

seven days at room temperature, and gave a negative test for peroxide; however, when heated at 170° for an hour and a half, the red solid decomposed to a mixture of white and yellow solids which gave the tests that would be expected of cesium superoxide. Both the potassium and cesium extracts decompose violently in water, with flashes of light accompanying the decomposition.

Analyses of the extracted potassium product indicate that the red solid contains about 55%  $K_2O$  and 45% available oxygen, *i. e.*, oxygen liberated upon complete decomposition, as compared with the values 54.1 and 45.9% calculated for the decomposition of  $KO_3$ . This fact would appear to substantiate to a large extent the findings of Kazarnovskii, Nikolskii and Abletsova<sup>6</sup> that the red solid is composed primarily of a substance having the formula  $KO_3$ ; hence, it should be termed potassium ozonide. In addition, thermal decomposition of the material at 50° for one hour liberates approximately the quantity of oxygen calculated for the decomposition of  $KO_3$  to  $KO_2$  (found, 16.0; calcd., 18.4). Measurement of the oxygen and iodine liberated when acidified potassium iodide solution is used as a decomposant indicates that the oxygen-iodine ratio is about 2.5:1. The solution remaining after aqueous decomposition of the red solid retains a very weak oxidizing power. Inasmuch as the behavior of this red solid differs from that of the sodium ozonate in that the latter is incapable of oxidizing acidified potassium iodide, considerable doubt exists that the potassium extract is a single chemical species.

Analyses of the extracted cesium products proved very inconclusive. The per cent. of  $Cs_2O$  was much higher than that calculated on the assumption that the red cesium solid was  $CsO_3$ . As in the case of the extracted potassium material, the results of oxygen-iodine determinations showed the oxygen-iodine ratio to be approximately 2.5:1. However, in this instance the oxidizing power displayed by the solid was in no way affected by aqueous

or acidic decomposition; the resulting solutions displayed the same amount of oxidizing action toward iodide ion as did the solid material. In this respect the behavior of the extracted potassium and cesium materials differ considerably. These observations would seem to lend weight to the thesis that the extracted material is not a single chemical species of the formula  $CsO_3$ , particularly in view of the fact that sodium ozonate does not oxidize iodide ion.

**Acknowledgment.**—The authors are indebted to Professor Arthur W. Davidson for his critical reading of this manuscript.

### Summary

Ozone-treated sodium hydroxide decomposes in water with evolution of oxygen, but does not liberate iodine from acidified potassium iodide solution. Ozonated potassium and cesium hydroxides also evolve oxygen upon decomposition in water, but liberate iodine from acidified iodide solution. Analyses of the gross products of ozonization of sodium and cesium hydroxides produce data which are most reasonably explained by assigning the formulas  $NaO_3$  and  $CsO_3$  to the colored, paramagnetic materials.

The colored products of ozonization of potassium and cesium hydroxides are soluble in liquid ammonia; evaporation to dryness of the resulting solutions produces red solid substances which decompose violently in water with evolution of oxygen, and liberation of energy in the form of light. Although analysis of the material extracted from ozone-treated potassium hydroxide appears to indicate that the red solid consists mainly of the compound  $KO_3$ , chemical behavior would seem to indicate that the extract is not a single chemical species. Analysis of the extracted cesium material even more strongly suggests the presence of another substance.

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RECEIVED JUNE 7, 1950

[CONTRIBUTION NO. 89 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

## Ionization and Hydration Equilibria of Periodic Acid<sup>1</sup>

BY C. E. CROUTHAMEL, A. M. HAYES AND D. S. MARTIN

### Introduction

Kinetic studies of the reaction between periodic acid and ethylene glycol<sup>2</sup> and other oxidation reactions involving periodate have large variations in their rates with temperature and hydrogen ion activity. A more detailed knowledge of the species present in solution should be of assistance in explaining these variations. The apparent ionization constants of periodic acid have already been evaluated at 25°.<sup>3</sup> No differentiation between the degree of hydration of ionic and molecular

species was made, thus the apparent ionization constants written in more general form would be

$$(a_{H^+})\Sigma a_1/\Sigma a_0 = K_1' \quad (1)$$

$$(a_{H^+})\Sigma a_2/\Sigma a_1 = K_2' \quad (2)$$

where  $a_{H^+}$  is the hydrogen ion activity, and  $\Sigma a_0$ ,  $\Sigma a_1$  and  $\Sigma a_2$  are, respectively, the sums of the activities of undissociated forms, singly charged and doubly charged ionic species. Since the ionization of three hydrogen ions was observed, the acid was designated as the hydrated species,  $H_3IO_6$ .

