

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary Systems $\text{KIO}_3\text{-KBr-H}_2\text{O}$ and $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$

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The following two systems have been investigated in order to continue the study undertaken at New York University of three-component systems involving salts found in the caliche of Chile, and in order to have more complete data on the formation of double salts by potassium iodate and sodium iodate. The discussion of this latter point will be taken up in a subsequent paper on compound formation between sodium iodate and sodium iodide.

The salts for these systems were prepared by recrystallization from the best available c. p. material, which, in the case of the bromides, usually contains from 0.5 to 1.0% of chloride. The purified salts were dried to the anhydrous state and kept continuously at 100° during use.

The experimental procedure used in obtaining the solubility data was the same as that described for previous similar investigations. Because of the slow attainment of equilibrium already observed in systems containing these iodates, the ternary complexes were given one to two weeks of stirring at the lower temperatures, and two to four days at higher temperatures (40–50°). This length of time allowed for the attainment of equilibrium was checked in several cases, and found to be sufficient, by analysis of the solution. The complexes for the system of potassium salts, in which no hydrates exist, were prepared and handled easily. In the system of sodium salts care had to be taken to seed each complex with the expected stable solid phase whenever possible, and to break up the caked hydrates which sometimes formed on mixing the salts with water in the preparation of the complexes. Nevertheless, metastability could not always be avoided.

The method of analysis of the saturated solution was the same in both systems. In one sample of the solution the iodate was determined by titration with standard thiosulfate. In another sample the total solid was determined by evaporation of the solution at 100° followed by one to two hours at 250° to expel the traces of water inclosed by the crystals of the bromide at lower temperatures. The concentration of the bromide was then determined by difference.

The solubilities of the pure salts reported below agree very closely with values recently reported in the literature.

System $\text{KIO}_3\text{-KBr-H}_2\text{O}$.—The results on this system are given in Table I, and the curves for the three isotherms are shown in condensed form, in Fig. 1.

TABLE I

Original complex,		Saturated solution,		Density	Solid phase
KBr	KIO ₃	KBr	KIO ₃		
wt. %	wt. %	wt. %	wt. %		
5°					
...	0.00	36.26	0.00	1.333	KBr
42.16	2.50	35.71	1.80	1.351	KBr + KIO ₃
37.94	7.10	35.72	1.80	1.352	KBr + KIO ₃
32.97	12.06	35.71	1.79	1.353	KBr + KIO ₃
	Av.	35.71	1.80	1.352	KBr + KIO ₃
27.02	13.03	30.50	1.77	1.290	KIO ₃
20.24	12.03	22.59	1.80	1.208	KIO ₃
12.81	15.11	14.80	1.95	1.136	KIO ₃
6.49	16.55	7.58	2.45	1.080	KIO ₃
0.00	...	0.00	5.186	1.043	KIO ₃
25°					
...	0.00	40.62	0.00	1.381	KBr
50.57	.81	40.28	.98	1.396	KBr
46.94	3.09	39.75	2.36	1.407	KBr + KIO ₃
41.03	9.04	39.75	2.36	1.408	KBr + KIO ₃
34.99	15.98	39.76	2.35	1.407	KBr + KIO ₃
	Av.	39.75	2.36	1.407	KBr + KIO ₃
29.97	15.07	34.38	2.47	1.341	KIO ₃
22.52	15.53	25.91	2.73	1.249	KIO ₃
15.02	16.50	17.40	3.26	1.168	KIO ₃
7.01	20.00	8.35	4.53	1.106	KIO ₃
0.00	...	0.00	8.452	1.071	KIO ₃
50°					
...	0.00	44.78	0.00	...	KBr
51.72	1.92	43.88	2.22	...	KBr
49.96	4.22	43.50	3.09	...	KBr + KIO ₃
38.02	17.02	43.50	3.06	...	KBr + KIO ₃
	Av.	43.50	3.07	...	KBr + KIO ₃
33.03	15.98	38.03	3.32	...	KIO ₃
26.64	16.04	30.57	3.87	...	KIO ₃
20.21	16.65	23.19	4.66	...	KIO ₃
13.57	18.03	15.65	5.89	...	KIO ₃
7.01	20.53	8.18	8.16	...	KIO ₃
0.00	...	0.00	13.20	...	KIO ₃

No double compound of the two salts is formed over the temperature range studied, the only solid phases at each temperature being anhydrous potassium bromide and anhydrous potassium iodate. For the determination of the composi-

tion of these solid phases, the method of algebraic extrapolation of tie-lines was used, making use of the composition of the saturated solution and that of the original complex. This method was again found to be very accurate, and to afford a good check on the accuracy of the analytical results, the average deviation of the extrapolated point from the true composition of the iodate or bromide being only 0.19%, the maximum 0.52%.

