Results

The measured heat contents above 298.16°K., expressed in defined cal. per mole of nickel chloride (129.60 g.), are listed in Table I and plotted in Fig. 1. Correction for condensation of nickel chloride vapor was applied as necessary, using the equation of Kelley.[5] This correction was negligible below 1100°K. and it never exceeded 0.2% at higher temperatures.

The trend in the heat content of the crystals is regular to 1281.1°K. Premelting became evident at 1286.6°K., and most of the substance was melted at 1300.8°K. (results labeled (a) in Table I). The adopted melting point is 1303°K., the temperature at which all the substance became molten. The heat of fusion was obtained as 18,470 cal./mole, yielding an entropy of fusion of 14.18 cal./deg./mole.

Measurements beyond 1336°K. were precluded by failure of the platinum–rhodium capsules, caused by the high vapor pressure of nickel chloride. From Kelley's[5] equations, in conjunction with the present results, it is estimated that the vapor pressure is about 3.5 atm. at this temperature.

The measured heat content of the crystals is represented to within an average deviation of 0.5% by the equation

$$H_T - H_{298.16} = 17.50T + 1.58 \times 10^{-3}T^2 + 1.19 \times 10^5T^{-1} - 5{,}757$$

For the short portion of the liquid range covered, the heat capacity is 24.00 cal./deg./mole, and the heat content is reproduced to within 0.2% by

$$H_T - H_{298.16} = 24.00T + 7{,}020$$

The previous data of Krestovnikov and Karetnikov[2] are mutually inconsistent to the extent of more than 10%, and they are 6% higher on the average than the present results.

Table II contains values of the molal heat content and entropy increments above 298.16°K. at even temperatures and at the melting point. The latter have been calculated to match the former by use of the method of Kelley.[3]

TABLE II

MOLAL HEAT CONTENT AND ENTROPY INCREMENTS ABOVE 298.16°K.

T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$	T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	1,800	5.18	1100	15,390	24.65
500	3,650	9.31	1200	17,510	26.50
600	5,545	12.76	1300	19,750	28.29
700	7,465	15.72	1303	19,820^{c}	28.34
800	9,400	18.30	1303	38,290^{l}	42.52
900	11,360	20.61	1350	39,420	43.37
1000	13,350	22.71			

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(5) K. K. Kelley, *U. S. Bureau of Mines Bull.* 383, 1935.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Catalytic Polarographic Waves of Hydrogen Peroxide. II. Kinetic Waves for the Peroxy Compounds of Molybdenum(VI), Tungsten(VI) and Vanadium(V)[1]

BY I. M. KOLTHOFF AND E. P. PARRY

Kinetic polarographic waves are observed in the systems molybdate or tungstate or vanadate with hydrogen peroxide. These kinetic waves are characterized by a pronounced maximum at about +0.15 to 0.3 volt *vs.* S.C.E. The maximum is not due to stirring or adsorption effects. The kinetic waves are observed at *p*H smaller than 6 where the active species are polymerized. The rate determining step is the reaction between some polymerized form with hydrogen peroxide to give the peroxy compound which is reduced instantaneously at the electrode. The kinetic currents have been studied as a function of concentration and kind of mineral acid, of *p*H and kind of buffer, of concentrations of hydrogen peroxide and of molybdate (W(VI) and V(V), respectively), of temperature and of height of mercury in the reservoir. In dilute mineral acids Mo, W and V give measurable kinetic currents even at concentrations as small as 10^{-6} *M*. In a phosphate buffer of *p*H about 5 molybdate can be detected (kinetic current) at a concentration of 10^{-7} *M* and vanadate of 10^{-8} *M*.

In a previous paper[2] the kinetic current observed in the ferric iron–hydrogen peroxide system was discussed. The ferrous iron formed at the electrode reacts with hydrogen peroxide to regenerate ferric iron which is again reduced at the electrode.

It has been found that molybdate in acid medium reacts with hydrogen peroxide with the formation of a peroxy compound which is reduced at positive potentials *versus* the saturated calomel electrode (S.C.E.). The rate of reaction of molybdate with hydrogen peroxide under proper conditions is so great that this ion, even at high dilutions, gives a measurable kinetic current produced by the reduction of the peroxy compound which is continuously reformed at the surface of the electrode

$$MoO_4^{=} + H_2O_2 \longrightarrow MoO_5^{=} + H_2O \qquad (1)$$

$$MoO_5^{=} + 2H^+ + 2e \longrightarrow MoO_4^{=} + H_2O \qquad (2)$$

For the sake of convenience, $MoO_4^{=}$ and $MoO_5^{=}$ are written in equations (1) and (2) although the molybdenum is undoubtedly present in different degrees of polymerization. Vanadate and tungstate with hydrogen peroxide give similar kinetic waves as molybdate.

This paper presents a study of the characteristics of the kinetic waves observed with these systems. The kinetic waves observed with mixtures of molybdate or vanadate and hydrogen peroxide in a phosphate buffer of *p*H about 5 are especially interesting. As little as 10^{-8} *M* molybdate or vanadate gives a measurable kinetic current, alluding to the use of this method for the trace detection of these ions. Analytical applications of kinetic currents will be described in subsequent papers.

Experimental

Apparatus and Materials.—The apparatus, including the capillary and most of the chemicals, were described previously.[2] As a source of molybdate, both sodium molybdate

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(1) From a Ph.D. Thesis submitted by E. P. Parry to the Graduate School of the University of Minnesota, 1950.

(2) I. M. Kolthoff and E. P. Parry, THIS JOURNAL, **73**, 3718 (1951).

