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Some Aqueous Ternary Systems Involving Univalent Iodates

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The aqueous ternary systems of $AgIO_3$ with each of the following salts were found to be simple at 25°: $LiIO_3$, $NaIO_3$, KIO_3, NH_4IO_3, $AgNO_3$. The solubility of $AgIO_3$ was determined at 25 and 45°. The solubility curve of a form of $LiIO_3$ stable above ~50–60° is reported, from 10 to 95°, as also the solubility, at 25°, of a form probably stable at that temperature. The system $AgIO_3$–I_2O_5–H_2O forms the incongruently soluble pyro-iodate $AgIO_3 \cdot I_2O_5$ at both temperatures studied, 25 and 45°. Similarities in the formulas of double compounds of iodates with iodic acid or with iodine pentoxide are discussed, and it is suggested that the compound previously described as $KIO_3 \cdot 2HIO_3$ is probably anhydrous, with the formula $KIO_3 \cdot I_2O_5$. The system $LiIO_3$–HIO_3–H_2O was studied at 25°. Unlike the other univalent iodates $LiIO_3$ does not form distinct compounds with HIO_3 or I_2O_5 at this temperature, but a solid solution. The limits of this solid solution do not extend to the simple components $LiIO_3$ and HIO_3, which are present as pure solid phases, but they do include the molar ratios of possible compounds of $LiIO_3$ with either HIO_3 or I_2O_5.

The first phase rule investigations on the solid compounds of iodic acid and the iodates were reported by Meerburg,[1] who determined the 30° isotherms of the ternary systems involving $NaIO_3$, KIO_3 and NH_4IO_3, respectively. In extension of this work we have studied the system $AgIO_3$–HIO_3–H_2O (more correctly, the system $AgIO_3$–I_2O_5–H_2O) at 25 and 45°, and the system $LiIO_3$–HIO_3–H_2O at 25°. At the same time some aqueous systems of $AgIO_3$ and other related salts were examined at 25°, and certain solubilities were determined, particularly that of one form of $LiIO_3$ from 10 to 95°.

All the univalent iodates studied form solid complexes with HIO_3 or I_2O_5 at room temperature. Both "acid iodates" or compounds of a salt with "HIO_3," and "pyro-iodates," compounds of salt and I_2O_5, are reported. $AgIO_3$ has now been found to form such a pyro-compound, with the formula $AgIO_3 \cdot I_2O_5$. $LiIO_3$ seems to be exceptional in forming, at 25°, a solid solution rather than any definite compound. Since the composition of the solid solution does not extend to the individual components, however, it is not possible to say whether it involves HIO_3 or I_2O_5, and it is possible that it may represent solid miscibility on the part of two or more actual compounds.

Materials and Analytical Methods.—Two samples of pure silver iodate were obtained by washing commercial preparations with warm, dilute nitric acid and water, followed by drying at 100°. A third sample was purified by recrystallization of commercial material together with solubility residues from an ammoniacal solution with nitric acid, followed by washing with water and drying at 100°. The purity of the samples, determined iodometrically, was 99.9–100.0%. Because of the low solubility of $AgIO_3$ and because of further difficulties from precipitation of AgI on undecomposed $AgIO_3$, the samples for analysis were dissolved completely in 50% aq. KI before treatment with dil. H_2SO_4. After the instant reduction of all the iodate in this manner, the liberated iodine was titrated with standard thiosulfate. The silver content of the first sample was also determined gravimetrically, with a result of 99.9% purity. For this purpose the sample, again first dissolved in a small volume of 50% aq. KI, was reduced to iodide with SO_2; after a hundredfold dilution of the solution, the precipitated AgI was filtered after boiling with some nitric acid.

Commercial NH_4IO_3 was recrystallized and vacuum-dried at 60–70°. Iodometric analysis with $Na_2S_2O_3$ gave 99.9% purity. C.P. samples of $NaIO_3$, KIO_3 and $AgNO_3$ were dried and used without further purification. The iodic acid used was ground to fine powder and dried at room temperature over anhydrone for one week. It was found 100.0% pure both alkalimetrically with NaOH (standardized with $KIO_3 \cdot HIO_3$ prepared according to Shaffer and Hartman[2]) and iodometrically with standard $Na_2S_2O_3$.

A second method used for determination of iodate, which will be referred to as iodometry with standard H_2SO_4, was the procedure, described in most analytical texts, in which the sample is titrated with standard acid in presence of excess of KI and $Na_2S_2O_3$, with methyl red as indicator. Since the equivalent weight of iodate is here six times that in respect to thiosulfate, this method was used for the analysis of the concentrated solutions of the system $LiIO_3$–HIO_3–H_2O. Both methods are very accurate, agreeing within 1/1000.

Some of the lithium iodate used was made by purification of two samples of commercial C.P. material, which assayed ~97% $LiIO_3$. One sample contained insoluble $Ba(IO_3)_2$ and gave an acid reaction. Part of it was simply recrystallized twice and part was neutralized with Kahlbaum LiOH before the second crystallization. The other sample contained insoluble Li_2CO_3 and gave an alkaline reaction; this was neutralized with iodic acid, followed by LiOH, before two recrystallizations. The rest of the salt used was made from Kahlbaum Li_2CO_3 and C.P. iodic acid, with final neutralization with some LiOH. Various turbidities appearing during the process were removed by filtration when possible and by boiling with activated carbon.

