

Some Factors Affecting the Precision of Polarographic Half-Wave Potential Measurements

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The experimental conditions required for the precise determination of polarographic half-wave potentials have been investigated and are discussed. The values of half-wave potentials vary with the characteristics of the dropping-mercury electrode in the case of reduction of metal ions to metal soluble in mercury. Consequently, it is necessary to specify the experimental condition whenever values for half-wave potentials are reported. With proper precautions it is possible to attain reproducibility within ± 0.2 millivolt in the measurements.

1. Introduction

The polarographic half-wave potential is of interest because of its use in the qualitative identification of electrode reactions. Of even greater interest, however, is its thermodynamic significance and its application to the problem of determining the complexity constants for complex ions [1,2].¹ In most cases the half-wave potential data presented in the literature have been precise to less than plus or minus several millivolts. While this is sufficient for qualitative purposes, it is not of the required precision for the other applications. The purpose of this investigation was to determine the precision with which it is possible to measure half-wave potentials and also to study the factors affecting the measurements. As the purpose of the work was to investigate methods by which precise values may be obtained and not to establish a precise half-wave potential spectrum, relatively few reducible materials were examined.

2. Experimental Measurements

All half-wave potential measurements were made with a manual arrangement, the circuit diagram of which is shown in figure 1. The voltage was applied to the cell by means of the slide wire (S) of a Sargent model XII or model XXI polarograph. The potential of the dropping-mercury electrode (DME) with respect to the saturated calomel reference electrode (REF) was measured with a precision potentiometer (Pot). The current was measured with an Ayrton shunt (SH) and a lamp and scale galvanometer (G_1). Galvanometer (G_2), the null indicator on the potentiometer, was a "spotlight" type of instrument. A system of B_2 , R_2 , R_3 , R_4 , and R_5 was included for the calibration of the galvanometer (G_1). This calibration current could be calculated from the voltage drop across R_1 and its known value of resistance.

The cell arrangement shown in figure 2 consisted of a 100-ml beaker fitted with a rubber stopper that contained inlet tubes for nitrogen for the removal of oxygen from the solution and holes for the access

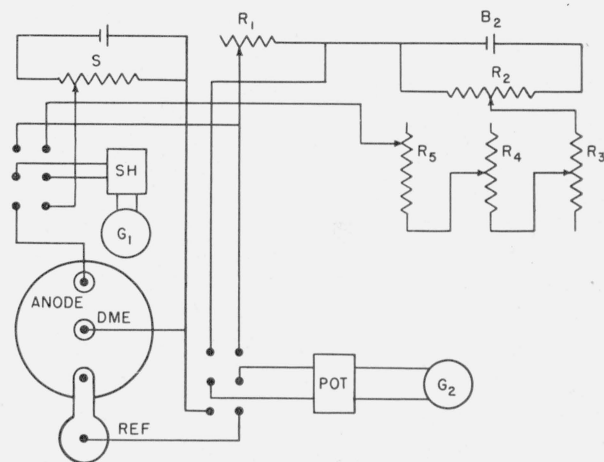


FIGURE 1. Manual arrangement for the measurement of half-wave potentials.

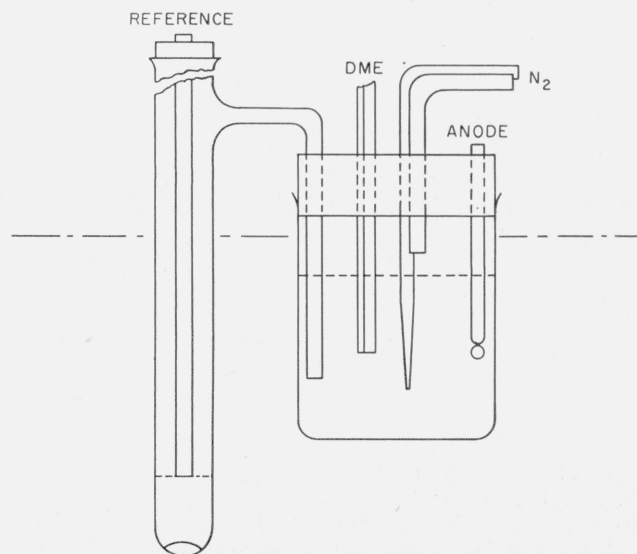


FIGURE 2. Polarographic cell used in half-wave potential measurements.

