sulfate. The values for the latter salt are compared with those of Åkerlöf in Table II, the same reference value being used at 0.1 *M*. The average difference between the two sets is 0.9% with a maximum difference of 1.6% at 1 *M* but there is no trend of the results away from one another.

A value of $\gamma = 0.441$ for 0.1 *M* potassium sulfate was taken from the computations of Redlich and Rosenfeld[5] who corrected freezing point data to 25°. The comparison with freezing point data at two other concentrations is good. The agreement with the e. m. f. data of Åkerlöf is also good except at one concentration, the average difference between the two sets of activity coefficients being 0.7%.

The activity coefficient curves of these four salts lie below that of calcium nitrate[6] and correspond to values of the closest distance of approach of the ions of approximately 3–4 Å. Thus considerable ionic association should occur and conductance data[7] show that the extent of association increases with the atomic weight of the cation, this being the order in which the activity coefficients decrease. The curve for sodium thiosulfate lies above that for sodium sulfate but below that for lithium sulfate. This suggests that, although ionic association occurs with sodium thiosulfate, it is less in extent than in the case of sodium sulfate and the distance of closest approach of the ions is somewhat greater, *i. e.*, the thiosulfate ion is slightly larger in this respect than the sulfate ion.

We wish to thank Professor H. S. Harned for his interest in this work and the Chemical Society (London) for a grant from the Research Fund.

Summary

Isopiestic vapor pressure measurements have been made to determine the osmotic and activity coefficients of lithium, sodium and potassium sulfate and sodium thiosulfate. The activity coefficients obtained for the sulfates agree within approximately 0.7% with those derived from e. m. f. measurements.

NEW HAVEN, CONN.
AUCKLAND, NEW ZEALAND
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[5] Landolt-Börnstein, "Tabellen," Zweiter Ergänzungsband, 1931, p. 1122.

[6] R. A. Robinson, THIS JOURNAL, **62**, 3130 (1940).

[7] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

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

The Reduction of Oxygen at the Dropping Mercury Electrode

BY I. M. KOLTHOFF AND C. S. MILLER[1]

Since the introduction of polarography by Heyrovsky it has been known that dissolved oxygen is reducible at the dropping mercury electrode.[2] In dilute electrolyte solutions the first reduction wave yields pronounced maxima, the suppression of which has been studied by Rasch,[3] Varasova,[4] Rayman[5] and Hamamoto.[6] Vitek[7] applied the polarograph to the determination of oxygen in waste gases. In recent years this method has gained popularity in the determination of oxygen in biologically important materials.[8] Vitek[9] determined the "reduction potentials" of oxygen by the 45° tangent method in various buffer and salt solutions. The first wave of oxygen corresponds to a reduction to hydrogen peroxide:

$$O_2 + 2H^+ + 2e \longrightarrow H_2O_2 \qquad (1)$$

or

$$O_2 + 2H_2O + 2e \longrightarrow H_2O_2 + 2OH^- \qquad (1a)$$

The second wave which is of equal height as the first one corresponds to the reduction of the peroxide to hydroxyl ions

$$H_2O_2 + 2e \longrightarrow 2OH^- \qquad (2)$$

or

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O \qquad (2a)$$

This second wave coincides with that produced by an equinormal solution of peroxide in the same medium. The first wave has a much steeper slope than the second one. In the literature it is often stated that the first wave corresponds to a reversible reaction while the reaction on the second wave is irreversible. In the present

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[1] From the experimental part of a thesis presented by C. S. Miller to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the Ph.D. degree (1940).

[2] J. Heyrovsky, *Trans. Faraday Soc.*, **19**, 785 (1924).

[3] J. Rasch, *Collection Czechoslov. Chem. Commun.*, **1**, 560 (1929).

[4] E. Varasova, *ibid.*, **2**, 8 (1930).

[5] B. Rayman, *ibid.*, **3**, 314 (1931).

[6] E. Hamamoto, *ibid.*, **5**, 427 (1933).

[7] V. Vitek, *Chimie et Industrie*, **29**, 215 (1933).

[8] H. G. Petering and F. Daniels, THIS JOURNAL, **60**, 2796 (1938); K. S. Karsten, *Am. J. Botany*, **25**, 14 (1938).

[9] V. Vitek, *Collection Czechoslov. Chem. Commun.*, **7**, 537 (1935).

paper it is shown that the reduction of oxygen to peroxide also occurs irreversibly. The effect of other constituents in the solution which react with hydroxyl ions formed in the reduction of oxygen at the dropping electrode from neutral unbuffered solutions has not been mentioned in the literature and is demonstrated in this paper. Some other observations in connection with the oxygen waves are also described.

