



# Chemical Equilibrium

(p. 275 - 348)



# Chemical Equilibrium

Static equilibrium exists when a system remains at a given point without active processes (rocks in a pile)

Dynamic equilibrium exists when two opposing processes occur at the **SAME RATE** and no visible change occurs (water in a bottle, evaporation rate and condensation rate are equal)



# Chemical Equilibrium

- Equilibrium DOES NOT mean that equal amounts of reactants and products exist, rather that both are present and the rates at which they are formed are equal

In chemical reactions equilibrium is DYNAMIC, the particles of reactants and products are always in motion even though change is not perceptible (think of hockey players)

# 3 types of dynamic equilibrium:

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- **1. Phase equilibrium:**
- When a substance is found in many phases within a system due to physical change (water bottle).

# 3 types of dynamic equilibrium:

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## 2. Solubility equilibrium:

- When a solute is dissolved in a solvent and an excess is in contact with the saturated solution (dissolving sugar in tea, excess sugar at the bottom)

# 3 types of dynamic equilibrium:

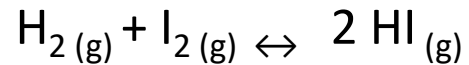
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## 3. Chemical equilibrium:

- When two opposing chemical reactions occur at the same rate, composition of the of the system unchanged

# In order for equilibrium to exist:

- **1.** Reaction must be reversible (eq. when  $r_{\text{dir}} = r_{\text{rev}}$ )



- **2.** System must be closed (no exchanges of matter)
- **3.** Macroscopic properties are constant  
(no visible change to colour, volume, pH, temperature and pressure)
- **4.** Reactants AND products are ALWAYS present

\*\*\*steady state system: may also appear to be at equilibrium, but system is open and exchanges matter or energy (water pouring into and draining out of a tub)



# Le Châtelier's principle

- If the conditions of an equilibrium system change, the system will react to oppose those changes and restore a new position of equilibrium

Three factors can influence the position of equilibrium:

- 1. concentration of reactants or products
- 2. temperature
- 3. pressure



# Le Châtelier's principle

- equilibrium can shift in favour of the reactants (left)  
therefore favouring the reverse reaction
- equilibrium can shift in favour of the products (right)  
therefore favouring the forward reaction
- adding a catalyst to a reaction does not shift the position of equilibrium, rather it allows equilibrium to be achieved more quickly



# The effect of changes in concentration

- Increasing concentration of a substance shifts equilibrium to the opposite side, as the system tries to decrease this concentration to compensate
  - Decreasing concentration of a substance shift equilibrium to the same side as the system tries to increase this concentration to compensate
-

Example:

What effect will the following changes have on the position of equilibrium and on the concentration of all substances in the reaction?



Change	[CO]	[H <sub>2</sub> ]	Direction of shift	[CH <sub>3</sub> OH]	Reaction favoured
Addition of H <sub>2</sub>					
Addition of CH <sub>3</sub> OH					
Removal of CO					
Removal of H <sub>2</sub>					
Removal of CH <sub>3</sub> OH					

# The effect of changes in temperature

- an increase in temperature always favours an endothermic reaction  
(adding heat is like adding a reactant)
- a decrease in temperature always favours an exothermic reaction  
(taking away heat is like taking away a product)

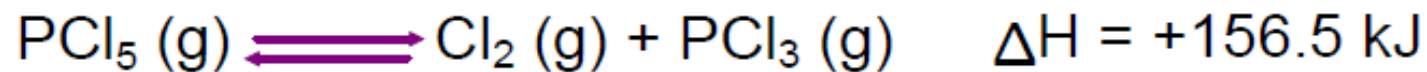


# The effect of changes in pressure

- In a gaseous system, an increase in pressure favours the reaction that produces the LEAST gas molecules
  - Conversely, a decrease in pressure favours the reaction that produces the MOST gas molecules
-

Example:

What are the effects of the following changes on the position of equilibrium and on the concentration of each substance in the reaction?



Change	[PCl <sub>5</sub> ]	Energy	Direction of shift	[Cl <sub>2</sub> ]	[PCl <sub>3</sub> ]	Reaction favoured
Increase temp.						
Decrease temp.						

