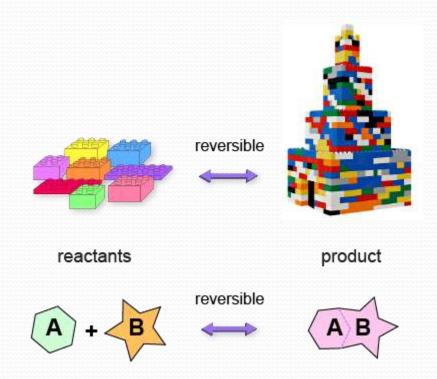
# Chapter 10 Part 1

Chemical equilibrium

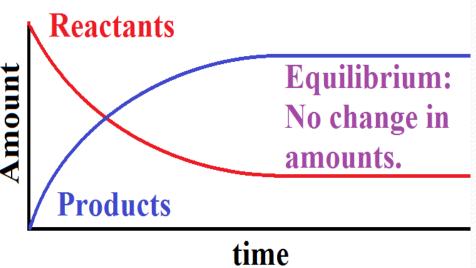
# **Chemical Equilibrium**

 Most chemical reactions are, at least to some extent, reversible.



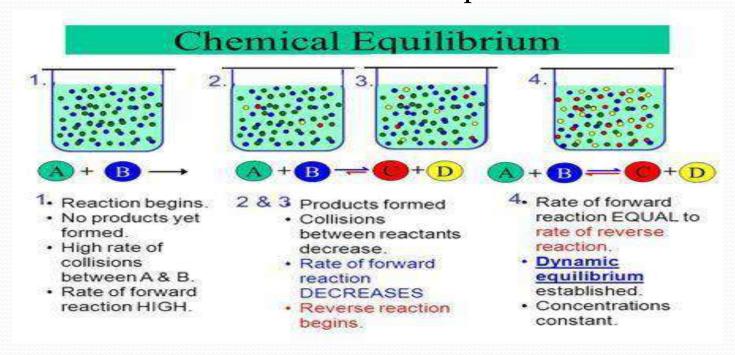
### **Chemical Equilibrium**

- At the start of a reversible process, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, the reverse process—that is, the formation of reactant molecules from product molecules—begins to take place.
- When the concentrations of the reactants and products no longer change with time, chemical equilibrium is reached. Here the rates of the forward and reverse reactions are equal.



# **Chemical Equilibrium**

- Chemical Equilibrium describes the state in which the rates of forward and reverse reactions are equal and the concentrations of the reactants and products remain unchanged with time.
- Note that a chemical equilibrium reaction involves different substances as reactants and products.



# **Equilibrium constant**

- This state of dynamic equilibrium is characterized by an equilibrium constant.
- By considering the following reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

- The equilibrium constant for the reaction at a particular temperature is  $K = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$
- *K* is a constant regardless of the equilibrium concentrations of the reacting species at a given temperature.
- The equilibrium constant also change with temperature.

### **Ways of Expressing Equilibrium Constants**

- Depending on the nature of reacting species, the equilibrium constant can be expressed in terms of molarities (Kc) or partial pressures (Kp).
- The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
- The relationship between Kp and Kc as

$$K_P = K_c(0.0821T)^{\Delta n}$$

 $\Delta n$  = moles of gaseous products - moles of gaseous reactants.

T= temperature in K°.

• Kp = Kc when  $\Delta_n$  = 0 as in the following reaction:

$$H_2(g) + I_2(g) \Longrightarrow 2HI(g)$$

# Homogeneous Equilibrium

• It refer to reactions in which all reacting species are in the same phase. An example of homogeneous gas-phase equilibrium is the dissociation of N2O4.

