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

The Use of the Dropping Mercury Electrode as an Indicator Electrode in Poorly Poised Systems

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(1) Müller and Baumberger[1] and Müller[2] have shown that the dropping mercury electrode can be used to measure the oxidation potential of the quinone–hydroquinone system. In their work the oxidation potential of the system was taken as that value of the potential of the dropping electrode at which the current flowing was zero. This procedure was found to give good results in the majority of practical cases where the solution used was reasonably well poised. However, when the same method was extended to very poorly poised (buffered) systems a fairly large error appeared to be made. Thus, in Müller's[2] work, a 10^{-1} *M* phosphate buffer of *p*H 6.9 gave a zero current potential at the dropping electrode corresponding to a *p*H 7.7 when the buffer was diluted by a factor of 10,000. A more probable value of the *p*H of this buffer diluted under ordinary conditions would be of the order of 6.7. It is our purpose in the first part of the present paper to offer an explanation for the apparent deviation.

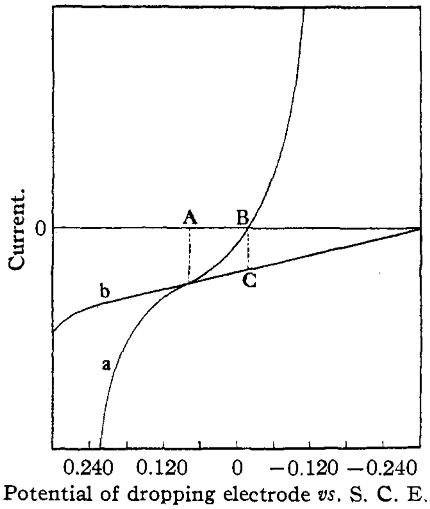

Fig. 1.—Diagram showing relation between oxidation potential and residual current in unbuffered quinhydrone solution.

Strictly speaking, the potential of the dropping electrode at which the current is zero does not correspond to the oxidation potential in the bulk of the solution because the residual current[3] is not being considered. The effect of the residual current can be best understood by reference to the following diagram. In Fig. 1 curve b represents the residual current of the medium and curve a is the current voltage curve of a poorly buffered quinhydrone solution (similar to Müller's[2] Fig. 3). The potential corresponding to point B is the zero current potential and is being taken as the oxidation potential of the system in the bulk of the solution. It is evident that at point B there is an anodic residual current of magnitude BC and therefore this residual current must be balanced by an equal cathodic current due to the reduction of quinone. This reduction produces hydroxyl ions at the poorly buffered interface causing an increase in the *p*H at the mercury surface over that in the bulk of the solution. The value of the potential at B therefore does not correspond to the oxidation potential in the bulk of the solution. The true oxidation potential in the bulk of the solution is that corresponding to point A where curves a and b intersect. As the buffer capacity of the system is increased curve a becomes steeper near B since the hydroxyl ions produced by the reduction of quinone have a smaller effect on the *p*H at the mercury surface and points A and B are drawn closer together until the error in the oxidation potential becomes negligible in well buffered systems.

In order to approximate the error caused by neglecting the residual current in poorly poised systems we have determined the c. v. curves of 0.1 *M* potassium nitrate solutions with and without 10^{-3} *M* quinhydrone. The experiments were carried out at 25 ± 0.03° with the manual apparatus used in previous work in this Laboratory.[3] The water used was distilled in a Pyrex still from alkaline permanganate the middle portion being collected and the latter then redistilled three times. The final sample was used immediately after collection. The quinhydrone used was a nicely crystalline product washed five times with 20 ml. portions of conductivity water and dried over phosphorus pentoxide. The hydroquinone

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(1) O. H. Müller and J. P. Baumberger, *Trans. Electrochem. Soc.*, **71**, 169 (1937).

(2) O. H. Müller, THIS JOURNAL, **62**, 2434 (1940).

