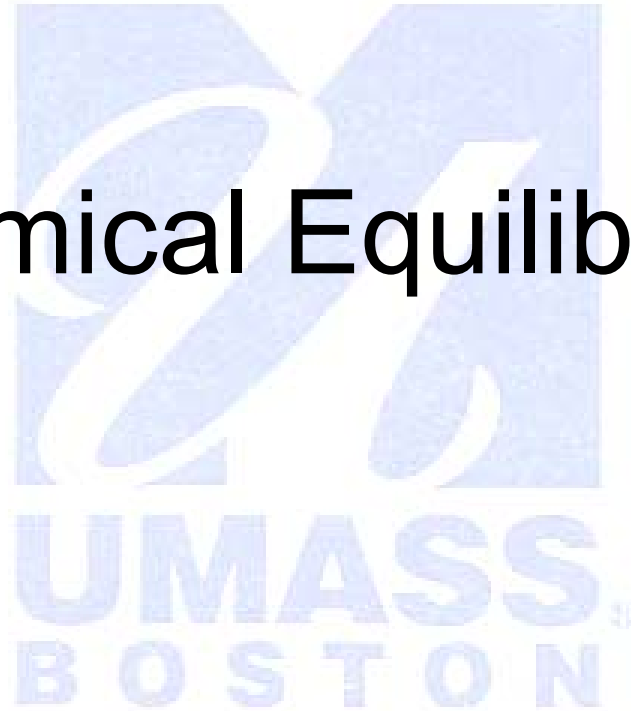


# Chemical Equilibrium



# Equilibrium

When the net reaction rate is equal to 0, the system becomes “dynamically equilibrium”.

Forward rate = Reverse rate

For reaction  $A + B \rightleftharpoons C + D$

$$K = \frac{[C][D]}{[A][B]}$$

$$k_f [A][B] = k_r [C][D]$$

$$K = \frac{[C][D]}{[A][B]} = \frac{k_f}{k_r}$$

# Equilibrium Constants

For the reaction:



The Equilibrium Constant:

- A, B are the reactants and C, D products
- a, b, c, d are the stoichiometry coefficients
- [ ] stands for concentration

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

*if A is gas*

$$K = \frac{[C]^c [D]^d}{P_a^a [B]^b}$$

**K tells us the position of equilibrium,  $K > 1$ , more C and D**

# The Units

- Standard State:
  - For solutes: 1 M (mol/Liter).
  - For gases: 1 bar (1 bar =  $10^5$  Pa = 0.98682atm).
  - For solvent: pure material.
- The unit in the equilibrium calculation:
  - Concentration of solutes: M (mol/liter)
  - Gases: bars
  - Pure material: unit (1)

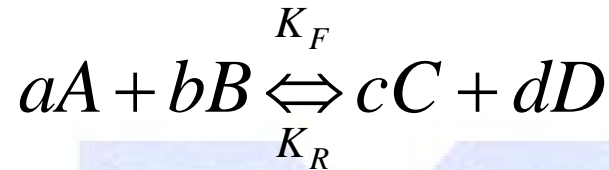
# The unit of equilibrium constant

- Equilibrium Constant  
 $K$  is dimensionless
- Why?
  - The  $[A]$ ,  $[B]$ ,  $[C]$  and  $[D]$  are ratios

$$[A] = \frac{\text{concentration of } A \text{ (M)}}{\text{standard state (1M)}}$$

$$P_a = \frac{\text{Pressure (bars)}}{\text{standard state (1bars)}}$$

# Forward and backward reactions



*forward reaction:*

$$K_F = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

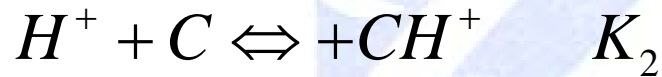
*Reverse reaction:*

$$K_R = \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

$$K_F = \frac{1}{K_R}$$

# Adding reactions

- If multiple reactions are added, the new  $K$  is the product of the individual values



$$K_3 = K_1 K_2 = \frac{[H^+][A^-]}{[HA]} \times \frac{[CH^+]}{[H][C]} = \frac{[A^-][CH^+]}{[HA][C]}$$

# Equilibrium of Water

- $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$   
autoprotolysis: self-ionization

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

- Where  $[\text{H}_2\text{O}]$ ?
- In the aqueous solution, at 25°C,  $K_w \equiv 1.0 \times 10^{-14}$



# Equilibrium and Thermodynamics

- $aA + bB \rightleftharpoons cC + dD$
- $\Delta G$  (Free energy) =  $\Delta H$  (enthalpy) -  $T\Delta S$  (entropy)
- $\Delta G = \Delta G^\circ + RT \ln Q$  where  $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$   
Q: reaction quotient  
When,  $Q=1$  standard state,  $\Delta G = \Delta G^\circ$   
When,  $\Delta G < 0$ , favor forward reaction  
When,  $\Delta G > 0$ , favor reverse reaction  
When,  $\Delta G = 0$ , reaction at equilibrium,  $K = Q$

$$\text{SO } \Delta G^\circ = - RT \ln K$$

$$K = e^{-\Delta G^\circ / RT}$$

# Le Châtelier's Principal

- When the equilibrium is disturb, the position of the reaction must shift to the direction which can partially off-set the disruption and try to bring the system back to equilibrium.

