caused by this approximate treatment are not large because of the shortness of the temperature intervals involved.

Log *K*, Δ*F*, Δ*H* and Δ*S* values for the dissociations are given in Table II. In Fig. 1, the log *K*(25°) values are plotted against the substituent constant, σ. The data from the present work are indicated by open circles while the data of McCullough and Eckerson are indicated by full circles. The sigma values employed for the disubstituted diphenylselenium dibromides are the sums of the two individual sigma values concerned (twice Hammett's sigma values in the cases of the symmetrically disubstituted compounds). The straight line shown is the result of a least squares treatment of all of the data and has a slope, ρ, of 2.2. This indicates a rather high susceptibility of the selenium–bromine bond to changes in electron density on the selenium atom.

The fact that all of the log *K* values lie reasonably close to a single straight line is convincing evidence of the additivity of the effects of a substituent on the first ring to those of a substituent on the second ring in this type of system.

Summary

1. Dissociation constants for a number of unsymmetrically substituted diphenylselenium dibromides in carbon tetrachloride solution have been determined and the values (as log *K*) are given in Table II.

2. The values of log *K* (25°) from the present study have been plotted together with those from an earlier study of symmetrically disubstituted dibromides against Hammett's substituent constant, σ. The fact that all log *K* values lie reasonably close to a single straight line with slope, ρ, of 2.2 shows that the σ value for a substituent on one ring is additive to that for a second substituent on the other phenyl group.

3. The quantities Δ*F*, Δ*H* and Δ*S* at 25° have been evaluated for the dissociations and are listed in Table II.

LOS ANGELES 24, CALIFORNIA RECEIVED MARCH 21, 1949

[CONTRIBUTION NO. 61 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Spectrophotometric Studies of Dilute Aqueous Periodate Solutions[1]

BY CARL E. CROUTHAMEL, HOMER V. MEEK, D. S. MARTIN AND CHARLES V. BANKS

The solubility behavior of various sparingly soluble periodates was found to be anomalous as interpreted through the equilibrium constants for the dilute aqueous periodate system as reported in the literature. Thus it was necessary to investigate these equilibria as a possible reason for the anomaly. Reinterpretation of this solubility behavior in light of the results of this investigation will be reported at a later date.

The ionization of periodic acid in aqueous solutions has been studied previously by various authors.[2,3] Giolitti[2a] and Partington and Bahl[3] found evidence of the dibasicity of periodic acid. Dubrisay[2b] found somewhat doubtful evidence of a third replaceable hydrogen. Rothmund and Drucker[4] reported the dissociation constant $K_1 = 2.3 \times 10^{-2}$ for paraperiodic acid, H_5IO_6. Rae[5] ran a conductometric titration of paraperiodic acid with sodium hydroxide and obtained two breaks. The first is in accord with the K_1 value reported by Rothmund and Drucker and from the second break he estimated that K_2 may be of the order of 10^{-6}. The literature generally concurs with the fact that paraperiodic acid, H_5IO_6, is the only solid periodic acid which is capable of existence in equilibrium with aqueous solutions of the acid. Hill[6] estimated a K_3 value of 4.6×10^{-11} using the previously reported values of K_1 and K_2 as a basis for his estimate.

In this study we have confirmed the previously reported value of $K_1 = 2.3 \times 10^{-2}$ and have assigned new values of $K_2 = 4.35 \times 10^{-9}$ and $K_3 = 1.05 \times 10^{-15}$. K_1 was confirmed from spectrophotometric studies, K_2 was estimated from spectrophotometric and potentiometric studies and K_3 was estimated using the method of Hill[6] and was confirmed by spectrophotometric data.

Aqueous solutions of periodate in the absence of interfering ions show an absorption maximum at 222.5 mμ in the ultraviolet region of the spectrum over a limited *p*H range. Since the start of this investigation MacDonald, Thompsett and Mead[7] reported an absorption maximum at 222 mμ and indicated that Beer's law was obeyed but neglected to mention the critical nature of *p*H. The full importance of *p*H is adequately described below.

Experimental

In the spectrophotometric studies a Beckman Quartz Spectrophotometer (Model DU) and a Cary Recording Spectrophotometer (Model 12) were employed. A Beckman Glass Electrode *p*H Meter (Model H-2) was used in carrying out the potentiometric titrations. Sources of periodate were paraperiodic acid manufactured by the

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[1] This document is based on work performed in the Ames Laboratory, Atomic Energy Commission.