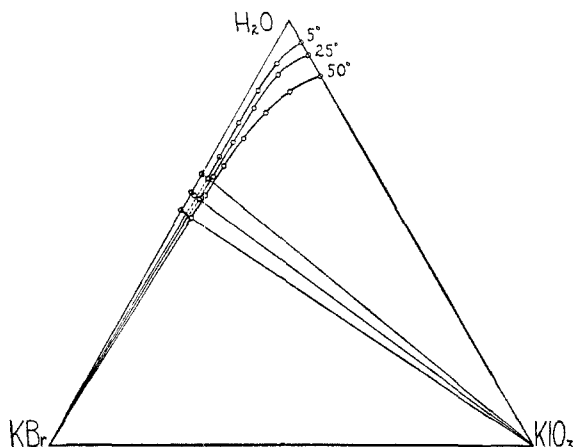


Fig. 1.—The system $\text{KIO}_3\text{-KBr-H}_2\text{O}$, at 5, 25 and 50°.

System $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$.—In the binary system $\text{NaBr-H}_2\text{O}$, the transition temperature between $\text{NaBr}\cdot 2\text{H}_2\text{O}$ and anhydrous NaBr is at 50.2°.¹ In the system $\text{NaIO}_3\text{-H}_2\text{O}$ there is a transition between $\text{NaIO}_3\cdot 5\text{H}_2\text{O}$ and $\text{NaIO}_3\cdot \text{H}_2\text{O}$ at 19.85° and one between $\text{NaIO}_3\cdot \text{H}_2\text{O}$ and anhydrous NaIO_3 at 73.4°.² In the ternary system two new phases appear: $2\text{NaIO}_3\cdot 3\text{NaBr}\cdot 15\text{H}_2\text{O}$ (D.S. 15), found at 5, 15, 25, 35 and still existing at 40°; and $2\text{NaIO}_3\cdot 3\text{NaBr}\cdot 10\text{H}_2\text{O}$ (D.S. 10), found to exist, over small ranges of concentration, at 40, 45 and 50°.

5° Isotherm.—The results for this temperature are presented in Table II, and shown graphically in Fig. 2.

The stable solid phases at this temperature are as follows: $\text{NaBr}\cdot 2\text{H}_2\text{O}$ for solutions between points a and b, $2\text{NaIO}_3\cdot 3\text{NaBr}\cdot 15\text{H}_2\text{O}$ (D.S. 15) for the curve b-c; and $\text{NaIO}_3\cdot 5\text{H}_2\text{O}$ from c to d. The points c and d and the curve between them are obtained if the complex, after preparation, is seeded with a crystal of the pentahydrate. If, however, the complexes, with compositions falling to the right of c, are not seeded at all, or are seeded with a crystal of the monohydrate of

(1) Scott and Durham, *J. Phys. Chem.*, **34**, 531 (1930).

(2) (a) Foote and Vance, *Am. J. Sci.*, **16**, 68 (1928); (b) Hill and Donovan, *THIS JOURNAL*, **53**, 934 (1931).

TABLE II
 $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$ AT 5°

	Original complex, wt. %		Saturated solution, wt. %		Density	Solid phase
	NaBr	NaIO ₃	NaBr	NaIO ₃		
a	...	0.00	45.08	0.00	1.489	$\text{NaBr}\cdot 2\text{H}_2\text{O}$
	50.05	1.02	45.04	.076	1.491	$\text{NaBr}\cdot 2\text{H}_2\text{O} + \text{D.S. 15}$
	46.66	4.06	45.00	.075	1.492	$\text{NaBr}\cdot 2\text{H}_2\text{O} + \text{D.S. 15}$
	43.66	6.99	45.07	.073	1.492	$\text{NaBr}\cdot 2\text{H}_2\text{O} + \text{D.S. 15}$
b	Ave.		45.04	.075	1.492	$\text{NaBr}\cdot 2\text{H}_2\text{O} + \text{D.S. 15}$
	41.96	6.98	43.99	.084	1.473	D.S. 15
	38.61	6.86	39.98	.124	1.415	D.S. 15
	34.47	6.95	35.04	.231	1.352	D.S. 15
	29.89	8.00	29.50	.584	1.287	D.S. 15
	25.41	5.99	24.56	1.09	1.238	D.S. 15
	22.87	6.99	23.53	1.27	1.229	D.S. 15 + $\text{NaIO}_3\cdot 5\text{H}_2\text{O}$
	23.79	6.54	23.49	1.28	1.230	D.S. 15 + $\text{NaIO}_3\cdot 5\text{H}_2\text{O}$
c	Ave.		23.51	1.28	1.230	D.S. 15 + $\text{NaIO}_3\cdot 5\text{H}_2\text{O}$
	20.99	7.06	22.95	1.25	1.225	$\text{NaIO}_3\cdot 5\text{H}_2\text{O}$
	16.96	6.52	18.42	1.13	1.175	$\text{NaIO}_3\cdot 5\text{H}_2\text{O}$
	12.92	6.98	14.13	1.09	1.132	$\text{NaIO}_3\cdot 5\text{H}_2\text{O}$
	9.48	6.99	10.37	1.13	1.097	$\text{NaIO}_3\cdot 5\text{H}_2\text{O}$
	4.52	7.53	4.97	1.44	1.052	$\text{NaIO}_3\cdot 5\text{H}_2\text{O}$
d	0.00	...	0.00	3.297	1.027	$\text{NaIO}_3\cdot 5\text{H}_2\text{O}$
	24.59	8.71	23.30	1.34	1.227	D.S. 15 (m) ^a
c'	22.34	8.03	21.71	1.78	1.215	D.S. 15 + $\text{NaIO}_3\cdot \text{H}_2\text{O}$ (m)
	19.03	9.48	20.78	1.74	1.204	$\text{NaIO}_3\cdot \text{H}_2\text{O}$ (m)
	15.45	7.06	16.39	1.85	1.162	$\text{NaIO}_3\cdot \text{H}_2\text{O}$ (m)
	11.58	7.04	12.26	2.03	1.123	$\text{NaIO}_3\cdot \text{H}_2\text{O}$ (m)
	6.49	8.57	6.97	2.52	1.079	$\text{NaIO}_3\cdot \text{H}_2\text{O}$ (m)
d'	0.00	...	0.00	5.479	1.050	$\text{NaIO}_3\cdot \text{H}_2\text{O}$ (m)

