21.4 Free Energy and Electrical Work

Relationship Between E_{cell} and ΔG_r

- **Electrical work (w)**

$$w = (\text{charge transferred}) \times (\text{voltage})$$

  - $n \rightarrow$ # mol e$^-$ transferred
  - $F \rightarrow$ charge of 1 mol e$^-$

| (charge transferred) $= nF$ |
| (voltage) $= E_{cell}$ |

$\Rightarrow w = -nFE_{cell}$ ($w < 0$ since the system does work)

  - ΔG is the maximum work the system can do, so

$$\Delta G = w_{max}$$

$\Rightarrow$ If the process is carried out reversibly ($w = w_{max}$)

$$\boxed{\Delta G_r = -nFE_{cell} \quad \text{and} \quad \Delta G_r^o = -nFE^o_{cell}}$$

  $\rightarrow F = 96485$ C/mol $\rightarrow$ **Faraday constant**

- ΔG_r, ΔG_r^o, E_{cell}, and E^o_{cell} are all dependent on T (superscripts, T, are omitted for simplicity)
- ΔG_r, ΔG_r^o are **extensive** properties
- E_{cell}, E^o_{cell}, E, and E^o are **intensive** properties

$\Rightarrow$ If a redox equation is multiplied by a number, ΔG is also multiplied, but E is not
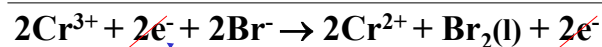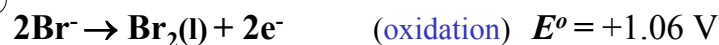
Example: Using E^o values from appendix D, calculate ΔG_r^o at 298 K for the reaction:

$$2Cr^{3+} + 2Br^- \rightarrow 2Cr^{2+} + Br_2(l)$$

$\rightarrow$ Find the redox couples in Appendix D (298 K):

$Cr^{3+} + e^- \rightarrow Cr^{2+}$ $\qquad E^o = -0.41$ V

$Br_2(l) + 2e^- \rightarrow 2Br^-$ $\qquad E^o = +1.06$ V

$\rightarrow$ Invert the 2nd half-reaction to match the overall eq.

$(+)$ $Cr^{3+} + e^- \rightarrow Cr^{2+}$ $\quad \times 2$ $\quad$ (reduction) $E^o = -0.41$ V

$\quad 2Br^- \rightarrow Br_2(l) + 2e^-$ $\qquad$ (oxidation) $E^o = +1.06$ V

$\quad 2Cr^{3+} + 2e^- + 2Br^- \rightarrow 2Cr^{2+} + Br_2(l) + 2e^-$

$\rightarrow$ Calculate E^o_{cell}

$E^o_{cell} = E^o_{cath} - E^o_{anod} = -0.41 - (+1.06) = -1.47$ V

$\rightarrow$ Calculate ΔG_r^o ($n = 2 \rightarrow$ # mol e$^-$ in overall eq.)

$\Delta G_r^o = -nFE^o_{cell} = -(2 \text{ mol}) \times (96485 \text{ C/mol}) \times (-1.47 \text{ V})$

$\Delta G_r^o = 2.84 \times 10^5$ C·V $= 2.84 \times 10^5$ J $= \boxed{+284 \text{ kJ}}$

$\Rightarrow \Delta G_r^o > 0$ and $E^o_{cell} < 0 \rightarrow$ the reaction is **non-spontaneous** at standard conditions

$\Rightarrow$ The reverse reaction is **spontaneous** at standard conditions

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Relationship Between E^o_{cell} and K

- From $\Delta G_r^o = -nFE^o_{cell}$ and $\Delta G_r^o = -RT\ln K$

$\rightarrow -nFE^o_{cell} = -RT \ln K$

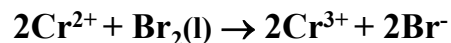$$\boxed{\Rightarrow \quad E^o_{cell} = \frac{RT}{nF} \ln K} \qquad K = e^{\frac{nFE^o_{cell}}{RT}}$$

