CHEMISTRY 225 SEMESTER 04-2011
HOMEWORK ON EQUILIBRIA - GENERAL

1) Write an expression for the equilibrium constant (K) for each of the following reactions:

a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

b) $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$

c) $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$

d) $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightleftharpoons 4H_2O(l) + Mn^{2+}(aq) + 5Fe^{3+}(aq)$

e) $Fe_3O_4(s) + 4H_2(g) \rightleftharpoons 4H_2O(g) + 3Fe(s)$

f) $2Fe(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightleftharpoons 2Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

g) $C_2H_5OH(l) \rightleftharpoons C_2H_5OH(g)$

h) $3O_2(g) \rightleftharpoons 2O_3(g)$

i) $Ag(s) + Fe^{3+}(aq) \rightleftharpoons Ag^+(aq) + Fe^{2+}(aq)$

j) $CaCO_3(s) \rightleftharpoons CO_2(g) + CaO(s)$

k) $Pb(s) + 2H^+(aq) \rightleftharpoons Pb^{2+}(aq) + H_2(g)$

l) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

m) $NH_3(aq) \rightleftharpoons NH_3(g)$

n) $H_2O(l) \rightleftharpoons H_2O(g)$

o) $2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$

p) $H_2O(s) \rightleftharpoons H_2O(l)$

q) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

2) For the system:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -98 \text{ kJ mol}^{-1}$$

state the effect on individual concentrations, equilibrium position, reaction rates and the value of K_c of
a) adding more oxygen.
b) increasing the pressure.
c) adding finely divided platinum, which acts as a catalyst.
d) increasing the temperature.

3) Chemical equilibrium is often described as *dynamic equilibrium*. Contrast dynamic equilibrium with static equilibrium, giving non-chemical examples in each case, and explain why chemical equilibrium is correctly described as dynamic.

4) Hydrogen and iodine are introduced into a sealed vessel at a temperature at which both are gases and allowed to react until equilibrium is reached. Sketch a graph of concentration against time showing the concentrations of hydrogen, iodine and hydrogen iodide. Sketch a second graph showing the rate of production of hydrogen iodide (one curve) and the rate of its reaction (ie. destruction) as a function of time.

5) The equilibrium constant (K_c) for the reaction

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

is 4. If in an equilibrium mixture [A] = 5, [B] = 2 and [D] = 4, find [C]

6) The equilibrium constant (K_p) for the reaction

$$2X(g \rightleftharpoons 3Y(g)$$

is 1/8. If P_x = 8 atm, find P_y

7) For the equilibrium $X(g) \rightleftharpoons Y(g) + Z(g)$, a 500 cm^3 flask contains 1 mol X, 1·5 mol Z and 2·5 mol Y in equilibrium together at 0®C. Find K_p for the reaction. If a second equilibrium mixture at the same temperature has P_x = 10 atm and P_y = 6 atm, find P_z.

8) When 60 g of ethanoic acid, CH_3COOH, are mixed with 46 g of ethanol, CH_3CH_2OH, the equilibrium amount of ethylethanoate, $CH_3COOCH_2CH_3$ formed is 58.7 g.
   a) Calculate K_c for the system:

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

   where water is NOT the solvent.
   b) What mass of ethylethanoate would be formed at the same temperature if 60 g of ethanoic acid are mixed with 23 g of ethanol?

9) a) An equilibrium mixture contains 2·0 mol of bromine, 1·25 mol of hydrogen and 0·5 mol of hydrogen bromide at a fixed temperature. Determine the equilibrium constants (K_c and K_p) for the reactions represented by

   i) $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

   ii) $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons HBr(g)$

   b) In another experiment conducted at this temperature, some HBr was admitted into an evacuated 2000 cm^3 vessel and when equilibrium was attained some had decomposed yielding 6·32 mol of bromine as one product.
   i) What was the concentration of each species present at equilibrium?
   ii) What mass of HBr was originally let into the vessel?

10) Suppose 3 mol of HCl and 2 mol of O_2 are introduced into a 5000 cm^3 vessel and the temperature held constant at 450®C until equilibrium is attained according to the reaction:

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g) \quad \Delta H = -113 \text{ kJ mol}^{-1}$$

   a) From this data, could the equilibrium constant be calculated? If so, find its value. If not, what further data would be needed?
   b) How will the value of K_p for the system at 450®C and 1 atm compare with that at 550®C and 1 atm?
   c) If the temperature is maintained at 450®C, but the system is permitted to expand so that the pressure is reduced to 0·5 atm, how will the relative concentrations at equilibrium compare with those at 450®C and 1 atm pressure?
   d) How will the value of K_p for the system at 450®C and 1 atm compare with that at 450®C and 0·5 atm?
   e) Show how the equilibrium constant expression for this reaction is related to those for the reactions:

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

11) In the following questions, consider the equilibrium:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

for which K_p = 1·70 at 250®C

a) If PCl_5 is 48·5% dissociated at 200°C, 1 atm, and 97% dissociated at 300°C, 1 atm, explain whether the decomposition reaction is exothermic, or endothermic.

b) If 1 mol of $PCl_5(g)$ is placed in a 1000 cm^3 flask at 250°C and allowed to come to equilibrium, find the equilibrium partial pressure of each species present.

c) If 5 mol of $PCl_5(g)$ were initially present as in (b) calculate the equilibrium partial pressure of each species.

d) Using your results from (b) and (c) or otherwise calculate the degree of dissociation of the PCl_5 in each case.

e) Proceed as in (b) and (c) for the following initial mixtures of species:
   i) 1 mol of PCl_3 and 1 mol of Cl_2.
   ii)0·5 mol of PCl_5 and 1 mol of Cl_2.

12) Calculate the reaction quotients in each of the following cases and decide whether the mixture has a tendency to form reactants or products.

a) A mixture that is 4·8 mM in $H_2(g)$, 2·4 mM in $I_2(g)$, and 2·4mM in HI(g) if $K_c = 49$ for

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

b) Equal concentrations of the three gases that appear in (a).

c) A mixture that is 1·0 M in ethanoic acid, 2·0 M in ethanol, 0·50 M in ethyl ethanoate, and 5·0 M in water in a non-aqueous solution. $K_c = 4·0$

13) 1g of ethanoic acid, when released into a 1500 cm^3 vessel and allowed to evaporate completely at 25®C gave rise to a pressure of 26·1 kPa. Calculate the degree of association of the ethanoic acid. (Ans. 0·103)

13) 0·92 g of a certain gaseous dimer occupies a volume of 342 cm^3 at 25®C and 1 atm pressure. If the dimer is 40% dissociated under these conditions, calculate the molar mass of the dimer and hence the monomer. (Ans. 92, 46 $gmol^{-1}$)

15) At elevated temperatures, aluminium chloride, Al_2Cl_6, reacts to form Al_3Cl_9 according to the equation:

$$3Al_2Cl_6(g) \rightleftharpoons 2Al_3Cl_9(g)$$

In an experiment at 454 K, the equilibrium partial pressure of Al_2Cl_6 is 1·00 atm, and the equilibrium partial pressure of Al_3Cl_9 is $1·02\times10^{-2}$ atm. Calculate the equilibrium constants, K_p and K_c of the above reaction at 454 K.

16) The compound 1,3-di-*t*-butylcyclohexane exists in two forms that are known as the "chair" and "boat" conformations because the shapes of the molecules resemble these objects. Equilibrium exists between these forms, represented by the equation:

chair ⇌ boat

At 580 K, 6·42% of the molecules are in the chair form. Calculate the equilibrium constant (K_c) for the reaction as written above.