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

Thermodynamic Significance of Polarographic Half-Wave Potentials of Simple Metal Ions at the Dropping Mercury Electrode

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The electrodeposition of simple (hydrated) metal ions at the dropping electrode is a chemically reversible process when the resulting metal is soluble in mercury, and may be represented by

$$M^{n+} + ne + Hg \rightleftharpoons M(Hg) \qquad (1)$$

where M(Hg) represents the amalgam formed on the surface of the mercury drops.[2] Heyrovsky and Ilkovic[3] have pointed out that if the foregoing reaction takes place reversibly the dropping electrode should be subject only to concentration polarization, and accordingly its potential at every point on a discharge wave should be given by

$$E_{d.e.} = E_a^0 - \frac{RT}{nF_y} \ln \frac{C_a \gamma_a}{C_0 \gamma_s} \qquad (2)$$

where C_a is the concentration of the amalgam formed on the surface of the mercury drops, C_0 is the concentration of the metal ions in the depleted layer of solution *at the surface* of the drops, γ_a and γ_s are, respectively, the activity coefficients of the metal in the amalgam and the metal ions in the solution, and E_a^0 is the standard potential of the amalgam, that is, the e. m. f. of the cell: Reference electrode / $M^{n+}(a = 1)$/M(Hg)$(a = 1)$ (I).

When an excess of an indifferent electrolyte is present so that the migration current is eliminated, the reducible metal ions reach the surface of the dropping electrode only by diffusion.[2,4] Representing the concentration of the reducible metal ions in the body of the solution by C, the current at any point on the polarographic wave by i, and the diffusion current by i_d, we have the relations[2,3]

$$i_d = KC \qquad (3)$$
$$i = K(C - C_0)$$

or

$$C_0 = \frac{i_d - i}{K} \qquad (4)$$

and

$$C_a = ki \qquad (5)$$

The validity of eq. 3, in which K is the diffusion current constant, has been amply demonstrated.[2,4]

The theoretical significance of K and the factors which influence it have been discussed in detail by Ilkovic[5] and Lingane and Kolthoff.[4] Equation 5 is simply a statement of the fact that the concentration of the amalgam at every point on the wave must be proportional to the current.

By substituting the foregoing relations into eq. 2 we obtain

$$E_{d.e.} = E_a^0 - \frac{RT}{nF_y} \ln \frac{\gamma_a k K}{\gamma_s} - \frac{RT}{nF_y} \ln \frac{i}{i_d - i} \qquad (6)$$

The half-wave potential is defined[3] as the value of $E_{d.e.}$ at the midpoint of the wave, and since the last log term becomes zero when $i = i_d/2$ eq. 6 may be written

$$E_{d.e.} = E_{1/2} - \frac{RT}{nF_y} \ln \frac{i}{i_d - i} \qquad (7)$$

and hence the half-wave potential is given by

$$E_{1/2} = E_a^0 - \frac{RT}{nF_y} \ln \frac{\gamma_a k K}{\gamma_s} \qquad (8)$$

It should be mentioned that the observed value of $E_{d.e.}$ includes a small iR drop in the solution. However, with concentrations of supporting electrolyte greater than about 0.01 M the resistance of a polarographic cell is generally less than 1000 ohms, and hence the iR drop is usually less than 0.001 v. per microampere, which is negligibly small.

When the resulting metal is not soluble in mercury it is simply deposited in the solid state on the surface of the dropping electrode, and in such a case the reduction of the metal ions will be given by

$$M^{n+} + ne \rightleftharpoons M(s) \qquad (9)$$

If this reaction would take place reversibly it readily can be derived that the equation of the polarographic wave should be

$$E_{d.e.} = E_M^0 - \frac{RT}{nF_y} \ln \frac{K}{\gamma_s} + \frac{RT}{nF_y} \ln (i_d - i) \qquad (10)$$

where E_M^0 is the ordinary standard potential of the metal. Quite obviously the curve of this equation is not symmetrical about the half-wave point, and therefore in this case the half-wave potential has no particular thermodynamic significance. The difficulty of obtaining reproduci-

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(2) For a detailed review of the fundamental principles of the polarographic method see I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1–94 (1939).