The final product was obtained by slow evaporation with stirring on a hot-plate. After decantation the crystals were filtered by suction and washed with water. Ground and dried at 110–180°, the product was found to be 99.9 to 100.1% pure by determination of lithium as Li_2SO_4 after reduction with SO_2, and by determination of iodate by titration with $Na_2S_2O_3$ and with H_2SO_4.

The determinations of solubilities, both binary and ternary, were made according to procedures usually followed in similar investigations, and a few minor variations will be indicated in connection with particular systems.

Solubility of $AgIO_3$, 25 and 45°.—These solubilities were determined by rotation of excess of solid with freshly boiled, distilled water in 250-ml. Pyrex bottles (glass-stoppered without grease) in large constant temperature water-baths. The solid used was first freed of very fine particles through warming and stirring with successive portions of concd. HNO_3 for an hour, followed by repeated washing and decantation with water. After rotation and settling of the solid, the liquid was sampled by means of calibrated 50-ml. delivery pipets fitted with filter paper tips. Samples showing any appreciable Tyndall effect gave high results and were therefore discarded. The solution was analyzed by determination of iodate with 0.01 *N* $Na_2S_2O_3$. In one experiment, rotation for 5 months gave, at 25°, 0.0506 g./l. (U, from unsaturation) and 0.0506 (S, from supersaturation); a second independent set of runs gave 0.512 and 0.0511

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(1) P. A. Meerburg, *Z. anorg. Chem.*, **45**, 324 (1905); also *Chem. Weekblad*, **1**, 474 (1904).

(2) P. A. Shaffer and A. F. Hartman, *J. Biol. Chem.*, **45**, 376 (1920); see also I. M. Kolthoff and L. H. van Berk, THIS JOURNAL, **48**, 2799 (1926).

(U), 0.0507 and 0.0509 (S) after 7 days. At 45° the results, after 2 days of stirring, were 0.0995 g./l. (U) and 0.0997 (S). Average values may be taken as 0.0508 g./l. at 25° and 0.0996 at 45°, or 0.00510 and 0.01006% by weight, respectively. With corrections for ionic strength neglected, the solubility product values would be 3.23×10^{-8} and 1.24×10^{-7}, respectively. The solubility at 25° agrees well with the most recent literature values,[3] which range from 0.0501 to 0.0507 g./l. at 25°. By interpolation, the literature values give ~0.10 g./l. at 45°.

Salt Systems at 25°.—The following five systems were studied at 25°: (1) $AgIO_3$–$LiIO_3$–H_2O; (2) $AgIO_3$–$NaIO_3$–H_2O; (3) $AgIO_3$–KIO_3–H_2O; (4) $AgIO_3$–NH_4IO_3–H_2O; (5) $AgIO_3$–$AgNO_3$–H_2O. The isotherms are all of the simplest type, with the individual salts, hydrated only for $NaIO_3 \cdot H_2O$, as the sole solid phases; there is no evidence of either compound formation or solid solution.

In systems 1–4 the concentration of $AgIO_3$ in the solutions containing the second salt was not detectable, all qualitative tests for silver in the solution being negative; hence the second salt was determined either through evaporation for total solid or through titration of total iodate.

In system 5, total solid was determined by evaporation to dryness after addition of a drop of concd. HNO_3, which, apparently by preventing reduction of silver, always gave pure white residues. The final weighed residue was taken up in water for determination of $AgIO_3$, whereupon $AgNO_3$ was calculated by difference. For iodate determination the solution of the residue was treated with HCl to precipitate AgCl and the filtrate was titrated with 0.01 *N* $Na_2S_2O_3$. Preliminary test of the procedure showed it to be dependable, leading to an uncertainty of about 0.003 in the final percentage of $AgIO_3$. The solubility of $AgIO_3$ was depressed to 0.009% at 22.65% $AgNO_3$, 0.006% at 48.47%, 0.035% at 70.43%, and 0.040–0.043% at 71.84% $AgNO_3$ (saturation).

The solubility of $LiIO_3$ is 43.86% (density 1.558); other densities are 1.227 at 23.25% and 1.553 at 43.37%. Although the average value found for the solubility of KIO_3 agrees with the average literature value, the individual determinations showed considerable scattering (8.428 to 8.504), a frequent observation with this salt, possibly attributable[4] to some colloidal behavior.[5] The solubility found for $NaIO_3 \cdot H_2O$, 8.44%, is lower than the most recent determination, 8.49%[6] (which was itself distinctly lower than all previously reported values, averaging ~8.6%). The present determination was made with monohydrate as the actual starting solid, with long periods of stirring, with both directions of equilibration, and, in some experiments, with special precautions, involving discarding of successive portions of saturated solution, to avoid colloidal particles.

