DETERMINATION OF MAGNESIUM

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Reading through the literature on the determination of magnesium, one finds various methods of procedure, and also varying statements regarding the properties of the precipitates formed. Practically all give the $MgNH_4PO_4 \cdot 6H_2O$ method for the separation of the magnesium from the solution, but they differ in the procedure of separation as well as in the method of drying, igniting, and weighing the precipitate.

This research is an attempt to check some of the statements regarding the properties of the precipitates. First, an attempt was made to determine the transition temperatures of $MgNH_4PO_4 \cdot 6H_2O$. The material was prepared by dissolving 20 g. of C.P. $MgCl_2 \cdot 6H_2O$ in about 1500 ml. of distilled water, adding 25 g. of NH_4Cl, making slightly acid with HCl, neutralizing by adding NH_4OH dropwise, adding NH_4OH to 1.5 molar and allowing to stand over night. The precipitate was then collected on a large Buechner funnel, washed free from chlorides, and dried at room temperature (24°C.).

Samples were then placed in a dilatometer tube with C.P. toluene. A check

sample of Rochelle salts was placed in a similar tube, and the two were placed side by side in a bath of glycerol. The temperature of the bath was raised one degree at a time and the readings of the rise in the tube were taken.

The rise per degree was quite uniform in both tubes up to 54°C., when the tube containing the Rochelle salts gave a sudden rise; but no rapid rise in the tube with the magnesium salt was noted until 85-86°C., at which temperature gas bubbles arose, rapidly forcing the liquid out of the tube.

Another method suggested by Hamrich, (J. Chem. Soc. 1589, 1920) was tried. Samples of the two hydrates were placed in toluene in test-tubes with thermometers, in a bath of glycerol. The glycerol bath was heated slowly with an electric heater, and the behavior of the crystals was watched very carefully at each rise in temperature. No change in either tube was noted until 54°C. when the crystals of Rochelle salts could be seen to crack and break down, while drops of moisture could be seen to collect around them. No change could be noted in the magnesium salt until 60°C. when an occasional bubble of gas would form around the crystals; but no noticeable action occurred until 85°, when the bubbling continued for several minutes. The gas given off at this temperature turned litmus blue and was evidently NH_3. Water would not boil off at this temperature and neither was any moisture noted around the crystals, as was noted with the Rochelle salts.

Effect of Heating at Different Temperatures

Six samples were prepared by taking 50 ml. (with a pipette) from a solution of $MgCl_2$ (made up 1 g. Mg. per liter), precipitated as above, and after standing over night, filtered into previously prepared and weighed Gooch crucibles marked A, B, C, D, E, F. After filtering, the samples were washed free from chlorides with 1.5 molar NH_4OH, allowed to dry on the suction for about 15 minutes, and then allowed to stand at room temperatures for one hour. Samples A, B, D, and F were placed in an electric oven at 75°C. Sample C was left in the desiccator over $CaCl_2$. After one hour the samples were removed from the oven, cooled in a desiccator, and weighed: A 0.4438; B 0.3574; D 0.4643, E 0.4952; and F 0.4595. C, which remained in the desiccator at room temperature, weighed 0.5017, which is nearly theoretical for the hexahydrate.

Samples A, B, C, and D were then placed in the oven at 75°C. and left over night. E and F remained in the desiccator. After cooling in the desiccator and weighing: values A 0.2976; B 0.3115; C 0.2955; D 0.3105; E 0.4940; and F 0.4595 were obtained. Samples were again placed in the oven, and the temperature was raised to 85°C. These were left for 24 hours, then cooled and weighed: A 0.2952; B 0.3005; C 0.2898; D 0.3009. These show only slight decrease in weight even at ten degrees rise in temperature. Samples C and D were replaced in the over at 85°C. and left another 24 hours with no further loss in weight.

Further Heating of Samples C and D						
24	hours	at	92°	C 0.2858	D	0.2875
24	"	"	115°	" 0.2754	"	0.2773
24	"	"	165°	" 0.2634	"	0.2624
24	"	"	300°	" 0.2458	"	0.2465
24	"	"	500°	" 0.2378	"	0.2380
24	"	"	700°	" 0.2376	"	0.2375
24	"	"	800°	" 0.2376	"	0.2375
24	"	"	900°	" 0.2376	"	0.2375

Loss on heating seemed to be complete at 700°C., as no further loss was noted up to 900°C. Also, 85°C. seemed to be the transition point of some definite compound.

