this system, between 5 and 73.4° (which is the binary transition temperature between $NaIO_3 \cdot H_2O$ and $NaIO_3$)

1. Between 5 and 15°	Solid phases D.S. 15, $NaIO_3 \cdot H_2O$ and $NaIO_3 \cdot 5H_2O$
2. At about 35°	Solid phases D.S. 15, $NaIO_3$, and $NaIO_3 \cdot H_2O$
3. Between 35 and 40°	Solid phases $NaBr \cdot 2H_2O$, 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 $NaBr \cdot 2H_2O$, 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 $NaIO_3 \cdot H_2O$)

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
BCFE	$NaIO_3 \cdot 5H_2O$	HIMLK	D.S. 10
CDGF	$NaIO_3 \cdot H_2O$	MLOP	NaBr
DGHI	$NaIO_3$	JKLON	$NaBr \cdot 2H_2O$

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 $2NaIO_3 \cdot 3NaBr \cdot 15H_2O$ and $2NaIO_3 \cdot 3NaBr \cdot 10H_2O$ 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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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

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 $NaIO_3 \cdot 5H_2O + NaI \cdot 2H_2O$ and $NaIO_3 \cdot 5H_2O + 2(NaI \cdot 2H_2O)$.

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:

$2NaIO_3 \cdot 3NaNO_3 \cdot 15H_2O$	$2NaIO_3 \cdot 3NaBr \cdot 15H_2O$
$2NaIO_3 \cdot 3NaCl \cdot 10H_2O$	$2NaIO_3 \cdot 3NaBr \cdot 10H_2O$

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.

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

(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).

The 2:3 molecular ratio of the salts in the above regular series is of course, the average of the 1:1 and 1:2 ratios reported for the solid solution; and the existence of two hydrates of the double salt in the case of sodium bromide showed that the same kind of behavior was probably taking place with the sodium iodide complex, causing an apparently continuous variation in the composition of the solid phase. Solely, then, because of the expectation of continued regularity in the combinations, and because the case of the solid solution appeared to be an otherwise inexplicable exception, it was decided to review the work on the ternary system $NaIO_3$–NaI–H_2O. Part of this system was therefore repeated, in a limited region—namely, the field of complex formation—for the purpose of picking out and separating the double salts. The results of this correction indicate the formation of three double salts, with the expected 2–3 molecular ratio of the salts, and with different degrees of hydration, again multiples of 5, thus strengthening still further the regularities seen in the above series of complexes based on sodium iodate. These new double salts are

$2NaIO_3{\cdot}3NaI{\cdot}20H_2O$ (D.S. 20)
$2NaIO_3{\cdot}3NaI{\cdot}15H_2O$ (D.S. 15)
$2NaIO_3{\cdot}3NaI{\cdot}10H_2O$ (D.S. 10)

The experimental procedure and analytical methods were exactly as described for previous similar work. Partial isotherms were determined at 20, 25, 40 and 55°. At all these temperatures the total range of existence, of the various complexes, on the ternary diagram is considerable, so that the method of algebraic extrapolation[5] for the determination of solid phases is found to be very accurate and useful in distinguishing the various hydrates of the complex salt.

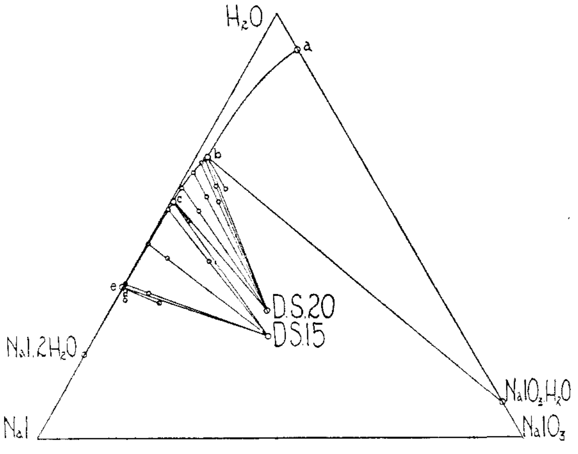

Fig. 1.—25° Isotherm: $NaIO_3$–NaI–H_2O.