The solubility of NH_4IO_3 was found to be 3.682% (density 1.026) at 25°, and 5.992% (density 1.037) at 45°. Solubilities at these temperatures have not previously been reported; however, the present values fall on a smooth curve with those reported at 30° (4.20%) by Meerburg[1] and at 15° (2.5%) and 101° (12.7%) by Rammelsberg.[7]

System $AgIO_3$–I_2O_5–H_2O; 25° and 45°.—The complexes in this system were made up from $AgIO_3$, HIO_3 and water. The liquids were sampled with delivery pipets at low concentration and with specific gravity pipets for high concentration. They were found to contain no significantly detectable concentration of $AgIO_3$ and hence the determination of acid with standard NaOH was calculated directly as either HIO_3 or I_2O_5. The determination, in a number of samples, both of acid and of iodate gave agreement within 1/1000, so that to this extent, at any rate, the absence of $AgIO_3$ in solution was confirmed. The densities obtained, many of them not listed in the table, may therefore be taken as those of solutions of iodic acid. They agree well, at 25°, with the values reported by Randall and Taylor[8] for the range 0–61% I_2O_5; those at higher concentrations are not considered as dependable as these. Equilibrium was in general proved by repeated analysis after further stirring following an initial period of about a week.

The data, in terms of weight percentage of $AgIO_3$ and I_2O_5 as components, are listed in Table I for the two temperatures studied, 25 and 45°. The stable relations at 25° are plotted, in the same units, in Fig. 1, from which the formation of a 1:1 compound is clear. The diagram for 45° is very similar to Fig. 1.

The compound formed more rapidly, and equilibrium was more easily attained, near the point *b*, the solution congruently saturated with compound and HIO_3 (or $I_2O_5 \cdot H_2O$), than near point *a*, the solution incongruently saturated with $AgIO_3$ and the compound. This difference would be expected if the formation of the compound depends on poly-iodate ions whose concentration would increase with that of iodic acid. At any rate, it was not possible to obtain equilibrium (except for one experiment at 45°) for complexes with compositions in the invariant region A-*a*-A·B as prepared from water, solid HIO_3 and solid $AgIO_3$, even though they were seeded with the compound and some were agitated at 100° for a few hours before being brought to 25 or 45°. The resulting metastable values have been omitted from both the table and the diagram. The invariant point *a* at both temperatures was finally obtained by direct equilibration of the actual solid phases, $AgIO_3$ and double compound, with solutions. Since the double compound was added as a wet residue from other experiments the total complex compositions for these points are estimated.

When the data were originally plotted in terms of HIO_3 as a component the tie-lines did not converge sharply at a point on the base of the triangle,

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(3) W. B. Baxter, This Journal, **43**, 615 (1921); I. M. Kolthoff and J. J. Lingane, *J. Phys. Chem.*, **42**, 133 (1938); N. C. C. Li and Ying-Tu Lo, This Journal, **63**, 394 (1941); R. M. Keefer and H. G. Reiber, *ibid.*, **63**, 689 (1941); P. F. Derr, R. M. Stockdale and W. C. Vosburgh, *ibid.*, **63**, 2670 (1941).

(4) A. E. Hill and J. E. Ricci, *ibid.*, **53**, 4305 (1931).

(5) J. W. McBain and S. S. Kistler, *J. Phys. Chem.*, **35**, 130 (1931).

(6) J. E. Ricci and W. F. Linke, This Journal, **69**, 1080 (1947).

(7) C. F. Rammelsberg, *Ann. Phys. und Chem.* (*Pogg.*), **44**, 555 (1838).

(8) M. Randall and M. D. Taylor, *J. Phys. Chem.*, **45**, 959 (1941).

TABLE I

SYSTEM $AgIO_3$ (=A)-I_2O_5 (=B)-H_2O (=W)

Saturated solution % B	Saturated solution Density	Total complex % A	Total complex % B	Solid phase
		At 25°		
19.51	1.203	3.03	18.96	A
36.89	1.455	9.99	33.17	A
48.64		2.99	47.21	A
52.11		22	45	A, A·B
52.09		20	46	A, A·B
54.12		14.96	54.06	A·B
55.20	1.864	5.00	55.02	A·B
59.78	1.999	8.00	58.81	A·B
63.04	2.12	5.01	62.15	A·B
63.72		10.01	61.67	A·B
64.69	2.18	5.00	63.57	A·B
65.70	2.22	5.00	64.48	A·B
67.82		5.00	66.39	A·B
68.85		5.00	67.35	A·B
69.86		5.00	68.29	A·B
71.00	2.45	5.00	69.24	A·B
71.42		5.50	69.25	A·B
71.54	2.48; point *b*, average of four			A·B, B·W
71.55		0.00	...	B·W
		At 45°		
34.55	1.410	20.01	27.53	A
40.40	1.512	19.97	32.21	A
46.43	1.637	20.00	36.98	A
47.44	1.653	10.00	42.68	A
48.42	1.681	8.99	44.10	A
49.53	1.702	5.00	46.96	A
49.95		21	44	A, A·B
49.94		22	42	A, A·B
49.94		5.01	49.81	A, A·B
50.45	1.727	5.01	50.75	A·B
50.99	1.737	5.00	51.24	A·B
51.55		5.00	51.71	A·B
52.73		15.00	53.11	A·B
54.24	1.820	5.00	54.08	A·B
55.30	1.849	5.00	55.03	A·B
56.29		5.01	55.98	A·B
57.44	1.911	5.01	56.93	A·B
61.10		15.01	58.82	A·B
66.74		15.00	62.59	A·B
70.64	2.42	5.01	68.76	A·B
71.69	2.47	4.98	69.71	A·B
72.05		14.95	66.21	A·B
73.24	2.54	5.00	71.14	A·B
74.02	2.58	2.00	74.00	A·B, B·W
73.89		0.00	...	B·W