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

The equilibrium constant is

$$K_{\rm c} = \frac{[{
m NO}_2]^2}{[{
m N}_2{
m O}_4]}$$
  $K_P = \frac{P_{
m NO}_2}{P_{
m N}_2{
m O}_4}$ 

 As another example of homogeneous equilibrium, the dissociation of acetic acid (CH<sub>3</sub>COOH) in water:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_{c} = \frac{[CH_{3}COO^{-}][H_{3}O^{+}]}{[CH_{3}COOH]}$$

# Example

- Methanol (CH<sub>3</sub>OH) is manufactured industrially by the reaction
   CO(g) + 2H<sub>2</sub>(g) ⇒ CH<sub>3</sub>OH(g)
- The equilibrium constant  $(K_c)$  for the reaction is 10.5 at 220°C. What is the value of  $K_p$  at this temperature?

$$K_P = K_c (0.0821T)^{\Delta n}$$

$$T = 273 + 220 = 493 \text{ K}$$

$$\Delta n = 1 - 3 = -2$$
.

$$K_P = (10.5)(0.0821 \times 493)^{-2}$$
  
=  $6.41 \times 10^{-3}$ 

# Heterogeneous Equilibrium

- A reversible reaction involving reactants and products that are in different phases leads to a **heterogeneous equilibrium**.
- Calcium carbonate is heated in a closed vessel, this equilibrium is attained:
   CaCO₃(s) ← CaO(s) + CO₂(g)
- The equilibrium constant is

$$K_{c} = [CO_{2}]$$
  $K_{P} = P_{CO_{2}}$   $\Delta n = 1$ 

• 2NaHCO<sub>3(s)</sub>
$$\rightleftharpoons$$
Na<sub>2</sub>CO<sub>3(s)</sub> +CO<sub>2(g)</sub> +H<sub>2</sub>O<sub>(g)</sub>

$$K_{c}=[H_{2}O][CO_{2}] k_{p}=P_{H_{2}O}.P_{CO_{2}}$$

# Heterogeneous Equilibrium

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$$K_{c}=[H_{2}O][CO_{2}] k_{p}=P_{H_{2}O}.P_{CO_{2}}$$

### The Form of K and the Equilibrium Equation

1. When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

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

$$ZNO_2(g) \Longrightarrow N_2O_4(g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$K_c' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K_c} = \frac{1}{4.63 \times 10^{-3}} = 216$$

 The value of K also depends on how the equilibrium equation is balanced.

$$\frac{1}{2}N_{2}O_{4}(g) \iff NO_{2}(g) \qquad K'_{c} = \frac{[NO_{2}]}{[N_{2}O_{4}]^{1/2}} \qquad 2N_{2}O_{4}(g) \iff 4NO_{2}(g) \qquad K'_{c} = \frac{[NO_{2}]^{4}}{[N_{2}O_{4}]^{2}}$$

$$N_{2}O_{4}(g) \iff 2NO_{2}(g) \qquad K_{c} = \frac{[NO_{2}]^{2}}{[N_{2}O_{4}]} \qquad N_{2}O_{4}(g) \iff 2NO_{2}(g) \qquad K_{c} = \frac{[NO_{2}]^{2}}{[N_{2}O_{4}]}$$

$$K'_{c} = \sqrt{K_{c}} \qquad K'_{c} = K_{c}$$

### **Calculating Equilibrium Concentrations from Kc**

• If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from a knowledge of the initial concentrations.

A mixture of 0.500 mol H<sub>2</sub> and 0.500 mol I<sub>2</sub> was placed in a 1.00-L stainless-steel flask at 430°C. The equilibrium constant  $K_c$  for the reaction  $H_2(g) + I_2(g) \iff 2HI(g)$  is 54.3. at this temperature. Calculate the concentrations of H<sub>2</sub>, I<sub>2</sub>, and HI at equilibrium.

Step 1: The stoichiometry of the reaction is 1 mol H<sub>2</sub> reacting with 1 mol I<sub>2</sub> to yield 2 mol HI. Let x be the depletion in concentration (mol/L) of H<sub>2</sub> and I<sub>3</sub> at equilibrium. It follows that the equilibrium concentration of HI must be 2x. We summarize the changes in concentrations as follows:

$$H_2 + I_2 \Longrightarrow 2HI$$
Initial (M): 0.500 0.500 0.000
Change (M):  $-x -x +2x$ 
Equilibrium (M): (0.500 - x) (0.500 - x) 2x
e equilibrium constant is given by