¹ Figures in brackets indicate the literature references at the end of this paper.

of the dropping-mercury electrode, the silver-silver-chloride working electrode (Anode), and the sidearm of the saturated calomel reference electrode (Ref). The Ag-AgCl anode, of the thermal-electrolytic type [3], had a large surface area to minimize polarization effects under the conditions of the measurements. This electrode was used because it was found that the silver-wire anodes frequently recommended were of insufficient surface area to prevent polarization effects. The saturated calomel electrode (S. C. E.) was so constructed that a large portion of it was immersed in the bath. The sidearm contained an agar plug saturated with KCl. All potential measurements were made with respect to this reference electrode.

A number of capillaries were used during the course of the investigation. A capillary of marine barometer tubing producing drops having a mass of 6.9 mg (*mt* value) was used in the investigation of the dependence of half-wave potential on concentration. In the determination of the dependence of the half-wave potential on capillary characteristics, the capillaries had *mt* values of 6.8, 8.8, 10.2, 32, and 64 mg, respectively. The first three of these were of marine barometer tubing and the last two were of the constricted type described by Taylor and Smith [4].

Before each series of runs, the cell was cleaned in a hot sulfuric-acid-potassium dichromate solution and then steamed for about 15 min. The stopper assembly was rinsed in distilled water and allowed to dry before it was placed in the cell. The Ag-AgCl electrode was stored between runs in 0.01 *N* HCl and before use was rinsed with distilled water and dried with a filter paper. The calomel electrode was stored with the sidearm immersed in saturated KCl and was treated in a similar manner before insertion in the cell.

Nitrogen was used to remove oxygen from the solutions. The gas was passed over hot copper to remove any traces of oxygen before introduction into the cell. While the measurements were being made, the nitrogen flowed over the surface to prevent oxygen from reentering the solution.

All measurements were made in a constant temperature bath maintained at $25 \pm 0.01^\circ \text{C}$.

Stock solutions of the metal ions used were made by dissolving weighed portions of the pure metals in acid, evaporating the solution to dryness several times to remove all of the acid, and then dissolving the residue in distilled water and diluting to the desired concentration. All other materials were reagent grade chemicals used without further purification.

The capacitance-conductance bridge network shown in figure 3 was assembled to measure the resistance of the cells and the change of resistance with applied voltage, drop time, etc. R_1 and R_2 are the ratio arms of the bridge and were equal to 500 ohms for the sensitivity used. The measuring arm of the bridge consisted of R_3 and C , a mica condenser variable in 0.001- μf steps from 0 to 1.11 μf .

A 1,000-ohm resistance, R_4 , was inserted to reduce the shunting effect of the potentiometer (P) on the detector (D). (P) was the slide wire of the model

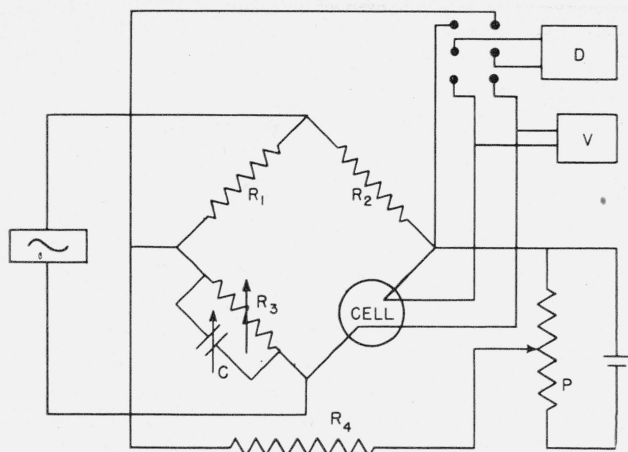


FIGURE 3. Circuit for the measurement of the resistance of the polarographic cell.

XII polarograph with the voltage increased to 5 v. The signal source was a beat frequency oscillator with an output voltage necessary to give 0.04 v across the cell. The voltmeter (V) used to measure the d-c voltage drop across the cell was a Beckman H-2 pH meter. The detector (D) was a cathode-ray oscillograph connected to the circuit so that it could be used as an a-c voltmeter across the cell, as well as the null point detector for the bridge. To study the variation of cell resistance with time, the bridge was set at some value greater than the minimum resistance and the time was recorded from the beginning of the drop until a balance was indicated. This was repeated at a series of R values until the curve shown in figure 4 was obtained.