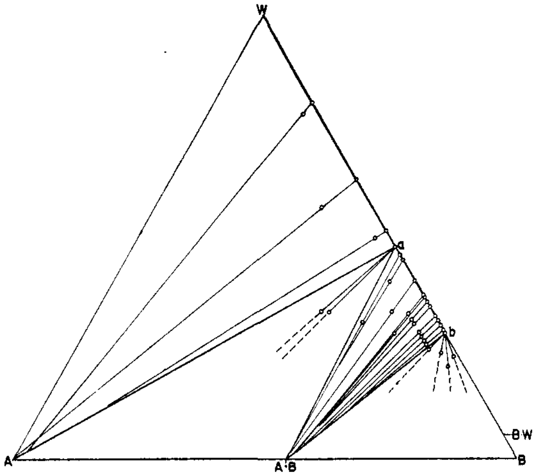

Fig. 1.—System $AgIO_3$(A)-I_2O_5(B)-H_2O (W) at 25°.

but fell, with some spreading, slightly to the right of the 1:2 molar ratio. (A 1:2 molar ratio of $AgIO_3$ to HIO_3 corresponds to a 1:1 ratio of $AgIO_3$ to I_2O_5.) Although the discrepancy from the compound composition "$AgIO_3 \cdot 2HIO_3$" was small, the analytical accuracy involved gave it significance. Since the tie-lines for the compound appeared, at both temperatures, to converge below the base of the diagram, with a negative percentage of water, the compound was suspected to involve I_2O_5 rather than HIO_3, and the data were therefore recalculated in the terms here presented. These tie-lines, fixed by compositions of liquid and total complex, were extrapolated algebraically[4] both to the base of the triangle of Fig. 1 and to the line connecting the points A and A·W, or "HIO_3." On the base line the twelve tie-lines at 25° give 54.57 ± 0.68% I_2O_5 (0.68 being the average deviation from the mean) while the thirteen tie-lines at 45° give 53.39 ± 0.48% I_2O_5. The theoretical value for $AgIO_3 \cdot I_2O_5$ is 54.14%. The extrapolations to the line A–A·W give 55.47 ± 0.91% I_2O_5 at 25° and 54.11 ± 1.02 at 45°, but the theoretical value for $AgIO_3 \cdot 2HIO_3$, or $AgIO_3 \cdot I_2O_5 \cdot H_2O$, is 52.60% I_2O_5. The agreement with the anhydrous formula is clearly so much better that we may take the compound to be the pyroiodate $AgIO_3 \cdot I_2O_5$.

Other Pyro- or Polyiodates.—The following is a list of apparently all the compounds between iodic acid or iodine pentoxide and other iodates reported in the literature:

Compound	Reference no.
$2NaIO_3 \cdot I_2O_5$	1
$NaIO_3 \cdot 2HIO_3(NaIO_3 \cdot I_2O_5 \cdot H_2O)$	1
$KIO_3 \cdot HIO_3(2KIO_3 \cdot I_2O_5 \cdot H_2O)$	1, 9, 10, 11, 12
$KIO_3 \cdot 2HIO_3(KIO_3 \cdot I_2O_5 \cdot H_2O)$	1, 9, 11, 12, 13
$KIO_3 \cdot I_2O_5$	13, 14
$RbIO_3 \cdot HIO_3(2RbIO_3 \cdot I_2O_5 \cdot H_2O)$	15
$RbIO_3 \cdot 2HIO_3(RbIO_3 \cdot I_2O_5 \cdot H_2O)$	13, 15
$RbIO_3 \cdot I_2O_5$	13
$2CsIO_3 \cdot I_2O_5$	15
$CsIO_3 \cdot I_2O_5 \cdot {}^1/_2H_2O$	15
$NH_4IO_3 \cdot 2HIO_3(NH_4IO_3 \cdot I_2O_5 \cdot H_2O)$	1, 16

In addition to these involving univalent iodates, we have also $Ba(IO_3)_2 \cdot I_2O_5$.[17]

The formation of these solid compounds may be taken as in a sense confirming the formation of poly-acid ions or of condensation in general in aqueous iodic acid, inferred from studies of its

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(9) A. Ditte, *Ann. chim. phys.*, [4] **21**, 47 (1870).

(10) J. C. G. de Marignac, *Ann. Mines*, [5] **9**, 32 (1856); [5] **12**, 66 (1857); reported in J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green, London, 1922, Vol. II, p. 335.

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(12) S. B. Smith, THIS JOURNAL, **69**, 2285 (1947); for details, Document 2389, Amer. Documentation Inst.

(13) U. Croatto and G. Bryk, *Gazz. chim. ital.*, **71**, 590 (1941).