Step 2: The equilibrium constant is given by

$$K_{\mathsf{c}} = \frac{[\mathbf{H}\mathbf{I}]^2}{[\mathbf{H}_2][\mathbf{I}_2]}$$

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$
$$x = 0.393 M$$

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.500 - 0.393) M = 0.107 M$$
  
 $[I_2] = (0.500 - 0.393) M = 0.107 M$   
 $[HI] = 2 \times 0.393 M = 0.786 M$ 

# **Factors That Affect Chemical Equilibrium**

- Change in concentration, pressure, or volume may alter the equilibrium position, but it does not change the value of the equilibrium constant. Only a change in temperature can alter the equilibrium constant.
- The rule, known as **Le Châtelier's** principle, states that if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as it tries to reestablish equilibrium.

#### Changes in Concentrations

At equilibrium all reactants and products are present in the reacting system. Increasing the concentrations of the products shifts the equilibrium to the left, and decreasing the concentration of the products shifts the equilibrium to the right.

For reactants, the opposite is true.

#### Changes in Pressure and Volume

Changes in pressure affect the concentrations of gases.

The greater the pressure, the smaller the volume, and vice versa. The increase in pressure increases concentration of gases, but the increase will be larger at the site of the reaction with more number of moles, so the reaction will proceed to the opposite site to decrease the effect of the stress.

For pressure decrease, the opposite is true

#### • Changes in Temperature

• If forward reaction is endothermic (absorbs heat,  $\Delta H^{\circ} > 0$ ):

heat 
$$+ N_2O_4(g) \longrightarrow 2NO_2(g)$$
  $\Delta H^{\circ} = 58.0 \text{ kJ/mol}$ 

- A rise in temperature favors the endothermic direction (from left to right of the equilibrium equation).
- A temperature decrease favors the reverse direction (from right to left of the equilibrium equation).
- For the exothermic reaction, the opposite is true.
- The Effect of a Catalyst
- A catalyst enhances the rate of a reaction but does not alter the equilibrium constant, nor does it shift the position of an equilibrium system.

Consider the following equilibrium process:

$$N_2F_4(g) \Longrightarrow 2NF_2(g)$$

$$\Delta H^{\circ} = 38.5 \text{ kJ/mol}$$

- Predict the changes in the equilibrium if
- (a) The reacting mixture is heated at constant volume;

The system will go from left to right and the equilibrium constant will increase from left to right

(b) Some N2F4 gas is removed from the reacting mixture at constant temperature and volume;

The system will go from right to left

(c) The pressure on the reacting mixture is decreased at constant temperature;

The system will go from left to right

(d) A catalyst is added to the reacting mixture.

A catalyst will not affect either the concentrations or the equilibrium constant.

# Chapter 10 part 2

Solubility equilibrium Acid- base equilibrium

# **Solubility Equilibrium**

• **Solubility equilibrium** is a type of dynamic hetrogenous equilibrium that exists when a chemical compound in the solid state is in chemical equilibrium with a solution of that compound.

$$AgCl(s) \Longrightarrow Ag^{+}(aq) + Cl^{-}(aq)$$

• The solubility product constant, Ksp, is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute (ionic compound) dissolves in water. The more soluble a substance is, the higher the Ksp value it has.

$$K_{sp} = [Ag^+][C1^-]$$

- The solubility product constant of a compound is the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.
- Molar solubility is the number of moles of solute per liter of solution.
- Molar solubility, solubility, and solubility product all refer to a saturated solution.

• 
$$MgF_2$$
  
•  $MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$   $K_{sp} = [Mg^{2+}][F^-]^2$   
•  $Ag_2CO_3$   
•  $Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$   $K_{sp} = [Ag^+]^2[CO_3^{2-}]$   
•  $Ca_3(PO_4)_2$ 

 $K_{\rm sp} = [{\rm Ca}^{2+}]^3 [{\rm PO}_4^{3-}]^2$ 

 $\operatorname{Ca}_3(\operatorname{PO}_4)_2(s) \Longrightarrow 3\operatorname{Ca}^{2+}(aq) + 2\operatorname{PO}_4^{3-}(aq)$ 