[2] (a) Giolitti, *Atti reale Accad. Lincei*, **14**, 217 (1905); (b) Dubrisay, *Compt. rend.*, **157**, 1150 (1913).

[3] Partington and Bahl, *J. Chem. Soc.*, 1088 (1934).

[4] Rothmund and Drucker, *Z. physik. Chem.*, **46**, 850 (1903).

[5] Rae, *J. Chem. Soc.*, 876 (1931).

[6] Hill, THIS JOURNAL, **65**, 1564 (1943).

[7] MacDonald, Thompsett and Mead, *Anal. Chem.*, **21**, 315 (1949).

G. Frederick Smith Chemical Company, Columbus, Ohio, and Baker and Adamson reagent grade potassium metaperiodate. The spectra obtained were found to be independent of the starting material in the absence of interfering substances. Ions which exhibited no interference were perchlorate, sodium and potassium. Ammonium ion exhibited no interference in concentrations attained by adjusting 10^{-4} *M* potassium metaperiodate up to *p*H of *ca.* 10.5 with filtered reagent grade ammonia solutions. Nitrate, sulfate and carbonate ions and carboxylate groups definitely interfere.

After originally establishing the nature of the absorption, solutions of both potassium metaperiodate and paraperiodic acid were scanned on the Cary instrument using 1.000 cm. silica cells at various *p*H values as adjusted with perchloric acid. Figure 1 shows the nature of the variation of the absorption spectra of solutions 1.01×10^{-4} *M* potassium metaperiodate at various *p*H values as adjusted by perchloric acid and using the Cary instrument. Figure 2 similarly shows the variation in the alkaline region of 1.05×10^{-4} *M* potassium metaperiodate at various *p*H values as adjusted by potassium hydroxide and unlike Fig. 1 these solutions are 10^{-2} *M* in sodium perchlorate. Isobestic points are apparent at approximately 213 mμ and 244 mμ. Solutions of paraperiodic acid gave absorption curves identical within experimental error when similarly adjusted in *p*H. Figure 3 is a plot of the optical densities at 222.5 mμ for solutions 1.009×10^{-4} *M* in potassium metaperiodate at various *p*H values as adjusted with perchloric acid or sodium hydroxide. The Beckman instrument (0.998 cm. silica cells) was used up to *p*H 12 but at higher *p*H the Cary instrument was used because it appears to be better suited to the measurement of very high optical densities. High optical densities at *p*H values above 12.0 were due to the fact that sodium hydroxide solutions of very high *p*H even though they contain only relatively small amounts of carbonate nevertheless absorb considerably at 222.5 mμ. The experimental values plotted in Curve 1, Fig. 3, above *p*H 12.0 represent the difference between optical densities of the periodate solutions at the *p*H values indicated and distilled water of the same *p*H values as adjusted by the same sodium hydroxide solution. As indicated on Fig. 3 the series of experimental optical density values above *p*H 12.0 represent Cary instrument readings converted to equivalent Beckman instrument readings. This was necessitated by the fact that different molecular extinction coefficients, ε, were found for the $H_3IO_6^{=}$ ion on the two instruments. This is explainable by the fact that th molecular extinction coefficient for this ion was determined not at an absorption maximum but at a wave length where the optical density is changing rapidly with wave length. Therefore minor discrepancies in the wave length scales of the two instruments would be reflected quite sensitively in the molecular extinction coefficients obtained for this ion. In the case of the $H_4IO_6^-$ ion no such discrepancy would be expected because the molecular extinction coefficient for this ion was determined at an absorption maximum where optical density is rather insensitive to wave length. Experimental values are in agreement with this explanation. In curve 1, Fig. 3, the ionic strength, μ, varies only as a consequence of the addition of perchloric acid or sodium hydroxide required in adjusting *p*H. The solutions for Curve 2, Fig. 3, differ from those of curve 1 only in that the former are all 0.0625 *M* in sodium perchlorate. Differences between curves 1 and 2 are due only to differences in ionic strength and experimental error. Table I lists observed and calculated data corresponding to Fig. 3.