^a m = metastable solid phase.

sodium iodate, a metastable isothermal diagram is obtained with the following solid phases: $\text{NaBr}\cdot 2\text{H}_2\text{O}$ between a and b; D.S. 15 for the solubility curve b to c'; and $\text{NaIO}_3\cdot \text{H}_2\text{O}$ for the

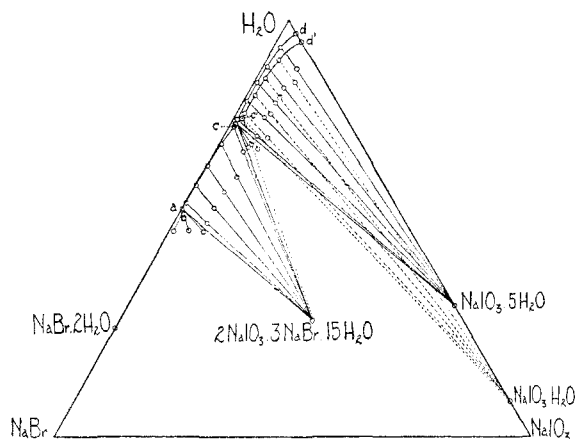


Fig. 2.—5° Isotherm: $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$.

curve c'-d'. The point c' is therefore a metastable isothermally invariant point, d is the stable solubility of $\text{NaIO}_3\cdot 5\text{H}_2\text{O}$, and d' is the metastable solubility of $\text{NaIO}_3\cdot \text{H}_2\text{O}$. This metastable solubility, 5.48%, was determined both by iodimetric titration and by evaporation of the solution to dryness.

These two separate hydrated forms of sodium iodate were distinguished and determined, at this temperature, not only by their very different

appearance in the solubility tubes, but also by means of the algebraic extrapolation of the tie-lines from the two curves c-d and c'-d'. Extrapolated to 68.74% NaIO₃, or NaIO₃·5H₂O, the five tie-lines for c-d gave an average deviation (from the theoretical 0.00% NaBr) of 0.11% in NaBr, with a maximum of 0.19%; the tie-lines for curve c'-d' were extrapolated to 91.66% NaIO₃, corresponding to NaIO₃·H₂O, giving an average deviation of 0.22% NaBr, with a maximum of 0.45%.

15° Isotherm.—Only part of this isotherm was studied, to determine the hydration of sodium iodate in the three-component system at this temperature. The results are given in Table III. Both the pentahydrate and the monohydrate appear in the system at this temperature.

TABLE III
NaIO₃-NaBr-H₂O at 15°

	Original complex, wt. %		Saturated solution, wt. %		Density	Solid phase
	NaBr	NaIO ₃	NaBr	NaIO ₃		
a	...	0.00	46.54 ^a	0.00	...	NaBr·2H ₂ O
c	26.17	9.04	27.15	1.91	1.278	D.S. 15 + NaIO ₃ ·H ₂ O
	20.48	8.51	22.08	2.05	1.219	NaIO ₃ ·H ₂ O
	17.12	9.05	18.54	2.20	1.184	NaIO ₃ ·H ₂ O
	12.43	9.02	13.41	2.53	1.136	NaIO ₃ ·H ₂ O
	8.16	10.01	9.16	2.69	1.101	NaIO ₃ ·5H ₂ O
	3.75	11.40	4.27	3.53	1.064	NaIO ₃ ·5H ₂ O
e	0.00	...	0.00	5.85 ^{ab}	1.051	NaIO ₃ ·5H ₂ O

25° Isotherm.—Table IV and Fig. 3. The solid phases at this temperature are: NaBr·2H₂O for solutions between points a and b; D.S. 15 for the curve b-c; and NaIO₃·H₂O for the curve c-d.

