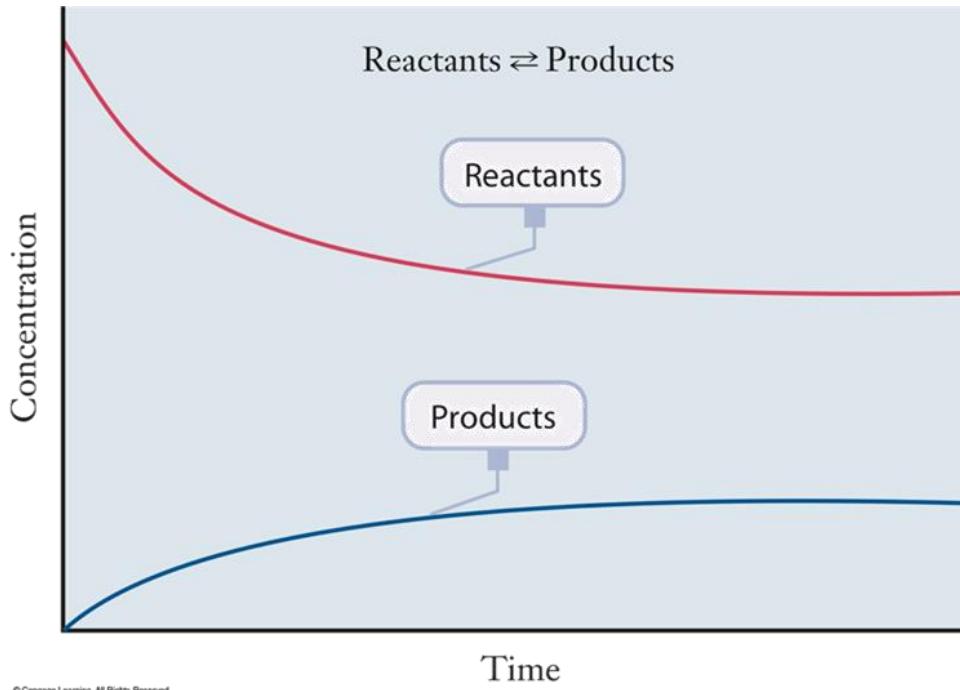
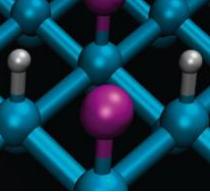


# Chapter 12

# Chemical Equilibrium

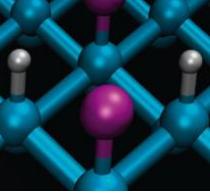


# Chemical Equilibrium



- A chemical system reaches equilibrium when the rate of the forward reaction equals the rate of the reverse reaction
- Concentrations of products and reactants do not change at equilibrium

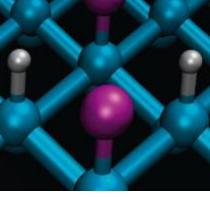
# Forward and Reverse Reactions



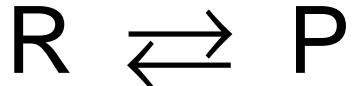
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- Water in an open system, such as a glass, will slowly evaporate, decreasing the amount of liquid water over time
- Water in a closed system, such as a covered glass, will establish a dynamic equilibrium, where the amount of liquid water present does not decrease over time

# Mathematical Relationships



- For any reaction involving reactants, R, and products, P, the chemical reaction is written at equilibrium with a double arrow

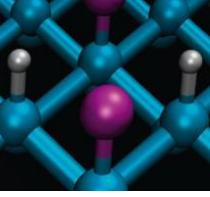


- Rate laws for the forward and reverse reaction can be written as

$$\text{Rate}_{\text{for}} = k_{\text{for}}[R]$$

$$\text{Rate}_{\text{rev}} = k_{\text{rev}}[P]$$

# Mathematical Relationships



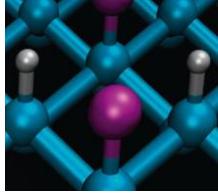
- At equilibrium, Rate<sub>for</sub> = Rate<sub>rev</sub>
  - Therefore,

$$k_{\text{for}}[R]_{\text{eq}} = k_{\text{rev}}[P]_{\text{eq}}$$

or

$$\frac{k_{\text{for}}}{k_{\text{rev}}} = \frac{[P]_{\text{eq}}}{[R]_{\text{eq}}}$$

# Equilibrium (Mass Action) Expression



- For the general chemical equation,



- ratio of concentrations, whether or not at equilibrium, can be defined, where Q is the **reaction quotient**

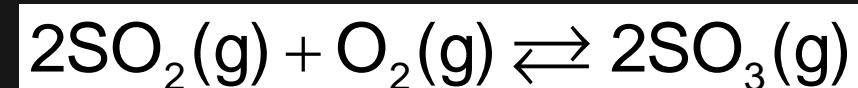
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- At equilibrium, the ratio becomes the **equilibrium expression**, and the corresponding value of Q is called the **equilibrium constant (K)**

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

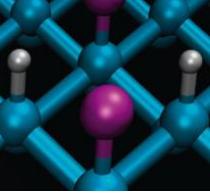
# Example Problem 12.1

- Write the equilibrium expression for this reaction

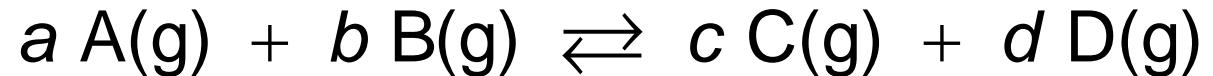


$$K = \frac{[\text{SO}_3]_{\text{eq}}^2}{[\text{SO}_2]_{\text{eq}}^2 \cdot [\text{O}_2]_{\text{eq}}}$$

