

necessary to calculate  $e$  since the time required to approach equilibrium closely enough is never more than ten minutes.

Table II shows a series of measurements over a resistance range of 10 to 50 megohms. Here  $e$  was calculated by Equation 3, neglecting the correction factor for leakage through the condenser. Charging times were chosen so that  $\Delta e_m$  from Equation 5 was about 1 millivolt if  $\Delta v$  is 0.1 millivolt.

### Summary

1. We have described a semi-deflection method of potentiometric measurement which may be used with cells having internal resistances as high as 50 megohms.

2. We have discussed the precautions necessary with work of this kind.

3. We have shown that when full precautions are taken measurements may be made with a precision of  $\pm 0.1$  millivolt when cell resistances are as high as 10 megohms, and with a precision of  $\pm 0.5$  millivolt with cell resistances as high as 50 megohms.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

## TERNARY SYSTEMS. VII. THE PERIODATES OF THE ALKALI METALS

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Following the discovery of periodic acid and the periodates, it was observed at an early date that the acid differed widely from the analogous perchloric acid in being distinctly polybasic and in the varying degrees of hydration of its hypothetical anhydride  $I_2O_7$ . The nomenclature most commonly adopted for classifying the various acids is, with slight modification, that of Blomstrand.<sup>1</sup>  $H_5IO_6$ , the hydrate of greatest water content, is known as para-periodic acid,  $H_8I_2O_{11}$  as di-para-periodic acid,  $H_5IO_5$  as meso-periodic acid,  $H_4I_2O_9$  as di-meso-periodic acid and  $HIO_4$  as meta-periodic acid. Although but two, or possibly three, of these acids are definitely known, salts derived from all of them have been reported; of these, the silver salts and the salts of the common alkali metals have been most thoroughly studied.<sup>2</sup> It does not appear, however, that the studies have been systematic in this nature; slight modifications in the conditions of preparation have given to the various investigators salts differing in their analyses and which were on that evidence assigned to the corresponding one of the five acids enumerated above. By such

<sup>1</sup> Blomstrand, *J. prakt. Chem.*, **34**, 433 (1886).

<sup>2</sup> See Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans Green and Co., N. Y., 1922, Vol. 2, p. 406.

methods the possibility of mixtures being regarded as pure salts is by no means excluded. It has seemed worth while to make a systematic investigation of the periodates of the two alkali metals, sodium and potassium, in order to determine with certainty just how many of those reported are true compounds. This can be completely determined, as far as salts crystallizing from water are concerned, by a study of the three component systems consisting of water, periodic acid and sodium hydroxide or potassium hydroxide, respectively, and the finished study should leave no doubt as to the compounds existing at the temperature selected. For reasons of convenience, however, since periodic acid is not easily prepared, the studies have been made with use of the meta-periodate of sodium or potassium (the most highly acidic salts known in each series) with water and the appropriate base; these show therefore all stable periodates more basic in composition than the meta-salt chosen. The possibility of more acidic salts will be mentioned later.

**Materials.**—The sodium periodate used in the experiments was prepared from pure sodium hydroxide, passing through the stage of the tri-sodium-para-periodate,  $\text{Na}_3\text{H}_2\text{IO}_6$ , which was eventually converted into the meta-periodate,  $\text{NaIO}_4$ . To a solution of pure sodium iodate five equivalents of sodium hydroxide was added and the solution stirred mechanically while a rapid stream of chlorine gas was passed through. The very insoluble sodium salt begins to precipitate within a few minutes. The stream of chlorine was continued until the solution gave an odor of hypochlorites and was nearly neutral; after the treatment with chlorine was interrupted, an additional equivalent of sodium hydroxide was added and the mixture well stirred for several hours. In the presence of an excess of base, which is essential to the formation of the tri-sodium salt, the reaction occurring is represented by the equation  $\text{NaIO}_3 + \text{Cl}_2 + 4\text{NaOH} \longrightarrow \text{Na}_3\text{H}_2\text{IO}_6 + 2\text{NaCl} + \text{H}_2\text{O}$ ; yields averaged above 80%. The solid salt was filtered on a Büchner funnel and washed repeatedly; because of its very low solubility, the loss on washing is negligible. In order to convert this salt to the meta-periodate,  $\text{NaIO}_4$ , it was treated with water and nitric acid in the ratio of 150 cc. of water and 45 cc. of concd. nitric acid to 100 g. of salt; the solution was heated until the salt dissolved completely, and then allowed to stand for twenty-four hours at room temperature. The crystals thus formed are of large size and even contour; because of their low rate of dissolving they could be washed rapidly on a Büchner funnel without considerable loss, and they analyze within 0.1% of the theoretical composition; the yields varied from 60 to 85%, dependent largely upon the time allowed for crystallization.

The potassium meta-periodate was likewise prepared from the iodate with four to five equivalents of base by oxidation with chlorine. Unlike the case of the sodium salt, the potassium salt is freely soluble in excess base, and does not appear in solid form until the solution has become nearly neutral. It was then, after cooling, rendered acid with a slight excess of sulfuric acid and allowed to stand until the insoluble meta-periodate,  $\text{KIO}_4$ , had precipitated. The yields obtained, after washing and drying, ran as high as 95%. As in the case of the sodium salt, the well-washed product analyzed always within 0.1% of the theoretical composition without the necessity for recrystallization.