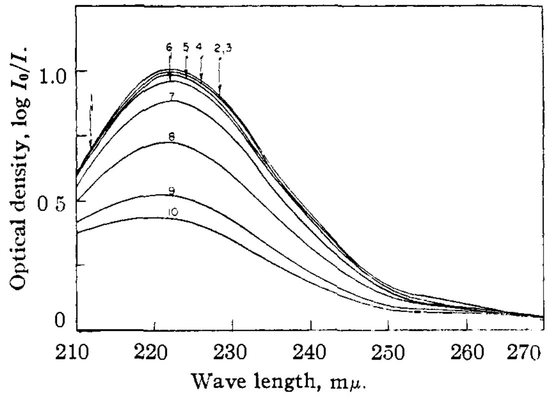

Fig. 1.—Absorption spectra of 1.01×10^{-4} *M* potassium periodate solutions at *p*H values: 1, 6.92; 2, 4.78; 3, 3.43; 4, 3.04; 5, 2.80; 6, 2.35; 7, 1.80; 8, 1.35; 9, 1.10.

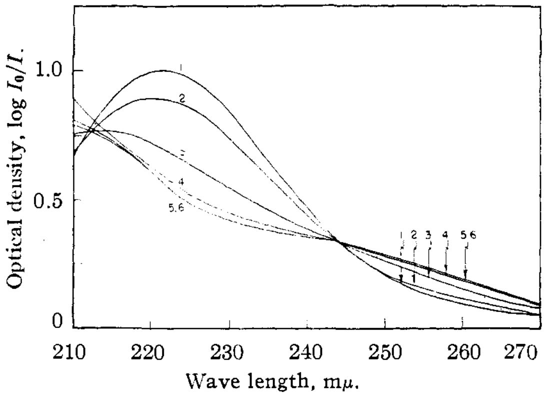

Fig. 2.—Absorption spectra of 1.05×10^{-4} *M* potassium periodate solutions at *p*H values: 1, 6.50; 2, 7.50; 3, 8.50; 4, 9.30; 5, 10.15; 6, 10.75.

Table I

Experimental and Calculated Data Corresponding to Fig. 3

*p*H	$\sqrt{\mu}$	γ_1	γ_2	γ_3	ΣD_i Calcd.	ΣD_i Exptl.
1.0[a]	0.32	0.770	0.359	0.225	0.403	0.405
2.0	.10	.900	.665	.650	.792	0.810
3.0	.033	.970	.885	.900	.983	1.000
4.0	.014	.988	.947	.950	1.013	1.017
5.0	.011	.992	.965	.955	1.014	1.020
6.0	.012	.990	.956	.952	1.013	1.016
7.0	.012	.990	.956	.952	0.996	1.010
8.0	.017	.985	.932	.930	.881	0.875
9.0	.020	.982	.922	.930	.666	.645
10.0	.020	.982	.922	.930	.599	.590
11.0	.035	.968	.872	.880	.591	.585
12.0	.10	.900	.665	.650	.590	.584
13.0	.32	.770	.359	.225	.579	.577
14.0	1.23	.585	.267	.060	.403	.390
1.0[b]	0.40	.740	.307	.150	.408	...
2.0	.27	.795	.405	.300	.811	.840
3.0	.25	.805	.428	.350	.987	.987
4.0	.25	.805	.428	.350	1.013	1.004
5.0	.25	.805	.428	.350	1.013	1.007
6.0	.25	.805	.428	.350	1.012	1.005
7.0	.25	.805	.428	.350	0.986	0.957
8.0	.25	.805	.428	.350	.823	.737
9.0	.25	.805	.428	.350	.637	.603
10.0	.25	.805	.428	.350	.595	.572
11.0	.25	.805	.428	.350	.591	.572

[a] Curve 1. [b] Curve 2.

