tions with other salts; and it should be possible to find a series of such combinations having sodium sulfate as the common constituent. An indication of the existence of another such combination has been found in the system Na_2SO_4–$NaBrO_3$–H_2O at 45°; this is being further investigated at present. Other anhydrous double salts of the type Na_2SO_4–NaX are $Na_2SO_4 \cdot NaF$, $3NaNO_3 \cdot 4Na_2SO_4$ and $3NaNO_3 \cdot 2Na_2SO_4$; ($NaNO_3 \cdot Na_2SO_4 \cdot H_2O$ is also reported). With salts of the type Na_2X, sodium sulfate seems to have a tendency to form solid solutions—for example, with Na_2S, Na_2SO_3, $Na_2S_2O_3$, Na_2CrO_4, and Na_2CO_3 (besides the compound $Na_2CO_3 \cdot 2Na_2SO_4$ in the case of the carbonate).[13]

It seems reasonable to expect that the study of such regular series of combinations, if they exist, may lead to information as to the properties of the constituent salts, or at least of the dominant salt, upon which this compound formation depends. For this purpose some additional combinations based on sodium sulfate will be studied, and perhaps also the series with sodium and potassium chlorate; series based on sodium bromate and on potassium bromate have been investigated, but these gave no compound formation at all, except for the indication of a complex with sodium sulfate, as already mentioned. The data on these series are presented in a subsequent paper.

Summary

1. The complex formed between sodium iodate and sodium iodide has been shown not to be a solid solution but to consist, in the temperature range between 20 and 55°, of three double salts: $2NaIO_3 \cdot 3NaI \cdot 20H_2O$, $2NaIO_3 \cdot 3NaI \cdot 15H_2O$ and $2NaIO_3 \cdot 3NaI \cdot 10H_2O$.

2. Certain regularities in the composition of the double salts based on sodium iodate are pointed out, and the possibility of finding other series of double salts with other salts as the dominant constituents is briefly discussed.

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[13] For $Na_2SO_4 \cdot NaF$: Foote and Schairer, THIS JOURNAL, **52**, 4202 (1930). The rest are all from "International Critical Tables."

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

Ternary Systems Involving Alkali Bromates

BY JOHN E. RICCI

Introduction.—The ternary systems involving combinations of sodium or potassium iodate together with the corresponding chloride, bromide, iodide, nitrate, or sulfate, plus water, have already been studied by various investigators. In all these ternary combinations involving sodium iodate, a complex, in the form of a double salt, in most cases hydrated, was found to form. These double salts of sodium iodate form a series showing on the whole some marked regularities of composition, which have been pointed out in a preceding paper.[1] But none of the five systems including potassium iodate showed any double salt formation whatever. In the system KIO_3–KI–H_2O which is now being studied in this Laboratory by Professor A. E. Hill and Mr. J. H. Wills, and in which a complex of the two salts had been more or less expected, the phase rule investigation gives no evidence of any association. The only double compounds of potassium iodate so far known are the complex tellurate $2KIO_3 \cdot Te(OH)_6$ and its acid salts with iodic acid which, as already pointed out,[1] appear to depend on a certain tendency of iodic acid, and not of potassium iodate. The fact of course that the tendency to form binary and ternary molecular compounds is distinctly more pronounced in the case of the sodium salts as compared to the corresponding potassium salts is not surprising.

The purpose of the measurements here reported was to establish any analogies that might be found to exist in the corresponding series with sodium bromate and potassium bromate, in respect to this property of forming molecular compounds. The results show that no double salts are formed at the temperatures studied, mostly 25°, both for the sodium bromate and for the potassium bromate series of systems. It is possible of course that such compounds may be found to exist at different temperatures in some of these systems; in fact, in incomplete data not here reported, there is evidence that there is some compound formation between sodium bromate

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[1] Ricci, THIS JOURNAL, **56**, 295 (1934).