(14) G. S. Serullas, *Ann. chim. phys.*, [2] **43**, 117 (1830).

(15) H. L. Wheeler, *Am. J. Sci.*, [3] **44**, 123 (1892).

(16) A. Ditte, *Ann. chim. phys.*, [6] **21**, 145 (1890).

(17) A. J. Freedman, Dissertation, New York University, 1948.

freezing point lowering, molecular conductivity, and ionic mobilities.[18] From this point of view the compound $AgIO_3{\cdot}I_2O_5$ might be considered as a triiodate, AgI_3O_8, and $KIO_3{\cdot}HIO_3$ as either a biiodate, KHI_2O_6, or a tetraiodate, $K_2I_4O_{11}{\cdot}H_2O$. But it is not possible, of course, to reason specifically from the formulas of the solids to probable formulas of condensed ions. In this connection we may note, for example, that in the case of the fairly soluble salt KIO_3, the familiar compound "$KIO_3{\cdot}HIO_3$" is precipitated from aqueous solution at 25° at a concentration as low as 0.38% HIO_3 and 7.77% KIO_3,[19] while no "poly-iodate" of silver appears until the iodic acid concentration reaches 54.9% (point *a* at 25°, in terms of HIO_3 as solute). The greatest regularity in the formulas of the solid compounds is, in fact, seen not from the point of view of possible ions of condensed acids, but on the basis of simple ratios of MIO_3 to I_2O_5, in compounds which may or may not be hydrated. All the formulas fall into two groups: $MIO_3{\cdot}I_2O_5$ and $2MIO_3{\cdot}I_2O_5$, in each case with or without one (one-half for the cesium compound) mole of water.

These observations suggest the question whether the compounds reported as $NaIO_3{\cdot}2HIO_3$, $NH_4IO_3{\cdot}2HIO_3$ and $KIO_3{\cdot}2HIO_3$ were correctly identified. For the first of these Meerburg reported direct analyses of the solid phase, but the other two were based on tie-lines which do not permit significant distinction between such formulas and the anhydrous pyroiodates, since the tie-lines did not originate in solutions of sufficiently high iodic acid content. In Table II, Smith's data for tie-lines originating from the two most concentrated solutions at each temperature are given, recalculated in terms of KIO_3, I_2O_5 and H_2O as the components.

TABLE II

PART OF SYSTEM KIO_3 (A)–I_2O_5 (B)–H_2O (W), FROM DATA OF S. B. SMITH[12]

Temp., °C.	Solution % A	Solution % B	Wet residue % A	Wet residue % B	% H_2O at 1A:1B
0	0.29	44.85	31.90	58.19	−0.62
	.30	61.14	32.41	60.45	+ .99
25	.38	53.84	29.94	59.32	− .11
	.34	64.24	29.24	62.48	−1.48
50	.83	55.36	29.80	59.20	−0.01
	.99	66.17	28.39	62.60	− .42

These tie-lines were then extrapolated algebraically to their intersections with the line $1KIO_3{:}1I_2O_5$; the result, in terms of %H_2O at the intersection, is given in the last column of the table. The average value is −0.28(± 0.57)% H_2O. Since the formula $KIO_3{\cdot}2HIO_3$ or $KIO_3{\cdot}I_2O_5{\cdot}H_2O$ requires 3.18% H_2O, it is clear that these tie-lines, which are the significant ones for the distinction, indicate the composition $KIO_3{\cdot}I_2O_5$. The solids in the system KIO_3–I_2O_5–H_2O in the temperature range 0–50° are therefore probably KIO_3, $KIO_3{\cdot}HIO_3$ (congruently soluble), $KIO_3{\cdot}I_2O_5$ (incongruently soluble) and HIO_3.[20]

System $LiIO_3$–HIO_3–H_2O at 25°.—For the analysis of the solutions the iodic acid content was determined by titration with standard NaOH, and the neutralized sample was then used for the determination of total iodate, either with standard $Na_2S_2O_3$ after suitable aliquoting or directly with standard H_2SO_4. The second, faster method was used for most of the work. The data are listed in Table III and plotted in Fig. 2.

TABLE III

SYSTEM $LiIO_3$–HIO_3–H_2O AT 25°

(A = $LiIO_3$; B = HIO_3; S.S. = solid solution)