(Baker reagent) and ammonium paramolybdate (B and A reagent) were used without further purification. With the same supporting electrolyte and the same concentration of molybdenum, identical results were obtained. For the experiments with tungstate and vanadate, reagent quality sodium tungstate (origin unknown), and C.P. ammonium metavanadate from the City Chemical Corporation, New York, were used without further purification. The phosphate buffer was prepared from B and A reagent potassium dihydrogen phosphate. A 1 *M* solution was prepared and sodium hydroxide was carefully added until the *p*H, measured after the desired dilution, was about 5. Sodium perchlorate was prepared by carefully neutralizing reagent perchloric acid (1 *M*) with sodium hydroxide. Measurements of *p*H were made on a Leeds and Northrup No. 7661-A1 *p*H meter.

Measurements were made at 25°. When measurements were made at potentials more positive than +0.05 volt *vs.* S.C.E., it was not necessary to remove oxygen from the solution. Its presence had no effect on the kinetic current.

Procedure.—Mixtures of hydrogen peroxide and molybdate (or tungstate or vanadate) oxidize mercury. In the absence of mercury such solutions are stable for at least 36 hours, but when mercury is present a noticeable decomposition occurs in from 5 to 15 minutes, depending on the acid and reagent concentrations and the kind of stirring. For this reason, the polarogram (or current readings) must be taken within five minutes after insertion of the electrode. The decomposition could be eliminated for longer periods of time by collecting the dropping mercury under carbon tetrachloride or chloroform.

Results

I. Molybdate. The Reduction of Peroxymolybdate.—Figure 1 (curve 2) represents a polarogram of an equimolar mixture of molybdate and hydrogen peroxide in 0.25 *M* sulfuric acid. The first wave is attributed to the reduction of peroxy molybdate to molybdate. The maximum which occurs at about +0.20 volt becomes more accentuated at higher peroxy molybdate concentrations as demonstrated in Fig. 2. The height of this maximum is not proportional to concentration. For example, at 25°, solutions containing equi-molar amounts of molybdate and hydrogen peroxide in 0.25 *M* sulfuric acid gave $i_{\max}/c$ values of 4.48 μA./millimole for an 8 × 10^{-4} *M* mixture, 3.88 for a 1.6 × 10^{-3} *M* mixture and 3.58 for a 2.4 × 10^{-3} *M* mixture.

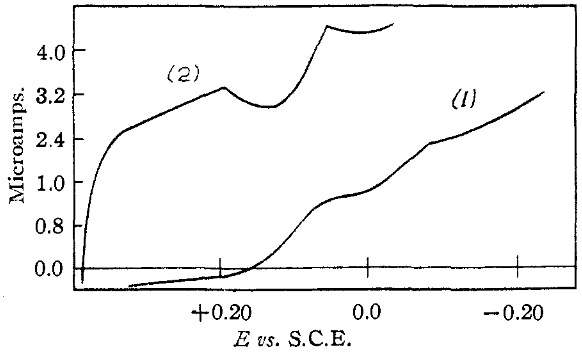

Fig. 1.—Polarogram showing the reduction of peroxy molybdate in 0.25 *M* sulfuric acid: (1) 8 × 10^{-4} *M* molybdate; (2) 8 × 10^{-4} *M* molybdate and 8 × 10^{-4} *M* hydrogen peroxide.

A solution containing 0.008 *M* molybdate and 0.004 *M* hydrogen peroxide in 0.25 *M* sulfuric acid gave a current of about 6.4 μa. at the maximum. The diffusion current of 0.004 *M* hydrogen peroxide in 0.25 *M* sulfuric acid is about 34 μa. Assuming that the formation of monoperoxy molybdate is complete,[3,4] it appears that the peroxy molybdate reduction is incomplete, and a true diffusion current region is not obtained at the potential corresponding to the maximum value of the current.

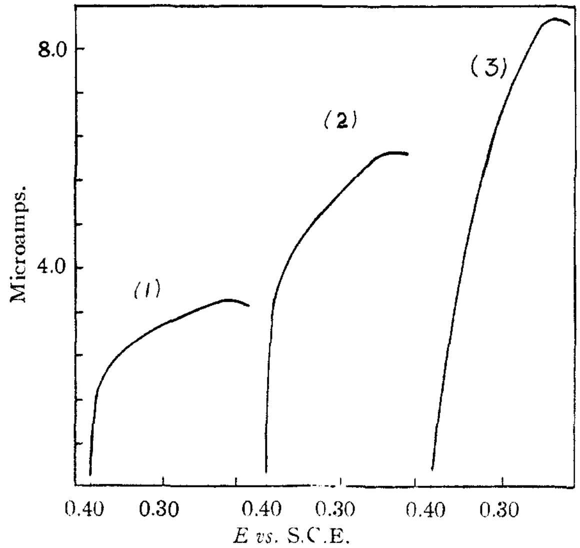

Fig. 2.—Polarograms of equimolar amounts of molybdate and hydrogen peroxide in 0.25 *M* H_2SO_4: (1) 8 × 10^{-4} *M*, (2) 1.6 × 10^{-3} *M*, (3) 2.4 × 10^{-3} *M*.

The Kinetic Wave in Acids.—The polarogram of a mixture 1.09 × 10^{-6} *M* in molybdate and 0.054 *M* in hydrogen peroxide in 0.25 *M* sulfuric acid is shown in curve 1 of Fig. 3. Curve 3 is the true kinetic current, obtained by subtracting from curve 1, the current due to the hydrogen peroxide reduction (curve 2). All values of the kinetic current reported in this paper refer to the maximum in the current-voltage curve. The decrease in kinetic current with increasing negative potential has been found to be typical of the kinetic currents of the peroxy compounds.

