Chemistry 104, Dr. Batterton
Help Sheet #9 – Chapter 16 - Equilibrium
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CHAPTER 16: EQUILIBRIUM

Nuggets: Equilibrium expression; Size of K; How K changes as rxn changes; Le Chatelier's principle; Reaction Quotient (Q)

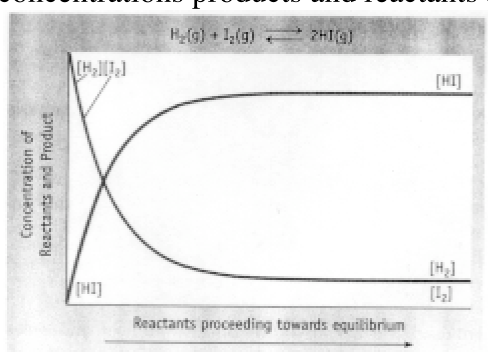
EQUILIBRIUM EXPRESSION and CONSTANT (K)

- K from kinetics with $rate_{forward} = rate_{reverse}$ which leads to

  $k_1/k_{-1} = [products]^{coefficient}/[reactants]^{coefficient}$ and $K = k_1/k_{-1}$
- Pure solids and liquids are ***not included*** in an equilibrium expression-their concentrations are constant.
- K is unitless (it is divided by a reference concentration which is not shown)
- K(T) since the rate constants, k_1 and k_{-1} are dependent on T
- Equilibrium expressions are written with products raised to the power of their stoichiometric coefficients divided by the reactants raised to their stoichiometric coefficients

  For example: $aA + bB \rightarrow cC \rightarrow \mathbf{K_c} = \frac{[C]^c}{[A]^a[B]^b}$

  where the values in [ ] are in molarity when K_c is used or atm when K_p is used
- At equilibrium *both* products and reactants exist
- Equilibrium occurs when the concentrations products and reactants are constant



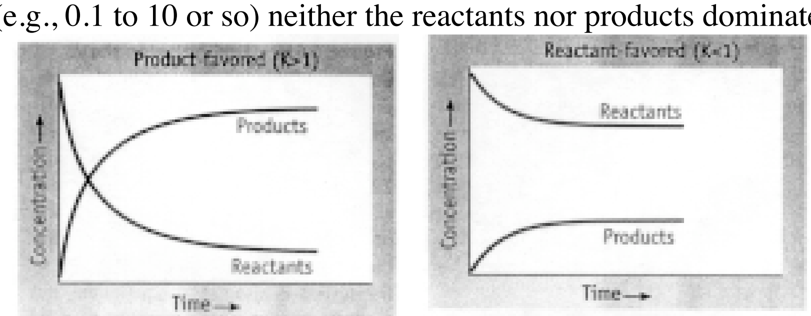
$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$
From *Chemistry and Chemical Reactivity*, Kotz and Treichel, pg 663, 2003.

SIZE OF K

If K is **large** (e.g., 1 x 10^5) the **products** are favored

If K is **small** (e.g., 1 x 10^{-5}) the **reactants** are favored

If K is close to 1 (e.g., 0.1 to 10 or so) neither the reactants nor products dominate



From *Chemistry and Chemical Reactivity*, Kotz and Treichel, pg 731, 2009.

REACTION QUOTIENT Q

Q can be used to determine if system is at equilibrium or if not which way the reaction goes (left or right) given initial concentrations

If Q > K reaction **goes to the left**
If Q < K reaction **goes to the right**
If Q = K reaction **is at equilibrium** and the reaction doesn't go either way

K_c versus K_p

K_c uses M while K_p uses atm; $K_p = K_c (RT)^{\Delta n}$ where Δn is the change in the number of gaseous moles; $\Delta n = n_{gas\ products} - n_{gas\ reactants}$; T is temperature in K, R = 0.0821; example: $C(s) + O_2(g) \rightarrow 2CO(g)$; Δn = 2 – 1 = 1 (Note: C(s) is not included because only gaseous moles are considered)

HOW K CHANGES AS THE REACTION CHANGES

1. Reverse a reaction: $K \rightarrow \frac{1}{K}$
2. Multiply a reaction by a constant c: $K \rightarrow K^c$
3. Reaction 1 + Reaction 2 = Reaction 3: $K_3 = K_1 \times K_2$

Le CHATILIER'S PRINCIPLE: reaction will shift in the direction to oppose the stress on the system
Factors affecting equilibrium:

1. **Concentration** of components in the equilibrium expression (not pure liquids or solids) add reactants or products to the system; way to think about: **[]↑ ⇒ []↓ ⇒ shift to []↓**
2. **Pressure** - change the pressure by changing the volume of a system; or just change the pressure without a method being described; way to think about: **P↑ ⇒ P↓ ⇒ n↓ ⇒ shift to n(g)↓** (only gaseous moles)
3. **Temperature** - heat a system or cool a system); an endothermic reaction means heat is a reactant (write "heat" on reactant side); an exothermic reaction means heat is a product (write "heat" as a product); recall ΔH > 0 → endothermic and ΔH < 0 → exothermic;
way to think about: **T↑ ⇒ T↓ ⇒ if exo, consume heat, T↓ ⇒ shift to L**

FACTORS NOT AFFECTING EQUILIBRIUM

1. Adding a **catalyst** (reaction speeds up but no shift in equilibrium)
2. Add a **pure liquid or a solid** to the system (since these don't appear in equilibrium expression, they don't affect the equilibrium)

Quadratic equation: from $ax^2 + bx + c = 0 \rightarrow \mathbf{x} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

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1. Write the K_c expression for the following:

a. $H_2(g) + I_2(g) \rightarrow 2HI(g)$
b. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
c. $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$
d. $C(s) + O_2(g) \rightarrow CO_2(g)$
e. $CS_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2S(g)$
f. $4H_2(g) + 4I_2(g) \rightarrow 8HI(g)$

2. a. How do we know when equilibrium is achieved?
b. What can you say about the relative rates of the forward and reverse reactions at equilibrium?
c. When a reaction has not reached equilibrium and is still proceeding to the *left*, what can you say about the relative rates of the forward and reverse reactions?

3. In which of the following reaction(s) will the products be most favored?

Rxn I: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $K = 10^{89}$

Rxn II: $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ $K = 49$

Rxn III: $AgCl \rightarrow Ag^+ + Cl^-$ $K = 2 \times 10^{-8}$

4. Calculate the equilibrium constant, K', for the reaction below in terms of K_1, K_2, and K_3

$2C(s) + H_2(g) \rightarrow C_2H_2(g)$ $K = K'$

given the individual equilibrium constants for the reactions below

$C_2H_2(g) + \frac{5}{2} O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$ $K = K_1$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $K = K_2$

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $K = K_3$

5. Calculate the equilibrium constant, K', for the reaction below in terms of K_1, K_2, and K_3

$N_2H_4(l) + CH_4O(l) \rightarrow CH_2O(g) + N_2(g) + 3H_2(g)$ $K = K'$

given the individual reaction standard enthalpy changes

$N_2H_4(l) + H_2(g) \rightarrow 2NH_3(g)$ $K = K_1$

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $K = K_2$

$CH_2O(g) + H_2(g) \rightarrow CH_4O(l)$ $K = K_3$

6. Why are solids and pure liquids not included in an equilibrium reaction?

7. Given the equilibrium concentrations for the reaction below, $[PCl_5] = 0.035$ M, $[PCl_3] = 0.0101$ M, $[Cl_2] = 0.0025$ M, what is the K value?

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

8. In a mixture at equilibrium a 0.45 L flask contains 2.8 g of N_2, 0.063 g H_2, and 0.85 g NH_3. What is the value for K for the following reaction?

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

9. Initially, there are 0.0625 moles of $COBr_2$ and 0.25 moles of CO in a 250ml flask. When the reaction has reached equilibrium, the final number of moles of CO is 0.26.

$COBr_2(g) \rightarrow CO(g) + Br_2(g)$

a. Calculate the final concentrations of $COBr_2$ and Br_2. b. Calculate K_c.

10. Initially, there is 1M N_2 and 1M O_2. When the reaction has reached equilibrium, the final concentration of N_2 is 0.9M. $N_2(g)$ $O_2(g) \rightarrow 2NO(g)$

a. Calculate the final concentrations of O_2 and NO. b. Calculate K_c.

11. Initially, there are 0.2M of $COCl_2$ and 2.0×10^{-3}M of CO in a 1.0 L flask.

$COCl_2(g) \rightarrow CO(g) + Cl_2(g)$

Calculate the final concentrations of $COCl_2$, CO and Cl_2 at equilibrium if $K_c = 2.22 \times 10^{-10}$. (Hint: Make an approximation in the calculation.)