The periodic acid used was prepared by the method used by Wells, Lamb<sup>3</sup> and others: the sodium salt was converted into (supposedly)  $\text{Ag}_3\text{IO}_6$  by long stirring with

<sup>3</sup> (a) Wells, *Am. Chem. J.*, **26**, 278 (1901); (b) Lamb, *ibid.*, **27**, 134 (1902).

three equivalents of silver nitrate solution, and the precipitate decomposed, after thorough washing, by a slow stream of washed chlorine gas passed into a cold aqueous suspension. After filtration from the silver chloride, the solution was evaporated to a small volume over a free flame and finally in a desiccator over sulfuric acid; the periodic acid crystallizes in the form of its hydrate  $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ , which may be dried over sulfuric acid without loss of water. Since no data have been recorded as to the solubility of this acid, it may be of use to state that analysis of the mother liquor shows the solubility to be about 53% at room temperature, and the density about 2.3.

The sodium hydroxide and potassium hydroxide used were Kahlbaum preparations, which were dissolved in water to a suitable concentration and standardized by titration against analyzed hydrochloric acid solutions, using methyl orange as indicator. The small carbonate content of the base was left out of consideration as having but a negligible influence upon the solubilities measured.

The periodates were analyzed by measuring their oxidizing action upon potassium iodide in acid solution; the thiosulfate solutions used were standardized against recrystallized potassium iodate. The free alkali present in the ternary solutions was determined by titration with standard sodium hydroxide solution, using methyl orange as indicator; the meta periodates are neutral to that indicator, as previously shown by others,<sup>4</sup> so that any excess alkali can be accurately determined.

### The Periodates of Potassium

The determination of the periodates of potassium consisted in the study of the action of potassium hydroxide upon the solubility of potassium meta-periodate. The experiments were conducted in a thermostat at 25°; weighed quantities of the meta-periodate were treated with measured quantities of potassium hydroxide solution and of water and rotated in glass stoppered test-tubes of Pyrex glass until equilibrium was attained; the time required did not exceed twenty-four hours in any case. Pipetted samples of the clear supernatant liquid were analyzed for periodate and for free base; from the volume of the pipetted liquid, density determinations of moderate accuracy could be calculated. The results are given in Table I.

TABLE I  
TERNARY SYSTEM  $\text{KIO}_4\text{-KOH-H}_2\text{O}$  AT 25°

| Complex taken      |                  | Saturated solution |                  |       | Density   | Solid phases |
|--------------------|------------------|--------------------|------------------|-------|---|--------------|
| $\text{KIO}_4$ , % | $\text{KOH}$ , % | $\text{KIO}_4$ , % | $\text{KOH}$ , % |       |   |              |
| 5.0                | 0.0              | 0.51               | 0.0              | 1.00  | $\text{KIO}_4$  |              |
| 5.0                | 1.0              | 4.12               | 1.01             | 1.044 | $\text{KIO}_4$  |              |
| 8.0                | 2.0              | 8.03               | 1.99             | 1.087 | $\text{KIO}_4$  |              |
| 15.0               | 4.0              | 10.32              | 2.55             | 1.116 | $\text{KIO}_4 + \text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$ |              |
| 20.0               | 6.0              | 13.15              | 4.55             | 1.165 | $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$                |              |
| 18.0               | 6.4              | 16.12              | 6.03             | 1.221 | $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$                |              |
| 21.6               | 8.3              | 20.8               | 8.0              | 1.326 | $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$                |              |
| 25.1               | 9.9              | 24.1               | 9.7              | 1.377 | $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$                |              |
| 31.0               | 12.0             | 28.9               | 11.9             | 1.484 | $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$                |              |
| 36.6               | 14.4             | 35.2               | 14.5             | 1.64  | $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$                |              |
| 44.0               | 16.0             | 39.0               | 16.4             | ...   | $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$                |              |
| 51.0               | 18.5             | 44.6               | 19.1             | ...   | $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$                |              |

<sup>4</sup> Rosenheim and Loewenthal, *Kolloid. Z.*, 25, 53 (1919); Loewenthal, "Inaugural Dissertation," Berlin, 1918.

From Table I and Fig. 1 the facts as to the periodates of potassium which are stable in contact with solution can easily be deduced. The sparingly soluble salt  $\text{KIO}_4$  has its solubility rapidly increased by the addition of potassium hydroxide; no common-ion effect in lessening its solubility can be detected. At the point  $b$  in Fig. 1, representing line 4 in the table, there is a change of solid phase, giving an isothermally invariant point. Further additions of potassium hydroxide give increasing concentrations of the second solid, which will be shown to be the ennea-hydrated potassium di-meso-periodate,  $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$ . The increase in solubility of this salt upon addition of potassium hydroxide is striking; in line 13 we have a total solubility increased to 87 times that of the original saturating salt.

