Chapter 6 Homework Questions

- 6.1 The standard Gibbs Energy of the reaction, H₂(g) + 3 N₂(g) ≈ 2 NH₃(g), is -32.9 kJ/mol at 25 °C. Calculate the value of ΔG for the following values of the reaction quotient, Q: (a) 0.01, (b) 1.0, (c) 10.0, (d) 100, 000, (e) 1,000,000 Estimate the value of the equilibrium constant, K, from the above data, and calculate the actual value of K.
- 6.2 Consider the gas phase reaction, $2 H_2O(g) \rightleftharpoons 2 H_2(g) + O_2(g)$. At 2257 K and p = 2.0 bar, H₂O is 1.77% dissociated. Calculate the equilibrium constant for this reaction.
- **6.3** Consider the reaction, $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$. The Gibbs Energy of Formation of $NH_3(g)$ is -16.5 kJ/mol at 298 K.

Calculate the reaction Gibbs Energy for the above reaction (at 298 K) when the partial pressures of the gases are; $p_{N2} = 3.0$ bar, $P_{H2} = 1.0$ bar, $P_{NH3} = 0.50$ bar. What is the spontaneous direction of the reaction under these conditions?

6.4 Consider the gas phase equilibrium, $3 A(g) \rightleftharpoons B(g) + 2 C(g)$. At 50 °C, the Gibbs Energy change for the reaction is -2.50 kJ/mol when the component pressures are: P_A =2.0 bar, P_B = 4.0 bar, P_C - 0.50 bar,

Calculate the value of the equilibriaum constant, K, at 50 °C.

- 6.5 Consider the gas phase dissociation equilibrium, $A(g) \rightleftharpoons B(g) + 3 C(g)$. At 25 °C, the percent dissociation is 30% at a total pressure of 2 bar. Calculate the equilibrium constant, K.
- 6.6 Consider the dissociation equilibrium, N₂O₄(g) ⇒ 2 NO₂(g). At 25 °C and p = 1 bar, N₂O₄ is 18.46% dissociated. The reaction enthalpy is constant at ΔH° = +56.2 kJ/mol.
 (a) Calculate the equilibrium constant, K, at 25 °C
 (b) Calculate K at 100 °C
- 6.7 For the gas phase reaction, $2 \text{ A} + \text{B} \rightleftharpoons 3 \text{ C} + 2 \text{ D}$, it was found that when 1.00 mol of A, 2.00 mol of B, and 1.00 mol of D were mixed and allowed to come to equilibrium at 25 °C, the resulting mixture contained 0.90 mol of of C at a total pressure of 4.0 bar.
 - (a) Calculate the equilibrium contant, K, for this reaction
 - (b) Calculate the Reaction Gibbs Energy, $\Delta_r G^o$, for this reaction at 25 °C.
- **6.8** The standard reaction enthalpy for the reaction, $Zn(s) + H_2O(g) \rightleftharpoons ZnO(s) + H_2(g)$, is approximately constant at 224. kJ/mol. The standard reaction Gibbs energy is +33 kJ/mol at 1280 K.

Determine the temperature at which the Equilibrium Constant for this reaction becomes greater than 1.

6.9 The equilibrium constant for the reaction, $A(g) \rightleftharpoons B(g)$, is temperature dependent and follows the equation:

ln K = A +
$$\frac{B}{T}$$
 + $\frac{C}{T^2}$, A = -1.0, B = -1100 K, C = 1.5x10⁵ K²
Calculate

(a) the Reaction Enthalpy, ΔH^o (in kJ/mol) at 180 oC

- (b) the Reaction Entropy, ΔS^o (in J/mol K) at 180 oC
- 6.10 For the gas phase equilibrium, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium constant is K = 4.5 at $150^{\circ}C$.

(a) If one puts PCl5(g) into a container with an initial pressure of Po = 3.0 bar, what are the pressures of PCl5(g) and PCl3(g) at equilibrium.

(b) Determine the Gibbs energy change for the when the partial pressures of the three gases are: P(PCl5) = 0.8 bar and P(PCl3) = 2.2 bar and P(Cl2) = 2.2 bar?

- 6.11 For the gas phase equilibrium, $2A(g) + B(g) \rightleftharpoons 2C(g)$, the equilibrium constant is $K = 1 \times 10^{-3}$. If one puts A and B into a vessel with initial pressures, Pinit(A) = Pinit(B) = 3. bar, determine the pressure of C at equilibrium? NOTE: You may assume that very little A and B react.
- 6.12 Consider the equilibrium, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The value of the equilibrium constant is K= 337 at 100 °C and K= 7.1x10⁻⁵ at 500 °C

(a) Determine the enthalpy (ΔH^{O}) and entropy (ΔS^{O}) changes for this reaction.

(b) Determine the value of the equilibrium constant at $300 \text{ }^{\circ}\text{C}$.

(c) At 500 $^{\text{O}}$ C, the initial pressures (before reaction to form NH₃) of N₂ and H₂ are 3.0 bar and 2.0 bar, respectively. Calculate the pressure of NH₃ at equilibrium [Note: You can make the assumption that very little NH3 is formed relative to the initial pressures of N2 and H2 to simplify your calculation].