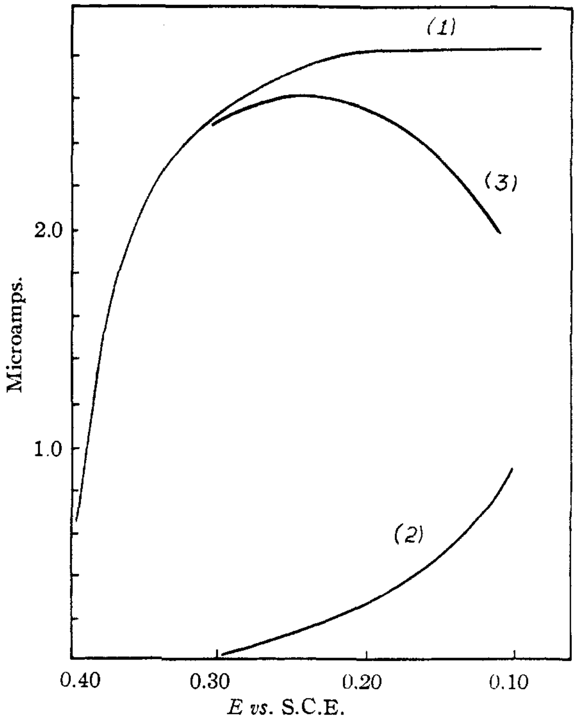

Fig. 3.—The kinetic wave for peroxymolybdate in 0.25 *M* sulfuric acid: (1) 1.09 × 10^{-6} *M* molybdate and 0.054 *M* hydrogen peroxide, (2) 0.054 *M* hydrogen peroxide only, (3) the kinetic wave, curve (1) less curve (2).

Effect of Kind of Acid and Concentrations of Acid, Molybdate and Hydrogen Peroxide.—Table I gives some typical

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(3) P. C. L. Thorne and E. R. Roberts, Ephraim's "Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 524.

(4) A. Rium and M. Martin Rodriquez, *Anales fis. y quim.*, **40**, 1034 (1944); *cf. C. A.*, **44**, 10561 (1950).

values of the kinetic current obtained in various mineral acids.

Table I

Kinetic Current Obtained in Various Acids of *p*H 0.7, 10^{-6} *M* in Molybdate; 0.054 *M* in H_2O_2, Temperature 25°

Acid	Potential at maximum	i_k, μa.
Nitric	0.35	2.7
Perchloric	.38	5.0
Sulfuric	.28	3.8
Phosphoric	.33	0.6

Sulfuric acid was chosen for a systematic study because the best defined waves were obtained in this acid.

From Fig. 4, it is evident that the plot of kinetic current *vs.* concentration of molybdate is linear for sulfuric acid concentrations between 0.25 and 1.0. The potential at which the maximum in the kinetic wave occurs was found to vary between 0.30 and 0.15 volt, being more positive at larger acid concentrations.

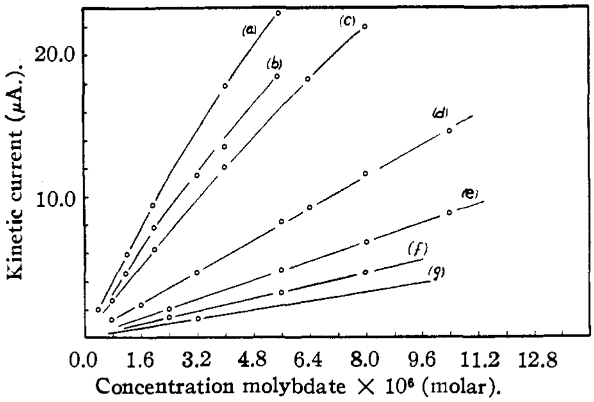

Fig. 4.—The peroxymolybdate kinetic current in various concentrations of sulfuric acid as a function of molybdate concentration, 0.037 *M* hydrogen peroxide: (a) 0.05 *M*, (b) 0.08 *M* plus 0.12 *M* sodium sulfate, (c) 0.1 *M*, (d) 0.25 *M*, (e) 0.50 *M*, (f) 0.80 *M*, (g) 0.975 *M*.

The variation of kinetic current with hydrogen peroxide concentration is given in Fig. 5. At all acid concentrations, a deviation from linearity occurs at hydrogen peroxide concentrations greater than 0.0372 *M*.

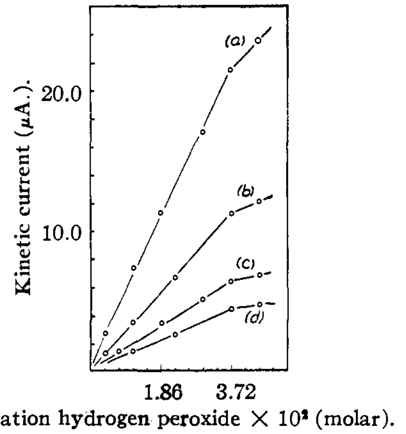

Fig. 5.—The peroxymolybdate kinetic current in various concentrations of sulfuric acid as a function of hydrogen peroxide concentration, 8.0 × 10^{-6} *M* molybdate: (a) 0.1 *M*, (b) 0.25 *M*, (c) 0.5 *M*, (d) 0.8 *M*.

Effect of *p*H.—It is impossible to determine unambiguously the effect of *p*H over a wide range because the kinetic current is very greatly affected by anions of the buffer. For example, curve 1 of Fig. 6 is the plot of the kinetic current *versus* *p*H over the *p*H range from 2 to 6 using biphthalate–perchloric acid and biphthalate-sodium hydroxide mixtures. (Small concentrations of perchlorate do not affect the kinetic current in biphthalate mixtures as demonstrated by Fig. 8.) Curve 2 was obtained using acetic acid–sodium acetate mixtures, while various concentrations of sulfuric acid gave curve 3. For curve 3 sodium sulfate was used to make the electrolyte concentration 0.2 *M* in the region of *p*H near 2.

