none-like ion to dehydroascorbic acid. The cupric ion concentration is maintained constant through oxidation by oxygen of the cuprous ion formed. An observed increase in the specific reaction rate during the course of the reaction is attributed to the accumulation of hydrogen peroxide formed through the oxidation of cuprous ion by oxygen.

A marked increase of the rate of the reaction upon the addition of ferric ion was observed.

PASADENA, CALIFORNIA RECEIVED APRIL 22, 1940

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

Mixed Potentials at the Dropping Mercury Electrode

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

When an electrode is placed in a solution and the system is not in oxidation–reduction equilibrium, the electrode potential measured by classical methods may be called a *mixed potential.* The dropping mercury electrode is ideally suitable for the measurement of such mixed potentials, as the electrode is renewed with each drop of mercury formed. When dealing with a depolarized electrode there is no net electrode reaction when the electrode is placed in the solution. This is no longer true when the electrode adopts a mixed potential. When such an electrode is placed in the solution, a cathodic and an anodic reaction occur, both yielding the same current. Although no current flows through the cell when the mixed potential is measured in the classical way, actually a cathodic reaction yielding a cathodic (positive) current and an anodic reaction yielding an anodic (negative) current occur, the positive and negative currents being of equal magnitude. Hence, under these conditions, the total current as indicated by the null point instrument is equal to zero.

Mixed potentials, as measured with the dropping mercury electrode, are of theoretical and practical interest as will be shown in this paper. In order to make clear the concept of mixed potentials at the dropping electrode we will consider a case which, for the sake of simplicity, is slightly idealized. In the experimental part mixed potentials and current–voltage curves actually measured will be given and interpreted. For the sake of simplicity we also neglect the very small effect of the charging or condenser current.[2] In Fig. 1 current ABC represents the current voltage curve obtained with the dropping electrode in an alkaline solution saturated with air. The cathodic (positive) current of oxygen starts at a potential A, and the diffusion current, BC, is attained at a potential of the dropping electrode corresponding to D. The anodic current AQ corresponds to the reaction $Hg + 2OH^- \longrightarrow Hg(OH)_2 + 2e$, and need not further be considered. In the same diagram (Fig. 1) we have represented the current voltage curve obtained in an air-free solution of an anion which depolarizes the dropping electrode at fairly negative potentials (in the diagram at E). Let EFG represent such a current voltage curve, say of dilute sulfide solution in alkaline medium. The anodic diffusion current FG is reached at a potential, H, of the d. e. We will now consider the current voltage curve when the mercury drops in the alkaline sulfide solution which is saturated with air. In Fig. 1 the diffusion current of sulfide is greater than that of oxygen. Coming from positive potentials we start with the anodic current IG of the hydroxyl ions, and at potentials more negative than G the diffusion current of sulfide is measured. When we have reached point G the potential has become equal to A, and at more negative po-

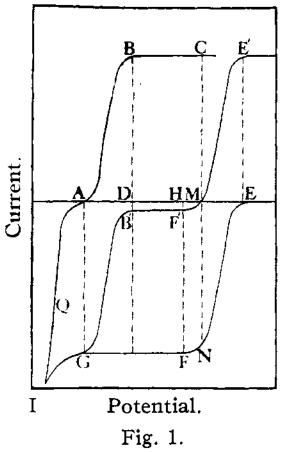

Fig. 1.

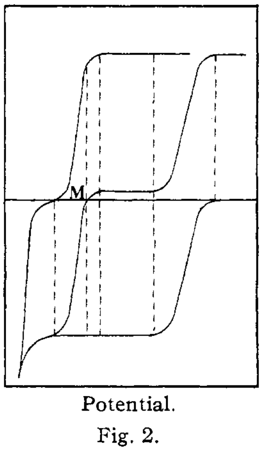

Fig. 2.

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[1] From the experimental work in a thesis submitted by C. S. Miller to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the doctor's degree (1940).

[2] Compare I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

tentials oxygen is being reduced. We now follow the c. v. curve $GB^1F^1ME^1$. The wave GB^1 corresponds to the reduction wave AB of oxygen, but it occurs at the anodic part of the c. v. curve. The reason for this paradoxical phenomenon is that simultaneously the reduction of oxygen and the oxidation of mercury to mercuric sulfide occur at the dropping electrode. The current measured is equal to the difference between the anodic diffusion current GF and the cathodic oxygen current over AB. The current becomes constant over the region B^1F^1, and is equal to the difference between the diffusion current of sulfide and of oxygen. At F^1 the potential corresponds to H. When the potential becomes more negative the diffusion current of sulfide is no longer obtained and the wave F^1ME^1 corresponds to the sulfide wave FNE, the part ME^1 of the anodic cyanide wave now being measured cathodically. Each value on the wave between M and E^1 now is equal to the difference between the diffusion current of oxygen and the anodic sulfide current at the particular potential. M indicates the *mixed* potential of the system, it simply represents the point on the current voltage curve where the cathodic diffusion current MC of oxygen is equal to the anodic sulfide current MN. This mixed potential is shifted to considerably more positive potentials if the diffusion current of oxygen is greater than that of the sulfide. This case is represented in Fig. 2.