Four more samples were prepared and filtered in the same manner as above, dried by suction, placed in the desiccator, left at room temperature for seven days, then weighed: G 0.4830; H 0.5164; I 0.5144; and J 0.5161. Sample G seemed to be an exception and was left in the desiccator. Sample I, of this set, and sample B, of the former set, were run for N_2 by the Kjeldahl method: I 0.0305 g. N_2 and B 0.0115 g. N_2. Sample I showed nearly the theoretical amount of N_2 for the hexahydrate, while B, which had been heated to 85°C. for 24 hours, lost two-thirds of its nitrogen. This shows that the loss in weight of samples heated above 85°C is not all water of hydration, as many have stated, but is also NH_3. Samples H and J were then heated in the muffle in 24 hour stages with the following results:

24	hours	at 300°	H 0.2476	J 0.2490
24	"	" 500°	" 0.2371	" 0.2383
24	"	" 600°	" 0.2361	" 0.2364
24	"	" 700°	" 0.2361	" 0.2360
24	"	" 800°	" 0.2361	" 0.2360

Another set of six samples were prepared as before. Three were left in the desiccator while the other three were placed in the oven at 60°C. then taken out and cooled in the desiccator and weighed at 24-hour intervals.

24	hrs.	at 60°	K 0.3547	L 0.3476	M 0.3340
48	"	" "	" 0.3024	" 0.3054	" 0.3040
72	"	" "	" 0.2994	" 0.3002	" 0.2978
96	"	" "	" 0.2979	" 0.2992	" 0.2978

Samples of N, I, and B Remaining in Desiccator

48 hours in Desiccator	N 0.5170	I 0.5198	B 0.5226
4 weeks in Desiccator	N 0.5161	I 0.5090	B 0.5200
10 weeks in Desiccator	N 0.5062	I 0.5046	B 0.5176

Samples N and B of the above were run for N_2 with the following results: N 0.308 and B 0.0315. These are just slightly above theoretical for the hexahydrate. Samples K, L, and M came to quite a constant weight after 96 hours at 60°C., supporting a statement by Warshaw that above 50°C., samples of hexahydrate, after 15 days, lost 41.75 per cent of their weight.

Six more samples were prepared as before. Three were placed in the oven at 75°C., and three were left in the desiccator. After 48 hours, the average weight from the oven was 0.2962, and the average weight of those in the desiccator was 0.5133. These samples were then run for N_2. Those from the desiccator averaged 0.0308, and those from the oven averaged 0.0116.

Again, samples heated in the oven over 50°C. and under 85°C. lose about 40 per cent of their weight, as suggested by Warshaw, but of this 40 per cent about two-thirds of their notrogen is included.

Comparison of Hot and Cold Methods

Six samples were prepared hot and made slightly acid with HCl; 40 per cent excess of $(NH_4)_2HPO_4$ was added, the solution was heated to boiling, then NH_4OH from a dropping funnel was added until alkaline, while stirring with an electric stirrer. It was cooled in ice water, made alkaline with NH_4OH to 1.5 molar, stirred for ten minutes, and allowed to stand for 24 hours. These samples were then filtered into prepared Gooch filters, dried, washed, placed in the electric furnace, heated to 900°C., cooled, and weighed. The precipitates were more crystalline than those prepared cold. They filtered more easily, and took less time to wash free from chlorides. The average weight was 0.2276.

Six samples were prepared in the same way except that they were cold. They were washed, dried, placed in the electric oven, and heated to 900°C. The average weight of these was 0.2304. The theoretical value for $Mg_2P_2O_7$ is 0.2289.

Summary

The cooling of the $MgNH_4PO_4 \cdot 6H_2O$ sample should be as rapid as posisble; the precipitation should be kept below 30°C.

The weight is retained for weeks in a desiccator if the temperature has previously been kept below 30°C. However, as much as two-thirds of the NH_3 is lost if the temperature goes above 50°C.

The hot precipitation gives slightly lower results than the cold, but it has the advantage of yielding larger crystals.