CHAPTER THIRTEEN

ELECTROCHEMICAL CELLS

The preceding chapter dealt primarily with the physical chemistry of electrolyte solutions; we now concern ourselves with the overall chemical process that occurs when electricity is passed through a conducting solution. The emphasis will be on the work associated with this overall change, as measured by the reversible cell potential. Since reversible work at constant temperature and pressure corresponds to a free energy change, we will thus be able to bring the emf of cells into the general scheme of thermodynamics. The chapter concludes with a discussion of irreversible electrode processes, that is, with the physical chemistry of the approach of ions to, and their reaction at, the surface of an electrode.

13-1 Definitions and Fundamental Relationships

A. Cell Conventions

An electrochemical cell has, as essential features, a current-carrying solution and two electrodes at which oxidation and reduction processes occur, respectively, as current flows. Figure 13-1 gives a schematic example of a fairly typical cell for this chapter; we have hydrogen and silver–silver chloride electrodes dipping into an aqueous solution of HCl. The hydrogen electrode, incidentally, typically consists of a platinized platinum metal surface arranged so that hydrogen gas bubbles past as it dips partly into the solution, the object being to provide the most intimate possible gas–solution–metal contact. Platinized platinum is merely platinum metal on which additional, very finely divided platinum has been deposited electrolytically; the result is a high area, catalytically active surface. A silver–silver chloride electrode consists of silver on which a fine-grained, adherent deposit of silver chloride has been placed, again electrolytically. The terminals of the cell might be connected to a motor, so as to provide electrochemical energy, or, in the laboratory, to a potentiometer circuit (see Section 13-2), so that the potential difference could be measured.
It is awkward to describe cells in a pictorial manner, and the conventional representation of the cell of Fig. 13-1 is

$$\text{Pt}/H_2(P\text{ atm})/HCl(m)/AgCl/Ag.$$ (13-1)

Equation (13-1) is known as a cell diagram. The rule is that one writes in order each successive phase that makes up the electrical circuit of the cell, using a diagonal bar to separate phases. One should in general specify not only the temperature of the cell, but also the composition of each condensed phase and the partial pressure of any gaseous one; we assume the general mechanical pressure to be 1 atm.

A potentiometric measurement on a cell will report a potential difference between the electrode terminals, and the second convention needed is that to specify the sign of this cell potential $\varepsilon$. There is some variation in practice and consequent ambiguity, and the least confusing way of stating the convention used here seems to be the following. We first define the cell reaction as the chemical change that occurs per faraday of electricity passed through the cell in the direction such that oxidation occurs at the left-hand electrode of the cell diagram. This electrode will be called the anode; it is also the electrode toward which anions migrate in the cell solution as they carry current. The right-hand electrode of the cell diagram is then the one at which reduction occurs, and it is called the cathode; it is also the electrode toward which cations migrate as they carry current. The cell reaction corresponding to (13-1) is

$$\begin{align*}
\text{anode} & \quad \frac{1}{2}H_2(1\text{ atm}) = H^+(m) + e^- \\
\text{cathode} & \quad AgCl + e^- = Ag + Cl^-(m) \\
\text{net} & \quad \frac{1}{2}H_2(1\text{ atm}) + AgCl = Ag + H^+(m) + Cl^-(m).
\end{align*}$$ (13-2)

Since the potential is a function of concentration as well as of the chemical species involved, statements of cell reactions should include the concentration or partial pressure of each substance.

The sign of $\varepsilon$ is now defined to be positive if the cell reaction occurs spontaneously in the direction written and to be negative if the reverse direction of reaction is the spontaneous one. In this particular example $\varepsilon$ would be positive.
That is, silver chloride is spontaneously reduced by hydrogen gas. Although the mechanical arrangement of the cell is such that the direct chemical reaction is prevented from occurring, the process will take place spontaneously when the electrode terminals are connected.

This last is an important feature of electrochemical cells. The cell reaction has to be spontaneous in one direction or the other, and the cell must always be so designed that the direct chemical reaction is physically prevented from occurring. In the case of the cell of Eq. (13-1) the reactants \( \text{H}_2 \) and \( \text{AgCl} \) are isolated at the separate electrodes. Another way in which direct chemical reaction is prevented is illustrated by the Daniell cell shown in Fig. 13-2; this consists of a zinc anode dipping into \( \text{ZnSO}_4 \) solution and a copper cathode dipping into \( \text{CuSO}_4 \) solution. The two solutions are separated by a porous diaphragm which allows electrical contact but prevents gross mixing. The cell diagram is then

\[
\text{Zn}/\text{ZnSO}_4(m_1)/\text{CuSO}_4(m_2)/\text{Cu}, \tag{13-3}
\]

where the dashed diagonal conventionally is used to indicate two miscible phases that are physically prevented from mixing. This situation will later be referred to as one of a liquid junction. The cell reaction is

\[
\begin{align*}
\text{anode} & : & \frac{1}{2}\text{Zn} & = \frac{1}{2}\text{Zn}^{2+}(m_1) + e^- \\
\text{cathode} & : & \frac{1}{2}\text{Cu}^{2+}(m_2) + e^- & = \text{Cu} \\
\text{net} & : & \frac{1}{2}\text{Zn} + \frac{1}{2}\text{Cu}^{2+}(m_2) & = \frac{1}{2}\text{Zn}^{2+}(m_1) + \frac{1}{2}\text{Cu}. \tag{13-4}
\end{align*}
\]

Again, the cell has been written in such a way that the cell reaction occurs spontaneously—if placed directly into the \( \text{CuSO}_4 \) solution, the zinc electrode would react as shown—and so the measured emf of this cell would be reported as positive.

To return to the matter of sign convention, we note that the usual source of confusion is in the plus and minus markings of electrodes. The cells of Figs. 13-1 and 13-2 are drawn so that in spontaneous action the left-hand electrode is the anode. This means that the anode bears a positive charge relative to the cathode at the solution end and a negative charge relative to the cathode at the exposed terminals. It is the terminals that are marked, hence it is the spontaneously operating
anode of a cell that bears the negative sign. To repeat, when we write a cell reaction the various signs and directions of flow are taken to be as shown in Fig. 13-3. If this is the spontaneous direction of flow, the $\mathcal{E}$ is reported as a positive number.\footnote{This is the traditional American convention—a very logical one for physical chemists. The SI convention is discussed in Section 13-CN-1.}

A further feature of electrochemical cells that are used in precise measurements is that they are \textit{reversible}. That is, the cell reaction must take place readily in either direction. If the cell is short-circuited, the reaction should proceed in its spontaneous direction; and if an external potential is applied which overrides the natural cell potential, then the reaction should just as readily proceed in the opposite direction. The reversible electrochemical cell is thus one which may be held in a state of dynamic balance by application of an external counterpotential just equal to $\mathcal{E}$. For example, in the case of the Daniell cell $\mathcal{E}$ is about 1.1 V if $m_1 = m_2 = 1$. External application of an opposing 1.1 V will just prevent reaction from occurring; a slightly smaller opposing potential will allow the cell reaction to occur as written, and a slightly larger opposing potential will make the reaction go in the opposite direction.

The customary way of determining $\mathcal{E}$ for a cell is, in fact, to find that opposing emf which puts the cell in balance. The procedure thus defines $\mathcal{E}$ as the reversible emf of the cell. If current is allowed to flow through the cell under conditions such that applied potential remains essentially equal to $\mathcal{E}$, then the work done is a reversible work. From the definition of potential, work in joules is given by $qV$, where $q$ is the amount of charge carried through potential difference $V$. The reversible work for an electrochemical cell is then $n\mathcal{E}$, where $n$ is the number of faradays passed through the cell.

For the Daniell cell as written in Eq. (13-4), the reversible work is 

\[
(96,487)(1.1) = 1.06 \times 10^5 \text{ J (} m_1 = m_2 = 1, \text{ and } 25^\circ \text{C})
\]

Had the reaction been written for 2 $\mathcal{F}$,

\[
Zn + Cu^{2+}(m_2) = Zn^{2+}(m_1) + Cu,
\]

the reversible work would be $2.12 \times 10^5 \text{ J}$, and had the reaction been written in the opposite direction, $\mathcal{E}$ would be reported as $-1.1 \text{ V}$ and the corresponding reversible work would be $-1.06 \times 10^5 \text{ J}$. Thus the sign of $\mathcal{E}$ and both the sign and magnitude of the reversible work depend on how the cell reaction is written.
A useful conversion factor is that for \( n = 1 \) an emf of 1 V = 23.06 kcal. This unit is sometimes called the electron-volt: 1 eV = 23.06 kcal mole\(^{-1}\).

### B. Thermodynamics of Cells

The reversible emf that is measured for a cell gives the reversible work associated with the cell reaction. Since this is reversible work at constant temperature and pressure, it is therefore the free energy change and, by Eq. (6-34), the sign convention is such that we must write

\[
\Delta G = -nF \bar{\varepsilon};
\]

that is, a positive cell emf corresponds to a spontaneous cell reaction and hence to a negative free energy change.

We may now rewrite several important equations of Section 7-4 in terms of emf's. Thus Eqs. (7-23) and (7-24) become

\[
\Delta S = nF \left( \frac{\partial \bar{\varepsilon}}{\partial T} \right)_p,
\]

and, since \( G = H - TS \) by definition, for a constant-temperature process we have

\[
\Delta H = \Delta G + T \Delta S,
\]

\[
\Delta H = -nF \left[ \bar{\varepsilon} - T \left( \frac{\partial \bar{\varepsilon}}{\partial T} \right)_p \right],
\]

\[
\Delta H^0 = -nF \left[ \bar{\varepsilon}^0 - T \left( \frac{\partial \bar{\varepsilon}^0}{\partial T} \right)_p \right].
\]

Equation (13-9) or (13-10) is known as the Gibbs–Helmholtz equation.

**Example.** The emf of the cell Cd/solution saturated with CdCl\(_2\)-2.5H\(_2\)O/AgCl/Ag is 0.6753 V at 25°C, and \( d\bar{\varepsilon}/dT = -0.00065 \) V K\(^{-1}\). If we write the cell reaction as \( \text{Cd} + 2\text{AgCl} = \text{CdCl}_2(\text{sat. soln.}) + 2\text{Ag} \), then \( \Delta S = (2)(96,487)(-0.00065) = -125 \) J or -29.9 cal K\(^{-1}\) mole\(^{-1}\), \( \Delta H = -(2)(96,487)(0.6753) = -1.303 \times 10^5 \) J or -31.14 kcal, and \( \Delta G = -(2)(96,487)(0.6753)(298.1) = -1.677 \times 10^5 \) J or -40.08 kcal (as compared with -39.5 kcal from thermochemical measurements).

An interesting point is that the \( q \) for a reversibly operating cell is given by \( T \Delta S; \) \( q \) would be -(29.9)(298.1) or -8.91 kcal in the example. In terms of Eq. (13-8) the measured \( q \) is given by \( \Delta H \) when the reaction occurs directly, as in a thermochemical experiment; in the reversible cell the energy \( \Delta G \) goes to do useful work, and the observed \( q \) is then determined by the entropy change. Thus the statement \( \Delta H = \Delta G + T \Delta S \) amounts to saying:

\[
\text{(total energy change)} = \text{(energy available to do work)} + \text{(energy not available to do work)}
\]
C. The Nernst Equation

A very important relationship is obtained as follows. For a general cell reaction

\[ aA + bB + \cdots = mM + nN + \cdots, \]

we have from Eq. (12-91) that

\[ \Delta G = \Delta G^0 + RT \ln Q_{th} \quad [\text{Eq. (12-91)}], \]

where, it will be remembered, \( Q_{th} \) has the same form as an equilibrium constant but contains the activities of the products and reactants as arbitrarily specified by the stated reaction. If the system is at equilibrium, however, \( \Delta G = 0 \), and we then obtain

\[ \Delta G^0 = -RT \ln K_{th} \quad [\text{Eq. (12-92)}], \]

where \( K_{th} \) is the thermodynamic equilibrium constant.

Combination of Eqs. (13-5) and (12-91) gives the Nernst equation:

\[ E = E^0 - \frac{RT}{nF} \ln Q_{th}. \quad (13-11) \]

Insertion of the numerical constants for 25°C yields

\[ E = E^0 - 0.02569 \ln Q_{th} = E^0 - \frac{0.05916}{n} \log Q_{th}. \quad (13-12) \]

Equation (13-11) is the central equation of electrochemistry. By means of it we can determine how the emf of a cell should vary with composition, and we can also determine \( E^0 \) for a cell reaction, which in turn enables us to obtain activity coefficients for electrolytes.

Example. The Nernst equation for the cell reaction of Eq. (13-2) is

\[ E = E^0 - 0.02569 \ln \frac{a_{H^+}a_{Cl^-}}{P_{H_2}}. \quad (13-13) \]

Ag and AgCl are in their standard states and hence have unit activity. The hydrogen pressure will be 1 atm, and, for the moment, we neglect activity coefficient effects, so Eq. (13-13) reduces to

\[ E = E^0 - 0.02569 \ln [H^+(Cl^-)] = E^0 - 0.05139 \ln m. \quad (13-14) \]

The observed emf of this cell is 0.49844 at 25°C and \( m = 0.005 \) and we may use the Nernst equation to calculate \( E \) for some other concentration, say 0.01 m. Since \( E^0 \) is a constant, it follows from Eq. (13-14) that

\[ E_{0.01m} = E_{0.005m} - 0.05139 \ln \frac{0.01}{0.005} = 0.46282. \]

The observed value is 0.46419, a difference we will shortly be attributing to the nonideality of aqueous HCl.

As a different kind of example, for the reaction of the Daniell cell, Eq. (13-4), we have

\[ E = E^0 - 0.02569 \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} = E^0 - 0.01285 \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}. \]

If Zn\(^{2+}\) and Cu\(^{2+}\) are at unit activity (or, very roughly, 1 m), \( E = 1.10 \) V at 25°C. This means that \( E^0 \) is also 1.10 V, since the log term is zero. If an excess of zinc metal is placed in a solution of copper sulfate which is initially at unit activity, the direct spontaneous reaction will occur to
form copper metal and zinc ion. Eventually the solution will consist of roughly 1 m or unit activity Zn\(^{2+}\) and some small equilibrium concentration of Cu\(^{2+}\). We can use the Nernst equation to calculate this last. Since the final state is at equilibrium, \(\Delta G\) and hence \(\Delta\) must be zero, and so

\[
\Delta\theta^0 = 1.10 = 0.01285 \ln \left( \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}/\text{equil}} \right)
\]

\[
= 0.01285 \ln \left( \frac{1}{a_{Cu^{2+}}/\text{equil}} \right).
\]

The equilibrium (Cu\(^{2+}\)) is then \(\exp(-1.10/0.01285)\), or about \(10^{-57}\) m(!).

