

Galvanic Cell and Free Energy

Cell Potential, Electrical Work

- The work that can be accomplished when electrons are transferred by emf, electromotive force, is defined in terms of a potential difference in volts between two circuits.
- emf = potential difference (V) = $\frac{\text{work (J)}}{\text{charge (C)}}$
- or $1 \text{ V} = 1 \text{ J/C}$
- Work is viewed from the point of view of the system.
- Therefore, $E = -w/q$ or $-w = qE$

Maximum work

- The maximum work is defined as
- $w_{\text{max}} = -q E_{\text{max}}$
- Achieving maximum work is impossible.
- In any real, spontaneous process, some energy is always wasted. The actual work realized is always less than the calculated maximum.

Free Energy

- Faraday's Constant (F) is defined as the charge of 1 mole of electrons.
- $F = 96,485 \frac{\text{C}}{\text{mol } e^-}$
- The purpose of a voltaic cell is to convert the free energy change of a spontaneous reaction into the KE of electrons moving through an external circuit.
- $w_{\text{max}} = \Delta G$

For a galvanic cell

- $\Delta G = -nFE$ or $\Delta G^\circ = -nFE^\circ$
- Where n is the number of moles of electrons transferred in the redox reaction.
- Note the units of F is C/mol, and the units of E, volts, is J/C
- $-nFE = (\text{mol})(\text{C/mol})(\text{J/C}) = \text{J}$
- This equation is in Joules, not Kilojoules!!

Spontaneity

- n and F are always positive.
- If $E_{\text{cell}} > 0$, then $\Delta G < 0$ and the process is thermodynamically favored. $K > 1$
- If $E_{\text{cell}} < 0$, then $\Delta G > 0$ and the process is not thermodynamically favored. $K < 1$
- If $E_{\text{cell}} = 0$, then $\Delta G = 0$ and the process is at equilibrium. $K = Q$

Calculating ΔG° for a Cell Reaction.

- Using the Standard Reduction Potential Chart, calculate ΔG° for the reaction
- $\text{Cu}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Fe}^{2+}(\text{aq})$
- Is the reaction thermodynamically favored?
- Predict whether 1 M HNO_3 will dissolve gold metal to form a 1 M Au^{3+} solution.
- Below is the half reaction of nitric acid acting as an oxidizing agent
- $4 \text{H}^+ + \text{NO}_3^- + 3 e^- \rightarrow \text{NO} + 2 \text{H}_2\text{O}$ $E^\circ = .96 \text{ V}$

Combining Reduction Potentials

- You can not add 2 reduction potentials together.
- Say you want
- $\text{Fe}^{3+}(\text{aq}) + 3 e^- \rightarrow \text{Fe}(\text{s})$ $E^\circ = ?$
- But you have
- $\text{Fe}^{3+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$ $E^\circ = .77 \text{ V}$
- $\text{Fe}^{2+}(\text{aq}) + 2 e^- \rightarrow \text{Fe}(\text{s})$ $E^\circ = -.44 \text{ V}$
- It makes sense that you could add them together, but it doesn't work out due to the different numbers of electrons.

Combining them

- However, by Hess's Law you can add ΔG values.
- $\Delta G = -nFE$
- $\text{Fe}^{3+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$ $E^\circ = .77 \text{ V}$
- $\Delta G = -1(96485) \cdot .77 \text{ V} = -74293.45 \text{ J}$
- $\text{Fe}^{2+}(\text{aq}) + 2 e^- \rightarrow \text{Fe}(\text{s})$ $E^\circ = -.44 \text{ V}$
- $\Delta G = -2(96485)(-.44) = 84906.8 \text{ J}$
- $\text{Fe}^{3+}(\text{aq}) + 3 e^- \rightarrow \text{Fe}(\text{s})$ $\Delta G = 10613.35 \text{ J}$
- Then solve for reduction potential
- $10613.35 \text{ J} = 3(96485) E$
- $E^\circ = -.04 \text{ V}$

The Relationship to the Equilibrium Constant

- $\Delta G^\circ = -R T \ln K$ and $\Delta G^\circ = -n F E^\circ_{\text{cell}}$
- therefore
- $-R T \ln K = -n F E^\circ_{\text{cell}}$
- When cadmium metal reduces Cu^{2+} in solution, Cd^{2+} forms in addition to copper metal. If $\Delta G^\circ = -143 \text{ kJ}$, calculate K at 25°C . What would be E°_{cell} in a voltaic cell that used this reaction?