Homework  
p. 298 # 1-4, 7  
p. 304-306 # 1, 2, 5

Answers p.298:

- 1 a) A: forward  
B: reverse  
C: forward  
D: reverse
- b) A: none  
B: forward  
C: none  
D: reverse
- c) A: forward  
B: forward  
C: forward  
D: reverse
2. a) reverse  
b) reverse  
c) forward  
d) none
3. decrease NH<sub>3</sub>
4. Yes
7. Add HCl, add O<sub>2</sub>, decrease Cl<sub>2</sub>, decrease H<sub>2</sub>O, increase temperature, increase pressure

**p. 304-306**

- 1 a) B  
b) A  
c) C
- 2a) reverse  
b) none  
c) forward  
d) reverse  
e) reverse  
f) none  
g) forward  
h) reverse  
i) forward
5. a) false  
b) false  
c) true  
d) true  
e) false  
f) false



# Equilibrium Constant ( $K_c$ )

- Demonstrates relationship between concentration of products and reactants at equilibrium. Concentrations are raised to the power of the stoichiometric coefficients.
  - We use only gaseous or aqueous concentrations
  - We omit the concentration of pure substances (either solid or liquid) as they remain constant throughout a reaction.
  - Concentrations are expressed in mol/L
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Given the following reaction:

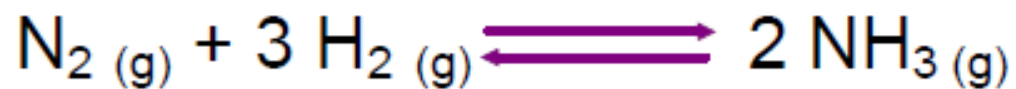


The equilibrium constant is calculated using the following expression:

$$K_c = \frac{[C]^3[D]}{[A]^2[B]^4}$$

### Example:

At 365.0 °C a mixture at equilibrium in a 6.00 L flask contains 1.62 moles H<sub>2</sub>, 0.546 moles N<sub>2</sub> and 0.0378 moles NH<sub>3</sub>. Calculate the K<sub>c</sub>.



**Example:**

At 125.0 °C, a system at equilibrium in a 3.0 L flask contains 0.056 moles I<sub>2</sub> and 0.12 moles Br<sub>2</sub>. What is the concentration of IBr if K<sub>c</sub> = 167.28?





# The value of the constant

- Because the constant is a ratio of products over reactants, if  $K$  is GREATER than 1, there are more products at equilibrium
  - If  $K$  is LESS than 1, there are more reactants at equilibrium
-



# Calculating equilibrium concentrations ICE tables

- Using Initial concentration, Change in concentration and Equilibrium concentrations we can find missing values
  - We can use the ratio of coefficients in the equation to determine change values in the table
  - We express concentrations in mol/L
  - We use equilibrium values to calculate  $K_c$
-

## Example #1:

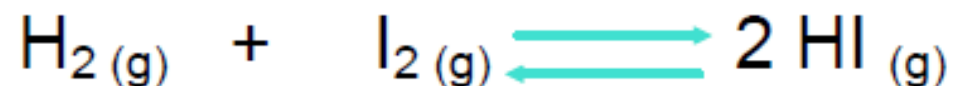
At a given temperature 8.0 moles of nitrogen oxide and 6.0 moles of oxygen are placed in a 4.0 L container. At equilibrium 3.0 moles of oxygen remain. Calculate  $K_c$ .



Initial			
Change			
Equilibrium			

## Example #2:

At a given temperature, the equilibrium constant for the following reaction is 34. Initially, 3.0 mol of hydrogen and 4.5 moles of iodine were placed in a 2.0 L container. What is the concentration of **EACH** substance at equilibrium. (use the quadratic equation, example p. 317)



