K_p & Q

Equillibrium Values
- Last class you were introduced to equilibrium and learned how to make calculations.
- K_{eq} or just K is a generic term and can be used with all types of equilibrium calculations.
  - K_c is the specific K value associated with concentration.
  - K_p is the specific K value associated with pressures.
  - K_{sp} is used when working with insoluble salts.
- Today we will look at the interrelation between K_c and K_p.

Equilibrium Expressions Involving Pressures
- In terms of partial pressure, the **equilibrium partial pressures of the gases equation** can be used. For the sample equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_{P} = \frac{(P_{NH3})^2}{(P_{N2}) x (P_{H2})^3}$$

  P represents the partial pressure of each gas.
- Example: The reaction for the formation of nitrosyl chloride: $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl$ The pressures at equilibrium were found to be: $P_{NO} = 0.60$ atm, $P_{Cl2} = 0.40$ atm and $P_{NOCl} = 2.20$ atm Calculate the K_p for the reaction.

$$K_{P} = \frac{(P_{NOCl})^2}{(P_{NO})^2 \, x \, (P_{Cl2})} \quad \rightarrow \quad \frac{(2.20)^2}{(0.60)^2(0.40)} \quad \rightarrow \quad \mathbf{K_p = 34}$$

- You try: Calculate K_P for the following: $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$ if $P_{HF} = 775$ mm Hg, $P_{H2} = 650$ mm Hg and $P_{F2} = 480$ mm Hg

- The relationship between K_c and K_p is: $\mathbf{K_p = K_c(RT)^{\Delta n}}$ Δn = the sum of the moles of gaseous product – sum of the moles of the gaseous reactants.
- Example: Calculate the K_c at 25°C for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ (from earlier example: $K_P = 34$)

  $K_P = K_c(RT)^{\Delta n}$
  $34 = K_c[(0.08206)(298)]^{-1}$
  $34 = K_c(0.0409)$
  $K_c = 830$
- You try: Calculate K_c and K_p at 40.0°C for the following equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
  $P_{N2} = 2.11$ atm, $P_{H2} = 1.65$ atm and $P_{NH3} = 3.45$ atm

Application of the Equilibrium Constant

- The tendency for a reaction to occur is indicated by the magnitude of the equilibrium constant. A value of K larger than 1 means that at equilibrium the reaction will consist of mostly products – the equilibrium lies to the right. A very small K value, one less than one, means that most of the system will be in the form of the reactants.
- The size of the K and the time required to reach equilibrium are not directly related. The time required to achieve equilibrium depends on reaction rate, which is determined by the size of the activation energy.
- When the reactants and products are mixed, it is useful to know whether the mixture is at equilibrium, or if not, the direction in which the system must shift to reach equilibrium. To determine the shift, the **reaction quotient, Q,** is used. The reaction quotient is obtained by applying the law of mass action using initial concentrations instead of equilibrium concentrations.
- To determine the direction a system will shift, compare the Q & K values for a reaction.
  - **If Q = K, the reaction is already at equilibrium.**
  - **If Q > K, the system shifts to the left and more reactants are formed until equilibrium is reached.**
  - **If Q < K, the system shifts to the right and more products are formed until equilibrium is reached.**
- Be sure to make proper relationships between Q_c and K_c and Q_p and K_p. Initial pressure relates to equilibrium pressure as initial concentration relates to equilibrium concentration.
- For example: For the synthesis of ammonia at 500°C, the equilibrium constant, K_c, is 6.0×10^{-2}. Determine the direction in which the system will shift to reach equilibrium in the following case:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\quad [N_2]_0 = 1.0 \times 10^{-5}$ M, $[H_2]_0 = 2.0 \times 10^{-3}$ M, $[NH_3]_0 = 1.0 \times 10^{-3}$ M.

$$Q = \frac{[NH_3]^2}{[N_2] \times [H_2]^3} \rightarrow \frac{[1.0 \times 10^{-3}]^2}{[1.0 \times 10^{-5}][2.0 \times 10^{-3}]^3} \rightarrow \mathbf{Q = 1.3 \times 10^7}$$

Since Q > K the reaction shifts to the left and ammonia decomposes to form nitrogen gas and hydrogen gas.

- You try: For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0×10^{-2}. Determine the direction in which the system will shift to reach equilibrium in the following case:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\quad [N_2]_0 = 5.0$ M, $[H_2]_0 = 1.0 \times 10^{-2}$ M, $[NH_3]_0 = 1.0 \times 10^{-4}$ M.

