYDRATING REAGENTS AT 125-175°

Desiccant	Temp., °C.	Percentage loss in weight				Fraction of water removed, %
		Time in hours				
		12	16	20	24	
Silica gel	125	1.81	2.57	7.9
"Hydralo"	150	9.06	9.27	28.6
"Hydralo"	175	10.71	10.38	32.0
P_2O_5	150	13.85	14.83	45.74
Anhydrone	150	21.01	21.66	66.81

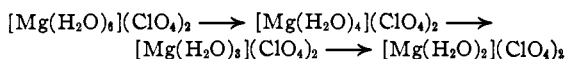
By examination of Table III it will be seen that over the temperature range 125-175° "Anhydrone" (anhydrous magnesium perchlorate) is the most efficient dehydrating agent of all commercially available desiccants whose efficiency is known to be such as to exert zero vapor pressure at ordinary temperature (barium oxide¹⁵ was not used in the comparisons). Even at 125° the dehydrating value of silica gel is negligible. "Hydralo" (dehydrated aluminum hydroxide) at 175° is capable of dehydrating hexaquo-magnesium perchlorate only to the formation of tetraquo-magnesium perchlorate. Phosphorus pentoxide at 150° is not nearly as rapid in its dehydration as Anhydrone at the same temperature. In the case of the use of Anhydrone, the lowest known hydrate of magnesium perchlorate (diaquo-magnesium perchlorate) was formed giving the theoretical loss in weight of 21.7%. The use of phosphorus pentoxide at 150° is not recommended since the vapor pressure of its water addition products is appreciable and results in the contamination of the sample dehydrated, vitiating results.

¹⁴ Smith and Rees, *Ind. Eng. Chem.*, **23**, 1328 (1931).

¹⁵ Booth and McIntyre, *Ind. Eng. Chem., Anal. Ed.*, **2**, 12 (1930).

For the experiments given in Table III, a vacuum metal desiccator was used which is to be described in a subsequent paper. It is to be noted that for these experiments in the comparison of the dehydrating efficiency of the various desiccants, hydrated magnesium perchlorate represents the most stable known hydrate for use in such work. Hydrated copper sulfate is ordinarily used but has a higher vapor pressure at comparable temperatures.

Finally, to show experimentally conditions under which the complete list of known hydrates of magnesium perchlorate can be formed, a stock of hexaquo-magnesium perchlorate was stored in a vacuum desiccator without dehydrating agent and kept at 50° with continuous evacuation. A pressure of 10–15 mm. was used for twenty-one days until the loss in weight was constant and tetraquo-magnesium perchlorate formed. The pressure was then reduced to 3–4 mm. and the dehydration completed at the same temperature. The results are shown in Fig. 3. The flat portions of the dehydration curve correspond to the successive dehydrations represented as



The stability of the triaquo derivative is seen to be less marked than of the remaining forms as indicated by slight break in the curve at the point corresponding to this composition. To carry the dehydration to completion a temperature of 150° or above to 250° must be employed.

Heat of Hydration of Various Forms of Hydrated Magnesium Perchlorate.—To show the increase in stability of magnesium perchlorate having various degrees of its coördination valences satisfied, the experimental determination of the heats of hydration and solution of the various forms was undertaken. For this purpose the glass reaction vessel shown in Fig. 2 was employed. The two partition cell of 150–200 cc. capacity is divided by use of the ring seal into a portion A, to contain the water used, separated from the reaction chamber B, which contains the particular form of magnesium perchlorate being examined, by the delivery tube C, which extends compartment B into C. The connection between B and C is made by perforating the thin bulb D using the glass plunger indicated. The method used in charging the sample into the reaction vessel consisted in preparing the particular hydrate of magnesium perchlorate to be used in a reaction tube terminating in a narrow neck which could be

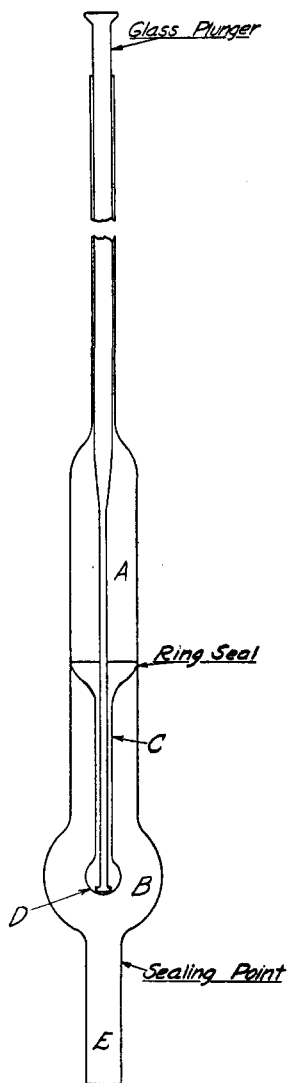


Fig. 2.

inserted within the reaction vessel through tube E. A weighed portion of hexaquo-magnesium perchlorate was dehydrated under the proper conditions to prepare the salt hydrate in question. The dehydration was carried out until, by noting that the loss in weight was the theoretical amount, the reaction was complete. Finally the narrow neck of the sample preparation tube was inserted within E and the apparatus turned upside down to deliver the sample to the calorimeter tube. This was then sealed off under vacuum at the point shown. Excess of water was then added at A and the glass plunger inserted, provided with a small rubber bulb at its upper extremity to provide manual circulation of the solution formed after the partition between sections A and B was broken.