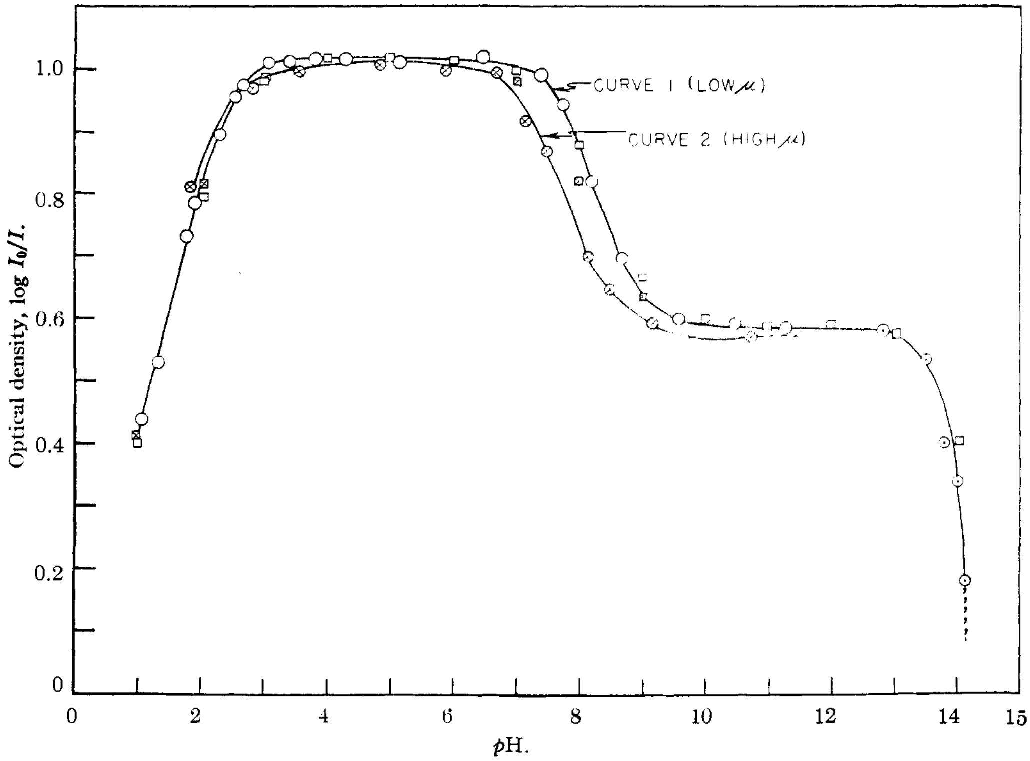

Fig. 3.—Variation of optical density at 222.5 mμ of solutions 1.009 × 10^{-4} M in potassium periodate at various pH values as adjusted with perchloric acid or sodium hydroxide using the Beckman instrument: curve 1, O, experimental (Beckman); ⊙, experimental, (Cary) converted to Beckman; □, calculated; curve 2, ⊗, experimental (Beckman); ⊠, calculated.

Figure 4 is a plot of the data obtained in the potentiometric titrations of two samples of paraperiodic acid with 0.2232 N potassium hydroxide using the Beckman pH Meter.

Discussion and Calculations

Aqueous solutions of periodate were found to follow Beer's law at given pH values from 1.0 to 10.5 at all wave lengths in the range where appreciable absorption occurs. The equilibria

$$H_5IO_6 \longleftrightarrow H_4IO_6^- + H^+,\ K_1 = \frac{a_{H^+}a_{H_4IO_6^-}}{a_{H_5IO_6}} \qquad \text{Eq. 1}$$

$$H_4IO_6^- \longleftrightarrow H_3IO_6^= + H^+,\ K_2 = \frac{a_{H^+}a_{H_3IO_6^-}}{a_{H_4IO_6^-}} \qquad \text{Eq. 2}$$

$$H_3IO_6^= \longleftrightarrow H_2IO_6^\equiv + H^+,\ K_3 = \frac{a_{H^+}a_{H_2IO_6^\equiv}}{a_{H_3IO_6^=}} \qquad \text{Eq. 3}$$

predict that the ratios of the activities of the various species remain constant at constant pH. Yet deviation from Beer's law might be caused by the variation of the activity coefficients in the solutions studied. In these solutions, however, either the ionic strength was so low that all activity coefficients were nearly 1.0 or the ionic strength was maintained constant by the addition of an electrolyte. In this work the pH value indicated by the glass electrode instrument, calibrated by means of three standard buffers of pH 4, 7 and 10, is taken as $-\log a_{H^+}$. For values less than 1.0 or greater than 12.0 the pH was calculated from the molar concentration of H^+ or OH^- and estimated values of activity coefficients.