12. If the initial concentration of NOBr is 1M and the K_c is 3.07 x 10^{-4}, what are the equilibrium concentrations of NO and Br_2? (Hint: Make an approximation in the calculation.)

$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$

13. K is 0.75 for the reaction $A(g) \rightarrow B(g) + C(g)$. If a 2.0 L flask contains 5.0mol A, how many ***mol*** of A, B, and C will exist once equilibrium is achieved?

14. For each of the following questions, determine if the system is at equilibrium or not. If not, which way will the reaction shift to reach equilibrium?

a. For the following reaction, K = 10.5.

$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$

The initial concentrations are: [CO] = 0.00135 M, $[H_2]$ = 0.00226 M, $[CH_3OH]$ = 1.33 M

b. For the following reaction, K = 4.8 x 10^3.

$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$

The starting concentrations are: [CO] = 0.02 M, $[H_2]$ = 0.60 M, $[CH_4]$ = 1.2 M, and $[H_2O]$ = 0.30 M.

c. For the following reaction, K = 8.

$2NO_2(g) \rightarrow N_2O_4(g)$

The starting concentrations of $[NO_2]$ and $[N_2O_4]$ are 0.50 M.

15. For the following *endothermic* reaction, which **direction** will the equilibrium shift if the following occur.

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

a. The amount of $CO_2(g)$ is decreased.
b. The reaction mixture is heated.
c. The amount of CO(g) is increased.
d. The amount of C(s) is increased.
e. The pressure is increased by reducing the volume.
f. The volume is increased.
g. A catalyst is added.
h. The amount of CO(g) is decreased.

16. $Zn(CN)_2$ is not very soluble in water, and when placed in water, only a small amount will dissolve as follows: $Zn(CN)_2(s) \rightarrow Zn^{+2}(aq) + 2CN^-(aq)$. When the following actions are done on this system, which direction will the reaction shift: left, right, or it will not shift?

a. NaCN is added to the container.
b. $Zn(CN)_2(s)$ is added to the container.
c. Water is added to the container.
d. $Zn(NO_3)_2(aq)$ is added to the container.

ANSWERS

1\. a. $K = \frac{[HI]^2}{[H_2][I_2]}$ b. $K = \frac{[NO_2]^2}{[NO]^2[O_2]}$ c. $K = \frac{[NO]^2[O_2]}{[NO_2]^2}$

d. $K = \frac{[CO_2]}{[O_2]}$ e. $K = \frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}$ f. $K = \frac{[HI]^8}{[H_2]^4[I_2]^4}$

2\. a. When the concentrations of the reactants and products no longer change.

b. The forward and reverse rates are equivalent at equilibrium.

c. The forward rate is greater than the reverse rate.

3\. Rxn I

4\. $\frac{(K_2)^2K_3}{K_1}$

5\. $K' = K_1/(K_2K_3)$

6\. Solids and pure liquids are not included in an equilibrium expression because their concentrations are constant and only chemicals whose concentrations can change are included.

7\. $K = 7.21 \times 10^{-4}$

8\. 166

9\. a. $[COBr_2] = 0.21$; $[Br_2] = 0.04$ M b. $K_c = 0.20$

10\. a. $[O_2] = 0.9$; $[NO] = 0.2$ b. 5×10^{-2}

11\. $[COCl_2] = 0.2M$, $[CO] = 2 \times 10^{-3}$, $[Cl_2] = 2 \times 10^{-8}$

12\. $[NO] = 8.50 \times 10^{-2}M$; $[Br_2] = 4.25 \times 10^{-2}M$

13\. With the quadratic equation: x = 1.045M; [A] = 2.5-x = 1.455M → 2.91mol A; [B] = x = 1.045M → 2.09mol B and 2.09 mol C

Without the quadratic equation: x = 1.369M; [A] = 2.5-x = 1.131M → 2.26mol A; [B] = x = 1.369M → 2.74mol B and 2.74 mol C

14\. a. $Q = 1.9 \times 10^8$; so Q > K; not at equilibrium; shifts left

b. Q = 83; so Q < K; not at equilibrium; shifts right c. Q = 2; so Q < K, not at equilibrium; shifts right

15\. a. left b. right c. left d. no change e. left f. right g. no change h. right

16\. a. left b. no shift c. right d. left