

11.3 Measurements of the reversible cell potential (Figure 11.5)

- ▶The **cell potential** measured under reversible conditions is directly related to the state functions **G, H, and S**.
- ▶The **reversible cell potential** (called **electromotive force, emf, 가역전위**), is determined in **Figure 11.5**.
- ▶The **dc source provides a voltage** to a **potentiometer (가변저항기)** circuit with a sliding contact.
- ▶The sliding contact is attached to the positive cell terminal and adjusted until the **current-sensing device (I)** shows a **null current**.
- ▶At null position, the applied voltage exactly opposes the cell potential. **The voltage measured is the reversible cell potential**.
- ▶If the sliding contact is moved to the left, the electron current will flow through the external circuit in one direction.
- ▶If the sliding contact is moved to to the right, the electron current will flow through the external circuit in the opposite direction, showing that the direction of the cell reaction has been reversed.
- Small change in applied voltage can reverse the spontaneity direction (Reversibility established)-

This measurement also demonstrates that the direction of spontaneous change can be reversed by changing the electrochemical potential of the electrons in one of the electrodes relative to that in the other electrode.

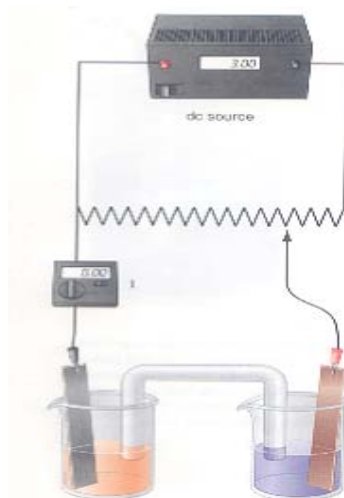


FIGURE 11.5
Schematic diagram showing how the reversible cell potential is measured.

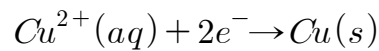
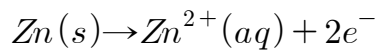
11.4 Chemical reactions in the electrochemical cells and the Nernst equation

By convention,

Anode \equiv The electrode at which oxidation occurs

Cathode \equiv The electrode at which reduction occurs

Cell voltage vs ΔG relationship



At equilibrium $\Delta G_R = \sum_i \nu_i \tilde{\mu}_i = 0$ (7)

$$\Delta G_R = \widetilde{\mu}_{\text{Zn}^{2+}} + \widetilde{\mu}_{\text{Cu}} - \widetilde{\mu}_{\text{Cu}^{2+}} - \widetilde{\mu}_{\text{Zn}} = \widetilde{\mu}_{\text{Zn}^{2+}}^o - \widetilde{\mu}_{\text{Cu}^{2+}}^o + RT \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$$

$$\Delta G_R = \Delta G_R^o + RT \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \quad (22)$$

For solid metal, activity=1, chemical potential=0 (element @ SS), z=0 being used.

For reversible reaction

$$dw_{rev} = (\varphi_2 - \varphi_1) dQ = \Delta\varphi dQ \quad (2)$$

$$\begin{aligned} dQ &= z F dn \quad \text{Charge transferred through the potentials} \\ &= - F dn \quad \text{for electron} \\ \rightarrow dw_{rev} &= - \Delta\varphi F dn = dG \end{aligned}$$

Note : At constant pressure (nonexpansible work)
 $dw_{rev} = dG$

$$\Delta G_R = - nF\Delta\varphi \quad (23)$$

$$= - nFE \quad (\text{For reversible reaction}) \quad (23)'$$

$$= - 2FE \quad (\text{For the above reactions}) \quad (23)''$$

n=Number of moles of electrons involved in the redox reaction.

$\Delta\varphi$ =Potential difference generated by the [spontaneous chemical reaction](#) for particular values of $a_{\text{Zn}^{2+}}$ and $a_{\text{Cu}^{2+}}$.

Replacing ΔG_R by $-2FE$ in 22 gives (Remember 2 electrons)

$$-2FE = \Delta G_R^o + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \quad (24)$$

For standard state condition, $a_i = 1$ (unit activity) and from 24 $\Delta G_R^o = -2FE^o$. (E^o =standard potential) Subing this back into (24) gives

$$E = E^o - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \quad (25)$$

For a general electrochemical reaction involving the transfer of n moles of electrons,

$$E = E^o - \frac{RT}{nF} \ln Q \quad (26) \quad \text{Nernst equation}$$

Q=reaction quotient = K at equilibrium given in Ch 10 as

$$K = \prod_i (a_i^{eq})^{\nu_i} \quad (35)$$

At 298K w/ $R=8.31\text{J/mol-K}$, $F=96,485\text{C/mol}$, Nernst eq becomes

$$E = E^o - \frac{0.05916\text{ V}}{n} \log_{10} Q \quad (27)$$

See Figure 11.6 for the plot of Nernst eq with different n .

From activities (Q) and $E^o \rightarrow$ emf (E) is calculated using Nernst eq.