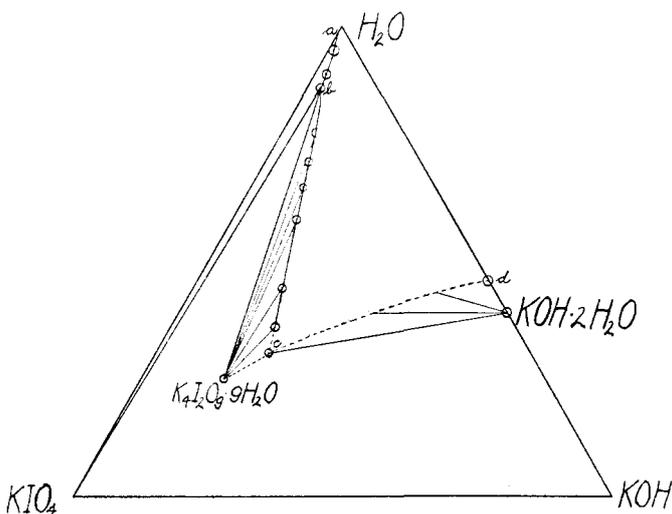


Fig. 1.—25° isotherm,  $\text{KIO}_4$ - $\text{KOH}$ - $\text{H}_2\text{O}$ .

Further additions of base caused the system to gelatinize, which of course put an end to further solubility measurements. It is clear, however, that the last experiment indicates a solution not far from the saturation point with respect to potassium hydroxide, which is shown schematically as the point  $c$ , with the solubility curve  $c$ - $d$  drawn schematically for the hydrated base. It is accordingly clear that two and only two periodates of potassium can be formed from aqueous solutions at 25°, and it is probable that at higher temperatures the same limitation exists as far as aqueous solutions are concerned. Kimmins's<sup>5</sup> salt,  $\text{K}_3\text{HI}_2\text{O}_9$ , and Ihre's<sup>6</sup>  $\text{K}_3\text{IO}_5 \cdot 4\text{H}_2\text{O}$  are not confirmed; it is probable that both are mixtures represented by the point  $b$  in Fig. 1, since they were formed in solutions in which the concentration of free base was not accurately known.

<sup>5</sup> Kimmins, *J. Chem. Soc.*, 51, 356 (1887); 55, 148 (1889).

<sup>6</sup> See Blomstrand, *Ber.*, 3, 316 (1870).

Some study was given to each of the two potassium salts prepared. The meta-periodate,  $\text{KIO}_4$ , has a strikingly low solubility for a potassium salt; the figure at  $25^\circ$ , calculated as moles per liter, is 0.0238; that of the corresponding perchlorate,  $\text{KClO}_4$ , is 0.152,<sup>7</sup> over six times as great. The

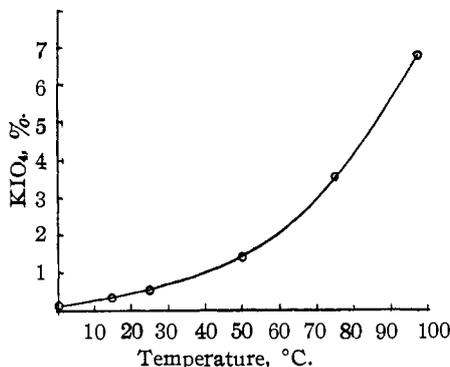


Fig. 2.—Solubility of  $\text{KIO}_4$ .

advantages of the use of this salt for the determination of potassium are clearly evident, especially because of the ease with which the periodate radical can be determined volumetrically and because of the high solubility of the corresponding sodium salt, which will be discussed later. It is understood that the details of such a method have been worked out at the laboratories of the University of Michigan. The solubility of the salt at a number of temperatures is given in Table II and shown in Fig. 2; measurements were made from solutions stirred by hand for brief periods, immersed in a water-bath with hand controlled temperature regulation.

TABLE II

SOLUBILITY OF  $\text{KIO}_4$  IN WATER

| Temp., $^\circ\text{C}$ . | 0.2   | 5.4  | 15.0  | 25.0  | 50.0 | 75.0 | 97.0 |
|---------------------------|-------|------|-------|-------|------|------|------|
| $\text{KIO}_4$ , %        | 0.169 | 0.21 | 0.334 | 0.510 | 1.44 | 3.59 | 6.83 |

The di-meso-periodate,  $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$ , should be congruently soluble according to Fig. 1, and therefore capable of recrystallization, which was found to be the case. For the analysis of the salt, including the water of hydration, the crystals were dried to constant weight in a miniature desiccator over the anhydrous salt;<sup>8</sup> the water content was then determined by heating in an electric oven at  $110^\circ$ ,  $\text{KIO}_4$  by the usual iodimetric method, and the excess base by titration with standard acid. The results follow.

*Anal.* Calcd. for  $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$ :  $\text{KIO}_4$ , 64.21;  $\text{K}_2\text{O}$ , 13.15;  $\text{H}_2\text{O}$ , 22.63. Found: 64.32, 13.23, 22.34.

There can be no question therefore, as to the composition of the salt. Its solubility was then determined as shown in Table III and in Fig. 3, the temperatures above  $25^\circ$  being hand controlled.

It is evident that the di-meso salt has both a high solubility and a high temperature coefficient of solubility. The figure found at  $25^\circ$  for the pure salt is in reasonably close agreement with the point *b* of Fig. 1, indicating

<sup>7</sup> Seidell, "Solubilities," D. Van Nostrand Co., New York 1919, p. 515.

<sup>8</sup> See Hill and Smith, *THIS JOURNAL*, **44**, 548 (1922).