UMASS  
BOSTON

# Adding reactant or product

For Reaction  $A \rightleftharpoons B$  at equilibrium

$$K = [B]/[A]$$

- If more A is added: In order to off-set the disruption, the reaction has to move forward to reduce amount of A.
- If more B is added: the reaction has to move backward to reduce amount of B.
- Does K change? Why?
- NO, because the K is a state function.

# Temperature change

$$\begin{aligned}K &= e^{-\Delta G^\circ / RT} = e^{-(\Delta H^\circ - T\Delta S^\circ) / RT} \\&= e^{(-\Delta H^\circ / RT + \Delta S^\circ / R)} \\&= e^{-\Delta H^\circ / RT} e^{\Delta S^\circ / R}\end{aligned}$$

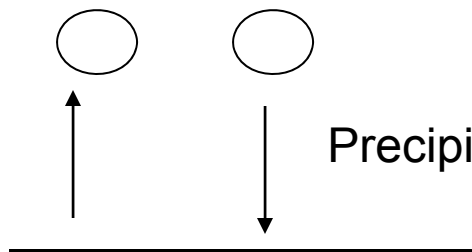
- For endothermic reaction,  $\Delta H^\circ > 0$ ,  $K$  increase when  $T$  increase. (heat +  $A \rightleftharpoons B$ )
- For exothermic reaction,  $\Delta H^\circ < 0$ ,  $K$  decrease when  $T$  increase. ( $A \rightleftharpoons B$  + heat)

# Solubility

- When dissolution rate  $>$  precipitation rate, solid dissolves.

- When dissolution rate = precipitation rate, solution become saturated (under the condition of sufficient amount of solid), the equilibrium is reached.

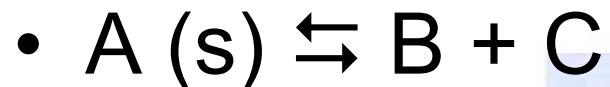
Dissolve



Precipitate

- The concentration of the solid = 1, so for  $A(s) \rightleftharpoons B + C$ ;  $K = [B][C] = K_{sp}$ , when the solution becomes saturated,  $K_{sp}$  is reached.

# Common Ion Effect

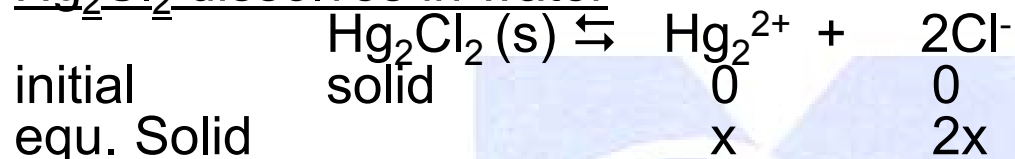


when the  $K_{sp}$  is reached, according to Le Châtelier's principal, adding more B or C can precipitate more A.



# Example

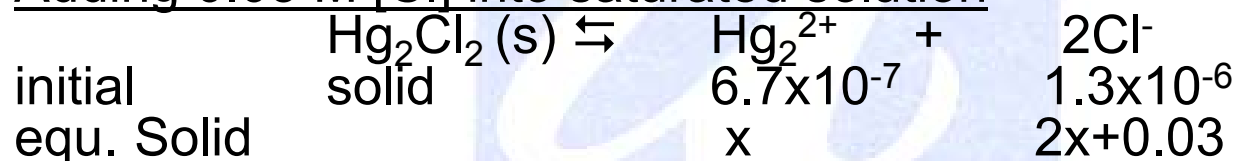
- Hg<sub>2</sub>Cl<sub>2</sub> dissolves in water



$$K_{\text{sp}} = x \cdot (2x)^2 = 1.2 \times 10^{-18} \rightarrow x = 6.7 \times 10^{-7} \text{ M}$$

$$[\text{Hg}_2^{2+}] = 6.7 \times 10^{-7} \text{ M}; [\text{Cl}^-] = 1.3 \times 10^{-6} \text{ M}$$

- Adding 0.03 M [Cl<sup>-</sup>] into saturated solution



$$K_{\text{sp}} = x \cdot (2x + 0.03)^2 = 1.2 \times 10^{-18} \rightarrow x = 1.3 \times 10^{-15} \text{ M}$$

$$[\text{Hg}_2^{2+}] = 1.3 \times 10^{-15} \text{ M}; [\text{Cl}^-] = 0.03 \text{ M} \text{ (2x is too small)}$$

- If more Hg<sub>2</sub>Cl<sub>2</sub> solid is added, according to Le Châtelier's principal, Hg<sub>2</sub><sup>2+</sup> + 2Cl<sup>-</sup> concentration should be higher, Is that right? Why?