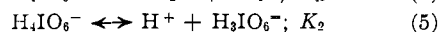
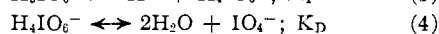
In the first paper<sup>2</sup> it was established that the absorption maximum at 2225 Å. was caused by univalent ions. Further examination of this peak under various conditions was interpreted to in-

(1) Work performed in the Ames Laboratory of the Atomic Energy Commission.

(2) Frederick R. Duke, *THIS JOURNAL*, **69**, 3054 (1947).

(3) C. E. Crouthamel, *et al.*, *ibid.*, **71**, 3031 (1949).

dicates that the single, dehydrated, univalent species,  $\text{IO}_4^-$ , is responsible for this absorption, and that solutions could be adjusted so that no interfering absorption was present. This made it possible to determine the molar extinction coefficient of this ion. In an analysis of the spectrophotometric absorption it was therefore possible to determine the concentration of this ion, a feature which permitted a detailed analysis of dehydration phenomena. The behavior in acid solutions was adequately described by the three equilibria



The constants for these reactions have been evaluated over a temperature range of 0–70° as have the apparent constants,  $K_1'$  and  $K_2'$ .

### Experimental

**Materials and Instruments.**—In the spectrophotometric studies a Cary Recording Spectrophotometer (Model 12) was employed. This instrument recorded directly the optical density of the solution, defined in this paper as  $\log I_0/I$ , where  $I_0$  and  $I$  represent the incident and transmitted light intensities, respectively. A Beckman glass electrode pH meter (model G) calibrated with standard buffer solutions was used for pH measurements. Solutions used in the ultraviolet absorption measurements were prepared from reagent grade samples of potassium metaperiodate manufactured by the G. F. Smith Chemical Co. and the General Chemical Co. No appreciable iodate was detectable by titration with standard thiosulfate in acid and in neutral buffered solutions. The oxidizing capacity of a weighed sample corresponded to a purity of better than 99.9%. Standard stock solutions of periodate were prepared by dissolving accurately weighed pure potassium metaperiodate in 500 ml. of solution. For the greatest accuracy standard solutions were prepared each day. Doubly distilled water from alkaline permanganate, specific conductance of  $0.9 \times 10^{-6}$  mho  $\text{cm}^{-1}$ , was used throughout. Methanol when used was purified by refluxing in alkali and iodine and redistilling. Dilute periodate solutions ( $2 \times 10^{-4}$  M) in methanol were stable for a day as measured by the spectrophotometer.

**2. Temperature Control.**—Absorption measurements with the Cary instrument at 32.5° and below were made by suitably controlling the room temperature and allowing sufficient time for the solutions and instrument to attain thermal equilibrium. Copper tanks, constructed so that they would fit into the sample chamber next to the silica cell, were filled with water at the proper temperature to act as a thermal ballast. At higher temperature the cell containing the sample was immersed in a water-bath at the correct temperature until thermal equilibrium was attained. The cell was then dried and placed in the sample chamber as quickly as possible. The time needed was from ten to fifteen seconds to transfer the cell, dry and make a measurement. Cooling rates were found to be less than 0.5–1°/min. in the temperature range of the measurements. Temperature fluctuations in these measurements made therefore a negligible contribution to the errors.

**3. Spectrophotometric Measurements.**—Potassium metaperiodate solutions at various pH values were scanned at different temperatures with the Cary Instrument using 1.000-cm. silica cells. The pH adjustments were made with perchloric acid or with carbonate free sodium hydroxide. Figures 1 and 2 are plots of the optical densities of various periodate solutions (*ca.*  $2 \times 10^{-4}$  M) at several pH values and temperatures. When necessary, corrections were made for volume changes by using density-temperature information for pure water. The optical density of pure potassium metaperiodate solutions in methanol-water mixtures were measured at 0°. These solutions were diluted to volume at this temperature to avoid differences in the coefficient of expansion caused by the varying solvent composition.

**4. Potentiometric Measurements.**—Potentiometric titrations of paraperiodic acid with 0.1795 N NaOH were made at temperatures of 0.5, 25.0 and 45.0°. For these

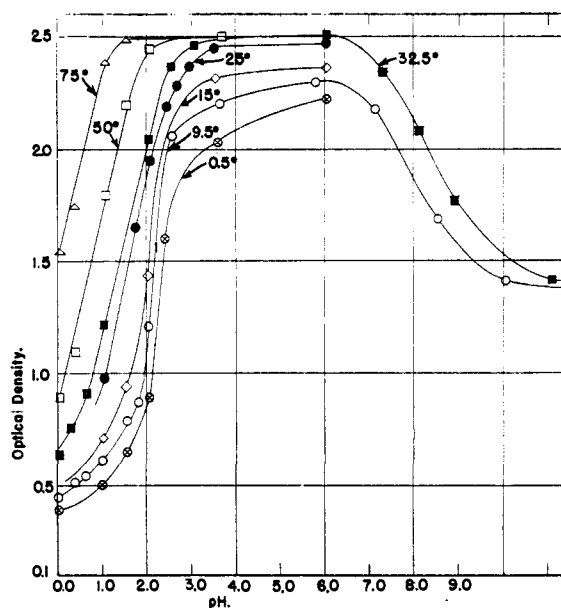


Fig. 1.—The optical density at 2225 Å. of potassium periodate solutions ( $2.37 \times 10^{-4}$  molar) vs. pH at various temperatures.