# **Examples**

- The solubility of calcium sulfate (CaSO<sub>4</sub>) is found to be 0.67 g/L. Calculate the value of *K*sp for calcium sulfate.
- The molar solubility of CaSO<sub>4</sub> [CaSO<sub>4</sub>]= 0.67/136 mole/L
   = 4.9 x 10<sup>-3</sup> M

[CaSO4] represent only the concentration of the dissolved solid

As each 1 mole of (CaSO<sub>4</sub>) give 1 mole for each of the ions,
 So

CaSO<sub>4(s)</sub> 
$$\rightleftharpoons$$
 Ca<sup>2+</sup><sub>(aq)</sub> + SO<sub>4</sub><sup>2-</sup><sub>(aq)</sub>  
S S S  
[CaSO<sub>4</sub>] = [Ca<sup>2+</sup>] = [SO<sub>4</sub><sup>2-</sup>] = 4.9x10<sup>-3</sup> M

$$K_{\rm sp} = [{\rm Ca}^{2+}][{\rm SO}_4^{2-}]$$
  
=  $(4.9 \times 10^{-3})(4.9 \times 10^{-3})$   
=  $2.4 \times 10^{-5}$ 

# **Examples**

• The Ksp of silver bromide (AgBr) is  $7.7 \times 10^{-13}$ . Calculate its molar solubility and solubility (g/L).

$$K_{sp} = [Ag^{+}][Br^{-}]$$
  
 $7.7 \times 10^{-3} = (s)(s)$   
 $s = \sqrt{7.7 \times 10^{-13}} = 8.8 \times 10^{-7} M$   
 $[Ag^{+}] = 8.8 \times 10^{-7} M$   
 $[Br^{-}] = 8.8 \times 10^{-7} M$ 

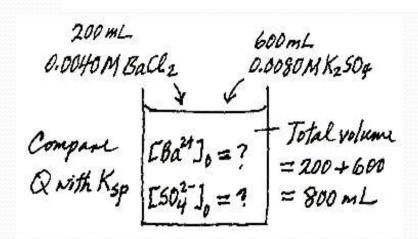
the molar solubility of AgBr also is  $8.8 \times 10^{-7} M$ .

# **Predicting Precipitation Reactions**

- We can predict whether a precipitate will form when we mix two solutions or add a soluble compound to a solution.
- We use Q, called the ion product, to represent the quantity obtained by substituting the initial concentrations of the ions into the Ksp expression.
  - Q < Ksp Unsaturated solution, no precipitation.
  - Q = Ksp Saturated solution, no precipitation.
  - Q > Ksp Supersaturated solution; precipitation occur.

# Example

• If exactly 200 mL of 0.0040 M BaCl2 are added to exactly 600 mL of 0.0080 M of potassium sulfate. Will a precipitate form? Given that:  $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$   $K_{50} = 1.1 \times 10^{-10}$ 



$$K_2SO_4(aq) + BaCl_2(aq) \rightarrow 2KCl(aq) + BaSO_4(s)$$
  

$$\therefore Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

For BaCl2, M1.V1 = M2.V2
 200 x 0.004 = M2 x 800

 $M_2 = 0.001 M = molar solubility of BaCl<sub>2</sub>= molar solubility of Ba<sup>+2</sup>$ 

For K2SO4, M1.V1 = M2.V2
 600 x 0.008 = M2 x 800

 $M_2 = 0.006 M = molar solubility of K2SO_4 = molar solubility of SO_4<sup>-2</sup>$ 

$$Q = [Ba^{2+}]_0[SO_4^{2-}]_0 = (1.0 \times 10^{-3})(6.0 \times 10^{-3})$$
$$= 6.0 \times 10^{-6}$$

 Q > Ksp, The solution is supersaturated because the value of Q indicates that the concentrations of the ions are too large. Thus, some of the BaSO<sub>4</sub> will precipitate out of solution. For BaCl2, M1.V1 = M2.V2
 200 x 0.004 = M2 x 800

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## **Theories of Acids and Bases**

#### A- The Arrhenius Theory of acids and bases

 Acids are substances that produce hydrogen ions in aqueous solution as HCl.

$$HCl_{(aq)}
ightarrow H_{(aq)}^+ + Cl_{(aq)}^-$$

 Bases are substances that produce hydroxide ions in aqueous solution as NaOH.

