

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF ST. STEPHENS COLLEGE AND OF  
NEW YORK UNIVERSITY]

## TERNARY SYSTEMS. XV. POTASSIUM IODATE, POTASSIUM NITRATE AND WATER. XVI. CALCIUM IODATE, SODIUM IODATE AND WATER

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### XV. POTASSIUM IODATE, POTASSIUM NITRATE AND WATER

Investigations of the ternary system consisting of sodium iodate, sodium nitrate and water have recently been made at Yale University<sup>1</sup> and at New York University.<sup>2</sup> The corresponding potassium salts are the subject of this investigation, giving information as to another of the systems of possible interest in relation to the Caliche.

The experimental conditions observed were, in general, those described in earlier papers of this series.<sup>2</sup> Measurements at 5 and 25° were conducted in the usual type of laboratory thermostat, those at 50° in a smaller thermostat of special construction. The salts used were commercial products of good quality, purified by recrystallization from water. The phase complexes used were made up by weight from salts and water and were rotated in closed tubes for periods from one week to two weeks (which time was shown by analysis of solutions to be sufficient for attainment of external equilibrium) in order to minimize the irregularities in solubility shown by the potassium iodate;<sup>3</sup> after the solid had settled, samples were withdrawn by pipet, analyzed iodimetrically for the iodate content and by evaporation to constant weight for the water content; the potassium nitrate was determined by difference. In Table I are given the data.

TABLE I  
THE SYSTEM  $\text{KIO}_3\text{-KNO}_3\text{-H}_2\text{O}$

Temp., °C.	Original complex		Saturated solution		Density	Solid phase
	$\text{KIO}_3$ wt., %	$\text{KNO}_3$ wt., %	$\text{KIO}_3$ wt., %	$\text{KNO}_3$ wt., %		
5	10.00	0.00	5.25	0.00	1.043	$\text{KIO}_3$
	10.00	5.00	3.29	5.36	1.060	$\text{KIO}_3$
	8.00	10.00	2.93	10.53	1.090	$\text{KIO}_3$
	7.00	13.00	2.89	13.53	1.110	$\text{KIO}_3$
	6.00	15.00				
	5.00	17.00	2.87	14.14	1.120	$\text{KIO}_3 + \text{KNO}_3$
	1.00	20.00	1.08	14.26	1.100	$\text{KNO}_3$
	0.00	20.00	0.00	14.43	1.097	$\text{KNO}_3$

<sup>1</sup> Foote and Vance, *Am. J. Sci.*, **18**, 375 (1929).

<sup>2</sup> Hill and Donovan, *This Journal*, **53**, 934 (1931).

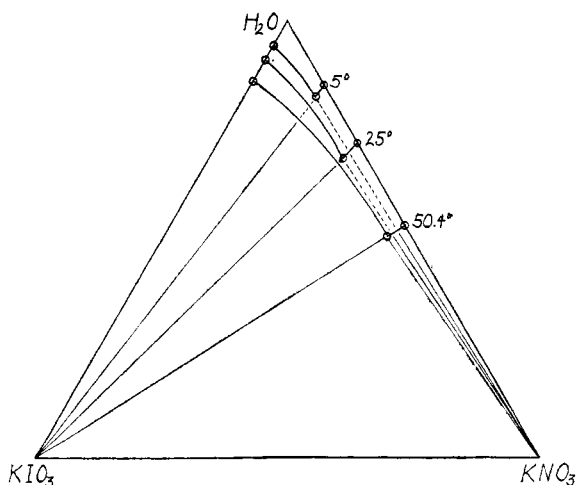
<sup>3</sup> Hill and Ricci, *ibid.*, **53**, 4305 (1931).

TABLE I (Concluded)

Temp., °C.	KIO <sub>3</sub> wt., %	KNO <sub>3</sub> wt., %	KIO <sub>3</sub> wt., %	KNO <sub>3</sub> wt., %	Density	Solid phase
25° <sup>a</sup>	20.00	0.00	8.46	0.00	1.072	KIO <sub>3</sub>
	15.00	5.00	5.92	5.48	1.084	KIO <sub>3</sub>
	22.13	7.00	5.25	8.51	1.110	KIO <sub>3</sub>
	15.00	15.00	4.57	16.77	1.156	KIO <sub>3</sub>
	21.44	14.96	4.48	18.19	1.160	KIO <sub>3</sub>
	...	...	4.21	26.84	1.232	KIO <sub>3</sub> + KNO <sub>3</sub>
	2.00	45.00	2.65	27.25	1.215	KNO <sub>3</sub>
	1.62	42.69	2.06	27.30	1.210	KNO <sub>3</sub>
	...	35.00	0.00	27.79	1.192	KNO <sub>3</sub>
50.4	20.00	...	13.35	...	1.110	KIO <sub>3</sub>
	20.00	15.00	7.32	17.42	1.167	KIO <sub>3</sub>
	10.00	30.00	5.79	31.43	1.259	KIO <sub>3</sub>
	13.63	34.55	5.30	37.83	1.31	KIO <sub>3</sub>
	15.00	35.00	5.17	39.17	1.33	KIO <sub>3</sub>
	15.00	38.00	4.91	42.42	1.35	KIO <sub>3</sub>
	...	...	4.75	44.23	1.37	KIO <sub>3</sub> + KNO <sub>3</sub>
	2.00	55.00	2.44	45.44	1.34	KNO <sub>3</sub>
	...	50.00	...	46.57	1.326	KNO <sub>3</sub>