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13-2 Experimental Procedures

A. The Potentiometer

The reader is referred to experimental texts for details, but the principle employed in the measurement of emf’s of cells should be described at least briefly. An elementary potentiometer arrangement is shown in Fig. 13-4. One sets up a closed circuit involving a working battery, usually a wet cell capable of delivering a reasonable amount of current without changing its voltage. The circuit contains a moderately high resistance, perhaps 1000 ohms, which is either in the form of a slide wire, or which may be tapped at close intervals. This resistance \(R\) then has an ohmic drop in potential \(iR\) across it. The electrochemical cell is connected as shown, with the electrodes in the same direction as for the working cell. One now moves the point of contact \(A\) until the galvanometer \(G\) shows no current flow. At this point the potential drop \(AB\) is the same as \(\theta\) for the cell.

The circuit is usually calibrated by means of a standard cell, or one of accurately known emf \(\theta_{\text{ref}}\). By determining point \(A'\) when the standard cell is in balance, one therefore knows the voltage drop \(A'B\). The desired emf is then \(\theta_{\text{ref}}(R_{AB}/R_{A'B})\).

In actual practice one adjusts subsidiary resistances in the circuit (not shown) in calibrating with the standard cell so that the tapped or slide wire resistance position \(A\) will read directly in volts.

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FIG. 13-4. A potentiometer circuit.
Potentiometric measurements are among the most accurate of physical chemistry. Cell potentials may be measured to about $10^{-5}$ V, the limiting accuracy usually being that of the voltage of the reference cell. If the unknown cell is one of very high resistance, then the sensitivity of the galvanometer may become the limiting factor. In the case of a pH meter, for example, the glass electrode may have $10^9$ ohms resistance, and one must use a vacuum-tube null-meter to detect the balance point (early users of pH meters struggled with quadrant electrometers).

The potentiometric method is a null method—when the circuit is balanced the galvanometer shows no current flow, and a slight shift in the position of the contact $A$ to one side or the other causes a galvanometer deflection in one direction or the other. A barely detectable galvanometer deflection need correspond to no more than perhaps $10^{-12}$ A, so the change in condition needed to reverse the current flow is very small and the measured potential is essentially the reversible one. If a relatively large current, say $10^{-5}$ A, is drawn through a cell, then the potential drops as various irreversible processes occur, such as polarization, discussed in Section 13-9. The magnitude of the measured potential is therefore at a maximum at zero current.

B. Standard Cells

The most widely accepted reference cell is the Weston cell, illustrated in Fig. 13-5. The anode consists of a layer of solid cadmium amalgam containing 12.5% cadmium, and the cathode consists of a pool of mercury layered with a thick paste of $\text{Hg}_2\text{SO}_4$. The solution is saturated with $\text{CdSO}_4 \cdot \frac{3}{2}\text{H}_2\text{O}$, with some excess crystals present on both sides, to maintain saturation. The cell diagram is

$$\text{Pt/Cd(Hg)/saturated CdSO}_4 \cdot \frac{3}{2}\text{H}_2\text{O}/\text{Hg/Pt}$$

and the corresponding cell reaction is

$$\frac{3}{2}\text{H}_2\text{O} + \text{Cd(amalgam)} + \text{Hg}_2\text{SO}_4(s) = \text{CdSO}_4 \cdot \frac{3}{2}\text{H}_2\text{O}(s) + 2 \text{Hg}.$$  

The emf at $25^\circ C$ is 1.0183 V; the temperature dependence is small, $-4.06 \times 10^{-5}$ V K$^{-1}$. 

![FIG. 13-5. The Weston cell.](image-url)
C. Reference Electrodes

An electrochemical cell consists essentially of the two parts defined by the two electrodes, and one often constructs a cell in which one electrode is that under investigation and the other is a conventional electrode of known properties. This last is called a reference electrode. A very common and easily constructed one is the calomel reference electrode, illustrated in Fig. 13-6(a). Platinum wire dips into a pool of mercury which is layered with a paste of Hg2Cl2, followed by a solution which is usually 0.1 N KCl, 1 N KCl, or saturated KCl. Electrolytic connection must be made to the rest of the cell, and this is done through a side arm in which the KCl solution has usually been stiffened with agar-agar or gelatine. This type of electrolytic connection is known as a salt bridge (see Special Topics section).

A complete cell might then appear as in Fig. 13-6(b). The cell diagram is

\[
\text{Pt}/\text{Hg}/\text{Hg}_{2}\text{Cl}_2(\text{s})/1\text{ N KCl or saturated KCl} / \text{HCl(m)}/\text{H}_2(1 \text{ atm})/\text{Pt}
\]

If the HCl is at unit activity, then

\[
\mathcal{E}_{298} = -0.280 \text{ V (1 N KCl)} \quad \text{and} \quad \mathcal{E}_{298} = -0.242 \text{ V (saturated KCl)}.
\]

The boundary between the KCl solution and that of the electrolyte of the second part of the cell is known as a liquid junction. Since ions are carrying the current in solution, passage of electricity means that ions move across the junction, just as in a transference experiment. In terms of this cell some K+ ions must move from the KCl solution into the HCl one, and some Cl- ions must move from a concentration \(m\) in the HCl to that in the KCl. Some net changes thus occur at the liquid junction, whose free energy requirement contributes to the emf of the cell as a whole. This contribution is known as the junction potential, and fortunately it is small if the bulk of the current is carried by oppositely charged ions of the same mobility. This is essentially the situation in the case of a KCl salt bridge; K+ and Cl- do have nearly the same mobility. The more detailed treatment of junction potentials is given in the Special Topics sections, and it is sufficient here to note that for most purposes the junction potential for a saturated KCl (or a concentrated NH4NO3) salt bridge can be neglected. However, this effect does impair the accuracy of a cell involving a calomel reference electrode.
Other reference electrodes include the hydrogen electrode itself, which is very accurate but somewhat inconvenient to use, and well-known reversible electrodes such as the silver–silver ion or the silver–silver chloride ones. For accurate work a reference electrode should be a direct part of the cell, but it may be more convenient to connect the electrode being studied to the reference electrode via a salt bridge and to either neglect or try to estimate the value of the junction potential.

13-3 Determination of $\varepsilon^0$ Values and Activity Coefficients

Equation (13-11) may be written in the form

$$\varepsilon = \varepsilon^0 - \frac{RT}{\overline{nF}} \ln Q - \frac{RT}{\overline{nF}} \ln Q_v,$$

(13-15)

where

$$Q_{th} = \frac{a_M^{m_1}a_N^{m_2} \cdots}{a_A^{n_1}a_B^{n_2} \cdots} \frac{(M)^{m_1}(N)^{m_2} \cdots}{(A)^{n_1}(B)^{n_2} \cdots} \frac{\gamma_M^{m_1}\gamma_N^{m_2} \cdots}{\gamma_A^{n_1}\gamma_B^{n_2} \cdots} = QQ_v.$$  

(13-16)

We now write

$$\varepsilon' = \varepsilon + \frac{RT}{\overline{nF}} \ln Q = \varepsilon^0 - \frac{RT}{\overline{nF}} \ln Q_v.$$  

(13-17)

The quantity $\varepsilon'$ is determined for a series of concentrations and plotted against concentration. At infinite dilution the activity coefficients and hence $Q_v$ approach unity, and $\ln Q_v$ approaches zero; the extrapolated value of $\varepsilon'$ is thus equal to $\varepsilon^0$.

The procedure may be illustrated for the cell corresponding to reaction (13-2)

![Graph](image_url)

**FIG. 13-7.** Determination of $\varepsilon^0_{298}$ for the cell Pt/H$_2$(1 atm)/HCl(m)/AgCl/Ag.
at 25°C. We write Eq. (13-14) in the form

\[ \varepsilon = \varepsilon^0 - 0.05139 \ln m - 0.05139 \ln \gamma_x \]

or

\[ \varepsilon' = \varepsilon + 0.05139 \ln m = \varepsilon^0 - 0.05139 \ln \gamma_x . \]  

(13-18)

According to the Debye–Hückel limiting law, Eq. (12-89), \( \ln \gamma_x \) should be proportional to \( \sqrt{m} \), so \( \varepsilon' \) is plotted against \( \sqrt{m} \) as shown in Fig. 13-7. Extrapolation to zero concentration gives \( \varepsilon^0_{298} = -0.22239 \) V. Having determined the \( \varepsilon^0 \) for the cell reaction, one may then insert its value back into Eq. (13-18) and thus obtain \( \gamma_x \) for HCl at each concentration.

This procedure illustrates how a number of very accurate values of \( \varepsilon^0 \) and of activity coefficients have been obtained. One may also, of course, estimate \( Q_v \) either theoretically or from other activity coefficient data and thus calculate \( \varepsilon^0 \) from the measured \( \varepsilon \).

### 13-4 Additivity Rules for Emf's. Standard Oxidation Potentials

Since the \( \varepsilon \) or \( \varepsilon^0 \) for a cell reaction is just the free energy change per equivalent, emf's obey essentially the same additivity rules as do free energies. For example,

\[
\begin{align*}
(a) & \quad \text{Zn} + 2\text{H}^+ = \text{Zn}^{2+} + \text{H}_2, \\
(b) & \quad \text{Cu} + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2, \\
(c) = (a) - (b) & \quad \text{Zn} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu}.
\end{align*}
\]

We know that \( \Delta G^0_{(c)} = \Delta G^0_{(a)} - \Delta G^0_{(b)} \), hence

\[-nF \varepsilon^0_{(c)} = -nF \varepsilon^0_{(a)} - (-nF \varepsilon^0_{(b)}),\]

or \( \varepsilon^0_{(c)} = \varepsilon^0_{(a)} - \varepsilon^0_{(b)} \). In general, if two cell reactions are added (subtracted), the resultant emf is the sum (difference) of those for the two reactions.

We make use of this attribute in much the same way as is done in formulating enthalpies and free energies of formation. First, all emf data are expressed as \( \varepsilon^0 \) relative to the hydrogen electrode as cathode. Second, a cell reaction is expressed as a combination of two half-cells. For example, reaction (a) is broken down as

\[
\begin{align*}
\text{Zn} = \text{Zn}^{2+} + 2e^- & \quad \varepsilon^0_{\text{Zn}/\text{Zn}^{2+}} \\
2\text{H}^+ + 2e^- = \text{H}_2 & \quad -\varepsilon^0_{\text{H}_2/\text{H}^+} \\
\text{Zn} + 2\text{H}^+ = \text{Zn}^{2+} + \text{H}_2 & \quad \varepsilon^0 = \varepsilon^0_{\text{Zn}/\text{Zn}^{2+}} - \varepsilon^0_{\text{H}_2/\text{H}^+}.
\end{align*}
\]

Thus any cell reaction may be written as the difference between two half-cell oxidation reactions and any \( \varepsilon^0 \) as the difference between two standard half-cell oxidation potentials. This combination of equations may therefore be written as

\[
\varepsilon^0_{(c)} = (\varepsilon^0_{\text{Zn}/\text{Zn}^{2+}} - \varepsilon^0_{\text{H}_2/\text{H}^+}) - (\varepsilon^0_{\text{Cu}/\text{Cu}^{2+}} - \varepsilon^0_{\text{H}_2/\text{H}^+})
\]

\[
\varepsilon^0_{(c)} = \varepsilon^0_{\text{Zn}/\text{Zn}^{2+}} - \varepsilon^0_{\text{Cu}/\text{Cu}^{2+}}.
\]
Some indirect estimates suggest that the absolute standard half-cell potential for \( \text{H}_2/\text{H}^+ \) is small, but it is apparent that its actual value is immaterial in combining equations, since it cancels out. The third step is, accordingly, to make the convenient, arbitrary assignment that \( \varphi_{\text{H}_2/\text{H}^+}^0 = 0 \) and to report the measured \( \varphi^0 \) values for reactions such as (a) and (b) as the actual values for the half-cells. Thus \( \varphi_{\text{Zn/Zn}^+}^0 = 0.763 \) and \( -0.337 \) for reactions (a) and (b), respectively, and we report that

\[
\varphi_{\text{Zn/Zn}^+}^0 = 0.763 \quad \text{and} \quad \varphi_{\text{Cu/Cu}^+}^0 = -0.337.
\]

Then \( \varphi_{\text{Zn/Zn}^+}^0 \) for reaction (c) is \( 0.763 - (-0.337) = 1.10 \mathrm{V} \); this result is independent of the assumption regarding \( \varphi_{\text{H}_2/\text{H}^+}^0 \).

The convention is that the emf of a cell is given by

\[
\varphi^0 = \varphi^0_{\text{left}} - \varphi^0_{\text{right}},
\]

where \( \varphi^0_{\text{left}} \) and \( \varphi^0_{\text{right}} \) are the standard oxidation potentials of the half-cells corresponding to the anode and cathode of the full cell, respectively.

The general mass of emf data has been reduced by means of this formalism and a number of standard half-cell potentials are given in Table 13-1. Their use follows the example just given. Each value is actually the \( \varphi^0 \) for the cell whose anode is the stated half-cell and whose cathode is the standard hydrogen electrode. The right-hand column of the table gives the corresponding standard electrode potentials, \( \varphi^0 \). This alternative definition is described in Section 13-CN-1.

As one other further example, the reaction

(c) \( 2\text{Hg} + 2\text{AgCl} = \text{Hg}_2\text{Cl}_2 + 2\text{Ag} \)

can be written as the difference between

(a) \( 2\text{Hg} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2 + 2\text{e}^- \), \( \varphi_{\text{Zn/Zn}^+}^0 = -0.2676 \)

and

(b) \( \text{Ag} + \text{Cl}^- = \text{AgCl} + \text{e}^- \), \( \varphi_{\text{Zn/Zn}^+}^0 = -0.2224 \).

Then \( \varphi_{\text{Zn/Zn}^+}^0 = -(0.2676) - (-0.2224) = -0.0452 \). Note that although we must multiply reaction (b) by 2 before subtracting it from reaction (a) in order to obtain reaction (c), we subtract the emf's directly. This is because an emf corresponds to the free energy change per faraday, so that all emf's are on the same basis.

There is one situation where the additivity procedure must be handled with care, namely in the combining of two half-cell reactions to give a third half-cell reaction. Each emf should be weighted by the number of faradays for which the half-cell reaction is written. As an example, consider the case

(a) \( \text{Fe} = \text{Fe}^{3+} + 2\text{e}^- \), \( \Delta G^0_{(a)} = -2F \varphi^0_{(a)} \),

(b) \( \text{Fe}^{2+} = \text{Fe}^{3+} + \text{e}^- \), \( \Delta G^0_{(b)} = -F \varphi^0_{(b)} \),

(c) \( \text{Fe} = \text{Fe}^{3+} + 3\text{e}^- \), \( \Delta G^0_{(c)} = -3F \varphi^0_{(c)} \).