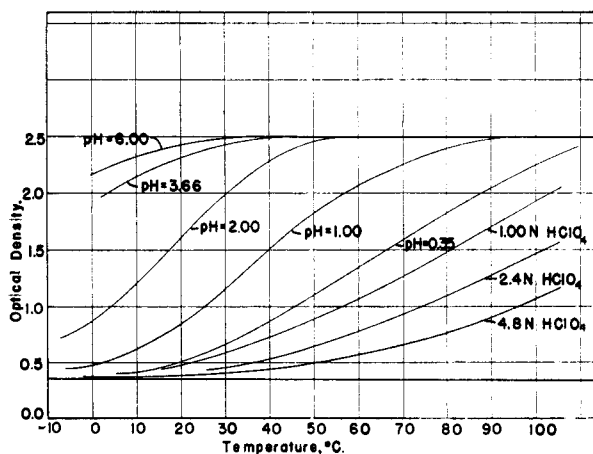


Fig. 2.—The optical density at 2225 Å. of potassium periodate solutions ( $2.37 \times 10^{-4}$  molar) vs. temperature for various acid concentrations.

measurements a Beckman model 1190 glass electrode and a Beckman model 1170 calomel electrode, recommended for use over this temperature range, were used with the model "G" pH meter.

Calibration was made at the proper temperature with standard buffer solutions after thermal equilibrium was attained. These curves are given in Fig. 3. Additional potentiometric titrations of paraperiodic acid with potassium hydroxide in various methanol-water mixtures at 25° (see Fig. 4) were performed.

### Discussion and Results

**I. Spectrophotometric Studies.**—Consideration of the plots of optical density at 2225 Å. (Figs. 1 and 2) led to the following observations: (1) The optical density of solutions at a pH value of 6, where essentially all the periodate would be present as monovalent ions, varied considerably with temperature and approached an upper limiting value at higher temperatures. (2) The optical density approached a lower limiting

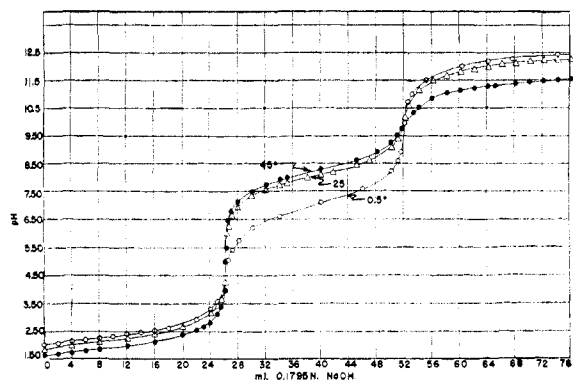


Fig. 3.—Potentiometric titration of aqueous periodic acid solutions with sodium hydroxide at various temperatures.

value at low  $pH$  values and low temperatures. (3) The optical density of solutions in the  $pH$  range 10.5–12 did not change appreciably with temperature from 0 to 50° when the volume changes of pure water were used to correct the concentrations. (4) Beer's law was obeyed at a given  $pH$  and temperature.

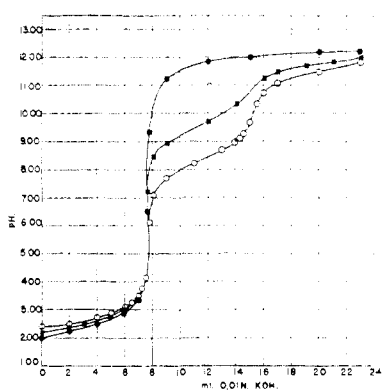


Fig. 4.—Potentiometric titrations of periodic acid with potassium hydroxide in various methanol-water mixtures at 25°: O, aq. soln. 25°; ●, 85%  $CH_3OH$  by vol.; ■, 40%  $CH_3OH$  by vol.