and sodium sulfate, at 45°. This however will be studied from the point of view of a possible series of combinations based on sodium sulfate, since the complex promises to prove similar to the compounds formed between sodium sulfate and sodium iodate. The fact appears clear that there is no series of double salts based on sodium bromate to be compared with the sodium iodate series; or, sodium iodate possesses a much greater tendency for the formation of double salts of the type RX–RX′ than does sodium bromate. This tendency on the part of any given salt for the formation of molecular compounds, it seems reasonable to suggest, may be correlated with such properties, among others, as its solubility and its extent of hydration, itself an index of molecular affinities. Since sodium bromate is much more soluble than sodium iodate (solubility of sodium bromate about 0.034; of sodium iodate about 0.013 mole fractions), the complex-forming tendency in this case is apparently not a function of the solubility. In respect to hydration, however, there is a correlation; while no hydrates of sodium bromate are known, sodium iodate forms both a mono- and a pentahydrate. That this correlation may be significant is also brought out by the relation seen between the degrees of hydration of the regular double salts of sodium iodate (which vary by 5 molecules of water, and are always multiples of 5) and the fact that sodium iodate exhibits a pentahydrate. Because the uncertainty is still great, it should be desirable to study the similar series for both sodium chlorate and potassium chlorate, both of which, although forming no hydrates, are more soluble than the corresponding bromates and iodates.

Experimental Procedure

The salts used were of the best available "C. P." grade and, with the exception of sodium iodide and potassium iodide, which were simply dried for use, they were all purified by recrystallization, particular care having been taken in purifying the bromates. The salts were all dried to the anhydrous state and kept constantly in a 100° oven.

The procedure for the solubility measurements and determination of solid phases was the same as that used in previous similar investigations. The ternary complexes were made up from weighed amounts of water and the two anhydrous salts for each system; these complexes were rotated in a large thermostat kept constant to ±0.01°, for about two days, a time found to be sufficient for equilibrium in all cases.

Samples of the saturated solution were withdrawn by means of a calibrated pipet provided with a folded filter paper at the tip. This afforded a determination of the density with a precision of about 0.1% in the case of the more dilute solutions, but less accurate for the more viscous solutions such as those of the iodides.

For the analysis of the solutions, the bromate was determined by titration with standard sodium thiosulfate, and the total solid by evaporation at 100° and drying at 250°, this giving the second salt by difference. A careful study of the method showed that it was accurate to within 0.2% even in the iodide–bromate combinations.

For the determination of 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 give a good check on the accuracy of the analytical methods. The average deviation of the extrapolated point from the true composition of the solid phases, in all the systems except those containing the iodides, is 0.13%, and the maximum deviation 0.53%. In the iodide systems the average deviation is 0.30%, maximum 0.67%.

Results

The solubilities of all the pure salts as reported below agree very closely with recently published solubility work and with values given in the "International Critical Tables." The only new values are those for sodium bromide at 10 and 45°, and the solubilities of sodium bromate and potassium bromate, which were determined between 5 and 50°, as given below in Table I and Fig. 1. The solid phase in the case of both bromates is the anhydrous salt. The solubilities for these salts listed in the "International Critical Tables" are incomplete, all given with a large probable error (±5%), and represent mostly very old work. Both sodium and potassium bromate were found to reach equilibrium rapidly in the solubility measurements, in contrast to the behavior of the corresponding iodates, where, partly because of the change of phase (occurring in the case of sodium iodate) and partly because of a possible but unexplained colloidal character of these iodates, the attainment of equilibrium is

TABLE I

SOLUBILITIES OF SODIUM BROMATE AND POTASSIUM BROMATE

Temp., °C.	NaBrO₃ Wt. % NaBrO₃ in satd. soln.	NaBrO₃ Density	KBrO₃ Wt. % KBrO₃	KBrO₃ Density
5	21.42	1.194	3.642	1.024
10	23.24	1.211	4.510	1.035
15	24.94	1.232	5.397	1 042
20	26.69	1.248	6.460	1.048
25	28.29	1.257	7.533	1.054
30	29.85	1.284	8.785	1.062
35	31.35	1.288	10.13	1.074
40	32.80	1.310	11.58	1.083
45	34.22	...	13.08	...
50	35.55	...	14.69	...

extremely slow. The solubilities of the bromates reported here were reached from both undersaturation and supersaturation, constant values being obtained within twenty-four hours under the conditions of the experiments.