<sup>a</sup> The 25° isotherm includes some results obtained by Dr. John E. Ricci.

The solubility of potassium nitrate in water at the three temperatures is within 0.1 to 0.3% of the figures given for the average of all previous investigations in the "International Critical Tables." The identity of

Fig. 1.—KIO<sub>3</sub>-KNO<sub>3</sub>-H<sub>2</sub>O.

the solid phases is established by the method of extrapolation of the tie-lines passing through the points for the composition of the solutions and those of the original complexes. Using the method of algebraic extrapola-

tion in order to secure a degree of accuracy not easily obtainable by graphic methods, it was found that the whole series of tie-lines passed through the points for the two pure anhydrous salts with an average deviation for all cases of 0.87%, the maximum being 3.56% in the least favorable case; in only five of the sixteen cases do the variations exceed 1%. Since the errors of the work are multiplied about tenfold in the extrapolation, it may be deduced that the concordance of the points with each other is within about 0.1% on the average.

The plot of the three solubility curves is shown in Fig. 1. At the temperatures studied, no compound formation appears similar to that found for the corresponding sodium salts,<sup>1,2</sup> which is in keeping with the known fact that double salts form less commonly with potassium salts than with sodium salts.

### XVI. CALCIUM IODATE, SODIUM IODATE AND WATER

The solubility of calcium iodate in water has previously been investigated by Mylius and Funk,<sup>4</sup> up to 100°; they found the hexahydrate the stable form up to about 32° and the monohydrate stable from that temperature up to 100°. Our investigation disclosed that there is a transition to the anhydrous salt at temperatures considerably below 100°, for which reason the solubility has been redetermined throughout. The salt was prepared by double decomposition of calcium nitrate and sodium iodate in water, washed, purified by recrystallization and the two hydrates obtained by slow cooling within the correct temperature range as given below; each sample was dried in a miniature desiccator over the next lower hydrate as desiccant, and was found on analysis to have the correct composition within a few tenths of a per cent. The anhydrous form was made by dehydration in an oven at 100°. In carrying out the solubility determinations, care was taken to use the correct solid phase in each instance, and the time allowed for equilibrium varied from one day at the highest temperature to two to three weeks (which time was shown by analysis of solution to be sufficient for attainment of external equilibrium) at the lower temperatures. By using metastable phases, several points for metastable equilibrium were obtained, in which the metastable solubility remained constant for as long a period as two weeks. Analysis of pipetted samples was conducted by the method of iodimetry. The results are given in Table II.

The graph of the results given in Fig. 2 shows clearly the existence of the three solid phases, with transition temperatures of about 35 and 57.5°; these were not determined by thermal means because of the marked metastability of the various forms. The anhydrous form, having a nearly flat solubility curve, was missed by Mylius and Funk; their figures for tem-

<sup>4</sup> Mylius and Funk, *Ber.*, **30**, 1724 (1897).

TABLE II  
SOLUBILITY OF CALCIUM IODATE IN WATER

Temp., °C.	Ca(IO <sub>3</sub> ) <sub>2</sub> , wt., %		Average	Solid phase
	From under-saturation	From super-saturation		
5	0.118	0.120	0.119	Ca(IO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
15	.194	.196	.195	Ca(IO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
25	.306	.307	.306	Ca(IO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
30	.384	.384	.384	Ca(IO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
35	.475	.477	.476	Ca(IO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O + Ca(IO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O
40	.584	...	.584	CaIO <sub>3</sub> ·6H <sub>2</sub> O (m) <sup>a</sup>
25	...	0.405	.405	Ca(IO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O (m)
40	0.514	.519	.517	Ca(IO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O
50	.589	.590	.590	Ca(IO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O
57.5	.621	...	.621	Ca(IO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O + Ca(IO <sub>3</sub> ) <sub>2</sub>
60	.652	...	.652	Ca(IO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O (m)
70	.811	...	.811	Ca(IO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O (m)
60	...	0.617	.617	Ca(IO <sub>3</sub> ) <sub>2</sub>
70	0.643	.645	.644	Ca(IO <sub>3</sub> ) <sub>2</sub>
80	.665	.665	.665	Ca(IO <sub>3</sub> ) <sub>2</sub>
90	.668	.668	.668	Ca(IO <sub>3</sub> ) <sub>2</sub>

<sup>a</sup> m, metastable.

peratures above 60° were doubtless due to the presence of the metastable monohydrate.