Since \( \Delta G^0_{(c)} = \Delta G^0_{(a)} + \Delta G^0_{(b)} \), it follows that \( \varphi^0_{(c)} = (2\varphi^0_{(a)} + \varphi^0_{(b)})/3 \). At 25°C, we get \( \varphi^0_{(c)} = [(2)(0.440) + (-0.771)]/3 = 0.036 \). The general equation is

\[
\varphi^0_{(c)} = \frac{n_{(a)} \varphi^0_{(a)} + n_{(b)} \varphi^0_{(b)}}{n_{(c)}},
\]

(13-20)
### TABLE 13-1. Standard Oxidation Potentials at 25°C

<table>
<thead>
<tr>
<th>Half-cell reaction</th>
<th>$E^{\circ}_{258}$</th>
<th>$E^{\circ}_{298}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li} = \text{Li}^+ + e^-$</td>
<td>3.045</td>
<td>-3.045</td>
</tr>
<tr>
<td>$\text{K} = \text{K}^+ + e^-$</td>
<td>2.925</td>
<td>-2.925</td>
</tr>
<tr>
<td>$\text{Ca} = \text{Ca}^{2+} + 2e^-$</td>
<td>2.87</td>
<td>-2.87</td>
</tr>
<tr>
<td>$\text{Na} = \text{Na}^+ + e^-$</td>
<td>2.714</td>
<td>-2.714</td>
</tr>
<tr>
<td>$\text{Mg} = \text{Mg}^{2+} + 2e^-$</td>
<td>2.37</td>
<td>-2.37</td>
</tr>
<tr>
<td>$\text{Al} = \text{Al}^{3+} + 3e^-$</td>
<td>1.66</td>
<td>-1.66</td>
</tr>
<tr>
<td>$\text{Zn} = \text{Zn}^{2+} + 2e^-$</td>
<td>0.763</td>
<td>-0.763</td>
</tr>
<tr>
<td>$\text{Fe} = \text{Fe}^{2+} + 2e^-$</td>
<td>0.440</td>
<td>-0.440</td>
</tr>
<tr>
<td>$\text{Cd} = \text{Cd}^{2+} + 2e^-$</td>
<td>0.403</td>
<td>-0.403</td>
</tr>
<tr>
<td>$\text{Pb} + \text{SO}_4^{2-} = \text{PbSO}_4 + 2e^-$</td>
<td>0.356</td>
<td>-0.356</td>
</tr>
<tr>
<td>$\text{TI} = \text{TI}^+ + e^-$</td>
<td>0.3363</td>
<td>-0.3363</td>
</tr>
<tr>
<td>$\text{Pb} = \text{Pb}^{2+} + 2e^-$</td>
<td>0.126</td>
<td>-0.126</td>
</tr>
<tr>
<td>$\text{Ag} + \text{I}^- = \text{AgI} + e^-$</td>
<td>0.156</td>
<td>-0.156</td>
</tr>
<tr>
<td>$\text{Fe} = \text{Fe}^{3+} + 3e^-$</td>
<td>0.036</td>
<td>-0.036</td>
</tr>
<tr>
<td>$\text{H}_2 = 2\text{H}^+ + 2e^-$</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$\text{Ag} + \text{Br}^- = \text{AgBr} + e^-$</td>
<td>-0.0713</td>
<td>0.0713</td>
</tr>
<tr>
<td>$\text{Cu}^+ = \text{Cu}^{2+} + e^-$</td>
<td>-0.153</td>
<td>0.153</td>
</tr>
<tr>
<td>$\text{Ag} + \text{Cl}^- = \text{AgCl} + e^-$</td>
<td>-0.22239</td>
<td>0.22239</td>
</tr>
<tr>
<td>Saturated calomel</td>
<td>-0.242</td>
<td>0.242</td>
</tr>
<tr>
<td>$2\text{Hg} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2 + 2e^-$</td>
<td>-0.2676</td>
<td>0.2676</td>
</tr>
<tr>
<td>Normal calomel</td>
<td>-0.280</td>
<td>0.280</td>
</tr>
<tr>
<td>0.1 N calomel</td>
<td>-0.3358</td>
<td>0.3358</td>
</tr>
<tr>
<td>$\text{Cu} = \text{Cu}^{2+} + 2e^-$</td>
<td>-0.337</td>
<td>0.337</td>
</tr>
<tr>
<td>$\text{Cu} = \text{Cu}^+ + e^-$</td>
<td>-0.521</td>
<td>0.521</td>
</tr>
<tr>
<td>$2\text{I}^- = \text{I}_2 + 2e^-$</td>
<td>-0.5355</td>
<td>0.5355</td>
</tr>
<tr>
<td>$2\text{Fe}^{2+} = \text{Fe}^{3+} + e^-$</td>
<td>-0.771</td>
<td>0.771</td>
</tr>
<tr>
<td>$2\text{Hg} = \text{Hg}_2^{2+} + 2e^-$</td>
<td>-0.789</td>
<td>0.789</td>
</tr>
<tr>
<td>$\text{Ag} = \text{Ag}^+ + e^-$</td>
<td>-0.7991</td>
<td>0.7991</td>
</tr>
<tr>
<td>$\text{Hg}_2^{2+} = 2\text{Hg}^{2+} + 2e^-$</td>
<td>-0.920</td>
<td>0.920</td>
</tr>
<tr>
<td>$2\text{Br}^- = \text{Br}_2 + 2e^-$</td>
<td>-1.0652</td>
<td>1.0652</td>
</tr>
<tr>
<td>$4\text{H}_2\text{O} = 4\text{OH}^- + 2\text{H}^+ + e^-$</td>
<td>$-1.23$</td>
<td>1.23</td>
</tr>
<tr>
<td>$\text{TI}^+ = \text{TI}^{2+} + 2e^-$</td>
<td>$-1.25$</td>
<td>1.25</td>
</tr>
<tr>
<td>$2\text{Cl}^- = \text{Cl}_2 + 2e^-$</td>
<td>$-1.36$</td>
<td>1.36</td>
</tr>
<tr>
<td>$\text{PbSO}_4 + 2\text{H}_2\text{O} = \text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^-$</td>
<td>$-1.685$</td>
<td>1.685</td>
</tr>
<tr>
<td>$2\text{F}^- = \text{F}_2 + 2e^-$</td>
<td>$-2.87$</td>
<td>2.87</td>
</tr>
</tbody>
</table>

Basic solutions

| $\text{SO}_4^{2-} + 2\text{OH}^- = \text{SO}_3^{2-} + \text{H}_2\text{O} + 2e^-$ | 0.93 | $-0.93$ |
| $\text{H}_2 + 2\text{OH}^- = 2\text{H}_2\text{O} + 2e^-$ | 0.8281 | $-0.8281$ |
| $\text{Ni} + 2\text{OH}^- = \text{Ni(OH)}_2 + 2e^-$ | 0.72 | $-0.72$ |
| $3\text{OH}^- = \text{H}_2\text{O} + \text{HO}_2^- + 2e^-$ | $-0.88$ | 0.88 |

---


*See Commentary and Notes section.*
where \( n \) denotes number of faradays. Whenever one has any question about combining cell emf’s, he should always do so first in terms of \( \Delta G \)'s since these are always additive.

### 13-5 Emf and Chemical Equilibria

#### A. Thermodynamic Relationships

Combination of Eqs. (13-5) and (12-92), \( \Delta G^0 = -RT \ln K_{th} \), gives an important relationship between the \( \varphi^0 \) for a cell and the equilibrium constant for the cell reaction:

\[
\varphi^0 = \frac{RT}{nF} \ln K_{th}
\]  

(13-21)

or, for 25°C

\[
\log K_{th} = \frac{n}{0.05917} \varphi^0.
\]  

(13-22)

Thus for \( n = 1 \), 0.059 V corresponds to one power of ten in \( K \).

#### B. Direct Applications

A very direct and useful application of the \( \varphi^0 \) values is to the treatment of oxidation-reduction equilibria in solution. The following examples illustrate typical situations.

**Example.** To what extent will Zn reduce 0.01 m \( \text{Fe}^{2+} \) at 25°C? The reaction is

\[
\text{Zn} + \text{Fe}^{2+} = \text{Zn}^{2+} + \text{Fe}^{0}
\]

and, from Table 13-1, \( \varphi^0_{298} = 0.763 - 0.440 = 0.323 \). Then

\[
K_{th} = \exp[(2)(0.323)/(0.02569)] = 8.3 \times 10^{10},
\]

or

\[
\text{Zn}^{2+} \approx 8.3 \times 10^{10} \times \text{Fe}^{2+}
\]

The reaction will go virtually to completion, or, if activity coefficients are neglected, until \( (\text{Zn}^{2+}) \) is essentially 0.01 m; the equilibrium \( (\text{Fe}^{2+}) \) is then \( 0.01/8.3 \times 10^{10} = 1.2 \times 10^{-11} \).

**Example.** To what extent should 0.01 m \( \text{Hg}^{2+} \) disproportionate into \( \text{Hg} \) and \( \text{Hg}^{2+} \) at 25°C? We combine the following half-cell reactions:

(a) \( \frac{1}{2}\text{Hg}^{2+} = \text{Hg}^{2+} + e^- \), \( \varphi^0_{(a)} = -0.920 \),

(b) \( \frac{1}{2}\text{Hg}^{2+} + e^- = \text{Hg}(l) \), \( \varphi^0_{(b)} = 0.789 \),

(c) \( \text{Hg}^{2+} = \text{Hg}^{2+} + \text{Hg}(l) \), \( \varphi^0_{(c)} = -0.131 \).

\[K_{th} = \exp(-0.131/0.02569) = 6.10 \times 10^{-8},\]

so we have

\[
6.10 \times 10^{-8} = \frac{(\text{Hg}^{2+})}{(\text{Hg}^2)} = \frac{(\text{Hg}^{2+})}{0.01 - (\text{Hg}^{2+})},
\]
from which \((\text{Hg}^{2+}) = 6.06 \times 10^{-3}\). The calculation supposes that some Hg(I) is formed or is present.

### 13-5 EMF AND CHEMICAL EQUILIBRIA

**C. Determination of Solubility Products**

Several of the half-cell reactions of Table 13-1 are written as the reaction of a metal with an anion to give a slightly soluble salt. The potential for such a half-cell reaction may be combined with the one for the simple oxidation of the metal, to give the solubility product of the salt. If we have

\[
\begin{align*}
(a) & \quad M + X^- = MX(s) + e^- , \quad \mathcal{E}_0 = \mathcal{E}_0^{(a)} , \\
(b) & \quad M = M^+ + e^- , \quad \mathcal{E}_0 = \mathcal{E}_0^{(b)} , \\
(c) = (b) - (a) & \quad MX(s) = M^+ + X^- , \quad \mathcal{E}_0 = \mathcal{E}_0^{(b)} - \mathcal{E}_0^{(a)} ,
\end{align*}
\]

then, neglecting activity coefficients, \(K_{sp} = \exp(\mathcal{E}_0/0.02569)\) at 25°C.

An alternative and sometimes very useful approach is the following. We write the Nernst equation for reaction (b):

\[
\mathcal{E}_{(b)} = \mathcal{E}_{(b)}^{0} - 0.02569 \ln a_{M^+} .
\tag{13-23}
\]

The potential at a metal-metal ion electrode must always reflect the chemical potential of that ion; in the presence of \(X^-\), \(MX(s)\) forms, which decreases \(a_{M^+}\) according to the solubility constant, \(a_{M^+} = K_{th}/a_{X^-}\). The standard potential of reaction (a) must therefore be the same as the potential of the metal–metal ion electrode for that value of \(a_{M^+}\) which is present when \(a_{X^-}\) is unity. Thus when \(a_{X^-}\) is unity \(\mathcal{E}_{(b)}^{0}\) in Eq. (13-23) may be replaced by \(\mathcal{E}_{(a)}^{0}\) and \(a_{M^+}\) by \(K_{th}\):

\[
\begin{align*}
\mathcal{E}_{(a)}^{0} &= \mathcal{E}_{(b)}^{0} - 0.02569 \ln K_{th} , \\
K_{th} &= \exp(\mathcal{E}_{(b)}^{0} - \mathcal{E}_{(a)}^{0})/0.02569 ,
\end{align*}
\]

which is the same result as before. This alternative treatment, although longer as presented here, becomes very advantageous when one is dealing with more complicated situations.

**Example.** Calculate the solubility product for \(\text{Ag}_2\text{SO}_4\) if \(\mathcal{E}_{298}^{0} = -0.627\) V for the cell

\[\text{Ag/Ag}_2\text{SO}_4/\text{H}_2\text{SO}_4(m)/\text{H}_2/\text{Pt.}\]

The \(\mathcal{E}^0\) is that for the half-cell reaction

\[2\text{Ag} + \text{SO}_4^{2-} = \text{Ag}_2\text{SO}_4 + 2e^- , \quad \mathcal{E}_{298}^{0} = -0.627.\]

Subtraction of this from

\[2\text{Ag} = 2\text{Ag}^+ + 2e^- , \quad \mathcal{E}_{298}^{0} = -0.799\]

gives

\[\text{Ag}_2\text{SO}_4 = 2\text{Ag}^+ + \text{SO}_4^{2-} , \quad \mathcal{E}_{298}^{0} = -0.172.\]

The solubility product is then \(\exp[(2)(-0.172)/0.02569] = 1.53 \times 10^{-6}\). Note that \(n = 2\) in this case.

Application of the alternative procedure is as follows. We write

\[\mathcal{E} = -0.799 - \frac{1}{2}(0.02569) \ln a_{\text{Ag}^+}.\]
When $a_{SO_4^{2-}}$ is unity, $\mathcal{E} = -0.627$ V, and $a_{Ag^+}^2 = K/a_{SO_4^{2-}} = K$, so

$$-0.627 = -0.799 - \frac{1}{2}(0.02569) \ln K,$$

which gives the same result as before.

### D. Determination of Dissociation Constants

The alternative procedure described in the treatment of solubility equilibria may be applied to a homogeneous equilibrium in solution. If a metal ion is complexed in solution, then the half-cell potential $M/M_2^+$ gives the activity of that ion, and this often allows the calculation of the equilibrium constant for complexation.