To interpret these observed facts, it was first necessary to assume that absorption of light at a wave length of 2225 Å. corresponds to an electron transition and should be characteristic of a given ionic or molecular species. The energy involved in the absorption of light of this wave length is so large that moderate temperature changes (*i.e.*, 0–100°) should have virtually no effect upon the population statistics of this process, *i.e.*, the extinction coefficient of a species should not be a function of temperature in the range observed. In such a case changes in optical density with temperature would be caused by a change of species. Subsequent experiments confirmed the validity of this assumption. The original choice of species was governed by the known chemistry of periodic acid and its salts. The known polybasicity of the acid and the fact that vacuum drying at 100° is necessary to prepare the meta acid led to the choice of  $H_5IO_6$  as the undissociated acid. The well known para- and metaperiodate

salts suggested the forms  $H_4IO_6^-$  and  $IO_4^-$  for the monovalent ions and this was later substantiated by the equilibrium behavior.

At a  $pH$  of 10.5 there was very little change in the optical density at 2225 Å. with temperature from 0 to 45° and Beer's law was obeyed in this region. These facts seem to indicate that dehydration involving dimerization (*i.e.*, as in the formation of  $I_2O_9$  species) was of no importance. However, a simple dehydration of the  $H_3IO_6^-$  to form  $HIO_5^-$  could occur and not cause apparent discrepancies in Beer's law at a given temperature. Also, if the extinction coefficient of the  $H_3IO_6^-$  and  $HIO_5^-$  ions are not appreciably different at 2225 Å., temperature variations of optical density would be very small. A study of the hydration equilibria of periodic acid in the alkaline region at high and low temperature is now in progress in this Laboratory and will be reported at a later date.

The equilibria necessary to describe the observed data have been given as (2), (3) and (4). It was also necessary to determine which species absorbed at 2225 Å. It was known<sup>3</sup> that the undissociated acid and the divalent ion did absorb at this wave length, however, the absorption by these species could be kept to less than 1% by proper  $pH$  adjustment. Analysis of the absorption curves for a potassium metaperiodate solution (at a  $pH$  of 5.80) at two temperatures (Fig. 5) showed that at wave lengths of 2225 Å. and greater only one species was absorbing within the accuracy of measurement. (Under these conditions at least 99.9% of the periodate present exists as some singly charged ion.) At wave lengths below this value two species were absorbing as shown by the isobestic point at 2050 Å. This was demonstrable since the ratio, optical density 25°/optical density 0°, remained constant for wave lengths of 2225 Å. and greater to within the accuracy possible, *ca.*  $\pm 5\%$ . The absorption was greatest at the higher temperature, hence this was associated with a dehydration process and the metaperiodate ion,  $IO_4^-$ , was assigned to this absorption.

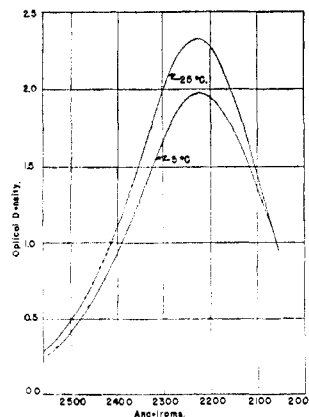


Fig. 5.—The optical density of a potassium periodate solution ( $pH$  5.80) as a function of wave length.

By plotting the optical densities of potassium metaperiodate solutions *versus* temperature (at a  $pH$  6) the extinction coefficient of the metaperiodate ion,  $IO_4^-$ , could be estimated. With this

information together with the total periodate in solution and the assumption that the activity coefficients of the two forms of monovalent ions were equal, the dehydration constant

$$K_D = (M_{\text{IO}_4^-} / M_{\text{H}_4\text{IO}_6^-}) a_{\text{H}_2\text{O}}^2 \quad (6)$$

could be computed. Figure 6 is a plot of the optical density *versus* temperature of these solutions. The limiting value at high temperatures

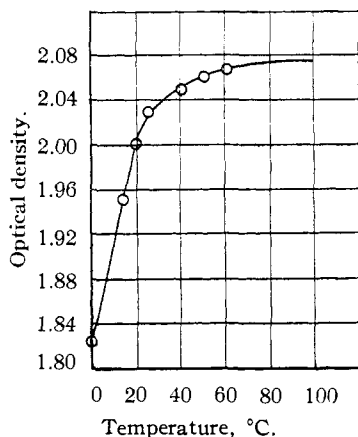


Fig. 6.—The optical density of potassium periodate ( $2.0 \times 10^{-4}$  molar and  $\text{pH } 6$ ) *vs.* temperature.

was used for the calculation of the value 10,700 as the molar extinction coefficient of  $\text{IO}_4^-$ . The test for the validity of reaction (4) was afforded by measurements of the variation of optical density, and hence of the  $(M_{\text{IO}_4^-} / M_{\text{H}_4\text{IO}_6^-})$  ratio with changes of the  $a_{\text{H}_2\text{O}}$  in water-methanol solutions. For the reaction considered, this ratio should satisfy the relation

$$\log (M_{\text{IO}_4^-} / M_{\text{H}_4\text{IO}_6^-}) = \log (a_{\text{IO}_4^-} / a_{\text{H}_4\text{IO}_6^-}) = \log K_D - 2 \log a_{\text{H}_2\text{O}} \quad (7)$$