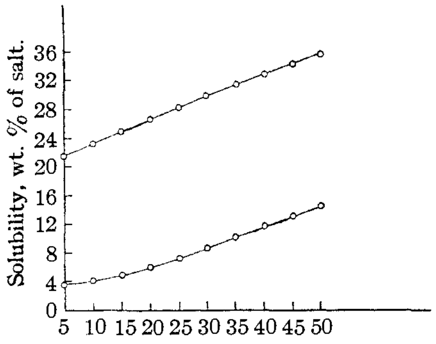

Fig. 1.—Solubilities of $NaBrO_3$ and $KBrO_3$.

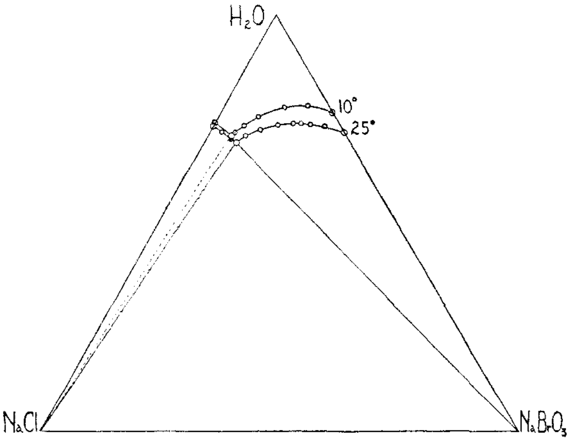

Fig. 2.—The system: $NaBrO_3$–NaCl–H_2O.

The results of the experiments with the three-component systems are given in Tables II–XI, and shown graphically for two of the systems in Figs. 2 and 3. The curves are of the simplest type in every case, the only solid phases being, in each case, those forms of the two salts, anhydrous or hydrated, which are stable at the stated temperatures.

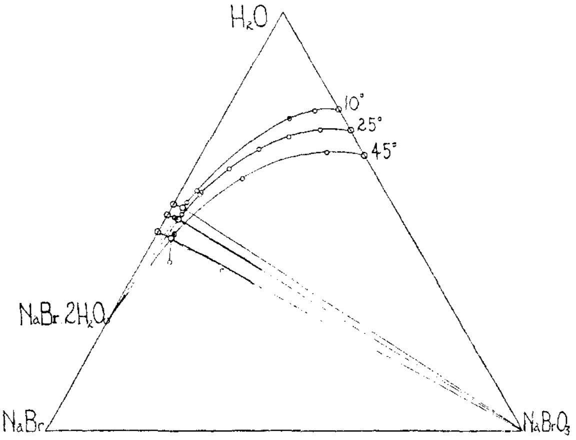

Fig. 3.—The system: $NaBrO_3$–NaBr–H_2O.

TABLE II

$NaBrO_3$–NaCl–H_2O

Original complex, wt. % NaCl	Original complex, wt. % NaBrO₃	Saturated solution, wt. % NaCl	Saturated solution, wt. % NaBrO₃	Density	Solid phase
		10°			
...	0.00	26.32[a]	0.00		NaCl
34.98	5.94	24.53	5.02	1.236	NaCl + NaBrO₃
30.02	10.96	24.53	5.02	1.233	NaCl + NaBrO₃
24.50	16.01	24.51	5.01	1.235	NaCl + NaBrO₃
Average		24.52	5.02	1.235	NaCl + NaBrO₃
19.96	19.95	23.61	5.32	1.229	NaBrO₃
17.08	22.95	20.75	6.41	1.213	NaBrO₃
13.08	26.00	16.15	8.58	1.199	NaBrO₃
7.97	29.01	9.84	12.75	1.192	NaBrO₃
4.00	31.99	4.85	17.28	1.193	NaBrO₃
0.00	...	0.00	23.24	1.211	NaBrO₃
		25°			
...	0.00	26.46	0.00	1.195	NaCl
40.03	2.00	25.55	2.48	1.215	NaCl
39.04	4.52	24.35	5.62	1.236	NaCl
38.98	6.02	23.93	6.92	1.247	NaCl + NaBrO₃
35.07	11.99	23.95	6.92	1.248	NaCl + NaBrO₃
31.99	17.98	23.93	6.92	1.246	NaCl + NaBrO₃
24.99	26.01	23.95	6.91	1.247	NaCl + NaBrO₃
18.01	32.47	23.92	6.91	1.249	NaCl + NaBrO₃
Average		23.94	6.92	1.247	NaCl + NaBrO₃
16.18	29.38	20.99	8.32	1.234	NaBrO₃
12.54	35.98	17.55	10.34	1.234	NaBrO₃
10.38	30.96	12.95	13.67	1.228	NaBrO₃
8.13	32.07	9.98	16.31	1.225	NaBrO₃
6.71	34.02	8.27	17.98	1.228	NaBrO₃
5.10	34.98	6.17	20.27	1.229	NaBrO₃
3.11	37.60	3.76	23.13	1.241	NaBrO₃
0.00	...	0.00	28.29	1.257	NaBrO₃