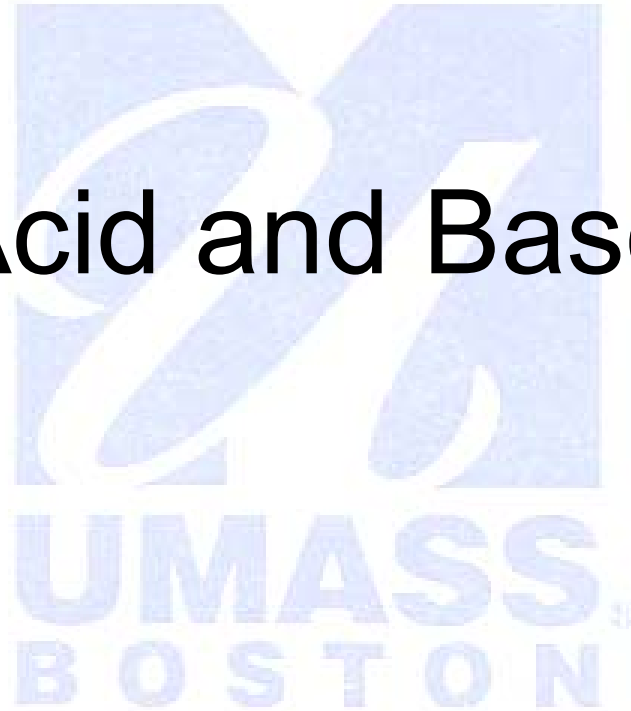
# Complex Formation

- Adding I<sup>-</sup> into Pb<sup>2+</sup> solution, PbI<sub>2</sub> becomes precipitated:  

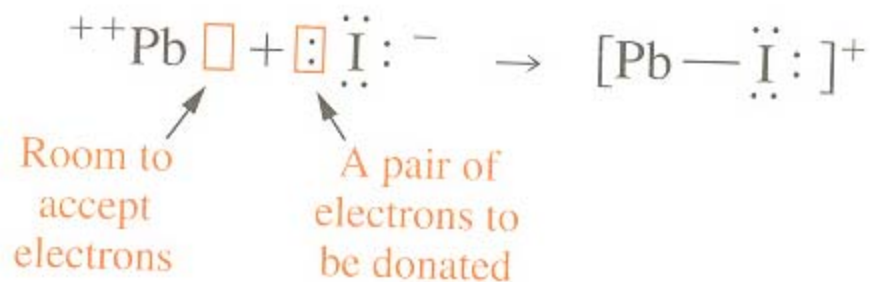
$$\text{PbI}_2(\text{s}) \leftrightarrow \text{Pb}^{2+} + 2\text{I}^- \quad K_{\text{sp}} = 7.9 \cdot 10^{-9} = [\text{Pb}^{2+}][\text{I}^-]^2$$
- Adding more I<sup>-</sup> will make PbI<sub>2</sub>(s) become dissolved. Because complex formation:
  - $\text{Pb}^{2+} + \text{I}^- \leftrightarrow \text{PbI}^+(\text{aq}) \quad K_1 = 100 = [\text{PbI}^+(\text{aq})]/[\text{Pb}^{2+}][\text{I}^-]$
  - $\text{Pb}^{2+} + 2\text{I}^- \leftrightarrow \text{PbI}_2(\text{aq}) \quad K_2 = 1400 = [\text{PbI}_2(\text{aq})]/[\text{Pb}^{2+}][\text{I}^-]^2$
  - $\text{Pb}^{2+} + 3\text{I}^- \leftrightarrow \text{PbI}_3^-(\text{aq}) \quad K_3 = 8300 = [\text{PbI}_3^-(\text{aq})]/[\text{Pb}^{2+}][\text{I}^-]^3$
  - $\text{Pb}^{2+} + 4\text{I}^- \leftrightarrow \text{PbI}_4^{2-}(\text{aq}) \quad K_4 = 30000 = [\text{PbI}_4^{2-}(\text{aq})]/[\text{Pb}^{2+}][\text{I}^-]^4$
- [Pb<sup>2+</sup>] is the same in all six of these equilibrium expressions. There can only be one [Pb<sup>2+</sup>] and one [I<sup>-</sup>] concentration
- Define soluble lead – any soluble species containing lead contributes to the total concentration of soluble lead.  
 Soluble lead = [Pb<sup>2+</sup>] + [PbI<sup>+</sup>(aq)] + [PbI<sub>2</sub>(aq)] + [PbI<sub>3</sub><sup>-</sup>(aq)] + [PbI<sub>4</sub><sup>2-</sup>(aq)]