This is an equation of a straight line with a slope of  $-2$  and an intercept,  $\log K_D$ , when  $\log (M_{\text{IO}_4^-} / M_{\text{H}_4\text{IO}_6^-})$  is plotted *versus*  $\log a_{\text{H}_2\text{O}}$ . Methanol was employed to vary the activity of water since it neither reacts with periodate nor absorbs appreciably at this wave length, and  $\text{pH}$  measurements showed that in methanol-water mixtures appreciable amounts of the undissociated acid were not formed. The activity of water in aqueous methanol mixtures was computed from known vapor composition information at  $25^\circ$ .<sup>4</sup> Solutions containing the same amount of potassium metaperiodate in various methanol-water mixtures at  $0^\circ$  were measured on the spectrophotometer and the resulting information is given in Fig. 7. The ratio  $(M_{\text{IO}_4^-} / M_{\text{H}_4\text{IO}_6^-})$  was calculated using the value for the extinction coefficient obtained by extrapolating the optical density curve *versus* mole fraction of water to zero. The extrapolation was necessary since at mole fractions of methanol greater than  $0.8$  it was apparent that interaction of the periodate with methanol became important. This extinction coefficient checked, within experi-

(4) J. B. Ferguson and W. S. Funnell, *J. Phys. Chem.*, **33**, 1 (1929).

mental error, the value obtained at high temperatures in aqueous solutions. Plotting of these data yielded a straight line with a slope of  $-2.0$  and the intercept value checked the value obtained for  $\log K_D$  at this temperature.

Values of the apparent first ionization constant,  $K_1'$ , were computed from the optical density- $\text{pH}$  curves shown in Fig. 2 using the method already described.<sup>3</sup> The  $\log K_1'$  was plotted *versus* the reciprocal of the absolute temperature in Fig. 8.  $\log K_D$  and  $\log (K_D + 1)$  were also plotted on this figure. If the constants  $K_1'$ ,  $K_D$  and  $K_1$  are taken as

$$K_1' = (a_{\text{H}^+})(a_{\text{IO}_4^-} + a_{\text{H}_4\text{IO}_6^-}) / a_{\text{H}_5\text{IO}_6} \quad (8)$$

$$K_1 = (a_{\text{H}^+})(a_{\text{H}_4\text{IO}_6^-}) / a_{\text{H}_5\text{IO}_6} \quad (9)$$

$$(a_{\text{IO}_4^-} / a_{\text{H}_4\text{IO}_6^-}) a_{\text{H}_2\text{O}}^2 = K_D \quad (10)$$

it follows that

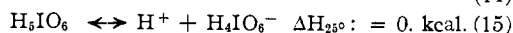
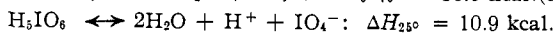
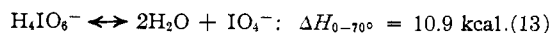
$$K_1' = K_1(K_D + 1) \quad (11)$$

or

$$\log K_1' = \log K_1 + \log (K_D + 1) \quad (12)$$

hence the  $\log K_1$  may be obtained by subtraction of  $\log (K_D + 1)$  from  $\log K_1'$ . The resulting values for  $\log K_1$  have been plotted in Fig. 8.

The slopes of these curves made possible the evaluation of the heat of reaction for



**II. Potentiometric Titrations.**—The determination of a true second ionization constant for

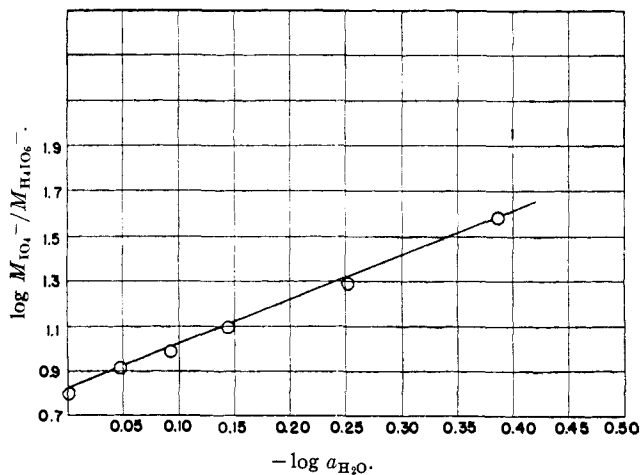


Fig. 7.—The  $\log M_{\text{IO}_4^-} / M_{\text{H}_4\text{IO}_6^-}$  *vs.*  $\log a_{\text{H}_2\text{O}}$  in various methanol-water mixtures at  $0^\circ$ .