[a] From "International Critical Tables."

TABLE III

$NaBrO_3$–NaBr–H_2O

Original complex wt. % NaBr	Original complex wt. % NaBrO₃	Saturated solution, wt. % NaBr	Saturated solution, wt. % NaBrO₃	Density	Solid phase
		10°			
...	0.00	45.89	0.00	1.492	NaBr·2H₂O
51.02	3.03	44.50	2.58	1.519	NaBr·2H₂O + NaBrO₃

TABLE III (*Concluded*)

Original complex, wt. %		Saturated solution, wt. %		Density	Solid phase
NaBr	$NaBrO_3$	NaBr	$NaBrO_3$		
47.11	7.99	44.54	2.58	1.516	$NaBr\cdot 2H_2O + NaBrO_3$
39.53	15.49	44.49	2.58	1.515	$NaBr\cdot 2H_2O + NaBrO_3$
Average		44.51	2.58	1.517	$NaBr\cdot 2H_2O + NaBrO_3$
37.00	16.52	43.09	2.83	1.498	$NaBrO_3$
33.50	17.99	39.40	3.55	1.452	$NaBrO_3$
9.48	29.94	11.10	14.46	1.240	$NaBrO_3$
4.57	32.94	5.33	18.73	1.220	$NaBrO_3$
0.00	...	0.00	23.24	1.211	$NaBrO_3$
		25°			
...	0.00	48.41	0.00	1.530	$NaBr\cdot 2H_2O$
53.31	1.50	47.37	1.90	1.546	$NaBr\cdot 2H_2O$
50.89	3.51	46.84	2.93	1.555	$NaBr\cdot 2H_2O + NaBrO_3$
49.90	9.88	46.81	2.94	1.558	$NaBr\cdot 2H_2O + NaBrO_3$
44.87	16.46	46.82	2.94	1.555	$NaBr\cdot 2H_2O + NaBrO_3$
38.22	24.89	46.81	2.94	1.553	$NaBr\cdot 2H_2O + NaBrO_3$
Average		46.82	2.94	1.555	$NaBr\cdot 2H_2O + NaBrO$
37.29	20.82	45.62	3.15	1.542	$NaBrO_3$
32.48	21.01	39.24	4.61	1.462	$NaBrO_3$
31.96	21.20	38.66	4.78	1.457	$NaBrO_3$
21.13	34.83	29.83	7.86	1.377	$NaBrO_3$
16.49	31.57	21.27	12.04	1.320	$NaBrO_3$
10.22	38.57	13.82	16.72	1.282	$NaBrO_3$
5.02	39.07	6.46	22.38	1.270	$NaBrO_3$
0.00	...	0.00	28.29	1.257	$NaBrO_3$
		45°			
...	0.00	52.55	0.00		$NaBr\cdot 2H_2O$
53.87	5.98	50.66	3.51		$NaBr\cdot 2H_2O + NaBrO_3$
44.05	18.04	50.70	3.50		$NaBr\cdot 2H_2O + NaBrO_3$
Average		50.68	3.51		$NaBr\cdot 2H_2O + NaBrO_3$
41.04	20.00	49.39	3.72		$NaBrO_3$
21.99	31.97	28.69	11.17		$NaBrO_3$
6.19	43.03	7.91	26.65		$NaBrO_3$
0.00	...	0.00	34.22		$NaBrO_3$