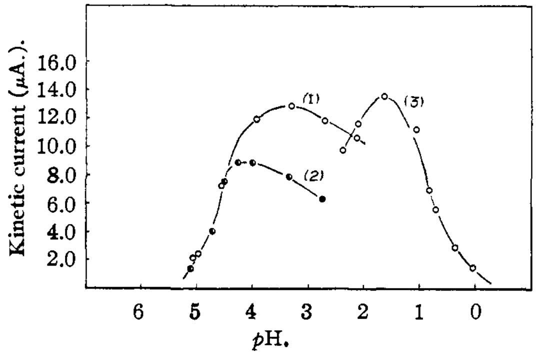

Fig. 6.—The peroxymolybdate kinetic current as a function of *p*H in various buffer mixtures: (1) 0.05 *M* biphthalate buffers, 4.0 × 10^{-6} *M* molybdate, 0.04 *M* hydrogen peroxide, (2) 0.2 *M* acetate buffers 3.2 × 10^{-6} *M* molybdate, 0.037 *M* hydrogen peroxide, (3) sulfuric acid (where necessary sodium sulfate used to make electrolyte concentration 0.2 *M*) 3.2 × 10^{-6} *M* molybdate, 0.037 *M* hydrogen peroxide.

Effect of Anions.—The effect of different concentrations of various anions on the kinetic current in sulfuric acid (Fig. 7) and in biphthalate and acetate buffers (Fig. 8) was determined. The potential at which the maximum kinetic current occurs depends on the kind and concentration of foreign anions and the supporting electrolyte, and was found to vary between 0.10 and 0.35 volt. Both sodium and potassium salts were used in some instances and there was no difference in the kinetic current obtained. The effect of other cations was not studied.

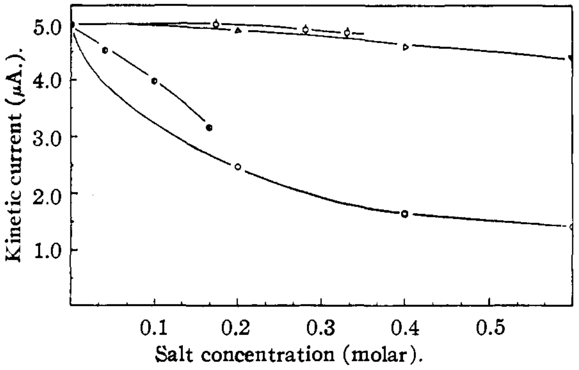

Fig. 7.—Effect of anions on the peroxymolybdate kinetic current, 0.25 *M* sulfuric acid, 2 × 10^{-6} *M* molybdate, 0.054 *M* hydrogen peroxide: O, nitrate; Δ, perchlorate; ◐, phosphate; ϙ, sulfate.

Effect of Maximum Suppressors.—From Table II it appears that gelatin, tylose and gum arabic decrease the kinetic current slightly (5 to 10%). Strongly adsorbed anionic detergents, like sodium decyl and lauryl sulfonates, do not affect the value of the maximum current, but they make the maximum somewhat more accentuated.

Effect of Temperature.—From the data of Table III the average temperature coefficient can be calculated. Its value is 5.6% per degree in the temperature interval from 20 to 25°.

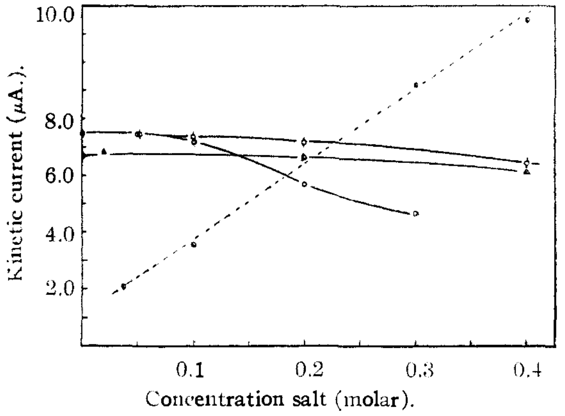

Fig. 8.—The peroxymolybdate kinetic current in buffer mixtures 4 × 10^{-6} *M* molybdate, 4 × 10^{-2} *M* hydrogen peroxide: O, kinetic current *vs.* biphthalate buffer concentration *p*H ~4.4; ϕ, effect perchlorate ion in 0.05 *M* biphthalate *p*H ~4.5; ◐, kinetic current *vs.* acetate buffer concentration *p*H ~4.5; Δ, effect perchlorate ion in 0.2 *M* acetate buffer; *p*H ~4.2.

Table II

Effect of Maximum Suppressors on the Kinetic Current, 2 × 10^{-6} *M* Molybdate, 4.3 × 10^{-2} *M* H_2O_2 in 0.25 *M* H_2SO_4, 0.005%

Maximum Suppressor Added

Suppressor	i_k	Suppressor	i_k	Suppressor	i_k
None	3.44	Gum arabic	3.24	Methyl red	3.40
Gelatin	3.33	Peptone	3.46	Thymol blue	3.46
Camphor	3.46	Thymol	3.48	0.01% Na decyl sulfonate	3.42
Tylose	3.20				

Table III

Dependence of Kinetic Current on Temperature, 0.25 *M* Sulfuric Acid

Concentration molybdate × 10^6	Concentration hydrogen peroxide × 10^2	i_k at 20°	i_k at 25°	i_k 25°/i_k 20°
2.0	5.35	3.35	4.40	1.32
3.0	5.35	5.17	6.82	1.32
5.0	5.35	8.12	10.44	1.29
5.0	2.14	3.45	4.62	1.34
5.0	3.21	5.24	6.92	1.32

Effect of Mercury Height.—A typical kinetic current should be independent of the height of mercury in the reservoir.[5] In 5 experiments with a solution 10^{-6} *M* in molybdate, 6.4 × 10^{-2} *M* in hydrogen peroxide and 0.25 *M* in sulfuric acid, the height of the mercury was decreased from 104 to 55 cm. The kinetic current measured in all experiments was 2.83 ± 0.02 microamperes.

