A SUMMARY OF ELECTRODE POTENTIALS[1]

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The purpose of presenting a summary of electrode potentials is four-fold. (1) To present explanation and discussion in a more complete form than will be possible in the pages of the International Critical Tables, (2) to receive helpful criticism (3) to point out needed researches to fill in gaps, and (4) to point out the necessity for employing easily duplicated and reversible reference electrodes.

The electrodes will be divided into four classes, (1) molal electrode potentials, (2) reference amalgam electrodes, (3) standard reference electrodes, and (4) oxidation-reduction electrodes. This constitutes an extension of Lewis and Randall's tables.[2] In addition, their example of expressing electrode potentials, calculated from the electromotive force of cells which contain no liquid potential, will also be followed, whenever such data exist. Thus cells which contain liquid potentials will be excluded from consideration whenever it is possible. The later references are usually given, in order that discussions of earlier work may be found.

I. SINGLE ELECTRODE POTENTIALS OF THE ELEMENTS

Conventions

I. The sign[3] of the electromotive force is such that the electromotive force is positive if the negative current tends to flow from

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[1] Contribution from the Department of Chemistry of the Massachusetts Institute of Technology.

The data in this paper will be the basis for the values of electrode potentials in the International Critical Tables.

[2] Lewis and Randall, Thermodynamics and the Free Energy of Chemical Substances. McGraw-Hill Book Co. 1923.

[3] Customary American usage. On the continent the reverse conventions are used.

right to left through the cell; also, the free energy increase, ΔF for the change of state occurring in the cell is given by the equation, $\Delta F = -NEF$.

II. The electromotive force of the molal hydrogen electrode H_2 (1 atm.), H^+ (unit activity) is zero.

III. The values for the electromotive force **E°**, of the half cells will be tabulated only for the substances in their standard states. The standard state for solids, liquids and gases is their state if the temperature is 25° and the pressure is one atmosphere. Unionized molecules and also ions are in their standard states if the temperature and pressure of the solution is 25° and one atmosphere and the concentrations are such that the activity is unity which is sometimes called "hypothetically molal." If the substances are not in their standard states, the symbols describing the cell will be followed by descriptive symbols in parentheses.

IV. The sign of the electromotive force of a given half cell is determined by reference to the hydrogen electrode, or other reproducible reference electrode. The cell consisting of a hydrogen electrode and the given half cell is expressed so that the negative current tends to pass from right to left through the cell. The electromotive force of the whole cell is then equal to the potential of the half cell at the negative pole minus the potential of the half cell at the positive pole. Thus, (**E** cell) =**E**(– pole) −**E**(+ pole).

$$E^\circ_{H_2} - E^\circ_{Cl_2} = E^\circ \text{ cell}$$

$$\begin{array}{cc} -\text{ pole} & +\text{ pole} \\ H_2,\ H^+ & Cl^-,\ Cl_2 \end{array}$$

$$E^\circ_{Na} - E^\circ_{H_2} = E^\circ \text{ cell}$$

$$\begin{array}{cc} -\text{ pole} & +\text{ pole} \\ Na,\ Na^+ & H^+,\ H_2 \end{array}$$

The cell is divided into two half cells, the electrode reactions of which combine to give the cell reaction.

ELECTRODE REACTION	E°	ELECTRODE REACTION	E°
$1/2\ H_2 = H^+ + E^-$	0.0000	$Na = Na^+ + E^-$	+2.9224
$E^- + 1/2\ Cl_2 = Cl^-$	−1.3594	$E^- + H^+ = 1/2\ H_2$	0.0000
$1/2\ H_2 + 1/2\ Cl_2 = H^+ + Cl^-$	+1.3594	$Na + H^+ = Na^+ + 1/2\ H_2$	+2.9224

Thus the potential of the chlorine electrode, Cl_2, Cl^-, which corresponds to the reaction, $Cl^- = 1/2\ Cl_2 + E^-$, is -1.3594 volts and the potential of the sodium electrode Na, Na^+, which corresponds to the reaction, $Na = Na^+ + \mathbf{E}^-$, is $+ 2.9224$ volts. In order to illustrate further this convention, the electromotive force of the cell will be calculated in which sodium chloride in its solution of unit activity is formed from the elements in their standard states.

ELECTRODE	E°	ELECTRODE REACTION
Na, Na^+	$+2.7125$	$Na \qquad = Na^+ + E^-$
Cl^-, Cl_2	$+1.3594$	$E^- + 1/2\ Cl_2 = Cl-$
Na, Na^+, Cl^-, Cl_2	$+4.0719$	$Na + 1/2\ Cl_2 = Na_2 + Cl^-$

The free energy increase, ΔF attending the formation of one mol of NaCl in its solution of unit activity is given by the equation $\Delta F^\circ = -\mathbf{NE^\circ F}$ and is numerically equal to $-93{,}955$ calories. This latter calculation illustrates the importance of a table of electrode potentials free from liquid potential corrections.

V. In order to obtain the potential of a half cell in which the substances are not in their standard states, the electrode reaction is written and the following formulae apply. Consider the chlorine electrode, Cl^- (C, molal), Cl_2 (P atm.) and its electrode reaction, $1/2\ Cl_2$ (P atm.) $+ E^- = Cl^-$ (C, molal).

$$\Delta F = \Delta F^\circ + RT \ln \frac{a(Cl^-)}{p^{\frac{1}{2}}(Cl_2)} = \Delta F^\circ + RT \ln \frac{\gamma C(Cl^-)}{p^{\frac{1}{2}}(Cl_2)}$$

$$\mathbf{E} = \mathbf{E}^\circ - \frac{\mathbf{RT}}{\mathbf{NF}} \ln \frac{a(Cl^-)}{p^{\frac{1}{2}}(Cl_2)} = \mathbf{E}^\circ - \frac{\mathbf{RT}}{\mathbf{NF}} \ln \frac{\gamma C(Cl^-)}{p^{\frac{1}{2}}(Cl_2)}$$