(3) J. Heyrovsky and D. Ilkovic, *Coll. Czech. Chem. Commun.*, **7**, 198 (1935).

(4) J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

(5) D. Ilkovic, *Collection Czech. Chem. Commun.*, **6**, 498 (1934); *J. chim. phys.*, *(France)* **35**, 129 (1938).

ble electrode potentials in the classical manner with metals that are insoluble in mercury (*e. g.*, metals of group VI in the periodic classification, the iron group, arsenic, vanadium, etc.) is well known, and chemical polarization and passivity phenomena are common in this group. Hence the reduction of such metals according to eq. 9 is in most cases probably not a reversible process. For these reasons the following discussion will be confined to those metals that are soluble in mercury, and whose ions are reduced at the dropping electrode according to eq. 1.

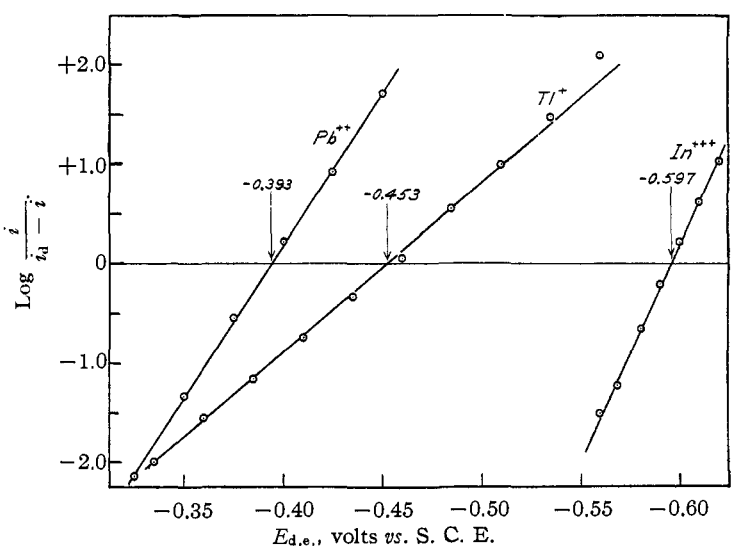

Fig. 1.—Log plots of observed current–voltage curves of thallous and lead ions in 0.1 *N* potassium chloride, and of indium ions in 1 *N* potassium chloride. The slopes of the three lines are Tl^{+} 0.059 v., Pb^{++} 0.033 v., and In^{+++} 0.023 v.

Equation 7 has been verified experimentally by Tomes[6] and Kolthoff and Lingane.[2] By plotting $E_{d.e.}$ against $\log i/(i_d - i)$ a straight line results, whose slope is equal to $2.3RT/nF_y$, and the value of $E_{d.e.}$ corresponding to a value of zero for the log term is the half-wave potential. This is demonstrated in Fig. 1, where the plots have been constructed from experimental current–voltage curves obtained by the writer, in the electrolysis of 0.002 *M* solutions of thallous, lead, and indium ions in the presence of an excess of potassium chloride. The current–voltage curves were obtained with the apparatus previously described.[2,4] As predicted by eq. 7, the experimental points fall on straight lines. The observed slopes of the three lines are, respectively, 0.059, 0.033, and 0.023 v. for the thallous, lead, and indium ions, in good agreement with the theoretical values which are 0.059, 0.030, and 0.020 v. for the discharge of uni-, di-, and trivalent ions. It is evident that eq. 7, and the fundamental assumption that the dropping electrode is subject only to concentration polarization in the discharge of metal ions according to eq. 1, are essentially correct.

(6) J. Tomes, *Coll. Czech. Chem. Commun.*, **9**, 12, 81, 150 (1937).