Using ICE Tables

At a certain temperature a 1.00 L flask initially contained 0.298 mol PCl_3 (g) and 8.70×10^{-3} mol PCl_5. After the system had reached equilibrium, 2.00×10^{-3} mol of $Cl_2(g)$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ Calculate the equilibrium concentrations of all species and the value of K_c.

Reaction	PCl_5	PCl_3	Cl_2	Note the bold values are the original
Initial	**8.70×10^{-3} M**	**0.298 M**	0	values. The values in the shaded
Change	-x	+x	+x	boxes were calculated.
Equilibrium	6.70×10^{-3} M	0.300 M	**2.00×10^{-3}**	

$$K = \frac{[0.300][2.00 \times 10^{-3}]}{[6.70 \times 10^{-3}]}$$

$$\mathbf{K_c = 8.96 \times 10^{-2}}$$

- You try: A 1.00 L flask was filled with 2.00 mol gaseous SO_2 and 2.00 mol gaseous NO_2 are heated. After equilibrium was reached, it was found that 1.30 mol gaseous NO was present. Assume that the reaction: $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$ occurs under these conditions. Calculate the value of the equilibrium constant, K_c, for this reaction.

Homework:

1. $$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
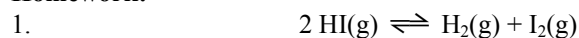
After a 1.0 mole sample of HI(g) is placed into an evacuated 1.0 L container at 700. K, the reaction represented above occurs. The concentration of HI(g) as a function of time is shown below.

(a) Write the expression for the equilibrium constant, K_c, for the reaction.

(b) What is [HI] at equilibrium?

(c) Determine the equilibrium concentrations of $H_2(g)$ and $I_2(g)$.

(d) On the graph above, make a sketch that shows how the concentration of $H_2(g)$ changes as a function of time.

(e) Calculate the value of the following equilibrium constants at 700. K.

  (i) K_c
  (ii) K_p

(f) At 1,000 K, the value of K_c for the reaction is 2.6×10^{-2}. In an experiment, 0.75 mole of HI(g),

0.10 mole of $H_2(g)$, and 0.50 mole of $I_2(g)$ are placed in a 1.0 L container and allowed to reach equilibrium at 1,000 K. Determine whether the equilibrium concentration of HI(g) will be greater than, equal to, or less than the initial concentration of HI(g). Justify your answer.
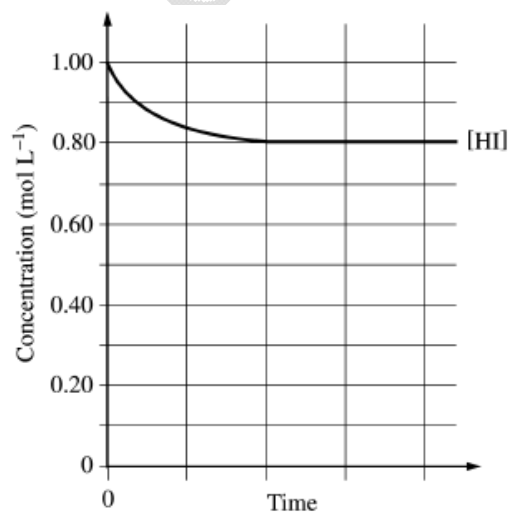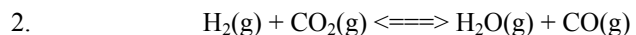
2. $$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$
When $H_2(g)$ is mixed with $CO_2(g)$ at 2,000 K, equilibrium is achieved according to the equation above.
In one experiment, the following equilibrium concentrations were measured.
$[H_2] = 0.20$ mol/L, $[CO_2] = 0.30$ mol/L, $[H_2O] = [CO] = 0.55$ mol/L
(a) What is the mole fraction of $CO(g)$ in the equilibrium mixture?
(b) Using the equilibrium concentrations given above, calculate the value of K_c, the equilibrium constant for the reaction.
(c) Determine K_p for this system.
(d) When the system is cooled from 2,000 K to a lower temperature, 30.0 percent of the $CO(g)$ is converted back to $CO_2(g)$. Calculate the value of K_c at this lower temperature.
(e) In a different experiment, 0.50 mole of $H_2(g)$ is mixed with 0.50 mole of $CO_2(g)$ in a 3.0-liter reaction vessel at 2,000 K. Calculate the equilibrium concentration, in moles per liter, of $CO(g)$ at this temperature.
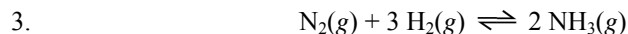
3. $$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
For the reaction represented above, the value of the equilibrium constant, K_p, is 3.1×10^{-4} at 700. K.
(a) Write the expression for the equilibrium constant, K_p, for the reaction.
(b) Assume that the initial partial pressures of the gases are as follows:
$pN_2 = 0.411$ atm, $pH_2 = 0.903$ atm, and $pNH_3 = 0.224$ atm.
    (i) Calculate the value of the reaction quotient, Q, at these initial conditions.
    (ii) Predict the direction in which the reaction will proceed at 700. K if the initial partial pressures are those given above. Justify your answer.
(c) Calculate the value of the equilibrium constant, K_c, for the above reaction using K_p.
(d) The value of K_p for the reaction represented below is 8.3×10^{-3} at 700. K.
    $$NH_3(g) + H_2S(g) \rightleftharpoons NH_4HS(g)$$
Calculate the value of K_p at 700. K for each of the reactions represented below.
    (i) $NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g)$
    (ii) $2\,H_2S(g) + N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_4HS(g)$ (Hint: Use Hess's Law and multiply K values)