**Example.** The potential for the cell

$\text{Cu}/0.02/\text{Cu(II) in 0.5/}\text{NH}_3/\text{normal calomel electrode}$

is 0.26 V at 25°C. [We use formalities since the copper is largely present as the complex $\text{Cu(NH}_3\text{)}_2^{2+}$ and we wish merely to describe the overall makeup of the solution.] We treat the left-hand electrode as a $\text{Cu/Cu}^{2+}$ electrode whose emf is determined by $a_{\text{Cu}^{2+}}$ in the solution: The emf of the cell is therefore written

$$\mathcal{E} = \mathcal{E}_{\text{Cu/Cu}^{2+}} - \mathcal{E}_{\text{ref}} - \frac{1}{2}(0.02569) \ln a_{\text{Cu}^{2+}}$$

or

$$0.26 = -0.337 - (-0.280) - \frac{0.02569}{2} \ln a_{\text{Cu}^{2+}},$$

$$a_{\text{Cu}^{2+}} = \exp \left(2\left(-0.317\right) \times \frac{0.02569}{2}\right) = 1.91 \times 10^{-11}.$$

Virtually all of the $\text{Cu}^{2+}$ is in the form of $\text{Cu(NH}_3\text{)}_2^{2+}$; therefore $(\text{NH}_3) = 0.5 - (4)(0.02) = 0.42$, and we evaluate the equilibrium constant as

$$K = \frac{(\text{Cu(NH}_3\text{)}_2^{2+})}{(\text{Cu}^{2+})(\text{NH}_3)^4} = \frac{0.02}{(1.91 \times 10^{-11})(0.42)^4} = 3.37 \times 10^{18}$$

(neglecting activity coefficients).

A number of equilibrium constants for the dissociation of complex ions have been determined in this way. We see in Section 13-8 that an analogous procedure may be applied to the determination of $a_{\text{H}^+}$ in a solution.

### 13-6 Concentration Cells

The term *concentration cell* is used to designate a cell whose net reaction involves only changes in composition of species (or of gas pressures) and no *net* oxidation or reduction. The $\mathcal{E}^0$ for such a cell must be zero since all species in the cell reaction are then to be at unit activity, in which case no change at all accompanies the passage of electricity.
A. Electrode Concentration Cells

A very straightforward type of concentration cell is the following:

\[ \text{Pt/H}_2(P_1)/\text{HCl}(m)/\text{H}_2(P_2)/\text{Pt}, \]

for which the cell reaction is

\[ \begin{align*}
\text{anode} & \quad \text{H}_2(P_1) = 2\text{H}^+(m) + 2e^-, \\
\text{cathode} & \quad 2\text{H}^+(m) + 2e^- = \text{H}_2(P_2), \\
\text{net reaction} & \quad \text{H}_2(P_1) = \text{H}_2(P_2),
\end{align*} \]

with

\[ \mathcal{E}_{298} = -\frac{0.02569}{2} \ln \frac{P_2}{P_1}. \]

In the case of a metal electrode the metal may be present as an amalgam:

\[ \text{Cd(x}_1, \text{ in Hg)/CdSO}_4(m)/\text{Cd(x}_2, \text{ in Hg),} \]

with

\[ \mathcal{E}_{298} = -\frac{0.02569}{2} \ln \frac{a_{x_2}}{a_{x_1}}. \]

B. Simple Electrolyte Concentration Cells

In a simple electrolyte concentration cell liquid junctions are avoided by setting up two opposing cells which differ only in their electrolyte concentration. The following is an example:

\[ \text{Ag/AgCl/HCl}(m_1)/\text{H}_2(1 \text{ atm})/\text{Pt—Pt}/\text{H}_2(1 \text{ atm})/\text{HCl}(m_2)/\text{AgCl}/\text{Ag}, \]

\[ \begin{align*}
\text{first anode} & \quad \text{Ag} + \text{Cl}^- (m_2) = \text{AgCl} + e^-, \\
\text{first cathode} & \quad \text{H}^+(m_1) + e^- = \frac{1}{2}\text{H}_2(1 \text{ atm}), \\
\text{second anode} & \quad \frac{1}{2}\text{H}_2(1 \text{ atm}) = \text{H}^+(m_2) + e^-, \\
\text{second cathode} & \quad \text{AgCl} + e^- = \text{Ag} + \text{Cl}^- (m_2), \\
\text{net reaction} & \quad \text{H}^+(m_1) + \text{Cl}^- (m_2) = \text{H}^+(m_2) + \text{Cl}^- (m_2).
\end{align*} \]

Note that it is important to write each ionic species separately if the electrolyte is in fact treated as fully dissociated. The emf for this cell is

\[ \mathcal{E}_{298} = -0.02569 \ln \frac{a_{\text{H}^+, m_2} a_{\text{Cl}^-, m_2}}{a_{\text{H}^+, m_1} a_{\text{Cl}^-, m_1}}, \]

\[ \mathcal{E}_{298} = -0.05139 \ln \frac{m_2}{m_1} - 0.05139 \ln \frac{\gamma^+, m_2}{\gamma^+, m_1}. \]

Cells of this type may be used to obtain the ratio of activity coefficients of an electrolyte at two different concentrations.
Electrolyte concentration cells having a liquid junction are discussed in the Special Topics section.

13-7 Oxidation-Reduction Reactions

We consider here the situation in which both the oxidized and reduced forms of the half-cell couple are solution species. Examples are the couples Fe\(^{2+}/\text{Fe}^{3+}\) and Cu\(^+/\text{Cu}^{2+}\). Both partners of the redox couple are in solution, and since they can be exposed only to one of the electrodes (or else the cell would be short-circuited), it is mandatory that the second electrode be connected by means of a salt bridge. Thus we have

\[ \text{Pt}/\text{Cu}^+(m_1), \text{Cu}^{2+}(m_2)/\text{standard calomel electrode}. \]

The potential of such a cell is given by the general form

\[ \mathcal{E} = \mathcal{E}_{\text{anode}}^\circ - \mathcal{E}_{\text{red}}^\circ - \frac{0.0592}{n} \ln \frac{a_{\text{oxid}}}{a_{\text{red}}}, \quad (13-24) \]

where the anode reaction is

\[ \text{M(red)} = \text{M(oxid)} + ne^- \]

and \(a_{\text{oxid}}\) and \(a_{\text{red}}\) refer to the activities of the oxidized and the reduced forms of the species of the redox couple, respectively. As mentioned in Section 13-2C, the presence of a liquid junction introduces some unavoidable inaccuracy in the measured emf. (See also the Special Topics section.)

Cells of this type have been used in the determination of the redox emf not only for metal ion couples but also for a variety of inorganic coordination compounds and for many organic systems. An example of the second type is the Fe(CN)\(_{3}^+\)/Fe(CN)\(_{6}^3-\) couple, for which \(\mathcal{E}_{298}^\circ = -0.36\) V, and an example of the latter is the couple

\[ [\text{HO--C}_4\text{H}_4\text{--OH}] = [\text{O=--C}_4\text{H}_4=\text{O}] + 2\text{H}^+ + 2e^-; \quad \mathcal{E}_{298}^\circ = -0.6994. \quad (13-25) \]

It will be seen in the next section that the quinone–hydroquinone couple is useful in pH determinations.

Returning to inorganic examples, we note that most elements exist in several oxidation states and that the potentials between these states are generally determined by cells of the type represented by Eq. (13-24). Table 13-2 summarizes a few of these emf relationships. The number between oxidation states is the standard oxidation potential at 25°C. We assume acid solutions and use H\(^+\) and H\(_2\)O as needed in writing the balanced half-cell reactions.

A cell corresponding to Eq. (13-24) may also be used to follow a redox titration. Let us say that ion \(M_1\) is initially present in reduced form and that an oxidizing agent, ion \(M_2\), is added progressively. The reaction

\[ M_1(\text{red}) + M_2(\text{oxid}) = M_1(\text{oxid}) + M_2(\text{red}) \]

occurs. We assume that the reaction is rapid so that at each stage of the titration the system is in equilibrium. Since there can be only one potential at the platinum anode, this means that \(a_{M_1(\text{oxid})}/a_{M_1(\text{red})}\) is always equal to \(a_{M_2(\text{oxid})}/a_{M_2(\text{red})}\).

The situation is most easily delineated by means of a concrete example. Consider the titration of Cu\(^+\) with Fe\(^{3+}\):

\[ \text{Cu}^+ + \text{Fe}^{3+} = \text{Cu}^{2+} + \text{Fe}^{2+}. \quad (13-26) \]
TABLE 13-2. Selected Standard Oxidation Potentials for the Elements in Their Various Valence States

\[
\begin{align*}
\text{Cr} & : \text{Cr}^{2+} \rightarrow \text{Cr}^{3+} \rightarrow \text{Cr}_2\text{O}_7^{2-} & 0.91 & 0.41 & -1.33 & -1.15 \\
\text{Mn} & : \text{Mn}^{2+} \rightarrow \text{Mn}^{3+} \rightarrow \text{MnO}_2 \rightarrow \text{MnO}_4^{2-} & 1.1 & -1.61 & -0.35 & -2.26 & -0.564 & \text{MnO}_4^{-} & \text{MnO}_4^{-} \\
\text{Fe} & : \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} & 0.44 & -0.771 & -0.537 & \text{Fe}^{3+} & \text{Fe}^{2+} \\
\text{Co} & : \text{Co}^{2+} \rightarrow \text{Co}^{3+} \rightarrow \text{Co}^{2+} \rightarrow \text{Co}^{3+} & -1.02 & -1.3 & \text{Co}^{3+} & \text{CoO}_{4}^{-} & \text{Ni} & \text{Ni}^{2+} \rightarrow \text{Ni}^{3+} \rightarrow \text{NiO}_{2} & -0.256 & -1.76 & \text{NiO}_{2} \\
\text{Cu} & : \text{Cu}^{+} \rightarrow \text{Cu}^{2+} & -0.41 & -0.152 & \text{Cu}^{2+} & \text{Cl}^{-} & \text{Cl}_{2} \rightarrow \text{Cl}^{-} \rightarrow \text{ClO}_{4}^{-} & -1.16 & -1.43 & -1.44 & -1.31 & -1.16 & \text{ClO}_{4}^{-} \\
\text{Br}^{-} & \rightarrow \text{Br}_{2} \rightarrow \text{HBrO} \rightarrow \text{BrO}_{3}^{-} & -1.07 & -1.19 & -1.49 & \text{BrO}_{3}^{-} & \text{I}^{-} & \text{I}_{2} \rightarrow \text{HIO} \rightarrow \text{IO}_{3}^{-} \rightarrow \text{H}_{2}\text{IO}_{6} & -1.45 & -1.14 & (-1.7) & \text{H}_{2}\text{IO}_{6}
\end{align*}
\]


The cell would be

\[ \text{Pt}/\text{Cu}^+ \text{(plus Cu}^{2+}, \text{Fe}^{3+}, \text{Fe}^{2+} \text{as the titration proceeds)/calomel reference electrode.} \]

The cell potential is \( \mathcal{E}_{\text{cell}} = \mathcal{E}_\text{Pt} - \mathcal{E}_\text{ref} \), where \( \mathcal{E}_\text{Pt} \) is the half-cell potential at the platinum electrode. The statement is that at all stages of the titration

\[ \mathcal{E}_\text{Pt} = \mathcal{E}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = \mathcal{E}_{\text{Cu}^{+}/\text{Cu}^{2+}}, \]

(13-27)

\[ \mathcal{E}_\text{Pt} = \mathcal{E}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = \mathcal{E}_{\text{Cu}^{+}/\text{Cu}^{2+}}, \]

(13-28)

where, for simplicity, activity coefficients are neglected. Equation (13-28) rearranges to

\[ \mathcal{E}_{\text{Cu}^{+}/\text{Cu}^{2+}} - \mathcal{E}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.05139 \ln \left( \frac{\text{Cu}^{2+}}{\text{Cu}^{+}} \right) (\text{Fe}^{3+}) = 0.618. \]

(13-29)

Equation (13-29) defines the equilibrium constant for reaction (13-26) and may be solved for each stage of the titration. One then inserts the equilibrium ratio of \((\text{Cu}^{2+})/(\text{Cu}^{+})\) or that of \((\text{Fe}^{3+})/(\text{Fe}^{2+})\) in Eq. (13-28) to give \( \mathcal{E}_\text{Pt} \) and thence \( \mathcal{E}_{\text{cell}} \).

At the end-point, \( \text{Fe}_{\text{tot}} = \text{Cu}_{\text{tot}} \), and since \( (\text{Fe}^{3+}) = (\text{Cu}^{2+}) \) by the stoichiometry of Eq. (13-26), it follows that \( (\text{Cu}^{+}) = (\text{Cu}^{2+}) \). Equation (13-29) then reduces to

\[ \mathcal{E}_{\text{Cu}^{+}/\text{Cu}^{2+}} - \mathcal{E}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.05139 \ln \left( \frac{(\text{Fe}^{3+})}{(\text{Fe}^{2+})} \right)_{\text{endpoint}}. \]

Insertion of this relationship into the right-hand side of Eq. (13-28) to eliminate the log term leads to

\[ \mathcal{E}_\text{Pt, endpoint} = \frac{1}{2}\left( \mathcal{E}_{\text{Fe}^{3+}/\text{Fe}^{2+}} + \mathcal{E}_{\text{Cu}^{+}/\text{Cu}^{2+}} \right). \]

(13-30)

Equation (13-30) gives the value of \( \mathcal{E}_\text{Pt} \), and hence of \( \mathcal{E}_{\text{cell}} \) at the endpoint. The plot of this particular titration is shown in Fig. 13-8, where \( F \) is the degree of progress of the titration.
13-8 Determination of pH

The term $pH$ was coined by S. Sorensen in 1909 to mean $-\log(H^+)$, and we have come to use the symbol $p(X)$ as an operator meaning $-\log X$, where $X$ may be a concentration, an activity, or an equilibrium constant; $pK_a$ means $-\log K_a$, for example. A potential measurement always reflects the activity of the species present, and only at infinite dilution can activity be equated with concentration. Potentiometric methods for $pH$ determination therefore measure some type of hydrogen ion activity, although it turns out that the exact nature of what is measured depends on the cell that is used. The modern procedure is to define $pH$ as essentially

$$pH = -\log a_{H^+}$$  \hspace{1cm} (13-31)

but with the exact meaning of $a_{H^+}$ determined by the cell used.

Consider first a cell such as (13-1):

$$\text{Pt}/H_2(1 \text{ atm})/HCl(m)/AgCl/Ag.$$  \hspace{1cm} (13-31)

The corresponding Nernst equation is

$$\varepsilon = \varepsilon^0 - 0.05139 \ln a_{H^+, \text{HCl}}.$$  \hspace{1cm} (13-32)

The procedure described in Section 13-3 allows the determination of $\varepsilon^0$, and so the cell measurements provide values for the mean activity of HCl in any solution, which might be thought to correspond to $a_{H^+}$. Suppose that now we replace the electrolyte by $[\text{HAc}(m_1) + \text{KCl}(m_2)]$. The $\varepsilon^0$ remains the same, as does Eq. (13-32). However, the calculated mean activity for HCl will now depend on both $m_1$ and $m_2$. Thus such a cell is not suited for $pH$ determination.