Measurements of the half-wave potential, $E_{1/2}$, were made in the following manner. The current and voltage were measured at a point about 0.1 v or more preceding the half-wave potential to establish a zero point for the wave, and at appropriate voltage increments up to and including the diffusion current plateau. Measurements on the supporting electrolyte alone at corresponding voltages gave values of the residual current, which were subtracted from the current readings above to give values of i . For values several tenths of a volt greater than the half-wave potential, the current is practically independent of the applied voltage (diffusion current plateau) and is designated the diffusion current, i_d . From these values of the current, $\log i/(i_d - i)$ was calculated and plotted with respect to the measured voltage. From this plot, the value of E at $\log i/(i_d - i) = 0$, when corrected for the voltage drop in the cell, corresponds to the half-wave potential. A typical plot is shown in figure 5. It may be seen that the curve is linear and that the reciprocal of the slope is 0.0306 v, in satisfactory agreement with the theoretical value of 0.0295 v. The value of R used in the correction for the iR drop is four-thirds of the minimum cell resistance corresponding to the average R during the life of the mercury drop.

3. Results

3.1. Variation of $E_{1/2}$ With the Characteristics of the Galvanometer Used on the Potentiometer

Measured values of the potential of the dropping electrode with respect to a reference electrode vary with time during the growth of the mercury drop due to the variation of voltage drop (iR) in the cell. It is not feasible to measure either the maximum or minimum value of this potential. Accordingly, the potentiometer is balanced at some average value as evidenced by the symmetrical deflection of the "null" galvanometer around its rest point. It is evident that such a potentiometric reading will be influenced by the characteristics of the null galvanometer and will approach the time average value when the characteristics are such that it can integrate the voltage variation that exists.

It was found that for the conditions given below, when the damping was near critical and the period of the galvanometer was of the same order as or greater than the drop time, there was no significant variation of $E_{1/2}$ with period of the galvanometer or with the damping. If the period was short or the damping resistance was very large, the values obtained for the half-wave potential were increased. Under these conditions the galvanometer does not integrate the voltage-time curve [5, 6], and the voltage read is no longer the average voltage corresponding to the average current. The conditions for the measurements were as follows: Drop time, 5.7 sec; reducible ion, 1 mM Cd; supporting electrolyte, 0.1 N HCl, 0.01 percent gel; $t=25^\circ\text{C}$; head 70 cm; marine barometer capillary; reference, S. C. E. The galvanometers and characteristics are listed below.

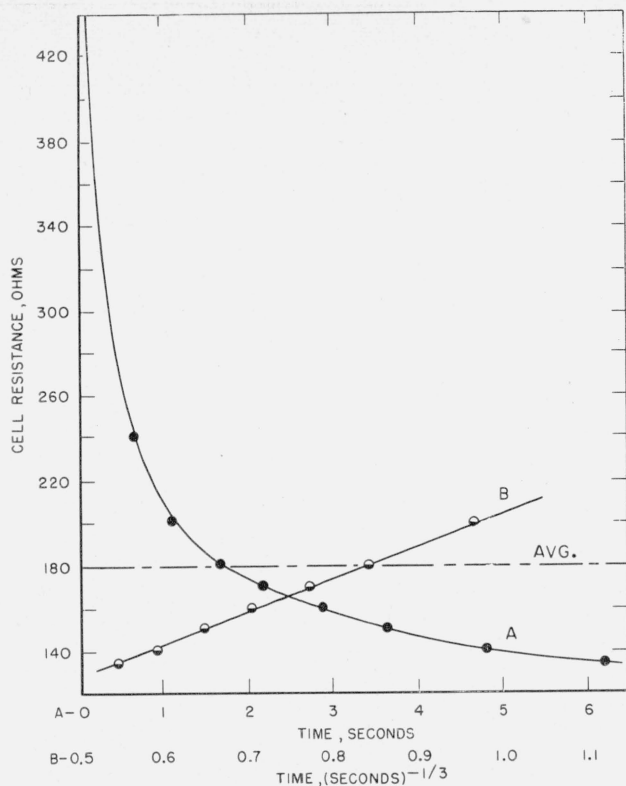


FIGURE 4. Electrical resistance of a dropping-mercury electrode.

