Chemical Equilibrium - Part A:

1. At 25^{o} C and 101.3 kPa one mole of hydrogen gas and one mol of chlorine gas are reacted in a stoppered reaction vessel. After a certain time, three gases are detected in the vessel. The molar ratios H_2 = 0.22, Cl_2 = 0.22, HCl = 1.56 do not change over an observable time period.
   a) Write an equation for the reaction ____
   b) What evidence suggests that a state of equilibrium exist?

   c) Explain the observations in terms of the DYNAMIC NATURE of the equilibrium system.

   d) Suggest THREE alternative explanations other than equilibrium to explain the constancy of macroscopic properties observed in (a)
   (1)

   (2)

   (3)

   (e) Can you suggest a way of distinguishing between the possible explanations given in questions (b) and (d)

   (1)

   (2)

   (f) Would equilibrium exist if the reaction vessel was left open to the air? Explain.

2. Explain the DYNAMIC NATURE of the following phase equilibria. Be specific.
   (1) Water and water vapour exist together in a closed vessel at constant temperature.

   (2) A saturated sugar solution with excess solid in a closed container at constant temperature.

3. (a) Explain the dependence of Le Chatelier's Principle on the rates of the forward and reverse reactions.

(b) What is the relationship between "equilibrium shift" and the product / reactant(P/R) ratio?

(c) If the equilibrium is "disturbed", what effect does this have on the position of the equilibrium or the "extend" of the equilibrium?

4. Given the following chemical equilibria: (Substances are all gases)

(1) $C_2H_6 \leftrightarrow H_2 + C_2H_4$

(2) $Br_2 + Cl_2 \leftrightarrow 2BrCl$ $\Delta H = + 14.63$ kJ

(3) $4NH_3 + 5O_2 \leftrightarrow 4NO + 6H_2O + 902.88$ kJ

(4) $H_2 + I_2 \leftrightarrow 2HI$

(5) $2SO_2 + O_2 \leftrightarrow 2SO_3$ $\Delta H = -192.28$ kJ

Complete the following table:

Reaction	Stress	Effect on Rates Rf and Rb	Shift of equilibrium position P/R ratio up or down
1	Increase in H_2 concentration		
2	Decrease temperature		
3	Increase temperature		
5	Increase temperature		
4	Decrease volume		
5	Add a solid catalyst. Vessel vol. constant		
5	Add a solid catalyst. Vessel vol. Vary		
5	Add some inert gas. i.e. He T and P is constant.		
5	Add some He volume constant		

5. The formation of ammonia from its elements occurs industrially by the Haber process.
   (1) Write the equation for the reaction ____
   (2) Use Le Chatelier's Principle to determine the ideal conditions of temperature and pressure for maximizing the yield of ammonia for industrial and commercial application.
   Pressure:

   Temperature:

   (3) Table 11a. Page 692 gives the yields of ammonia in the Haber Process as a function of temperature and pressure. Explain why the industrial conditions do not correspond to the conditions of maximum yield as given by the table.

6. $2SO_2 + O_2 \leftrightarrow 2SO_3$ (all are gases) K = 43.6
   (a) Write the equilibrium law expression for this reaction

   (b) The units of K are ____________________

   (c) What is the equilibrium constant for the reverse reaction?

7. The water gas reaction: $CO_2 + H_2 \leftrightarrow CO + H_2O$ (all are gases) was carried out at 900°C with the following results. P = Partial pressure

Trial	P_{CO}	P_{H2O}	P_{CO2}	P_{H2}
1	0.352	0.352	0.648	0.148
2	0.266	0.266	0.234	0.234
3	0.186	0.686	0.314	0.314

   (a) Write the equilibrium law expression for this reaction K_p =

   (b) Verify that the expression in (a) is indeed a numerical constant using the equilibrium constant based on partial pressures.
   Solution:

8. Equilibrium constants are given for the following reactions.
   (1) $CH_3COOH_{(aq)} \leftrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$ $K_1 = 1.8 \times 10^{-5}$
   (2) $CdS_{(s)} \leftrightarrow Cd^{2+}_{(aq)} + S^{2-}_{(aq)}$ $K_2 = 7.1 \times 10^{-28}$
   (3) $H^+ + HS^- \leftrightarrow H_2S_{(aq)}$ $K_3 = 1.0 \times 10^{7}$
   Which reaction as written with the information given above, is the most spontaneous i.e the product are favoured over the reactants? Explain why.

9.(a) Entropy is defined as

____

____

(b) For each of the following processes, predict, with reasoning, whether the entropy of the system increases or decreases when the reactants forms products.

(1) $2H_2O_{(g)} + O_{2(g)} \leftrightarrow 2H_2O_{(g)}$

(2) $MgCO_{3(s)} + 2H_3O^+_{(aq)} \leftrightarrow Mg^{2+}_{(aq)} + 3H_2O_{(l)} + CO_{2(g)}$

(3) $Ag^+_{(aq)} + Cl^-_{(aq)} \leftrightarrow AgCl_{(s)}$

(4) $Cl_{2(g)} \leftrightarrow 2Cl_{(g)}$

(5) $NH_{3(g)} + HCl_{(g)} \leftrightarrow NH_4Cl_{(s)}$

(6) $NH_4NO_{3(s)} \leftrightarrow NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)}$

10.(a) The two driving factors affecting the extend of a reaction are entropy and enthalpy. A reaction would be very spontaneous and have a very high K if in proceeding to the right entropy __________________ and enthalpy ______________________. These are the two governing principles for all chemical reactions.
(b) Explain using these principles why the melting of ice at 273 K is a spontaneous process even though the reaction is endothermic.