Initial			
Change			
Equilibrium			

## Homework

p. 318-319: # 2, 3, 7, 8, 10, 11, 13, 15, 21

### Answers:

2)  $1.9 \times 10^{-2}$

3)  $2.4 \times 10^{-4}$

7)  $2.9 \times 10^{-3}$

8) A, B, C

10) constant is very large, lots of products

11 a) FORWARD

b) REVERSE

c) FORWARD

d) REVERSE

13. a) LEFT

b) RIGHT

c) LEFT

d) LEFT

15) 0.11 mol

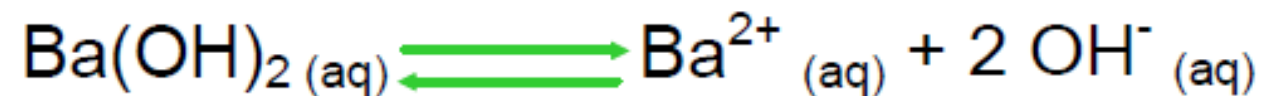
21) 1.19



# Acids and Bases

- An acid dissociates in water to form an  $\text{H}^+$  ion (otherwise written as  $\text{H}_3\text{O}^+$ , hydronium ion) and a negatively charged ion (conjugate base)
- A base dissociates in water to form an  $\text{OH}^-$  ion and a positively charged ion (conjugate acid)

For example:



## Calculating pH and pOH

- $\text{pH} = -\log [\text{H}^+]$
- $\text{pOH} = -\log [\text{OH}^-]$
- $[\text{H}^+] = 1 \times 10^{-\text{pH}}$
- $[\text{OH}^-] = 1 \times 10^{-\text{pOH}}$
- $\text{pH} + \text{pOH} = 14$
- $[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$

## Practice

Calculate pH:

1.  $[H^+] = 2.67 \times 10^{-3}$

2.  $[H^+] = 4.72 \times 10^{-4}$

3.  $[OH^-] = 3.76 \times 10^{-9}$

4.  $[OH^-] = 8.24 \times 10^{-11}$

Calculate  $[H^+]$ :

1.  $pH = 6.24$

2.  $pH = 4.72$

3.  $pOH = 9.57$

4.  $pOH = 11.24$

5.  $[OH^-] = 3.89 \times 10^{-8}$

6.  $[OH^-] = 5.63 \times 10^{-10}$

## Homework

p. 339-340: # 7, 8, 9, 11, 12, 21

### Answers

7) acidic,  $\text{H}_3\text{O}^+$ :  $1.9 \times 10^{-5}$  mol/L,  $\text{OH}^-$ :  $5.2 \times 10^{-10}$  mol/L, pOH: 9.28

8) pH 6.8, solution is close to neutral

9) basic,  $\text{H}_3\text{O}^+$ :  $6.5 \times 10^{-9}$  mol/L,  $\text{OH}^-$ :  $1.5 \times 10^{-6}$  mol/L, pH: 8.18

11)  $\text{H}_3\text{O}^+$ :  $1.9 \times 10^{-3}$  mol/L,  $\text{OH}^-$ :  $5.4 \times 10^{-12}$  mol/L

12) acidic, pH 3.54

21) a) 4.43,  $2.7 \times 10^{-10}$ , 9.57, acidic

b)  $3.9 \times 10^{-11}$ ,  $2.6 \times 10^{-4}$ , 3.69, basic

c)  $1.41 \times 10^{-13}$ , 12.85, 1.15, basic

d)  $7.94 \times 10^{-6}$ , 5.10,  $1.3 \times 10^{-9}$ , acidic

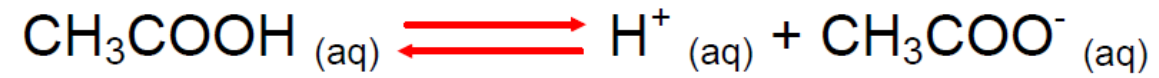
Acidity and  
Basicity  
Constant  
( $K_a$ ,  $K_b$ )

- represents the degree to which an acid or base dissociates into ions
- the greater the dissociation, the stronger the acid, the higher the value of the constant
- we cannot judge the strength of an acid strictly based on pH, we must look at the dissociation constant as it takes into consideration the initial concentration of the acid
- to calculate percent dissociation of an acid we use the following formula:

$$\text{percent ionization} = \frac{[\text{H}^+](\text{at eq.})}{[\text{HA}] (\text{initial})} \times 100$$

## Example #1

At equilibrium, a solution of 2.0 M acetic acid ( $\text{CH}_3\text{COOH}$ ) has a pH of 1.87. Calculate  $K_a$  and percent dissociation.