$\rightarrow$ **At 298 K, $RT/F = 0.0257$ V**

$$\boxed{\Rightarrow \quad E^o_{cell} = \frac{0.0257}{n} \ln K} \qquad K = e^{\frac{nE^o_{cell}}{0.0257}}$$

$\rightarrow \ln K = 2.303 \times \log K$ and $0.0257 \times 2.303 = 0.0592$

$$\boxed{\Rightarrow \quad E^o_{cell} = \frac{0.0592}{n} \log K} \qquad K = 10^{\frac{nE^o_{cell}}{0.0592}}$$

Example: Using E^o values from appendix D, calculate K at 298 K for the reaction:

$$2Cr^{2+} + Br_2(l) \rightarrow 2Cr^{3+} + 2Br^-$$

→ This is the reverse of the reaction in the previous example ($E^o_{cell} = -1.47$ V from previous example)

→ $E_{reverse} = -E_{forward}$

$\Rightarrow E^o_{cell} = -(-1.47\ V) = +1.47\ V$ and $n = 2$

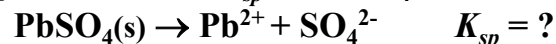$$\Rightarrow K = e^{\frac{nE^o_{cell}}{0.0257}} = e^{\frac{2\times1.47}{0.0257}} = 4.8\times10^{49}$$

→ $E^o_{cell} > 0$ → the reaction is **spontaneous** at standard conditions
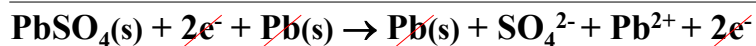
→ $K \gg 1$ → the products are favored at equilibrium

Interrelationship between ΔG_r^o, E^o_{cell}, and K

ΔG^0	K	E^0_{cell}	Reaction at standard-state conditions
<0	>1	>0	Spontaneous
0	1	0	At equilibrium
>0	<1	<0	Nonspontaneous

$\Delta G^0 = -nFE^0_{cell}$

$\Delta G^0 = -RT \ln K$

$E^0_{cell} = \frac{RT}{nF} \ln K$
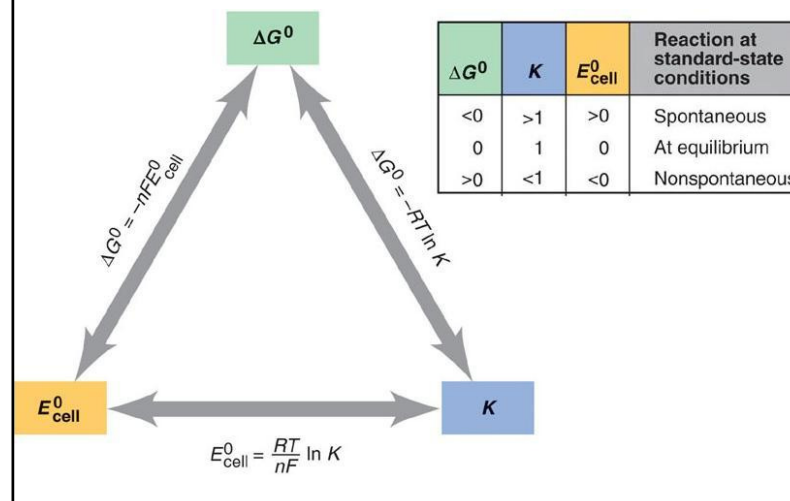
Example: Calculate K_{sp} of **PbSO$_4$** at 298 K.

$$PbSO_4(s) \rightarrow Pb^{2+} + SO_4^{2-} \qquad K_{sp} = ?$$

→ Not a redox reaction, but it can be represented as a sum of two redox half-reactions

$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}$ (reduction) $E^o = -0.36$ V

$Pb(s) \rightarrow Pb^{2+} + 2e^-$ (oxidation) $E^o = -0.13$ V

$\overline{PbSO_4(s) + 2e^- + Pb(s) \rightarrow Pb(s) + SO_4^{2-} + Pb^{2+} + 2e^-}$