However, an equilibrium such as

$$2H_3IO_6^= \longleftrightarrow I_2O_9^{==} + 3H_2O,\ K_4 = \frac{a_{I_2O_9^{==}}a^3_{H_2O}}{a^2_{H_3IO_6^=}} \qquad \text{Eq. 4}$$

does predict a departure from Beer's law at any pH value at which this equilibrium is of importance, because the activities of the $I_2O_9^{==}$ and $H_3IO_6^=$ ions are raised to different powers in the expression for K_4. Therefore this equilibrium is of no importance up to a pH of 10.5 and is probably never appreciably involved in dilute aqueous solutions of periodates. The formulation $K_4I_2O_9 \cdot 9H_2O$ frequently encountered in the literature[8] is probably better represented as $K_2H_3IO_6 \cdot 3H_2O$. Reactions of simple hydration or dehydration of the various periodate species involved in Equations 1, 2 and 3 predict no departure from Beer's law and are not considered in this work. Treatment of the data obtained using only K_1, K_2 and K_3 accounts completely for the variation of the optical densities of the solutions with pH.

A molecular extinction coefficient was estimated for H_5IO_6 using a solution of known periodate concentration and 1.14 M in perchloric acid. Molecular extinction coefficients for $H_4IO_6^-$ and

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(8) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 39.

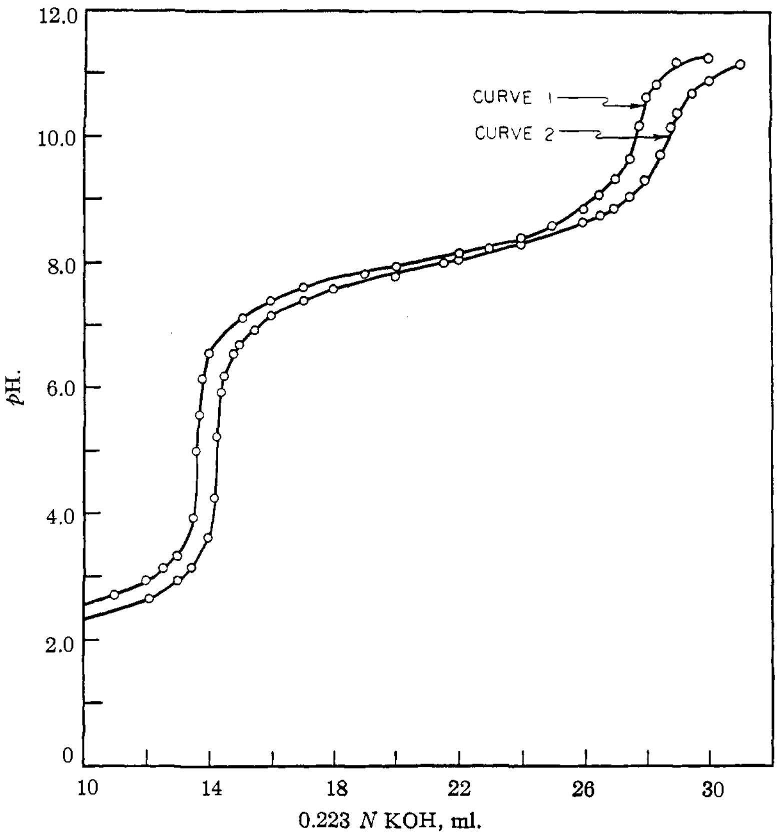

Fig. 4.—Potentiometric titration curves of paraperiodic acid.

$H_3IO_6^{=}$ were estimated from the wide plateaus obtained in dilute acid and dilute alkaline solution respectively in the plot of optical densities *vs.* *p*H for known concentrations of periodate. Table II lists the molecular extinction coefficients estimated for the various species of periodate using both the Cary and Beckman instruments.

Table II

Molecular Extinction Coefficients at 222.5 mμ of the Various Periodate Species in Dilute Aqueous Solution

Instrument	$\epsilon_0 \times 10^{-3}$	$\epsilon_1 \times 10^{-3}$	$\epsilon_2 \times 10^{-3}$	$\epsilon_3 \times 10^{-3}$
Beckman	2.18	10.08	5.24	0.00
Cary	2.18	9.97	5.86	0.00

Good agreement was obtained except in the case of $H_3IO_6^{=}$ and the probable reason for this has already been cited (see Experimental). This is not unexpected since Ewing and Parsons[9] have shown relative discrepancies of half this magnitude among ten Beckman instruments themselves at constant band width.