Apparatus

The manual apparatus[10] was used in all the experiments. Current voltage curves were determined in a thermostat at 25.00 ± 0.05°. A new and handy dipping type of (saturated) calomel electrode was used, as shown in Fig. 1. The side tube F making connection between the dropping electrode compartment G and the reference electrode receiver E was filled with a stiff 3% agar gel containing a 10^{-1} *M* electrolyte such as potassium chloride. In cases in which the latter salt interferes with the electrolysis in G another salt is used instead. The liquid in E consisted of a 1 *M* electrolyte solution such as potassium nitrate. The saturated calomel electrode ABCD was placed into this salt solution just before the experiments were carried out. The wide tube D sealed into the calomel half cell was filled with a 3% agar gel saturated with potassium chloride. The magnitude of the surface of the mercury in the saturated half cell was about 8 sq. cm. The electrode, therefore, remained practically completely depolarized during the determination of current-voltage curves. Even when the experiments lasted for one hour or more we never noticed changes of the potential of the reference electrode greater than 0.1 to 0.2 mv. The resistance of the entire cell was very small. Actual measurements of the resistance according to Ilkovic[11] showed it to be of the order of 300 to 400 ohms when the concentration of the solution of the strong electrolyte in G was at least 0.1 *N*.

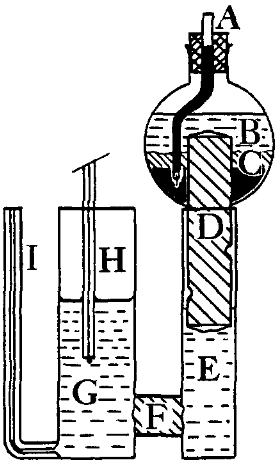

Fig. 1.—Electrolysis cell and calomel electrode.

The drop time of the capillary used was in general 4.00 seconds (in distilled water saturated with air) and the mass of mercury delivered per second (m) was 2.863 mg.

Results

Typical current–voltage curves of oxygen obtained in 0.01 *N* potassium chloride solutions saturated with air are given in Fig. 2. Curve 1 shows the very pronounced maximum of the first oxygen wave; after the maximum is reached the current drops steeply and becomes equal to the first diffusion current at a potential of about −0.5 v. (*vs.* S. C. E.) while at about −0.6 v. the second oxygen wave starts. The latter is drawn out over a long range of potentials, the second diffusion current not being reached until the potential is about −1.4 v. Curve 2 shows that the oxygen maximum is completely suppressed by the addition of 0.01% of thymol to the solution. This maximum suppressor hardly affects the shape of the second (peroxide) wave. In most of our work the oxygen maximum was suppressed by the addition of thymol, or a trace of methyl red.

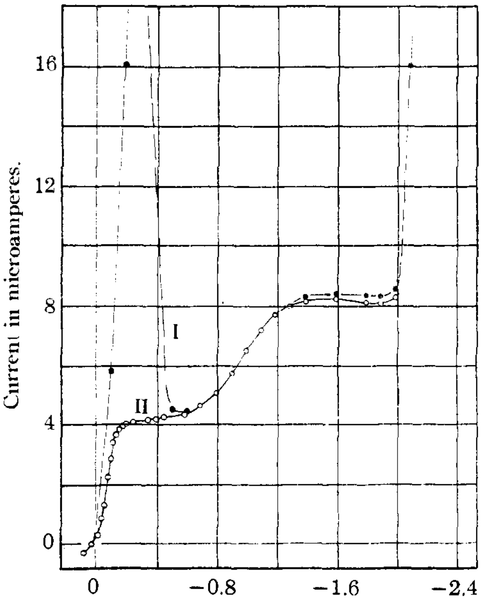

Fig. 2.—Reduction of oxygen at the dropping electrode in air-saturated 0.1 *N* potassium chloride solution: Curve I, without maximum suppressor; Curve II, in the presence of 0.01% thymol.