$\text{H}_5\text{IO}_6$  from spectrophotometric data would require further analyses of the spectra in the alkaline region. However by a treatment similar to the above where

$$K_2 = (a_{\text{H}^+}) a_2 / a_{\text{H}_4\text{IO}_6^-} \quad (16)$$

and

$$K_2' = (a_{\text{H}^+}) a_2 / (a_{\text{H}_4\text{IO}_6^-} + a_{\text{IO}_4^-}) \quad (17)$$

the following expression can be obtained which corrects for the dehydration of the univalent ion

$$K_2 = K_2'(K_D + 1) \quad (18)$$

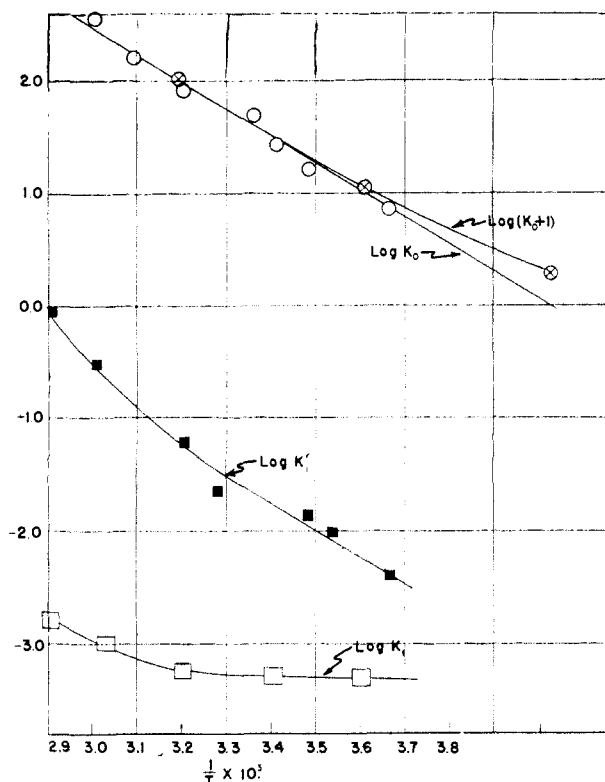


Fig. 8.— $\log K_D$ ;  $\log (K_D + 1)$ ;  $\log K'$  and  $\log K_1$  vs.  $1/T$ .

Values of  $K_2'$  were calculated from the series of potentiometric titrations with solutions thermostated at 0.5, 25.0 and 45.0° (Fig. 3) by the methods used previously.<sup>3</sup> Values of  $K_2$  and  $K_2'$  from these experiments have been included in Table I. It should be noted that the apparent constant  $K_2'$  at 25° agreed closely with the constant obtained from the spectrophotometer data in the preceding paper.

TABLE I  
(Values of  $K_2$  and  $K_2'$ )

$-\log K_2'$	$T, ^\circ\text{C.}$	$\log (K_D + 1)$	$-\log K_2$
7.40	0.5	0.95	6.45
8.40	25.0	1.61	6.69
8.65	45.0	2.15	6.50

The value of  $\Delta H$  obtained from plotting  $\log K_2'$  versus  $1/T$  was approximately  $-11$  kcal. at room temperature. This corresponded to the heat effect of the dehydration reaction of the monovalent ion and indicates that at near room temperatures the major portion of the divalent ion can be described as  $\text{H}_3\text{IO}_6^=$ . The values of  $K_2$  remain essentially constant over the temperature range within the accuracy of measurement, again, agreeing with the characteristics of other oxyacids.

Figure 4 shows potentiometric titrations made in methanol-water mixtures. An unusual effect was observed here since the  $p\text{H}$  values in methanol-water mixtures were lower than in water. The dehydrating effect of methanol apparently overcame the usual effect of depression of the ionization of the acid when methanol is used. In this regard it is also well to point out that metaperiodic

acid,  $\text{HIO}_4$ , would be expected to be a very strong acid similar to perchloric.

Theoretical treatment<sup>5a,b</sup> have indicated that two properties appear to classify the inorganic oxygen acids with respect to ionization constants into distinct groups. First, the formal charge on the central atom and, second, the number of non-hydroxyl oxygen atoms in the molecule. Iodine in periodic acid has a formal charge of,  $m = 1$  and the non-hydroxyl oxygen atoms are,  $n = 1, 2, 3$  for  $\text{H}_5\text{IO}_6$ ,  $\text{H}_4\text{IO}_6^-$  and  $\text{H}_3\text{IO}_6^=$  species, respectively. Using the semi-empirical expression derived by Ricci,<sup>5</sup>  $pK = 8.0 - m(9.0) + n(4.0)$  an improved correlation is obtained between calculated and observed values when the true ionization constants are used. In Table II a summary of the ionization constants is given.