By substituting $\gamma_0M_0,\gamma_1M_1,\gamma_2M_2$ and γ_3M_3 for the activities of H_5IO_6, $H_4IO_6^-$, $H_3IO_6^{=}$ and $H_2IO_6^{\equiv}$, respectively, in equations 1, 2 and 3 and solving these equations for the molar concentrations of the various periodate species the following equation may be written for the total periodate concentration, assuming that $\gamma_0 = 1$

$$M_{\text{total}} = M_0 + \frac{K_1M_0}{\gamma_1 a_{H^+}} + \frac{K_1K_2M_0}{\gamma_2 a^2_{H^+}} + \frac{K_1K_2K_3M_0}{\gamma_3 a^3_{H^+}} \quad \text{Eq. 5}$$

The activity coefficients as functions of the ionic strength were estimated in the following manner for all points except for *p*H 14. For γ_1, values of $\gamma_\pm$ for aqueous potassium chloride solutions[10] were used. Values for γ_2 were calculated from values of $\gamma_{C_2O_4^=}/\gamma_{Cl^-} \times \gamma_{HC_2O_4^-}$ indicated in the potentiometric evaluation of the second ionization constant of oxalic acid[11] together with the values of γ_1. The activity coefficient, γ_3, was calculated in the conventional manner from values of $\gamma_\pm$ reported for various rare earth chlorides.[12] For *p*H of 14, γ_1 was taken from values of $\gamma_\pm$ for sodium hydroxide and γ_2 was calculated from values of $\gamma_\pm$ for alkaline earth halides tabulated by Harned and Owen.[13] The values of K_1, K_2 and K_3 are quite easily estimated from equation 5 and the following relation for the optical density

$$D = l\left[\epsilon_0 M_0 + \frac{\epsilon_1 K_1 M_0}{\gamma_1 a_{H^+}} + \frac{\epsilon_2 K_1 K_2 M_0}{\gamma_2 a^2_{H^+}} + \frac{\epsilon_3 K_1 K_2 K_3 M_0}{\gamma_3 a^3_{H^+}}\right] \quad \text{Eq. 6}$$

since a_{H^+} is known from *p*H measurements, M_{total} is known from chemical analysis, l is the cell thickness in cm. and ϵ_3 is very nearly zero. In this way the values for K_1, K_2 and K_3 which gave the best agreement between experimental and calculated optical density values at low ionic strength were found to be

$$K_1 = 2.30 \times 10^{-2}$$
$$K_2 = 4.35 \times 10^{-9}$$
$$K_3 = 1.05 \times 10^{-15}$$

The value of K_1 thus determined agrees exactly with previously reported values.[4,5] The value of K_2, a new constant, was substantiated from the potentiometric titration data shown in Fig. 4 in the following manner.

From equation 2 it follows that

$$K_2 = a_{H^+} \text{ when } \frac{a_{H_3IO_6^=}}{a_{H_4IO_6^-}} = \frac{\gamma_2 M_2}{\gamma_1 M_1} = 1 \quad \text{Eq. 7}$$

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[9] Ewing and Parsons, *Anal. Chem.*, **20**, 423 (1948).

[10] Shedlovsky and MacInnes, This Journal, **59**, 503 (1937).

[11] Pinching and Bates, *J. Research Natl. Bur. Standards*, **40**, 405 (1948).

[12] Robinson, This Journal, **59**, 84 (1937); *Trans. Faraday Soc.*, **35**, 1229 (1939).

[13] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 567.

Knowing the total quantity of periodate, the volume of solution, how the assumed values for γ_1 and γ_2 vary with ionic strength, and how the ratio of M_2: M_1 varies with ml. of base added, the condition where Eq. 7 is satisfied was evaluated by a series of successive approximations. This condition was found to occur where $\sqrt{\mu}$ was *ca.* 0.25 and

$$\frac{M_2}{M_1} = \frac{\gamma_1}{\gamma_2} = \frac{0.805}{0.428} = 1.88$$

This molar ratio corresponds to *p*H values of 8.24 and 8.26 on curves 1 and 2, respectively, in Fig. 4. This gives a value of $K_2 = 5.6 \times 10^{-9}$ which, in view of the uncertainties involved in γ_1 and γ_2, is in good agreement with the value of $K_2 = 4.35 \times 10^{-9}$ obtained from the spectrophotometric studies.