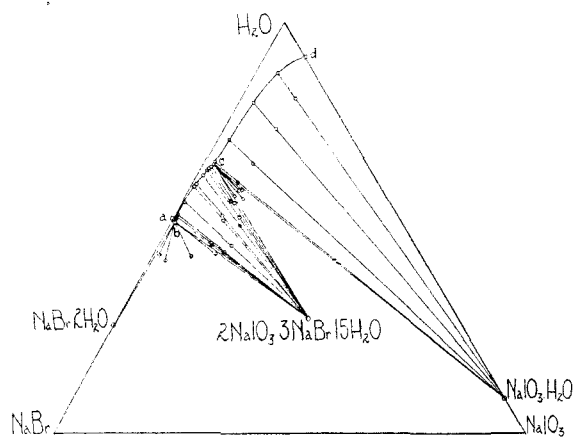


Fig. 3.—25° Isotherm: NaIO₃-NaBr-H₂O.

35° Isotherm (Partial).—Table V. At this temperature there is still only one double salt, D.S. 15, and a new phase, anhydrous sodium iodate, has appeared. The three complexes

(3) By interpolation from "International Critical Tables."

TABLE IV
NaIO₃-NaBr-H₂O at 25°

	Original complex, wt. %		Saturated solution, wt. %		Density	Solid phase
	NaBr	NaIO ₃	NaBr	NaIO ₃		
a	...	0.00	48.41	0.00	1.530	NaBr·2H ₂ O
	55.02	1.61	48.23	.42	1.538	NaBr·2H ₂ O + D.S. 15
	54.82	3.19	48.17	.42	1.536	NaBr·2H ₂ O + D.S. 15
	47.42	8.61	48.21	.42	1.541	NaBr·2H ₂ O + D.S. 15
	43.07	12.97	48.22	.42	1.534	NaBr·2H ₂ O + D.S. 15
b	Av.	...	48.21	.42	1.537	NaBr·2H ₂ O + D.S. 15
	43.50	10.99	47.73	.42	...	D.S. 15
	43.11	11.00	47.35	.42	1.522	D.S. 15
	41.23	14.97	46.73	.45	1.509	D.S. 15
	39.04	15.45	43.58	.55	1.472	D.S. 15
	37.45	10.98	39.55	.86	1.417	D.S. 15
	36.99	10.01	38.83	.95	1.406	D.S. 15
	34.42	14.93	36.61	1.31	1.380	D.S. 15
	33.48	13.07	35.23	1.51	1.367	D.S. 15
	33.47	10.04	34.62	1.66	1.360	D.S. 15
	33.14	10.97	34.34	1.71	1.359	D.S. 15
	32.16	10.00	32.79	2.13	1.344	D.S. 15 + NaIO ₃ ·H ₂ O
	30.72	12.02	32.72	2.15	1.343	D.S. 15 + NaIO ₃ ·H ₂ O
	30.13	10.72	32.56	2.18	1.343	D.S. 15 + NaIO ₃ ·H ₂ O
	29.94	10.97	32.63	2.17	1.343	D.S. 15 + NaIO ₃ ·H ₂ O
c	Av.	...	32.68	2.16	1.343	D.S. 15 + NaIO ₃ ·H ₂ O
	29.76	9.52	32.44	2.17	1.338	NaIO ₃ ·H ₂ O
	23.99	10.52	26.39	2.35	1.266	NaIO ₃ ·H ₂ O
	14.99	11.03	16.49	3.00	1.172	NaIO ₃ ·H ₂ O
	7.15	11.50	7.78	4.46	1.104	NaIO ₃ ·H ₂ O
d	0.00	...	0.00	8.569	1.075	NaIO ₃ ·H ₂ O

which gave this solid phase were all seeded with NaIO₃·H₂O before being rotated in the thermostat. Nevertheless because of the known difficulty with which sodium iodate changes to the monohydrate, and because the range of stability of the anhydrous sodium iodate even at 40°, in this system, is very limited, it cannot be stated with certainty here that anhydrous sodium iodate is a stable and not a metastable solid phase at 35°. At any rate the quintuple point involving the three solids D.S. 15, NaIO₃ and NaIO₃·H₂O, must be close to 35°.