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

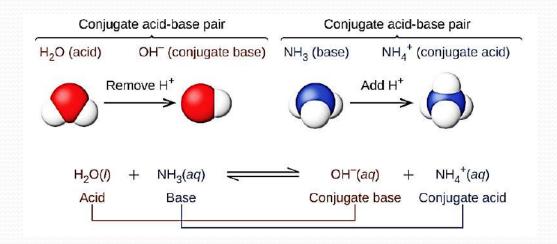
- Limitation of the Arrhenius Definition of Acids and Bases
- The Arrhenius definition can only describe acids and bases in an aqueous environment

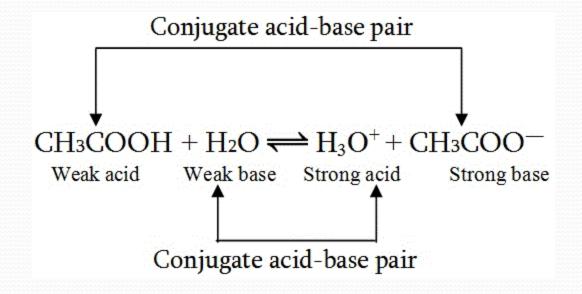
#### B- The Brønsted-Lowry Theory of acids and bases

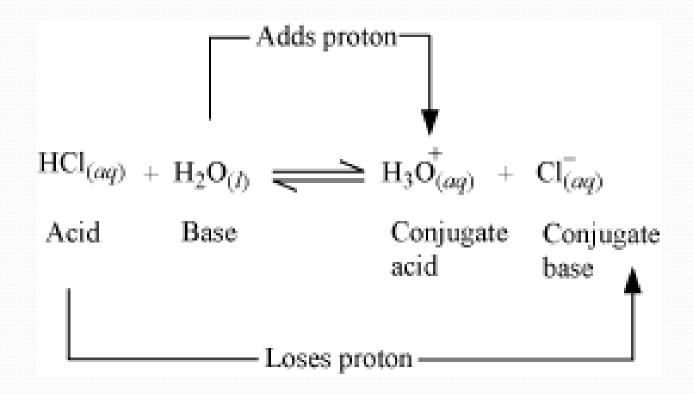
- An acid is a proton (hydrogen ion) donor. We call the product that remains after an acid donates a proton the conjugate base of the acid (This species is a base because it can accept a proton to re-form the acid).
- A base is a proton (hydrogen ion) acceptor. We call the product that results when a base accepts a proton the conjugate acid of the base (This species is an acid because it can give up a proton and thus re-form the base)

# **Conjugate Acid-Base Pairs**

$$\begin{array}{c} ...\\ H-N-H+H-O: \\ \downarrow \\ H \end{array} \longmapsto \begin{bmatrix} H\\ \downarrow \\ H-N-H\\ \downarrow \\ H \end{bmatrix}^+ + H-O: -\\ ...\\ NH_3(aq) + H_2O(l) \\ base_1 \qquad acid_2 \qquad NH_4^+(aq) + OH^-(aq) \\ acid_1 \qquad base_2 \end{array}$$







# **Bronsted** acids

• **Monoprotic acids**; that is, each unit of the acid yields one hydrogen ion upon ionization:

$$\operatorname{HCl}(aq) \longrightarrow \operatorname{H}^+(aq) + \operatorname{Cl}^-(aq)$$
 $\operatorname{HNO}_3(aq) \longrightarrow \operatorname{H}^+(aq) + \operatorname{NO}_3^-(aq)$ 
 $\operatorname{CH}_3\operatorname{COOH}(aq) \Longrightarrow \operatorname{CH}_3\operatorname{COO}^-(aq) + \operatorname{H}^+(aq)$ 

- The ionization of acetic acid is incomplete (note the double arrows), it is a weak electrolyte. For this reason it is called a weak acid
- On the other hand, HCl and HNO<sub>3</sub> are strong acids because they are strong electrolytes, so they are completely ionized in solution (note the use of single arrows).