Next, consider the cell

$$\text{Pt}/H_2(1 \text{ atm})/\text{solution} /\text{calomel electrode}.$$
This emf is

\[ \varepsilon_{298} = -\varepsilon_{\text{ref}} - 0.02569 \ln a_{H^+} = -\varepsilon_{\text{ref}} + 0.05916 \text{pH} \] (13-33)

and it appears that our goal is achieved. The problem is that \( \varepsilon_{\text{ref}} \) contains the junction potential at the solution/KCl interface (see Section 13-2C and Special Topics section) and is not rigorously measurable. What is actually done is to determine \( \varepsilon_{\text{ref}} \) such that \( a_{H^+} \) corresponds to \((H^+)\gamma_\pm\) as observed, by independent means, to apply to various solutions of weak acids. In effect, it is assumed, not quite correctly, that \( \gamma_{H^+} = \gamma_\pm \); it is also assumed, not quite correctly, that the junction potential incorporated in \( \varepsilon_{\text{ref}} \) will not vary with the nature of the solution studied.

The result of all this is that the operational definition of pH is given by Eq. (13-33) with the \( \varepsilon_{\text{ref}} \) values of Table 13-1 for the various calomel reference electrodes. The definition allows very precise pH measurements, but ones whose accuracy is subject to some, but probably not much uncertainty so long as fairly dilute solutions are involved. The interpretation of pH in concentrated solutions or in nonaqueous solvents can be quite a problem.

The hydrogen electrode is a demanding one to use experimentally; the platinized platinum can be poisoned (lose its catalytic ability due to adsorption of solution components), so that the electrode fails to function well. An alternative pH-determining cell is that corresponding to Eq. (13-25):

\[
\text{Pt/solution with quinone (Q) plus hydroquinone (H}_2\text{Q)/calomel electrode.}
\]

One convenience is that quinone forms a 1:1 compound with hydroquinone, quinhydrone, so that by dissolving the compound in the solution to be tested, one establishes equal concentrations of both species. With the added assumption that, being nonelectrolytes, their activity coefficients will be unity, the Nernst term, \((RT/nF)\ln(a_Q/a_{H_2Q})\), drops out and one has for \(25^\circ\text{C}\)

\[ \varepsilon_{298} = -0.6994 - \varepsilon_{\text{ref}} + 0.05916 \text{pH} \] (13-34)

(subject to the same reservations about liquid junctions as stated earlier).

The most widely used pH-determining cell is that known as the pH meter or glass electrode. The cell diagram is

\[
\text{glass membrane}
\]

\[
\text{reference electrode} \quad // \quad \text{in solution A} \quad // \quad \text{unknown solution} \quad // \quad \text{calomel electrode},
\]

(13-35)

where the anode may be either Ag/AgCl or a calomel electrode, but with the solution buffered at some constant pH. The glass membrane has the property of passing essentially only hydrogen ions, and, per faraday, the cell reaction is

\[
\text{H}^+(\text{solution A}) = \text{H}^+(\text{unknown solution})
\]

so

\[ \varepsilon_{298} = \text{constant} + 0.05916 \text{pH} , \] (13-36)

where the constant contains \( \varepsilon^0 \) for the cell, a constant Nernst term, and the junction potential. In practice, one calibrates the pH meter scale by measuring the emf when a known buffer solution is used in place of the unknown solution,
and one finds that it gives almost the same pH values for other solutions as a hydrogen electrode does [see Dole (1941) and Bates (1954) for details]. Recently other ion-selective membranes have been developed that pass only one or another cation or anion, and an electrode incorporating such a membrane allows the determination of a $pM$ or a $pX$, where $M$ or $X$ is the ion passed. The selectivity is not always rigorous, however, and one must test such electrodes carefully in the actual situation before accepting the results of their use.

**13-9 Irreversible Electrode Processes**

The material so far has dealt with reversible emf’s, the experimental measurements being made under conditions of virtually no current flow through the cell. Practical applications of electrochemistry, except for standard reference cells, involve appreciable current flows and we now encounter a new set of phenomena which involve irreversible processes. One is that of overvoltage, important in electrodepositions and also in the study of the kinetics of electrode reactions. Another is polarography, discussed in the Special Topics section.

**A. Electrodeposition**

Electrodeposition is the production of an electrolysis product, usually a metal, on a preparative scale. The situation is illustrated in Fig. 13-9. When a potential is applied across the terminals of a cell very little happens until a critical voltage is reached, beyond which the current increases about linearly with potential. This is what occurs: Suppose that we have two platinum wires dipping in an HCl solution. The cell reaction and reversible potential are

- Anode: $2Cl^-(m) = Cl_2(P) + 2e^-$
- Cathode: $2H^+(m) + 2e^- = H_2(P)$

and

\[
\delta = \delta^0 - \frac{RT}{2F} \ln \frac{1}{a^{2}_{HCl}} - \frac{RT}{2F} \ln(a_{H_2} a_{Cl_2}),
\]  

(13-37)
where \( \varphi^0 = -1.3595 \) V at 25°C. This would, in principle, be established if hydrogen and chlorine gas were bubbling past the respective electrodes, so that \( a_{\text{H}_2} \) and \( a_{\text{Cl}_2} \) corresponded to a \( P \) of 1 atm.

In the present experiment, however, no gases are being supplied, and \( P \) is initially zero, so that \( \varphi \) is some large positive number, infinity in theory. When the electrodes are inserted into the solution and connected, but with no potential applied some fluctuation will decide one to be the anode and the other the cathode, and some minute amount of electrolysis will occur, forming a little dissolved hydrogen and chlorine next to the electrodes and bringing their local activities up to some low, but nonzero value. The activity of the dissolved gases is far below that for 1 atm pressure and no bubbles can form, but the dissolved gases will diffuse steadily away from the electrodes into the solution. The result is that a small current will flow, and if a very sensitive probe could be used, each electrode would be observed to have some potential relative to the probe. The electrodes are said to be polarized, and the small current is called the residual polarization current.

If we now apply a small potential \( V \) between the electrodes, additional electrolysis will take place, building up \( a_{\text{H}_2} \) and \( a_{\text{Cl}_2} \) so that a back emf \( \varphi' \) develops in opposition to the applied potential difference. The increased hydrogen and chlorine activities lead to an increased diffusion rate away from the electrodes and a consequent increase in the very low steady-state current. We thus observe section 1–2 of the curve shown in Fig. 13-9. With continued increase in applied voltage \( a_{\text{H}_2} \) and \( a_{\text{Cl}_2} \) will become equal to the value of the gases at 1 atm, and actual bubble formation will occur. Then \( \varphi' \) is at its maximum value \( \varphi'_{\text{max}} \) and cannot increase further, and beyond this point the increase in applied potential goes into an ohmic potential drop through the solution, that is, \( V - \varphi'_{\text{max}} = iR \). The section 2–3 of the plot is thus linear.

This analysis indicates that extrapolation of the linear portion of the plot of Fig. 13-9 gives \( \varphi'_{\text{max}} \); this is called the decomposition potential. Ideally, \( \varphi'_{\text{max}} \) is equal to \( \varphi_{\text{rev}} \) for the cell, but in practice it may be more positive, and the difference between the two is then called the overvoltage. In electrodeposition one is operating in this linear region, and although the reversible potential is the ideal decomposition potential, in practice one must know what the overvoltage will be.

Suppose that we wish to deposit cadmium from a 0.1 m solution of a cadmium salt at \( p\text{H} \) 7. The reversible potential for the reaction

\[
\text{Cd}^{2+} + 2e^- = \text{Cd}
\]

will be, at 25°C and with activity coefficient effects neglected,

\[
\varphi_{\text{Cd}} = -0.402 - \frac{0.02569}{2} \ln \left( \frac{1}{0.1} \right) = -0.432 \text{ V}
\]

The value for hydrogen, that is, \( \varphi \) for evolving hydrogen gas, is

\[
\varphi_{\text{H}_2} = 0 - \frac{0.02569}{2} \ln \left( \frac{10^{-7}}{10^{-7}} \right) = -0.414 \text{ V}
\]

One thus expects the evolution of hydrogen to occur first as potential is applied to the electrolysis cell and that, in fact, it would be virtually impossible to cause cadmium metal to deposit on the electrode. The actual situation is just the reverse because the overvoltage for hydrogen evolution from a cadmium surface is about 0.5 V; as a consequence, the cadmium deposits and no hydrogen evolution occurs.

Some representative hydrogen evolution overvoltages are as follows: platinized platinum, zero or small; smooth platinum, 0.09; silver, 0.15; copper, 0.23; lead, 0.64; zinc, 0.70; and mercury, 0.78 (for zero current). An interesting observation is that the hydrogen overvoltage parallels the heat of adsorption of atomic hydrogen on the metal. The overvoltage thus seems to be related to the energy required to produce surface hydrogen atoms as the intermediate to \( \text{H}_2 \) formation.

### B. Theory of Overvoltage

The excess of an applied potential over the reversible decomposition potential, or the overvoltage, is usually given the symbol \( \eta \), and Fig. 13-9 could be redrawn so as to show a plot of \( i \) versus \( \eta \). However, there are three general types of contribution to an observed overvoltage, only two of which are of fundamental interest. As mentioned earlier, the linear portion of Fig. 13-9 arises primarily from the Ohm's law drop in potential across the solution and is trivial from a theoretical point of view. Second, as active decomposition occurs, electrolysis products accumu-
late and reactants are depleted in the vicinity of the electrode; the effect is to change $\varepsilon_z$ from the reversible value calculated for the average compositions. This contribution to $\eta$ is known as concentration polarization, and is of practical but not much theoretical interest (see Special Topics section). We wish to concentrate on that portion of $\eta$ due to the intrinsic chemistry of the electrode process itself, often called activation polarization.

The experimental method is illustrated in Fig. 13-10. The desired current $i$ is passed through the electrode to be studied $\varepsilon_z$ by means of the circuit $\varepsilon_{\text{right}} - \varepsilon_{\text{left}}$ and the potential variation at $\varepsilon_z$ is measured by means of the separate potentiometer circuit $\varepsilon_{\text{right}} - \varepsilon_{\text{right}}$. Thus the ohmic contribution is essentially eliminated, and, with good stirring, most of the concentration polarization. The commutator device shown allows $\eta$ to be measured either during current flow or immediately after cessation of flow; in this last case that portion of $\eta$ due to activation polarization will often decay exponentially with time.

Activation polarization usually obeys an equation due to J. Tafel in 1905, known as the first law of electrode kinetics:

$$\eta = a + b \ln i.$$  \hspace{1cm} (13-38)

A derivation of Eq. (13-38) is given in the Special Topics section, but the qualitative basis for it is that there is some slow step in the electrode process which involves an energy barrier, so that a Boltzmann factor $\exp\left(-\Delta G^*/RT\right)$ determines $i$. The applied potential acts to lower the level of this barrier, and hence the increased current is logarithmically related to $\eta$.

---

**COMMENTARY AND NOTES**

**13-CN-1 Standard Oxidation Potential $\theta^0$ and Standard Electrode Potential $\nu^0$**

We have used the standard oxidation potential $\theta^0$ throughout this chapter, and an alternative quantity, the standard electrode potential $\nu^0$, should be mentioned. This last is defined according to the recommendations of an international commission of 1953 as follows. A cell is made up of the particular electrode and a hydrogen electrode, and the half-cell electrode potential is that of the reversible potential difference between the terminals of the electrodes. Referring to Fig. 13-3, we see that if the half-cell operates spontaneously as the anode, the potential at its terminal is negative, and its electrode potential is therefore reported as negative. The standard electrode potential is defined the same way as to sign, but, of course, with all species now in their standard states.

The standard electrode potential is, by this definition, a property of the half-cell (relative to the hydrogen electrode), and its sign is therefore independent of the direction in which one writes the half-cell reaction. In determining $\theta^0$ for a cell, one writes the cell diagram as usual, and, by definition,

$$\theta^0 = \nu^0_{\text{right}} - \nu^0_{\text{left}}.$$  \hspace{1cm} (13-39)

By this definition $\theta^0$ is positive if the cell reaction, with the left-hand electrode taken to be the anode, is spontaneous; there is no change in this respect.

The system used here compares with that just given as follows. The standard oxidation potential is positive for a half-cell if, relative to the hydrogen electrode, the spontaneous reaction of the half-cell is one of oxidation. For some other

Commutator

$$\Phi_i$$

$$\Phi_j$$

Potentiometer

$$\Phi_k$$

cell $\varepsilon^0$ is, by this definition,

$$\varepsilon^0 = \varepsilon^0_{\text{left}} - \varepsilon^0_{\text{right}}$$  \[\text{Eq. (13-19)}]\]

The standard oxidation potential is always associated with the half-cell reaction written as an oxidation; the standard potential for a half-cell written as a reduction is called the standard reduction potential. In effect, $\psi^0$ values are the same in sign and in use as standard reduction potentials. Their values, included in Table 13-1, are thus always the negative of the $\varepsilon^0$ values.

The system used in this chapter, that of $\varepsilon^0$ values, is the one employed by Latimer (1952) in his definitive book on oxidation potentials and is the traditional one in the United States. The $\psi^0$ system conforms more to the European tradition of signing an electrode according to the potential at its terminal. This writer feels that the first convention, the one used here, is better suited to the physical chemist interested in electrode reactions and in viewing the potential of an electrode in solution rather than at its terminal. It is also consistent with the sign convention for the emf of a whole cell. Both these potentials are positive if the cell reaction proceeds spontaneously with the left-hand electrode as anode. Likewise, the $\varepsilon^0$ for a half-cell is positive if the cell reaction is spontaneous with the half-cell written as the left-hand electrode or anode and the hydrogen half-cell as the cathode.

**13-CN-2 Storage Batteries**

Electrochemical cells have great practical application. They are called primary cells if electrical energy is supplied on a one-time basis and secondary cells or storage batteries if an external source of energy is required to charge them.
One common type of storage battery is the lead–sulfuric acid cell for which the electrode reactions are

\[
\text{anode: } \quad \text{Pb} + \text{H}_2\text{SO}_4 = \text{PbSO}_4(s) + 2\text{H}^+ + 2\text{e}^-, \\
\text{cathode: } \quad \text{PbO}_2(s) + \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- = \text{Pb} + \text{PbSO}_4(s) + 2\text{H}_2\text{O}.
\]

The net reaction is

\[
\text{PbO}_2(s) + \text{PbSO}_4 + 2\text{H}_2\text{SO}_4 = 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}.
\]

The potential is about 2 V; most lead storage batteries consist of several cells in series. The Leclanché dry cell has a potential of about 1.6 V and consists of a carbon electrode surrounded by manganese dioxide and graphite immersed in a starch paste containing zinc chloride and excess solid ammonium chloride. The electrode reactions of this cell are

\[
\text{anode: } \quad \text{Zn} + 2\text{NH}_3 = \text{Zn(NH}_3)_2^+ + 2\text{e}^-, \\
\text{cathode: } \quad 2\text{MnO}_2 + 2\text{NH}_4^+ + 2\text{e}^- = \text{Mn}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{NH}_3.
\]

The lead storage battery loses a good deal of power under high loads and, of course, is very heavy. A more expensive, but otherwise very attractive storage battery has been in use in Europe for many years, and, more recently, in the United States. This is the Jungner nickel–cadmium battery, which consists of nickel and cadmium electrodes and a KOH or other alkali electrolyte. The cell reactions are

\[
\text{anode: } \quad \text{Cd} + 2\text{OH}^- = \text{Cd(OH)}_2 + 2\text{e}^-,
\]

\[
\text{cathode: } \quad \text{Ni(OH)}_3 + \text{e}^- = \text{Ni(OH)}_2 + \text{OH}^-.
\]

The net reaction is

\[
\text{Cd} + 2\text{Ni(OH)}_3 = \text{Cd(OH)}_2 + 2\text{Ni(OH)}_2.
\]

Notice that the electrolyte serves merely as a vehicle for the transportation of OH\(^-\) ions. The Ni–Cd battery is rechargeable and can deliver very high currents without appreciable loss of power. An important use is in battery-powered tools and appliances.