The results are given in Table I, and shown graphically in Figs. 1 and 2; the diagram for 20° would be very similar to the 25° figure. In the column headed "Extrapolation" is given the result of the algebraic extrapolation of the tie-lines connecting saturated solution with original complex, to the percentage of sodium iodate calculated for the solid phase indicated in the next column. The figure given represents the deviation in per cent. of sodium iodide from the theoretical value calculated for the same solid phase. The agreement is seen to be generally very close.

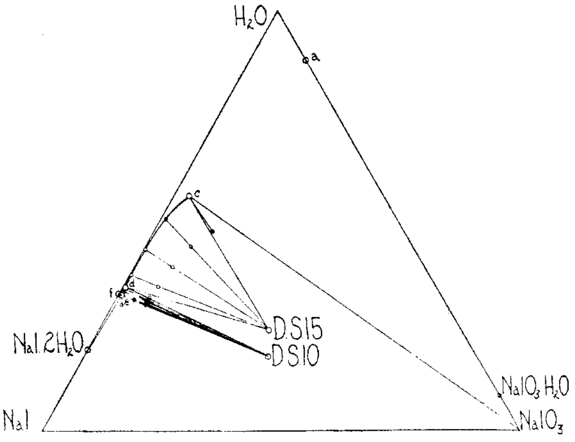

Fig. 2.—40° Isotherm (partial): $NaIO_3$–NaI–H_2O.

The two salts sodium iodate and sodium iodide therefore form three double salts, or one double salt with three different degrees of hydration. At 20 and 25°, the two forms $2NaIO_3{\cdot}3NaI{\cdot}20H_2O$ and $2NaIO_3{\cdot}3NaI{\cdot}15H_2O$ occupy the field of compound formation. Between 25 and 40°, the next isotherm studied, D.S. 20 disappears and D.S. 10 makes its appearance; so that at 40° the field of compound formation is taken up by the two forms D.S. 15 and D.S. 10, as seen in Fig. 2. The relationships of these double salts at still higher temperatures were not investigated further, except in a limited region at 55°, enough to show only that the range of existence of D.S. 10 is considerably enlarged at that temperature. The purpose of the experiments at 55° was principally to substantiate further the composition of the phase reported as D.S. 10 at 40°.

The formulas of the two higher hydrates of the double salt are based on the analysis of crystals formed by the slow evaporation of solutions falling

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(5) Hill and Ricci, THIS JOURNAL, **53**, 4305 (1931).

