THE HYDRATES, TRANSITION TEMPERATURES AND SOLUBILITY OF SODIUM IODATE.

H. W. FOOTE AND JOHN E. VANCE.

Contribution from the Department of Chemistry, Yale University.

Sodium iodate has been reported by various investigators as forming, from water solution, no less than seven hydrates, besides the anhydrous salt.[1] No investigation along modern lines has been carried out to determine the stable hydrates, their transition temperatures and solubility. In the present investigation this data has been obtained between the freezing point of the saturated solution and about 90°. No stable hydrate exists above 73.4°.

Material and Method of Analysis. The sodium iodate used was a very pure commercial product having a composition closely approximating the monohydrate. It was recrystallized before use. In the analysis of solutions and residues, iodate was determined by adding to the solution an excess of potassium iodide, acidifying with sulphuric acid and titrating with standard sodium thiosulphate solution. When more convenient, the water (instead of the iodate) in a solid residue could be determined by heating at 120-140°. The iodate is entirely stable at the latter temperature.

Transition Temperatures. Preliminary determinations by means of cooling curves (between 25° and the eutectic temperature) and dilatometer observations (between 5° and 95°) indicated only two transition temperatures, one slightly below 20° and the other below 90°. The change of the unstable into the stable form immediately above and below the higher transition temperature is exceedingly slow, and for this reason we were unable to determine this temperature accurately either by the dilatometer or by a cooling curve. The slowness of transformation, however, rendered it possible to determine the solubility of the two forms concerned, both above and below the transition point, thus obtaining metastable as well as stable systems. The solubility curves are fortunately quite different in slope and the intersection gives the transition temperature 73.4° with considerable accuracy (see Fig. 1). The solid phases in equilibrium at this temperature are $NaIO_3.H_2O$ and $NaIO_3$.

[1] For a review of the literature on the subject see, for instance, Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 2, p. 334.

The solid phases at the lower transition temperature are $NaIO_3.H_2O$ and $NaIO_3.5H_2O$. They transform into each other very readily. This temperature was determined by (1) a thermal method, (2) by the dilatometer, and (3) by the solubilities. By the first method, nearly equal weights of the two hydrates were mixed with a solution already saturated at approximately the right temperature and placed in a vacuum-jacketed flask. Due to the heat of transformation, the system adjusts itself at the transition temperature. Approaching this temperature from above and below, the values 19.7° and 19.55° were obtained. By means of the dilatometer, the value 19.85° was obtained. From the solubility results which are given below, the value 20.3° can be derived. The average of all four determinations is 19.85°.

Hydrates. In principle, the determination of all the stable hydrates of a salt is exceedingly simple when the transition temperatures are known. All that is necessary is to allow the salt to crystallize at a temperature within its stable range, and determine its composition.

Two samples of the hydrate which is stable below 19.85° were obtained by crystallization below this temperature. They were removed from solution and dried quickly in a cold room. Analyses gave 68.58 and 68.68 per cent of $NaIO_3$. The compound $NaIO_3.5H_2O$ contains 68.72 per cent of $NaIO_3$.

Numerous analyses of the monohydrate, which was found to be the only stable hydrate above 19.85°, were made on samples obtained from solutions at various temperatures within the stability range of this hydrate. This was done because of the other hydrates, particularly the compound $NaIO_3.1\frac{1}{2}H_2O$, which are mentioned in the literature.[2] While the dilatometer showed no irregular expansion throughout the range between 19.85° and 73.4°, indicating that no transition occurred, it seemed highly desirable to show by analysis that only one form, the monohydrate, existed. In some cases, the solid residue from a solubility determination was used for analysis. In others, the salt was allowed to crystallize from solution at the temperature indicated. Averages of closely agreeing results at each temperature were as follows:

Temperature:	20°	25°	30°	35°	40°	60°
Percent $NaIO_3$:	91.71*	91.70†	91.76†	91.34*	91.81*	91.91†

* From a solubility residue.
† By slow crystallization.

[2] Meerburg (Z. anorg. Chem. **45**, 324 (1905) assumed this hydrate was the stable form at 30° in investigating the system $NaIO_3$-HIO_3-H_2O.

The calculated percentage of $NaIO_3$ in the compounds $NaIO_3.H_2O$ and $NaIO_3.1\frac{1}{2}H_2O$ are 91.65 and 87.89 respectively. The results appear to be quite sufficient to show that only the former exists.

To determine when the anhydrous salt was present in the solubility determinations at the higher temperatures, the solid was filtered on a warm Gooch crucible, washed quickly with alcohol and dried between filter papers. This method of obtaining the solid gave entirely satisfactory results as the change from monohydrate to the anhydrous salt (and the reverse) is slow. The residues were either analyzed or tested in a closed tube for water.

Solubility. The solubility was determined in duplicate at each temperature chosen, approaching equilibrium from (1) supersaturated and (2) undersaturated solutions. The mixtures were shaken in a thermostat from four to six hours. Constant solubility, within narrow limits, showed that equilibrium had been reached. The usual precautions were adopted in removing samples for analysis. Following are the results:

SOLUBILITY OF SODIUM IODATE.