By setting the second differential of eq. 7, *i. e.*

$$\frac{d^2E}{di^2} = \frac{RT}{nF_y}\left(\frac{1}{i^2} - \frac{1}{(i_d - i)^2}\right)$$

equal to zero, it is found that the curve of eq. 7 has a point of inflection when $i = i_d/2$. The polarographic wave is therefore symmetrical about the half-wave point, and $E_{1/2}$ coincides with the true inflection point of the curve.[3]

It has been found experimentally[2,3] that the half-wave potential is entirely independent of the geometrical characteristics of the particular capillary that is used, the rate of flow of mercury, and the drop time. Therefore, it is evident from eq. 8 that the product kK is constant and independent of these factors. Although both k and K are individually dependent on the properties of the capillary, the rate of mercury flow, and the drop time, the effect of these factors on k must be inversely proportional to their effect on K, so that the product kK remains constant. It is also an experimental fact[2,3] that the half-wave potential is constant and independent of the concentration of the reducible metal ions, provided that the composition of the solution with respect to foreign salts, *i. e.*, γ_s, is kept constant. It is evident, therefore, that the half-wave potential is a characteristic property of the reducible ions, and it has definite thermodynamic significance.

Influence of the Concentration of Supporting Electrolyte on the Half-Wave Potential.—Since the activity coefficient, γ_s, of the reducible metal ions decreases with increasing ionic strength, it is to be expected from eq. 8 that $E_{1/2}$ should be shifted somewhat to more negative values with increasing concentration of supporting electrolyte. This is actually observable experimentally, as shown by the data in Table I obtained by the writer.

TABLE I

HALF-WAVE POTENTIALS OF THALLOUS, ZINC, CADMIUM, AND LEAD IONS IN VARIOUS CONCENTRATIONS OF SUPPORTING ELECTROLYTE

Half-wave potentials in volts referred to the saturated calomel electrode at 25°.

Supporting electrolyte	Tl^+	Zn^{++} $E_{1/2}$	Pb^{++}	Cd^{++}
0.02 *N* KNO_3	−0.451	−0.988		−0.572
0.1 *N* KNO_3	.459	0.997	−0.388	.578
1 *N* KNO_3	.477	1.012	.405	.586
0.02 *N* KCl		−0.988	− .377	− .578
0.1 *N* KCl	−0.459	0.995	.396	.599
0.25 *N* KCl	.466		.402	
1 *N* KCl	.480	−1.022	.435	.642

These data were obtained by the manual method of measurement and with the cells that have already been described,[2,4] and $E_{d.e.}$ was measured directly against an external saturated calomel reference electrode during the electrolysis. The concentration of the metal ions was 5×10^{-4} *M* or smaller, the current at the half-wave point was less than 2 microamp., and hence the correction for the *iR* drop in the solution was negligibly small. The $E_{1/2}$ values are reproducible to about ±2 mv.

The negative shift of the $E_{1/2}$ values with increasing ionic strength is of the order of magnitude predicted by eq. 8, when potassium nitrate is used as supporting electrolyte. The half-wave potential of thallous ions is the same in potassium nitrate and potassium chloride media at the same ionic strength, but with the other metal ions the negative shift is considerably greater in potassium chloride than in potassium nitrate solutions, due to complex ion formation between the divalent metal ions and chloride ions. It is well known that the half-wave potentials of metal ions are shifted to more negative values by complex formation.[2,3] In potassium nitrate solutions there is no appreciable complex formation, and only the ionic strength effect is operative.

Thermodynamic Interpretation of the Half-Wave Potential.—In order to interpret the half-wave potentials thermodynamically, it is convenient to compare them with the ordinary standard potentials of the metals. Consider the cell $M(s)/M^{n+}/M(Hg)$ two phase (II), in which the left electrode is the solid metal, and the right electrode is its saturated two-phase amalgam. Let $a_{satd.}$ be the activity of the metal in the saturated liquid amalgam in contact with a solid phase which may be either the pure metal, or a solid compound, or solid solution, of the metal and mercury. The e. m. f. of this cell is given by

$$E_{II} = E_a^0 - E_M^0 - \frac{RT}{nF_y} \ln a_{satd.} \qquad (11)$$

where E_M^0 is the ordinary standard potential of the metal, that is, the e. m. f. of the cell: Reference electrode/$M^{n+}(a = 1)$/M(s) (III).