Multiple Choice Homework:

1. $CuO(s) + H_2(g) \Longleftrightarrow Cu(s) + H_2O(g)$; $\Delta H = -2.0$ kilojoules
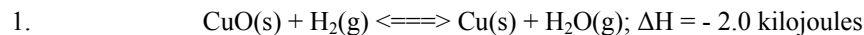
When the substances in the equation above are at equilibrium at pressure P and temperature T, the equilibrium can be shifted to favor the products by

(A) increasing the pressure by means of a moving piston at constant T
(B) increasing the pressure by adding an inert gas such as nitrogen
(C) decreasing the temperature
(D) allowing some gases to escape at constant P and T
(E) adding a catalyst

2. In which of the following systems would the number of moles of the substances present at equilibrium NOT be shifted by a change in the volume of the system at constant temperature?

(A) $CO(g) + NO(g) \Longleftrightarrow CO_2(g) + \frac{1}{2} N_2(g)$ (B) $N_2(g) + 3 H_2(g) \Longleftrightarrow 2 NH_3(g)$
(C) $N_2(g) + 2 O_2(g) \Longleftrightarrow 2 NO_2(g)$ (D) $N_2O_4(g) \Longleftrightarrow 2 NO_2(g)$
                     (E) $NO(g) + O_3(g) \Longleftrightarrow NO_2(g) + O_2(g)$

3. $4 HCl(g) + O_2(g) \Longleftrightarrow 2 Cl_2(g) + 2 H_2O(g)$
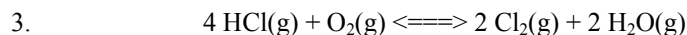
Equal numbers of moles of HCl and O_2 in a closed system are allowed to reach equilibrium as represented by the equation above. Which of the following must be true at equilibrium?

        I. [HCl] must be less than [Cl_2].
        II. [O_2] must be greater than [HCl].
        III. [Cl_2] must equal [H_2O].

(A) I only   (B) II only   (C) I and III only   (D) II and III only   (E) I, II, and III

4. $2 SO_3(g) \Longleftrightarrow 2 SO_2(g) + O_2(g)$
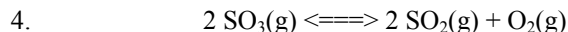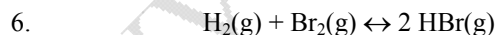
After the equilibrium represented above is established, some pure O_2 (g) is injected into the reaction vessel at constant temperature. After equilibrium is reestablished, which of the following has a lower value compared to its value at the original equilibrium?

(A) K_{eq} for the reaction
(B) The total pressure in the reaction vessel.
(C) The amount of SO_3 (g) in the reaction vessel.
(D) The amount of O_2 (g) in the reaction vessel.
(E) The amount of SO_2 (g) in the reaction vessel.

5. $W(g) + X(g) \rightarrow Y(g) + Z(g)$
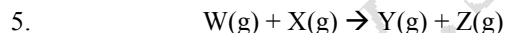
Gases W and X react in a closed, rigid vessel to form gases Y and Z according to the equation above. The initial pressure of W(g) is 1.20 atm and that of X(g) is 1.60 atm. No Y(g) or Z(g) is initially present. The experiment is carried out at constant temperature. What is the partial pressure of Z(g) when the partial pressure of W(g) has decreased to 1.0 atm?