TABLE I

Temp., °C.	Original complex, wt. %		Saturated solution, wt. %		Density	Extrapolation	Solid phase
	NaI	$NaIO_3$	NaI	$NaIO_3$			
20	31.47	6.98	30.43	1.58	1.318	−0.82% NaI	D.S. 20
	38.01	7.04	38.26	0.513	1.409	− .25	D.S. 20
	52.12	7.06	54.96	.062	1.686	+ .32	D.S. 15
	57.34	7.00	61.36	.042	1.811	+ .58	D.S. 15
25 a	0.00	...	0.00	8.569	1.075		$NaIO_3 \cdot H_2O$
b	31.53	10.00	31.57	2.42	...		$NaIO_3 \cdot H_2O$ + D.S. 20
	33.68	7.50	33.06	1.96	1.355	− .77	D.S. 20
	34.75	9.97	34.29	1.62	...	−1.19	D.S. 20
	36.67	6.93	36.56	1.18	1.391	−0.15	D.S. 20
	39.98	6.99	40.42	0.704	1.443	+ .90	D.S. 20
c	43.00	6.00	43.91	.455	1.494		D.S. 20 + D.S. 15
	43.50	15.01	46.06	.314	...	− .38	D.S. 15
	52.01	6.06	54.42	.102	1.605	− .19	D.S. 15
	59.85	6.08	63.71	.069	1.884	+ .67	D.S. 15
	59.01	9.49	64.67	.079	...	No D.S. 10	D.S. 15 + $NaI \cdot 2H_2O$
	65.35	2.20	64.72	.71	...		D.S. 15 + $NaI \cdot 2H_2O$
d	Av.		64.70	.75			D.S. 15 + $NaI \cdot 2H_2O$
e	...	0.00	64.71	.00	1.904		$NaI \cdot 2H_2O$
40 a	0.00	...	0.00	11.70[1]			$NaIO_3 \cdot H_2O$
b	...	...	...	...			$NaIO_3 \cdot H_2O$ + $NaIO_3$
c	40.44	12.00	40.84	3.02		No D.S. 20	$NaIO_3$ + D.S. 15
	46.27	9.48	48.26	0.95		−0.11%	D.S. 15
	52.77	8.00	56.16	.36		+ .26	D.S. 15
	58.04	7.52	62.52	.30		+ .41	D.S. 15
d	61.39	7.00	65.39	.32			D.S. 15 + D.S. 10
	61.72	6.98	65.54	.31		−0.19%	D.S. 10
	62.07	7.00	65.95	.31		− .09	D.S. 10
	62.44	7.00	66.40	.31		− .08	D.S. 10
	62.68	6.99	66.63	.30		+ .17	D.S. 10
	62.88	7.00	66.89	.30		+ .13	D.S. 10
	64.79	3.95	66.97	.30		+ .33	D.S. 10
e	67.90	2.01	67.10	.30			D.S. 10 + $NaI \cdot 2H_2O$
f	...	0.00	67.35	.00			$NaI \cdot 2H_2O$
55	57.91	7.48	60.97	.82		− .27	D.S. 10
	60.15	7.18	63.59	.67		− .31	D.S. 10
	62.97	7.03	66.78	.60		+ .44	D.S. 10
	64.07	6.99	68.03	.61		+ .63	D.S. 10
	64.94	6.99	69.11	.59		+ .48	D.S. 10

on the solubility curves of the respective solids, at room temperature. The crystals of D.S. 20 were so large and well formed that they could not have been contaminated with any but negligible quantities of mother liquor; some of these crystals —hexagonal—are 1.3 cm. long and over 0.65 cm. in cross section. Their analysis is given in Table II-A. The analysis of the D.S. 15 crystals, which were much smaller, was corrected according to the method of A. E. Hill,[6] and is given in Table II-B. The extremely limited range of stability of the lowest hydrate, $2NaIO_3 \cdot 3NaI \cdot 10H_2O$, at 40°, and its very incongruent solubility relationships, made it too difficult to obtain crystals of the double salt by slow evaporation of its saturated solution. The analysis reported for it in Table II-C was made on two residues of ternary complexes at 40°; specifically, those containing 62.44 and 62.88% of sodium iodide, respectively. The errors seen in the results are to be expected from the difficulty of separating the very fine crystals from the hot, rapidly crystallizing solution containing about 67% of solid. Nevertheless the 2:3:10 ratio is evident, and the composition is further confirmed by the extrapolation of the tie-lines, as reported in the table, especially in the experiments at 55°. The extrapolations at the latter temperature are more significant since there is greater convergence of the tie-lines, due to the expanded range of stability of the double salt at the higher temperature.

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(6) Hill, THIS JOURNAL, **52**, 3823 (1930).

TABLE II

A. $2NaIO_3 \cdot 3NaI \cdot 20H_2O$

	Observed molecular ratio		Average	Theoretical
Sample	1	2		
$NaIO_3$	1.99	1.89	1.95	2
NaI	3.00	3.00	3.00	3
H_2O	19.74	19.88	19.81	20

B. $2NaIO_3 \cdot 3NaI \cdot 15H_2O$

Sample	1	2		
$NaIO_3$	2.07	1.85	1.96	2
NaI	3.00	3.00	3.00	3
H_2O	14.87	15.12	15.00	15

C. $2NaIO_3 \cdot 3NaI \cdot 10H_2O$

Sample	1	2		
$NaIO_3$	2.00	2.00	2.00	2
NaI	3.31	3.02	3.17	3
H_2O	9.96	9.32	9.64	10

Double Salts Based on $NaIO_3$.—The following is a list of the known double salts of sodium iodate with salts of the type NaX.