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

was treated similarly. The potassium nitrate was a C. P. product recrystallized three times from conductivity water. The experiments were carried out in a Pyrex cell, the air being removed by the use of purified (air and carbon dioxide free) nitrogen. An external saturated calomel electrode was used as an anode, connection being made to the electrolysis cell with a 0.1 *M* potassium nitrate agar bridge. An *iR* correction was avoided by measuring the potential of the dropping electrode against a separate saturated calomel electrode, connection to the electrolysis cell being made by a second 0.1 *M* potassium nitrate bridge.

In Table I a few of the experimental values of interest in this particular case are given.

TABLE I

π	+0.150	+0.100	+0.050	0.00	−0.025	−0.050
i_r	− .16	− .14	− .12	− .12	− .09	− .05
i	− .26	− .18	− .12	− .10	+ .04	+ .19

π = potential of dropping electrode against S. C. E. in volts. i_r = residual current in microamp. obtained in 0.1 *M* potassium nitrate alone. i = current in microamp. observed in 0.1 *M* potassium nitrate plus 10^{-3} *M* quinhydrone. + signifies a reduction current and − an oxidation current.

From a plot of these results the zero current potential of the 10^{-3} *M* quinhydrone solution was found to be at −0.0215 v. This corresponds to the potential at point B in Fig. 1 and the *p*H calculated was 8.0. The true oxidation potential, corresponding to point A in Fig. 1, was found to be +0.050 v. and this gives a *p*H value of 6.8. In order to check this value the potential of a bright platinum electrode was measured in this solution at the same time. Its value was +0.0400 v. which corresponds to a *p*H of 7.0. Hence it is shown that the correct *p*H can be approximated with the dropping electrode if the proper correction for the residual current is made. However, this method is more involved than the classical method. The same considerations hold for other poorly poised systems. The oxidation potential of such systems can be measured with the dropping electrode if part of the c. v. curve is obtained and corrected for the residual current as illustrated above. This is hardly a simple procedure.

(2) In the interpretation of the half-wave potentials of quinhydrone obtained in unbuffered or poorly buffered solutions Müller did not find values of the potentials corresponding to the expected values of the *p*H at the electrode surface. Quite correctly he points out that at the half-wave potential of the anodic wave (oxidation of hydroquinone) the ratio of quinone to hydroquinone is not 1:1 but 3:1. This change in the ratio involves a correction of 0.24 in the *p*H instead of the 0.5 which Müller applies in his Table I and possibly in his Table III. Even after proper correction the half-wave potentials do not correspond to those expected by Müller. Our experimental results are in essential agreement with those of Müller.[2] In the following discussion it is shown that the deviations can be quantitatively accounted for.

For the sake of simplicity we will only consider the anodic wave because an analysis of the cathodic wave is too involved due to the liberation of hydroxyl ions at the electrode, part of which react with the hydroquinone to form uni- and divalent anions of this acid. In considering the anodic wave of 0.001 *M* hydroquinone or 0.001 *M* quinhydrone in 0.1 *M* potassium nitrate Müller calculates the expected hydrogen ion concentration at the electrode to be 0.001 *M* at the half-wave potential on the basis of the reaction

$$C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2 + 2H^+ + 2e$$

A more detailed consideration of the conditions at the dropping electrode shows that this calculation is not correct. The proper calculation of the interfacial concentration of hydrogen ions in oxidations or reductions involving hydrogen ions is of general importance in polarographic work and is given below. The average rate at which hydroquinone is being removed from the electrode surface is proportional to $\bar{i}$, where $\bar{i}$ is the average current during the life of the drop. Following the derivations of Ilkovic[4] or MacGillavry and Rideal[5] we find that the average rate at which hydroquinone is being supplied to the electrode surface is given by $k'D_{\mathrm{Hy}}^{1/2}([\mathrm{Hy}] - [\overline{\mathrm{Hy}}]_0)$, where k' is a constant depending upon the characteristics of the capillary, D_{Hy} is the diffusion coefficient of the hydroquinone, [Hy] is the concentration of hydroquinone in the bulk of the solution and $[\overline{\mathrm{Hy}}]_0$ is the average concentration of hydroquinone at the electrode surface. Since these rates must be equal we get the relation

$$\bar{i} = kD_{\mathrm{Hy}}^{1/2}([\mathrm{Hy}] - [\overline{\mathrm{Hy}}]_0) \qquad (1)$$