(A) 0.20 atm   (B) 0.40 atm   (C) 1.0 atm   (D) 1.2 atm   (E) 1.4 atm

6. $H_2(g) + Br_2(g) \leftrightarrow 2 HBr(g)$

At a certain temperature, the value of the equilibrium constant, K, for the reaction represented above is 2.0×10^5. What is the value of K for the <u>reverse</u> reaction at the same temperature?

(A) -2.0×10^{-5} (B) 5.0×10^{-6} (C) 2.0×10^{-5} (D) 5.0×10^{-5} (E) 5.0×10^{-4}

7. For the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H° < 0$
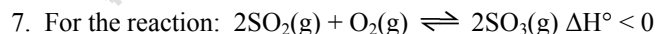
Which change(s) will increase the fraction of $SO_3(g)$ in the equilibrium mixture?

        1. Increasing the pressure
        2. Increasing the temperature
        3. Adding a catalyst

(A) 1 only   (B) 2 only   (C) 3 only   (D) 1 and 3 only   (E) 1, 2 and 3

Questions 8 and 9 should both be answered with reference to this reaction, for which $\Delta H°$ is negative.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$
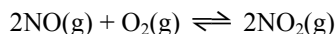
8. Which would increase the partial pressure of $NO_2(g)$ at equilibrium?
(A) decreasing the volume of the system
(B) adding a noble gas to increase the pressure of the system
(C) removing some $NO(g)$ from the system
(D) adding an appropriate catalyst
(E) none of the above

9. At a certain temperature the equilibrium concentrations for this system are: $[NO] = 0.52M$; $[O_2] = 0.24M$; $[NO_2] = 0.18M$. What is the value of K_C at this temperature?
(A) 0.063   (B) 0.50   (C) 1.4   (D) 2.0   (E) 1.0

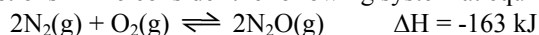10. $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$ $\Delta H = + 51.8$ kJ
Which would increase the equilibrium quantity of $HI(g)$?
Assume the system has reached equilibrium with all three components present.
    I. increasing pressure
    II. increasing temperature
    III. decreasing volume
(A) I only   (B) II only   (C) III only   (D) Both I and II   (E) I, II and III

For questions 11-16 consider the following system at equilibrium:
$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g) \qquad \Delta H = -163 \text{ kJ}$$
    and select from the following choices:
        a. to the right
        b. to the left
        c. neither
        d. in both directions
        e. cannot be determined from information provided

11. In which direction will the system move in order to reestablish equilibrium if the temperature is raised?
12. In which direction will the system move in order to reestablish equilibrium if the volume is increased?
13. In which direction will the system move in order to reestablish equilibrium if O_2 is added?
14. In which direction will the system move in order to reestablish equilibrium if a catalyst is added?
15. In which direction will the system move in order to reestablish equilibrium if N_2O is removed?
16. In which direction will the system move in order to reestablish equilibrium if a sample of Kr is added?

17. 6.0 moles of chlorine gas are placed in a 3.0 L flask at 1250 K. At this temperature, the chlorine molecules begin to dissociate into chlorine atoms. What is the value of K_c, if 50.% of the chlorine molecules dissociate when equilibrium has been achieved?
(A) 12.0   (B) 6.0   (C) 4.0   (D) 3.0   (E) 1.0

18. A sample of 0.1973 mole of nitrogen gas is confined at 37° C and 0.216 atmosphere. What would be the pressure of this sample at 15° C and the same volume?
(A) 0.0876 atm   (B) 0.175 atm   (C) 0.201 atm   (D) 0.233 atm   (E) 0.533 atm

19. A 3.00-liter flask initially contains 1.50 mol of gas A and 0.450 mol of gas B. Gas A decomposes according to the following reaction: $3A \rightleftharpoons 2B + C$ The equilibrium concentration of gas C is 0.100 mol/L. Determine the equilibrium concentration of gas A.
(A) 0.500 M   (B) 0.100 M   (C) 0.200 M   (D) 0.300 M   (E) none of these

20. The equilibrium constant for the reaction: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 26 at 50ºC. What is the K_c
for: $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ at the same temperature?
(A) 0.34   (B) 1.8×10^4 (C) 0.038   (D) 5.7×10^{-5} (E) 2.9