Remedial Problem Set: Chemical Equilibrium 92

Part A

1. Each of the following reactions has come to equilibrium. In this system using "Le Chatelier's Principle" predict the shift in equilibrium with appropriate reasoning.

(1) $2H_2O_{(g)} + 2NO_{(g)} \leftrightarrow N_{2(g)} + 2H_2O_{(g)}$	Total pressure increases
(2) $SO_{2(g)} + \frac{1}{2} O_{2(g)} \leftrightarrow SO_{3(g)} + 96.14$ kJ	Temperature is increased
(3) $P_{4(s)} + 6H_{2(g)} \leftrightarrow 4PH_{3(g)}$	Some $H_{2(g)}$ is added
(4) $FeO_{(s)} + CO_{(g)} \leftrightarrow Fe_{(s)} + CO_{2(g)}$	Some Fe is added and volume of container is kept constant
(5) $NH_{3(g)} + HCl_{(g)} \leftrightarrow NH_4Cl_{(s)}$	The volume of the system is increased

2. Given the equilibrium $Fe^{3+}_{(aq)} + SCN_{(aq)} \leftrightarrow FeSCN^{2+}_{(aq)}$. What is the effect on colour intensity of the solution if NaF(s) is added? The following equilibrium has a very high K. It is known that Fe^{3+} reacts with F^- ions. $Fe^{3+}_{(aq)} + 6F^-_{(aq)} \leftrightarrow [FeF_6]^{3-}_{(aq)}$

3. What experimental conditions of pressure and temperature will give the best yields of $HCl_{(g)}$?

4. Explain how the tendencies towards minimum enthalpy and maximum entropy affect the following:
$Br_{2(s)} \leftrightarrow 2Br_{(l)} \quad \Delta H = +67.72$ kJ/mol

Part B 100

1. Silver chloride is sparingly soluble in water represented by this equation:
   $AgCl_{(s)} \leftrightarrow Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$
   What is the effect on the position of the equilibrium if more AgCl solid is added to the system? Explain.

2. Calcium carbonate dissociates according to this equation:
   $CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$

   (1) Write the equilibrium constant expression for this reaction

   (2) What would happen to the vapour pressure of CO_2 if some solid calcium carbonate or calcium oxide were added at constant temperature and constant container volume? Explain

3. When 1 mole of $NH_{3(g)}$ and 0.4 mol of $N_{2(g)}$ are placed in a five litre container and allowed to reach equilibrium at a certain temperature , it is found that 0.78 mol of NH_3 is present. The reaction is
   $NH_{3(g)} \leftrightarrow 3H_{2(g)} + N_{2(g)}$

   (1) Calculate the number of moles of hydrogen and nitrogen gases at equilibrium.

   (2) Calculate the concentration of each product and reactant present.

4. The equilibrium constant for $2X_{(g)} \leftrightarrow Y_{(g)} + Z_{(g)}$ is 3.0. How many moles of X are present at equilibrium when 1.00 mol of each of Y and Z are placed in a 5 L container.

5. When 0.04 mol of PCl_5 is heated to 250°C in a 1 litre vessel, an equilibrium is established in which the concentration of Cl_2 is 0.025 mol/L. Find the equilibrium constant value for the reaction.
   $PCl_{5(g)} \leftrightarrow PCl_{3(g)} + Cl_{2(g)}$

6. At a given temperature, analysis of an equilibrium mixture shows that the concentrations in mol/L of SO_2, SO_3, NO_2 and NO are 4.0, 3.0, 0.5 and 2.0 respectively. How many moles of NO_2 must be added to increase the concentration of SO_3 by 1.0 mol/L at constant temperature? The reaction is
   $SO_{2(g)} + NO_{2(g)} \leftrightarrow SO_{3(g)} + NO_{(g)}$

7. Will there be a net reaction when 2.5 moles of PCl_5, 0.60 moles of Cl_2, 0.60 moles of PCl_3 are placed in a 1 litre vessel and heated to 250^{o} C. If so which reaction (forward or reverse) takes place? Explain.

8. At a specific concentration the substance AO_2 is 10% dissociated at a given temperature as follows:
   $4AO_2 \leftrightarrow 2A_2O_3 + O_2$
   For these conditions, how many moles of EACH component will be present in a mixture at equilibrium if 2 moles of A_2O_3 and 1 mol of O_2 are present initially?

9. Predict the spontaneity of the following reactions by using the Gibbs Free Energy equation to approximate the sign of G
   (1) $H_2O_{(l)} \leftrightarrow H_{2(g)} + ½ O_{2(g)}$ ΔH = +284.24 kJ/mol; $T\Delta S$ = +41.8 kJ

   (2) $C_6H_{14(g)} \leftrightarrow 6C_{(s)} + 7H_{2(g)}$ ΔH = + 163.02 kJ/mol; $T\Delta S$ = -167.2 kJ

   (3) $2Fe_{(s)} + ½ N_{2(g)} \leftrightarrow Fe_2N_{(s)}$ ΔH = -3.76 kJ/mol; $T\Delta S$ = -14.63 kJ

   (4) $N_{2(g)} + 2O_{2(g)} \leftrightarrow 2NO_{2(g)}$ ΔH = =67.72 kJ/mol; $T\Delta S$ = (analyse equation and determine sign)