 A diprotic acid, each unit of the acid gives up two H<sup>+</sup> ions, in two separate steps

$$\mathbf{H}_2 SO_4(aq) \longrightarrow \mathbf{H}^+(aq) + \mathbf{H} SO_4^-(aq)$$
  
 $\mathbf{H} SO_4^-(aq) \Longleftrightarrow \mathbf{H}^+(aq) + \mathbf{S}O_4^{2-}(aq)$ 

Triprotic acids, which yield three H+ ions

$$\mathbf{H_3PO_4}(aq) \Longrightarrow \mathbf{H^+}(aq) + \mathbf{H_2PO_4^-}(aq)$$
 $\mathbf{H_2PO_4^-}(aq) \Longrightarrow \mathbf{H^+}(aq) + \mathbf{HPO_4^{2-}}(aq)$ 
 $\mathbf{HPO_4^{2-}}(aq) \Longrightarrow \mathbf{H^+}(aq) + \mathbf{PO_4^{3-}}(aq)$ 

### **Bronsted bases**

• Sodium hydroxide (NaOH) and barium hydroxide Ba(OH)<sub>2</sub> are strong electrolytes. This means that they are completely ionized in solution:

NaOH(s) 
$$\xrightarrow{\text{H}_2\text{O}}$$
 Na<sup>+</sup>(aq) + OH<sup>-</sup>(aq)  
Ba(OH)<sub>2</sub>(s)  $\xrightarrow{\text{H}_2\text{O}}$  Ba<sup>2+</sup>(aq) + 2OH<sup>-</sup>(aq)

• The OH<sup>-</sup> ion can accept a proton as follows:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

- Thus, OH<sup>-</sup> is a Brønsted base.
- Ammonia (NH<sub>3</sub>) is classified as a Brønsted base because it can accept a H<sup>+</sup> ion

$$NH_3(aq) + H_2O(l) \Longrightarrow NH_4^+(aq) + OH^-(aq)$$

# Molecular Structure and the Strength of Acids

• In this series of **binary acids** (through a group, the atomic size increases), the weaker the bond (H—X), the stronger the acid. So that the strength of the acids increases as follows:

$$HF \leq HC1 \leq HBr \leq HI$$

• In this series of binary acids (through a period, the electronegativity increases), the greater attraction of the bonding electron pairs (H—X), so easier to dissociate the H<sup>+</sup>, the stronger the acid. So that the strength of the acids increases as follows:

Oxoacids contain hydrogen, oxygen, and one other element Z, which occupies a central position.

• Oxoacids having the same central atom but different numbers of oxygen. Within this group, acid strength increases as the number of oxygen atoms increases.

$$HC1O_4 > HC1O_3 > HC1O_2 > HC1O$$

• Oxoacids having different central atoms but have the same number of oxygen. Within this group, acid strength increases with increasing electronegativity of the central atom.

# C- Lewis acids and bases

- According to Lewis's definition, a base is a substance that can donate a pair of electrons, and an acid is a substance that can accept a pair of electrons.
- The significance of the Lewis concept is that it is much more general than other definitions; it includes as acid-base reactions many reactions that do not involve Brønsted acids.

- Consider, for example, the reaction between boron trifluoride (BF3) and ammonia. The B atom in BF3 is sp2-hybridized. The vacant, unhybridized 2p orbital accepts the pair of electrons from NH3.
- Note that a coordinate covalent bond is formed between the B and N atoms.

• The hydration of carbon dioxide to produce carbonic acid can be understood in the Lewis framework

#### The Ion Product of Water

• Water is a very weak electrolyte, but it does undergo ionization to a small extent:

 $H - O: + H - O: \Longrightarrow \begin{bmatrix} H - O - H \\ H \end{bmatrix}^{+} + H - O:^{-}$ 

• This reaction is sometimes called the autoionization of water. At equilibrium:  $K_{\mathbf{w}} = [\mathbf{H}_{3}\mathbf{O}^{+}][\mathbf{O}\mathbf{H}^{-}] = [\mathbf{H}^{+}][\mathbf{O}\mathbf{H}^{-}]$ 

where Kw is called the ion-product constant.