An important type of primary cell is the fuel cell. A simple example is the cell

\[
\text{Pt/H}_2(\text{g})/\text{electrolyte/O}_2(\text{g})/\text{C},
\]

for which the net reaction is just \(\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}\). Much current research is being carried out on the development of suitable electrodes for the reversible combustion of hydrocarbons so as to obtain electrical energy directly from a reaction such as \(\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}\). The electrode reactions should be nearly reversible, high current densities are desirable, and a means must be provided for removing the products of the electrode reaction. It has not yet been possible to meet these requirements in a fully satisfactory manner, although results with experimental fuel cells have been encouraging.

### 13-CN-3 Thermodynamic Quantities for Aqueous Ions

We have completed, with this chapter, the presentation of the various experimental approaches by which we obtain thermodynamic quantities for aqueous
electrolytes. The thermochemical approach is summarized in Section 5-5B and standard enthalpies of formation of aqueous electrolytes and of individual ions are given in Table 5-3; it will be recalled that these latter are based on the convention that $\Delta H^0_{298} = 0$ for H$^+$ ion.

The free energy of formation of an aqueous electrolyte may be determined from either solubility or emf data. As an example of the first method, the solubility of KCl is 4.82 M at 25°C and the mean activity coefficient in the saturated solution is 0.588; the standard free energy of solution is the solubility equilibrium constant, or

$$\Delta \mu^0 = -RT \ln K = -2RT \ln a_{\text{sat}}$$

$$= -(2)(1.98)(298) \ln[(4.82)(0.588)] = -1.23 \text{ kcal mole}^{-1}.$$  

The value of $\Delta H^0$ of solution (at infinite dilution since this is the reference condition) is 4.11 kcal mole$^{-1}$, and on combination of the two results, $\Delta S^0$ of solution is 18.0 cal K$^{-1}$ mole$^{-1}$. In the case of AgCl the corresponding calculation might be based on the thermodynamic solubility constant, as determined from emf data, whose temperature dependence would give $\Delta S^0$ directly.

Absolute standard entropies for a number of electrolytes have been determined by one or another of these methods and one now adopts the convention that $S^0$ of H$^+$ ion is zero. This allows the entropy data to be reported for individual ions, and a selection of such values is given in Table 13-3. The standard free energies of formation of the various ions are included in the table; again that for H$^+$ ion is taken to be zero. One may use tables such as Table 13-3 in combination with those for standard entropies and free energies of formation of pure compounds to obtain $\delta^0$ values for half-cells not previously measured.


<table>
<thead>
<tr>
<th>Ion</th>
<th>$S^0$ (cal K$^{-1}$ mole$^{-1}$)</th>
<th>$\Delta \mu^0$ (kcal mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>(0.0000)</td>
<td>(0.0000)</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>3.4</td>
<td>-70.22</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>14.4</td>
<td>-62.59</td>
</tr>
<tr>
<td>K$^+$</td>
<td>24.5</td>
<td>-67.46</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>17.67</td>
<td>18.43</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>-2.52</td>
<td>-37.59</td>
</tr>
<tr>
<td>F$^-$</td>
<td>-2.3</td>
<td>-66.08</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>13.2</td>
<td>-31.35</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>19.29</td>
<td>-24.57</td>
</tr>
<tr>
<td>I$^-$</td>
<td>26.14</td>
<td>-12.35</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>43.2</td>
<td>-2.47</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>4.1</td>
<td>-177.34</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>-12.7</td>
<td>-126.22</td>
</tr>
</tbody>
</table>

13-CN-4 Electrocapillarity. Absolute Electrode Potentials

A very interesting electrochemical effect is that of the change in interfacial tension with applied potential. Not many interfaces allow an accurate study of this effect, however, because an attempt to apply a potential difference often results in electrolysis or in electrolytic transport across the interface. An especially well-adapted system is that of the mercury-electrolyte solution interface. This is highly polarizable, meaning that applied potentials result in little electrolysis in the absence of easily reducible ions, and, since mercury is a liquid, the interfacial tension can be observed by the methods of capillarity.

The typical experimental observation is illustrated in Fig. 13-11, which shows the mercury–solution interfacial tension to increase, go through a maximum, and then decrease as potential is applied. The experimental arrangement is that depicted in Fig. 13-12; a mercury reservoir terminates in a fine capillary tube and the position of the meniscus is viewed through a traveling microscope. Since the contact angle glass–mercury–solution is obtuse, there is a capillary depression [note Eq. (8-37)], so a positive head of mercury is needed to force the meniscus toward the end of the tapering capillary tube. The electrical connection is from the mercury through a source of potential to a calomel electrode and thence to the electrolyte solution. Measurement of the head required to maintain the meniscus yields the capillary depression and hence the surface tension at the mercury–solution interface. It is the variation of this surface tension with applied potential that is reported in Fig. 13-11; the abscissa is the potential relative to that at the maximum, called the rational potential.

The thermodynamic explanation of the electrocapillarity effect is that the derivative of surface tension with respect to potential gives the surface charge density $\sigma$:

$$\frac{\partial \gamma}{\partial V} = -\sigma.$$  \hspace{1cm} (13-40)

Just as the adsorption of a surfactant at an interface lowers the interfacial tension,

![Graph](https://example.com/graph.png)  

so does the concentration of charge at an interface. At the maximum the derivative in (13-40) is zero and so therefore must be the surface charge density; this suggests that the absolute potential difference across the interface is also zero. The voltage applied to reach this electrocapillarity maximum therefore just balances the natural potential difference between the phases. This applied potential difference is 0.48 V if the electrolyte is one not apt to interact with the mercury surface, such as potassium carbonate or sulfate, which implies that the absolute half-cell potential of the calomel electrode is —0.48 V (as compared to —0.28 V on the hydrogen scale).

The problem is that even though the charge density must be zero at the electrocapillarity maximum, there will still be adsorbed and polarized solvent and solute molecules, so that $\Delta \phi$, the galvanic potential difference across the interface, is not necessarily zero. Notice, for example, that the position of the electrocapillarity maximum shown in Fig. 13-11 varies with the nature of the electrolyte as the anion is changed; the same happens if the cation is varied or if the solvent medium is altered.

Various other attempts have been made to determine absolute half-cell potentials, but, as in this case, certain unprovable assumptions are always involved. It does seem likely, though, that the absolute values are not greatly different from those reported on the hydrogen scale.

SPECIAL TOPICS

13-ST-1 Liquid Junctions

The existence and importance of the potential at a liquid junction have been noted in several places in this chapter. The detailed treatment is somewhat specialized, however, and has therefore been placed in this section. We consider
first the potential of a cell having a liquid junction and then some aspects of the electrochemistry of the liquid junction itself.

A. Concentration Cells with a Liquid Junction

The least complicated type of cell which has a liquid junction is a concentration cell since the electrode reactions are then the same, except for a difference in concentration of the electrolyte across the junction. The general cell diagram is

\[ \text{anode/solution at } m_1/\text{solution at } m_2/\text{cathode}, \]

where the dashed line means that the two solutions are in electrolytic contact but are somehow prevented from mechanical mixing. This may be by means of a porous diaphragm, as in the Daniell cell of Fig. 13-2, or by a stiffening of one of the solutions at its point of contact with the other by agar-agar or gelatine, as is done in a salt bridge.

An example of a concentration cell with a liquid junction is the following:

\[ \text{Pt/H}_2(1 \text{ atm})/\text{HCl}(m_1)/\text{HCl}(m_2)/\text{H}_2(1 \text{ atm})/\text{Pt}, \]  

anode reaction \( \frac{1}{2}\text{H}_2(1 \text{ atm}) = \text{H}^+(m_1) + e^- \),
cathode reaction \( \text{H}^+(m_2) + e^- = \frac{1}{2}\text{H}_2(1 \text{ atm}) \),
net reaction \( \text{H}^+(m_2) = \text{H}^+(m_1) \).

(13-41)

(13-42)

The emf of a cell corresponds to the free energy change associated with the sum of all processes occurring per faraday of electricity passed through the cell. Current is carried by the ions in the solution, which means that \( t_+ \) equiv of hydrogen ion must cross the junction from left to right and \( t_- \) equiv of chloride ion must do so from right to left, where \( t \) denotes transference number (see Section 12-6). The changes that occur in addition to the electrode reactions are then

\[ t_+\text{H}^+(m_1) = t_+\text{H}^+(m_2), \quad t_-\text{Cl}^-(m_2) = t_-\text{Cl}^-(m_1). \]

(13-43)

The sum of process (13-42) and processes (13-43) is

\[ t_+\text{H}^+(m_2) + t_-\text{Cl}^-(m_2) = t_+\text{H}^+(m_1) + t_-\text{Cl}^-(m_1), \]

(13-44)

bearing in mind that \( t_+ + t_- = 1 \). The corresponding Nernst equation is

\[ \frac{\Delta G}{nF} = -RT \ln \frac{a_{\text{H}^+}^{t_+}a_{\text{Cl}^-}^{t_-}}{a_{\text{H}^+}^{t_1}a_{\text{Cl}^-}^{t_2}} \]

or

\[ \frac{\Delta G}{nF} = -2t_-RT \ln \frac{a_{\text{H}^+}^{t_1}a_{\text{Cl}^-}^{t_2}}{a_{\text{H}^+}^{t_1}a_{\text{Cl}^-}^{t_2}}. \]

(13-45)

If \( m_1 \) and \( m_2 \) are 0.1 and 0.01, respectively, then the \( \gamma_\pm \) values are 0.796 and 0.904, respectively, and the \( t_- \) values are 0.1686 and 0.1749, respectively. The
average value of \( t_- \) is 0.1717, and the emf of the cell at 25°C is calculated to be

\[
\varepsilon = -(2)(0.1717)(0.02569) \ln \frac{(0.1)(0.796)}{(0.01)(0.904)} = -0.1919.
\]

The overall cell reaction is the sum of processes (13-42) and (13-43), and the separate Nernst expressions for these are

\[
\varepsilon_E = -\frac{RT}{\mathcal{F}} \ln \frac{a_{H^+,m_1}}{a_{H^+,m_2}}
\]

and

\[
\varepsilon_j = -t_+ \frac{RT}{\mathcal{F}} \ln \frac{a_{H^+,m_2}}{a_{H^+,m_1}} - t_- \frac{RT}{\mathcal{F}} \ln \frac{a_{Cl^-,m_1}}{a_{Cl^-,m_2}}.
\]

Inspection confirms that the sum of Eqs. (13-46) and (13-47) gives Eq. (13-45); thus

\[
\varepsilon = \varepsilon_E + \varepsilon_j.
\]

The emf for the cell can therefore be viewed as made up of two terms: that due to the electrode reactions \( \varepsilon_E \), and the junction potential \( \varepsilon_j \), which gives the work associated with the transport of ions across the liquid junction.

We can extend the preceding numerical example to the calculation of \( \varepsilon_E \) and \( \varepsilon_j \) only by making some assumption regarding individual ionic activity coefficients. If, for example, we assume that \( \gamma_{H^+} = \gamma_{Cl^-} = \gamma_\pm \), then Eqs. (13-46) and (13-47) give \( \varepsilon_E = -0.05588 \text{ V}, \varepsilon_j = 0.03669 \text{ V} \). The junction potential represents a major correction in this case.

In using Eq. (13-45), an average value of \( t_- \) for the two concentrations was used. It turns out that the correct average is not the simple arithmetic one, and the work done in transporting an ion across the junction actually involves the integral

\[
RT \int_{m_1}^{m_2} t_- d(ln a_\pm),
\]

so that the corrected version of Eq. (13-45) is

\[
\varepsilon = -2 \frac{RT}{\mathcal{F}} \int_{m_1}^{m_2} t_- d(ln a_\pm).
\]

A study of cells of this type evidently permits the determination of transference numbers as a function of concentration.

As a last point, the overall cell reaction will depend on whether the electrodes are reversible to the anion or to the cation. Thus for the cell

\[
\text{Ag/AgCl/HCl(m_1)}/\text{HCl(m_2)/AgCl/Ag}
\]

Eqs. (13-45) and (13-49) would have \( t_+ \) rather than \( t_- \), and \( \varepsilon_E \) would have the opposite sign. The numerical example would then give

\[
\varepsilon = \varepsilon_E + \varepsilon_j, \quad \text{or} \quad 0.09257 = 0.05588 + 0.03669.
\]

The sign of the junction potential remains the same. Thus, although we analyze
in detail each specific concentration cell to determine the correct overall cell reaction, the junction potential remains the same for any given junction.

### B. Junction Potentials

Equation (13-47) simplifies considerably if activity coefficient effects are neglected. We then obtain

\[
\varepsilon_j = (t_+ - t_-) \frac{RT}{\mathcal{F}} \ln \frac{m_1}{m_2}.
\]

This form brings out the important point that \( \varepsilon_j \) depends on \( t_+ - t_- \). It is largely with this factor in mind that one expects the junction potential to be small in the case of a KCl bridge; \( t_+ \) for 1 m KCl is 0.488, and so \( t_+ - t_- \) is only 0.024. The same situation applies in the case of NH\(_4\)NO\(_3\), an electrolyte that is used in a salt bridge if it is not desirable that Cl\(^-\)-ion-containing solution have contact with the electrolyte of the half-cell being studied.

If various electrolytes are present on either side of a liquid junction, then the total work of transporting ions across the junction per faraday, which gives \( \varepsilon_j \), depends on weighted averages or integrals such as that of Eq. (13-48). By using concentrated KCl in the salt bridge, one ensures that the important \( t_i \) will be those of K\(^+\) and Cl\(^-\), so that \( \varepsilon_j \) will not be very sensitive to the nature of the more dilute electrolyte solution of the half-cell into which the salt bridge dips. The analysis makes it clear, however, that although we can reduce a junction potential to a fairly small value, cells with liquid junctions retain a residual uncertainty in the interpretation of their emf’s and one which is difficult to analyze exactly.