## Example #2

Calculate the pH of a 0.40 M solution of nitric acid ( $\text{HNO}_3$ ) if  $K_a = 1.76 \times 10^{-5}$ . (use the quadratic formula)





HW p. 339-340 # 20, 22, 23, 33, 39

\*\*\*Use reference table on p.421

Answers:

20)  $\text{pH} = 3.41$

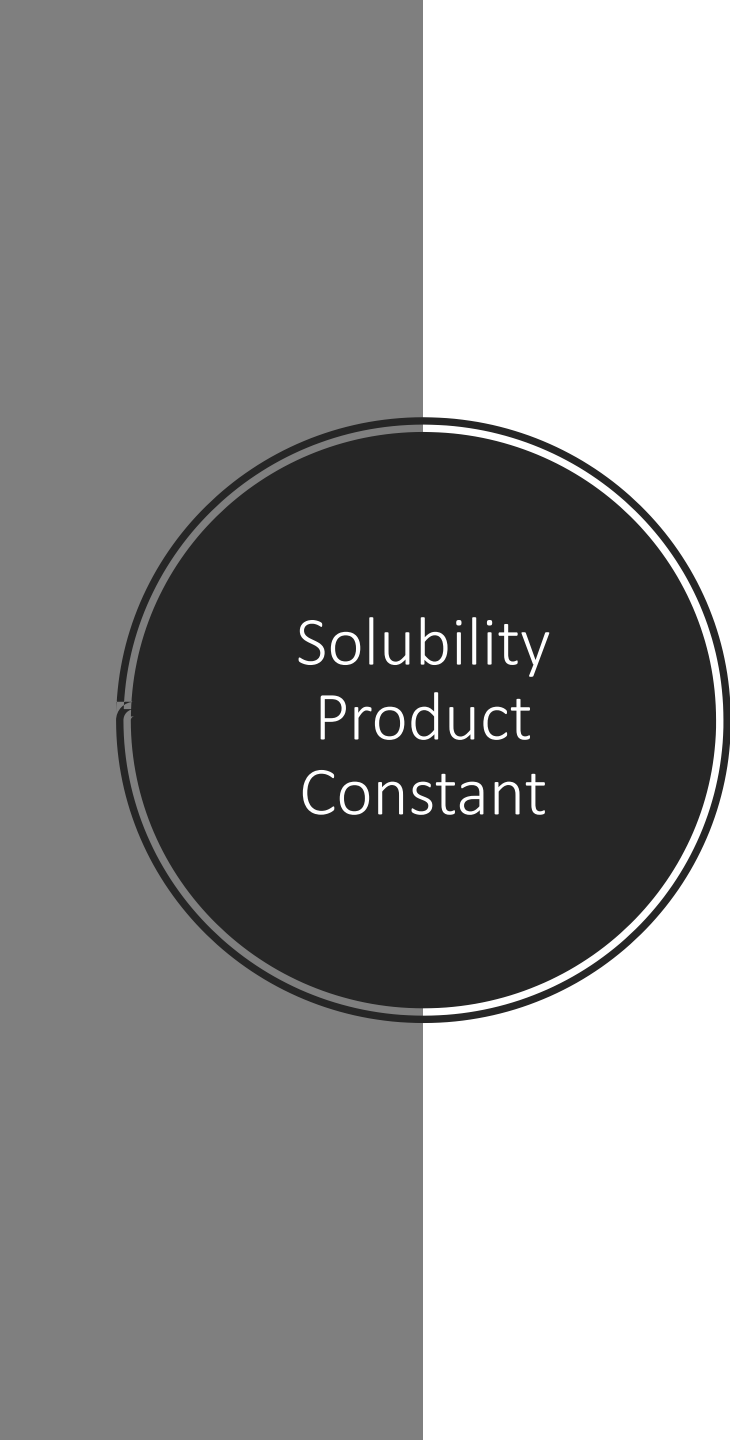
22) percent dissociation =  $0.47\%$

23)  $\text{pH} = 2.6$

33)  $\text{pH} = 11.13$

39) Strong acid = high degree of dissociation

Weak acid = low degree of dissociation



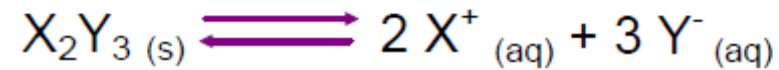
## Solubility Product Constant

- solubility indicates the maximum amount of solute that can dissolve in a given amount of liquid
- solubility of a solid is expressed in mol/L
- solubility equilibrium exists when a saturated solution contains non-dissolved solute at the bottom of a container
- this indicates that the rate of dissolution is equal to the rate of re-crystallization

## Solubility Product Constant

- remember that when solving for the constant, we do not take into consideration the concentration of solids
- therefore the constant is calculated as the product of the concentration at equilibrium of the two products (and thus the name  $K_{sp}$ )

