Applications of Chemical Equilibrium

- Van't Hoff Equation (Temperature dependence of K_{eq})
- Calculations of Equilibrium
  - Charge and mass balance
  - Applications to pH: Henderson-Hasselbalch
- Electrochemistry and Free Energy
- Application: DNA Melting

Van't Hoff Equation

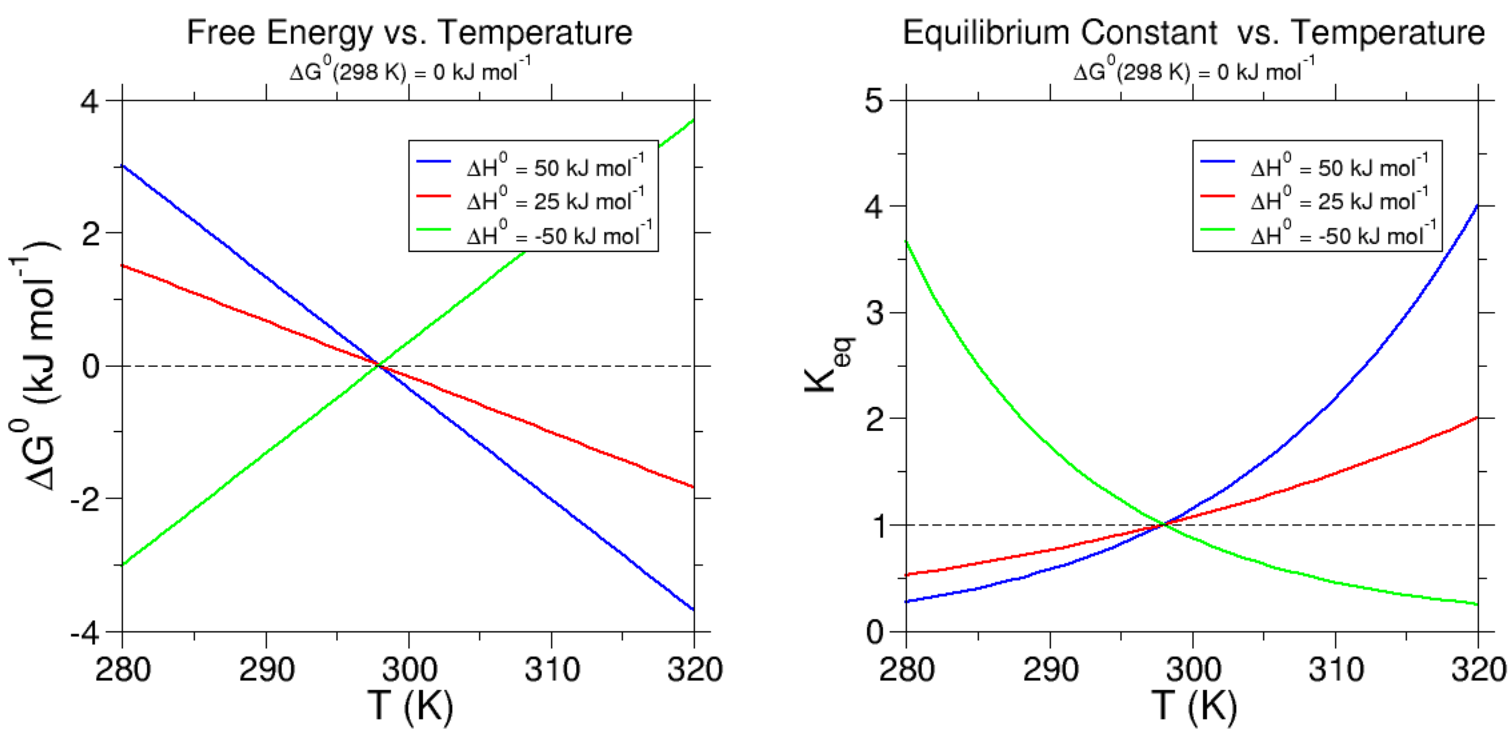
- Temperature dependence of ΔG (lecture 4-2):