TABLE V
NaIO₃-NaBr-H₂O at 35°

	Original complex, wt. %		Saturated solution, wt. %		Solid phase
	NaBr	NaIO ₃	NaBr	NaIO ₃	
a	...	0.00	50.48 ^a	0.00	NaBr·2H ₂ O
	51.54	4.05	50.04	1.01	NaBr·2H ₂ O + D.S. 15
	47.44	7.00	50.00	1.02	NaBr·2H ₂ O + D.S. 15
b	Av.	...	50.02	1.02	NaBr·2H ₂ O + D.S. 15
	46.52	7.52	49.46	1.03	D.S. 15
	44.96	7.97	47.82	1.08	D.S. 15
	43.39	9.01	46.46	1.18	D.S. 15
	42.00	9.47	44.96	1.30	D.S. 15
	39.95	9.99	42.59	1.60	D.S. 15
	38.41	10.48	40.55	1.98	D.S. 15
	36.66	10.97	38.11	2.63	D.S. 15
c	By extrapolation	...	38.1	2.6	D.S. 15 + NaIO ₃ (m?)
	35.05	10.99	38.30	2.70	NaIO ₃ (m?)
	33.26	11.51	36.52	2.81	NaIO ₃ (m?)
	31.55	11.50	34.51	2.95	NaIO ₃ (m?)
e	0.00	...	0.00	10.55 ^b	NaIO ₃ ·H ₂ O

40° Isotherm.—Table VI and Fig. 4. The solid phases at this temperature are as follows: NaBr·2H₂O for solutions between a and b; 2Na-

$\text{IO}_3 \cdot 3\text{NaBr} \cdot 10\text{H}_2\text{O}$ (D.S. 10), for the curve b-c; D.S. 15 for the curve c-d; NaIO_3 for the curve d-e; and $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ for the curve e-f. The double salt $2\text{NaIO}_3 \cdot 3\text{NaBr} \cdot 10\text{H}_2\text{O}$ is described later. The interesting point in this 40° isotherm is the existence of anhydrous sodium iodate as a solid phase for certain concentrations of solution. The existence of this as a stable phase 33° or more below its transition temperature in the binary system with water was also found in the system $\text{NaIO}_3\text{-NaI-H}_2\text{O}$.⁴ In the present system it also shows metastable existence, at 40° , in regions where D.S. 15 or $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ should be the solid phase, and it may, as already mentioned, even be stable at 35° .

TABLE VI
 $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$ AT 40°

	Original complex,		Saturated solution,		Solid phase
	wt. % NaBr	wt. % NaIO ₃	wt. % NaBr	wt. % NaIO ₃	
a	...	0.00	51.5 ⁵	0.00	NaBr·2H ₂ O
	53.46	4.53	50.84	1.37	NaBr·2H ₂ O + D.S. 10
	47.62	11.00	50.84	1.37	NaBr·2H ₂ O + D.S. 10
b	Av.		50.84	1.37	NaBr·2H ₂ O + D.S. 10
	47.80	7.99	50.37	1.39	D.S. 10
	45.96	12.00	50.43	1.42	D.S. 10
	46.93	7.99	49.38	1.53	D.S. 10
	44.89	11.97	48.41	1.71	D.S. 10
c	44.15	12.50	47.95	1.77	D.S. 10 + D.S. 15
	43.43	12.49	47.96	1.80	D.S. 15
	43.63	9.98	46.82	1.89	D.S. 15
	41.96	12.51	45.93	2.00	D.S. 15
	42.10	10.00	44.86	2.13	D.S. 15
	40.55	9.98	43.37	2.48	D.S. 15
	39.39	12.31	42.38	2.59	D.S. 15
	38.96	12.47	42.10	2.65	D.S. 15 + NaIO ₃
	38.49	12.49	41.82	2.72	D.S. 15 + NaIO ₃
d	Av.		41.96	2.69	D.S. 15 + NaIO ₃
	37.90	13.01	42.44	2.52	NaIO ₃ (m)
	37.17	12.48	41.36	2.59	NaIO ₃
	35.94	12.55	40.05	2.63	NaIO ₃
e	By extrapolation				
	about		39.5	2.65	NaIO ₃ + NaIO ₃ ·H ₂ O
	34.28	12.56	37.73	2.75	NaIO ₃ (m)
	33.56	12.48	37.29	2.80	NaIO ₃ (m)
	34.95	12.47	39.06	2.68	NaIO ₃ ·H ₂ O
	32.50	13.00	36.79	2.62	NaIO ₃ ·H ₂ O
	28.21	13.51	32.08	2.77	NaIO ₃ ·H ₂ O
	23.78	14.00	27.16	3.04	NaIO ₃ ·H ₂ O
	18.12	14.50	20.65	3.65	NaIO ₃ ·H ₂ O
f	0.00	...	0.00	11.70 ^{2b}	NaIO ₃ ·H ₂ O

45° Isotherm (Partial).—Table VII. At this temperature the solid phases are the same as at 40° , with the exception of D.S. 15 which has disappeared between 40 and 45° . At this temperature again sodium iodate appears as a metastable phase in the region in which D.S. 10 is stable.