The activity and the activity coefficient are "a" and "γ" respectively, which are employed instead of concentration for precise calculation. However, the lack of precise information concerning the activities of the individual ions considerably hampers accurate calculation of the potential of half cells. This difficulty can be easily avoided by combining two half cells into a cell in such a way as to avoid liquid potentials. Except for oxidation-reduction cells, the electromotive force of the complete cell, in which the substances exist in states other than their standard states, may be accurately evaluated with the aid of a table of activity coefficients. Suppose that the electromotive force of a cell consisting of sodium and chlorine electrodes in a saturated solution of sodium chloride were desired. The molality is 6.12 and the activity coefficient 1.013(2). If the sodium chloride solution is of unit activity, the electromotive force of the cell is 4.0719 volts. The change of state is $Na + 1/2\ Cl_2 = Na^+ + Cl^-$ and the equation relating the electromotive force to the state of the substance is $\mathbf{E} = \mathbf{E}^\circ\ \frac{\mathrm{RT}}{\mathbf{NF}} \ln \frac{a_2(\mathrm{NaCl})}{p\frac{1}{2}\mathrm{Cl}_2}$. Since the activity of the 6.12 molal NaCl solution is the square of the product of the molality and the activity coefficient 1.013, the electromotive force of the cell Na, $NaCl(sat)Cl_2$ containing the saturated solution is 3.9781 volts. The necessity of using the activities of the dissolved solute instead of the individual activities of the ions is to be especially noted in a cell of the type H_2, H_2SO_4, $Hg_2SO_4(s)$, Hg. This feature is more than offset by the advantage gained in that the half cell offers the most compact method of accurately tabulating electromotive force data.

In table 1 is the list of electrode potentials summarized by Lewis and Randall,[2] which are based upon their activity coefficients.

II. REFERENCE AMALGAM ELECTRODES FOR METALS

The fact that two-phase amalgam electrodes are employed in standard cells in place of pure solid metal electrodes is a strong argument for using the former type of electrodes in exact electromotive force measurements. Greater reproducibility with less effort and without analysis of two-phase amalgams are the principal advantages over the solid metal electrodes. If the electromotive force of a cell whose electrodes consist of the pure metal and the two-phase amalgam has been carefully measured, the results obtained with the reference two-phase amalgam electrode can easily be corrected.

TABLE 1

Single electrode potentials at 25°

	ELECTRODE	ELECTRODE REACTION	E°
1	Li, Li^+	$Li = Li^+ + E^-$	2.957_8
2	Rb, Rb^+	$Rb = Rb^+ + E^-$	2.924_2
3	K, K^+	$K = K+ + E^-$	2.922_4
4	Na, Na^+	$Na = Na^+ + E^-$	2.712_5
5	Zn, Zn^{++}	$Zn = Zn^{++} + 2E^-$	0.758_1
6	Fe, Fe^{++}	$Fe = Fe^{++} + 2E^-$	0.44_1
7	Cd, Cd^{++}	$Cd = Cd^{++} + 2E^-$	0.397_6
8	Tl, Tl^+	$Tl = Tl^+ + E^-$	0.336_3
9	Sn, Sn^{++}	$Sn = Sn^{++} + 2E^-$	0.13_6
10	Pb, Pb^{++}	$Pb = Pb^{++} + 2E^-$	0.12_2
11	Pt, H_2, H^+	$1/2\,H_2 = H^+ + E^-$	0.000_0
12	Cu, Cu^{++}	$Cu = Cu^{++} + 2E^-$	-0.344_8
13	Hg, Hg_2^{++}	$2\,Hg = Hg_2^{++} + 2E^-$	-0.798_6
14	Ag, Ag^+	$Ag = Ag^+ + E^-$	-0.799_5
15	Pt, I_2, I^-	$I^- = 1/2\,I_2 + E^-$	-0.535_7
16	Pt, Br_2, Br^-	$Br^- = 1/2\,Br_2 + E^-$	-1.065_9
17	Pt, Cl_2, Cl^-	$Cl^- = 1/2\,Cl_2 + E^-$	-1.359_4
18	Pt, H_2, OH^-	$1/2\,H_2 + OH^- = H_2O = E^-$	$+0.828_0$
19	Ba (Hg), Ba^{++} (1)	$Ba\,(Hg) = Ba^{++} + 2E$	1.837_6
20	Sr (Hg), Sr^{++} (1)	$Sr\,(Hg) = Sr^{++} + 2E$	1.790_8

(1) Danner, *J. Am. Chem. Soc.*, **46**, 2385 (1924).

Thus in order to measure the potential of cell III, in which the reaction, $Zn(s) + Hg_2SO_4(s) = ZnSO_4(xm) + 2\,Hg$, tends to take place, it is necessary only to measure the electromotive force of cell II, and add to it the value of cell I.

I. Zn(s), Zn^{++}, Zn(Hg) (2 phase)
II. Zn(Hg) (2 phase), $ZnSO_4(xm)$, $Hg_2SO_4(s)$, Hg
III. Zn(s), $ZnSO_4(xm)$, Hg_2SO_4, Hg

In table 2 are listed values of the potentials of several pure metals against their two-phase amalgams.

III. STANDARD REFERENCE ELECTRODES

This section contains a compact summary of very useful data. In the main, these half cells are free from liquid potential corrections. Instead of choosing the final most probable values for these half cells, the data of different observers are exhibited in order to illustrate the usefulness of this method of intercomparison, the advisability of the discontinuance of certain reference electrodes, and the necessity of the use of oxygen free electrolytes in practically all cells.

TABLE 2

Reference amalgam electrodes

CELL	E.M.F. AT 25°	$\Delta E/\Delta T$	REFERENCE
Na, Na$^+$, Na(Hg)	0.782_1		1, 5, 8, 11
Cd, Cd^{++}, Cd(Hg)	0.050_5	−0.000244	2, 3, 7, 9, 13
Zn, Zn^{++}, Zn(Hg)	0.004_7		3, 14
Pb, Pb^{++}, Pb(Hg)	0.005_7	0.000016	6
Tl, Tl$^+$, Tl(Hg)	0.002_4	0.000032	6, 12, 14
Cu, Cu^{++}, Cu(Hg)	0.002_4	−0.000138	10
CdPb(Hg), Cd^{++}, Cd(Hg)	0.001_1	0.000027	15
CdSn(Hg), Cd^{++}, Cd(Hg)	0.001_0	0.000032	15
CdBi(Hg), Cd^{++}, Cd(Hg)	0.001_7	0.000080	15
CdCu(Hg), Cd^{++}, Cd(Hg)	0.000005	0.0000005	15