TABLE III  
SOLUBILITY OF  $K_4I_2O_9$  IN WATER

| Temp., °C. | $K_4I_2O_9$ , % | Density of soln. | Solid phases                        |
|------------|-----------------|------------------|-------------------------------------|
| 0.3        | 3.5             | 1.032            | $K_4I_2O_9 \cdot 9H_2O$             |
| 15.0       | 7.7             | 1.073            | $K_4I_2O_9 \cdot 9H_2O$             |
| 25.0       | 12.3            | 1.118            | $K_4I_2O_9 \cdot 9H_2O$             |
| 37.5       | 22.0            | 1.216            | $K_4I_2O_9 \cdot 9H_2O$             |
| 50.0       | 35.0            | 1.395            | $K_4I_2O_9 \cdot 9H_2O$             |
| 65.0       | 50.1            | ...              | $K_4I_2O_9 \cdot 9H_2O$             |
| 78         | 61.7*           | ...              | $K_4I_2O_9 \cdot 9H_2O + K_4I_2O_9$ |
| 98.6       | 61.1            | ...              | $K_4I_2O_9$                         |

that the salt does not form as a solid phase until the ratio of base to acid in the solution is almost exactly that which occurs in the salt itself. The solubility curve shows a sharp break at about  $78^\circ$ , which is the temperature of the transition  $K_4I_2O_9 \cdot 9H_2O \rightleftharpoons K_4I_2O_9 + \text{solution}$ . This temperature was obtained by a study of cooling curves, but could not be obtained with high precision, owing to delayed transformation and also possibly to slight decomposition, since the hot solutions gradually acquired a slightly yellow tinge, although free iodine could not be detected in them by the starch test. That the compound existing above  $78^\circ$  is the anhydrous form and not some lower hydrate is indicated by the evidence (just short, it may be claimed, of proof) that the moist ennea-hydrate, placed over the anhydrous form, does not lose water to form any lower hydrate, as shown above. If this evidence be accepted, it follows that the ennea-hydrate is to be regarded as a true salt-hydrate, and not in any sense an acid salt of the para series, as has been sometimes proposed.

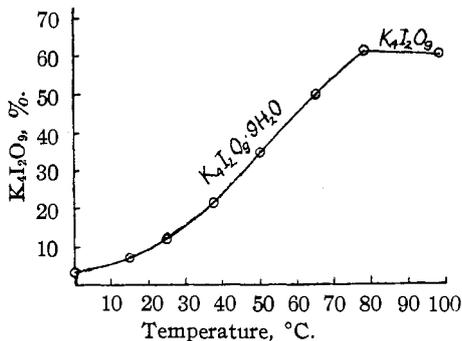


Fig. 3.—Solubility of  $K_4I_2O_9$ .

### The Periodates of Sodium

To determine the periodates of sodium which are stable in contact with aqueous solution, the  $25^\circ$  isotherm was studied by the same method used for the potassium salts. The results are given in Table IV.

The results are in striking contrast with those of Table I. First, with regard to the experiments themselves, it was found that a very long time is required for equilibrium to be attained; from one to three weeks' stirring was used for the experiments in which  $Na_2H_3IO_6$  is the solid phase and it is by no means certain that complete equilibrium was always reached. For this reason the figures for  $NaIO_4$  content of the solution, while showing a



$\text{Na}_2\text{H}_3\text{IO}_6$ , upon addition of the smallest quantity of sodium hydroxide (line 2). In the solution obtained no free base could be detected, although the titration would easily show amounts smaller than 0.01%. The isothermally invariant point *b*, shown in Fig. 4, is therefore too close to the side of the triangle to be shown to scale. Further additions of base give  $\text{Na}_2\text{H}_3\text{IO}_6$  as the solid phase until the point *c* of Fig. 4 is reached, corresponding to line 10 of Table IV, beyond which the stable phase is the more basic para-periodate,  $\text{Na}_3\text{H}_2\text{IO}_6$ . The experiments were discontinued at the point where there was present 30% of sodium hydroxide, without the appearance of any new phase; there are, therefore, three and only three sodium periodates found by precipitation from aqueous solution, namely,  $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{H}_3\text{IO}_6$  and  $\text{Na}_3\text{H}_2\text{IO}_6$ . Col. 6 of Table IV shows the

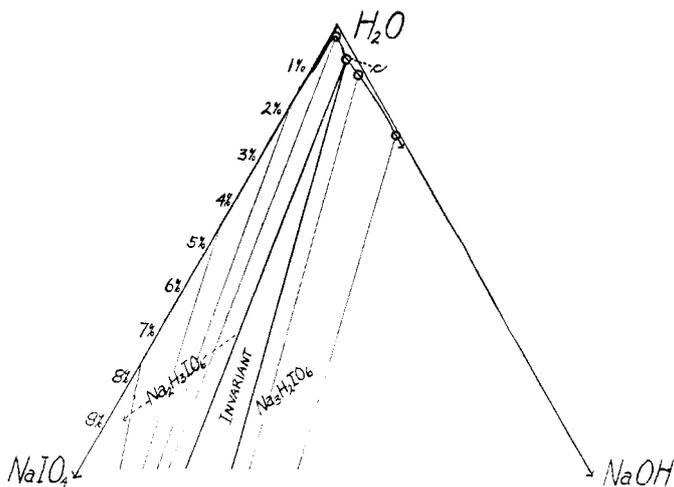


Fig. 5.—Partial isotherm at 25°,  $\text{NaIO}_4$ - $\text{NaOH}$ - $\text{H}_2\text{O}$ .

sodium hydroxide content of the salts, by algebraic extrapolation of the tie lines; the results are in good agreement with the calculated values of 14.71% and 27.22% for the two salts, taking into consideration the great length of the lines extrapolated. The partial isotherm shown in Fig. 5 shows in greater detail the pitch of the tie lines for the two compounds.