If we express the composition of the amalgam in terms of mole fraction of the metal, *N*, and designate the *solubility* of the metal in mercury by $N_{satd.}$ and the corresponding activity coefficient by $\gamma_{satd.}$, we obtain from eq. 11

$$E_a^0 = E^0 + E_{II} + \frac{RT}{nF_y} \ln N_{satd.}\, \gamma_{satd.} \qquad (12)$$

By substituting this expression for E_a^0 into eq. 8 we find that the difference between the half-wave potential of a metal ion and its ordinary standard potential is given by

$$E_{1/2} - E_M^0 = E_{II} + \frac{RT}{nF_y} \ln N_{satd.}\, \gamma_{satd.} - \frac{RT}{nF_y} \ln \frac{\gamma_s kK}{\gamma_s} \qquad (13)$$

The first two terms on the right side of this equation are thermodynamic terms, but the last term involves the kinetics of the electroreduction.

In the case of metals which do not form solid compounds or solid solutions with mercury, *e. g.*, zinc, E_{II} is zero. In general, however, when the metal forms a solid compound or solid solution with mercury, E_{II} is equal to $-\Delta F/nF_y$, where ΔF is the free energy increase in the formation of the solid M_xHg_y, according to the reaction

$$xM(s) + yHg(l) \rightleftharpoons M_xHg_y(s) \qquad (14)$$

It is evident, therefore, that the difference between $E_{1/2}$ and E_M^0 depends on three distinct factors; the affinity of the metal for mercury (ΔF of reaction 14), the solubility of the metal in mercury, and the kinetic term *kK*.

A comparison of the half-wave potentials and the ordinary standard potentials of several metal ions is given in Table II. The values of $E_{1/2}$ given for the first four metal ions are the values obtained with 0.1 *N* potassium nitrate as the supporting electrolyte (Table I). The $E_{1/2}$ values of sodium and potassium ions were taken from the compilation given by Heyrovsky and Ilkovic[3]; they were obtained by using tetra-substituted alkylammonium salts as the supporting electrolyte.

It will be noted that the difference between $E_{1/2}$ and E_M^0 is greatest in the case of the alkali metals, due to their great affinity for mercury. In these cases the difference is due chiefly to the large value of E_{II}, and the second and last terms in eq. 13 are of subordinate importance. On the

TABLE II

COMPARISON OF HALF-WAVE POTENTIALS AND STANDARD ELECTRODE POTENTIALS OF SEVERAL METAL IONS

The values of $E_{1/2}$ and E^0_M are in volts with respect to the saturated calomel electrode at 25°.

Ion	$E_{1/2}$	E^0_M	$E_{1/2} - E^0_M$	E_{II}	$N_{satd.}$	$\gamma_{satd.}$	kK, calcd.
Tl^+	−0.459[a]	−0.582	+0.123	+0.003[c]	0.435[i]	7.75[i]	0.025
Pb^{++}	− .388[a]	− .372	− .016	.006[d]	.0143[k]	0.717[k]	.033
Cd^{++}	− .578[a]	− .647	+ .069	.051[e]	.0953[i]	.216[i]	.0025
Zn^{++}	− .997[a]	−1.008	+ .011	0[f]	.0638[m]	.756[m]	.011
Na^+	−2.12[b]	−2.961	+ .84	.780[n]	.0538[g]	1.28[g]	.005
K^+	−2.14[b]	−3.170	+1.03	1.001[h]	.0254[h]	5.52[h]	.036

[a] In 0.1 N KNO_3; see Table I. [b] Heyrovsky and Ilkovic, ref. 3. [c] Richards and Daniels, THIS JOURNAL, **41**, 1732 (1919). [d] Gerke, *ibid.*, **44**, 1684 (1922). [e] Hulett, *Trans. Am. Electrochem. Soc.*, **7**, 333 (1905). [f] Clayton and Vosburgh, THIS JOURNAL, **58**, 2093 (1936). [g] Bent and Swift, *ibid.*, **58**, 2216 (1936). [h] Bent and Gilfillan, *ibid.*, **55**, 3989 (1933). [i] Teeter, *ibid.*, **53**, 3917, 3927 (1931). [j] Lewis and Randall, "Thermodynamics," p. 267. [k] Hoyt and Stegeman, *J. Phys. Chem.*, **38**, 753 (1934). [l] Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, 1936. [m] Pearce and Eversole, *J. Phys. Chem.*, **32**, 209 (1928). [n] Bent and Forziati, THIS JOURNAL, **58**, 2220 (1936).