(1) Allmand and Pollack, *J. Chem. Soc.*, **115**, 1020 (1919).
(2) Cohen, *Z. Physik. Chem.*, **34**, 612 (1900).
(3) Cohen and Moesvald, *Z. Physik. Chem.*, **95**, 285 (1920).
(4) Cohen and Tombrock, *Verslag. Akad. Wetenschappen Amsterdam*, **18**, 17 (1909).
(5) Danner, *J. Am. Chem. Soc.*, **44**, 2832 (1922).
(6) Gerke, *J. Am. Chem. Soc.*, **44**, 1684 (1922).
(7) Hulett, *Trans. Am. Electrochem.* Soc., **7**, 353 (1905).
(8) Lewis and Kraus, *J. Am. Chem Soc.*, **32**, 1459 (1910).
(9) Obata, *Proc. Phys. Math. Soc. Japan*, [3] **3**, 64 (1921).
(10) Obata, *Proc. Phys. Math. Soc. Japan*, [3] **2**, 225 (1921).
(11) Richards and Conant, *J. Am. Chem. Soc.*, **44**, 601 (1922).
(12) Richards and Daniels, *J. Am. Chem. Soc.*, **41**, 2452 (1919).
(13) Richards and Lewis, *J. Am. Chem. Soc.*, **28**, 1 (1899).
(14) Richards and Smyth, *J. Am. Chem. Soc.*, **44**, 324 (1922).
(15) Vosburgh, Unpublished Measurements.

Conventions

I. The conventions for half cells, as the calomel electrode which consists of an insoluble salt and a soluble ion, are the same as for the half cells in section I.

$$\mathrm{Hg(1)},\ \mathrm{Hg_2Cl_2(s)},\ \mathrm{Cl^-}(a = 1),\ E = E^\circ - \frac{RT}{NF} \ln a(\mathrm{Cl^-})$$

II. In order to place half-cells of the *soluble salt* type, such as Na(s), NaCl(s), NaCl(sat. sol.) in the table with other half cells, and also because of the lack of activity data in saturated solution of soluble salts, a new and arbitrary convention will be employed. This convention relates to the magnitude of the electromotive force of such an electrode of the type just mentioned. The convention is that the total electromotive force of a cell containing a soluble salt electrode is equal to the difference of the electromotive force, **E′** of the insoluble salt half cell and the standard electromotive force, **E°**, of the reference electrode. As an illustration consider the cell, Na(s), NaCl(s), NaCl(sat. sol.) Hg_2Cl_2, Hg, which contains no liquid potential. The electromotive force of the whole cell, **E**, is related to **E′** Na(s), NaCl(s), NaCl(sat. sol.) and to **E°** (Cl^-, Hg_2Cl_2, Hg) by the equation, $\mathbf{E} = \mathbf{E}' - \mathbf{E}°$.[4]

This equation appears to indicate the existence of a liquid potential between the saturated sodium chloride solution and a solution of sodium chloride of unit activity. Such is not the case, since the cell under discussion has for its electrolyte saturated sodium chloride throughout the whole cell. It is understood that an electrode, (Na(s), NaCl(s), NaCl (sat. sol.) should be combined with chloride ion reference electrodes and not with other types such as the mercurous sulphate, mercury half cell. In order to distinguish soluble salt half cells from the insoluble salt type and also because of the abitrariness of the convention, no electrode reactions will be tabulated for the soluble salt electrodes.

In table 3 each cell will be followed by not more than four references—namely, (1) the reference to the author, (2) the reference

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[4] There is an alternative method for stating this convention in terms of the single electrode potential of the metal and the activity of the saturated salt solution. It can be briefly illustrated for this particular case by the equation, $\mathbf{E}' = \mathbf{E}°\ (\mathrm{Na}) - \mathbf{E}°\ (\mathrm{Hg},\ Hg_2Cl_2,\ Cl^-) - \frac{\mathbf{RT}}{\mathbf{NF}} \ln a_2(\mathrm{NaCl}) - \mathbf{E}°(\mathrm{Hg},\ Hg_2Cl_2,\ Cl^-) = \mathbf{E}°\ (\mathrm{Na}) - \frac{\mathbf{RT}}{\mathbf{NF}} \ln a_2(\mathrm{NaCl})$. All the changes in electromotive force of the whole cell, due to changes in concentration of the electrolyte are thus found to be collected in the potential of the soluble salt half cell.