(a) Plot of resistance-time variation during the life of a 7-mg drop and at a drop time of 6.2 sec.

(b) Demonstration that the resistance varies with $(\text{time})^{-1/3}$.

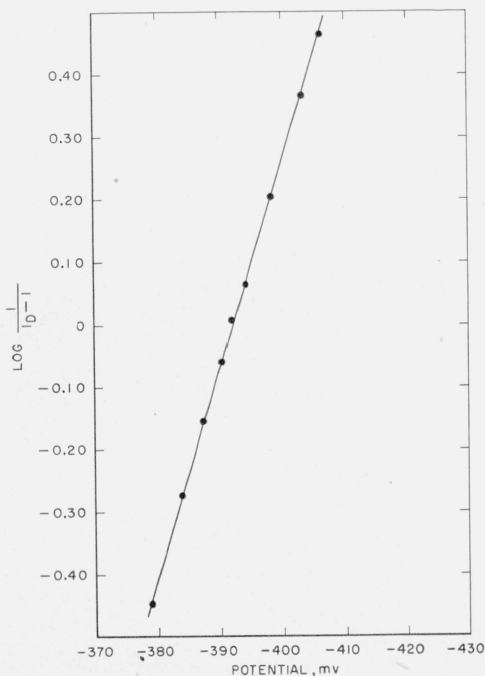


FIGURE 5. Plot of potential of the DME versus $\log i/(i_a - i)$ from which the half-wave potential is obtained.

NBS galvanometer	Period	Critical damping resistance	Damping resistance
3568-----	1.85	43	10; 43; ∞
16350-----	3.83	2,700	700; 2,700; ∞
10442-----	5.26	43,000	10,000; 43,000; ∞
5705-----	15.5	21,000	21,000; ∞

The magnitude of the error from this source is not large but is significant in precise measurements. The maximum error to be expected is of the order of one-half of the iR correction and would be obtained when using a balance indicator of very short period, for example, an oscilloscope. When using the galvanometer with period of 1.85 sec and infinite damping resistance, errors in the half-wave potential of 1 mv were observed. On the other hand, with the galvanometer of 15.5-sec period, half-wave potential measurements were practically independent of the damping resistance used.

3.2. Measurement of Resistance

It was found that, as a practical matter, the resistance measurements needed for the iR drop correction may be made with sufficient accuracy on the supporting electrolyte, by the use of a small 1,000-cps conductance bridge with an "electronic-eye" detector, provided that the capacity balance is closely maintained. As shown in figure 4, the resistance varies as the minus one-third power of time, in accord with theory. The average value of the resistance is four-thirds of the minimum value, occurring at the time of dislodgment of the drop.

Measurements of resistance with no applied d-c potential were found to be applicable over the range of potential used, since the variation of resistance with potential is small, and the accuracy of measurement decreases with the potential. The resistance was found not to vary significantly with drop time. For example, with a capillary for which $mt=8.8$ at drop times of 3.92, 3.12, 2.58, 2.22, 1.94, and 1.74 sec, the resistances were 195, 196, 197, 196, 197, and 197 ohms, respectively.

With a reducible ion in the solution, the behavior of the resistance and capacitance at the half-wave potential was generally in accord with the observations of other investigators [7, 8]. However, as this phenomenon had no direct bearing on this investigation, it was not pursued in detail.

3.3. Variation of $E_{1/2}$ With the Concentration of Reducible Ion

Measurements of half-wave potentials for this study were made with a marine barometer capillary with a drop weight of 6.9 mg and at a drop time of 5.8 sec. The temperature was held at $25 \pm 0.01^\circ \text{C}$. for all runs. Measurements made on Cd^{++} in 1.0 N KCl and 0.1 N HCl , and on Pb^{++} in 0.1 N KCl and 0.1 N HCl show no significant variation of $E_{1/2}$ with concentration of reducible ion from 0.5 mM to 5.0 mM. However, the correction for the iR drop is very important in these measurements, being as large as 5 mv for the most concentrated solutions. A typical plot in figure 6 shows curves before