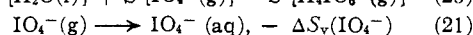
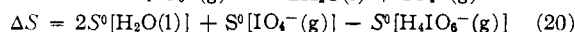
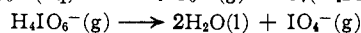
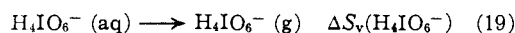
TABLE II

COMPARISON OF OBSERVED AND CALCULATED VALUES OF THE IONIZATION CONSTANTS OF PERIODIC ACID AT 25°

	Apparent <sup>3</sup> $pK$	True $pK$ (this paper)	Calcd. <sup>5</sup> $pK$
$pK_1$	1.6	3.3	3.0
$pK_2$	8.4	6.7	7.0
$pK_3$	14.3	...	11.0

It is interesting to note that the first apparent ionization constant of carbonic acid has a very small value because of a hydration equilibria between carbon dioxide and the undissociated acid as reported first by McBain<sup>6</sup> and later investigators.<sup>7,8</sup>

From the equilibrium constant  $K_D$  and  $\Delta H_D$  for the dehydration of  $\text{H}_4\text{IO}_6^-$ , the entropy change,  $\Delta S_D$  was computed to be 44 e.u. Contributions to this entropy change were indicated by resolving the reaction into three steps.



$\Delta S_v$  represents the entropy change for the hypothetical process of taking one mole of the ion in question from its standard state in aqueous solution to a standard state of ideal vapor at one atmosphere. This quantity for various ions has been discussed by Frank and Evans.<sup>9</sup> Using  $S^\circ[\text{H}_2\text{O}(\text{l})] = 16.75$  e.u.<sup>10</sup> and calculating by the methods of statistical mechanics a value of  $-12.5$  e.u. for  $S^\circ[\text{IO}_4^-(\text{g})] - S^\circ[\text{H}_4\text{IO}_6^-(\text{g})]$ ,<sup>11</sup> the differ-

(5) (a) A. Kossiakoff and D. Harker, *THIS JOURNAL*, **60**, 2047 (1938); (b) John E. Ricci, *ibid.*, **70**, 109 (1948).

(6) McBain, *J. Chem. Soc.*, **101**, 814 (1912).

(7) G. A. Mills and H. C. Urey, *THIS JOURNAL*, **62**, 1019 (1940).

(8) A. R. Olson and P. V. Youle, *ibid.*, **62**, 1027 (1940).

(9) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(10) W. F. Giaque and J. W. Stout, *THIS JOURNAL*, **58**, 1144 (1936).

(11) The  $\text{IO}_4^-$  was assumed to be tetrahedral with I-O distances of 1.79 Å. From a set of estimated tetrahedral frequencies the vibrational contribution to the entropy was calculated to be 11 e.u. The  $\text{H}_4\text{IO}_6^-$  was assumed to have the oxygens arranged octahedrally with all I-O distances equal to 1.93 Å. The O-H distances were taken as 0.97 Å. and the I-O-H angles as 105°. The vibrational entropy was calculated to be 16 e.u. from a set of estimated octahedral frequencies and a treatment of the hydrogens' motion as restricted rotation around the I-O bond with a very high two-maximum barrier. The symmetry of the ion was taken to be  $D_{4h}$ ,  $\sigma = 8$ .

ence in  $\Delta S_v$  for the two species would be

$$S_v(\text{H}_4\text{IO}_6) - S_v(\text{IO}_4^-) = 44 - 33.5 + 12.5 = 23 \text{ e. u.} \quad (22)$$

This difference would seem to be surprisingly high. A part of the difference might be explained as due to loss of rotational entropy in the cage of the solvent. However, a fairly large fraction of it would still have to be accounted for as due to a difference of the two ions in destroying the structure of the solvent, the  $\Delta S_{st}$  discussed by Frank and Evans.

### III. Solubility of Potassium Metaperiodate.

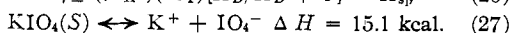
Inconsistencies exist in the solubility values reported for  $\text{KIO}_4$  in the literature. The early values of T. V. Barker<sup>12a,b</sup> are apparently too high when compared with the later values of A. E. Hill<sup>13</sup> and J. H. Jones.<sup>14</sup> From equilibria 9 and 17 it can be seen that the solubility of potassium metaperiodate should be increased by both excess acid and alkali. Thus it is not surprising to find that potassium hydroxide does not depress the solubility of potassium metaperiodate salt according to the common ion effect.<sup>13</sup> Also it is known that strong acids dissolve potassium metaperiodate quite readily. Using the data of Hill<sup>13</sup> and Jones<sup>14</sup> for the solubility of potassium metaperiodate the solubility product at various temperatures has been calculated. The following equations should apply to solutions of potassium metaperiodate with no excess acid or alkali ( $p\text{H}$  6–6.8).