The Kinetic Wave in Phosphate Buffer.—Curve (a) of Fig. 9 illustrates the wave in a phosphate buffer of *p*H near 5. The possibility that the wave is not kinetically controlled, but caused by stirring phenomena was investigated by suspending talcum powder in the solution and closely observing the drop with a magnifying lens during electrolysis. No stirring could be observed at the drop surface.

Curve (b) of Fig. 9 is for the reduction of 10^{-3} *M* molybdate in the phosphate buffer. The reduction of molybdate begins at a potential which is 0.3 volt more negative than that at the maximum of the kinetic wave; therefore, the mechanism for the kinetic current (curve (a)) is assumed to involve the reduction and reformation of a complex peroxyphosphomolybdate.

The potential at which the maximum current is obtained was found to vary slightly with the *p*H and buffer concentration, but was independent of molybdate and hydrogen peroxide concentrations.

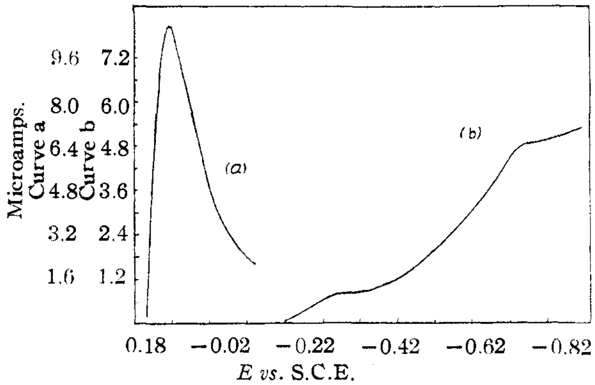

Fig. 9.—The peroxymolybdate kinetic wave in 0.1 *M* phosphate buffer: (a) 1.6 × 10^{-6} *M* molybdate, 0.012 *M* hydrogen peroxide; *p*H 4.90; (b) 1 × 10^{-3} *M* molybdate only, *p*H 5.10.

Effect of Molybdate and Hydrogen Peroxide Concentrations and of Foreign Anions.—The kinetic current is a linear function of molybdate concentration in the range from 2 × 10^{-7} to 1.6 × 10^{-6} *M*, but is not linear with hydrogen peroxide concentration (Fig. 10).

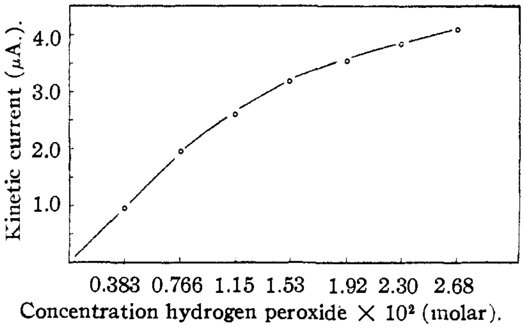

Fig. 10.—The peroxymolybdate kinetic current in 0.1 *M* phosphate buffer as a function of hydrogen peroxide concentration; *p*H 5.40, 8.0 × 10^{-7} *M* molybdate.

The potassium dihydrogen phosphate used in making the buffer was found to contain a trace of vanadium which was not removed by recrystallization (*v.i.*). The presence of this ion gave a small "blank" wave (*i.e.*, a wave was found for solutions containing buffer and hydrogen peroxide only). A correction has been applied in the above experiments to account for this "blank."

Foreign anions have qualitatively the same decreasing effect on the kinetic current as when dilute sulfuric acid is the medium.

II. **Tungstate.**—Tungstate reacts with mineral acids to form insoluble tungstic acid (except concentrated halogen acids). The reaction is rather slow in dilute (0.25 *M*) acids, a turbidity resulting after about 45 minutes in a 10^{-3} *M* tungstate solution. When hydrogen peroxide and tungstate are present together, no turbidity results even after an hour indicating that the peroxy tungstate which is formed is soluble at this concentration in mineral acids.

In the determination of the kinetic current, experiments were made with nitric, perchloric and sulfuric acids as supporting electrolytes. The largest kinetic current is obtained in sulfuric acid. For example, for a solution containing 3.6 × 10^{-5} *M* tungstate and 0.02 *M* hydrogen peroxide, currents of 4.6, 3.7 and 2.6 μa. were obtained in 0.25 *M* H_2SO_4, 0.2 *M* HNO_3 and 0.2 *M* $HClO_4$, respectively.

The reduction of peroxy tungstate (Fig. 11 curve 1) and the kinetic current obtained with the tungstate–hydrogen peroxide system (Fig. 11 curve 3) are very similar to those observed with the molybdate system. The kinetic current is not a linear function of tungstate concentration in 0.2 *M* nitric acid, 0.2 *M* perchloric acid, nor in sulfuric acid at con-

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[5] R. Brdicka and K. Wiesner, *Collection Czech. Chem. Commun.*, **12**, 39 (1947).

centrations varying from 0.8 to 0.1 *M*. Likewise the kinetic current is not a linear function of hydrogen peroxide concentration in 0.25 *M* sulfuric acid.