The value of K_3, also a new constant, agrees, within experimental error, with the value of K_3 obtained from K_1 and K_2 using the method of Hill.[6]

Activity Coefficients.—The magnitudes of the differences between Curves 1 and 2 in Fig. 3 are much greater than predicted differences due to such changes in ionic strength, using normal γ_1 and γ_2 values. This suggests an abnormal decrease of the actual activity coefficients of the $H_4IO_6^-$ and $H_3IO_6^=$ ions, particularly the latter, with increasing ionic strength. For this reason values of K_1 and K_2 were calculated from the data for low ionic strength where errors due to such abnormalities would be very small. Estimates of the actual γ_1 and γ_2 values at the ionic strengths indicated may be made from the magnitudes of the differences between the two curves.

Analytical Significance.—From these studies it is quite obvious that for the analytical determination of periodate (in the absence of interfering substances) spectrophotometrically, *p*H is a very important factor. Inspection of the plot of optical density at 222.5 mμ *versus* *p*H shows clearly that a *p*H of *ca.* 5.0 is the optimum *p*H to use in acid solutions for this determination. For solutions of low ionic strength *p*H values of 5.0 ± 1.5 are quite satisfactory, the optical density not varying appreciably in this region. Concentrations as low as 10^{-7} molar in periodate should be detectable using 5.00-cm. silica cells. In the event that it is desirable to determine periodate spectrophotometrically in alkaline solutions, *p*H values between *ca.* 10.5 and 12.5 are desirable. Such analysis leads to a sacrifice in sensitivity of the method at 222.5 mμ because of the lower molecular extinction coefficient of the $H_3IO_6^=$ ion as compared to that of the $H_4IO_6^-$ ion used in the lower *p*H range. This disadvantage may be eliminated by simply carrying out the analysis at a somewhat lower wave length, *i. e.*, at a wave length nearer to or at which the $H_3IO_6^=$ ion shows an absorption maximum.

Summary

It was shown that most probably any equilibria involving the formation of the dimesoperiodate ion, $I_2O_9^{==}$, is of no importance in dilute aqueous solutions. Three simple equilibria involving stepwise dissociation of paraperiodic acid, H_5IO_6, account completely for the variation of the ultraviolet absorption spectra of dilute aqueous solutions of periodate with *p*H. K_1[4,5] was substantiated and new estimates of K_2 and K_3 were made from spectrophotometric studies. K_2 was substantially confirmed by potentiometric studies and K_3 was confirmed by the method of Hill.[6] Evidence was shown for abnormal activity coefficients of $H_4IO_6^-$ and $H_3IO_6^=$ ions with increasing ionic strength. Recommendations were made for the spectrophotometric determination of periodate in slightly acid and alkaline solutions.

AMES, IOWA RECEIVED APRIL 4, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORQUIMA S. A., SÃO PAULO, BRAZIL]

The Acid Properties of Iron Tetracarbonyl Hydride

BY P. KRUMHOLZ AND H. M. A. STETTINER

It has been shown previously[1] that the reaction between iron pentacarbonyl and alkalies does not produce, as assumed by Hieber,[2] the free iron tetracarbonyl hydride but its monobasic salts. The acid behavior of iron carbonyl hydride could be confirmed later by preparing salts with complex amine cations.[3] Some of them, as shown by Hieber,[4] behave in solution as strong electrolytes. Meanwhile Hieber[4] stated that structures as $[Fe(CO)_4H]^-$ are not stable and only can be stabilized by the formation of salts with complex cations, that the alkaline solutions of the hydride contain aquo salts rather than normal salts not yet prepared,[5] and that the formation of metal derivatives of $Fe(CO)_4H_2$ is by far not as general as it is supposed to be in an ordinary formation of salts.

In order to destroy any doubts regarding the behavior of iron carbonyl hydride as an ordinary acid we tried to determine its dissociation constant[6] by potentiometric titration of its salts with

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(1) F. Feigl and P. Krumholz, *Monatsh.*, **59**, 314 (1932).

(2) W. Hieber and F. Leutert, *Z. anorg. Chem.*, **204**, 145 (1932).

(3) F. Feigl and P. Krumholz, *ibid.*, **215**, 242 (1933).

(4) W. Hieber and E. Fack, *ibid.*, **236**, 83 (1938).

(5) The monosodium salts prepared by F. Feigl and P. Krumholz, ref. 1, as alcoholates could not be freed completely from alcohol.

(6) A. A. Blanchard, *Chem. Rev.*, **21**, 3 (1937), assumed that the dissociation constant of cobalt tetracarbonyl hydride should be about 10^{-6}.