The question may be raised what the mixed potential would be if the diffusion current of oxygen and of sulfide were the same. In this case the current would remain zero over a potential range between D and H (Fig. 1), in other words, the electrode potential would have any value between D and H. This case cannot be realized as we have neglected the charging or condenser current of the dropping mercury.[2] Although the latter is very small there is only one potential at which the current is zero, even if i_d of oxygen were equal to that of the sulfide.

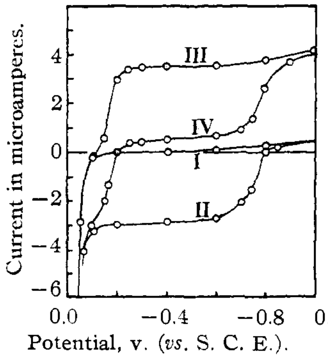

Fig. 3.—I, NaOH 10^{-1} *N*, Me Red 10^{-6} *M*, air free; II, same as I with ($S^=$) 7 × 10^{-4} *M*; III, same as I but air saturated; IV, same as III with ($S^=$) 7 × 10^{-4} *M*.

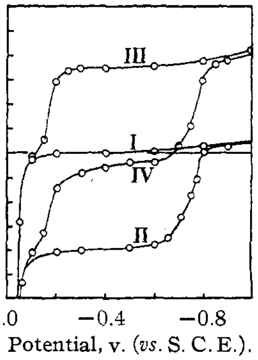

Fig. 4.—I, NaOH 10^{-1} *N*, Me Red 10^{-6} *M*, air free; II, same as I with ($S^=$) 9.5 × 10^{-4}; III, same as I but air saturated; IV, same as III with 9.5 × 10^{-4} *M* ($S^=$).

The shifting of cathodic waves to the anodic region and vice versa is also of practical importance in polarography. In practical polarography a large pool of mercury at the bottom of the electrolysis cell is often used as an anode. The potential of this anode is affected by the medium in which the electrolysis is carried out. In chloride solutions its potential is close to that of the calomel electrode at the same chloride concentration. In the presence of much cyanide its potential is much more negative. In order to take this anode potential into account, an "indicator or pilot substance" whose half wave potential is unaffected by the cyanide, is often added. As such, the addition of thallium has been recommended[3] when the electrolysis is carried out in cyanide medium. Although it is true that the half wave potential of thallium is not affected by cyanide, the cathodic wave measured with the dropping electrode in a solution of thallium containing much cyanide is not that of thallium, but part of the anodic wave of cyanide. This is made clear in Fig. 7.

Experimental

The manual polarographic equipment described by Kolthoff and Lingane[2] was used to obtain the data presented in this paper. The electrolysis cell and dropping electrode used are described by Lingane and Laitinen.[4] All potentials are referred to the saturated calomel electrode at 25°. The reagents were the analytical grade of either Merck or Mallinckrodt. A trace of methyl red was always added to suppress maxima.

In Figs. 3 and 4 are presented current voltage curves obtained with air saturated solutions of 0.1 *N* sodium hydroxide with air free sodium sulfide solutions in the same medium and with air saturated solutions containing different concentrations of sulfide. In Fig. 3 the sulfide wave is smaller than the oxygen wave while in Fig. 4 the reverse is true.

It is seen that in the critical range a small change of the sulfide concentration in the mixture with oxygen results in a large change of the "mixed" or null potential. In Fig. 3 the sulfide concentration was 7 × 10^{-4} *M* and the mixed

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(3) H. Hohn, "Chemische Analysen mit dem Polarographen," J. Springer, Berlin, 1937.

(4) J. J. Lingane and H. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

potential −0.200 volt. In Fig. 4 the sulfide concentration was 9.5×10^{-4} M and the mixed potential was −0.670 volt. At a sulfide concentration of 8.3×10^{-4} M the diffusion current of oxygen would be equal to that of sulfide. From the idealized curves in Fig. 1 and 2 one would infer that in such a mixture the mixed potential would be undefined between −0.25 and −0.6 v. Actually the measured diffusion currents are not perfectly constant over any range of potentials and there always will be a definite mixed potential. However, the latter will vary greatly with slight changes in the ratio of oxygen and sulfide at the critical ratio.