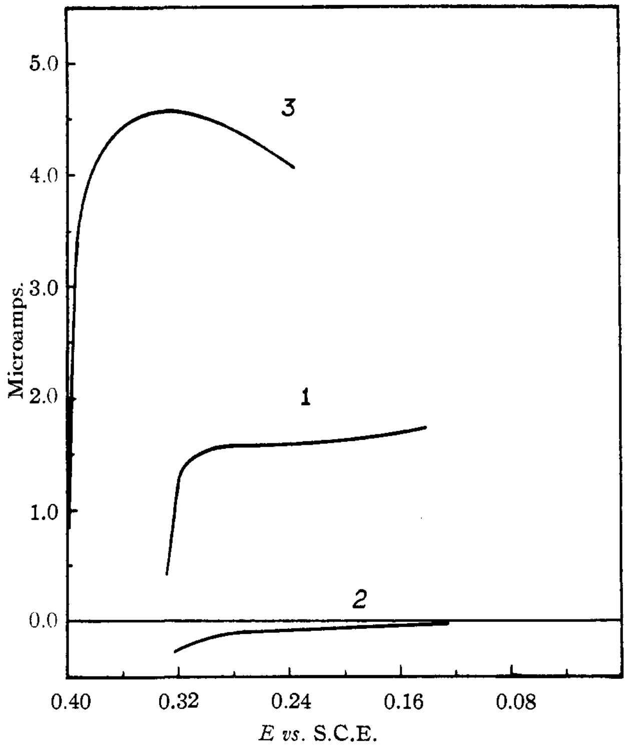

Fig. 11.—Polarogram showing reduction of peroxy tungstate and the kinetic wave of the tungstate–hydrogen peroxide system in 0.25 *M* sulfuric acid: (1) 3.2×10^{-8} *M* tungstate and 3.2×10^{-3} *M* hydrogen peroxide; (2) 3.2×10^{-3} *M* tungstate only; (3) 3.6×10^{-5} *M* tungstate, 0.0203 *M* hydrogen peroxide.

Tungstate in a phosphate buffer of *p*H near 5 gives a very small wave compared to molybdate and vanadate. For example, a 0.1 *M* buffer of *p*H 4.9 being 0.007 *M* in hydrogen peroxide gave a kinetic current of 1.2 μa. for 8×10^{-6} *M* tungstate, 6.5 μa. for 1.6×10^{-6} *M* molybdate and 18.6 μa. for 8×10^{-7} *M* vanadate. A further study of the tungstate wave in phosphate buffer was not undertaken.

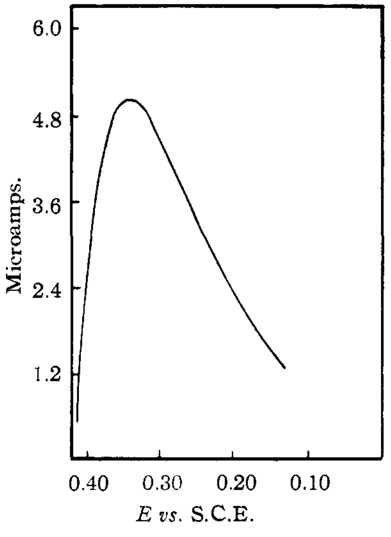

Fig. 12.—The peroxyvanadate kinetic current in 0.1 *M* sulfuric acid; 4×10^{-5} *M* vanadate, 0.041 *M* hydrogen peroxide.

III. Vanadate. The Kinetic Wave in Acids. Effect of Vanadate, Hydrogen Peroxide and Sulfuric Acid Concentrations.—The kinetic wave for this ion is shown in Fig. 12. Since the polarographic wave for acid solutions of vanadium (+5) begins at the dissolution potential of mercury,[6] it is not certain whether the kinetic current involves (1) a reduction of peroxy vanadate to vanadate at the electrode with subsequent reformation by reaction with hydrogen peroxide (as in molybdate and tungstate), (2) reduction of V(+5) to V(+4) at the electrode with subsequent reoxidation by hydrogen peroxide, or (3) a combination of both processes. The latter mechanism would seem to be most probable.

It is observed that the current falls off with increasing negative potential after reaching a maximum value (at about +0.33 volt). The potential at which this maximum occurs was found to be independent of acid, vanadate and hydrogen peroxide concentrations.

In the investigated concentration range between 0.025 and 0.4 *M* the kinetic current is a linear function of vanadate concentration in sulfuric acid (see Fig. 13). Likewise a linearity was observed with hydrogen peroxide concentrations up to 4×10^{-2} *M* peroxide in both 0.1 and 0.25 *M* sulfuric acid. Qualitatively similar results were obtained with perchloric in place of sulfuric acid.

The Kinetic Wave in Phosphate Buffer. Effect of Vanadate Concentration.—The kinetic wave obtained with vanadate is similar to that of molybdate (see Fig. 9). The height of the wave was found to be a linear function of vanadate concentration in the range from 2×10^{-8} to 1.8×10^{-7} *M*. This great sensitivity for vanadate suggests the use of this wave for the detection and determination of traces of the ion.

Polarograms of solutions of hydrogen peroxide in the phosphate buffer containing no added vanadium showed a kinetic wave of 1.3 microamperes. Spectroscopically, a trace of vanadium was found in the potassium dihydrogen phosphate. The height of the wave corresponded to the presence of 0.6 p.p.m. V in the salt. Successive recrystallization failed to remove the impurity.

Effect of *p*H of Buffer, Maximum Suppressors and Foreign Anions.—From Fig. 14 it is evident that the kinetic current has a maximum value in a rather narrow region of *p*H near 5. In making analytical use of such a kinetic current it is apparent that careful control of *p*H is necessary.

Maximum suppressors and foreign anions have qualitatively the same effect as on the kinetic current of molybdate in sulfuric acid.