other hand, in the case of thallium E_{II} is negligibly small, but the solubility of thallium in mercury is large, so that the difference between $E_{1/2}$ and E^0_M is determined practically entirely by the last two terms in eq. 13.

The solubilities of the various metals in mercury at 25° are listed in the sixth column of the table, in terms of mole fraction, and the corresponding activity coefficients are given in the seventh column. The values of $\gamma_{satd.}$ are based on infinite dilution ($\gamma_a = 1$) as the standard state.

The last column contains approximate values of kK for the various metals calculated by means of eq. 13 from the observed differences between $E_{1/2}$ and E^0_M, and the experimental values of E_{II}, $N_{satd.}$, and $\gamma_{satd.}$ given in the table. In this calculation it was assumed that the activity coefficient of the univalent ions is 0.8, and that of the divalent ions 0.5, at an ionic strength of 0.1 M in potassium nitrate solutions.[7] Since we had no exact knowledge, *a priori*, regarding the concentration of the amalgams formed on the surface of the mercury drops, it was assumed that the concentrations of the amalgams were so small, under the usual conditions of a polarographic experiment, that γ_a was equal to unity. Because of this uncertainty the calculated values of kK can only be considered as approximations, but they are sufficiently accurate to indicate at least the order of magnitude of the constant k.

Although the observed values of $E_{1/2} - E^0_M$, and E_{II}, vary from a few millivolts up to one volt, and the activities of the saturated solutions of the metals in mercury vary widely from 0.01 in the case of lead up to 3.5 in the case of thallium, the calculated values of kK are all of the same order of magnitude. Unfortunately, no independent experimental method for determining k has yet been discovered, so that a more direct test of eq. 13 is not possible at the present time. However, the uniformity of the various calculated values of kK constitutes good indirect evidence of the validity of eq. 13.

The diffusion current constant K for the metal ions in Table II is of the order of magnitude of 5 microamp. per millimole per liter, with capillaries of the usual dimensions.[2,4] Hence the apparent value of k, from the data in Table II, is of the order of 0.005 mole fraction per microamp. for most of the metals. If we express the composition of the amalgams in volume concentration units, the apparent value of k is of the order of 300 mmol. per liter per microamp. This rather large value of k indicates that the deposited metal atoms remain close to the surface of the drop during its life, and that diffusion into the body of the drop is relatively slow. At the present time our knowledge of the diffusion processes in the mercury drops is so meager and incomplete that any attempt at a more detailed interpretation of these results at this time would be pure conjecture.

(7) J. Kielland, THIS JOURNAL, **59**, 1675 (1937).

Summary

The equation of the current–voltage curves in the electrodeposition of metal ions at the dropping mercury electrode has been discussed. When the reduced metal is soluble in mercury the dropping electrode is subject only to concentration polarization.

Experimental data have been presented which demonstrate that the half-wave potentials of metal ions are shifted somewhat to more negative values with increasing ionic strength of the solution.

The characteristics of the half-wave potential have been discussed, and an equation was derived relating the half-wave potentials to the ordinary standard potentials of the metals. The difference between the polarographic half-wave potential of a simple metal ion and the ordinary standard potential of the metal was shown to be a function of three distinct factors: (1) the affinity of the metal for mercury; (2) the solubility of the metal in mercury; and (3) the kinetics of the diffusion processes in the solution and in the mercury drops.