Each of the three sodium salts has been studied. The meta-periodate exists as a trihydrate and in anhydrous form as shown in Table V.

It was found that this salt is very slow in coming to equilibrium with its aqueous solutions and that the transition from the anhydrous form to the hydrate is also greatly delayed; the experiments, therefore, were conducted in the usual thermostat at the lower temperatures and at the higher temperatures in an electric oven, containing a large vessel of glycerin as a temperature buffer, into which the test-tube of solution was dipped and stirred mechanically from outside the oven. By making the heating

TABLE V  
 SOLUBILITY OF  $\text{NaIO}_4$  IN WATER

| Temp., °C. | $\text{NaIO}_4$ , wt., % | Density of soln. | Solid phases  |
|------------|--------------------------|------------------|---|
| 5.8        | 3.93                     | 1.048            | $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$                 |
| 15.0       | 7.2                      | 1.060            | $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$                 |
| 20.0       | 9.3                      | 1.073            | $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$                 |
| 25.0       | 12.62                    | 1.103            | $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$                 |
| 30.0       | 16.6                     | 1.143            | $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$                 |
| 31.5       | 18.2                     | 1.161            | $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$                 |
| 33.0       | 19.6                     | 1.175            | $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$                 |
| [34.5]     | [21.3]                   | ...              | $\text{NaIO}_4 \cdot 3\text{H}_2\text{O} + \text{NaIO}_4$ |
| 31.5       | 19.8                     | 1.173            | $\text{NaIO}_4$ (metastable)                              |
| 33.0       | 20.6                     | 1.185            | $\text{NaIO}_4$ (metastable)                              |
| 35.0       | 21.5                     | 1.192            | $\text{NaIO}_4$   |
| 36.0       | 21.8                     | 1.196            | $\text{NaIO}_4$   |
| 38.0       | 22.6                     | 1.202            | $\text{NaIO}_4$   |
| 44.2       | 24.9                     | 1.218            | $\text{NaIO}_4$   |
| 51.5       | 28.0                     | 1.251            | $\text{NaIO}_4$   |

element of the oven appropriate in size, the temperature changes in the glycerin bath were kept within  $0.1^\circ$ . The time required for equilibrium, if the stable solid phase is present, varies from one to two days; but if a change of phase is to be completed, a week or more may be necessary. The results of lines 9 and 10 were obtained after twenty-four hours and forty-eight hours' stirring, respectively; in line 9 the solubility is in perfect alignment with the results for the anhydrous salt, though metastable at this temperature, while in line 10 there has been a slight fall from that required for the metastable curve, indicating the very slight transformation to the hydrate which has occurred in two days. The transition temperature,  $34.5^\circ$ , is obtained from the intersection of the two curves, using the equation  $\text{Solubility} = 8.53 + 0.37t$  for the anhydrous form and  $\text{Solubility} = 4.017 - 0.0758t + 0.0167t^2$  for the hydrate. Efforts to find the transition by cooling or warming curves gave no indication of the transition at any temperature, however carefully managed.

The composition of the hydrate, as previously shown by Barker,<sup>9</sup> was confirmed by bringing a sample of moist crystals to constant weight over the anhydrous form. Analysis gave the water by loss on heating as 20.0%; calcd. for  $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ , 20.17%.

The secondary sodium para-periodate,  $\text{Na}_2\text{H}_3\text{IO}_6$ , has a very low solubility; by independent experiments made with a recrystallized sample, the solubility at  $25^\circ$  was found to be 0.23%, somewhat higher than the figure (0.157%) given by Rosenheim and Loewenthal.<sup>4</sup> This is, as far as I am able to find, the least soluble sodium salt known, and its use for the detection and estimation of sodium is easily possible; the sharp contrast with the solubilities of the potassium salt is favorable for such a separation,

<sup>9</sup> Barker, *J. Chem. Soc.*, **93**, 15 (1908).

since in neutral or acid solution the potassium salt ( $KIO_4$ ) is insoluble and the sodium salt ( $NaIO_4$ ) soluble, while in alkaline solution the potassium salt ( $K_4I_2O_9$ ) is freely soluble and the sodium salt ( $Na_2H_3IO_6$ ) very insoluble.