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H(T_2^{-1} - T_1^{-1})$$

- If this is true for *any* ΔG, it must be true for $\Delta \bar{G}^0$, too: express $\Delta \bar{G}^0$ in terms of K_{eq}

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R}(T_2^{-1} - T_1^{-1})$$

Van't Hoff Equation



- Since $K = \frac{[\text{products}]}{[\text{reactants}]}$, bigger K favors products

Solving Equilibrium Problems

- Model System: Sodium Acetate Buffer

$$HOAc \rightarrow H^{+} + OAc^{-}$$

- Useful constants:

$$K_w = [H^+][OH^-] = 10^{-14}$$

$$K_A = \frac{[H^+][OAc^-]}{[HOAc]} = 1.8 \times 10^{-5}$$

(alternatively, $pK_A = 4.74$)

Solving Equilibrium Problems: Tips

- Write out balanced chemical equation
- Set up table:
  - Initial concentrations
  - Change (conserve mass & charge)
  - Final conditions → expression for K
- Check units and make sure you've answered the question
- If activities are needed (i.e. $a_A \neq [A]$), use them in the equilibrium expression instead of concentrations

Electrochemistry and Galvanic Cells

- Certain chemical reactions result in transfer of electrons from one compound to another (oxidation-reduction)

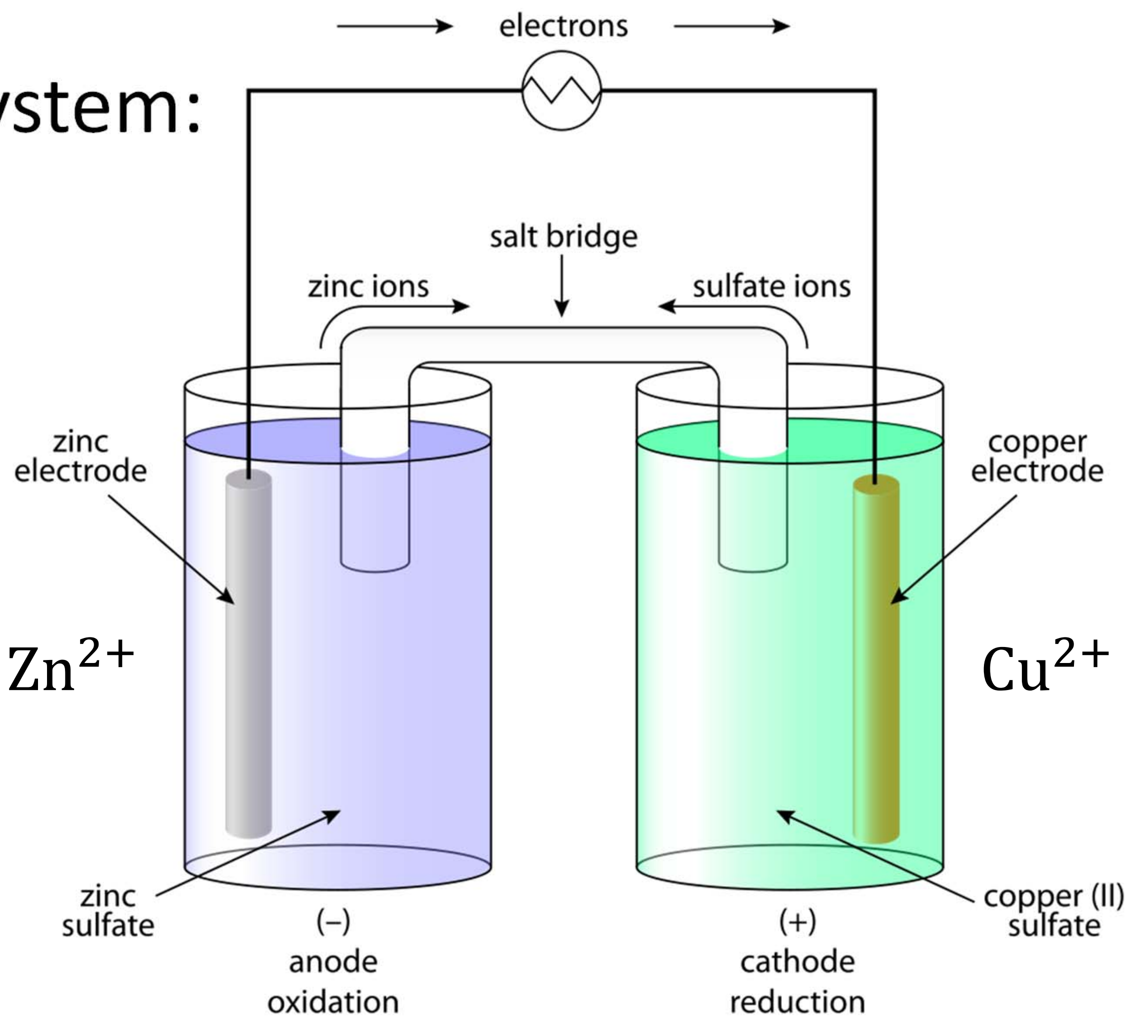
- **What if:** What if we could couple electron transfer to current going through a wire?