TABLE IV

$NaBrO_3$–NaI–H_2O AT 25°

Original complex wt. %		Saturated solution, wt. %		Density	Solid phase
NaI	$NaBrO_3$	NaI	$NaBrO_3$		
...	0.00	64.71	0.00	1.904	$NaI\cdot 2H_2O$
66.64	1.99	63.98	1.17	1.911	$NaI\cdot 2H_2O + NaBrO_3$
63.67	5.98	64.00	1.17	1.913	$NaI\cdot 2H_2O + NaBrO_3$
60.06	10.06	63.93	1.16	1.920	$NaI\cdot 2H_2O + NaBrO_3$
56.15	13.49	64.00	1.17	1.916	$NaI\cdot 2H_2O + NaBrO_3$
Average		63.95	1.17	1.914	$NaI\cdot 2H_2O + NaBrO_3$
47.44	24.89	62.13	1.30	1.874	$NaBrO_3$
50.00	18.94	60.65	1.44	1.836	$NaBrO_3$
45.00	20.02	54.89	2.23	1.727	$NaBrO_3$
35.08	29.99	48.11	3.62	1.619	$NaBrO_3$
32.42	25.05	40.76	5.78	1.521	$NaBrO_3$
24.49	30.98	32.21	8.92	1.438	$NaBrO_3$
13.00	36.96	17.32	16.57	1.332	$NaBrO_3$
0.00	...	0.00	28.29	1.257	$NaBrO_3$

TABLE V

$NaBrO_3$–$NaNO_3$-H_2O AT 25°

Original complex wt. %		Saturated solution, wt. %		Density	Solid phase
$NaNO_3$	$NaBrO_3$	$NaNO_3$	$NaBrO_3$		
...	0.00	47.87	0.00	1.384	$NaNO_3$
55.97	2.01	46.50	2.43	1.405	$NaNO_3$
53.42	5.08	44.46	6.04	1.432	$NaNO_3$
47.84	10.20	42.57	9.39	1.455	$NaNO_3 + NaBrO_3$
40.86	15.15	42.60	9.37	1.455	$NaNO_3 + NaBrO_3$
Average		42.59	9.38	1.455	$NaNO_3 + NaBrO_3$
33.90	23.15	39.57	10.23	1.441	$NaBrO_3$
27.45	26.03	32.54	12.41	1.387	$NaBrO_3$
21.00	30.06	25.54	14.94	1.353	$NaBrO_3$
15.02	33.01	18.48	17.79	1.314	$NaBrO_3$
9.01	36.98	11.33	21.25	1.288	$NaBrO_3$
4.00	40.05	5.00	24.92	1.270	$NaBrO_3$
0.00	...	0.00	28.29	1.257	$NaBrO_3$

TABLE VI

$NaBrO_3$–Na_2SO_4–H_2O AT 25°

Original complex wt. %		Saturated solution, wt. %		Density	Solid phase
Na_2SO_4	$NaBrO_3$	Na_2SO_4	$NaBrO_3$		
...	0.00	21.90	0.00	1.205	$Na_2SO_4\cdot 10H_2O$
27.56	2.49	20.48	3.34	1.225	$Na_2SO_4\cdot 10H_2O$
26.07	5.15	19.17	7.06	1.254	$Na_2SO_4\cdot 10H_2O$
25.20	7.82	17.94	10.79	1.275	$Na_2SO_4\cdot 10H_2O$
24.00	10.48	16.94	14.11	1.303	$Na_2SO_4\cdot 10H_2O$
24.43	13.98	16.46	15.87	1.319	$Na_2SO_4\cdot 10H_2O + NaBrO_3$
21.61	18.70	16.43	15.86	1.316	$Na_2SO_4\cdot 10H_2O + NaBrO_3$
16.49	27.08	16.47	15.83	1.320	$Na_2SO_4\cdot 10H_2O + NaBrO_3$
13.38	31.69	16.45	15.85	1.312	$Na_2SO_4\cdot 10H_2O + NaBrO_3$
Average		16.45	15.85	1.317	$Na_2SO_4\cdot 10H_2O + NaBrO_3$
9.95	34.17	12.35	18.71	1.303	$NaBrO_3$
6.77	35.43	8.28	21.72	1.288	$NaBrO_3$
3.28	38.29	4.09	24.96	1.284	$NaBrO_3$
0.00	...	0.00	28.29	1.257	$NaBrO_3$