In the study of the properties of this secondary sodium salt, some interesting facts as to its hydration were observed. When formed by precipitation from  $NaIO_4$  and  $NaOH$  solutions, the precipitate is usually amorphous in part, and upon drying over sulfuric acid to a constant weight it is found to contain from 2 to 3% of water in excess of that calculated by formula. This finding is in accordance with the results of Rammelsberg,<sup>10</sup> whose analysis shows the salt to be low in periodate and therefore high in water, but not in accord with the analyses of Loewenthal,<sup>4</sup> who worked, however, with exceedingly small samples of the salt (0.030 to 0.099 g.), which may have resulted in obscuring the fact of high water content. On putting the samples in a drying oven at  $100^\circ$ , it was observed that there was a somewhat rapid loss of water for the first two days (0.4 to 0.6%), and following that a quite regular loss continuing for at least three months, at a rate of about 0.01% per day, during which time the composition passed through that of the para-periodate and evidently the formation of a pyro salt began. The results of analyses of two 10g. samples are given in Table VI. Sample 1 was apparently amorphous, and showed continuous loss of water while Sample 2, more definitely crystalline, lost water only up to the point of the composition of the di-sodium salt.

TABLE VI  
DEHYDRATION OF  $Na_2H_3IO_6$   
Sample No. 1 (amorphous)

|                                   | Calcd.,<br>% | Dried over<br>$H_2SO_4$ , % | Dried at $100^\circ$ , days |         |         |         |
|-----------------------------------|--------------|-----------------------------|-----------------------------|---------|---------|---------|
|                                   |              |                             | 10                          | 50      | 75      | 100     |
| $NaIO_4$                          | 78.66        | 76.91                       | ...                         | 78.61   | 79.17   | 80.09   |
| $NaOH$                            | 14.72        | 14.74                       | ...                         | 14.91   | 15.23   | 15.56   |
| $H_2O$                            | 6.62         | ( 8.35)                     | ...                         | ( 6.48) | ( 5.60) | ( 4.35) |
| Water lost at $100^\circ$         | ...          | ...                         | ...                         | 1.56    | 2.23    | 3.86    |
| Sample No. 2 (partly crystalline) |              |                             |                             |         |         |         |
| $NaIO_4$                          | 78.66        | ...                         | 77.75                       | 78.24   | 78.38   | 78.36   |
| $NaOH$                            | 14.72        | ...                         | 14.87                       | 15.01   | 15.03   | 15.24   |
| $H_2O$                            | 6.62         | ...                         | ( 7.38)                     | ( 6.75) | ( 6.57) | ( 6.40) |
| Water lost at $100^\circ$         | ...          | ...                         | 0.68                        | 1.12    | 1.30    | 1.30    |

During this entire period the samples were weighed weekly. It is apparent, therefore, that the salt (at least in its amorphous form) can contain more than the stoichiometrical proportion of water, that the loss of water (both the excess and that of the stoichiometric compound) is appreciable at  $100^\circ$  under atmospheric conditions of aqueous pressure and that the vapor pressure of the excess water and that of the true

<sup>10</sup> Rammelsberg, *Pogg. Ann.*, **134**, 368 (1868).

compound are sensibly the same. The loss of water was not observed by Rammelsberg<sup>10</sup> to occur until a temperature of 185° had been reached. With well crystallized samples of the salt, however, no excess of water, within the limits of the analysis, could be found. Recrystallization was accomplished by dissolving the salt by lengthy boiling in water (its solubility at 100° being about 0.4%) and evaporating the saturated solution to about one-fourth its original volume; because of the well-developed property of forming supersaturated solutions, this could be accomplished without any precipitation. On standing at room temperature for a period of days, the salt precipitated in well-formed, small crystals; analysis of these samples gave the calculated stoichiometric composition for all three components within  $\pm 0.1\%$ . It is also to be deduced from the low vapor tensions here indicated that the water in the stoichiometric compound is held by primary valence as water of composition, and not by secondary valence as water of hydration; the compound is therefore to be classed as a para-periodate and not as a hydrated di-meso-periodate, as has sometimes been proposed.<sup>11</sup>

In order to determine whether the ratio of the two components,  $\text{NaIO}_4$  and  $\text{NaOH}$ , varies in the compound, through adsorption from an excess in solution, four experiments were conducted similar to those of Table IV, but with quantities of the components chosen so that the extrapolation of the tie lines should be subject to smaller error, that is, with a larger proportion of solid phase in the complex. Arranging to have about 10% of solid present, the four tests were made to contain the following molar ratios of  $\text{NaOH}$  to  $\text{NaIO}_4$ : 0.8, 1.0, 1.1 and 1.2, respectively. After agitation in the thermostat for ten days, the liquid phases were carefully analyzed; algebraic extrapolation of the tie lines showed that the solid phases contained the following slight variations from the theoretical quantities of  $\text{NaOH}$ :  $-0.40\%$ ,  $+0.24\%$ ,  $+0.07\%$ ,  $-0.07\%$ . These figures contain the error of the analysis of the solution multiplied nearly ten times, and because of their small magnitude and irregular direction seem to me to be negligible and to prove that there is no sensible variation of these two components in the compound. Analysis of these solids, and of others, gave a molar ratio of  $\text{NaIO}_4$  to  $\text{NaOH}$  of 1 to 1  $\pm 2\%$ . These findings are in agreement with those of Loewenthal.<sup>4</sup>

Passing to the tertiary sodium salt,  $\text{Na}_3\text{H}_2\text{IO}_6$ , it will be seen from Fig. 5 that the salt does not possess congruent solubility. It can be formed only when there is excess sodium hydroxide in the solution, which excess can be calculated from the results of Table IV, line 10; expressed as a molar ratio of  $\text{NaIO}_4$  to  $\text{NaOH}$ , it has the high value 1:9.2. The pure salt, therefore, cannot be recrystallized from water; depending upon whether the amount of water is greater or less, it will either be completely

