

TABLE IV
ANALYSIS OF TERNARY COMPOUND

	Uncorrected analysis, %	Corrected analysis, %	Calculated for $2\text{NaIO}_3 \cdot 3\text{NaNO}_3 \cdot 15\text{H}_2\text{O}$
NaIO_3	42.06	42.60	42.97
NaNO_3	28.91	28.00	27.69
H_2O	29.03	29.40	29.34

The upper temperature limit for the ternary compound is at about 9.6° , as found by thermal measurements—in sufficient agreement with Foote and Vance's figure 9.8° , accurate measurements not being possible because of the apparently slow formation of the compound. It is obvious that the existence of this compound will have an important influence upon the separation of sodium nitrate and sodium iodate at any temperature below this point.

Summary

1. Solubility measurements are given for sodium iodate in water between 5 and 50° , and for the three-component system consisting of sodium iodate, sodium nitrate and water at 5 , 25 and 50° .

2. The stable hydrates of sodium iodate are the pentahydrate below 20° , and the monohydrate above that temperature to its transition to the anhydrous form.

3. Hydrated sodium iodate does not reach equilibrium with its solution, from both undersaturation and supersaturation, within twenty-six days or more.

4. In the ternary system below 9.8° there exists a double salt of the formula $2\text{NaIO}_3 \cdot 3\text{NaNO}_3 \cdot 15\text{H}_2\text{O}$.

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TERNARY SYSTEMS. X. MAGNESIUM IODATE, MAGNESIUM NITRATE AND WATER¹

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For the work upon this ternary system, knowledge of the two binary systems of a single salt and water are necessary. Investigations of the solubility of magnesium nitrate in water have been conducted by Chodnew,² Lescoeur,³ Ditte,⁴ Ordway⁵ and Funk,⁶ the latter determined that only

¹ The material of this paper was presented by Samuel Moskowitz in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

² Chodnew, *Ann.*, 71, 241 (1849).

³ Lescoeur, *Ann. chim. phys.*, [7] 7, 419 (1896).

⁴ Ditte, *ibid.*, [5] 18, 320 (1879); *Compt. rend.*, 89, 641 (1879).

⁵ Ordway, *Am. J. Sci.*, [2] 27, 16 (1859).

⁶ Funk, *Ber.*, 32, 96 (1889); *Z. anorg. Chem.*, 20, 395 (1899).

two hydrates have stable existence, $\text{Mg}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ from -29 to -18° , and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from -18° to its congruent melting point at 90° . We have not repeated this work. For magnesium iodate and water it was found that the work of Millon,⁷ Ditte⁸ and Mylius and Funk⁹ should omissions, for which reason the work has been repeated.

Magnesium Iodate and Water.—Magnesium iodate was prepared according to the method of Millon,⁷ by neutralizing an aqueous solution of iodic acid with magnesium carbonate and evaporating the slightly acidified solution at above 40 – 50° for four days, which gave a copious crystallization of the tetrahydrate. The crystals were washed with water, air dried, ground and placed in a desiccator; here there developed an outstanding peculiarity of the compound. The tetrahydrate loses only an inappreciable weight of water at room temperature over sulfuric acid or phosphorus pentoxide; a sample of 220 g. lost about 1 mg. per day over concentrated sulfuric acid, and a sample of 67 g. lost about 0.6 mg. per day over phosphorus pentoxide. Samples kept in an oven at 110° lost rapidly for a few days, but could not be brought to an anhydrous condition in a month, the residual water being about 0.5% for finely ground samples and considerably larger for coarse samples. Mylius and Funk report the tetrahydrate as stable at 80° . These results at room temperature and even at the higher temperature are most striking in view of the fact, later shown, that the hydrate has a transition temperature at about 57.5° and therefore has a vapor tension at that temperature equal to that of the saturated solution, which may be calculated by Raoult's law as approximately 128 mm. Either the vapor tension curve for this hydrate is astonishingly steep, or the hydrate shows a remarkable degree of metastability with regard to dehydration; we are inclined to accept the latter view as the better interpretation. Samples which had been over the desiccating agent for several weeks were analyzed by titration and found to have the composition $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ within the errors of titration. This material was later used in the three-component work as of constant and known composition, since efforts to prepare the anhydrous compound by oven treatment had not been successful.