TABLE VII

$KBrO_3$–KCl–H_2O AT 25°

Original complex, wt. %		Saturated solution, wt. %		Density	Solid phase
KCl	$KBrO_3$	KCl	$KBrO_3$		
...	0.00	26.36	0.00	1.179	KCl
34.99	1.30	25.93	1.48	1.187	KCl
31.97	4.07	25.90	1.61	1.197	$KCl + KBrO_3$
28.04	8.01	25.89	1.60	1.189	$KCl + KBrO_3$
25.59	12.98	25.88	1.61	1.190	$KCl + KBrO_3$
Average	...	25.89	1.61	1.192	$KCl + KBrO_3$
20.98	17.10	24.87	1.65	1.183	$KBrO_3$
16.50	17.97	19.71	1.97	1.147	$KBrO_3$
12.01	19.03	14.45	2.44	1.112	$KBrO_3$
7.47	20.07	9.03	3.24	1.082	$KBrO_3$
3.62	20.54	4.33	4.63	1.058	$KBrO_3$
0.00	...	0.00	7.533	1.054	$KBrO_3$

TABLE VIII

$KBrO_3$–KBr–H_2O AT 25°

Original complex, wt. %		Saturated solution, wt. %		Density	Solid phase
KBr	$KBrO_3$	KBr	$KBrO_3$		
...	0.00	40.62	0.00	1.381	KBr
50.53	.99	40.08	1.20	1.389	KBr
45.91	4.10	40.00	1.43	1.392	$KBr + KBrO_3$
41.25	6.02	39.99	1.43	1.393	$KBr + KBrO_3$
35.01	15.99	39.99	1.43	1.392	$KBr + KBrO_3$
Average	...	39.99	1.43	1.392	$KBr + KBrO_3$
30.07	15.04	34.82	1.62	1.328	$KBrO_3$
22.48	15.51	26.05	2.06	1.237	$KBrO_3$
15.00	16.54	17.48	2.73	1.161	$KBrO_3$
6.52	20.21	7.82	4.29	1.089	$KBrO_3$
0.00	...	0.00	7.533	1.054	$KBrO_3$

TABLE IX

$KBrO_3$–KI–H_2O AT 25°

Original complex, wt. %		Saturated solution, wt. %		Density	Solid phase
KI	$KBrO_3$	KI	$KBrO_3$		
...	0.00	59.76	0.00	1.718	KI
66.99	3.00	59.15	.96	1.728	$KI + KBrO_3$
58.98	11.00	59.22	.96	1.727	$KI + KBrO_3$
48.45	19.99	59.22	.96	1.730	$KI + KBrO_3$
Average	...	59.20	.96	1.729	$KI + KBrO_3$
46.96	20.07	58.14	.99	1.707	$KBrO_3$
40.03	21.05	50.06	1.21	1.565	$KBrO_3$
31.46	20.64	38.99	1.63	1.402	$KBrO_3$
23.05	21.09	28.60	2.17	1.278	$KBrO_3$

TABLE IX (*Concluded*)

Original complex, wt. %		Saturated solution, wt. %			
KI	$KBrO_3$	KI	$KBrO_3$	Density	Solid phase
15.15	21.95	18.85	2.96	1.182	$KBrO_3$
7.03	23.15	8.77	4.54	1.103	$KBrO_3$
0.00	...	0.00	7.533	1.054	$KBrO_3$

TABLE X

$KBrO_3$–KNO_3–H_2O AT 25°

Original complex, wt. %		Saturated solution, wt. %			
KNO_3	$KBrO_3$	KNO_3	$KBrO_3$	Density	Solid phase
...	0.00	27.71	0.00	1.193	KNO_3
38.10	2.25	27.27	2.64	1.211	KNO_3
35.06	4.48	27.01	3.90	1.228	$KNO_3 + KBrO_3$
29.49	9.57	27.01	3.90	1.225	$KNO_3 + KBrO_3$
23.13	18.04	27.01	3.90	1.223	$KNO_3 + KBrO_3$
Average		27.01	3.90	1.225	$KNO_3 + KBrO_3$
20.05	16.98	23.17	4.00	1.193	$KBrO_3$
14.55	17.99	16.98	4.23	1.148	$KBrO_3$
9.43	19.02	11.10	4.64	1.110	$KBrO_3$
4.29	20.01	5.05	5.61	1.074	$KBrO_3$
0.00	...	0.00	7.533	1.054	$KBrO_3$