The following experiment shows conclusively that hydroxyl ions are formed at the surface of the dropping mercury during the reduction of oxygen to peroxide (see equation 1a) and of the latter on the second wave. Curve 2 in Fig. 3 gives the current voltage curve of an air-free solution of 0.001 *M* hydrochloric acid in 0.1 *M* potassium chloride containing a trace of methyl red. The diffusion current after correction for the residual current at a potential of −1.8 v. was 12.85 microamperes. Curve 1 gives the c. v. curve of the same solution after saturation with air. It is seen that the diffusion current of the hydrogen

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(10) I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

(11) D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **4**, 480 (1932).

ions is considerably reduced and is now equal to the original value minus the sum of the two diffusion currents of oxygen. If the experiment is carried out with half the concentration of acid no hydrogen wave is found at all in the air-saturated solution. The number of hydrogen ions reaching the electrode at a potential of −1.8 v. is the same in the presence and in the absence of air. However, the number of hydrogen ions which is removed chemically at the surface of the electrode is equal to the number of hydroxyl ions formed in the oxygen reduction.

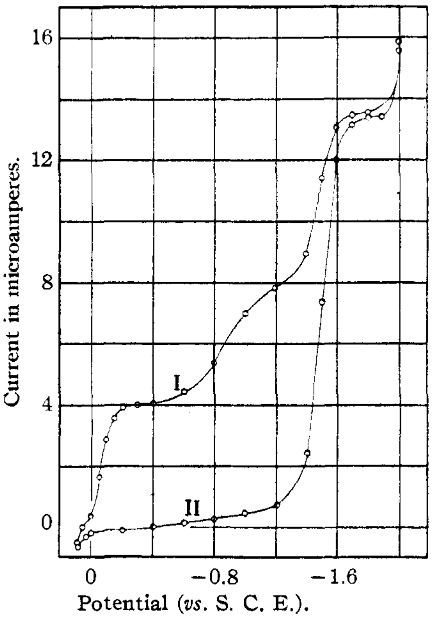

Fig. 3.—Formation of hydroxyl ions in the reduction of oxygen: Curve I, 0.001 *M* HCl in 0.1 *M* KCl, air-saturated with trace of methyl red; Curve II, same as Curve I in air-free solution.

In practical work the interference that may be caused by the formation of hydroxyl ions in the reduction of oxygen may have to be considered. In Fig. 4 curve 1 is the c. v. curve of an air-free solution of 0.001 *M* cadmium chloride in 0.1 *M* potassium chloride (with trace of methyl red). Curve 2 is the c. v. curve of the same solution after saturation with air. In the first place it is seen that the slope of the first oxygen wave is considerably affected by the presence of cadmium (comp. with Fig. 3 and Fig. 2). When the current in the reduction of oxygen has become equal to about 2 microamperes the first oxygen wave becomes much drawn out. Before the first diffusion current (at 4 microamperes) is reached the discharge of cadmium starts. The change of the slope of the oxygen wave is undoubtedly due to the fact that when the current is 2 microamperes the hydroxyl ions formed react with the cadmium ions giving rise to the formation of a film of cadmium hydroxide (or basic cadmium salt) at the surface of the electrode which interferes with the further reduction of oxygen. The summation of the individual waves of oxygen and cadmium is given by the dotted curve in Fig. 4. It is clear that the currents in the mixture at potentials between −0.8 and −1.9 v. are much smaller than those which might be expected if there were no precipitation of cadmium. That the abnormalities are due to precipitation of cadmium hydroxide is evident from curve 3 (Fig. 4) which gives the currents obtained with the air-saturated cadmium solutions in 0.1 *N* hydrochloric acid instead of in 0.1 *N* potassium chloride.

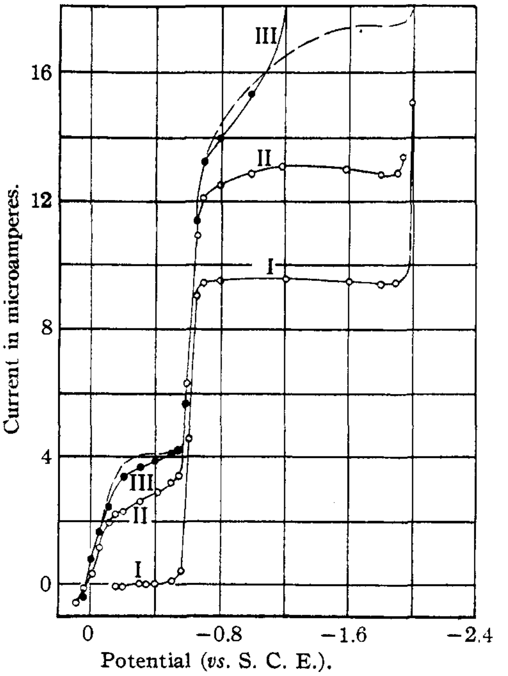

Fig. 4.—Effect of hydroxyl ions formed in the reduction of oxygen upon the cadmium wave: Curve I, 0.001 *M* $CdCl_2$ in 0.1 *M* KCl, air-free; Curve II, same as Curve I, but air-saturated; Curve III, 0.001 *M* $CdCl_2$ in 0.1 *M* HCl, air-saturated; dotted curve, summation of cadmium and oxygen waves.