The calorimeter tube (Fig. 2) was provided with two copper bands around sections A and B having copper fins soldered to them bent at such an angle as to give circulation to the water of the calorimeter when a vertical movement of the calorimeter reaction chamber was employed. The calorimeter tube was a large cylindrical Dewar flask inserted within a still larger cylindrical Dewar flask and the latter placed in a can from which it was separated by infusorial earth and the outside of the can encased in felt. The calorimeter tube was mounted in a support which was provided with a mechanism to impart a vertical movement with an amplitude of 5 cm. The plunging mechanism was operated by use of a motor and pulley and the speed was 30-40 vertical displacements per minute. A weighed portion of water was placed in the inside Dewar flask and a Beckmann thermometer within the same flask. The movement of the calorimeter tube with its stirring mechanism attached stirred the bath water and when the condition of temperature equilibrium of the whole system was obtained the partition between the water chamber A (of the reaction vessel) and the reaction chamber B was broken by a gentle downward thrust on the plunger, the time noted, and the temperature rise plotted. The results of the various determinations are given in Table IV.

TABLE IV

HEAT OF SOLUTION OF ANHYDROUS MAGNESIUM PERCHLORATE AND ITS HYDRATES
Calorimeter water used in each case, 830 g.

Material	Dehydration analysis Loss in weight in %		Sample, g.	Rise in temp., °C.	Molecular heat of solution, calories	Mg(ClO ₄) ₂ heat of hydration, calories per gram mole
	Calcd.	Found				
[Mg(H ₂ O) ₆](ClO ₄) ₂	7.4560	-0.02	-738	...
			7.8013	-.025	-881	...
					Av. -809	
[Mg(H ₂ O) ₄](ClO ₄) ₂	10.86	10.3	9.2558	+0.29	7678	8487
			9.5981	+.28	7149	7958
			8.0483	+.22	6698	7507
					Av. 7984	
[Mg(H ₂ O) ₂](ClO ₄) ₂	21.73	21.77	6.0588	+0.52	18466	19275
			7.0998	+.60	18182	18991
			7.3193	+.63	18521	19330
					Av. 19199	
Mg(ClO ₄) ₂	32.60	32.70	7.3531	+1.24	31247	32056
			7.9880	+1.355	31430	32239
			7.6863	+1.37	33021	33830
					Av. 32708	

From an examination of Table IV it is noted that heat of hydration of anhydrous magnesium perchlorate ("Anhydrone") is practically the same as the heat of reaction¹⁶ between the ordinary amorphous form of phosphorus pentoxide and water (33,000 calories per gram mole). Since the heat of reaction evolved in the saturation of the coordinate covalences of the magnesium ion of magnesium perchlorate is approximately equal to the heat of solution of phosphorus pentoxide in water, which is a covalence reaction phenomenon, the equality between these two dehydrating agents (Anhydrone and phosphorus pentoxide) in drying intensity would be predicted and has been established. The heat of reaction involved in the saturation of the first two coordination covalences of the magnesium ion is much greater than that for the saturation of the second pair and the saturation of the last pair results in still less heat evolved. The increase in heat

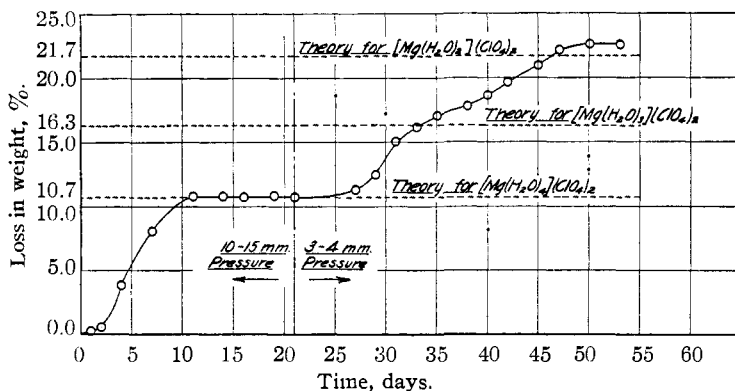


Fig. 3.—Vacuum dehydration of $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, no desiccant, pressures 10-15 and 3-4 mm.

evolved upon hydration of the successively lower forms would be predicted from the increase in temperature required to show a measurable vapor pressure for the same forms. Thus, tetraquo-magnesium perchlorate shows its first appreciable vapor pressure at 50° . The diaquo form shows its first appreciable vapor pressure at 135° . If the heat of hydration of the former is taken as 8000 calories per gram mole, the heat of hydration of the latter would be estimated at 21,500 calories as compared with the value found of 19,200 calories. Conversely, if the heat of hydration of the anhydrous form is 33,000 calories, it would not be expected that the diaquo form would show an appreciable vapor pressure under 200° , which is found to be experimentally justified.