Incidentally, it may be mentioned that the behavior of a mixture of sulfide and oxygen at the dropping electrode may be made the basis of a new type of *amperometric titration*. This type of titration is unique in this respect that the substance titrated and the "reagent" do not react chemically during the titration. If to an oxygen solution in 0.1 N sodium hydroxide successive amounts of a sulfide solution were added at an applied potential of −0.45 ± 0.1 volt, the positive current would be found to decrease and become zero at the point where the diffusion current of the added sulfide has become equal to that of the oxygen. From the Ilkovic expression of the diffusion current[2] it can be inferred that zero current is reached when in the mixture $C_{\text{oxygen}}\sqrt{D_{\text{oxygen}}} = C_{\text{sulfide}}\sqrt{D_{\text{sulfide}}}$, D representing the diffusion coefficient. Such titrations are of limited practical application but of considerable theoretical significance. Making use of the above principles such titrations also could be carried out potentiometrically.

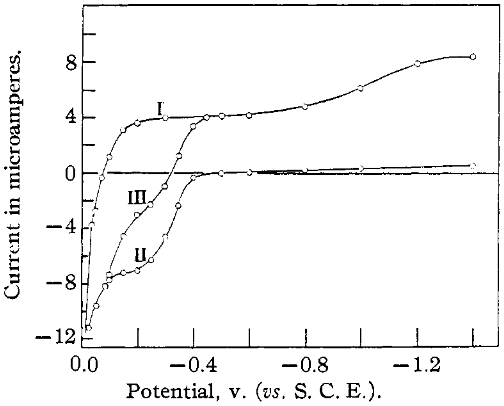

Fig. 5.—I, KCl 10^{-1} N, NaOH 10^{-2} N, Me Red 10^{-6} M, air saturated; II, KCl 10^{-1} N, NaOH 10^{-2} N, Me Red 10^{-6} M, KCN 10^{-3} N, air free; III, same as II but air saturated.

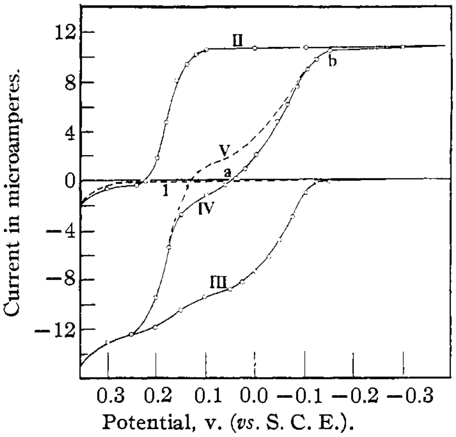

Fig. 6.—Cyanide and quinone waves in acetate buffer, pH 4.7: I, buffer with KNO_3 10^{-1} N, air free; II, same as I with quinone 10^{-3} M; III, same as I with KCN 2×10^{-3} M; IV, same as II with KCN 2×10^{-3} M; V, algebraic summation of II and III.

Mixed potentials are also measured in mixtures of oxygen and cyanide in dilute sodium hydroxide. Curve 3 in Fig. 5 gives the current-voltage curve of such a mixture. In Fig. 6 another example of a mixed potential is given in an air-free mixture of quinone and hydrogen cyanide at a pH of 4.7. Curve 5 represents the algebraic summation of the cathodic quinone wave (curve 2) and the anodic cyanide wave (curve 3). This theoretical curve 5 does not coincide exactly with curve 4, which was actually measured in the mixture, since there was a slight loss of hydrogen cyanide. It is quite evident from Fig. 6 that ab (curve 4) is not the reduction wave of quinone but the anodic wave of cyanide. Such an apparent shift of the reduction wave has been discussed in the introduction of this paper. It also occurs in an alkaline mixture of thallium and cyanide as is evident from Fig. 7. The reduction wave of 0.001 M thallous chloride in 0.1 N cyanide (containing an excess of sodium hydroxide) occurs at such large negative currents that it cannot be measured. The cathodic wave (curve 2) in the mixture again corresponds to part of the anodic cyanide wave. Apparently, the half wave potential of thallium is shifted from −0.46 v. (referred to the satd. calomel electrode) to a value of −0.59 v. in the 0.1 N cyanide solution. This fact should be considered when thallium is used as an "indicator ion" in solutions containing cyanide.

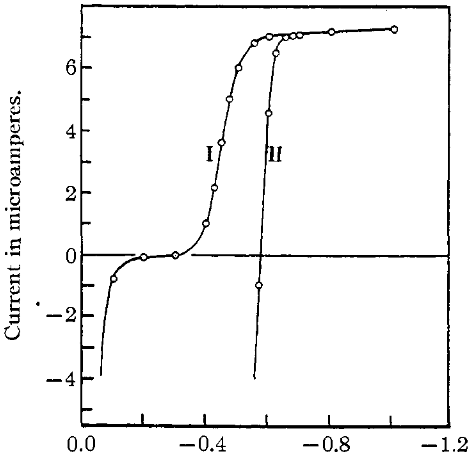

Fig. 7.—I, TlCl 10^{-3} N, NaOH 10^{-1} N; II, same as I with KCN 10^{-1} N.

