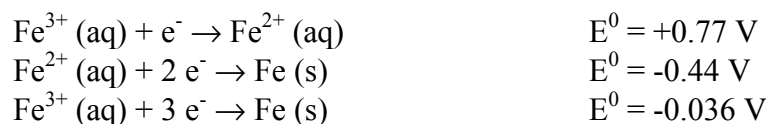


CHEM 121
Spring 2006
Quiz 11

Name: _____

1. (7 Points) Calculate $\Delta G_f^0(\text{Fe}^{2+}, \text{aq})$ from the following standard reduction potentials assuming that $\Delta G_f^0(e^-, \text{aq}) = 0$. You are given that $\Delta G = -n \cdot F \cdot E$, $F = 96485 \text{ C/mole}$ and $1 \text{ V} = 1 \text{ J/C}$.



For the second reaction ΔG^0 can be written in terms of ΔG_f^0 for the reactants and products.

$$\Delta G^0 = \Delta G_f^0(\text{Fe}, \text{s}) - \Delta G_f^0(\text{Fe}^{2+}, \text{aq}) - \Delta G_f^0(e^-, \text{aq})$$

This simplifies to this expression.

$$\Delta G^0 = -\Delta G_f^0(\text{Fe}^{2+}, \text{aq})$$

Since this is a redox reaction ΔG^0 can be related to E^0 as follows.

$$-nFE^0 = -\Delta G_f^0(\text{Fe}^{2+}, \text{aq})$$

$$\Delta G_f^0(\text{Fe}^{2+}, \text{aq}) = nFE^0 = (2) \left(96485 \frac{\text{C}}{\text{mole}} \right) \left(-0.44 \frac{\text{J}}{\text{C}} \right) = -85. \frac{\text{kJ}}{\text{mole}}$$

$\Delta G_f^0(\text{Fe}^{2+}, \text{aq})$ is -85. kJ/mole.

2. (4 Points) The synthesis of many unstable or metastable compounds (such as BeH_2 , whose ΔG_f is positive) is accomplished by a reaction pathway that involves the formation of a salt (in the case of BeH_2 , LiCl was formed). Why?

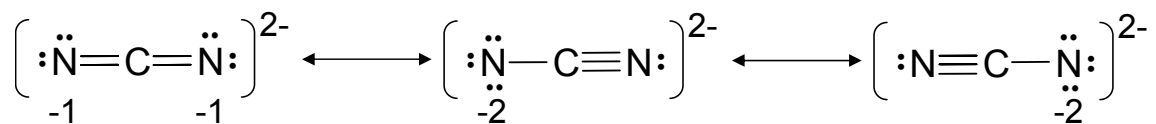
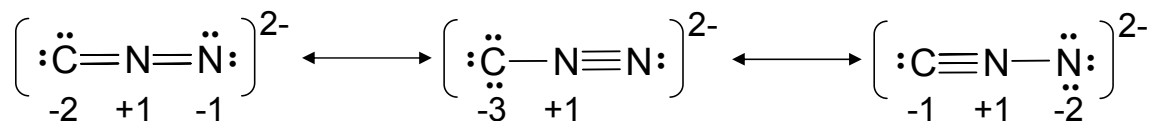
The negative ΔG_f for the salt (resulting from the large E_{lattice}) drives the unfavorable reaction to form the unstable compound.

3. (10 Points) CaC_2 reacts with N_2 to give calcium cyanamide, CaCN_2 , which contains the linear cyanamide ion, CN_2^{2-} . There are two possible ways in which the atoms in CN_2^{2-} can be attached to each other. Draw a Lewis dot structure for each of the possibilities (including contributing resonance structures). Use the Lewis dot structures to predict which structure is more likely to be more accurately reflect the bonding in the CN_2^{2-} ion.

Determine total number of valence electrons.

C	4
2 N	2 x 5 = 10
-2 charge	+2
Total	16

The two possible structures are frameworks are C–N–N and N–C–N. The resonance structures for each framework are shown below. The formal charges are shown below the individual atoms.



The bottom set of resonance structures best match the criteria set forth in the Electroneutrality Principle (minimizes number of atoms with formal charge, puts negative charge on more electronegative atom and does not separate charge as badly as the first set does). Therefore, we conclude that the CN_2^{2-} ion is best described by the second set of resonance structures.

4. (7 Points) An aqueous solution that is 1.00% NaCl by mass has a density of 1.071 g/cm³ and an osmotic pressure of 7.83 atm at 25.0 °C. What fraction of the moles of NaCl in this solution exist as ion pairs? Osmotic pressure is given by $\pi = i \cdot M \cdot R \cdot T$, where i is the van't Hoff factor, M is the solution's molarity, $R = 0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$ and T is the temperature.