In Fig. 5 c. v. curves of about 0.0009 *M* lead nitrate in air-free and air-saturated electrolyte solutions are given. Qualitatively the results are comparable to those obtained with cadmium. Recently, it was noticed by Strnak[12] that *traces* of

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(12) F. Strnak, *Collection Czechoslov. Chem. Commun.*, **11**, 391 (1939).

lead in neutral oxygen solutions greatly increase the oxygen maximum (first wave) and that they displace the peroxide wave to more positive potentials. This lead effect was found to disappear when the lead concentration had become equal to 0.001 *N*. Strnak, however, does not make any mention of the "abnormal" waves in neutral mixtures of lead and oxygen, the abnormalities being caused by precipitation of basic lead salts.

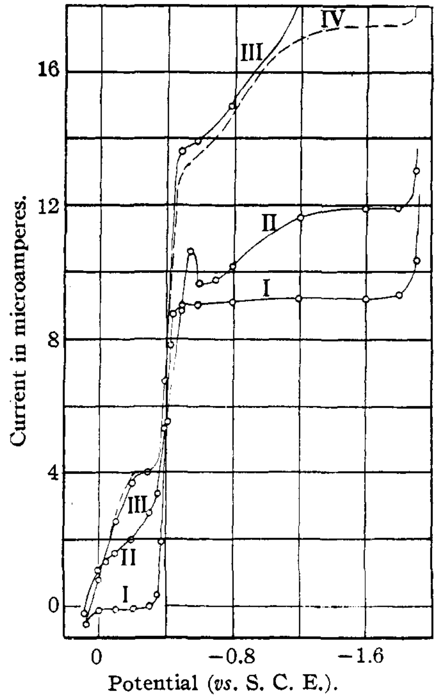

Fig. 5.—Effect of oxygen upon lead wave: Curve I, 0.0009 *M* lead nitrate in 0.1 *N* KNO_3, air-free; Curve II, same, but air-saturated; Curve III, 0.0009 *M* $Pb(NO_3)_2$ in 0.1 *N* HNO_3, air-saturated; Curve IV, summation of oxygen and lead waves.

Diffusion Coefficient of Oxygen.—With the aid of the Ilkovic[13] equation

$$i_d = 0.63nFCm^{2/3}t^{1/6}D^{1/2}$$

in which $n = 2$, *F* the Faraday, *C* the concentration in moles per ml., *m* the weight of mercury flowing from the capillary per second and *t* the drop time, the diffusion coefficient *D* can be calculated. In our experiments at 25.00° we used a 0.1 *M* solution of potassium nitrate which was saturated with air. Under the experimental conditions the concentration of oxygen was 2.62×10^{-4} *M*. The first diffusion current was 4.10 microamperes, and the product of $m^{2/3}t^{1/6}$ was 0.02513 g.$^{2/3}$ sec.$^{1/6}$. From these data we calculate a value of D_{O_2} at 25° of 2.6×10^{-5} cm.^{2} sec.$^{-1}$.

The Irreversible Reduction of Oxygen on the First Wave.—If the reaction given by equation (1) were reversible, the potential π at each point of the first wave would be determined by the expression

$$\pi = \text{const.} + \frac{RT}{2F} \ln \frac{[O_2]_0[H^+]_0^2}{[H_2O_2]_0} \qquad (3)$$

in which the subscript zero denotes concentrations at the surface of the electrode. Introducing the relations between $[O_2]_0$, $[H_2O_2]_0$ on the one hand and i_d and i on the other we find that

$$\pi = \pi_{1/2} + \frac{RT}{2F} \ln \frac{i_d - i}{i} + \frac{RT}{F} \ln [H^+]_0 \qquad (4)$$