• In pure water at 25C, the concentrations of both ions are equal and found to be 1.0 x 10<sup>-7</sup> M. Thus,

$$K_{\rm w} = [{\rm H}^+][{\rm OH}^-] = 1.0 \times 10^{-14}$$

 In practice, we can change the concentration of either H<sup>+</sup> or OHions in solution, but we cannot vary both of them independently. This mean increase the H<sup>+</sup> conc. accompanied by decrease in OHconc. and vice versa.

# pH—A Measure of Acidity

• The concentrations of H<sup>+</sup> ions in aqueous solutions are frequently very small numbers and therefore inconvenient to work with. A more practical measure called pH:

$$pH = -log[H_3O^+]$$
 or  $pH = -log[H^+]$ 

Acidic solutions:  $[H^+] > 1.0 \times 10^{-7} M$ ,  $pH < 7.00$ 

Basic solutions:  $[H^+] < 1.0 \times 10^{-7} M$ ,  $pH > 7.00$ 

Neutral solutions:  $[H^+] = 1.0 \times 10^{-7} M$ ,  $pH = 7.00$ 

- Notice that pH increases as [H+] decreases.
- Similarly, we define pOH as:

Neutral solutions:

$$pOH = -log[OH^{-}]$$

The relationship between pH and pOH is

$$pH + pOH = 14.00$$

## Weak Acids and Acid Ionization Constants

 Consider a weak monoprotic acid, HA. Its ionization in water is represented by:

$$HA(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + A^-(aq)$$
  $HA(aq) \Longrightarrow H^+(aq) + A^-(aq)$ 

The equilibrium expression for this ionization is

$$K_{\rm a} = \frac{[{\rm H_3O^+}][{\rm A}^-]}{[{\rm HA}]}$$
 or  $K_{\rm a} = \frac{[{\rm H}^+][{\rm A}^-]}{[{\rm HA}]}$ 

- where Ka, the acid ionization constant, is the equilibrium constant for the ionization of an acid at a given temperature. The strength of the acid HA is measured quantitatively by the magnitude of Ka. The larger Ka, the stronger the acid.
- Only weak acids have Ka values associated with them.

 Diprotic and polyprotic acids ionize in a stepwise manner, that is, they lose one proton at a time. An ionization constant expression can be written for each ionization stage.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
  $K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$   $4.2 \times 10^{-7}$   $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$   $K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$   $4.8 \times 10^{-11}$ 

- For a given acid, the first ionization constant is much larger than the second ionization constant, and so on.
- This trend is reasonable because it is easier to remove an H<sup>+</sup> ion from a neutral molecule than to remove another H<sup>+</sup> from a negatively charged ion derived from the molecule.

#### **Weak Bases and Base Ionization Constants**

- The ionization of weak bases is treated in the same way as the ionization of weak acids.
- When ammonia dissolves in water, it undergoes the reaction

$$NH_3(aq) + H_2O(l) \Longrightarrow NH_4^+(aq) + OH^-(aq)$$

• The base ionization constant (Kb), is the equilibrium constant for the ionization reaction,

$$K_{\mathbf{b}} := \frac{[\mathbf{NH}_{4}^{+}][\mathbf{OH}^{-}]}{[\mathbf{NH}_{2}]}$$

• The larger Kb, the stronger the base. Only weak bases have Kb values associated with them.

# The Relationship Between Conjugate Acid-Base Ionization Constants

$$CH_{3}COOH(aq) \rightleftharpoons H^{+}(aq) + CH_{3}COO^{-}(aq)$$

$$K_{a} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]}$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

write the base ionization constant as

$$K_{\rm b} = \frac{\rm [CH_3COOH][OH^-]}{\rm [CH_3COO^-]}$$

The product of these two ionization constants is given by

$$K_{a}K_{b} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]} \times \frac{[CH_{3}COOH][OH^{-}]}{[CH_{3}COO^{-}]}$$
  
=  $[H^{+}][OH^{-}]$   
=  $K_{w}$