Determine the molarity of NaCl formula units in the solution.

$$\left(\frac{1.00 \text{ g}}{100.00 \text{ g solution}} \right) \left(\frac{1.071 \text{ g solution}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ cm}^3}{1 \text{ mL}} \right) \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) \left(\frac{1 \text{ mole}}{58.443 \text{ g}} \right) = 0.183 \text{ M}$$

Determine the concentration of particles (Na⁺, Cl⁻ and NaCl ion pairs) in the solution from the osmotic pressure. We can ignore the van't Hoff factor here.

$$\pi = M \cdot R \cdot T$$

$$M = \frac{\pi}{R \cdot T} = \frac{7.83 \text{ atm}}{(0.082057 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15 \text{ K})} = 0.320 \text{ M}$$

In 1.00 L of solution we will have dissolved 0.183 moles of NaCl formula units and this will result in 0.320 moles of particles (Na⁺, Cl⁻ and NaCl ion pairs).

Let x be the number of moles of NaCl that dissociated, resulting in x moles of Na⁺ and x moles of Cl⁻ being formed. Let y be the moles of the NaCl ion pairs. We can then write the following equations.

$$2x + y = 0.320 \text{ moles}$$

$$x + y = 0.183 \text{ moles}$$

Solving for x and y gives $x = 0.137$ moles and $y = 0.046$ moles.

The fraction of NaCl formula units that exist as ion pairs is $\frac{0.046 \text{ moles}}{0.183 \text{ moles}} = 0.25$.

Or, 25% of the NaCl exist in solution as ion pairs!

5. (10 Points) Attach problem 8-72.

The equilibrium is $\text{Ag}_2\text{SO}_4 (\text{s}) \rightleftharpoons 2 \text{Ag}^+ (\text{aq}) + \text{SO}_4^{2-} (\text{aq})$.

a. in pure water.

	$\text{Ag}_2\text{SO}_4 (\text{s})$	$2 \text{Ag}^+ (\text{aq})$	$\text{SO}_4^{2-} (\text{aq})$
Initial	-----	0	0
Change	-----	+2 x	+x
Equilibrium	-----	2x	x

$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$$

$$1.2 \times 10^{-5} = [2x]^2 [x]$$

$$x = 0.014 \text{ M}$$

In pure water the solubility of Ag_2SO_4 is 0.014 M.

b. in 0.100 M AgNO_3 .

	$\text{Ag}_2\text{SO}_4 (\text{s})$	$2 \text{Ag}^+ (\text{aq})$	$\text{SO}_4^{2-} (\text{aq})$
Initial	-----	0.100	0
Change	-----	+2 x	+x
Equilibrium	-----	0.100 + 2x	x

$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$$

$$1.2 \times 10^{-5} = [0.100 + 2x]^2 [x]$$

Assume that x is negligible with respect to 0.100.

$$x = 1.2 \times 10^{-3} \text{ M}$$

Check.

$$\frac{1.2 \times 10^{-3}}{0.100} \times 100 = 1.2\%$$

This is less than 5%, so the assumption is valid.

The solubility of Ag_2SO_4 in 0.100 M AgNO_3 is 1.2×10^{-3} M.

c. in 0.20 M K_2SO_4 .

	$Ag_2SO_4 (s)$	$2 Ag^+ (aq)$	$SO_4^{2-} (aq)$
Initial	-----	0	0.20
Change	-----	+2 x	+x
Equilibrium	-----	2x	0.20+x

$$K_{sp} = [Ag^+]^2 [SO_4^{2-}]$$

$$1.2 \times 10^{-5} = [2x]^2 [0.20 + x]$$

Assume that x is negligible with respect to 0.20.

$$x = 3.9 \times 10^{-3} \text{ M}$$

Check.

$$\frac{3.9 \times 10^{-3}}{0.200} \times 100 = 1.2\%$$

This is less than 5%, so the assumption is valid.

The solubility of Ag_2SO_4 in 0.100 M $AgNO_3$ is 3.9×10^{-3} M.

6. (10 Points) Attach problem 11-48.

Since adding the reactions gives the reaction that we seek, adding the ΔG for each reaction gives ΔG for the final half reaction. We can then convert ΔG for the half reaction back to E^0 for the half reaction.



Known values from tables: $E_1^0 = +0.80 \text{ V}$ and $K_{\text{sp}} = 1.5 \times 10^{-16}$.

$$-n \cdot F \cdot E_3^0 = -n \cdot F \cdot E_1^0 + -R \cdot T \cdot \ln K$$

$$E_3^0 = \frac{n \cdot F \cdot E_1^0 + R \cdot T \cdot \ln K}{n \cdot F}$$

$$E_3^0 = \frac{(1) \left(96485 \frac{\text{C}}{\text{mole}} \right) \left(+0.80 \frac{\text{J}}{\text{C}} \right) + \left(8.31451 \frac{\text{J}}{\text{C} \cdot \text{mole}} \right) (298.15 \text{ K}) (\ln(1.5 \times 10^{-16}))}{(1) \left(96485 \frac{\text{C}}{\text{mole}} \right)}$$

$$E_3^0 = \frac{77.18 \times 10^3 \frac{\text{J}}{\text{mole}} + -90.323 \times 10^3 \frac{\text{J}}{\text{mole}}}{\left(96485 \frac{\text{C}}{\text{mole}} \right)} = \frac{-13.14 \times 10^3 \frac{\text{J}}{\text{mole}}}{\left(96485 \frac{\text{C}}{\text{mole}} \right)} = -0.14 \text{ V}$$

This half reaction has E^0 equal to -0.14 V.