Example:



$$K_{sp} = [X^+]^2[Y^-]^3$$

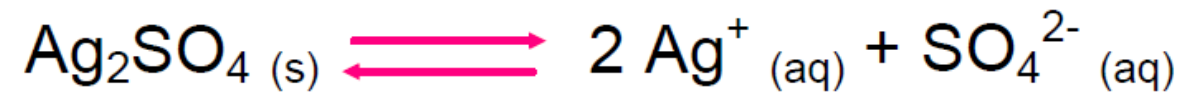
## Example #1

Calculate the concentration of barium ions and sulfate ions in a saturated solution of barium sulfate given that  $K_{sp} = 1.1 \times 10^{-10}$ .



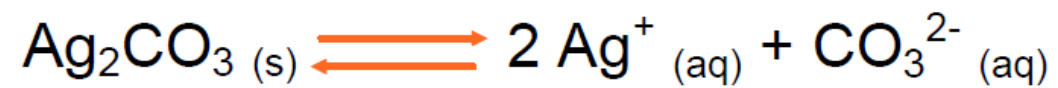
## Example #2

Calculate the concentration of both ions in a saturated solution of silver sulfate given that  $K_{sp} = 1.5 \times 10^{-4}$ .



### Example #3

The solubility of  $\text{Ag}_2\text{CO}_3$  is  $3.6 \times 10^{-3}$  g/100.0 ml at ambient temperature, calculate  $K_{sp}$ .



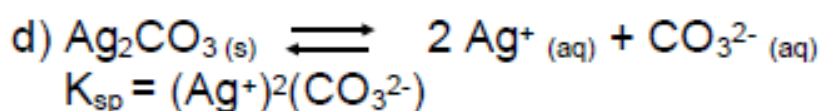
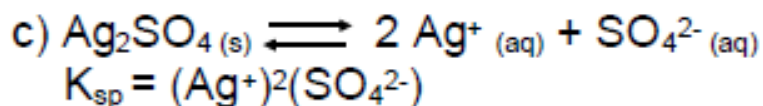
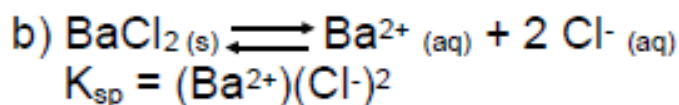
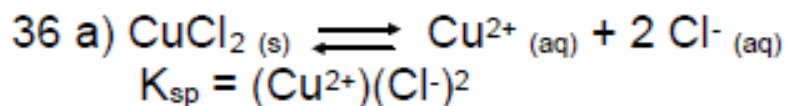
## HW

p. 340 #36, 37, 38

p. 346-348: # 21, 38, 42, 47

Answers:

p. 340:



37)  $K_{sp} = 2.3 \times 10^{-16}$

38)  $K_{sp} = 3.2 \times 10^{-11}$

p. 346-348

21) B

38) a)  $1.6 \times 10^{-6}$     b)  $4.5 \times 10^{21}$  molecules/L

42) 129 times more lead ions

47)  $K_{sp} = 1.1 \times 10^{-37}$