13-ST-2 Polarization at Electrodes. Polarography

Three types of polarization effects were noted in Section 13-9: ohmic, concentration, and activation. We now discuss these last two in more detail.

### A. Activation Polarization

The Tafel equation (13-38), which relates the activation polarization component of the overvoltage to the current \( i \), may be accounted for in terms of the following analysis. Consider a general electrode reaction

\[
e^{-} + O \text{ (oxidized state)} = R \text{ (reduced state)},
\]

where, as illustrated in Fig. 13-13, the oxidized state must pass through some high-energy intermediate \( I \) in the process of being reduced. We write an equation analogous to Eq. (8-65) for the rate of the forward process:

\[
R_t = \left[ \frac{kT}{h} \exp\left( -\frac{\Delta G_I^{0\Delta}}{RT} \right) \right] \quad (O),
\]

where \( \Delta G_I^{0\Delta} \) is the standard free energy change to go from O to I. It will be known
in the next chapter as the free energy of activation. Similarly, the rate of the back reaction is

\[ R_b = \left[ \frac{kT}{h} \exp\left( -\frac{\Delta G^0_t}{RT} \right) \right] (R). \] (13-52)

The presence of a potential difference \( \phi \) between the electrode and the solution contributes to \( \Delta G^0_t \) and we write this last as the sum of a chemical component and an electrical one:

\[ \Delta G^0_t = \Delta G^0_{t,\text{chem}} - \alpha \mathcal{F} \phi, \] (13-53)

which allows that only some of this potential difference is effective; this fraction is called the transfer coefficient \( \alpha \). The current part due to the forward reaction is then

\[ i_t = \left[ \frac{kT}{h} \exp\left( -\frac{\Delta G^0_{t,\text{chem}}}{RT} \right) \exp\left( \frac{\alpha \mathcal{F} \phi}{RT} \right) \right] (O), \] (13-54)

where current is in faradays per square centimeter per second. At equilibrium there will be equal and opposite currents in the two directions, or \( i_t^0 = i_b^0 = i^0 \), where \( i^0 \) is known as the exchange current, and \( \phi \) has the value \( \phi^0 \) and corresponds to \( \mathcal{E}^0 \). Then

\[ i^0 = \left[ \frac{kT}{h} \exp\left( -\frac{\Delta G^0_{t,\text{chem}}}{RT} \right) \exp\left( \frac{\alpha \mathcal{F} \phi^0}{RT} \right) \right] (O). \] (13-55)

Combination of Eqs. (13-54) and (13-55) gives

\[ i_t = i^0 \exp\left( \frac{\alpha \mathcal{F} (\phi - \phi^0)}{RT} \right) - i^0 \exp\left( \frac{\alpha \mathcal{F} \eta}{RT} \right), \] (13-56)

where \( \eta \) is the overvoltage. Equation (13-56) may be written in the form

\[ \ln i = \ln i^0 + \frac{\alpha \mathcal{F} \eta}{RT}, \]

which rearranges to the Tafel equation.

In a stricter analysis, an equation analogous to Eq. (13-54) is written for \( i_b \),

\[ \text{FIG. 13-13. Mechanism for activation polarization.} \]
Negative \[ 0 \rightarrow \text{Positive} \]

\[ \eta \]

**FIG. 13-14. A general current versus voltage diagram.**

with \( i = i_t - i_0 \); the effect is to alter the coefficient of \( \eta \) in Eq. (13-56) to give

\[
i = i_0 \left[ \exp \left( \frac{\alpha F \eta}{RT} \right) - \exp \left( - \frac{(1 - \alpha) F \eta}{RT} \right) \right]. \tag{13-57}
\]

As the equation suggests, the situation is symmetric; \( \eta \) may be positive or negative, so that the electrode reaction is driven either forward or backward. Figure 13-14 shows the general behavior of Eq. (13-57).

This treatment, although somewhat sketchy, is designed to indicate how the detailed study of overvoltage effects can lead to information about the intrinsic rate of the electrode reaction, through \( i^\circ \), and the energy of the reaction barrier. As an example, although the mechanism for the reduction of \( \text{H}_3\text{O}^+ \) ion at a metal electrode is still not fully elucidated, the evidence suggests that the rate-determining step is probably the reaction of \( \text{H}_3\text{O}^+ \) with the metal surface to give adsorbed hydrogen atoms and water:

\[
\text{H}_3\text{O}^+ + \text{M} + e^- = \text{M-H} + \text{H}_2\text{O}.
\]

**B. Concentration Polarization**

The preceding analysis was based on the assumption that the rate-limiting step of the electrode process was some activated chemical reaction at the electrode surface. Another process must become rate-controlling at sufficiently high current densities, namely the rate of diffusion of reactant to and of product away from the electrode surface. If the reaction is one of the deposition of a metal from solution, only the rate of diffusion of the metal ion to the electrode is to be considered.
Recalling Eq. (2-65) and the discussion of Section 10-7B, we can write

\[ J = -\mathcal{D} \frac{dC}{dx}, \]  

(13-58)

where \( J \) is now in moles per square centimeter per second. If there is an excess of inert electrolyte in the solution so that the ion being reduced carries little of the current, the potential term in Eq. (12-121) will not be important and \( \mathcal{D} \) will be a constant, equal to the ion diffusion coefficient as given by Eq. (12-119). Further, a reasonable approximation to the physical situation is that the stirring conditions leave a thin stagnant layer of thickness \( \delta \) within which \( C \) varies linearly from \( C_b \), the bulk solution concentration, to \( C_s \), the concentration at the electrode surface. We expect the linear variation of \( C \) with \( x \) since in a steady-state condition \( J \) is constant, and since \( \mathcal{D} \) is constant, so must be \( dC/dx \). Equation (13-58) then becomes

\[ id = zJ = -z\mathcal{D}(C_b - C) / \delta, \]  

(13-59)

where \( id \) is the diffusion current density in faradays per square centimeter per second and \( z \) is the valence number of the metal ion being discharged. Under the conditions of the preceding subsection it is assumed that \( \mathcal{D}/\delta \) is large enough that \( C_b = C \), and the observed current is determined by the rate of the chemical reduction reaction at the electrode, \( i_a \). That is, under steady-state conditions there is no accumulation of material in the diffusion zone and \( id = i_a \). As the overvoltage is increased, \( i_a \) decreases by Eq. (13-57), and \( C_b \) drops enough for \( id \) to match the increase in \( i_a \). The maximum possible diffusion rate \( id_{(\text{max})} \) is reached when \( C_b \) has dropped to zero. Further increase in the overvoltage cannot increase the current any further, and the plot of \( i \) versus \( V \) must level off at \( id_{(\text{max})} \), or at

\[ id_{(\text{max})} = z\mathcal{D}C / \delta. \]  

(13-60)

Thus the effect of concentration polarization is to give a maximum current which is proportional to the concentration of the ion being discharged.

If a mixture of potentially reducible ions is present, again with a supporting electrolyte, that is, an excess of inert electrolyte, present, then as the applied reducing potential is increased the first metal ion begins to deposit, reaches its \( i_{(\text{max})} \), and the second metal ion begins to deposit at some higher potential, and reaches its \( i_{(\text{max})} \), so that the plot of \( i \) versus \( V \) is as shown in Fig. 13-15. The characteristic deposition potential for each ion could be identified as in Fig. 13-9 but when one is operating in the diffusion-controlled region \( C_b \) and hence \( \phi_{\text{rev}} \) is changing with \( V \) so that one obtains a sinusoidal rather than a linear \( i \) versus \( V \) plot. Consequently, it is much more accurate to pick the potential at the half-way point of the step, or the half-wave potential \( V_{1/2} \), as the characteristic one.

Since the overvoltage \( \eta \) is given by

\[ \eta = \phi - \phi_{\text{rev}} = -\frac{RT}{2\mathcal{F}} \ln \frac{C_b}{C}, \]  

(13-61)
where ohmic polarization is neglected, as are activity coefficient terms, we can solve for $C^*/C$. Also, combination of Eqs. (13-59) and (13-60) gives

$$i_d = i_{d\text{ (max)}} \left(1 - \frac{C^*}{C}\right).$$  \hspace{1cm} (13-62)

The result is

$$\frac{i_d}{i_{d\text{ (max)}}} = 1 - \exp \left(-\frac{z\mathcal{F} \eta}{RT}\right).$$  \hspace{1cm} (13-63)

Equation (13-63) gives a symmetric curve such as shown in Fig. 13-15, for which $V_{1/2}$ occurs at the inflection point.

C. Polarography

The preceding analysis suggests that we could analyze for metal ions in solution by obtaining experimental $i$ versus $V$ curves, each limiting diffusion current giving the concentration of a particular ion, the ion being identified by its $V_{1/2}$. This procedure is indeed used. To maintain $\delta$ more constant than is possible by stirring

![Fig. 13-16. Schematic diagram of a polarographic cell.](image-url)
the solution, a common practice is to use a rotating electrode. There is still a problem with accumulation of reduction products, and a very ingenious alternative procedure was devised by J. Heyrovsky in 1922.

The basic experimental features of the Heyrovsky polarograph are shown in Fig. 13-16. The cathode is a mercury drop that is steadily growing at the tip of a capillary immersed in the electrolyte solution, and the anode is a large pool of mercury. By having a tiny drop as the anode surface, concentration polarization effects can be made to develop at relatively small currents; the large area of the anode pool of mercury essentially eliminates concentration polarization at its surface. As each drop grows and falls the anode surface is steadily kept fresh and reproducible, and with a supporting electrolyte the same general analysis applies as for a stationary electrode.

A typical polarogram is shown in Fig. 13-17. The oscillations are a result of the successive appearance of new drops at intervals of a few seconds; currents may be only microamperes in order of magnitude. Each step is called a polarographic wave and is characterized by its half-wave potential $V_{1/2}$ and diffusion current $i_{d(\text{max})}$. The detailed algebraic analysis is complicated by the situation of an expanding cathode surface, and an equation derived by D. Ilkovic in 1938 will be given without the derivation:

$$i_{d(\text{max})} = 70.82 zw (\frac{3}{4} t) (\frac{1}{6}) (\frac{1}{3}) C,$$

(13-64)

where $z$ is the valence number of the ion, $w$ is the flow of the mercury in grams per second, $t$ is the drop time in seconds, and $C$ is the concentration in moles per liter. Equations have also been derived for the half-wave potential, but this remains essentially an empirically determined quantity for each species.

Polarography is capable of measuring ion concentrations as low as $10^{-4} \text{ M}$ and is a rapid as well as a sensitive analytical tool. The physical chemist uses it to study the chemistry of reduction (or of oxidation) processes. One can determine from the diffusion current whether the reduction occurs as a one- or as a two-

![FIG. 13-17. A typical polarogram.](image-url)
electron step. If complexing ions are added to the solution, both the reduction potentials and the formation constants of complex ions can be found. With a commutator to interrupt the applied voltage, chemical rate processes can be followed.

A modern variant of polarography uses a fixed (not a dropping mercury) electrode and current is recorded as the voltage is changed at a fixed rate. In *cyclic voltammetry* the voltage sweep is first in one direction and then in the other. Sweep rates of up to 100 V sec\(^{-1}\) may be used. An idealized voltammogram is shown in Fig. 13-18. On the forward sweep (upper curve) reduction products are formed and on the backward sweep (lower curve) these are oxidized. About the same information is obtained as in ordinary polarography but, in addition, much can be learned about the nature and the reaction kinetics of the reduction product.

![Typical cyclic voltammogram for a reversible redox couple.](image)


**GENERAL REFERENCES**


Activity coefficient effects are to be neglected in Exercises and Problems unless specifically noted otherwise. Assume 25°C unless otherwise specified. Take as exact numbers given to one significant figure.

13-1 The emf of the cell Pb/PbCl₂(s)/KCl(µ)/Hg₂Cl₂(s)/Hg is 0.5357 V at 25°C and increases with temperature by 1.45 × 10⁻⁴ V K⁻¹. Write the electrode and overall cell reactions and calculate ΔG°, ΔH°, ΔS°, and qrev.

   Ans. Pb + Hg₂Cl₂ = PbCl₂ + 2Hg(l), ΔG° = -103.4 kJ,
   ΔS° = 28.0 J K⁻¹, ΔH° = -95.1 kJ, qrev = 8.34 kJ.

13-2 The emf for the cell Cd/0.1 m Cd(NO₃)₂, 0.01 m AgNO₃/Ag is -0.446 V at 25°C. Calculate θ° for this cell.

   Ans. -0.357 V.

13-3 Calculate θ° for the cell Ag/AgI(s)/0.1 m HI/H₂(1 atm)/Pt.

   Ans. 0.038 V.

13-4 Calculate θ° and K at 25°C for the reaction Tl + Ag⁺ = Tl⁺ + Ag.

   Ans. θ° = 1.135 V, K = 1.56 × 10¹⁹.

13-5 Calculate K for the reaction 1/2Cd + Tl⁺ = 1/3Cd²⁺ + Tl and the ratio (Cd²⁺)/(Tl⁺) if excess Cd is added to a solution which is 0.1 m in Tl⁺.

   Ans. K = 13.4 M⁻¹/₂; 2.76.

13-6 Calculate θ° for the half-cell reaction Tl = Tl³⁺ + 3e⁻.

   Ans. -0.721 V.

13-7 Obtain θ° for the half-cell Mg + C₂O₄²⁻ = Mg(C₂O₄)²⁺ + 2e⁻ given that Ksp = 9.0 × 10⁻³ for Mg(C₂O₄)²⁺.

   Ans. 2.49 V.

13-8 What fraction of Ag(CN)₂⁻ is dissociated into Ag⁺ in 1 × 10⁻³ M CN⁻ if θ° = 0.289 V for the half-cell Ag + 2 CN⁻ = Ag(CN)₂⁻ + e⁻? (Neglect the hydrolysis of CN⁻.)

   Ans. 4.0 × 10⁻¹⁸ (!).
13-9 Calculate $\mathcal{E}^{\circ}_{298}$ for the following concentration cells: (a) Na(Hg, $x_{\text{Na}} = 0.1$)/NaCl($m = 0.1$)/Na(Hg, $x_{\text{Na}} = 0.01$); (b) Pt/H$_2$(P = 0.1 atm)/HCl($m = 0.1$)/H$_2$(P = 0.01 atm)/Pt; (c) Ag/AgBr(s)/HBr($m = 0.1$)/H$_2$(1 atm)/Pt—Pt/H$_2$(1 atm)/HBr($m = 0.01$)/AgBr(s)/Ag. 

*Ans.* (a) 0.0592 V, (b) 0.0296 V, (c) 0.1183 V.

13-10 Calculate $\mathcal{E}^{\circ}$ for the cell in Exercise 13-9(b). 

