## Equilibrium problems (calculator required)

1. For the equilibrium

   $$CO_2(g) \rightleftharpoons CO(g) + 1/2O_2(g)$$

   $K_c = 1.72 \times 10^{-46}$ at 25°C.

   a) Evaluate $K_P$ at 25°C. **[$8.56 \times 10^{-46}$]**
   b) If a flask initially containing only 1.00 bar of $CO_2$ is allowed to come to equilibrium, what will be the equilibrium pressure of each species?
   **[$P_{CO2}$ = 1 bar; $P_{CO}$ = $1.1 \times 10^{-30}$ bar; $P_{O2}$ = $5.7 \times 10^{-31}$ bar]**
   c) Do you expect that this reaction will be exothermic or endothermic? Why? **[endo]**

2. Bromine and chlorine both dissolve in carbon tetrachloride, whereupon they react (slowly) to form BrCl:

   $$Br_2(CCl_4) + Cl_2(CCl_4) \rightleftharpoons 2BrCl(CCl_4)$$

   Under equilibrium conditions at 25°C, $[Br_2] = [Cl_2] = 0.0043$ M, and [BrCl] = 0.0114 M.
   a) Evaluate the equilibrium constant for this reaction at 25°C. **[7.03]**
   b) If 0.078 moles of BrCl were added to the equilibrium mixture above, what would be the new equilibrium concentrations of all species present? Assume 1 L of solution.
   **[$Br_2$] = [$Cl_2$] = 0.02107 M; [BrCl] = .05586 M**

3. Predict the effect each of the following would have on the equilibrium reaction:

   $$CoCl_4^{-2}(aq) + 6H_2O(l) \rightleftharpoons Co(H_2O)_6^{+2}(aq) + 4Cl^-(aq) \qquad \Delta H = -14 \text{ kJ}$$

   Indicate your choice by writing shift **R**ight, shift **L**eft, or **N**o change:
   a) Adding concentrated HCl ______
   b) Heating the reaction ______
   c) Adding $AgNO_3$ (AgCl is insoluble) ______
   d) Adding water ______

**[L L R R]**

4. The ionization of water is an equilibrium process for which $K_c = 1.0 \times 10^{-14}$ at 25°C:

   $$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H = +55.8 \text{ kJ}$$

   Determine the [$H^+$] in water at 50°C. **[$2.39 \times 10^{-7}$]**

5. The normal boiling point of methanol is 64.65°C and its enthalpy of vaporization is 37.85 kJ/mol. What is its vapour pressure at 21.0°C? **[**102.8 mmHg]

6. Ammonium carbamate, $NH_4CO_2NH_2$, dissociates according to the exothermic reaction:

   $NH_4CO_2NH_2\,(s) \rightleftharpoons 2\,NH_3\,(g) + CO_2\,(g)$  $K_p = 4.62 \times 10^{-4}$ at 25°C

   a) If 1.00 g of ammonium carbamate is placed in a 1.00 L sealed, evacuated flask at 25°C, calculate the total pressure in the flask at equilibrium. **($P_T$ = 0.146 bar)**
   b) What mass of ammonium carbamate will be left at equilibrium in the experiment described in part a)? **(0.84 g)**
   c) If 1.00 g of ammonium carbamate is placed in the same 1.00 L evacuated flask and some $CO_2$ is added so that the partial pressure of $CO_2$ at equilibrium is 1.00 atm, calculate the partial pressure of $NH_3$ when the system comes to equilibrium at 25 °C. **(0.0214 bar)**

7. The fastest growing use of methanol is to make the octane enhancer, methyl *tert*-butyl ether. Today all methanol is produced by the reaction of carbon monoxide and hydrogen. The value of $K_p$ for this reaction is $1.3 \times 10^{-4}$ at 300.°C.
   a) Write the equilibrium reaction for the production of methanol.
      **($2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$)**
   b) What is the value of $K_c$ at 300.°C? **(0.30)**
   c) In which direction will this reaction shift if the temperature is raised, given that the $\Delta H°_{rxn}$ = -90.7 kJ. Explain! **(shifts to left because heat is a product when rxn. is exothermic, try to use up "excess" heat to re-establish eqm.)**
   d) In the industrial process, the stoichiometric ratio of CO to $H_2$ is used. If the reaction is carried out at an initial total pressure of 300. bar, what are the initial partial pressures of CO and $H_2$? **(100. bar CO, 200. bar $H_2$)**