$E^o_{cell} = E^o_{cath} - E^o_{anod} = -0.36 - (-0.13) = \textbf{-0.23 V}$

$$\Rightarrow K_{sp} = e^{\frac{nE^o_{cell}}{0.0257}} = e^{\frac{2\times(-0.23)}{0.0257}} = 1.7\times10^{-8}$$

$\Rightarrow E^o_{cell} < 0$ → the dissolution of **PbSO$_4$** is non-spontaneous at 298 K ($K_{sp} \ll 1$)

The Effect of Concentration on E_{cell}

• The **Nernst equation** – gives the variation of the cell potential with composition

$$\Delta G_r = \Delta G_r^o + RT \ln Q$$

$$\Delta G_r = -nFE_{cell} \quad \text{and} \quad \Delta G_r^o = -nFE^o_{cell}$$

$$\Rightarrow -nFE_{cell} = -nFE^o_{cell} + RT \ln Q$$

$$\boxed{E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q}$$

→ **At 298 K**

$$\boxed{E_{cell} = E^o_{cell} - \frac{0.0257}{n}\ln Q} \qquad \boxed{E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log Q}$$

- The Nernst equation applies also to half-reactions (E and E^o are used instead of E_{cell} and E^o_{cell})

Example: Calculate the electrode potential of the Cu^{2+}/Cu redox couple at 298 K, if the concentration of Cu^{2+} is 0.025 M.

$$Cu^{2+} + 2e^- \rightarrow Cu(s) \qquad E^o = +0.34 \text{ V}$$
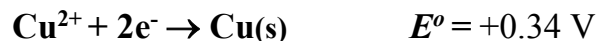
$\rightarrow$ Use the Nernst eq. to get E

$\rightarrow Q = 1/[Cu^{2+}] = 1/0.025$ and $n = 2$

$$E = E^o - \frac{0.0257}{n}\ln Q = +0.34 - \frac{0.0257}{2}\ln\left(\frac{1}{0.025}\right)$$

$$E = +0.34 - 0.047 = \boxed{0.29 \text{ V}}$$

E_{cell} in Relation to Q and K

➤ From $E_{cell} = E^o_{cell} - (RT/nF) \ln Q$:

⇒ If $Q < 1$ (more reactants), $\ln Q < 0$, and $E_{cell} > E^o_{cell}$

⇒ If $Q > 1$ (more products), $\ln Q > 0$, and $E_{cell} < E^o_{cell}$

⇒ If $Q = 1$ (standard state), $\ln Q = 0$, and $E_{cell} = E^o_{cell}$

➤ Combining $E_{cell} = E^o_{cell} - (RT/nF) \ln Q$ with $E^o_{cell} = (RT/nF) \ln K$ leads to:

$\rightarrow E_{cell} = (RT/nF) \ln K - (RT/nF) \ln Q$

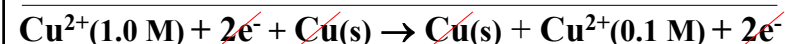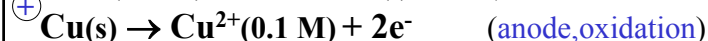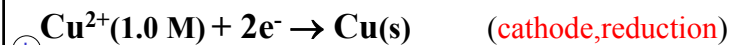⇒ If $Q < K$, $E_{cell} > 0$ → forward reaction is spontaneous