$$(M_{\text{IO}_4^-}/M_{\text{H}_4\text{IO}_6^-}) = K_D \quad (23)$$

$$[K_D/K_D + 1]M_T = M_{\text{IO}_4^-} \quad (24)$$

$$(a_{\text{K}^+})(a_{\text{IO}_4^-}) = K_{sp} \quad (25)$$

$$\gamma_{\pm}^2(M_{\text{K}^+})(M_T)[K_D/K_D + 1] = K_{sp} \quad (26)$$



Where  $M_T$  is the total periodate concentration, moles/liter, in solution and  $\gamma_{\pm}$  is the mean activity coefficient calculated by Jones.<sup>14</sup> Using the solubility data of Jones for potassium metaperiodate at 25° where

$$\gamma_{\pm} = 0.866, M_{\text{K}^+} = M_T^{25^\circ} = 0.02248 \text{ and } K_D = 40. \\ (3.77 \times 10^{-4}) [(K_D)/(K_D + 1)] = 3.70 \times 10^{-4} = K_{sp}^{25^\circ}$$

(12) (a) T. V. Barker, *J. Chem. Soc.*, **93**, 15 (1908); (b) "International Critical Tables," Vol. 4, p. 239.

(13) A. E. Hill, *THIS JOURNAL*, **50**, 2678 (1928).

(14) J. H. Jones, *ibid.*, **69**, 536 (1947).

At lower temperatures, 0°, the value of  $K_D$  becomes less than 10 and the effect of the hydration equilibria on  $K_{sp}$  is more pronounced. In Fig. 9 is plotted the  $\log K_{sp}$  versus  $1/T$ . These values were calculated using the solubility data of Hill<sup>13</sup> and the solubility product equation (25). The heat of reaction (27) was calculated from the slope of this curve.

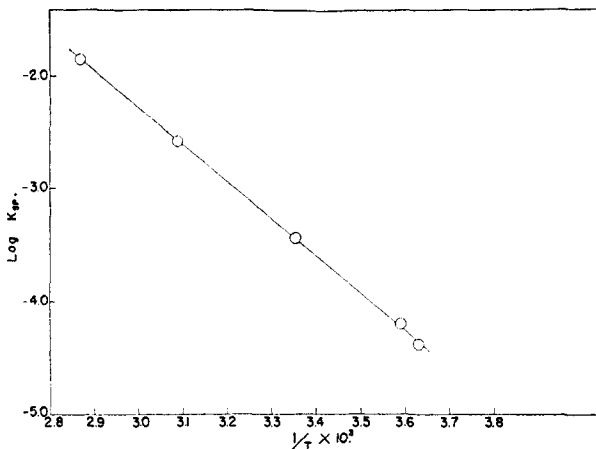


Fig. 9.— $\log K_{sp}$  for potassium metaperiodate vs.  $1/T$ .

### Summary

Variations in the absorption characteristics of periodate solutions with  $p\text{H}$  and temperature have been used to better determine the species present in dilute aqueous solutions. The species  $\text{H}_5\text{IO}_6$ ,  $\text{H}_4\text{IO}_6^-$ ,  $\text{IO}_4^-$  and  $\text{H}_3\text{IO}_6^{2-}$  and their equilibria were sufficient to completely explain the spectrophotometric and potentiometric data of periodate solutions in  $p\text{H}$  ranges 0–7 and temperature ranges 0–70°. Apparent and true constants for these ionization and hydration equilibria have been evaluated at 25° as

$$a_{\text{H}^+}(a_{\text{H}_4\text{IO}_6^-})/a_{\text{H}_5\text{IO}_6} = K_1 = 5.1 \times 10^{-4}$$

$$a_{\text{H}^+}(a_{\text{H}_3\text{IO}_6^{2-}})/a_{\text{H}_4\text{IO}_6^-} = K_2 = 2.0 \times 10^{-7}$$

$$(a_{\text{IO}_4^-}/a_{\text{H}_4\text{IO}_6^-}) a^2_{\text{H}_2\text{O}} = K_D = 40$$

$$[a_{\text{H}^+}(a_{\text{IO}_4^-} + a_{\text{H}_4\text{IO}_6^-})]/a_{\text{H}_5\text{IO}_6} = K_1' = 2.3 \times 10^{-2}$$

$$a_{\text{H}^+}(a_{\text{H}_3\text{IO}_6^{2-}})/(a_{\text{IO}_4^-} + a_{\text{H}_4\text{IO}_6^-}) = K_2' = 4.35 \times 10^{-9}$$

AMES, IOWA

RECEIVED MAY 18, 1950