8. A flask initially contains only NOBr gas. Once heated to a temperature T, 34.0 % of the original gas decomposes via the following equation to give a total pressure of 0.25 bar at equilibrium:

   $2\,NOBr\,(g) \rightleftharpoons 2\,NO(g) + Br_2\,(g)$

   a) Determine the original pressure of NOBr in the flask. **(0.21 bar)**
   b) What is the value of $K_p$ at this temperature T? **($9.6 \times 10^{-3}$)**
   c) If the value of $K_c$ at this temperature T is $3.87 \times 10^{-4}$, determine the temperature T. **(25°C)**

9. For the equilibrium:

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

At a given temperature $T_1$, $K_p = 2.25$. An unknown quantity of pure $PCl_5(g)$ is placed in an evacuated flask at a temperature $T_1$.when equilibrium is established, the partial pressure of $PCl_5\,(g)$ is 0.25 bar.

a) What are the partial pressures of $PCl_3$ and $Cl_2$ at equilibrium? **(0.75 bar)**
b) Determine the original pressure of $PCl_5$ (before any reaction) and the % dissociation of $PCl_5$. **(1.00 bar, 75 %)**
c) What is the value of $K_c$ for the process if $T_1$ equals 375 °C? **(0.0418)**

10. For the following system:

$C\,(s) + CO_2\,(g) \rightleftharpoons 2\,CO\,(g)$

At 700. °C in a 2.00 L flask there are 0.100 moles of CO, 0.200 moles of $CO_2$, and 0.400 moles of C at equilibrium. At 600. °C, an additional 0.0400 moles of C forms at equilibrium.

a) The process as written is: exothermic or **endothermic**.
b) Determine the value of $K_c$ at 600. °C and 700. °C. **($K_c$ = 0.0250 at 700. °C, $8.3 \times 10^{-4}$ at 600. °C)**
c) An additional 0.200 moles of C is added to the flask at 600. °C. What will be the effect on:

| | | | | |
|---|---|---|---|---|
| i) | $K_c$ | increase | decrease | **no effect** |
| ii) | $P_{CO}$ | increase | decrease | **no effect** |
| iii) | $P_{CO_2}$ | increase | decrease | **no effect** |

11. Consider the equilibrium:

$4\,NH_3\,(g) + 5\,O_2\,(g) \rightleftharpoons 4\,NO_2\,(g) + 6\,H_2O(l) \quad \Delta H° = -1381\text{ kJ}$

Predict whether the equilibrium amount of $NH_3$ will increase or decrease and the direction that the reaction will shift in order to establish a new equilibrium if:

a) the volume of the system is decreased **(↓,shifts to right)**
b) the temperature of the system is increased **(↑,shifts to left)**
c) some $O_2$ is added to the container **(↓,shifts to right)**
d) some He is added to the container **(no effect)**
e) some $NH_3$ is added to the container **(↑, shifts to right)**
f) some $H_2O$ is removed from the container **(no effect as long as some water remains)**

12. 0.024 mole of $N_2O_4$ was introduced into a 0.375 L flask at 25°C. Determine the equilibrium concentrations of $N_2O_4$ and $NO_2$ at 25.0 °C. **($N_2O_4$ = 0.056 M; $NO_2$ = 0.016 M)**

$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$ $\qquad K_c = 4.61 \times 10^{-3}$ at 25°C

13. 0.150 mol of antimony sulfide and 0.500 mol of $H_2$ were placed in a 500 mL flask and heated to 713 K. What are the equilibrium concentrations of $H_2$ and $H_2S$ at 713 K?
**([$H_2$] = 0.570 M; [$H_2S$] = 0.430 M)**

$Sb_2S_3\ (s) + 3\ H_2\ (g) \rightleftharpoons 2\ Sb\ (s) + 3\ H_2S\ (g)$ $\qquad K_c = 0.429$ at 713 K

14. 0.100 mol of $H_2$ and 0.100 mol of HI were placed in a 1.00 L container and heated to 445 °C. Determine all equilibrium concentrations. **([$H_2$] = 0.102 M; [$I_2$] = 1.81 × 10 $^{-3}$ M, [HI] = 0.0964 M))**

$H_2\ (g) + I_2\ (g) \rightleftharpoons 2\ HI\ (g)$ $\qquad K_c = 50.2$ at 445 °C