Temperature	Grms. $NaIO_3$ in 100 gms. Solution. I	II	Average	Solid Phase
0.0°	2.39	2.46	2.42	$NaIO_3.5H_2O$
10.0	4.39	4.40	4.39	" "
15.0	5.87	5.88	5.88	" "
20.0	7.87	7.82	7.84	$NaIO_3.1H_2O$
25.0	8.65	8.66	8.66	" "
30.0	9.63	9.63	9.63	" "
35.0	10.58	10.55	10.57	" "
40.0	11.70	11.71	11.71	" "
49.9	14.13	13.99	14.06	" "
57.8	15.97	15.86	15.91	" "
69.6	19.05	19.00	19.03	" "
79.0*	21.91	21.74	21.82	" "
67.0*	18.98	19.10	19.04	$NaIO_3$
70.6*	19.55	19.57	19.56	"
75.8	20.48	20.49	20.49	"
80.6	21.22	21.26	21.24	"
87.6	22.12	22.32	22.22	"
90.3	23.02	23.03	23.03	"

* Metastable system.

The average results have been plotted in the diagram, Fig. 1. In Fig. 2 the logarithm of the solubility has been plotted against 1000/T, where T is the absolute temperature. As might be expected, the results for the pentahydrate and the anhydrous salt fall very nearly on a straight line, as the temperature range in each case is small. The linear relation for the

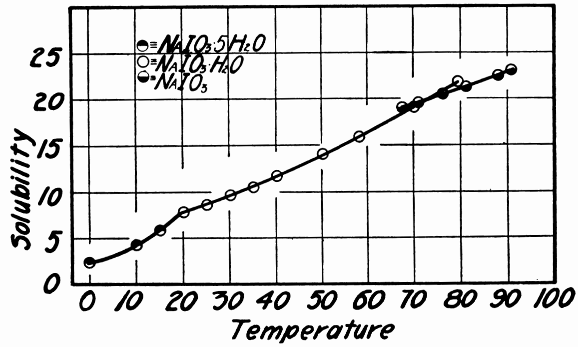

Fig. 1.

monohydrate is evident between 20° and 50° but the results diverge somewhat above this temperature. This may be shown also by calculating the solubility from the equation of

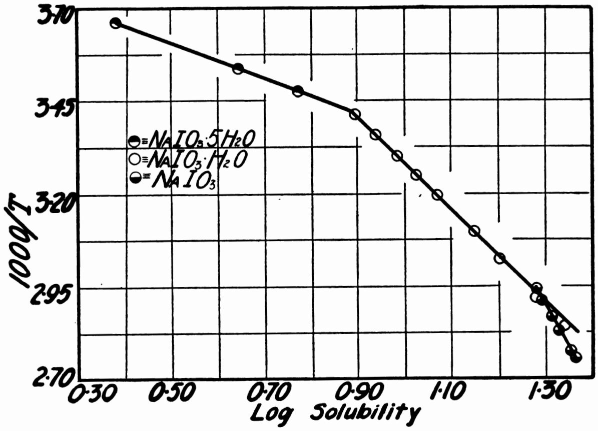

Fig. 2.

the straight line between the points at 20° and 49.9°. This equation is the following:

$$\text{log solubility} = 3.6344 - \frac{802.8}{T} \qquad (1)$$

By means of this equation, we have calculated the solubility of the monohydrate at the temperatures where the solubility was determined. The following table gives a comparison between the calculated and observed values:

Temperature	Solubility (Calculated)	Solubility (Determined)	Difference
20°	(7.84)	7.84	..
25	8.71	8.66	.05
30	9.66	9.63	.03
35	10.66	10.57	.09
40	11.73	11.71	.02
49.9	(14.06)	14.06	..
57.8	16.13	15.91	.22
69.6	19.55	19.03	.52
79.0	22.58	21.82	.76

The corresponding equation for the solubility of the pentahydrate, based on the results at 0° and 15°, is:

$$\log \text{solubility} = 7.7793 - \frac{2019}{T} \qquad (2)$$

The transition temperature calculated from these two equations is 20.3°, which is the value mentioned previously under transition temperatures as calculated from the solubility. The higher transition temperature, 73.4°, is taken directly from the plotted solubility results, as the logarithmic relation for the monohydrate at the higher temperatures is not a straight line.

The freezing point of the saturated solution is −0.35°. The solubility at this temperature has been calculated from equation (2). The solubility at 19.85°, the lower transition temperature, is calculated from equation (1), while the corresponding value for the higher transition temperature 73.4° has been taken directly from the plotted results.

The results are as follows:

	Percent of $NaIO_3$ in solution	Solid Phases
−0.35°	2.38	Ice and $NaIO_3.5H_2O$
19.85°	7.83	$NaIO_3.5H_2O$ and $NaIO_3.H_2O$
73.4°	20.00	$NaIO_3.H_2O$ and $NaIO_3$.

SUMMARY.

1. The stable hydrates of sodium iodate are $NaIO_3.5H_2O$ and $NaIO_3.H_2O$.

2. The two transition temperatures in the system occur at 19.85° where $NaIO_3.5H_2O$ and $NaIO_3.H_2O$ are in equilibrium, and at 73.4°, where $NaIO_3.H_2O$ and $NaIO_3$ are in equilibrium.

3. The solubility of sodium iodate has been determined between 0° and 90.3°.

Sterling Chemistry Laboratory,
Yale University,
New Haven, Conn.