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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

Mutarotation of Tetramethyl-α-d-glucopyranose and Tetramethyl-α-d-mannopyranose

BY B. CLIFFORD HENDRICKS AND ROBERT E. RUNDLE

In a previous paper,[1] a study of the complexity of the mutarotation of *d*-galactopyranose was reported. In this communication a study of the analogous glucose and mannose sugars is presented.

The mutarotation of tetramethyl-α-*d*-glucopyranose has been investigated by Purdie and Irvine,[2] Lowry and co-workers[3–5] and Böeseken and Couvert[6] in water and other solvents. These workers, however, gave direct attention to the reaction order of the sugars' mutarotations at only one temperature. The mutarotation of tetramethyl-α-*d*-mannopyranose has been previously reported,[7] though only incidentally.

A systematic study of the unmethylated α-*d*-glucose[8] does not support the reported[9] complex mutarotation of α-*d*-glucose. The authors proposed to learn whether methylation and mutarotation at or near 0° would give evidence of mutarotation complexity.

Since there is a paucity of data upon tetramethylmannose they prepared and followed the mutarotation of tetramethyl-α-*d*-mannopyranose also.

The two sugars were prepared as indicated in a previous paper.[10] The properties of the tetramethyl-α-*d*-glucopyranose used were: initial rotations, $[\alpha]^0D$ +104.0; $[\alpha]^{25}D$ +104.0; equilibrium rotations: $[\alpha]^0D$ +80.4; $[\alpha]^{25}D$ + 84.8 and m. p. 92.5–93.5°. The constants for the tetramethyl-α-*d*-mannopyranose used were m. p. 49–50°; initial rotations: $[\alpha]^0D$ +11.5; $[\alpha]^{25}D$ +6.3; equilibrium rotations: $[\alpha]^0D$ +2.5 and $[\alpha]^{25}D$ −0.2.

(1) Hendricks and Rundle, THIS JOURNAL, **60**, 3007 (1938).
(2) Purdie and Irvine, *J. Chem. Soc.*, **85**, 1070 (1904).
(3) Lowry and Richards, *ibid.*, **127**, 138 (1925).
(4) Jones and Lowry, *ibid.*, 720 (1926).
(5) Richards, Faulkner and Lowry, *ibid.*, 1733 (1927).
(6) Böeseken and Couvert, *Rec. trav. chim.*, **40**, 354 (1921).
(7) Drew, Goodyear and Haworth, *J. Chem. Soc.*, 1237 (1927).
(8) Isbell and Pigman, *Bur. Standards J. Research*, **18**, 141 (1937).
(9) Worley and Andrews, *J. Phys. Chem.*, **32**, 307 (1928).
(10) Hendricks and Rundle, THIS JOURNAL, **60**, 2563 (1938).

TABLE I

MUTAROTATION OF TETRAMETHYL-α-*d*-GLUCOPYRANOSE AT 25°

2.4298 g. of sugar in 25 ml. of water

Time Min.	Time Sec.	Rotation obsd.	$(k_1 + k_2) \times 10^3$ calcd.
7	15	19.60	
9	0	19.49	
11	15	19.32	9.00
13	50	19.15	8.57
20	30	18.71	8.84
25	0	18.46	8.75
34	50	17.98	8.70
49	0	17.42	8.75
62	25	17.02	8.78
88	15	16.50	8.81
104	0	16.25	9.17
125	0	16.07	9.20
	∞	15.75	
			Av. 8.86 ± 0.34

TABLE II

MUTAROTATION OF TETRAMETHYL-α-*d*-GLUCOPYRANOSE AT 1.0°

2.819 g. of sugar in 25 ml. of water

Time Min.	Time Sec.	Rotation obsd.	$(k_1 + k_2) \times 10^3$ calcd.
9	15	25.32	
10	45	25.30	
18	10	25.24	0.754
25	30	25.18	.644
32	30	25.12	.786
40	50	25.03	.864
58	20	24.90	.829
81	45	24.82	.670
166	30	24.26	.709
255	0	23.78	.707
293	0	23.62	.693
424	0	23.14	.661
575	0	22.64	.660
646	0	22.46	.651
748	0	22.18	.662
	∞	20.68	
			Av. 0.715 ± 0.149