TABLE 3

Standard reference electrodes†

	ELECTRODE	ELECTRODE REACTION	E° AT 25°	REFERENCE
1	Na(Hg), NaCl(s), (sat)		1.835_4	6, III 31, 0
2	Al(Hg), $Al(OH)_3$(s), OH^-	Al(Hg) + 3 OH^- = $Al(OH)_3$ + 3 E^-	1.6_2	12, III 36, 0
3	Zn(Hg), $ZnSO_4 \cdot 7\ H_2O$(s), (sat.)		0.799_3	34, III 35
4a	Cd(Hg), $CdCl_2$, (sat.)		0.40_{13}	25, III 31
4b	Cd(Hg), $CdCl_2$, (sat.)		0.40_{08}	23, III 13
5a	Cd(Hg), $CdBr_2 \cdot 4\ H_2O$(s), (sat.)		0.41_{99}	25, III 33
5b	Cd(Hg), $CdBr_2 \cdot 4\ H_2O$(s), (sat.)		0_{5166}	23, III 14
6a	Cd(Hg), CdI_2, (sat.)		0.45_{36}	35, III 27a
6b	Cd(Hg), CdI_2, (sat.)		0.45_{52}	25, III 34a
6c	Cd(Hg), CdI_2, (sat.)		0.45_{75}	23, III 15
6d	Cd(Hg), CdI_2, (sat.)		0.45_{76}	36, III 15, O
7a	Cd(Hg), $CdSO_4 \cdot 8/3\ H_2O$, (sat.)		0.397_1	25, III 35
7b	Cd(Hg), $CdSO_4 \cdot 8/3\ H_2O$, (sat.)		0.434_6	23, III 16
8	Cd(Hg), $Cd(OH)_2$(s), OH^-	Cd(Hg) + 2 OH^- = $Cd(OH)_2$ + 2 E^-	0.76_1	20, III 36
9	Cd(Hg), CdO(s), OH^-	Cd(Hg) + 2 OH^- = CdO + H_2O + 2 E^-	0.72_6	20, III 36
10	Tl(Hg), TlCl(s), Cl^-	Tl(Hg) + Cl^- = TlCl + E^-	0.552_1	8, III 25
11	Tl, TlI(s), I^-	Tl + I^- = TlI + E^-	0.77_{03}	16, I 15 la le
12	Tl(Hg), Tl_2SO_4(s), SO_4^-	Tl(Hg) + $SO_4^=$ = Tl_2SO_4 + 2 E^-	0.436_0	13, III 25, 0
13	Pb(Hg), $PbCl_2$(s), Cl—	Pb(Hg) + 2Cl^- = $PbCl_2$ + 2 E^-	0.259_9	8, III 31, 0
14	Pb(Hg), $PbBr_2$(s), Br^-	Pb(Hg) + 2 Br^- = $PbBr_2$ + 2 E^-	0.368_3	9, I 16, 0
15	Pb(Hg), PbI_2(s), I^-	Pb(Hg) + 2 I^- = PbI_2 + 2 E^-	0.357_9	8, I 17, 0
16	Pb(Hg), $PbSO_4$(s), SO_4^-	Pb(Hg) + $SO_4^=$ = $PbSO_4$ + 2 E^-	0.343_3	11, III 35
17	Pb, PbS(s), H_2S(1 atm.), H^+	Pb + H_2S = PbS + 2 H^+ + 2 E^-	-0_{070}	17, III 28, la
18a	Pb, PbO(red), OH^-	Pb + OH^- = PbO + H_2O + 2E^-	0.578_6	32, I 11, le, 0
18b	Pb, PbO(red), OH^-	Pb + 2 OH^- = PbO + H_2O + 2 E^-	0.58_{29}	2, III 36, le
19	Pb, PbO(yellow), OH^-	Pb + 2 OH^- = PbO + H_2O + 2 E^-	0.57_{55}	2, III 36, le

20	Pb(Hg), PbO(hydrate), OH^-		0.56_7	7, III 36, 1e
21a	Cu(Hg), CuCl(s), Cl^-	$Cu(Hg) + Cl^- = CuCl + E^-$	-0.1_{405}	3, III 31
21b	Cu, CuCl(s), Cl^-	$Cu(Hg) + Cl^- = CuCl + E^-$	-0.1_{21}	21, I 11, 1e
22a	Cu(Hg), $CuSO_4 \cdot 5\ H_2O$, (sat.)		-0.268_4	24, III 35
22b	Cu(Hg), $CuSO_4 \cdot 5\ H_2O$, (sat.)		-0.268_4	26, III 35
23	Cu, CuS(s), H_2S(1 atm.), H^+	$Cu + H_2S = CuS + 2\ H^+ + 2\ E^-$	$+0_{259}$	17, III 28, 1o
24	Cu, Cu_2O(s), OH^-	$2\ Cu + 2\ OH^- = Cu_2O + H_2O + 2\ E^-$	0.34_4	1, III 31
25a	Ag (elec. fine crystals), AgCl (ppted), Cl^-	$Ag + Cl^- = AgCl + E^-$	-0.224_5	8, III 31
25b	Ag (elec. powder), AgCl (Chem. ppt.), Cl^-	$Ag + Cl^- = AgCl + E^-$	-0.223_4	37, I 11
25c	Ag(elec. plate), AgCl(elec.), Cl^-	$Ag + Cl^- = AgCl + E^-$	-0.223_4	39, I 11
25d	Ag(Reduc. oxide), AgCl(elec.), Cl^-	$Ag + Cl^- = AgCl + E^-$	-0.223_3	38, I 11
26a	Ag(elec.), AgBr(elec.), Br^-	$Ag + Br^- = AgBr + E^-$	-0.0_{732}	19, I 11
26b	Ag(elec.), AgBr(elec.), Br^-	$Ag + Br^- = AgBr + E^-$	-0.1_{784}	28, I 3
27a	Ag(elec. fine crystals), AgI(ppted.), I^-	$Ag + I^- = AgI + E^-$	$+0.15_{01}$	8, III 15, 0
27b	Ag(elec. fine crystals), AgI(ppted.), I^-	$Ag + I^- = AgI + E^-$	0.15_{13}	27, I 11
27c	Ag(elec. fine crystals), AgI(ppted.), I^-	$Ag + I^- = AgI + E^-$	0.15_{22}	22 I 11
27d	Ag(elec. fine crystals), AgI(ppted.), I^-	$Ag + I^- = AgI + E^-$	0.1_{634}	35, III 15
28	Ag, Ag_2S(s), H_2S(s), H_2S(1 atm.) + H^-	$2\ Ag + H_2S = Ag_2S + 2\ H^- + 2\ E^-$	0.036_6	22, I 11
29	Ag, $AgBrO_3$(s), BrO_3^-	$Ag + BrO_3^- = AgBrO_3 + E^-$	-0.68_0	29, I 14, 1o
30	Ag, Ag_2CO_3(s), $CO_3 =$	$2\ Ag + CO_3 = Ag_2CO_3 + 2\ E^-$	-0.50_0	33, III 31, 1o
31	Hg, Hg_2Cl_2(s), Cl^-*	$2\ Hg + 2\ Cl^- = Hg_2Cl_2 + 2\ E^-$	-0.270_0*	18
33	Hg, Hg_2Br_2(s), Br^-	$2\ Hg + 2\ Br^- = Hg_2Br_2 + 2\ E^-$	-0.13_{68}	10, III 31, 1o
34a	Hg, Hg_2I_2(s), I^-	$2\ Hg + 2\ I^- = Hg_2I_2 + 2\ E^-$	0.04_{32}	4, III 33, 1o
34b	Hg, Hg_2I_2(s), I—	$2\ Hg + 2\ I- = Hg_2I_2 + 2\ E^-$	0.04_{14}	25, III 6a
34c	Hg, Hg_2I_2(s), I^-	$2\ Hg + 2\ I^- = Hg_2I_2 + 2\ E^-$	0.040_4	36, III 15, 0
35	Hg, Hg_2SO_4(s), SO_4=	$2\ Hg + SO_4^= = Hg_2SO_4 + 2\ E^-$	-0.621_3	18
36	Hg, HgO(red), OH^-	$Hg + 2\ OH^- = HgO + H_2O + 2\ E^-$	-0.098_4	18
37	Hg, HgO(yellow), OH^-	$Hg + 2\ OH^- = HgO + H_2O + 2\ E^-$	-0.099_1	5, III 36