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

(5) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

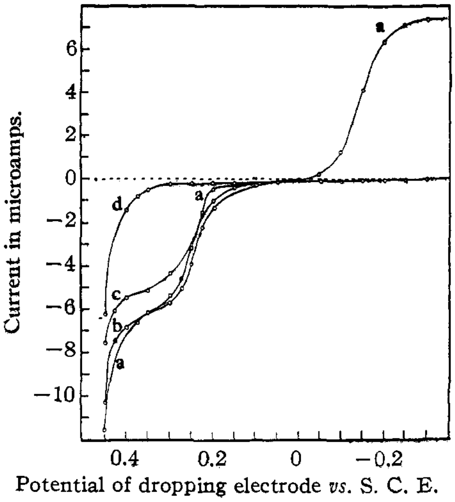

Fig. 2.—C. V. curves in 0.1 *M* potassium nitrate solutions: (a) 0.001 *M* in quinhydrone, $m = 2.02$ mg. per sec., $t = 2.44$ sec. (at $\pi = +0.375$ v.); (b) 0.001 *M* hydroquinone, $m = 2.02$, $t = 2.44$; (c) 0.001 *M* hydroquinone, $m = 1.15$, $t = 4.20$; (d) residual current in medium, $m = 2.02$, $t = 2.44$.

We also find that the average rate at which quinone is being supplied to the electrode is proportional to $\bar{i}$ and the average rate at which it is being removed is given by $k'D_{\mathrm{Q}}^{1/2}([\overline{\mathrm{Q}}]_0 - [\mathrm{Q}])$ where these symbols have meanings analogous to those given above for the hydroquinone case. Again equating these rates we find.

$$\bar{i} = kD_{\mathrm{Q}}^{1/2}([\overline{\mathrm{Q}}]_0 - [\mathrm{Q}]) \qquad (2)$$

In a similar way we find for the hydrogen ions

$$\bar{i} = {}^1/_2 kD_{\mathrm{H}^+}^{1/2}([\overline{\mathrm{H}}^+]_0 - [\mathrm{H}^+]) \qquad (3)$$

(The $^1/_2$ appears because of the reaction $C_6H_4OH_2 \rightleftarrows C_6H_4O_2 + 2H^+ + 2e$.) The Ilkovic equation[4] gives us the relation

$$i_{\mathrm{d}} = kD_{\mathrm{Hy}}^{1/2}[\mathrm{Hy}] \qquad (4)$$

From these equations we readily find the relations

$$[\overline{\mathrm{Hy}}]_0 = [\mathrm{Hy}]\left(1 - \frac{\bar{i}}{kD_{\mathrm{Hy}}^{1/2}[\mathrm{Hy}]}\right) = [\mathrm{Hy}]\,\frac{id - \bar{i}}{i_{\mathrm{d}}} \qquad (5)$$

$$[\overline{\mathrm{Q}}]_0 = \frac{D_{\mathrm{Hy}}^{1/2}}{D_{\mathrm{Q}}^{1/2}}([\mathrm{Hy}] - [\overline{\mathrm{Hy}}]_0) + [\mathrm{Q}] \qquad (6)$$

$$[\overline{\mathrm{H}}^+]_0 = \frac{D_{\mathrm{Hy}}^{1/2}}{D_{\mathrm{H}^+}^{1/2}}\,2([\mathrm{Hy}] - [\overline{\mathrm{Hy}}]_0) + [\mathrm{H}^+] \qquad (7)$$