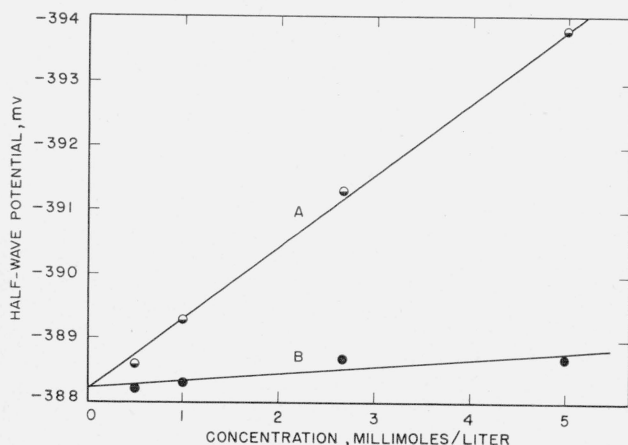


FIGURE 6. Variation of $E_{1/2}$ with concentration (A) and the same data after the iR drop has been corrected (B).

(A) and after (B) the iR correction has been made.

It was found that moving the reference electrode from one position to another in the cell did not affect the potential measured with respect to the dropping-mercury electrode. A separate experiment was performed, using a cell in which three compartments filled with 0.1 N KCl were separated by tubes containing agar plugs of several hundred ohms resistance. Silver-silver-chloride electrodes were placed in the end compartments and a potential was applied. It was found that the portion of the fall of potential between the electrodes, as measured by a reference electrode, depended on its distance between them. In this case, however, the resistance at the surface of the Ag-AgCl electrodes is small, whereas that of the intervening medium is large; therefore, the greater part of the potential drop occurs across the solution and not at the electrode interface. In the case of the DME, the resistance of the drop interface is large and that of the intervening medium is relatively small, so that the greater part of the potential drop occurs across the interface. It is not possible, therefore, to place the reference electrode close enough to the drop to exclude measuring this fall of potential. For this reason the half-wave potential must be corrected for iR drop, although no cell current is involved.

3.4. Variation of $E_{1/2}$ With Capillary Characteristics

In the reduction of a metal ion to metal soluble in mercury, the half-wave potential has been found to vary with the drop time and size of drop of the electrode, other factors remaining constant. This variation is approximately linear with drop time for a given electrode, as is shown in figure 7. However,

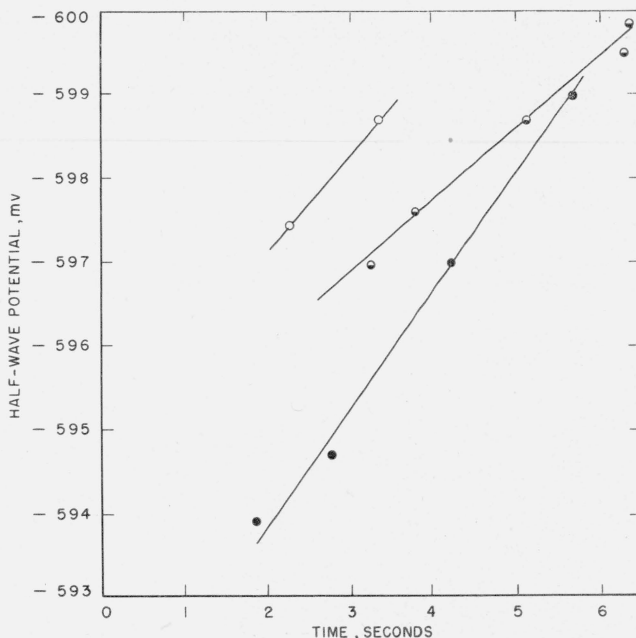


FIGURE 7. Variation of $E_{1/2}$ with capillary characteristics in the case of Cd in 0.1 N KCl , 0.01 percent gel.

●, Capillary 8.8; ◐, capillary 32; ○, capillary 64.

no simple relation appears to exist between the curves obtained for the several electrodes studied. The metal ions Cd^{++} , Pb^{++} , and Tl^{++} have been used in this investigation with capillaries having mt values of 6.8, 8.8, 10.2, 32, and 64 mg, respectively. In the case of homogeneous electrode reactions in-

TABLE 1. Half-wave potential of Cd for a series of capillaries and drop times

The supporting electrolyte is 0.1 N KCl and 0.01 percent gelatin, except where noted. (Temperature, 25.0° C)