TABLE 3—*Continued*

	ELECTRODE	ELECTRODE REACTION	E° AT 25°	REFERENCE
38	Au, Au^{+++}	$Au = Au^{+++} + 3\ E^-$	-1.3_6	15
39a	As, $As_2O_3(s)$, H^+	$2\ As + 3\ H_2O = As_2O_3 + 6\ H^+ + 6\ E^-$	-0.234_0	31, I 11, 1e
39b	As, $HAsO_2$, H^+	$As + 2\ H_2O = HAsO_2 + 3\ H^+ + 3\ E^-$	-0.237_5	31, I 11, 1e
40a	Sb, $Sb_2O_3(s)$, H^+	$Sb + 3\ H_2O = Sb_2O_3 + 6\ H^+ + 6\ E^-$	-0.15_2	30, I 11, 1e
40b	Sb, SbO^+. H^+	$Sb + H_2O = SbO^+ + 2\ H^+ + 3\ E^-$	0.21_2	30, I 11, 1e
41a	Bi, BiOCl(s), $H^+ + Cl^-$	$Bi + Cl^- + H_2O = BiOCl + 2\ H^+ + 3\ E^-$	-0.155_9	21, I 11, 1e
41b	Bi, BiOCl(s), $H^+ + Cl^-$	$Bi + Cl^- + H_2O = BiOCl + 2\ H^+ + 3\ E^-$	-0.14	14, III 31, 1o

(1) Allmand, *J. Chem. Soc.*, **95**, 2151 (1909).
(2) Applebey and Reed, *J. Chem. Soc.*, **121**, 2129 (1922).
(3) Bronsted, *Z. Physik. Chem.*, **80**, 206 (1912).
(4) Bugarsky, *Z. Anorg. Chem.*, **14**, 145 (1897).
(5) Cohen, *Z. Physik. Chem.*, **34**, 69 (1900).
(6) Danner, *J. Am. Chem. Soc.*, **44**, 2832 (1922).
(7) Gerke, Unpublished measurements.
(8) Gerke, *J. Am. Chem. Soc.*, **44**, 1684 (1922).
(9) Gerke and Gordon, Unpublished measurements.
(10) Goodwin, *Z. Physik. Chem.*, **13**, 652 (1894).
(11) Henderson and Stegeman, *J. Am. Chem. Soc.*, **40**, 84 (1918).
(12) Heyrovsky, *J. Chem. Soc.*, **117**, 27 (1920).
(13) Ishikawan, *J. Chem. Soc.* Japan, **43**, 560 (1922).
(14) Jelinek and Kuhn, *Z. Physik. Chem.*, **105**, 337 (1923).
(15) Jersa and Jelinek, *Chem. Listy*, **18**, 1 (1924).
(16) Jones and Schumb, *Proc. Am. Acad. Arts Sci.*, **56**, 199 (1921).
(17) Knox, *Trans. Faraday Soc.*, **25**, 2 (1909).
(18) Lewis and Randall, Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill. (1923).
(19) Lewis and Storch, *J. Am. Chem. Soc.*, **39**, 2544 (1917).
(20) McRay, Thesis 1917, Mass. Inst. Technology.
(21) Noyes and Chow, *J. Am. Chem. Soc.*, **40**, 739 (1918).

(22) Noyes and Free, *J. Am. Chem. Soc.*, **42**, 476 (1920).
(23) Obata, *Proc. Phys. and Math. Soc. Japan*, [3] **3**, 64 (1921).
(24) Obata, *Proc. Phys. and Math. Soc. Japan*, [3] **2**, 225 (1921).
(25) Oeholm, *Acta Soc. Scientiarum Fennicae*, **41**, 1 (1913).
(26) Oeholm, *Medd. K. Vetenskapsakad.* Nobelinst., **5**, 1 (1919).
(27) Pearce and Fortsch, *J. Am. Chem. Soc.*, **45**, 2852 (1923).
(28) Pearce and Hart, *J. Am. Chem. Soc.*, **43**, 2483 (1921).
(29) Reedy, *J. Am. Chem. Soc.*, **43**, 1440 (1921)
(30) Schuhmann, *J. Am. Chem. Soc.*, **46**, 52 (1924).
(31) Schuhmann, *J. Am. Chem. Soc.*, **46**, 1444 (1924).
(32) Smith and Woods, *J. Am. Chem. Soc.*, **45**, 2632 (1923).
(33) Spencer and LaPla, *Z. Anorg. Chem.*, **65**, 10 (1909).
(34) Steinwehr, *Z. Instrk.*, **33**, 321 (1913).
(35) Taylor and Perrot, *J. Am. Chem. Soc.*, **43**, 484 (1921).
(36) Vosburgh, Unpublished measurements.
(37) Linhart, *J. Am. Chem. Soc.*, **41**, 1175 (1919).
(38) Noyes and Ellis, *J. Am. Chem. Soc.*, **39**, 2532 (1917).
(39) Scatchard, Unpublished Measurements.

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* The activity coefficients used in this table are those of Lewis and Randall (ref. 18).