50° Isotherm.—Table VIII. The binary transition temperature for $\text{NaBr} \cdot 2\text{H}_2\text{O}$ -NaBr is 50.2° ; therefore $\text{NaBr} \cdot 2\text{H}_2\text{O}$ must be a solid

(4) Hill, Willson and Bishop, THIS JOURNAL, 55, 520 (1933).

(5) Interpolated from data of Scott and Durham, Ref. 1.

TABLE VII
 $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$ AT 45°

	Original complex,		Saturated solution,		Solid phase
	wt. % NaBr	wt. % NaIO ₃	wt. % NaBr	wt. % NaIO ₃	
a	...	0.00	52.55	0.00	NaBr·2H ₂ O
b	53.92	7.33	51.79	1.81	NaBr·2H ₂ O + D.S. 10
	46.96	9.99	49.91	2.08	D.S. 10
	By extrapolation				
	about		49.5	2.5	D.S. 10 + NaIO ₃
	46.91	9.08	50.29	2.56	NaIO ₃ (m)
	45.16	9.50	48.64	2.51	NaIO ₃
	42.36	10.09	45.95	2.50	NaIO ₃
	39.77	9.10	42.63	2.58	NaIO ₃
d					NaIO ₃ + NaIO ₃ ·H ₂ O
e	0.00	...	0.00	12.83 ⁶	NaIO ₃ ·H ₂ O

phase of the ternary system at 50° . That anhydrous sodium bromide is also a stable solid phase,

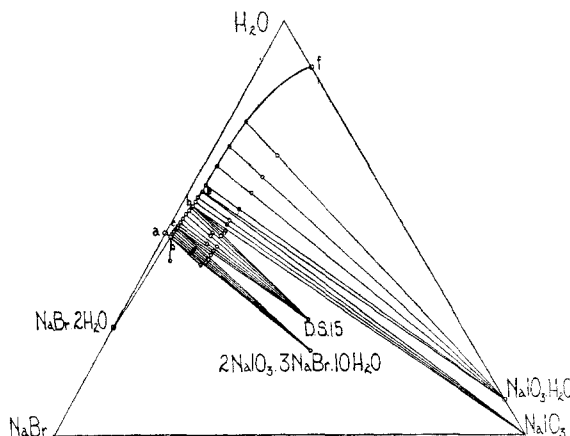


Fig. 4.— 40° Isotherm: $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$.

in equilibrium with solutions near the isothermally invariant point c, Table VIII, is known from the

TABLE VIII
 $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$ AT 50°

	Original complex,		Saturated solution,		Solid phase
	wt. % NaBr	wt. % NaIO ₃	wt. % NaBr	wt. % NaIO ₃	
a	...	0.00	53.63	0.00	NaBr·2H ₂ O
b	By extrapolation		53.0(+)	1.67(-)	NaBr·2H ₂ O + NaBr
	60.02	1.34	52.97	1.57	NaBr
c	55.94	3.00	52.57	2.37	NaBr + D.S. 10
	49.95	8.00	52.39	2.40	D.S. 10
	48.53	10.99	52.12	2.40	D.S. 10
	47.96	10.98	51.40	2.49	D.S. 10
	47.49	11.02	50.97	2.62	D.S. 10 + NaIO ₃
	48.01	9.02	50.90	2.63	D.S. 10 + NaIO ₃
	46.62	11.93	50.91	2.64	D.S. 10 + NaIO ₃
d	Av.		50.93	2.63	D.S. 10 + NaIO ₃
	46.98	8.99	50.30	2.60	NaIO ₃
	44.50	9.01	47.72	2.54	NaIO ₃
	41.50	9.52	44.74	2.56	NaIO ₃
	38.38	9.99	41.56	2.67	NaIO ₃
	35.63	10.02	38.56	2.86	NaIO ₃
	29.95	10.59	32.41	3.41	NaIO ₃
	24.03	11.51	26.02	4.30	NaIO ₃
	20.86	15.46	23.54	4.73	NaIO ₃
e	18.98	15.73	21.46	5.15	NaIO ₃ + NaIO ₃ ·H ₂ O
	17.98	12.59	19.75	4.93	NaIO ₃ ·H ₂ O
	17.83	12.48	19.57	4.86	NaIO ₃ ·H ₂ O
	11.94	14.55	13.28	6.28	NaIO ₃ ·H ₂ O
	5.99	16.51	6.63	9.03	NaIO ₃ ·H ₂ O
f	0.00	...	0.00	13.49	NaIO ₃ ·H ₂ O

(6) Interpolated from Hill and Donovan, Ref. 2b.

extrapolation of the tie-line for the first ternary complex in this table. This tie-line crosses the line of 100% sodium bromide at 0.03% NaIO_3 , showing that sodium bromide is the solid phase for a solution containing 1.57% NaIO_3 , at 50° . Therefore there must be an isothermally invariant point, b, on the solubility curve between 0 and 1.57% NaIO_3 , where both sodium bromide and $\text{NaBr}\cdot 2\text{H}_2\text{O}$ are in equilibrium with the same solution. The other isothermally invariant points for the 50° diagram are all directly determined values.