Capillary (mt value)	Drop time	$E_{1/2}$
<i>mg</i>	<i>sec</i>	<i>v</i>
8.8	1.90	-0.5939
8.8	2.82	-0.5947
8.8	4.25	-0.5970
8.8	5.70	-0.5990
32	3.26	-0.5970
32	3.78	-0.5976
32	5.14	-0.5987
32	6.38	-0.5995
32	6.68	-0.5999
64	2.32	-0.5974
64	3.36	-0.5987
6.9	5.8	-0.5958
6.9 (0.1 N HCl)	5.8	-0.6015
6.9 (1.0 N KCl)	5.8	-0.6432

TABLE 2. Half-wave potential of Pb for a series of capillaries and drop times

The supporting electrolyte is 0.1 N KCl and 0.01 percent gelatin, except where noted. (Temperature, 25.0° C)

Capillary (mt value)	Drop time	$E_{1/2}$
<i>mg</i>	<i>sec</i>	<i>v</i>
8.8	1.92	-0.3882
8.8	2.90	-0.3891
8.8	4.30	-0.3906
8.8	5.74	-0.3923
32	3.20	-0.3918
32	4.32	-0.3917
32	4.86	-0.3921
32	6.38	-0.3927
64	2.28	-0.3913
64	3.42	-0.3922
6.9 (0.1 N HCl)	5.8	-0.3953
6.9	5.8	-0.3885

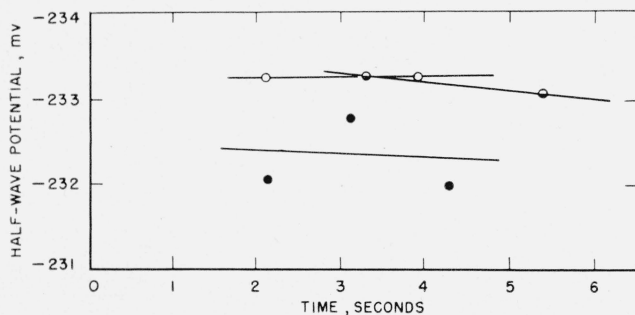


FIGURE 8. Variation of $E_{1/2}$ with capillary characteristics in the case of the Fe^{2+} , Fe^{3+} system in 1.0 M K_2O_4 , 0.01 percent gel.

●, Capillary 8.8; ●, capillary 32; ○, capillary 64.

volving reduction from a higher to a lower oxidation state, in which the dropping electrode acts as an indicator electrode, there is no variation with drop time and only slight variation with drop size, as is shown in figure 8. The supporting electrolytes were: for Pb, Cd, and Tl, 0.1 N KCl, 0.01 percent gel; for Fe, 1.0 M $\text{K}_2\text{C}_2\text{O}_4$, 0.01 percent gel; for quinhydrone, 0.04 M Na_2HPO_4 , 0.027 M NaH_2PO_4 . The $E_{1/2}$ values obtained for all cases are shown in tables 1, 2, 3, 4, and 5.

TABLE 3. Half-wave potential of Tl for a series of capillaries and drop times

The supporting electrolyte is 0.1 N KCl and 0.01 percent gelatin. (Temperature 25.0° C)

Capillary (mt value)	Drop time	$E_{1/2}$
<i>mg</i>	<i>sec</i>	<i>v</i>
6.8	4.24	-0.4573
6.8	5.30	-0.4601
6.8	6.56	-0.4629
8.8	2.88	-0.4519
8.8	4.82	-0.4560
8.8	5.64	-0.4598
10.2	2.14	-0.4538
10.2	3.10	-0.4555
10.2	4.24	-0.4584
32	3.28	-0.4587
32	4.34	-0.4593
32	5.34	-0.4600
64	2.22	-0.4593
64	3.22	-0.4598

TABLE 4. Half-wave potentials of the Fe^{2+} , Fe^{3+} system for a series of capillaries and drop times

The supporting electrolyte is 1.0 M $\text{K}_2\text{C}_2\text{O}_4$ and 0.01 percent gelatin. (Temperature 25.0° C)

Capillary (mt value)	Drop time	$E_{1/2}$
<i>mg</i>	<i>sec</i>	<i>v</i>
10.2	2.14	-0.2321
10.2	3.08	-0.2328
10.2	4.26	-0.2320
32	3.28	-0.2333
32	5.42	-0.2331
64	2.10	-0.2333
64	3.92	-0.2333

TABLE 5. Half-wave potential of the Quinhydrone system for a series of capillaries and drop times