† The value, −0.2700 for the calomel electrode is based on concordant measurements in 0.1 M HCl and upon the activity coefficient 0.814 for 0.1 HCl derived from Lewis and Randall's interpretation of Linhart's measurements on the cell, H_2, HCl, AgCl, Ag. Recently, Randall and Vanselow, *J. Am. Chem. Soc.* **46**, 2418 (1924), have obtained a value, 0.809 for the activity coefficient of 0.1 M HCl from freezing point measurements. Still more recently, Scatchard (unpublished) has carefully analyzed the electromotive force measurements of Linhart and of his own and also the freezing point measurements of Randall and Vanselow. His interpretation gives 0.801 from electromotive force and 0.804 from freezing point for the activity coefficient of 0.1 M HCl. The true value for the electromotive force of the calomel electrode should be some value between the values −0.2700 ($\gamma = 0.814$) and −0.2692 ($\gamma = 0.801$). Doubt is cast upon the present value, − 0.2700. A change in the value of the calomel electrode, due to a change in the value of the activity coefficient of hydrochloric acid, would not only affect most all of the values of standard electrode potentials of chlorides but many of the values of bromides and iodides as well. The author believes it best to defer such a change in the values of the electrode potentials until after discussion has taken place. It must be borne in mind that the calomel electrode in table 3 may be in error by as much as 0.0008 volts.

to other standard reference electrodes which were used in evaluating the given one, (3) the type of liquid junction correction existing in the experimental potential, and (4) the letter, O, indicates that dissolved oxygen was not present in the cell electrolyte. For example, the electromotive force of cell III 1 in table 3 was derived from reference 6 in section III and with the aid of half cell III 31 in table 3. It has no liquid potential correction and dissolved oxygen was not present in the cell electrolyte. Liquid potential corrections will be classified as lo, lc, and le, respectively. The ordinary type K Cl; $NaNO_3$ will be designated as "lo;" the concentration cell type HCl, c_1; HCl, c_2 as "lc" and the electrode type as "le." The latter type which is sometimes unavoidable is eliminated in the second cell.

Tl(Hg), TlCl(s), KCl, Hg_2Cl_2(s), Hg(l)
Tl(Hg), TlCl(s), KCl, Hg_2Cl_2(s) + TlCl(s), Hg

IV. OXIDATION-REDUCTION ELECTRODE POTENTIALS

There are two outstanding difficulties in the interpretation of oxidation-reduction potential half cells. The first difficulty consists of the incomplete elimination of liquid potentials and the second consists of the lack of precise data on the activity of an electrolyte in the presence of one or more electrolytes. In the main, the published data in this field abounds with unnecessary liquid potential corrections which cannot be precisely computed.

There are two general classes of reversible oxidation-reduction potential half cells, namely, (1) those in which liquid potentials are not necessary, and (2) those in which liquid potentials can be reduced to a negligible value by a careful choice of relative concentrations of electrolytes. As an illustration of the first class, consider the two half cells III 16 and IV 14 combined to make a cell. The cell reaction is $Pb(Hg) + PbO_2 + 2\ H_2SO_4 = 2\ PbSO_4 + 2\ H_2O$ and no liquid potential exists in the cell, due to the insolubility of lead sulphate and lead dioxide. However, if half cells III 13 and IV 14 were combined, a liquid potential would exist at the boundary of the sulphuric and hydrochloric acids.

The combination of half cells III 31 and IV 11 results in the cell reaction

$$2\ Hg + 4\ H^+ + 2\ Cl^- + MnO_2 = Hg_2Cl_2 + Mn^{++} + 2\ H_2O$$

or

$$2\ Hg + 4\ HCl + MnO_2 = Hg_2Cl_2 + MnCl_2 + 2\ H_2O$$

This cell has no liquid potential, due to the insolubility of manganese dioxide, if manganous chloride and hydrochloric acid are used as the electrolyte throughout the whole cell. In the case of the lead, lead sulphate, lead dioxide cell, sulphuric acid is the cell electrolyte. With the aid of a table of activity coefficients, it is possible to precisely calculate the change of electromotive force of the cell with a change of concentration of sulphuric acid. On the other hand, in cells III 31 and IV 11 mentioned above, the electrolyte is a mixture of manganous chloride and hydrochloric acid and the calculation of the electromotive force at different concentrations involves data on the activity coefficients of both electrolytes in the presence of each other.

The second class of oxidation-reduction potential half cells involves liquid potentials which can be made negligible by a careful choice of relative concentrations of electrolytes. The $Fe^{++} - Fe^{+++}$ potential may be studied in either of the following types of cells:

Pt, $FeCl_2$ 1.0 M + $FeCl_3$ 0.001 M, $FeCl_2$ 1.0 M, Hg_2Cl_2, Hg
Pt, $FeCl_2$ 0.001 M + $FeCl_3$ 0.001 M + HCl 1.0 M, HCl 1.0 M, Hg_2Cl_2, Hg

In either cell the cell reaction may be written:

$$FeCl_2 + 1/2\ Hg_2Cl_2 = FeCl_3 + Hg$$

The precise interpretation of such results requires a knowledge of the activities of ferric chloride in the presence of ferrous chloride in the first cell and in ferrous chloride and hydrochloric acid in the second cell.

Most of the values for oxidation and reduction potential half cells tabulated in table 4 were derived from cells in which unnecessary liquid potentials exist and can be regarded as rough provisional values, pending the results of more precise research.