For an unbuffered solution at the half-wave potential we therefore have

$$[\overline{\mathrm{Hy}}]_0 = \frac{1}{2}[\mathrm{Hy}] \qquad (8)$$

$$[\overline{\mathrm{Q}}]_0 = \frac{D_{\mathrm{Hy}}^{1/2}}{D_{\mathrm{Q}}^{1/2}}\,\frac{1}{2}[\mathrm{Hy}] + [\mathrm{Hy}] \text{ (In a quinhydrone solution)} \qquad (9)$$

$$[\overline{\mathrm{Q}}]_0 = \frac{D_{\mathrm{Hy}}^{1/2}}{D_{\mathrm{Q}}^{1/2}}\,\frac{1}{2}[\mathrm{Hy}] \text{ (In a hydroquinone solution)} \qquad (10)$$

$$[\overline{\mathrm{H}}^+]_0 = \frac{D_{\mathrm{Hy}}^{1/2}}{D_{\mathrm{H}^+}^{1/2}}[\mathrm{Hy}] \qquad (11)$$

Since the potentials of the dropping electrode have been measured against a saturated calomel electrode, we also have the relation

$$p\mathrm{H} = \frac{0.4532 - \pi^{1/2}}{0.0591} + \frac{1}{2}\log\left(\frac{[\overline{\mathrm{Q}}]_0}{[\overline{\mathrm{Hy}}]_0}\right)_{\text{at } \pi^{1/2}} \qquad (12)$$

In order to verify these equations c. v. curves of the following solutions were run as described in part I; 0.1 *M* potassium nitrate with 0.001 *M* hydroquinone (at two different values of the drop time and mass of mercury per second) and 0.1 *M* potassium nitrate with 0.001 *M* quinhydrone. The results are given in Fig. 2. After correcting all currents for the residual current of the 0.1 *M* potassium nitrate solution, the half-wave potentials and the diffusion currents were determined. The masses of mercury per second and the drop times were also measured at the diffusion currents. The Ilkovic equation (4) was used to calculate[2] D_{Hy} and D_{Q} from the observed values of the diffusion currents, the concentrations, the drop times and the masses of mercury per second. The values found at 25° were

$D_{\mathrm{Hy}} = 7.4 \pm 0.2 \times 10^{-6}$ cm.^{2} sec.$^{-1}$; $D_{\mathrm{Q}} = 8.6 \pm 0.2 \times 10^{-6}$ cm.^{2} sec.$^{-1}$

A value of 9.32×10^{-5} sq. cm. sec.$^{-1}$ for D_{H^+} at 25° was taken from Kolthoff and Lingane.[3] Using these values equations (8), (9), (10), (11) and (12) may be evaluated. The pH should then be given by the relations

$$p\overline{\mathrm{H}}_0 = 0.23 + \frac{0.4532 - \pi^{1/2}}{0.0591} \text{ (for quinhydrone solutions)} \qquad (13)$$

$$p\overline{\mathrm{H}}_0 = -0.02 + \frac{0.4532 - \pi^{1/2}}{0.0591} \text{ (for hydroquinone solutions)} \qquad (14)$$

$$p\overline{\mathrm{H}}_0 = 0.56 - \log[\mathrm{Hy}] \qquad (15)$$

The results are given in Table II where $p\mathrm{H}_0$ observed has been calculated from equation (13) for curve a and from equation (14) for curves b and c. pH calculated has been evaluated using equation (15).

TABLE II

Curve	$\pi^{1/2}$	$p\overline{\mathrm{H}}_0$ obsd.	$p\overline{\mathrm{H}}_0$ calcd.	Drop time
a	+0.255	3.6 ± 0.1	3.6	2.44
b	+ .238	3.6 ± .1	3.6	2.44
c	+ .239	3.6 ± .1	3.6	4.20

The agreement is remarkably good and it is evident that the rapid diffusion of hydrogen ions accounts quantitatively for the apparent discrepancy, noted in Müller's[2] paper, between the "calculated" and observed values of the *p*H. The shift of the half-wave potential with a change in drop time, which is not to be expected on the basis of equations (5), (6) and (7), was not found by us as evidenced by curves b and c. It is possible that such an effect might exist at very small drop times, but in exact work small drop times should be avoided.