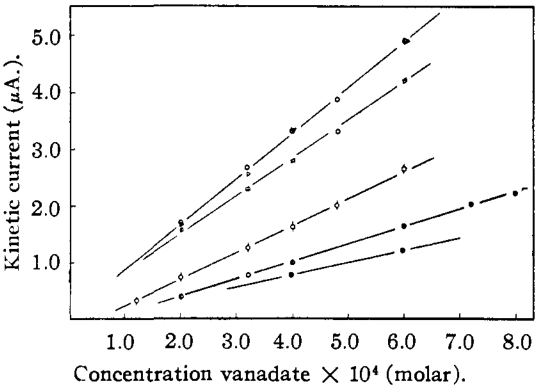

Fig. 13.—The peroxyvanadate kinetic current as a function of vanadate concentration: 0.04 *M* hydrogen peroxide: O, 0.1 *M* sulfuric acid; Δ, 0.2 *M* Na_2SO_4 and 0.05 *M* H_2SO_4; □, 0.025 *M* H_2SO_4 and 0.23 *M* Na_2SO_4; Ó, 0.25 *M* H_2SO_4; ◐, 0.4 *M* H_2SO_4; ●, 0.56 *M* H_2SO_4.

Discussion

Assuming that the mechanism for the molybdate kinetic wave is described by equations (1) and (2), the kinetic current according to Brdicka[5] is given by

[6] J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).

$$i_k = 2F\mu qk10^3[H_2O_2][\text{molybdate}]$$

where F is the faraday, μ the thickness of the layer in which reaction (1) is presumed to occur, q the average area of the surface of the mercury drop, k the velocity constant for reaction (1), $[H_2O_2]$ and [molybdate] concentrations in moles/liter, and i_k the kinetic current in microamperes.

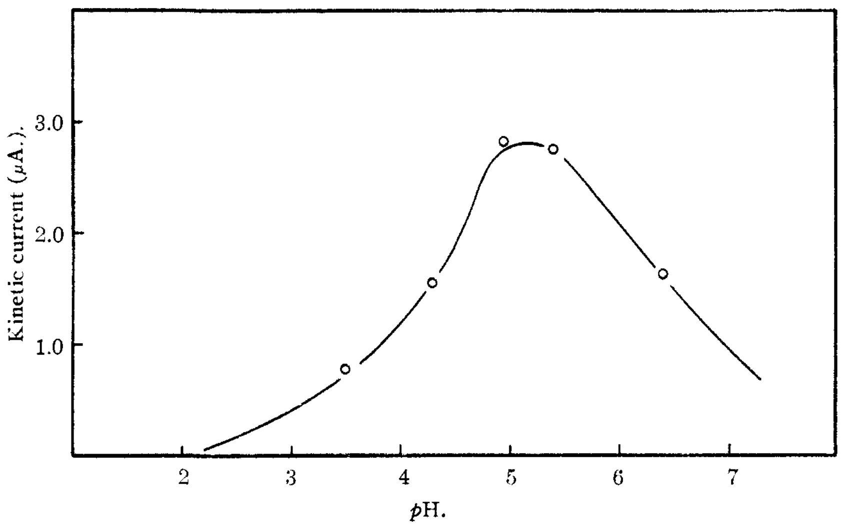

Fig. 14.—The peroxyvanadate kinetic current in 0.05 M phosphate buffer as a function of pH; 8 × 10^{-8} M vanadate, 0.0075 M hydrogen peroxide.

This equation indicates that the kinetic current should be a linear function of molybdate concentration. This relation was found to hold at sulfuric acid concentrations between 0.25 to 1.0 M (see Fig. 4), and in a phosphate buffer of pH 5 (Fig. 10). The deviations from linearity observed at acid concentrations between 0.25 and 0.05 M are attributed to changes in the degree of association of the polymolybdates in this region.

The chemistry of Mo(VI) is very complex, and the literature contains many contradictory statements regarding the type of poly ions which exist at various pH values. For example, Jander[7] and Rosenheim[8] state that the ion $MoO_4^=$ exists uniquely at pH 7 and above, while with increasing acidity, the ions $Mo_3O_{11}^{-4}$, $Mo_6O_{21}^{-6}$, $Mo_{12}O_{41}^{-10}$, and $Mo_{24}O_{78}^{-12}$ are formed. At pH beyond 1, the molybdenum exists mainly as a cation. Travers and Malaprade[9] and Doucet[10] believe that the $MoO_4^=$ ion exists uniquely at a pH above 7, but $Mo_4O_{13}^{-2}$ and $Mo_7O_{24}^{-6}$ are formed at decreasing pH. Bye[11] agrees with the latter authors, but also claims that the ion $Mo_6O_{20}^{-4}$ is formed at relatively high acidities. Similar statements are made concerning the types of peroxy molybdate in solution.[12]

Many of the contradictory statements in the literature undoubtedly may be attributed to the great effect that molybdate concentration, ratio of acid to molybdate concentration, indifferent electrolytes, temperature, and other such factors have on the degree of polymerization. Nothing is known about the kinds of molybdate and peroxy molybdate species present in the very dilute solutions used in the present work, and a quantitative interpretation of the kinetic current must await a better understanding of the chemistry of molybdenum(VI) and the peroxy compounds formed by it.

From the fact that no kinetic current is obtained at pH values higher than 6 (see Fig. 6), it can be concluded that either the monomeric $MoO_4^=$ species does not produce a kinetic current by reactions (1) and (2) (*i.e.*, a more polymerized species is necessary), or reaction (1) is acid catalyzed. However, this catalyzed reaction alone cannot account for the observed phenomena and it must be assumed that polymeric forms of molybdate (and of V and W) play a part.

In those instances in which no strict proportionality of the kinetic current with the molybdate concentration was observed (0.05 to 0.25 M sulfuric acid) it must be assumed that the ratio of molybdates of different degree of polymerization varies with the analytical concentration of molybdate and that the various species react with a different rate with hydrogen peroxide.