The solid phases for this temperature are therefore as follows: $\text{NaBr}\cdot 2\text{H}_2\text{O}$, for solutions between a and b; anhydrous sodium bromide for the curve b-c; D.S. 10 for c-d; anhydrous NaIO_3 for d-e, and $\text{NaIO}_3\cdot \text{H}_2\text{O}$ for e-f.

The Double Salt $2\text{NaIO}_3\cdot 3\text{NaBr}\cdot 15\text{H}_2\text{O}$.—The formula of this salt is based on the analysis of crystals formed by the slow evaporation at 25° of

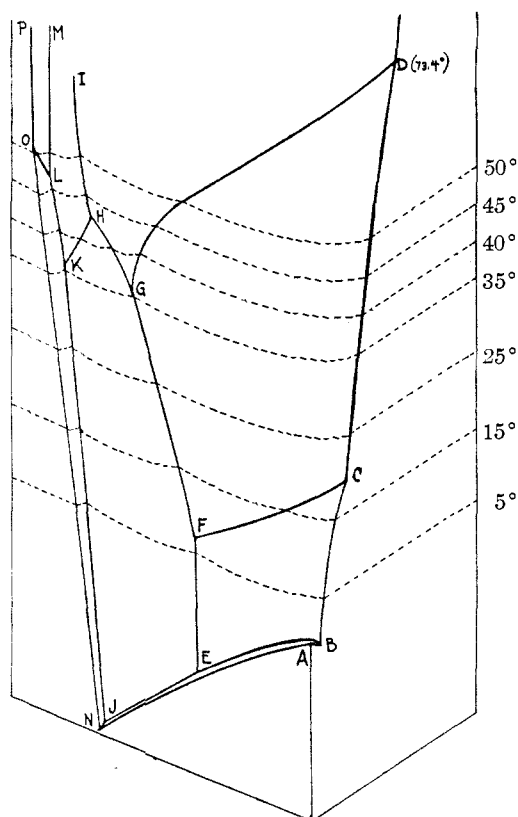


Fig. 5.—System $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$.

three solutions with compositions corresponding to points on the curve b-c at 25° , *i. e.*, calculated to be in equilibrium with the double salt. The crystals obtained, hexagonal plates, were large and well formed, up to 1.6 cm. long. When a sufficient quantity of crystals had formed, samples

of the solutions were removed for analysis, and the crystals were filtered, dried with filter paper and centrifuged. Samples were immediately weighed out for analysis, and the remainder placed over a dehydrating agent consisting of partially dried residues of the same double salt. All three samples came to constant weight within fourteen days. This determination of the quantity of mother liquor contaminating the crystals was used in correcting the analysis of the crystals according to the method described by A. E. Hill.⁷ The results are given in Table IX-A.

The Double Salt $2\text{NaIO}_3\cdot 3\text{NaBr}\cdot 10\text{H}_2\text{O}$.—This formula is based on the analysis of two residues from ternary complexes at 50° . One of these cases (the third ternary complex of Table VIII, 49.95% NaBr and 8.00% NaIO_3) gave some unusually well-formed crystals of salt. The complex was made up by mixing anhydrous sodium iodate, anhydrous sodium bromide, and water, heating to dissolve the greater part of the salts, and breaking up the caked hydrate $\text{NaBr}\cdot 2\text{H}_2\text{O}$ which formed at first. After four hours of stirring (rotating the closed tube) at 50° , uniform, distinct crystals of the double salt had formed, hexagonal plates, 2 to 3 mm. in diameter and 0.5 mm. in thickness, so completely transparent in the center that they appeared perforated while in the saturated solution. It is believed that the analysis of such distinct crystals should be sufficiently dependable even though they had to be removed from a 50° solution containing over 50% of sodium bromide. The results of the analysis, which was carried out exactly as in the case of D.S. 15, and similarly corrected, are given in Table IX-B.

TABLE IX
ANALYSIS OF DOUBLE SALTS
A, $2\text{NaIO}_3\cdot 3\text{NaBr}\cdot 15\text{H}_2\text{O}$

Sample	Observed molecular ratio			Average	Theoretical
	1	2	3		
NaIO_3	2.00	2.00	2.00	2.00	2
NaBr	3.04	3.03	3.02	3.03	3
H_2O	15.15	14.79	15.13	15.02	15

B, $2\text{NaIO}_3\cdot 3\text{NaBr}\cdot 10\text{H}_2\text{O}$

Sample	Observed molecular ratio		Average	Theoretical
	1	2		
NaIO_3	2.00	2.00	2.00	2
NaBr	3.25	3.07	3.16	3
H_2O	9.95	9.87	9.91	10

Omitting the eutectics, where ice is a solid phase, there are the following quintuple points in