Saturated solution % A	Saturated solution % B	Saturated solution Density	Total complex % A	Total complex % B	Solid phase	% $LiIO_3$ in solid
43.86	0.00	1.558	. . .	0.00	A	
43.96	1.03	1.579	49.99	1.00	A	
43.96	3.13	1.620	48.80	2.93	A	
43.83	6.67	1.697	50.01	6.00	A	
43.56	11.18	1.797	50.00	10.00	A	
43.08	16.65	1.923	49.00	15.00	A	
42.49	20.89	2.027	44.99	20.00	A	
41.48	26.56		44.98	24.99	A	
40.81	28.80	2.237	55.00	22.00	A	
40.42	30.78	2.300	41.99	29.98	A	
40.16	31.40	2.312	54.96	23.99	A + S.S	
40.25	31.30	2.310	52.50	26.27	A + S.S.	
40.16	31.30	2.311	54.99	26.50	A + S.S.	82.4
(40.19	31.33	2.311)	← aver. (*a*);			
			point (*c*) →		A + S.S.	(78.7)
39.75	32.46	2.334	50.54	29.46	S.S.	78.2
39.57	32.65	2.340	52.98	28.99	S.S.	77.8
38.84	34.58	2.385	47.96	31.98	S.S.	76.0
38.53	35.42		39.94	34.98	S.S.	76
37.21	38.25	2.475	46.99	35.00	S.S.	74.0
37.13	38.52	2.476	47.49	35.00	S.S.	74.0
36.18	40.29	2.525	36.97	39.99	S.S.	74
36.28	40.38		47.00	36.50	S.S.	72.9
35.35	42.23	2.567	46.50	38.00	S.S.	71.5
34.70	43.54	2.602	46.00	39.01	S.S.	71.0
34.09	44.79	2.636	45.50	40.00	S.S.	70.5
33.62	45.60		35.00	44.99	S.S.	71
33.48	46.00		44.99	41.00	S.S.	69.8
32.89	47.02	2.695	42.00	43.00	S.S.	68.9
32.81	47.25	2.702	44.48	42.00	S.S.	69.0
29.86	52.74	2.848	35.00	49.99	S.S.	67.3
27.25	57.45	2.979	32.88	54.09	S.S.	65.2
(26.84	58.15	2.995)	← av.(*b*); point			
			(*d*) →		S.S. + B	(65.0)
26.76	58.19	2.993	31.89	55.11	S.S. + B	64.4
26.95	58.10	2.993	27.99	58.96	S.S. + B	
26.82	58.15	2.998	25.99	60.96	S.S. + B	
25.91	58.56	2.961	19.99	67.97	B	
21.08	61.25	2.827	18.99	64.97	B	
16.48	63.91		14.00	68.97	B	
10.20	68.09	2.609	9.00	71.97	B	
7.23	70.19		6.00	75.00	B	
3.50	72.92	2.514	3.00	75.97	B	
1.24	74.62	2.487	1.00	77.93	B	
0.00	75.40		0.00	. . .	B	

The liquids were sampled with 1-ml. specific gravity pipets. Solutions with at least 20% H_2O could still be pulled through filter paper tips for separation from solid. Those with less water were too viscous for such filtration, and were sampled only after sufficient settling. When the

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(18) See, for example, N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, 1950, pp. 1228–1229.

(19) From the data of S. B. Smith, ref. 12 (on microfilm service).

(20) Prof. S. B. Smith has commented, in a private communication, that even if $KIO_3{\cdot}I_2O_5$ is the solid phase in the region involved in Table II, it is still possible that the solid is $KIO_3{\cdot}2HIO_3$ at lower concentrations of I_2O_5.

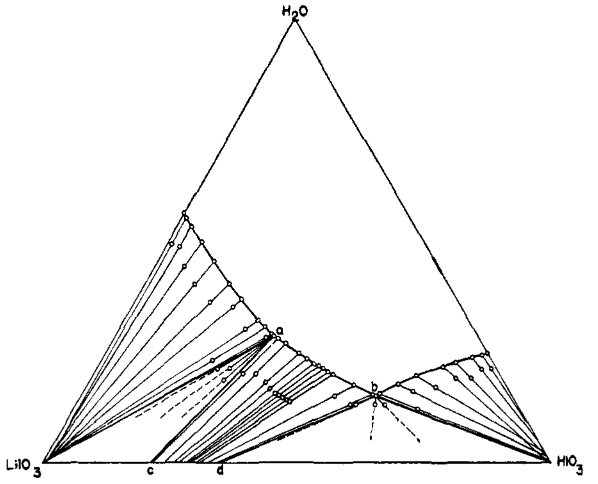

Fig. 2.—System $LiIO_3$–HIO_3–H_2O at 25°.

crystals were not too fine, one or two days of settling sufficed. So much time was otherwise required for settling that the solid–liquid mixture was alternately centrifuged for one minute and replaced in the water-bath for five minutes, until sufficient clear supernatant liquid was available for sampling. The viscosity was so high that even without filtration the withdrawal of a 1-ml. sample required up to 30 minutes.

The densities are plotted against the iodic acid concentration in Fig. 3. The relative values of these densities are significant even though the accuracy of the determinations of the highest values is probably not high.

Equilibrium was reached in 2 to 8 weeks depending on the composition and the amount of solid involved; equilibrium was checked on a few representative complexes, including the most viscous, in each series prepared, before the whole series was analyzed. For saturation with the solid solution equilibrium was checked on each solution, the agreement being 1/1000. In most cases equilibrium was approached presumably from supersaturation because it was necessary to heat the complex to break up the solid cake formed on mixing the components. Since the caking depended somewhat on the order of mixing, some of the points were obtained from undersaturation by variation of this order.

Supersaturation in respect to HIO_3 as solid phase was always very persistent, and the solutions on the solubility curve of HIO_3 were all seeded with the solid before stirring at 25°. In some cases in which the preheating of the complexes led to such marked supersaturation the solutions were so viscous that the liquid barely flowed when the tubes were inverted. For a few of the worst cases the rotation of the tubes was started at ~45°, where the liquids were less viscous, and the temperature of the water-bath was slowly lowered to 25° over a period of 30 hours, the tubes being seeded with HIO_3 at ~36°.