For the solubility determinations, excess salt was treated with distilled water in glass-stoppered pyrex tubes; for the lower temperatures the tubes were rotated in a water thermostat, constant to about 0.03° . For temperatures above 50° the tubes were inserted in an air thermostat and stirred by means of a brass paddle on a mechanical stirrer; a mercury seal served to minimize evaporation. Filtered samples were withdrawn by calibrated pipets at the lower temperatures and weighed to give approximate figures for density; at the higher temperatures the samples were forced through a tube into a weighing bottle by air pressure, crystallization being easily avoided because of the marked metastability. At the lower temperatures, one to three days of stirring were found to give equilibrium from undersaturation, while from supersaturation long periods were needed. Seeding with a crystal of decahydrate was resorted to below 13° . Where the change from the tetrahydrate to the anhydrous form occurs, four days of stirring were required at 80° and two days at 90° ; at 70° the solid phase used was anhydrous salt, obtained at the higher temperatures, equilibrium being reached within one day. Analysis of the centrifuged solid phase obtained at 90° was in good agreement with the requirements for the anhydrous form. The results are given in Table I and shown in Fig. 1.

The solubility figures were obtained by titrating with standard thio-sulfate the iodine freed by action of the samples upon potassium iodide

⁷ Millon, *Ann. chim. phys.*, [3] 9, 422 (1843).

⁸ Ditte, *ibid.*, [6] 21, 154 (1890).

⁹ Mylius and Funk, *Ber.*, 30, 172 (1897).

TABLE I
SOLUBILITY OF MAGNESIUM IODATE IN WATER

Temp., °C.	Wt., % of $Mg(IO_3)_2$ in satd. soln.	Density	Solid phase	Temp., °C.	Wt., % of $Mg(IO_3)_2$ in satd. soln.	Density	Solid phase
-0.36	3.18	1.026	$I_{10} + \text{ice}$	40	10.51	1.090	I_4
+5	4.39	1.034	I_{10}	50	12.05	1.115	I_4
10	5.87	1.049	I_{10}	57.5	13.1	...	I_4
15	7.79	1.073	$I_{10} \text{ (m)}$	70	15.7	...	$I_4 \text{ (m)}$
5	6.09	1.047	$I_4 \text{ (m)}$	90	19.6	...	$I_4 \text{ (m)}$
10	6.68	1.060	$I_4 \text{ (m)}$	60	13.2	...	I
15	7.29	1.065	I_4	70	13.3	...	I
25	8.55	1.075	I_4	80	13.4	...	I
35	9.83	1.086	I_4	90	13.5	...	I

solution with sulfuric acid. In the fourth column of the above table, the abbreviation I_{10} is used for the decahydrate, I_4 for the tetrahydrate, I for the anhydrous form; (m) indicates that the solid phase was metastable, by interpretation of Fig. 1. The system is, therefore, found to show the

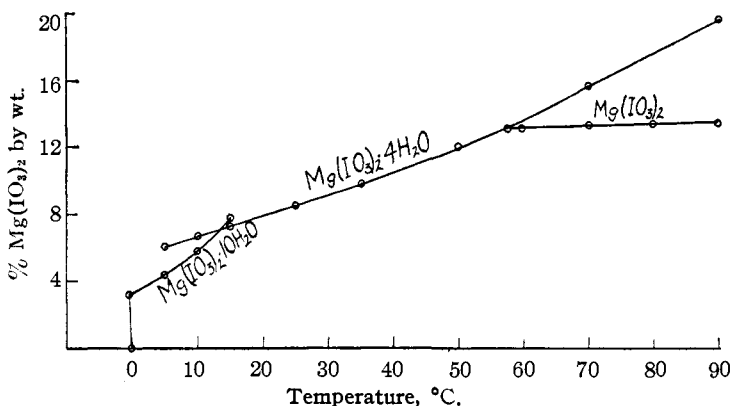


Fig. 1.—Solubility of magnesium iodate.

following invariant points: a eutectic at -0.36° found by the usual thermal means, a transition of the decahydrate to the tetrahydrate at 13.3° (by interpolation), and a transition of the tetrahydrate to the anhydrous form at 57.5° . Because of the great tendency toward metastability, confirmation of these transition points by thermal means was not possible. Whether or not the remarkable behavior of the tetrahydrate is connected with the possible poly-basidity of iodic acid and the constitution of the compound as an acid salt rather than a true hydrate would be mere speculation in the absence of other data.

