## **Equilibrium Problems (no calculator)**

You can do these problems with or without a calculator. The answers here were calculated without a calculator.

1. For the equilibrium

 $A(g) = B(g) + \frac{1}{2}C(g)$ 

 $K_c = 4.0 \text{ x } 10^{-13} \text{ at } 27^{\circ}C.$ 

- a) Evaluate K<sub>P</sub> at 27°C. [2.0 x 10<sup>-12</sup>]
- b) If a flask initially containing only 1.00 bar of A(g) is allowed to come to equilibrium, what will be the equilibrium pressure of each species?  $[P_A = 1 \text{ bar}; P_B = 2.0 \text{ x } 10^{-8} \text{ bar}; P_C = 1.0 \text{ x } 10^{-8} \text{ bar}]$
- 2. Bromine and chlorine both dissolve in carbon tetrachloride, whereupon they react (slowly) to form BrCl:

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

Under equilibrium conditions at some temperature,  $[Br_2] = [Cl_2] = 0.50$  M, and [BrCl] = 0.10 M.

- a) Evaluate the equilibrium constant for this reaction at 25°C. [0.040 or 1/25]
- b) If 0.22 moles of BrCl were added to the equilibrium mixture you found in (a), what would be the new equilibrium concentrations of all species present? Assume 1 L of solution. ([Br2] = [Cl2] = 0.60 M; [BrCl] = 0.12 M)
- 3. Predict the effect each of the following would have on the reaction (initially at equilibrium):

 $CoCl_{4}^{-2}(aq) + 6H_2O(l) \implies Co(H_2O)_{6}^{+2}(aq) + 4Cl^{-1}(aq) \qquad \Delta H^{\circ} = -14 \text{ kJ}$ 

Indicate your choice by writing shift <u>R</u>ight, shift <u>L</u>eft, or <u>N</u>o change:

- a) Adding HCl gas
  b) Heating the reaction
  c) Adding AgNO<sub>3</sub> (AgCl is insoluble)
- d) Adding water

[LLRR]

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

 $H_2O(1) \implies H^+(aq) + OH^{-1}(aq) \qquad \Delta H = +57 \text{ kJ}$ 

Should  $K_w$  be larger or smaller at 75 than at 25? How do you know? Determine the approximate  $K_w$  of water at 75°C. [about 2 x 10<sup>-13</sup>]

- 5. The normal boiling point of a liquid is 67°C and its enthalpy of vaporization is 34 kJ/mol. What is its vapour pressure (in atmospheres) at 27°C? **[about 0.2]**
- 6. Solid compound A decomposes according to the endothermic reaction:

A(s) = 2B(g) + C(g)  $K_p = 1.08 \times 10^{-4}$ 

- a) If 50.0 mmol of A(s) is placed in a 6.10-L sealed, evacuated flask at 25°C, calculate the total pressure in the flask at equilibrium. (9.0 x 10<sup>-2</sup> bar)
- b) How many millimoles of A(s) will be left at equilibrium in the experiment described in part (a)? (42.5)
- c) If some A(s) is placed in a 6.10-L evacuated flask at 25°C and some C(g) added so that the partial pressure of C(g) at equilibrium is 1.00 bar, calculate the equilibrium partial pressure of B(g) in the system. (about 1 x 10<sup>-2</sup> bar)
- d) What is the value of  $K_p$  for the equilibrium:

 $4B(g) + 2C(g) \implies 2A(s)$ 

(about 9 x 10<sup>7</sup>)

e) If the equilibrium B(g) = D(g) has equilibrium constant  $K_p = 5.0 \times 10^{-3}$ , determine the equilibrium constant for the reaction

(about 3 x 10<sup>-9</sup>)

- 7. The fastest growing use of methanol (CH<sub>3</sub>OH) is to make the octane enhancer methyl tertbutyl ether. Today all methanol is produced (as a gas) by the reaction of carbon monoxide and hydrogen. The value of  $K_p$  for this reaction is (about) 2.0 x 10<sup>-4</sup> at 327.°C.
  - a) Write the equilibrium reaction for the production of methanol.
     (2H<sub>2</sub>(g) + CO(g) → CH<sub>3</sub>OH(g))
  - b) What is the value of  $K_c$  at 327.°C? (about 0.5)
  - c) In which direction will this reaction shift if the temperature is raised, given that the  $\Delta H^{\circ}_{rxn} = -90.7 \text{ kJ}$ ? Explain! (shifts to left because heat is a product when rxn. is exothermic, try to use up "excess" heat to re-establish equilibrium.)
  - d) In the industrial process, the stoichiometric ratio of CO to H<sub>2</sub> 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<sub>2</sub>? (100. bar CO, 200. bar H<sub>2</sub>)
- 8. A flask initially contains only NOBr gas. Once heated to a temperature T, 20.0 % of the original gas decomposes via the following equation to give a total pressure of 0.33 bar at equilibrium:

 $2\text{NOBr}(g) \implies 2\text{NO}(g) + \text{Br}_2(g)$ 

- a) Determine the original pressure of NOBr in the flask. (0.30 bar)
- b) What is the value of  $K_p$  at this temperature T? (1.9 x 10<sup>-3</sup> or 3/1600)
- c) If the value of  $K_c$  at this temperature T is 3.9 x 10<sup>-5</sup>, determine the temperature T. (600 K)
- 9. For the equilibrium:

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

At some temperature  $T_1$ ,  $K_p = 2.25$ . An unknown quantity of pure PCl<sub>5</sub>(g) is placed in an evacuated flask and heated to  $T_1$ . When equilibrium was established, the partial pressure of PCl<sub>5</sub>(g) was found to be 0.25 bar.

- a) What were the partial pressures of  $PCl_3$  and  $Cl_2$  at equilibrium? (0.75 bar)
- b) Determine the original pressure of PCl<sub>5</sub> (before any reaction) and the percent dissociation of PCl<sub>5</sub> at equilibrium. (1.00 bar, 75 %)
- c) What is the value of  $K_c$  for the reaction if  $T_1$  is 327°C? (about 5 x 10<sup>-2</sup>)

10. For the following system:

 $C(s) + CO_2(g) \implies 2CO(g)$ 

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<sub>c</sub> at 600.°C and 700.°C. (K<sub>c</sub> = 0.0250 at 700.°C, 8.3 x 10<sup>-4</sup> 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)   | Kc               | increase | decrease | no effect |
|------|------------------|----------|----------|-----------|
| ii)  | Pco              | increase | decrease | no effect |
| iii) | P <sub>CO2</sub> | increase | decrease | no effect |

11. Consider the equilibrium:

 $4NH_3(g) + 5O_2(g) = 4NO_2(g) + 6H_2O(l) \Delta H^\circ = -1381 \text{ kJ}$ 

Predict whether the equilibrium number of moles of NH<sub>3</sub> will increase or decrease and the direction that the reaction will shift in order to establish a new equilibrium if:

- i) the volume of the system is decreased  $(\downarrow$ ,shifts to right)
- ii) the temperature of the system is increased  $(\uparrow, \text{shifts to left})$
- iii) some  $O_2$  is added to the container ( $\downarrow$ ,shifts to right)
- iv) some He is added to the container (no effect)
- **v**) some NH<sub>3</sub> is added to the container ( $\uparrow$ , shifts to right)
- vi) some H<sub>2</sub>O is removed from the container (no effect as long as some water remains)
- 12. 0.50 moles of  $N_2O_4$  were introduced into a 0.25 L flask. Determine the equilibrium concentrations of  $N_2O_4$  and  $NO_2$  if  $K_c$  for the equilibrium

 $N_2O_4(g) \implies 2NO_2$ 

is  $5.0 \ge 10^{-7}$ . (N<sub>2</sub>O<sub>4</sub> = 2.0 M; NO<sub>2</sub> = 1.0  $\ge 10^{-3}$  M)

13. Some antimony sulfide and 500 mmol of H<sub>2</sub> were placed in a 500 mL flask and heated. What were the equilibrium concentrations of H<sub>2</sub> and H<sub>2</sub>S once equilibrium had been reached?

 $Sb_2S_3(s) + 3H_2(g) \implies 2Sb(s) + 3H_2S(g)$   $K_c = 0.216$ 

 $([H_2] = 0.625 \text{ M}; [H_2S] = 0.375 \text{ M})$ 

14. 0.100 mol of  $H_2$  and 0.100 mol of HI were placed in a 1.00 L container and heated. Determine the equilibrium concentrations of all species.

 $H_2(g) + I_2(g) = 2HI(g)$   $K_c = 5.0 \times 10^9$ 

 $([H_2] = [HI] = 0.100 \text{ M}, [I_2] = 2.0 \text{ x } 10^{-11} \text{ M})$