From the temperature coefficient of the kinetic current in 0.25 M sulfuric acid, the energy of activation of the reaction between molybdate and hydrogen peroxide is calculated to be about 10,000 cal./mole. Values obtained by this method are only approximate, as has been shown previously.[2]

The kinetic waves observed with molybdate, tungstate and vanadate are all characterized by a pronounced maximum which is not due to stirring. Capillary active substances, and especially anionic detergents (lauryl sulfonate), which may be expected to be strongly adsorbed on the mercury–solution interface, hardly affect the kinetic current. Therefore, the maximum and the pronounced decrease of the kinetic current with increasing negative potentials cannot be attributed to adsorption or desorption effects. It seems that the rate of the reaction which determines the kinetic current is greatly affected by the potential of the electrode.

Our knowledge of the various forms of tungstates[13]

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and vanadates[14] and the respective peroxy compounds[15] is also inadequate, and no quantitative interpretation of the effect of the various factors presented in this paper can be given.

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The Determination of Consecutive Formation Constants of Complex Ions from Polarographic Data

BY DONALD D. DEFORD[1] AND DAVID N. HUME[2]

A method for the mathematical analysis of the change in half-wave potential of a metal ion with changes in the concentration of the complexing agent is derived. The identification of the successive complex ions formed and the determination of their formation constants are thus made possible.

The polarograph has been extensively used in the study of complex ions which are reversibly electroreduced at the dropping mercury electrode. If a metal ion forms only one complex over a considerable range of ligand concentration, it is possible to determine from a plot of half-wave potential against the logarithm of ligand concentration, the number of ligands bound in the complex, and by the shift in half-wave potential from that of the simple ion, the dissociation constant.[3] Hitherto, data derived from systems involving mixtures of consecutively formed complex ions have not been interpretable. During the last ten years a great deal of interest has been developed in the study of consecutively formed complex ions largely through the pioneering work of Bjerrum.[4] Leden[5] has described an ingenious and useful method of taking and interpreting potentiometric data for the evaluation of consecutive formation constants. In this paper is described a method of mathematical analysis of the shift of half-wave potential with ligand concentration which makes possible the identification of the successive complex ions formed and the evaluation of their formation (or dissociation) constants. The sign conventions are those of reference 3.

For complex ions of a metal which is soluble in mercury, the reduction to the metallic state (amalgam) at the dropping mercury electrode may be represented by

$$\mathrm{MX_j}^{+(n-jb)} + n\mathrm{e} \rightleftarrows \mathrm{M(amalgam)} + j\mathrm{X}^{-b} \quad (1)$$

where X^{-b} is the complex-forming substance. For convenience, this reaction may be regarded as the sum of the partial reactions

$$\mathrm{MX_j}^{+(n-jb))} \rightleftarrows \mathrm{M}^{+n} + j\mathrm{X}^{-b} \quad (2)$$

and

$$\mathrm{M}^{+n} + n\mathrm{e} \rightleftarrows \mathrm{M(amalgam)} \quad (3)$$

where M^{+n} symbolizes the simple (hydrated) metal ions. If the electrode reactions are reversible, the potential of the dropping electrode is given by

$$E_{\mathrm{d.e.}} = E_{\mathrm{a}}^0 - \frac{RT}{nF}\ln\frac{C_{\mathrm{a}}^0 f_{\mathrm{a}}}{C_{\mathrm{M}}^0 f_{\mathrm{M}}} \quad (4)$$

where C_{a}^0 is the concentration of the amalgam at the electrode surface, C_{M}^0 is the concentration of simple metal ions at the electrode surface, and the f's are the corresponding activity coefficients. Since the amalgams formed at the electrode surface are very dilute, f_{a} may be considered to be unity and will be neglected hereafter.

If the formation of the complex ions is rapid and reversible, then for each individual complex

$$C_{\mathrm{MX_j}} f_{\mathrm{MX_j}} = K_{\mathrm{j}} C_{\mathrm{M}} f_{\mathrm{M}} (C_{\mathrm{X}})^j (f_{\mathrm{X}})^j \quad (5)$$

where K_{j} is the formation constant of the complex $\mathrm{MX_j}^{+(n-j\mathrm{b})}$, $C_{\mathrm{MX_j}}$ is the concentration of the complex in the body of the solution, C_{M} is the concentration of the simple metal ion in the body of the solution, C_{X} is the concentration of the complex-forming substance, and the f's are the corresponding activity coefficients. Also

$$C_{\mathrm{MX_j}}^0 f_{\mathrm{MX_j}} = K_{\mathrm{j}} C_{\mathrm{M}}^0 f_{\mathrm{M}} (C_{\mathrm{X}})^j (f_{\mathrm{X}})^j \quad (6)$$

where the zero superscripts refer to concentrations at the electrode surface. It is assumed that the complex-forming substance is present in relatively large excess so that the concentration of this substance at the electrode surface is virtually equal to the concentration in the body of the solution.

Addition of the equations for the individual complexes as represented by equation (6) and rearrangement of the resulting equation shows that

$$C_{\mathrm{M}}^0 f_{\mathrm{M}} = \frac{\sum\limits_{\mathrm{j}} C_{\mathrm{MX_j}}^0}{\sum\limits_{\mathrm{j}} \frac{K_{\mathrm{j}}(C_{\mathrm{X}})^{\mathrm{j}}(f_{\mathrm{X}})^j}{f_{\mathrm{MX_j}}}} \quad (7)$$

Combination of equations (4) and (7) gives

$$E_{\mathrm{d.e.}} = E_{\mathrm{a}}^0 - \frac{RT}{nF}\ln\frac{C_{\mathrm{a}}^0 \sum\limits_{\mathrm{j}} \frac{K_{\mathrm{j}}(C_{\mathrm{X}})^j(f_{\mathrm{X}})^j}{f_{\mathrm{MX_j}}}}{\sum\limits_{\mathrm{j}} C_{\mathrm{MX_j}}^0} \quad (8)$$

When an excess of supporting electrolyte is pres-

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