(d) Determine the Gibbs energy change for the reaction at 500 ^{O}C for $P_{N2}=P_{H2}=0.2$ bar and $P_{NH3}=2.5$ bar

- **6.13** Use the Reduction Potential Table below to calculate the equilibrium constants for the following two reactions:
 - (a) $Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2 Sn^{2+}(aq)$ (b) $Sn(s) + 2 AgCl(s) \rightleftharpoons SnCl_2(aq) + 2 Ag(s)$

Reduction Reaction	Ered ^o
$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2 e^{-} \rightarrow \operatorname{Sn}^{2+}(\operatorname{aq})$	+0.15 V
$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2 e^{-} \rightarrow \operatorname{Sn}(s)$	-0.14 V
$2 \operatorname{AgCl}(s) + 2 e^{-} \rightarrow 2 \operatorname{Ag}(s) + 2 \operatorname{Cl}(aq)$	+0.22

6.14 The solubility products of two sparingly soluble Bromide (Br⁻) salts are: AgBr - Ksp = $5.4x10^{-13}$, HgBr₂ - Ksp = $6.2x10^{-20}$ Consider a solution which initially contains $5.0x10^{-5}$ M Ag⁺(aq) and $5.0x10^{-5}$ M Hg²⁺(aq). KBr (a strong electrolyte) is added until [Br⁻] = $2.0x10^{-8}$ M. Which of the above salts (AgBr and HgBr₂) will precipitate?

6.15 Mercury(I) Sulfate, Hg₂SO₄, is a sparingly soluble salt with Ksp = 6.5×10^{-7} . If 1200 mL of 0.010 M K₂SO₄(aq) is mixed with 800 mL of 0.020 M HgNO₃(aq), calculate the concentrations of [Hg⁺] and [SO₄²⁻] in the resulting solution and **determine whether or not** Hg₂SO₄(s) will precipitate.

6.16 The standard reduction potentials of $Br_2(l)$ and $Hg^{2+}(aq)$ are +1.07 V and +0.86 Volts, respectively Consider the electrochemical cell, $Br^{-}(0.005 \text{ M})|Br2(l)||Hg^{2+}(2.5 \text{ M})|Hg(l).$

(a) Write the balanced equation for this reaction, and indicate the number of electrons transfered.

(b) Calculate the standard cell potential, E^{O} cell, for the reaction.

- (c) Calculate the equilibrium constant for the reaction at $25 {}^{\rm O}$ C.
- (d) Calculate the cell potential under the conditions shown above.
- 6.17 The standard reduction potentials of $Mg^{2+}(aq)$ and $Al^{3+}(aq)$ are -2.37 V and -1.66 Volts, respectively. Consider the electrochemical cell,

 $Mg(s)|Mg^{2+}(1.8 M)||Al^{3+}(0.001 M)|Al(s).$

(a) Write the balanced equation for this reaction, and indicate the number of electrons transfered.

- (b) Calculate the standard cell potential, E^{O} cell, for the reaction.
- (c) Calculate the equilibrium constant for the reaction at $25 {}^{\text{O}}\text{C}$.
- (d) Calculate the cell potential under the conditions shown above.

6.18 The EPA recommended maximum concentration of Zn^{2+} [M(Zn) = 65.4 g/mol] in drinking water is 5. mg/L. The amount of Zn in a sample of water can be determined by measuring the voltage of an electrochemical cell in which the reference electrode (cathode) has a standard concentration [say, 0.20 M Zn(NO3)2] and the sample electrode (anode) has the water sample. This cell can be designated as: $Zn(s)|Zn^{2+}(xx M)||Zn^{2+}(0.20 M)|Zn(s)$.

The cell potential was measured as +0.078 V. Determine the concentration of Zn^{2+} in the sample, in mg/L.

6.19 An electrochemical cell is prepared with 0.50 M Pb(NO3)2(aq) in the reference compartment (cathode) and a saturated solution of lead iodate, Pb(IO3)2(aq), in the sample compartment (anode). The measured cell voltage is: 0.120 V.

Calculate the Solubility Product, Ksp, of Pb(IO3)2.

6.20 An electrochemical cell is prepared with 0.25 M AgNO₃(aq) in the reference compartment (cathode) and a saturated solution of silver phosphate, Ag3PO4(aq), in the sample compartment (anode). The measured cell voltage is: 0.195 V.

Calculate the Solubility Product, K_{sp}, of Ag₃PO₄.

6.21 Consider the electrochemical cell reaction: $Hg_2Cl_2(aq) + H_2(g) \rightleftharpoons 2 Hg(l) + 2 HCl(aq)$. The standard cell potential is temperature dependent and given by: $E^{o}_{cell} = a - b/T^2$ where a = 0.313 V and $b = 5.0 \times 10^7$ V/K²., T is temperature in Kelvins.

For this reaction, calculate: (a) $\Delta_r G^o$, (b) $\Delta_r S^o$, (c) $\Delta_r H^o$