<sup>11</sup> Rammelsberg, *Ber.*, 1, 70 (1869).

hydrolyzed to the secondary salt, or (if the total complex falls within the invariant area of Fig. 5) to a mixture of the two salts. This fact as to influence of the excess base explains why the preparation of sodium periodate by action of chlorine upon sodium iodate in presence of sodium hydroxide has sometimes given the secondary sodium salt,<sup>12</sup> sometimes the tertiary,<sup>13</sup> and sometimes a mixture,<sup>5</sup> no other explanation is needed to clear up the discrepancies. In order to confirm these conclusions as to the hydrolysis of the tertiary salt, independent experiments were carried out; a sample complex of  $\text{Na}_3\text{H}_2\text{IO}_4$  and water falling within the area of saturation for the salt  $\text{Na}_2\text{H}_3\text{IO}_6$  (Fig. 5) was agitated for a week's time at 25°; the supernatant liquid showed upon analysis a ratio of 2.3 moles of  $\text{NaOH}$  to 1 of  $\text{NaIO}_4$ , indicating that the hydrolysis had occurred. Since it was found that the hydrolysis was slow at room temperature, a similar complex was boiled with water for two and one-half hours and then allowed to stand overnight at room temperature; the liquid phase showed upon analysis substantially the same

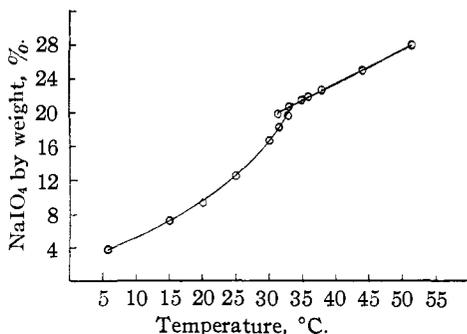


Fig. 6.—Solubility of  $\text{NaIO}_4$ .

ratio of the components as given above, and the solid phase, filtered and dried, was found to contain 78.16% of  $\text{NaIO}_4$ , corresponding to a 91.5% conversion into  $\text{Na}_2\text{H}_3\text{IO}_6$ .

The water content of the tertiary salt was found, as in the case of the secondary salt, to depend upon the crystalline character of the solid. If precipitated rapidly and in amorphous condition, it may contain up to 2% of water, which is not lost over sulfuric acid; moreover, it is driven off at 100° much more slowly than in the case of the secondary salt. Experiments continued over several months gave an average daily loss of only 0.002%. If the salt is allowed to precipitate from only moderately supersaturated solutions, formed from  $\text{NaIO}_4$  and  $\text{NaOH}$ , a crystalline form occurs which has the stoichiometrical composition. As a matter of interest, the preparation of the salt by action of chlorine upon the iodate, as given earlier in the paper, apparently occurs at a rate giving a crystalline precipitate, which analyzes as practically 100% pure. The ratio of  $\text{NaOH}$  to  $\text{NaIO}_4$  in various samples was found to be stoichiometric within the errors of the analysis. It was found also, in accordance with the experiments of Loewenthal,<sup>4</sup> that there is no detectable adsorption of sodium

<sup>12</sup> Rosenheim and Liebknecht, *Ann.*, **308**, 53 (1899).

<sup>13</sup> Ihre (Blomstrand), *Ber.*, **3**, 316 (1870).

hydroxide from solution containing the base in excess; the figures of Col. 6 of Table IV indicate, indeed, a deficiency of base, but this variation is probably due to the method of experimentation necessary for solubility determinations; an excess of the solid meta-periodate was present, which on treatment with sodium hydroxide solution doubtless became crusted with the very insoluble trisodium salt, preventing further action upon the interior parts of the crystals. Material formed by precipitation, however, never showed variation in this direction.

It is also to be deduced that the trisodium salt, which shows so very low an aqueous tension, is to be regarded as a salt of the para series, and not a hydrated meso salt ( $\text{Na}_3\text{IO}_5 \cdot \text{H}_2\text{O}$ ). It appears, then, that the only stable sodium periodates forming from aqueous solution are the meta-periodate (as a trihydrate and in anhydrous form) and the disodium salt and the trisodium salt of para-periodic acid; the several others listed in Mellor's "Treatise"<sup>12</sup> cannot be confirmed. In view also of the very low aqueous tension of the two last named salts, it seems necessary to classify them as stated, and Mellor's preference for regarding them as hydrated di-meso salts or meso-salts cannot be sustained. Walden's<sup>14</sup> measurements of the electrical conductivity of solutions made from periodic acid and sodium hydroxide are in solutions supersaturated with respect to the two salts described above and illustrate the marked metastability of these solutions; however justified may be his deductions as to the condition of the dissolved salts, they have no bearing upon the composition of the solid phases and there is therefore no evidence for the existence, as a solid, of the salt  $\text{Na}_5\text{IO}_6$ .

### Acid Periodates

It being well known that the nearly related alkali salts of iodic acid form double compounds or acid salts with free iodic acid, such as  $\text{KIO}_3 \cdot \text{HIO}_3$ , experiments were conducted to determine whether a similar condition exists in the case of the periodates. Samples of the two meta-periodates were agitated in the thermostat with varying amounts of periodic acid and the solutions analyzed after equilibrium had been attained, as shown in Table VII.