*Ans.* 0.0348 V.

13-11 Calculate $\mathcal{E}^{\circ}$ for the cell Ag/AgCl(s)/0.1 m HCl/H$_2$(1 atm)/Pt, using activity coefficient data from Chapter 12. 

*Ans.* −0.352 V.

13-12 A pH meter gives a reading of 200 mV when measuring a solution whose hydrogen ion activity is considered to be $10^{-4}$; what is the hydrogen ion activity of a solution for which the meter reads 100 mV? (Assume 25°C.)

*Ans.* pH = 2.31.

**PROBLEMS**

13-1 $\mathcal{E}^{\circ}_{298}$ is −1.46 V for the half-cell Pb$^{2+}$ + 2H$_2$O = PbO$_2$(s) + 4H$^+$ + 2e$^−$. Using additional data as needed from Table 13-1, calculate (a) $\mathcal{E}^{\circ}_{298}$ for the half-cell Pb + 2H$_2$O = PbO$_2$(s) + 4H$^+$ + 4e$^−$ and (b) $K$ for the reaction 2Pb$^{2+}$ + 2H$_2$O = Pb + PbO$_2$(s) + 4H$^+$.

13-2 The cell Cu/CuCl(s)/KCl(0.100 m)/Cl$_2$(1 atm)/C has a potential of 1.234 V at 25°C.

(a) Calculate the solubility product for CuCl in water at 25°C.

(b) What is the concentration of cuprous ion at the anode of this cell?

13-3 Given that $\mathcal{E}^0 = 0.152$ for Ag + I$^-$ = AgI + e$^-$ at 25°C and is −0.800 for Ag = Ag$^+$ + e$^-$, calculate the solubility product for AgI.

13-4 The voltage of the cell Ag/Ag$_2$SO$_4$(s)/saturated solution of Ag$_2$SO$_4$ and Hg$_2$SO$_4$/Hg is 0.140 V at 25°C and its temperature coefficient is 0.00015 V°C$^{-1}$.

(a) Give the cell reaction.

(b) Calculate the free energy change for the cell reaction.

(c) Calculate the enthalpy change for the cell reaction.

(d) Calculate the entropy change for the cell reaction.

(e) Does the cell absorb or emit heat as the cell reaction occurs? Calculate the number of calories per mole of cell reaction.

(f) One mole each of Hg, Ag$_2$SO$_4$(s), Hg$_2$SO$_4$(s), and some saturated solution of the two salts are mixed. What solid phases finally will be present and in what amounts?

13-5 $\mathcal{E}$ for the cell Ag/AgCl/ZnCl$_2$(m)/Zn is −1.240 V at 25°C and −1.260 V at 35°C, if $m = 1 \times 10^{-4}$ m. Write the cell reaction and calculate $\Delta G$, $\Delta H$, and $\Delta S$ for this reaction at 30°C.

13-6 Write the cell diagram for a cell whose $\mathcal{E}$ could be used to determine the solubility product for Ag$_2$SO$_4$(s). What additional information would be needed besides the measured emf?

13-7 Given the cell

Ag/AgNO$_3$(0.00100 m)/AgNO$_3$(0.00100 m), KCN (0.004 m)/Ag,
whose emf is $-0.767$ V at 25°C:

(a) Write the electrode and net cell reactions.
(b) Calculate the equilibrium constant for $\text{Ag}^+ + 2\text{CN}^- = \text{Ag(CN)}_2^-$ (neglect activity coefficient effects). The double dashed diagonal denotes a salt bridge which (it is hoped) makes the junction potential negligible.

13-8 At 25°C, $\varepsilon$ for the cell $\text{Pb}/\text{PbSO}_4(\text{s})/\text{H}_2\text{SO}_4(0.00200 \text{ m})/\text{H}_2(1 \text{ atm})/\text{Pt}$ is 0.125 V. Calculate the solubility product of PbSO$_4$ at 25°C.

13-9 Calculate the percentage of mercury in the mercuric state in a solution of mercuric nitrate that is in equilibrium with liquid mercury.

13-10 Calculate the solubility product of ferrous hydroxide from the cell $\text{Fe(s)}/\text{Fe(OH)}_2(\text{s})/\text{Ba(OH)}_2(0.05 \text{ m})/\text{HgO(s)}/\text{Hg}$. $\varepsilon_{298} = 0.973$ V.

13-11 Molecular weights are given in kg in the SI system; thus, the molecular weight of O$_2$ is 0.032 kg. In going from the cgs to the SI system, state whether the numerical value of each of the following is changed, and if it is, calculate the new value. (a) Avogadro’s number. (b) Faraday's number. (c) $\varepsilon$ for the cell $\text{Pt}/\text{H}_2(1 \text{ atm})/\text{HCl}/\text{AgCl}/\text{Ag}$. (d) $\Delta G^0$ for the cell reaction in (c). (e) $\varepsilon$ at 25°C for the cell $\text{Pt}/\text{H}_2(1 \text{ atm})/\text{HCl}(0.001 \text{ m})/\text{AgCl}/\text{Ag}$. What would your answers be had the molecular weight of O$_2$ been defined as 32 kg mole$^{-1}$ (and m had been kg molecular weights per 1000 kg of solvent)?

13-12 It is desired to separate Cd$^{2+}$ from Pb$^{2+}$ by electrodeposition from a solution which is 0.1 m in each ion and at pH 2. Calculate the sequence in which Cd and Pb metals and H$_2$ are produced and the concentrations of the various species in solution when a new stage of electrolysis occurs. Include overvoltage effects in considering H$_2$ evolution.

13-13 R. Ogg found $\varepsilon = -0.029$ V at 25°C for the cell

$$\text{Hg}/\left(\text{mercurous nitrate (0.01 N)}\right)/\left(\text{mercurous nitrate (0.001 N)}\right)/\text{HNO}_3(0.1 \text{ m})/\text{Hg}.$$ 

What is the formula for mercurous ion? Show how your conclusion follows from this information.

The actual dissociation constant for $\text{Hg}^{2+} = 2\text{Hg}^+$ is not known, but suppose that $\varepsilon$ for this cell is found to be $-0.059$ V when the higher and lower mercurous nitrate normalities are $2 \times 10^{-4}$ and $3 \times 10^{-4}$, respectively. Calculate $K_{\text{diss}}$ for $\text{Hg}^{2+}$ from this data. (In both parts of the problem neglect any junction potential.)

13-14 Calculate the emf of the following cells (neglect activity coefficient effects):

(a) $\text{Pt}/\text{H}_2(0.1 \text{ atm})/\text{H}_2\text{SO}_4(1 \text{ m})/\left(\text{K}_4\text{Fe(CN)}_6(0.01 \text{ m})\right)/\text{Au}$. 

(b) $\text{Au}/\text{O}_2(0.2 \text{ atm})/\left(\text{H}_2\text{SO}_4(1 \text{ m})\right)/\left(\text{H}_2\text{O}_2(0.1 \text{ m})\right)/\text{H}_2\text{SO}_4(1 \text{ atm})/\text{Pt}$. 

(c) $\text{Ag}/\text{AgBr}/\text{HBr}(0.01 \text{ m})/\text{H}_2(0.5 \text{ atm})/\text{Pt}$. 

Neglect junction potentials.

13-15 If copper and silver are negligibly soluble in each other as solids, approximately what must be the concentration of Ag$^+$ in a solution in which Cu$^{2+}$ is at unit activity in order that the two metals may be plated out together in electrolysis? At what potential will this occur, on the assumption that oxygen is formed at the anode at an overvoltage of 0.50 V at 1 atm pressure from a solution of pH 5? Assume 25°C.
CHAPTER 13: ELECTROCHEMICAL CELLS

13-16 At 25°C, $\varepsilon$ for the cell Pt/H$_2$(1 atm)/HCl(m)/AgCl/Ag is as follows (Harned and Ehlers, 1932):

<table>
<thead>
<tr>
<th>$m$</th>
<th>0.01002</th>
<th>0.01010</th>
<th>0.01031</th>
<th>0.04986</th>
<th>0.05005</th>
<th>0.09642</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$ (V)</td>
<td>0.46376</td>
<td>0.46331</td>
<td>0.46228</td>
<td>0.38582</td>
<td>0.38568</td>
<td>0.35393</td>
</tr>
</tbody>
</table>

Calculate $\varepsilon^o$ for the cell by the extrapolation method, and then the activity coefficients for HCl at these concentrations and plot them against $\sqrt{m}$; compare the limiting slope with the value from theory.

13-17 At 25°C, $\varepsilon$ for the cell

$$\text{Ag/AgCl/NaCl(m)/NaHg(amalgam)\textbar NaHg (amalgam)/NaCl(0.100 m)/AgCl/Ag}$$

is as follows:

<table>
<thead>
<tr>
<th>$m$</th>
<th>0.200</th>
<th>0.500</th>
<th>1.000</th>
<th>2.000</th>
<th>3.000</th>
<th>4.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{258}$ (V)</td>
<td>0.03252</td>
<td>0.07584</td>
<td>0.10955</td>
<td>0.14627</td>
<td>0.17070</td>
<td>0.19036</td>
</tr>
</tbody>
</table>

The mean activity coefficient of 0.100 m NaCl is 0.773. Calculate the mean activity coefficients of NaCl in solutions of these concentrations and plot the values against the square root of $m$.

13-18 At 25°C, $\varepsilon$ for the cell Pb/PbSO$_4$(s)/H$_2$SO$_4$(m)/H$_2$(1 atm)/Pt changes with the molality of the sulfuric acid as follows:

<table>
<thead>
<tr>
<th>$m$</th>
<th>0.00100</th>
<th>0.00200</th>
<th>0.00500</th>
<th>0.01000</th>
<th>0.02000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{298}$ (V)</td>
<td>0.1017</td>
<td>0.1248</td>
<td>0.1533</td>
<td>0.1732</td>
<td>0.1922</td>
</tr>
</tbody>
</table>

By the extrapolation method, obtain $\varepsilon^o$ for this cell. From this value calculate the thermo-dynamic solubility product for PbSO$_4$.

13-19 At 25°C, $\varepsilon$ for the cell Pt/H$_2$(1 atm)/ m Ba(OH)$_2$/Ba(amalgam)/0.1200 m Ba(OH)$_2$/H$_2$(1 atm)/Pt is as follows:

<table>
<thead>
<tr>
<th>$1000 m$</th>
<th>2.45</th>
<th>7.93</th>
<th>15.09</th>
<th>49.70</th>
<th>199.60</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$ (V)</td>
<td>-0.1245</td>
<td>-0.0840</td>
<td>-0.0630</td>
<td>-0.0254</td>
<td>+0.0144</td>
</tr>
</tbody>
</table>

(a) Write the cell reaction (each electrode separately and then the net reaction).
(b) By means of the appropriate extrapolation procedure, calculate the mean activity coefficient for 0.1000 m Ba(OH)$_2$.

13-20 Suppose that the atomic weight of carbon is defined as 12 kg mole$^{-1}$. Explain whether this redefinition would affect the values of $\varepsilon$ and $\varepsilon^o$ for the cell Pb/PbCl$_2$(s)/KCl(10 g liter$^{-1}$)/HgCl$_2$(s)/Hg at 25°C.

13-21 The pH of a solution may be found with the use of a hydrogen electrode and a calomel half-cell. Suppose that the pH of a certain buffer solution is measured at a high altitude such that the ambient pressure is 600 Torr but that the observer neglects this aspect and calculates the pH assuming the pressure of the hydrogen bubbling past the electrode to be 1 atm. If he reports a pH of 5.50, what is the correct pH of the solution?

13-22 Calculate the free energy of formation of AgCl(s) using the solubility product for AgCl and data from Table 13-3.

13-23 Calculate $\Delta G^o$ for the reaction H$_2$O(l) = H$^+$ + OH$^-$ at 25°C given that the free energy of formation of liquid water is $-56.69$ kcal mole$^{-1}$ and using Table 13-3.

13-24 A thallous (Tl$^+$) solution is titrated with ceric (Ce$^{4+}$) solution. The reaction is

$$\text{Tl}^+ + 2\text{Ce}^{4+} = \text{Tl}^{3+} + 2\text{Ce}^{3+}.$$
Calculate the half-cell potential at 25°C for the reaction \( \text{Tl}^+ = \text{Tl}^{3+} + 2e^- \) at the end-point (that is, the equivalence point of the titration) given:

\[
\begin{align*}
\text{Ce}^{4+} &= \text{Ce}^{3+} + e^-,
\delta^o &= -1.60 \text{ V}, \\
\text{Tl}^+ &= \text{Tl}^{3+} + 2e^-,
\delta^o &= -1.23 \text{ V}.
\end{align*}
\]

As a calculator problem, obtain the titration curve for 0.1 \( m \) \( \text{Tl}^+ \) titrated with 0.1 \( m \) \( \text{Ce}^{4+} \).

13-25 Calculate the equilibrium concentration of ferric ion at 25°C in a solution which is 0.01 \( f \) in \( \text{Hg(NO}_3)_2 \) and 0.01 \( f \) in \( \text{Fe(NO}_3)_3 \). Use the Debye–Hückel limiting law to estimate activity coefficients.

### SPECIAL TOPICS PROBLEMS

13-1 Calculate \( \delta \), \( \delta_E \), and \( \delta_J \) at 25°C for the cell

\[
\text{Na(dilute Hg amalgam)/NaCl(0.01 m)}/\text{NaCl(0.001 m)}/\text{Na(dilute Hg amalgam)}. 
\]

13-2 Calculate the emf’s of concentration cells with transference for the following electrolytes in 0.01 \( m \) and 0.001 \( m \) solution, respectively, with appropriate silver chloride or mercurous sulfate electrodes: (a) \( \text{CaCl}_2 \); (b) \( \text{La}_2(\text{SO}_4)_3 \).

13-3 Calculate the emf of the following cells with transference at 25°C:

(a) \( \text{Ag/AgCl/CaCl}_2(0.01 m)}/\text{CaCl}_2(0.001 m)/\text{AgCl/Ag} \).

(b) \( \text{Hg/Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4(0.01 m)}/\text{K}_2\text{SO}_4(0.001 m)/\text{Hg}_2\text{SO}_4/\text{Hg} \).

13-4 Given the cell \( \text{Ag/Ag}_2\text{SO}_4(s)/\text{Na}_2\text{SO}_4(m_2)/\text{Na}_2\text{SO}_4(m_1)/\text{Ag}_2\text{SO}_4(s)/\text{Ag} \), and that \( t_+ = 0.38 \) for both \( \text{Na}_2\text{SO}_4 \) concentrations, (a) write the anode and cathode reactions per faraday, and the net cell reaction, and (b) obtain the expressions for \( \delta_E \) and \( \delta_J \) and calculate the ratio \( \delta_J/\delta_E \). Neglect activity coefficient corrections.