Hence if the reaction were reversible and equilibrium were attained at each point on the first wave, it is expected in buffer solutions, in which $[H^+]_0$ can be taken equal to the hydrogen ion concentration in the bulk of the solution, that $\pi_{1/2}$ would shift 59.1 mv. per unit change of the *p*H. Also, in a particular buffer solution, the line obtained on plotting π against log $(i_d - i)/i$ should be straight and have a slope of 0.0296 at 25°. In Fig. 6 are given the half wave potentials of the first and second waves of oxygen obtained in Clark and Lubs buffer solutions which were saturated with oxygen at *p*H values between 1 and 10. Evidently there is no relation between the *p*H and the half wave potentials of both waves. The relation given by expression (4) does not hold and the reaction given by equation (1) is not potential determining on the first wave. The half wave potential of the first wave and the slope of the latter seem to be affected by the kind and concentrations of anions present. The

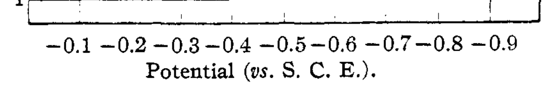

Fig. 6.—Half-wave potentials of first and second (peroxide) waves of oxygen in buffers of various *p*H.

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(13) D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934).

effect is particularly pronounced in the case of biphthalate. When biphthalate was added to an acetate buffer with a *p*H of 4 the half wave potential of the first wave shifted considerably to more negative potentials. Further experiments were carried out in mixtures of potassium nitrate and nitric acid with a total nitrate concentration of 1 *N*, in sulfuric acid–potassium sulfate mixtures with a total sulfate of 1 *N* and in some acetate buffers with a *p*H varying between 4 and 6. In none of these cases was there a relation between the half wave potential and the *p*H. In none of the cases was a straight line found upon plotting π against $\log (i_d - i)/i$, but in some cases straight lines were obtained by using $\log (i_d - i)/\sqrt{i}$ against π. In these cases the slope of the lines was 0.106. From the measurements described it is not possible to derive a mechanism which quantitatively accounts for the relation between the potential and the current on the first oxygen wave.

A preliminary study of oxygen maxima confirmed results reported in the literature.[3,4,5,6] However, we could not confirm Heyrovsky's[14] rule that maxima occurring at potentials at which the mercury carries a positive charge are greatly suppressed in the presence of small concentrations of anions of a high valence. We have studied the effects of potassium ferrocyanide and sodium citrate in this respect and found their effects are comparable to those of potassium chloride. As an illustration the effects observed with sodium citrate are given in Fig. 7. Cations of high valence did not have a marked effect on the maxima either.

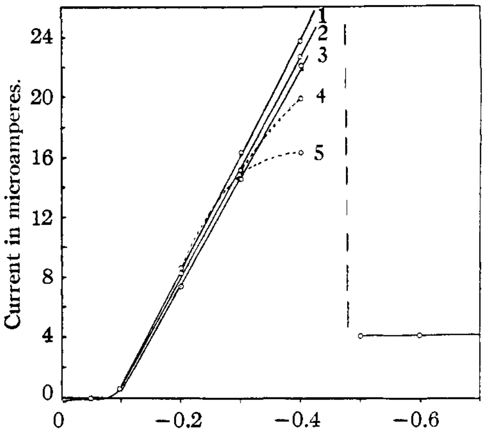

Fig. 7.—Effect of sodium citrate on maximum of oxygen in 0.002 *M* sodium hydroxide: I, no citrate; II, 1 × 10^{-4} *M* citrate; III, 5 × 10^{-4} *M;* IV, 10^{-3} *M;* V, 2 × 10^{-3} *M.*

Summary

1. The reaction occurring on the first oxygen wave

$$O_2 + 2H^+ + 2e \longrightarrow H_2O_2 \text{ or } O_2 + 2H_2O + 2e \longrightarrow H_2O + 2OH^-$$

is irreversible. There is no relation between the *p*H and the half wave potentials of the first and second oxygen waves. The slopes of both waves correspond to irreversible reactions.

2. The formation of hydroxyl ions has to be considered in polarographic analyses of air-saturated unbuffered neutral solutions which contain constituents which react with hydroxyl ions.

3. The diffusion coefficient of dissolved oxygen at 25° has been calculated to be 2.6 × 10^{-5} cm.^{2} sec.$^{-1}$.

4. Anions of higher valence were not found to have a greater effect upon the "positive" oxygen maximum than univalent anions have.

MINNEAPOLIS, MINNESOTA RECEIVED DECEMBER 12, 1940

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[14] J. Heyrovsky, "A Polarographic Study of the Electrokinetic Phenomena of Adsorption, Electroreduction and Overpotential Displayed at the Dropping Mercury Cathode," Actualités scientifiques et industrielles, No. 90, Hermann et Cie., Paris, 1934.