TABLE 4

Oxidation-reduction electrode potentials

	ELECTRODE	ELECTRODE REACTION	E° AT 25°	REFERENCE
1	Pt, H_3AsO_3, H_3AsO_4, H^+	$H_3AsO_3 + H_2O = H_3AsO_4 + 2\,H^+ + 2\,E^-$	-0.49_8 (equil)	(22)
2	Pt, Ce^{+++}, Ce^{++++}	$Ce^{+++} = Ce^{++++} + E^-$	-1.5_5	(3)
3a	Pt, Co^{++}, Co^{+++}	$Co^{++} = Co^{+++} + E^-$	-1.81_7	(11)
3b	Pt, Co^{++}, Co^{+++}	$Co^{++} = Co^{+++} + E^-$	-1.77_6 (at 0°)	(20)
4	Hg, Cr^{++}, Cr^{+++}	$Cr^{++} = Cr^{+++} + E^-$	$+0.40_0 \left(-0.065 \log \frac{Cr^{+++}}{Cr^{++}}\right)$	(7)
5	Pt, Cu_2O, $Cu(OH)_2$, OH^-	$Cu_2O + 2\,OH^- + H_2O = 2\,Cu(OH)_2 + 2\,E^-$	0.08_2	(1)
6	Pt, Cu_2O, CuO(aged), OH^-	$Cu_2O + 2\,OH^- = 2\,CuO + H_2O + 2\,E^-$	0.15_4	(2)
7a	Pt, Fe^{++}, Fe^{+++}	$Fe^{++} = Fe^{+++} + E^-$	-0.7_{38} (including liq. pot.)	(14)
7b	Pt, Fe^{++}, Fe^{+++}	$Fe^{++} = Fe^{+++} + E^-$	-0.74_7 (equil.)	(14)
8	Pt, $K_4Fe(CN)_6$, $K_3Fe(CN)_6$	$K_4Fe(CN)_6 = K_3Fe(CN)_6 + K^+ + E^-$	-0.489_0	(12)
9	Pt, $Br_2(l)$, BrO_3^-, H^+	$1/2\,Br_2 + 3\,H_2O = BrO_3^- + 6\,H^+ + 5\,E^-$	-1.49_1	(18)
10	Pt, $I_2(s)$, IO_3^-, H^+	$1/2\,I_2 + 3\,H_2O = IO_3^- + 6\,H^+ + 5\,E^-$	-1.19_7	(19)
11	Pt, Mn^{++}, MnO_2, H^+	$Mn^{++} + 2\,H_2O = MnO_2 + 4\,H^+ + 2\,E^-$	-1.33_2	(21)
12	Pt, MnO_4^{--}, MnO_4^-	$MnO_4^{--} = MnO_4^- + E^-$	-0.66_4	(17)
13	Pt, MnO_2, MnO_4^{--}, OH^-	$MnO_2 + 4\,OH^- = MnO_4^{--} + 2\,H_2O + 2\,E^-$	-0.71_8 (equil)	(15)
14	Pt, $PbSO_4$, PbO_2, H^+, $SO_4^=$	$PbSO_4 + 2\,H_2O = PbO_2 + 4\,H^+ + SO_4^= + 2\,E^-$	-1_7	(10)
15	Pt, PbO, PbO_2, OH^-	$PbO + 2\,OH^- = PbO_2 + H_2O + 2\,E^-$	-0_{27}	(8)
16	Hg, Sn^{++}, Sn^{++++}	$Sn^{++} = Sn^{++++} + 2\,E^-$ (+ 0.011Cl)	$-1.25_6 \left(-0.03 \log \frac{Sn^{++++}}{Sn^{++}}\right)$	(5)
17	Hg, Ti^{++}, Ti^{+++}	$Ti^{++} = Ti^{+++} + E^-$	-0.3_7	(6)
18	Pt, Ti^{+++}, $Ti(SO_4)_2$, $SO_4^=$	$Ti^{+++} + 2\,SO_4^= = Ti(SO_4)_2 + E^-$	-0.0_4	(4)
19	Pt, Tl^+ Tl^{+++}	$Tl^+ = Tl^{+++} + 2\,E^-$	-1.2_{11}	(9)
20	Pt, UO_2SO_4, $U(SO_4)_2$, $SO_4^=$	$U(SO_4)_2 + 2\,H_2O = UO_2SO_4 + 4\,H^+ + SO_4^= + 2\,E^-$	-0.3_{58}	(13)
21	Pt, VSO_4, $(VO)_2SO_4$, H^+, $SO_4^=$	$VSO_4 + H_2O = 1/2(VO)_2SO_4 + 2\,H^+ + 1/2\,SO_4^= + E^-$	$+0.2_1$	(16)
22	Pt, $(VO)_2SO_4$, $VOSO_4$, $SO_4^=$	$1/2\,(VO)_2SO_4 + 1/2\,SO_4^= = VOSO_4 + E^-$	-0.3_0	(16)
23	Pt, $(VO)SO_4$, HVO_3, H_2SO_4	$VOSO_4 + 2\,H_2O = HVO_3 + H_2SO_4 + E^-$	-0.9_2	(16)

(1) Allmand, *J. Chem. Soc.*, **95,** 2151 (1909).
(2) Allmand, *J. Chem. Soc.*, **97,** 603 (1910).
(3) Bauer and Glaesnner, *Z. Elektrochem.*, **9,** 534 (1903).
(4) Diethelm and Foerster, *Z. Physik. Chem.*, **62,** 138 (1908).
(5) Forbes and Bartlett *J. Am. Chem. Soc.*, **36,** 2030 (1914).
(6) Forbes and Hall, *J. Am. Chem. Soc.*, **46,** 385 (1924).
(7) Forbes and Richter, *J. Am. Chem. Soc.*, **39,** 1140 (1917).
(8) Glasstone, *J. Chem. Soc.*, **121,** 1456 (1922).
(9) Grube and Herman, *Z. Elektrochem.*, **26,** 291 (1920).
(10) Kendrick, *Z. Elektrochem.*, **7,** 52 (1900).
(11) Lamb and Larson, *J. Am. Chem. Soc.*, **42,** 2024 (1921).
(12) Lewis and Sargent, *J. Am. Chem. Soc.*, **31,** 355 (1909).
(13) Luther and Michie *Z. Elektrochem.*, **14,** 826 (1908).
(14) Noyes and Brann, *J. Am. Chem. Soc.*, **34,** 1016 (1912).
(15) Ruby, *J. Am. Chem. Soc.*, **43,** 294 (1921).
(16) Rutter, *Z. Anorg. Chem.*, **52,** 368 (1907).
(17) Sackur and Taegener, *Z. Elektrochem.*, **18,** 718 (1912).
(18) Sammet, *Z. Physik. Chem.*, **53,** 678 (1905).
(19) Sammet, *Z. Physik. Chem.*, **53,** 641 (1905).
(20) St. Jahn, *Z. Anorg. Chem.*, **60,** 292 (1908).
(21) Tower, *Z. Physik. Chem.*, **32,** 566 (1900).
(22) Washburn and Strachan, *J. Am. Chem. Soc.*, **35,** 681 (1913).

DISCUSSION

It may be interesting to quote a few statistics, which can be obtained from the tables of electrode potentials. Only thirty-two of the ninety-two elements are found in the tables. Only twenty elements, including both electropositive and electronegative enter directly into reversible electrode reactions. In a broad sense it is apparent that electromotive force measurements have been applied to only a rather limited number of elements in the periodic table.

Although many elements have been studied, which have been found to give irreversible electrodes, the field of precise electromotive force measurements is still fertile and well worth cultivating. For example, practically all of the oxidation-reduction potential electrodes need to be more precisely reinvestigated with the purpose of obtaining more accurate and interpretable measurements. A glance at the tables will show that cells containing solid salts and solutions of carbonates, phosphates and sulphides have received but scant attention.