(7) HILL, THIS JOURNAL, 52, 3823 (1930).

this system, between 5 and 73.4° (which is the binary transition temperature between $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ and NaIO_3)

- | | |
|-------------------------|--|
| 1. Between 5 and 15° | Solid phases D.S. 15, $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ and $\text{NaIO}_3 \cdot 5\text{H}_2\text{O}$ |
| 2. At about 35° | Solid phases D.S. 15, NaIO_3 , and $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ |
| 3. Between 35 and 40° | Solid phases $\text{NaBr} \cdot 2\text{H}_2\text{O}$, D.S. 10, and D.S. 15 |
| 4. Between 40 and 45° | Solid phases D.S. 10, D.S. 15, and NaIO_3 |
| 5. Between 45 and 50° | Solid phases $\text{NaBr} \cdot 2\text{H}_2\text{O}$, NaBr , and D.S. 10 |
| 6. Between 50 and 73.4° | Solid phases NaBr , D.S. 10, and NaIO_3 (disappearance of D.S. 10, if D.S. 10 disappears before $\text{NaIO}_3 \cdot \text{H}_2\text{O}$) |

No attempt has been made to determine the exact temperatures of these various quintuple points; the overlapping of the temperature ranges for the existence of the two double salts, and the already known difficulty in obtaining true equilibrium in systems containing sodium iodate (particularly where the phase is either the anhydrous form or the monohydrate), indicate that little accuracy could be expected from such an attempt.

Space Model.—In Fig. 5 the entire system is represented as a solid model with a triangular

base, plotting temperature as ordinate. The dotted lines show the solubility isotherms. The invariant points in both the binary and ternary systems are represented by lettered dots. The fields and corresponding solid phases are as follows

ABEJN	Ice	EFGHKJ	D.S. 15
BCPE	$\text{NaIO}_3 \cdot 5\text{H}_2\text{O}$	HIMLK	D.S. 10
CDGF	$\text{NaIO}_3 \cdot \text{H}_2\text{O}$	MLOP	NaBr
DGHI	NaIO_3	JKLON	$\text{NaBr} \cdot 2\text{H}_2\text{O}$

Summary

1. Solubility measurements are given for the system KIO_3 – KBr – H_2O at 5, 25 and 50°; no double salt formation is found in this system.

2. The system NaIO_3 – NaBr – H_2O has been studied at various temperatures between 5 and 50°. Two double salts, with the formulas $2\text{NaIO}_3 \cdot 3\text{NaBr} \cdot 15\text{H}_2\text{O}$ and $2\text{NaIO}_3 \cdot 3\text{NaBr} \cdot 10\text{H}_2\text{O}$ were found to exist in this system, the first at lower temperatures, to about 40°, the second at higher temperatures, from a little below 40°.

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Compound Formation between Sodium Iodate and Sodium Iodide

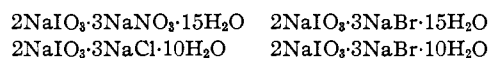
BY JOHN E. RICCI

The general purpose of these phase rule studies on the formation of double compounds between salts is to find, if possible, what properties of the constituent salts determine the formation, first of all, and then the composition and stability of the double salts. Before this can be done it is necessary, of course, to find more evidence of regularity, in occurrence and composition, in any series of double salts containing one common given salt. Hence it was thought desirable to clarify and add further to the data on double salts formed by sodium iodate, which salts are found in part to constitute a series showing certain interesting regularities.

The complex formed between sodium iodate and sodium iodide was recently reported as a solid solution by Hill, Willson and Bishop,¹ the composition of the solid solution being given as ranging between the stoichiometric ratios $\text{NaIO}_3 \cdot 5\text{H}_2\text{O} + \text{NaI} \cdot 2\text{H}_2\text{O}$ and $\text{NaIO}_3 \cdot 5\text{H}_2\text{O} + 2(\text{NaI} \cdot 2\text{H}_2\text{O})$.

(1) Hill, Willson and Bishop, *THIS JOURNAL*, **55**, 520 (1933).

With sodium nitrate,² sodium chloride,³ and sodium bromide,⁴ the following definite compounds have already been reported, forming a short series with very evident regularities of composition:



In view of the similarity of all these combinations, the reported solid solution for the combination with sodium iodide seemed to be too strange an exception. From the close similarity between sodium iodide and sodium bromide both as to solubility and as to hydration, and purely from probability considerations, not only would one expect a similar behavior in respect to this complex formation, but one could almost predict, from the above table, the composition of the double salts of sodium iodide and sodium iodate.

(2) Foote and Vance, *Am. J. Sci.*, **18**, 376 (1929); Hill and Donovan, *THIS JOURNAL*, **53**, 934 (1931).

(3) Foote and Vance, *Am. J. Sci.*, **17**, 425 (1929).

(4) Ricci, *THIS JOURNAL*, **56**, 290 (1934).