The Effects of Concentration on E

- For the cell reaction
- $2\text{Al}(s) + 3\text{Mn}^{2+}(\text{aq}) \rightleftharpoons 2\text{Al}^{3+}(\text{aq}) + 3\text{Mn}(s)$
 $E^\circ_{\text{cell}} = 0.48 \text{ V}$
- predict whether E_{cell} is larger or smaller than E°_{cell} for the following cases.
- a) $[\text{Al}^{3+}] = 2.0 \text{ M}$, $[\text{Mn}^{2+}] = 1.0 \text{ M}$
- b) $[\text{Al}^{3+}] = 1.0 \text{ M}$, $[\text{Mn}^{2+}] = 3.0 \text{ M}$

Nernst Equation

- The Nernst equation gives the relationship between the cell potential and the concentrations of cell components.
- $E = E^\circ - \frac{RT}{nF} \ln Q$
- Calculations with this equation have been removed from the AP test, however, qualitative understanding of how concentration affects a cell are still on the test.
- **DO NOT USE LeCHÂTELIER'S PRINCIPLE!!!**
- LeChâtelier's Principle requires you to start from equilibrium, then shift! A cell at equilibrium is dead!

Use K vs Q to qualitatively explain Nernst

- K must be greater than 1, if the cell works.
- **Q values are never negative, at standard state $Q = 1$.**
- During the reaction, concentrations proceed from reactant to product so Q increases and approaches K .
- For Q values less than 1, the concentration of reactant are higher. Increased reactant concentration increases rate of reaction, increasing the E_{cell} compared to E°_{cell} .
- When $Q < 1$, $[\text{reactant}] > [\text{product}]$, and therefore $E_{\text{cell}} > E^\circ_{\text{cell}}$.

Continued effect of Q

- For Q values higher than 1, the concentration of product are higher than reactant.
- Decreased reactant concentration means a slower reaction! So will E_{cell} decrease.
- When $Q > 1$, $[\text{reactant}] < [\text{product}]$, and therefore $E_{\text{cell}} < E^\circ_{\text{cell}}$.
- When $Q = 1$, $[\text{reactant}] = [\text{product}]$, $E_{\text{cell}} = E^\circ_{\text{cell}}$.

Manipulating Nernst

- $E = E^\circ - \frac{RT}{nF} \ln Q$
- $E^\circ - E = \frac{RT}{nF} \ln Q$
- "RT/nF" will always be a positive value.
- At standard state $Q = 1$, $\ln Q = 0$ and $E^\circ = E$
- If $Q > 1$ (more product) $\ln Q$ will be positive therefore $E^\circ > E$
- If $Q < 1$ (more reactant) $\ln Q$ will be negative therefore $E^\circ < E$

K and Q

- At equilibrium, $K = Q$ and $E_{\text{cell}} = 0$.
- At equilibrium, the components in the two cell compartments have the same free energy, and $\Delta G = 0$.
- At this point, the cell can no longer do work!

Problems

- Consider a cell based on the reaction
- $\text{Fe}(s) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Cu}(s)$
- If $[\text{Cu}^{2+}] = 1.30 \text{ M}$, what $[\text{Fe}^{2+}]$ is needed to increase E_{cell} to 1.03V at 25°C ?

Describe the cell based on the following half-reactions:

- $\text{VO}_2^+ + 2\text{H}^+ + e^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$
 $E^\circ = 1.00 \text{ V}$
- $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$
 $E^\circ = -0.76 \text{ V}$
- where $T = 25^\circ \text{C}$
- $[\text{VO}_2^+] = 2.0 \text{ M}$
- $[\text{H}^+] = 0.50 \text{ M}$
- $[\text{VO}^{2+}] = 0.01 \text{ M}$
- $[\text{Zn}^{2+}] = 0.1 \text{ M}$

Concentration Cells

- Concentration cells are constructed with the exact same half-reactions, with the exception of a difference in concentrations.
- **Voltages are typically small** as electrons are transferred from the cell of higher concentration to the cell of lower concentration.
- $E_{\text{cell}}^{\circ} = 0.00 \text{ V}$, but these never deal with standard conditions because concentrations are not standard (not 1 M).

Calculating the Potential of a Concentration Cell.

- A concentration cell is built using two Au/Au³⁺ half-cells. In half-cell A, [Au³⁺] = $7.0 \times 10^{-4} \text{ M}$, and in half-cell B, [Au³⁺] = $2.5 \times 10^{-2} \text{ M}$. What is E_{cell} , and which electrode is the anode?