The Ternary System.—The phase complexes used in the study of the ternary system were made from weighed amounts of magnesium iodate tetrahydrate, water and an analyzed solution of purified magnesium

nitrate nearly saturated at room temperature; the latter solution was used since it is impossible to dehydrate crystallized magnesium nitrate without hydrolytic decomposition. In a few instances it was necessary to use magnesium nitrate hexahydrate which had been partially dehydrated, in

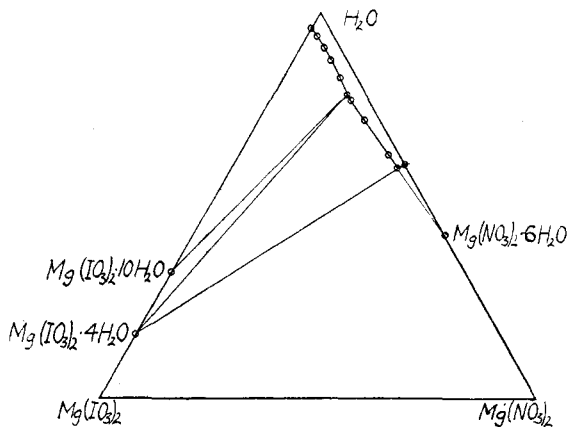


Fig. 2.—5° Isotherm: $\text{Mg}(\text{IO}_3)_2$ - $\text{Mg}(\text{NO}_3)_2$ - H_2O .

order to reduce the water content of the complex. The materials were agitated in the thermostat at the desired temperature for periods of one to three days. For the analysis of the ternary solutions, the method of iodimetry was used to give part of the necessary data, but evaporation to

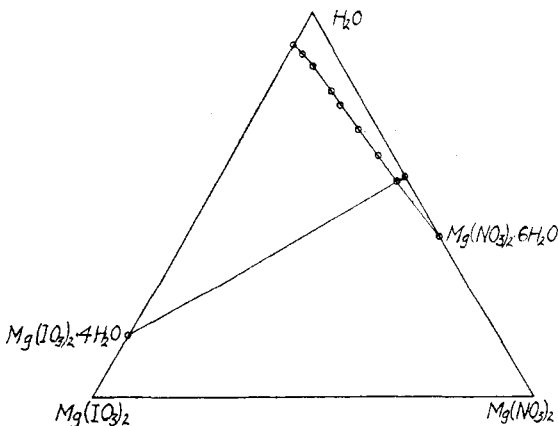


Fig. 3.—25° Isotherm: $\text{Mg}(\text{IO}_3)_2$ - $\text{Mg}(\text{NO}_3)_2$ - H_2O .

dryness for the water content was found impossible for the two reasons stated—incomplete dehydration of the iodate and hydrolysis of the nitrate. A determination of total magnesium was therefore necessary for the calculation of the composition of the solutions. Investigation of solutions

of known magnesium content showed that precipitation as magnesium ammonium phosphate and weighing either as the hexahydrate or by conversion to magnesium pyrophosphate gave distinctly high results; the same was true, though to a much less degree, of the values obtained by igniting the salts to form magnesium oxide. The method used, which gave results only 0.25% low with a known solution, consisted in evaporation on a steam-bath with excess sulfuric acid, finally raising the temperature over a burner to a dull red for a brief time, and weighing the residue as $MgSO_4$.

Table II gives the results obtained at 5, 25 and 50°. The curves are plotted in Figs. 2, 3 and 4.