It is to be noted that since the temperature of dehydration of diaquo-magnesium perchlorate must be greater than 135° , anhydrous magnesium

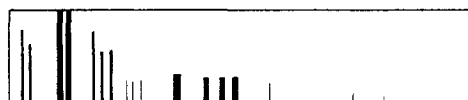
¹⁶ Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1928, Vol. VIII, p. 943.

perchlorate is a perfect drying agent up to this temperature. The use of the latter drying agent at temperatures between 50 and 135° therefore prevents the formation of higher hydrates than the diaquo form and facilitates regeneration of the spent desiccant.

x-Ray Powder Diffraction Patterns of Hydrated Magnesium Perchlorates.—For this study a polychromatic molybdenum radiation produced by a standard outfit together with a Hull Quadrant Cassette with a filter of zirconium dioxide was employed. The method of charging the capillary tubes with the samples in question was a problem because of their extreme deliquescence. The process employed was as follows.

A piece of 15-mm. Pyrex tubing about 7 or 10 cm. in length was drawn out on one end to a capillary of about 6.3 cm. length and a half to one mm. bore. A sample of

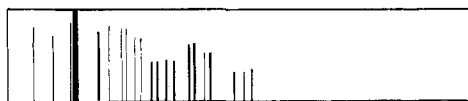
magnesium perchlorate hexahydrate, which had been thoroughly ground, together with five or six $\frac{3}{16}$ -inch steel ball bearings, was placed in the large part of the tube. The large end of the tube was then drawn down in the flame and a long piece of 6-mm. glass tubing sealed on. The whole thing was then placed in an electric oven at the desired temperature with the long glass tube extending out through the top of the oven. This tube was connected to a vacuum pump with a weighed anhydrous tube in the line. By regulating the temperature of the oven the desired dehydration of the hexahydrated material could be brought about and this could be followed by the increased weight of the drying tube. When the theoretical loss for the production of the desired hydrate had occurred, the system was removed from the oven, rolled and shaken in order to effect grinding, and the capillary packed by tapping the material gently down into it. When this was completed the capillary was



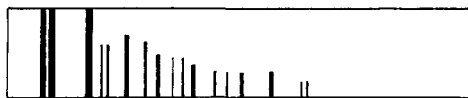
Anhydrous.



Diaquo.



Tetraquo.



Hexaquo.

Fig. 4.

fused off near the large tube. Later a sample was removed from the large tube and analyzed. This gave a double check on the constitution of the material in the capillary tube.

The results from the x-ray powder diffraction photographs are shown by reference to Fig. 4. It will be seen from an examination of the results from the various samples that separate and distinct patterns are shown for each form and the deviation is least pronounced in the comparison of the hexaquo and tetraquo forms. The x-ray examination of the various hydrates of magnesium perchlorate cannot be extended to include Laue

diffraction patterns until a process is developed for the preparation of individual crystals of the various types for examination. This problem is complicated by the fact that the lower hydrates cannot be prepared in aqueous solution by ordinary processes because of the high temperature required. The x-ray powder patterns indicate the existence of the various forms associated with marked distinctions in structural relationships.

Assistance on the part of Professor G. L. Clark in the x-ray studies is gratefully acknowledged.

Summary

1. The structural relationships existing between the numerous forms of the hydrated perchloric acids have been discussed and the experimental justification for the conclusions drawn has been indicated.

2. Two new forms of hydrated magnesium perchlorates, diaquo- and tetraquo-magnesium perchlorate, were predicted from a study of the various hydrates of perchloric acid and the conditions for their preparation described.

3. Vapor pressure studies involving the use of the various forms of hydrated magnesium perchlorates have been made and the dehydrating efficiency of the anhydrous form compared to that of other highly intensive desiccants.

4. x-Ray powder diffraction patterns of the various hydrates of magnesium perchlorate have been prepared.

URBANA, ILLINOIS

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THE ENTROPIES OF SOME SIMPLE POLYATOMIC GASES CALCULATED FROM SPECTRAL DATA

BY RICHARD M. BADGER AND SHO-CHOW WOO

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Introduction

Knowledge of the nature of the energy levels of diatomic molecules has now advanced to such a state that when appropriate data are available it is possible to calculate specific heats and entropies with great accuracy and with results in which we may be entirely confident, as has been shown by comparisons between calculated values and those obtained from specific heat data.

The polyatomic molecule in most cases offers considerably greater difficulties, and for those of the most general type there is as yet probably no case in which data are available for making any exact calculation. However, in two special cases the computation becomes very much sim-