- **We could measure chemical work (dw^* and ΔG) by measuring the electrical work!**
  - Doesn't work for all reactions, even all redox reactions

Electrochemistry and Galvanic Cells

- The system:

$Zn \rightarrow 2e^{-} + Zn^{2+}$



$Cu^{2+} + 2e^{-} \rightarrow Cu$

http://en.wikipidia.com/wiki/Galvanic_cell

Electrochemistry and Galvanic Cells

- Overall Reaction is:

$$\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$$

- Equilibrium constant (at equlibrium):

$$K_{eq} = \left(\frac{[\mathrm{Zn^{2+}}][\mathrm{Cu}]}{[\mathrm{Zn}][\mathrm{Cu^{2+}}]}\right)_{\mathrm{eq}}$$

Pure Substance

Pure Substance

- Reaction quotient (not at equilibrium):

$$Q = \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]}$$

Electrochemistry and Galvanic Cells

- As before, we know (at const T, P):

$$\Delta \bar{G} = \Delta \bar{G}^0 + RT \ln Q$$

- But from physics, we know that $\Delta \bar{G}$ is related to *voltage* (1 V = 1 J C^{-1}):

$$\Delta G = -m\mathcal{E}$$

  – *m* is the amount of charge (in Coulombs) accelerated through a voltage difference of $\mathcal{E}$

- A simple conversion factor (F) gets us to moles of e^-

$$\Delta \overline{\mathrm{G}} = -nF\mathcal{E}$$

Electrochemistry and Galvanic Cells

- Converting our "Gibbs equation" to volts:

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{nF} \ln Q$$

- Special notes:
  - This is called the "Nernst Equation"
  - F is "Faraday's number," or 96,485 C mol^{-1}
  - *n* is the **total # of moles of electron per mole of reaction** (remember $d\alpha$ reaction variable)
  - Positive voltage is a spontaneous process

Electrochemistry Example

- Copper/Silver Galvanic Cell:

$$\mathrm{Ag}^{+} + e^{-} \rightarrow \mathrm{Ag} \qquad \mathcal{E}^{0} = 0.799\ \mathrm{V}$$

$$\mathrm{Cu}^{2+} + 2e^{-} \rightarrow \mathrm{Cu} \qquad \mathcal{E}^{0} = 0.337\ \mathrm{V}$$

- What is the standard state free energy for a Cu/Ag galvanic cell? Is Ag the cathode or the anode?