TABLE II
SYSTEM: $Mg(NO_3)_2$ - $Mg(IO_3)_2$ - H_2O

Temp.	Original complex		Saturated solution		Density	Solid phase
	Wt., % $Mg(NO_3)_2$	Wt., % $Mg(IO_3)_2$	Wt., % $Mg(NO_3)_2$	Wt., % $Mg(IO_3)_2$		
5°	0.00	...	0.00	4.39	1.034	I_{10}
	2.19	11.35	2.49	3.93	1.053	I_{10}
	4.89	10.18	5.45	3.92	1.076	I_{10}
	8.03	8.96	8.86	4.03	1.105	I_{10}
	12.38	7.65	13.10	4.26	1.149	I_{10}
	16.43	6.77	17.00	4.55	1.184	$I_{10} + I_4$
	12.22	24.39				
	13.51	25.66	18.52	4.44	1.197	I_4
	17.95	24.30	24.08	3.95	1.244	I_4
	33.53	4.54	34.21	2.82	1.333	I_4
	38.36	6.69	38.10	2.39	1.368	$I_4 + N_6$
	41.48	0.40	39.02	0.46	1.352	N_6
00	39.25	.00	1.347	N_6
	0.0	...	0.00	8.55	1.075	I_4
	3.26	12.12	3.49	7.35	1.089	I_4
	6.91	10.91	7.31	6.66	1.116	I_4
13.37	12.23	14.60	5.66	1.171	I_4	
17.14	10.86	18.48	5.14	1.202	I_4	
24.00	9.82	25.81	4.20	1.261	I_4	
29.14	13.62	33.50	3.25	1.325	I_4	
...	...	41.00	2.46	1.398	$I_4 + N_6$	
...	...	41.60	0.90	1.380	N_6	
...	0.00	42.03	.00	1.378	N_6	
25°	0.00	...	0.00	12.05	1.115	I_4
	6.88	16.69	7.78	9.00	1.141	I_4
	13.95	14.49	15.17	7.31	1.186	I_4
	21.62	14.18	24.35	5.58	1.253	I_4
	28.21	14.01	32.15	4.36	1.321	I_4
	34.79	11.62	38.82	3.57	1.368	I_4
	44.41	3.13	...	$I_4 + N_6$
	45.27	1.52	...	N_6
	...	0.00	46.09	0.00	...	N_6
	50°	0.00	...	0.00	12.05	1.115
6.88		16.69	7.78	9.00	1.141	I_4
13.95		14.49	15.17	7.31	1.186	I_4
21.62		14.18	24.35	5.58	1.253	I_4
28.21		14.01	32.15	4.36	1.321	I_4
34.79		11.62	38.82	3.57	1.368	I_4
...		...	44.41	3.13	...	$I_4 + N_6$
...		...	45.27	1.52	...	N_6

N_6 represents $Mg(NO_3)_2 \cdot 6H_2O$

The solid phases at these three temperatures are determined beyond question by the extrapolation of the tie-lines from the composition of the saturated solution through the composition of the original complex used. At 5° there are found not only the hexahydrated magnesium nitrate and the decahydrated magnesium iodate, but also the tetrahydrated magnesium iodate in those solutions where the vapor tension has been greatly lowered by the highly soluble magnesium nitrate. At 25° only the two salts, each stable in water at this temperature, are found. At 50° the

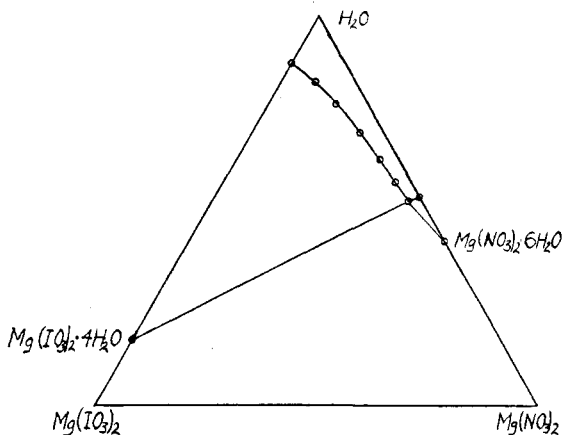


Fig. 4.—50° Isotherm: $\text{Mg}(\text{IO}_3)_2$ - $\text{Mg}(\text{NO}_3)_2$ - H_2O .

same condition prevails; were it not for the strange behavior of the magnesium iodate tetrahydrate already stated, one would be ready to predict that the anhydrous form should also appear, since the high concentration of magnesium nitrate obviously lowers the vapor tension greatly. The extrapolated tie-lines however point to the tetrahydrate as solid phase in every instance.

Summary

1. It is found that magnesium iodate and water give not only the decahydrate and tetrahydrate previously known, but also an anhydrous form stable in contact with water above 57.5°.

2. The solubility of magnesium iodate in water has been determined from -0.36° , the eutectic temperature, to $+90^\circ$.

3. Ternary isotherms have been studied for magnesium iodate, magnesium nitrate and water at 5, 25 and 50°. No double compounds have been found.

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