1. With $NaNO_3$[2]	$2NaIO_3 \cdot 3NaNO_3 \cdot 15H_2O$
2. With NaCl[3]	$2NaIO_3 \cdot 3NaCl \cdot 10H_2O$
3. With NaBr[4]	$2NaIO_3 \cdot 3NaBr \cdot 15H_2O$ $2NaIO_3 \cdot 3NaBr \cdot 10H_2O$
4. With NaI	$2NaIO_3 \cdot 3NaI \cdot 20H_2O$ $2NaIO_3 \cdot 3NaI \cdot 15H_2O$ $2NaIO_3 \cdot 3NaI \cdot 10H_2O$

With HIO_3[7] there are two compounds, $NaIO_3 \cdot 2HIO_3$ and $2NaIO_3 \cdot I_2O_5$. With salts of the type Na_2X, it forms double salts only in the case of Na_2SO_4: $NaIO_3 \cdot 3Na_2SO_4$ and $NaIO_3 \cdot 4Na_2SO_4$.[8] There is no compound formation with Na_2CO_3,[9] $Na_2C_2O_4$;[10] moreover, no compounds are formed with $Mg(IO_3)_2$[5] or KIO_3.[5]

The regularity in the combinations with sodium nitrate and with the three halides is so marked that one hesitates to classify the combinations with iodic acid and with sodium sulfate simply as exceptions. It seems more likely that the regular combinations constitute, or are members of, a series depending primarily on the properties of sodium iodate, and only secondarily on the properties of the second salt in the combination; or, a series based on sodium iodate; while the two apparently irregular cases of combinations with iodic acid and sodium sulfate would appear to represent instances of series the characteristics of which are determined by iodic acid and sodium sulfate, respectively.

In the regular sodium iodate series here shown, sodium iodate is so to speak the dominant member of the double salt. It is the common salt of the series, and the 2–3 molecular ratio runs through the whole series. The hydration varies regularly, by 5 molecules of water, and is in each case a multiple of 5. This in itself points to the influence of sodium iodate, which crystallizes as $NaIO_3 \cdot 5H_2O$ below 19.8°. This series of salts then is to a great extent independent of the other salts—the regressive member—with which the iodate is combined; for since sodium nitrate has no hydrates, and the three halides have dihydrates only, it is evident that with 3 molecules of each in a molecule of the double salt there is no way of relating the hydration of the double salt to the hydration of these secondary salts. Moreover, that the regularities of this series of salts is significant is brought out by what has already been stated in reference to the correction of the sodium iodide system; for it was sufficient, in the writer's experience, to examine the list for the nitrate, chloride and bromide cases, to be quite certain beforehand as to what would be found in the iodide system.

It is suggested then that the combinations with iodic acid, which are so different in character from those showing what we may call the sodium iodate regularities, must indicate the influence of the other constituent, iodic acid. Some confirmation that this is probably so is seen in the fact that iodic acid gives other similar anhydrous complex salts:[7] $KIO_3 \cdot HIO_3$ and $KIO_3 \cdot 2HIO_3$; and $NH_4IO_3 \cdot 2HIO_3$. Here again then we find some regularity in a series containing iodic acid as the common constituent. Moreover, with the exception of the double salt $2KIO_3 \cdot Te(OH)_6$, a compound illustrating certain properties of telluric acid,[11] this combination with iodic acid is the only complex known to be formed by potassium iodate,[5,12] showing that its formation is essentially a property of iodic acid and not of potassium iodate.

As to the apparently very irregular combinations with sodium sulfate it is evident that they cannot be explained by any tendency of sodium iodate since the latter does not generally form complexes with salts of the type Na_2X. Such anhydrous combinations, then, with uneven molecular ratios such as 1:3 and 1:4 should represent a tendency of sodium sulfate in its combina-

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(7) Meerburg, *Z. anorg. Chem.*, **45**, 324 (1905).

(8) Foote and Vance, *Am. J. Sci.*, **19**, 203 (1930).

(9) Foote and Vance, *ibid.*, **25**, 499 (1933).

(10) Foote and Vance, *ibid.*, **26**, 16 (1933).

(11) Pauling, THIS JOURNAL, **55**, 1895 (1933).

(12) Hill and Brown, *ibid.*, **53**, 4316 (1931).

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).