TABLE VII

SOLUBILITY OF META-PERIODATES IN THE PRESENCE OF PERIODIC ACID AT 25°

| Saturating salt | Complex taken |                         | Saturated solution |               | Density |
|-----------------|---------------|-------------------------|--------------------|---------------|---------|
|                 | Wt. % of salt | Wt. % of $\text{HIO}_4$ | Wt. % of salt      | Wt. % of acid |         |
| $\text{KIO}_4$  | Excess        | 0.0                     | 0.51               | 0.00          | 1.000   |
| $\text{KIO}_4$  | 0.982         | 1.171                   | 0.355              | 1.157         | 1.014   |
| $\text{KIO}_4$  | 1.04          | 2.81                    | 0.261              | 2.83          | 1.023   |
| $\text{NaIO}_4$ | Excess        | 0.0                     | 12.62              | 0.0           | 1.103   |
| $\text{NaIO}_4$ | 13.77         | 4.93                    | 11.43              | 5.23          | 1.150   |

<sup>14</sup> Walden, *Z. physik. Chem.*, **2**, 49 (1888).

It will be seen that the addition of free acid produces a marked diminution in the solubility of potassium periodate, qualitatively in accord with the common-ion effect of the periodate ion but in direct contrast with the effect of free base previously shown to cause an increase in solubility. Such a decrease in solubility indicates the probable non-existence of a double compound of the nature of an acid periodate of potassium. The results in the case of the sodium salt are to be interpreted in the same fashion. It did not seem worth while, with this evidence, to complete the isotherms through all possible concentration ranges.

### The Periodates of Lithium and Ammonium

Periodates of lithium have previously been prepared only by action of periodic acid upon lithium hydroxide. Attempts were made<sup>15</sup> to prepare such salts by action of chlorine upon lithium iodate in the presence of lithium hydroxide, in imitation of the methods so successful for the sodium and potassium salts. The products of the reaction were certain very insoluble substances, proved to be periodates by the correct ratio of oxidizing oxygen to iodine content, but containing large and irregular quantities of lithium hydroxide, so that stoichiometrical formulas were not to be thought of. The explanation probably lies in the fact, clearly demonstrated by Rosenheim and Loewenthal,<sup>4</sup> that lithium periodate adsorbs the hydroxide very strongly from its solutions. It appears, therefore, that this method of preparing lithium periodate is not possible, unless devices for maintaining a correct concentration of base during the preparation were worked out, which would be a matter of some difficulty.

Attempts<sup>16</sup> to prepare ammonium periodate by action of chlorine on ammonium iodate in the presence of ammonium hydroxide were wholly unsuccessful; no periodate was obtained and the iodate remained unchanged. It seems probable that in ammonia solutions the hydroxyl-ion concentration is insufficient to permit the oxidation of iodate ion to periodate ion, a reaction which thus far has been found to occur only in strongly basic solutions.

The conditions for the formation of pyro-salts of sodium periodate, by dehydration of the para-periodates, are being studied in this Laboratory, and the composition of the periodates of silver is also under investigation.

### Summary

1. A 25° isotherm has been studied for the system consisting of  $KIO_4$ , potassium hydroxide and water. The stable salts of potassium found to

<sup>15</sup> Experiments by Mr. H. E. Wolf, thesis for the B.S. degree, New York University, 1928.

<sup>16</sup> Experiments by Mr. San W. Wong, thesis for B.S. degree, New York University, 1928.

form from aqueous solutions are two only, and of the formulas  $\text{KIO}_4$  and  $\text{K}_4\text{I}_2\text{O}_9 \cdot 9\text{H}_2\text{O}$ .

2. The solubility of the two potassium salts in water has been measured between the temperatures of 0 and  $100^\circ$ . The latter salt undergoes a transition to the anhydrous form at about  $78^\circ$ .

3. A  $25^\circ$  isotherm has been studied for the system consisting of  $\text{NaIO}_4$ , sodium hydroxide and water. The stable sodium salts which form from aqueous solution are three only, and of the formulas  $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{H}_3\text{IO}_6$  and  $\text{Na}_2\text{H}_2\text{IO}_6$ .

4. The solubility of sodium meta-periodate,  $\text{NaIO}_4$ , has been measured between the temperatures of 5 and  $50^\circ$ . A transition point between the hydrate and the anhydrous form occurs at  $34.5^\circ$ .

5. The wide difference in the solubilities of the sodium and potassium salts may be used as a means for the analytical separation of potassium and sodium.

6. The secondary sodium periodate,  $\text{Na}_2\text{H}_3\text{IO}_6$ , is found, when in an amorphous condition, to hold a few per cent. of water with a vapor tension apparently as low as that of the compound; at  $100^\circ$  the rate of loss of water, adsorbed or of composition, averages about 0.01% per day under atmospheric aqueous pressures. The tertiary sodium salt also adsorbs water, and the rate of loss of water adsorbed or of composition is about one-fifth as great.

7. Action of periodic acid upon the meta-periodates was not found to produce acid salts.

8. Lithium periodate could not be formed in a pure state, and ammonium periodate could not be formed at all by the oxidation of the iodates by chlorine in presence of the appropriate base.

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