Summary

1. The significance of "mixed potentials" at the

dropping mercury electrode is explained. Various examples of current–voltage curves in mixtures which yield mixed potentials have been given.

2. Although thallous thallium does not react chemically with cyanide its "apparent" reduction wave is shifted to more negative potentials in the presence of cyanide.

3. The principle of a new type of amperometric titration in which the substance titrated and the titrating agent do not react chemically has been described.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 11, 1940

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The 20° Isotherm of the Ternary System: Manganous Nitrate–Nitric Acid–Water

BY WARREN W. EWING AND CHARLES F. GLICK

This investigation of the ternary system manganous nitrate–nitric acid–water was undertaken to confirm or discover the existence of certain hydrates of manganous nitrate, in conjunction with vapor pressure and freezing point measurements on this salt which are being made in this Laboratory. No mention of any previous investigation of this system occurs in the literature. According to Mellor,[1] Funk's solubility data indicate the existence of a hexahydrate and a trihydrate of manganous nitrate. Ditte reported a monohydrate and a hemipentahydrate, although the existence of the latter is unconfirmed. Guntz and Martin reported the preparation of anhydrous manganous nitrate by various chemical methods.

Experimental

Saturated solutions were prepared, and both liquid and moist solid phases were analyzed for nitric acid and manganous nitrate.

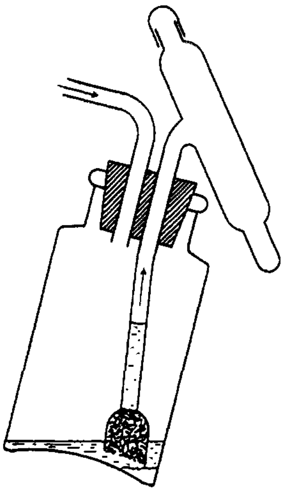

Fig. 1.—Isothermal filtering device.

Materials.—A solution of C. P. manganous nitrate, containing about 50% manganous nitrate, was concentrated over concentrated sulfuric acid in a vacuum desiccator until the solution yielded a thick slush of hexahydrate crystals at 10°. The mother liquor was removed from this slush by suction on a large sintered glass filter. The crystallization was repeated twice more. The moist crystals were dried over concentrated sulfuric acid in a vacuum desiccator until their composition reached about 80% manganous nitrate; for higher compositions phosphorus pentoxide was used as the desiccant. Prolonged drying over phosphorus pentoxide yields pure anhydrous manganous nitrate, a faintly pink powder which dissolves in water without leaving a residue. This indicates that this method of preparation does not change the salt to an insoluble basic form, as is the case with zinc nitrate.

C. P. nitric acid was prepared by distillation from a mixture of two volumes of sulfuric acid and one volume of nitric acid. This distillate was redistilled in a 75 cm. Vigreux column; the fraction distilling at 82° was collected. This product was pale amber in color and gave an analysis of 101% acid.

Preparation and Treatment of Samples.—Manganous nitrate and nitric acid of the appropriate concentrations were mixed together to give samples of the desired concentrations. The samples were prepared in two ounce wide-mouth bottles and the ground glass stoppers were sealed with paraffin. They were rotated in a water thermostat at 20.00 ± 0.02° for at least four hours. Due to the complexity of the system, it was not possible to prepare exactly duplicate samples in order to approach equilibrium from two directions, but samples very nearly the same, prepared from the hot side and from the cold side, yielded solubility data which were concordant. Furthermore, some samples were rotated as much as eight hours and again concordant data were obtained. These concordant results proved that four hours was ample time to establish equilibrium.

The saturated solution phase was removed by filtration. For a viscous solution and a coarsely granular solid phase, the glass wool filter, Fig. 1, was used. The sample bottle and the filter tube were inclined as shown to permit filtration of most of the liquid phase, even though this be present in small quantity. For a non-viscous solution and a fine, powdery solid phase, another filter was used, similar to the first except that a sintered glass micro filter replaced the bell of glass wool. In using either filter, compressed air was supplied to the inlet tube, since filtration by suction caused vaporization of nitric acid. The filtrate collected in the well of the receiver and was immediately available for analysis without interruption of the filtration.

Method of Analysis.—The residues were prepared for analysis by two different methods. Those consisting of hexahydrate were melted at 30–35° without danger of vaporization of nitric acid. Those consisting of lower

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[1] Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Vol. XII, Longmans, Green and Co., London, 1932, p. 440.