# Acid and Base

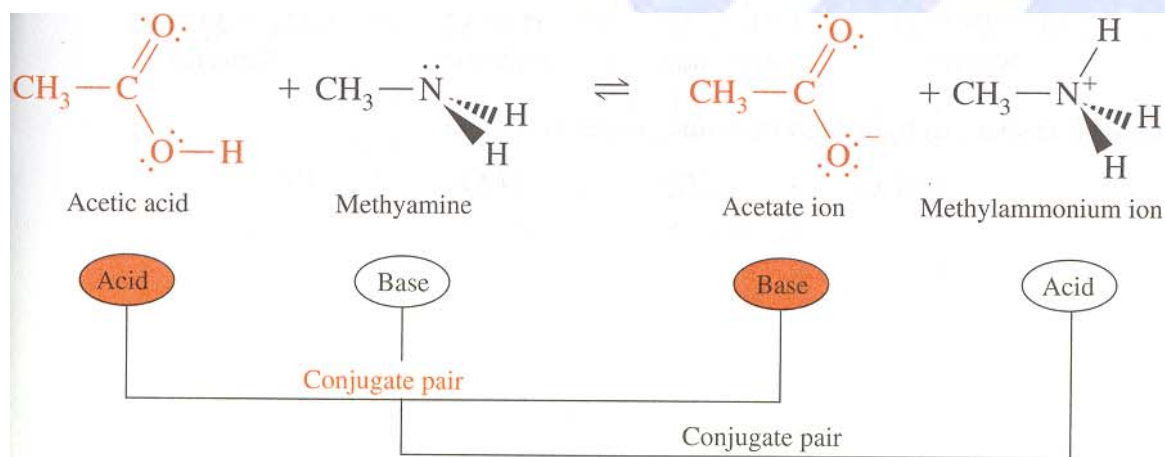
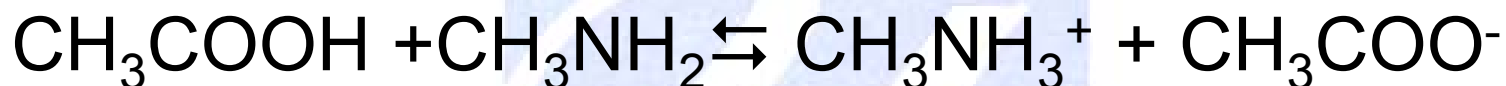


- Lewis acid and base  
 Lewis acid: orbit to accept electron pair  
 Lewis base: a pair of electron to be donated



- Protic acid and base  
 Acid: proton donor HCl  
 Base: proton acceptor NaOH
- Conjugate acid and base are related by the gain or loss of one proton

# Acid – base reaction:



Conjugate acids and bases are related by the gain or loss of one proton. In these structures, a solid wedge is a bond coming out of the plane of the page and a dashed wedge is a bond to an atom behind the page.

# pH

**In aqueous solution,  $[H^+][OH^-] \equiv 10^{-14}$  at 25 °C**

- Definition:  $pH = -\log[H^+]$ ; acidity of solution
- For pure water:  $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$  (25°C)  
So  $[H^+] = [OH^-] = 10^{-7}$ ;  $pH = -\log(10^{-7}) = 7$
- In acidic solution, e.g.  $[H^+] = 10^{-4}$ ,  $pH = 4$
- In alkaline solution, e.g.  $[OH^-] = 10^{-4}$   
 $[H^+] = K_w / [OH^-] = 10^{-14} / 10^{-4} = 10^{-10}$ ;  $pH = 10$
- $pH > 7$  alkaline;  $pH < 7$  acidic

# Strength of acid and base

- Strong acid or base: it can be completely dissociated in the solution, e.g. in water



- Weak acid or base: it can only be partially dissociated in the solution e.g.



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

(acid dissociation constant)

# Strength of acid and base

- Dissociation Vs. Dissolution
- Hydrogen Halides HCl, HBr and HI are strong acid.
- HF is specially



# Strength of acid and base

- Solution consists of:
  - Salt formed by strong acid and strong base is neutral, e.g. NaCl (HCl/NaOH)
  - Salt formed by strong acid and weak base is acidic e.g. NH<sub>4</sub>Cl (NH<sub>4</sub>OH/HCl)  
$$\text{NH}_4\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+ + \text{Cl}^-$$
  - Salt formed by weak acid and strong base is basic, e.g. CH<sub>3</sub>COONa (CH<sub>3</sub>COOH/NaOH)  
$$\text{CH}_3\text{COONa} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{Na}^+ + \text{OH}^-$$

# At low concentration systematic treatment is needed