A word should be said about the method of determination of an electrode potential. One of the most important electrodes is the calomel electrode, since many values of electrode potentials are dependent upon it. Its value depends upon concordant measurements of electromotive force in 0.1 molal hydrochloric acid, the activity coefficient of the hydrochloric acid and the convention that the electromotive force of the molal hydrogen electrode is zero. At the present time there is a uncertainty in the value of the activity coefficient of hydrochloric acid of not greater than one and one-half per cent, which is reflected as an uncertainty of not more than 0.0008 volts in the potential of the molal calomel electrode. This difficulty in the case of hydrochloric acid will be soon disposed of, since accurate measurements on its activity coefficient exist. Existing data show that the activity coefficients of hydrobromic and hydroiodic acids in solutions more dilute than 0.1 molal are identical with those of hydrochloric acid. Hence the electrode potentials in solutions of bromides and iodides are also subject to a correction depending upon the value selected for hydrochloric acid. Data for the activity of sulphuric acid exists, but are not quite as accurate as those of hydrochloric acid. These form the fundamental basis for the electrode potentials in solutions of chlorides, bromides, iodides and sulphates. The question arises as to the method of evaluating electrode potentials in solutions of phosphates, sulphides, carbonates, chromates, thiocynates, oxalates, cyanides, etc., since the use of the hydrogen electrode is precluded in most of these solutions. Future experimentations in this field will require not only measurements of electromotive force, but also determinations of activity coefficients of electrolytes.

Of chief importance to workers in this field of investigation is a knowledge of what not to do, rather than a set of very detailed directions. In order to secure measurements which will permit precise interpretation, the main difficulties to avoid are impurities such as dissolved oxygen, liquid potentials and irreversible electrodes. The solid metal, insoluble salt electrodes constitute a class of electrodes which are found to be not accurately duplicated as to electromotive force. Examples of this class are the electrodes Ag, AgCl(s), Cl^- (III 25a, b, c, and d), Ag, AgBr(s), Br^- (III 26 a and b), and Ag, AgI(s), I^-(III 27 a, b, c, and d). The lack of agreement in these electrodes strongly suggests the discontinuance of their use in accurate electromotive force measurements. On the other hand, electrodes of the calomel type with oxygen free solutions strongly recommend themselves for these uses. Similarly, in the case of the solid metals Na, Cd, Zn, Pb, Tl and Cu the two-phase amalgam, solid salt type electrodes, which are used in standard cell construction, are preferable for ease of reproducibility of electromotive force. In the following table are listed cell electrolytes and corresponding reference electrodes, some of which have been carefully studied and are known to be easily duplicated.

CELL ELECTROLYTE	ELECTRODE
H^+ in absence of oxidizing agents	Pt, H_2, H^+
OH^-	Pt, H_2, OH^- or Hg, HgO, OH^-
Cl^-	Hg, Hg_2Cl_2, Cl^-
Br^-	Hg, Hg_2Br_2, Br^-
I^-	Pb (Hg), PbI_2, I^-
$SO_4^{=}$	Hg, Hg_2SO_4, SO_4,$^{=}$ or
$SO_4^{=}$	Pb (Hg), $PbSO_4$, $SO_4^{=}$

Moreover, liquid potentials can easily be avoided by the selection of the proper reference electrode. Thus, in the study of solutions containing iodide ions a lead amalgam, lead iodide electrode would prove satisfactory.

Of great importance are the criteria of irreversibility of electrodes. These have been summarized by Luther[5] and are summarized below.

I. Fluctuations in electromotive force.

II. Two electrodes in the same solution which give different electromotive force.

III. Changes of electromotive force on shaking.

IV. Changes in electromotive force not proportional to the logarithm of the concentration.

Of equal, if not greater importance than reversibility of electrodes is the fidelity with which the cell registers the tendency for the desired cell reaction to take place. Thermodynamics has placed in our hands a powerful tool for deciding as to the purity of the desired cell reaction. These criteria are listed below.

I. The free energy increase of the cell reaction which is calculated from the electromotive force should be identical with the free energy increase which is calculated from equilibrium measurements.

II. Identical potentials for half cell derived from measurements of different workers using different reference electrodes.

III. Identical electrochemical and thermochemical heats of reaction.

IV. Identical entropy increases for the cell reaction from electrometric and heat capacity data.

The use of these thermodynamic tools will be briefly illustrated with two examples. The oxygen electrode is irreversible, due to the fact that no satisfactory catalyst has been found which will sufficiently increase the rates of the electrode reaction. The degree of reversibility of this electrode was not known until its potential was calculated from equilibrium measurements[6,7]. Two

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[5] *Z. Elektrochem.*, **13**, 289 (1907).

[6] Nernst, *Z. Elktrochem.*, **12**, 693 (1906).

[7] Lewis, *J. Am. Chem. Soc.*, **28**, 158 (1906).

authors found by different calculations that the then accepted value for the potential of the oxygen electrode was at least a tenth of a volt too low.

The cell, $Pb(Hg)_2$, $PbBr_4$, $Pb(ClO_4)_2$, $PbBr_2$, $Br_2(1)$, in which the desired cell reaction is $Pb(Hg) + Br_2(1) = PbBr_2(s)$ presents an excellent opportunity to ascertain if the desired cell reaction actually tends to take place. This cell, which should contain no liquid potential, behaved well experimentally both as to reproducibility of electromotive force and temperature coefficient. The potential of the half cell III 14 should be between those of III 13 and III 15. The electrometric value, −67,480 calories for the heat of formation of lead bromide does not compare well with Thomsen's −64,465 calories. Also, the electrometric increase of entropy attending the formation of one mol of lead bromide from the elements is −18.4 cal. per deg. in contrast to the value −8.9 cal. per deg. from heat capacity data. In view of these discrepancies, it seems almost certain that the desired change in state does not tend to take place in this cell. The lead-lead bromide electrode is being studied by Mr. James R. Geddes of this laboratory by means of another cell.

SUMMARY

I. A summary of electrode potentials has been tabulated in four groups, (1) molal electrode potentials, (2) reference amalgam electrodes, (3) standard reference electrodes, and (4) oxidation-reduction electrodes.

II. For the practical selection of a proper reference electrode a short table of reproducible and easily duplicated standard reference electrodes was included.