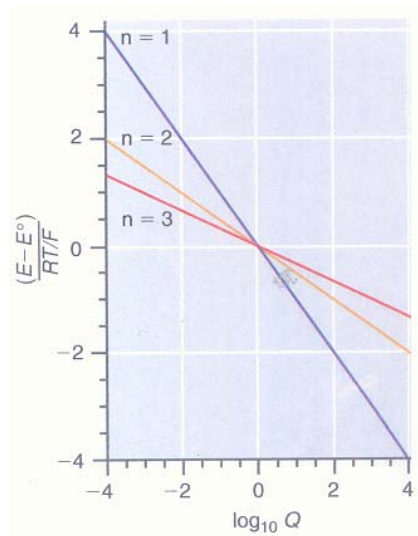
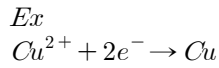


FIGURE 11.6

The cell potential E varies linearly with $\log Q$. The slope of a plot of $(E - E^\circ)/(RT/F)$ is inversely proportional to the number of electrons transferred in the redox reaction.

In the above, Nernst eq has been derived for [overall cell reaction](#), but it could be derived for a [half-cell](#) as follow. The equilibrium condition for (28) is given by (29).



$$\begin{aligned} \mu_{\text{Ox}^{n+}} + nF\phi_{\text{Ox}^{n+}} (=0) + n\widetilde{\mu}_{e^-} &= \mu_{\text{Red}} + z(=0)F\phi_{\text{Red}} (=0) \\ \rightarrow \\ \mu_{\text{Ox}^{n+}} + n\widetilde{\mu}_{e^-} &= \mu_{\text{Red}} \quad (29) \end{aligned}$$

Subing $\widetilde{\mu}_{e^-} = -\phi F_{\text{Ox/Red}}$ into (29)

$$\begin{aligned} \mu_{\text{Ox}^{n+}}^\circ + RT \ln a_{\text{Ox}^{n+}} - nF\phi_{\text{Ox/Red}} &= \mu_{\text{Red}}^\circ + RT \ln a_{\text{Red}} \\ \phi_{\text{Ox/Red}} &= \frac{\mu_{\text{Ox}^{n+}}^\circ - \mu_{\text{Red}}^\circ}{nF} - \frac{RT}{nF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}^{n+}}} \\ E_{\text{Ox/Red}} &= E_{\text{Ox/Red}}^\circ - \frac{RT}{nF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}^{n+}}} \quad (30) \end{aligned}$$

Problem 2

For the half-cell reaction $\text{AgBr}(s) + e^- \rightarrow \text{Ag}(s) + \text{Br}^-(aq)$, $E^\circ = +0.0713\text{V}$ (Table 11.1-Standard reduction potential). Using this result and $\Delta G_f^\circ(\text{AgBr}, s) = -96.9\text{ kJ mol}^{-1}$, determine $\Delta G_f^\circ(\text{Br}^-, aq)$.

Solution:

$$\Delta G_R^\circ = -nFE^\circ = \Delta G_f^\circ(\text{Br}^-, aq) - \Delta G_f^\circ(\text{AgBr}, s)$$

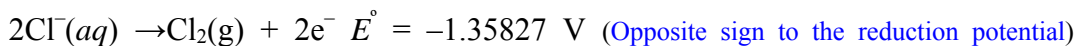
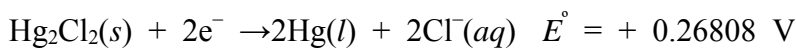
$$\Delta G_f^\circ(\text{Br}^-, aq) = \Delta G_f^\circ(\text{AgBr}, s) - nFE^\circ$$

$$\Delta G_f^\circ(\text{Br}^-, aq) = -96.9\text{ kJ mol}^{-1} - 1\text{ mol} \times 96485\text{ C mol}^{-1} \times 0.0713\text{ V} = -103.8\text{ kJ mol}^{-1}$$

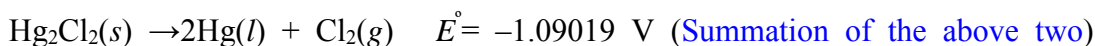
Problem 13

Calculate $\Delta G_{\text{reaction}}^\circ$ and the equilibrium constant at 298.15 K for the reaction $\text{Hg}_2\text{Cl}_2(s) \rightarrow 2\text{Hg}(l) + \text{Cl}_2(g)$.

Solution (Data from Table 11.1)



Net reaction



$$\Delta G_{\text{reaction}}^\circ = -nFE^\circ = -2 \times 96485\text{ C mol}^{-1} \times 1.09019\text{ V} = 210.4\text{ kJ mol}^{-1}$$

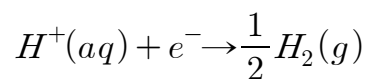
$$\ln K = \frac{nF}{RT} E^\circ = -\frac{2 \times 96485\text{ C mol}^{-1} \times 1.09019\text{ V}}{8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 298.15\text{ K}}$$
$$= -85.002$$

$$K = 1.21 \times 10^{-37}$$

EXAMPLE PROBLEM 11.1

Calculate the potential of the H^+/H_2 half-cell when $a_{H^+} = 0.770$ and $f_{H_2} = 1.13$.

Solution



$$E = E^o - \frac{0.05916 V}{n} \log_{10} \frac{a_{H^+}}{\sqrt{f_{H_2}}} = 0 - \frac{0.05916 V}{1} \log_{10} \frac{0.770}{\sqrt{1.13}} = 0.0083 V$$