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Summary

1. The oxidation potential of poorly poised systems can be determined with the dropping mercury electrode, if proper correction is made for the residual current. Neglecting this correction may lead to large errors.

2. When hydrogen ions are produced at the dropping mercury electrode during an electrolysis the surface concentration of hydrogen ions can be calculated by a proper consideration of the diffusion and current relations. Equations have been derived which were in excellent agreement with experimental results.

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The Solubility of Lead Iodide in Solutions of Potassium Iodide–Complex Lead Iodide Ions

BY OSCAR E. LANFORD AND SAMUEL J. KIEHL

The solubility of lead iodide is increased by the addition of iodide ion after a certain definite minimum solubility has been reached. This fact has been demonstrated conclusively by Burrage,[1] by Van Klooster and Balon[2] and by Demassieux and Roger.[3] Furthermore, this behavior has been interpreted generally to be due to the formation of complex ions of lead and iodine, to which some authors,[1,3,4] although the data available are insufficient to establish composition, have ascribed the formula PbI_3^-,—possibly because double salts of the type $RI \cdot PbI_2 \cdot xH_2O$ have been identified as solid phases during equilibrium studies on such solutions while solid phases of double salts in which the molar ratio of alkali iodide to lead iodide is greater than one to one have not been encountered[1,2,3,4] in these investigations.

So to verify experimentally the formula of the ion, PbI_3^-, and to ascertain whether other complex lead iodide ions are formed in solutions of lead iodide and potassium iodide and to determine, if possible, their nature, a series of solubility measurements was made. Whereupon not only was evidence found for the existence of PbI_3^- but also for $PbI_4^{=}$ as well—both in significant amount. Moreover, their respective stability constants and standard free energies of formation were evaluated.

Materials and Procedure

Lead iodide and potassium iodide both of a high degree of purity were crystallized three times from water. All other reagents used in this investigation, although of the highest purity obtainable, were tested as an assurance that no other substances which would affect the results were present.

A colorimetric method was employed for the determination of lead. The sample containing between 0.4 and 1.0 mg. of lead was placed in a 100-ml. volumetric flask and 0.5 ml. of 3 *N* sodium acetate added. This operation was followed successively by the addition of 20 cc. of a 50% solution of sucrose, 4 ml. of 6 *N* hydrochloric acid, and 4 ml. of a saturated solution of hydrogen sulfide. The solution of hydrogen sulfide was freshly prepared from carefully washed commercially available gas. The resulting solution was thoroughly mixed, 5 ml. of 6 *N* ammonia added, and made to volume with constant agitation and intermixing. A brown color appeared after the addition of ammonia.

A Pulfrich photometer equipped with a violet (s43, λ = 4300) filter was used to measure the extinction coefficient of the above solution contained in a three-centimeter cell. A blank solution containing all the reagents was present in the other side of the instrument.

To evaluate the solubility of lead iodide a calibration curve was made for the instrument by using standard solutions of lead nitrate and lead iodide. In making the curve the extinction coefficient was plotted against the lead content in the above solution. A straight line for solutions containing not more than 1.0 mg. of lead in 100 ml. of solution, which was the most concentrated solution

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(1) L. J. Burrage, *J. Chem. Soc.*, 1703 (1926).

(2) H. S. Van Klooster and P. A. Balon, THIS JOURNAL, **56**, 591 (1934).

(3) N. Demassieux and Roger, *Compt. rend.*, **204**, 1818 (1937).

(4) L. J. Burrage, *Chem. News*, **134**, 85 (1937).