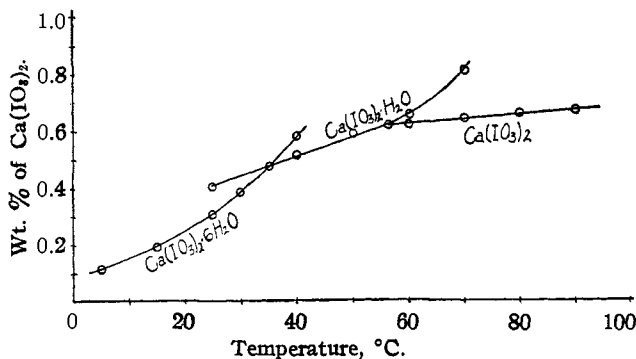


Fig. 2.—Ca(IO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O.

The ternary system was studied at a single temperature only. The samples were rotated for about two weeks, to minimize the supersaturation with respect to sodium iodate which has been noted in earlier investigations.<sup>2</sup> Pipetted samples were analyzed for total iodate by the method of iodimetry, and for calcium by precipitation with ammonium oxalate. The figures are given in Table III.

The results are also graphed in Fig. 3. By extrapolation of the tie-lines, it becomes apparent that the hexahydrate of calcium iodate is the only

TABLE III  
THE SYSTEM  $\text{Ca}(\text{IO}_3)_2\text{-NaIO}_3\text{-H}_2\text{O}$  AT  $25^\circ$

Original complex		Saturated solution		Density	Solid phase
$\text{Ca}(\text{IO}_3)_2$ wt., %	$\text{NaIO}_3$ wt., %	$\text{Ca}(\text{IO}_3)_2$ wt., %	$\text{NaIO}_3$ wt., %		
..	0.00	0.306	0.000	...	$\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$
4.97	.50	.084	.522	1.00	$\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$
4.99	4.99	.000	5.29	1.041	$\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$
1.00	12.04	.000	8.58	1.074	$\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NaIO}_3 \cdot \text{H}_2\text{O}$
0.00	...	.000	8.58	...	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$

stable phase of that salt appearing, and that the common ion from sodium iodate reduces its solubility to an amount too small to be determined for the greater part of the isotherm; 10-g. samples failed to give a weighable precipitate on treatment with ammonium oxalate. The composition at the isothermally invariant point is the same as for saturation with sodium iodate alone, within the errors of analysis. Because of the lack of compound formation and the low solubility of the calcium salt, it was thought unnecessary to complete isotherms at other temperatures.

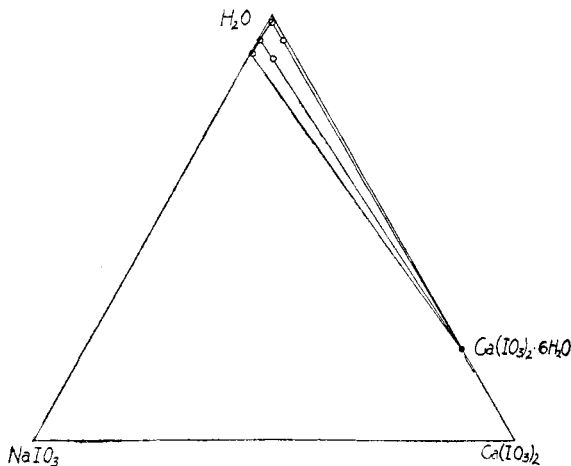


Fig. 3.— $\text{Ca}(\text{IO}_3)_2\text{-NaIO}_3\text{-H}_2\text{O}$ .

### Summary

The ternary system consisting of potassium iodate, potassium nitrate and water has been studied at  $5$ ,  $25$  and  $50.4^\circ$ ; there is no compound formation. The solubility of calcium iodate in water has been redetermined from  $5$  to  $90^\circ$ ; a new transition from the monohydrate to the anhydrous form has been found to occur at  $57.5^\circ$ . The ternary isotherm of calcium iodate, sodium iodate and water at  $25^\circ$  has been studied.

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