The solid phases are seen from Fig. 2 to be pure $LiIO_3$, a solid solution of intermediate composition, and pure HIO_3. The tie-lines converge with satisfactory sharpness at the compositions of the simple solids $LiIO_3$ and HIO_3. The break in the liquid curve at point *a*, for twofold saturation with $LiIO_3$ and the limiting solid solution *c*, is vague in the plot of Fig. 2, but it is brought out in the density plot of Fig. 3. The limiting compositions of the solid solution, points *c* and *d*, may be estimated from a Roozeboom type of distribution diagram, in which the weight ratio of the salts in the liquid phase is plotted against the ratio in the solid phase. Extrapolation of the curve for saturation with solid solution to the compositions *a* and *b* in the liquid phase gives 78.7% $LiIO_3$ at point *c* and 65.0% $LiIO_3$ at point *d*.

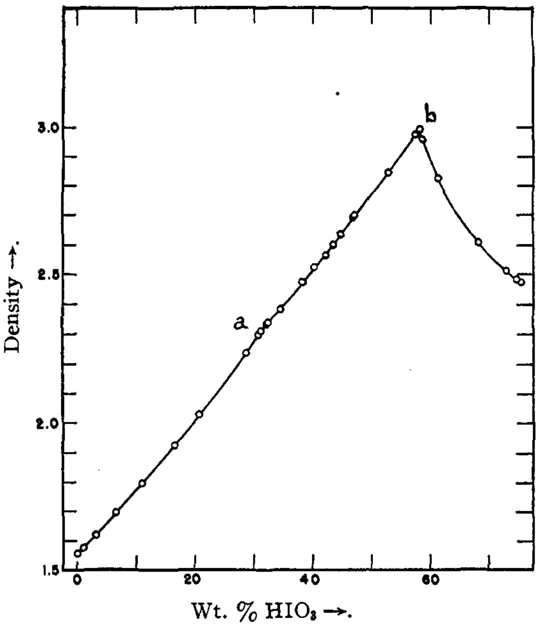

Fig. 3.—Density of saturated solution, system $LiIO_3$–HIO_3–H_2O at 25°.

This solid solution is of the unusual type noted in the system Na_2SO_4–$NaBrO_3$–H_2O, studied from 37.5 to 52°[21]; with point "*d*" containing only ~10% $NaBrO_3$ at 37.5° it would be difficult to attribute that solid solution to solid miscibility of binary compounds of reasonable formulas. In the present case the limits *c* and *d* are such that it is more probable that the solid solution is formed between definite compounds, although whether they would be compounds of $LiIO_3$ with HIO_3 or with I_2O_5 cannot be determined from the data. The limits *c* and *d* cover approximately the ratios 1.8 to 3.6 $LiIO_3/HIO_3$; in terms of $LiIO_3$, I_2O_5 and H_2O as components, the corresponding limits cover the ratios 4.8 to 9.1 $LiIO_3/I_2O_5$.

Under microscopic examination the crystals of the solid solution appeared as long hexagonal rods similar to those of the form of $LiIO_3$ stable at 25°, as observed on samples both from binary and from ternary solubility experiments. The solid solution crystals differed only in that their ratio of length to width was usually about twice that of the $LiIO_3$ crystals.

Solubility of $LiIO_3$.—Many measurements were made in an attempt to determine the stable solubility curves of the forms of $LiIO_3$ from 10 to 95°. The crystallization of the form or forms stable in

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(21) J. B. Ricci, This Journal, 57, 805 (1935).

the lower range (10 to ~50°) is so slow, however, that all that could be reasonably read from the results is a curve attributable to a form stable above ~50–60°. This form, crystallizing in small octahedra, persists metastably evidently down to 10°, and its solubility curve, with some points approached from undersaturation, some from supersaturation, and a few from both directions, was determined from 10 to 95°. For each point the solid phase was examined microscopically and found to be always the same. The values, listed in Table IV, fall on a smooth curve with a minimum solubility near 85°. These values represent measurements agreeing on repeated analysis with continued stirring at each temperature. The density of the solution at 24.95°, with 45.33% $LiIO_3$, was 1.587. Many widely scattered and unreproducible "solubilities" lower than the values on this curve were observed at temperatures below 55°, and one higher than the curve at 60° but none below the curve at temperatures above 50°. It is probable, therefore, that the form involved is stable above and unstable below ~50–60°.