TABLE XI

$KBrO_3$–K_2SO_4–H_2O AT 25°

Original complex, wt. %		Saturated solution, wt. %			
K_2SO_4	$KBrO_3$	K_2SO_4	$KBrO_3$	Density	Solid phase
...	0.00	10.76	0.00	1.083	K_2SO_4
20.04	1.51	10.12	1.69	1.094	K_2SO_4
20.01	3.01	9.45	3.40	1.103	K_2SO_4
20.03	5.16	9.34	4.00	1.108	$K_2SO_4 + KBrO_3$
14.06	10.00	9.36	4.00	1.108	$K_2SO_4 + KBrO_3$
9.11	16.01	9.35	4.01	1.108	$K_2SO_4 + KBrO_3$
Average		9.35	4.00	1.108	$K_2SO_4 + KBrO_3$
7.13	16.53	8.20	4.27	1.100	$KBrO_3$
4.73	17.51	5.44	5.02	1.083	$KBrO_3$
2.30	18.97	2.67	6.08	1.066	$KBrO_3$
0.00	...	0.00	7.53	1.054	$KBrO_3$

Summary

1. The three-component systems consisting of water and the following pairs of salts have been studied at 25°: $NaBrO_3$–NaCl (also at 10°); $NaBrO_3$–NaBr (also at 10 and 45°); $NaBrO_3$–NaI; $NaBrO_3$–$NaNO_3$; $NaBrO_3$–Na_2SO_4; $KBrO_3$–KCl; $KBrO_3$–KBr; $KBrO_3$–KI; $KBrO_3$–KNO_3; $KBrO_3$–K_2SO_4. Double salt formation has not been found in any of these cases at the temperatures here reported.

2. These series of systems are briefly compared with the corresponding series involving sodium iodate and potassium iodate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. XLI. Electrolytic Preparation of Rare Earth Amalgams. 3. Amalgams of Lanthanum, Neodymium, Cerium, Samarium and Yttrium. Metallic Lanthanum, Neodymium and Cerium by Thermal Decomposition of Their Amalgams

BY E. E. JUKKOLA WITH L. F. AUDRIETH AND B. S. HOPKINS

Previous investigations[1] have shown that certain rare earth metal amalgams may be prepared readily by the electrolysis of their salts in various non-aqueous solvents using a mercury cathode. Subsequently it was found that lanthanum amalgam could be decomposed thermally to give the metal in a state of high purity.[2]

Since the preparation of the amalgams and their decomposition may be carried out using relatively small quantities of materials—a factor which must be considered in researches dealing with the rare earths—it was deemed advisable to investigate more thoroughly the conditions governing amalgam formation. The present paper gives the results of such a study and includes preliminary observations in the extension of this method to the preparation of the amalgams of samarium and yttrium.

Experimental[3]

Amalgams of lanthanum, neodymium, cerium, samarium and yttrium may be prepared conveniently by electrolysis at room temperatures of concentrated solutions of the anhydrous chlorides in absolute ethyl alcohol as solvent using a mercury cathode. Other solvents, such as glacial acetic acid and the higher alcohols, were found to be too poorly conducting to be of any use. Methyl alcohol was found to be fairly satisfactory. Electrolysis of aqueous solutions resulted in some amalgam formation, but was accompanied in every case by precipitation of considerable quantities of the basic salt.

Attempts were made to use other rare earth salts as electrolytes. Sulfates were too slightly soluble in ethyl alcohol, while nitrates suffered reduction at the cathode. Acetates, both in glacial acetic acid and in alcohol, gave no amal-

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[1] Audrieth, Jukkola, Meints aud Hopkins, THIS JOURNAL, **53**, 1805 (1931).

[2] Meints, Hopkins and Audrieth, *Z. anorg. allgem. Chem.*, **211**, 237 (1933).

[3] See Refs. 1 and 2 for details concerning apparatus and procedure.