⇒ If $Q > K$, $E_{cell} < 0$ → reverse reaction is spontaneous

⇒ If $Q = K$, $E_{cell} = 0$ → reaction is at equilibrium

Concentration Cells

- **Concentration cell** – contains the same redox couple in both the anode and cathode half-cells
  - The anode and cathode are the same
    $\Rightarrow E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0$
  - The concentrations of the components are different in the two half-cells $\Rightarrow E_{cell} = 0 - (RT/nF) \ln Q \neq 0$
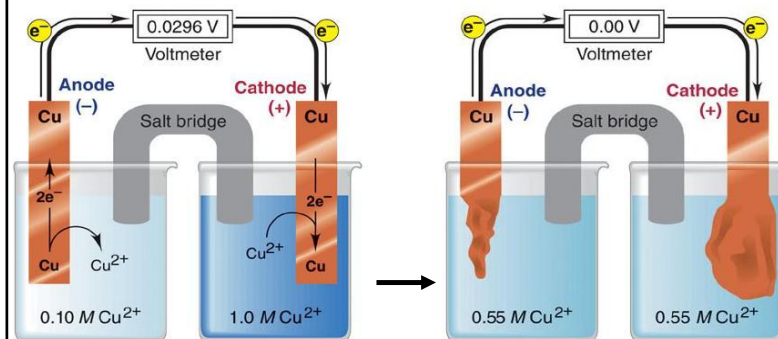
Example: Cu^{2+}/Cu concentration cell ($E^o_{Cu} = 0.34$ V)

$$Cu^{2+}(1.0 \text{ M}) + 2e^- \rightarrow Cu(s) \qquad \text{(cathode,reduction)}$$
$$^{(+)}Cu(s) \rightarrow Cu^{2+}(0.1 \text{ M}) + 2e^- \qquad \text{(anode,oxidation)}$$
$$\overline{Cu^{2+}(1.0 \text{ M}) + 2\cancel{e^-} + \cancel{Cu(s)} \rightarrow \cancel{Cu(s)} + Cu^{2+}(0.1 \text{ M}) + 2\cancel{e^-}}$$
$$E^o_{cell} = E^o_{Cu} - E^o_{Cu} = +0.34 - (+0.34) = \mathbf{0 \text{ V}}$$

$$E_{cell} = E^o_{cell} - \frac{0.0257}{n}\log Q = 0 - \frac{0.0592}{2}\log\left(\frac{0.1}{1.0}\right)$$

$$E = 0 - \frac{0.0592}{2}(-1) = 0 + 0.0296 = \mathbf{0.0296 \text{ V}}$$

→ The cell continues to work until $[Cu^{2+}]$ is equalized in the two half-cells and E_{cell} decreases to zero

- **Ion-selective** electrodes – have potentials that are directly related to the concentration of specific ions such as H^+ (*pH*), K^+, F^-, Cl^-, Br^-, …

Example: Calculate the *pH* of a solution in which the potential of the $H^+ \mid H_2(g,1atm) \mid Pt$ electrode is $E = -0.15$ V.

$$2H^+ + 2e^- \rightarrow H_2(g,1atm) \qquad E^o = 0.00 \text{ V}$$
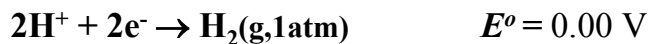
$$Q = \frac{P_{H_2}}{[H^+]^2} = \frac{1 \text{ atm}}{[H^+]^2} \qquad\qquad n = 2$$

$$E = E^o - \frac{0.0592}{n} \log Q = 0 - \frac{0.0592}{2} \log\left(\frac{1}{[H^+]^2}\right)$$

$$E = -\frac{0.0592}{2} \log\left(\frac{1}{[H^+]^2}\right) = -\frac{0.0592}{2} \log [H^+]^{-2}$$

$$E = -\frac{(-2) \times 0.0592}{2} \log [H^+] = -0.0592\, pH$$

$$\Rightarrow pH = \frac{E}{-0.0592} = \frac{-0.15}{-0.0592} = 2.5$$

– The potential of an ion-selective electrode is measured by combining it in a cell with a **reference electrode** having a well known and constant electrode potential such as the **calomel** ($Hg/Hg_2Cl_2/Cl^-$) or the $Ag/AgCl/Cl^-$ electrodes

– Optionally, the ion-selective electrode can be operated in a concentration cell with the same electrode immersed in a solution with known concentration as a reference