TABLE IV

SOLUBILITY OF ONE FORM OF $LiIO_3$ (OCTAHEDRAL CRYSTALS)

U, undersaturation; S, supersaturation; *m*, metastable

Temp., °C.	Solubility wt. % $LiIO_3$	Approach from
9.93	47.19 (*m*)	U
20.24	45.86 (*m*)	S
24.95	45.33 (*m*)	U & S
29.94	44.89 (*m*)	U
34.95	44.45 (*m*)	U
40.00	44.12 (*m*)	U
45.00	43.84 (*m*)	U & S
50.06	43.51 (*m*)	S
55.1	43.35 (?)	U
60.2	43.10	U
65.3	43.00	U
75.5	42.82	U
85.5	42.76	S
95.1	42.85	U

Most attention was given to 25°, where a long-constant value of 43.86% was obtained with several different samples of starting material. This is lower than the value in Table IV, and therefore must pertain to a form stable (relatively) at 25°. Whether it is the most stable form at 25°, however, cannot be said, although its solubility does agree fairly well with the value (~44.0%) extrapolated from the solubility curve of $LiIO_3$ in the system $LiIO_3$–HIO_3–H_2O as presented in Table III and Fig. 2. It also agreed in crystalline appearance with the $LiIO_3$ solid phase obtained in the ternary system, in the form of long hexagonal rods, as already mentioned. It is probably the form studied crystallographically by Zachariasen and Barta.[22] Since this solid is definitely anhydrous according to Fig. 2, we may infer that the higher temperature form involved in Table IV must also be anhydrous.

For comparison, we note that the solubility values in the literature are few, at scattered temperatures, and sometimes with no information concerning the purity of the salt and the attainment of equilibrium. Lühdemann[23] reported 42.18% at 10°; Heydweiler[24] gave values of 23.5 and 38.3%, for two forms, at 18°; Grüneisen[25] reported 38% at 18°; Mylius and Funk[26] reported 44.6% at 18°. In addition a hydrate of the salt was also reported ($LiIO_3 \cdot H_2O$, at ~60°) by Ditte,[16] although it has not again been mentioned.

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[22] W. H. Zachariasen and F. A. Barta, *Phys. Rev.*, **36**, 1693 (1930); **37**, 1326 (1931).

[23] R. Lühdemann, *Z. physik. Chem.*, **B29**, 133 (1935).

[24] A. Heydweiler, *Ann. Physik*, **37**, 741 (1912).

[25] E. Grüneisen, *Wissensch. Abh. Phys.-Techn. Reichsanst.*, **4**, 246 (1905).

[26] F. Mylius and R. Funk, *Ber.*, **30**, 1716 (1897).

NEW YORK, N. Y. RECEIVED NOVEMBER 29, 1950

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Some Aqueous Salt Systems Involving Fluosilicates

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The solubility relations in several aqueous systems, some ternary and one quaternary, involving fluosilicates are reported for 25°. The isotherm of the system K_2SiF_6–KBr–H_2O shows the saturating solid K_2SiF_6 to be anhydrous. The three ternary systems involving the salt pairs $(NH_4)_2SiF_6$–$MgSiF_6$, $SrCl_6$–$SrSiF_6$, and $(NH_4)_2SiF_6$–$SrSiF_6$ were studied with 0.5% aqueous H_2SiF_6 as solvent, to prevent hydrolytic precipitations. The first two are simple, with $(NH_4)_2SiF_6$, $MgSiF_6 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $SrSiF_6 \cdot 2H_2O$ as sole solid phases. The third pair forms a congruently soluble double salt the formula of which seems to be $(NH_4)_2SiF_6 \cdot 6SrSiF_6$. In connection with these systems the solubilities of $(NH_4)_2SiF_6$ and $SrSiF_6 \cdot 2H_2O$ in presence of H_2SiF_6, up to ~30%, were also determined. The three systems containing the pairs NH_4–NH_4Cl, NH_4Cl–$(NH_4)_2SiF_6$, and NH_4F–$(NH_4)_2SiF_6$ were studied with pure water as solvent. The first two are simple, the only solids being the anhydrous salts. The third involves the already known incongruently soluble double salt $NH_4F \cdot (NH_4)_2SiF_6$. The 25° isotherm of the quaternary system NH_4F–NH_4Cl–$(NH_4)_2SiF_6$–H_2O has two solutions of threefold saturation. One is a transition point in isothermal evaporation, with the phase reaction $(NH_4)_2SiF_6 + \text{liquid} \rightleftarrows NH_4Cl + NH_4F \cdot (NH_4)_2SiF_6 + H_2O\nearrow$, and the other is the congruent drying-up point for the solids $NH_4F + NH_4Cl + NH_4F \cdot (NH_4)_2SiF_6$.

The literature contains little information on solubility equilibria of the fluosilicates. Solubilities of a number of fluosilicates, some of them of uncertain dependability, are cited in Mellor's "Treatise,"[1] in Seidell's "Solubilities,"[2] and in a compilation by Carter of values known to 1930.[3] Carter also reported some further measurements, in particular the solubilities of the sodium, potassium and barium salts from 0 to ~80°. No double salts of the fluosilicates are mentioned other than the compound $NH_4F \cdot (NH_4)_2SiF_6$. This was first prepared

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[1] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York, N. Y., 1925, Vol. VI, pp. 944–958.

[2] A. Seidell, "Solubilities of Inorganic and Organic Substances," D. Van Nostrand Co., New York, N. Y., 1940, Vol. I, pp. 810, 970, 1098. A few further individual solubilties have since been reported in the literature.

[3] R. H. Carter, *Ind. Eng. Chem.*, **22**, 886 (1930).