The supporting electrolyte is 0.04 M Na_2HPO_4 and 0.027 M NaH_2PO_4 pH=7.0. (Temperature 25.0° C)

Capillary (mt value)	Drop time	$E_{1/2}$
<i>mg</i>	<i>sec</i>	<i>v</i>
10.2	2.06	+0.0510
10.2	2.98	+0.0518
10.2	4.18	+0.0507
32	3.24	+0.0498
32	5.38	+0.0493
64	1.98	+0.0500
64	2.68	+0.0499

4. Discussion

The results of this investigation show that the half-wave potential may vary significantly with the characteristics of the dropping electrode. Because variations of several millivolts can occur, it is important that the characteristics of the electrode be reported, in addition to information concerning the supporting electrolyte and temperature, to give the measurements their full significance. The importance of the correction for the iR drop in the cell is also emphasized.

Strehlow and Stackelberg [9] have predicted variation in $E_{1/2}$ with drop time caused by stirring effects within the Hg drop and the resultant disturbance of diffusion conditions for the amalgam. The variation of $E_{1/2}$ observed in this investigation in the case of the reduction of metal ions to an amalgam, and the lack of such variation in oxidation-reduction systems are in accord with this theory. The order of magnitude is such that a few percent change in the concentration of the amalgam at the surface would account for the variation observed. The problem of a quantitative treatment of this phenomenon is under study.

It has been shown by other investigators [10] that the half-wave potential is dependent on the capillary in the case of irreversible reactions. In the present case, however, the linearity of the $\log i/(i_a - i)$ versus E plot, and the near theoretical slope obtained, attest to the reversibility of the reactions studied and eliminate irreversibility as the cause of the variations.

In order to attain reproducibility within ± 0.2 mv in half-wave potential measurements, several sources of error must be considered. The temperature of the cell and of the reference electrode must be known and held constant to within $\pm 0.1^\circ$ C, since the temperature coefficients are approximately 0.8 mv/ $^\circ$ C in each case. The residual current must be determined from measurements on a cell containing supporting electrolyte only, and the corresponding correction applied to the limiting current at each point. Fortunately, moderate errors in the residual current can be tolerated, as it is only a small fraction of the total current in the usual case.

The largest sources of error arise in the evaluation of the $\log i/(i_a - i)$ versus E relationship and in the determination of the voltage drop in the cell. With respect to the first, comparison of graphical methods with least squares adjustment of the data shows agreement in the two methods to ± 0.1 mv. The simple plotting procedure can thus be relied on within this limit of precision. The magnitude of the iR correction depends on both the current and the cell resistance. In measurements of half-wave potential, cells should be designed to offer minimum electrical resistance, and the design used in this work appears to approach the optimum from this point of view. Such cells have resistances of the order of a few hundred ohms (largely interfacial resistance) which can be readily measured with ordinary equipment to within 3 to 4 percent. The magnitude of

the diffusion current depends on both the size of the dropping electrode and the concentration of the electrolyzable material. However, since the resistance of the cell decreases with increase of the size of the drop, with corresponding increase in the current, it is not difficult to choose a combination so that the uncertainty in the iR correction will not exceed ± 0.1 mv, except in the case of the largest electrodes, where errors of several times this amount may result.

An important source of error in the measurement of half-wave potentials is the junction potential of the reference electrode-solution interface. This error may be of the order of several tenths of a millivolt and has been recently discussed by Vlcek [11]. No corrections for junction potentials have been made in this study, as they would be only approximate and would not affect the precision.

5. Summary

The sources of error in half-wave potentials have been investigated and found to lie chiefly in the correction for the iR drop in the solution and in the actual reproducibility of current and voltage measurements. When proper precautions are exercised, it is possible to obtain values reproducible to within ± 0.2 mv.

The half-wave potential is shown to vary with the size of drop and with the drop time of the electrode in the case of the reduction of metallic ions to metal soluble in the mercury electrode. On the other hand, much less variation was observed in homogeneous electrode reactions in which the dropping-mercury electrode acts as an indicator electrode. Accordingly, the observed variations are attributed to stirring effects within the drop and the resulting disturbance of diffusion conditions for the amalgam formed in heterogeneous reactions. In view of the large variations found, values of half-wave potential are not significant unless the characteristics of the electrode used for the measurements are reported.

6. References

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