# Gas Phase Equilibria: $K_p$ versus $K_c$

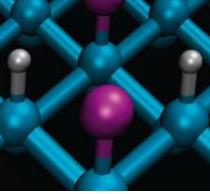


- Equilibrium expressions can be written for gas phase reactions using partial pressures
  - $K_p$  is the equilibrium constant in terms of partial pressures



$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

# Gas Phase Equilibria: $K_p$ versus $K_c$

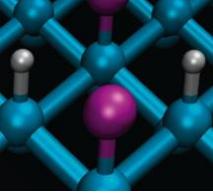


- The values of  $K_c$  and  $K_p$  are not necessarily equal
- The relationship between  $K_c$  and  $K_p$  is:

$$K_p = K_c \times RT^{(\Delta n_{\text{gas}})}$$

- $\Delta n_{\text{gas}}$  represents the change in the number of moles of gas from the reactants to the products
- Only when  $\Delta n_{\text{gas}} = 0$  does  $K_p = K_c$
- All equilibrium constants in this text are based on molar concentrations
- The subscript “c” will not be used when writing K values

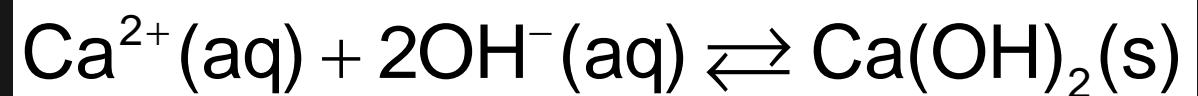
# Homogeneous and Heterogeneous Equilibria



- **Homogeneous equilibria:** Reactants and products are in the same phase, either gaseous or aqueous
- **Heterogeneous equilibria:** Reactants and products are in different phases
  - Reactants and products that are either liquid or solid do not appear in the equilibria constant expression because their concentrations are constant
    - The concentration of a solid or liquid does not change because these substances are pure

## Example Problem 12.2

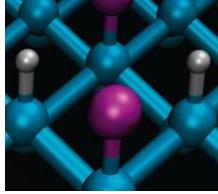
- Calcium hydroxide will precipitate from solution by the following equilibrium:



- Write the equilibrium expression for this reaction

$$K \equiv \frac{1}{[\text{Ca}^{2+}]_{\text{eq}} [\text{OH}^-]_{\text{eq}}^2}$$

# Numerical Importance of the Equilibrium Expression



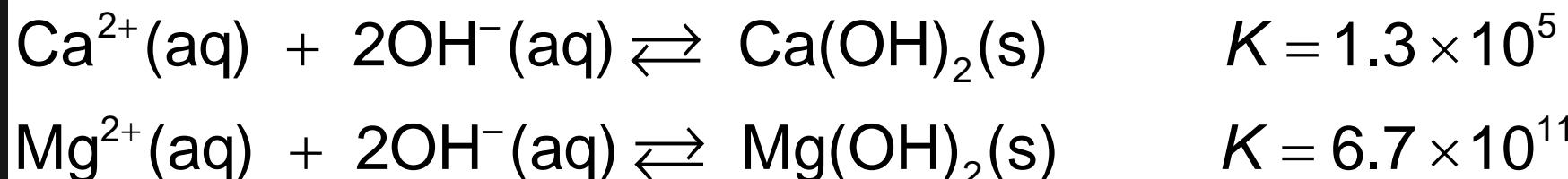
- The size of the equilibrium constant indicates the direction a chemical reaction will likely proceed

$$K = \frac{\text{[products]}}{\text{[reactants]}}$$

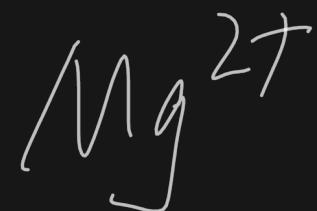
- For large values of  $K (K \gg 1)$ , products are favored
- For small values of  $K (K \ll 1)$ , reactants are favored

## Example Problem 12.3

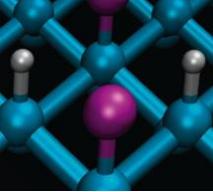
- In Example Problem 12.2, we saw that hydroxide ions precipitate with calcium. Magnesium ions show similar behavior. The two pertinent equilibria are:



Which ion is more likely to precipitate hydroxide from a solution, assuming roughly equal concentrations of calcium and magnesium ions?

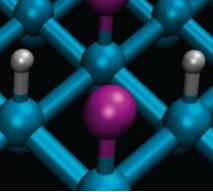


# Units and the Equilibrium Constant



- The equilibrium constant  $K$  is dimensionless
  - The concentrations used to calculate the equilibrium constant are divided by the standard concentration of 1 M, which has no numerical consequence
  - A dimensionless  $K$  is required when  $K$  is used as the argument in a natural log function

# Equilibrium Concentrations

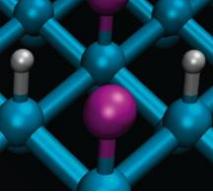


- The equilibrium concentrations of reactants and products for a chemical reaction can be predicted using the balanced chemical equation and known equilibrium constants

- Three basic features for the strategy used in any equilibrium calculation
  - ① Write a balanced chemical equation for the relevant equilibrium or equilibria
  - ② Write the corresponding equilibrium expression or expressions  $K_e = \dots$
  - ③ Create a table of concentrations with all reacting species as columns and the following rows: initial concentration, change in concentration, and final concentration

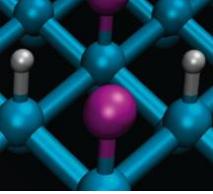
Initial	A	B	c	D
final	b			

# Equilibrium Concentrations

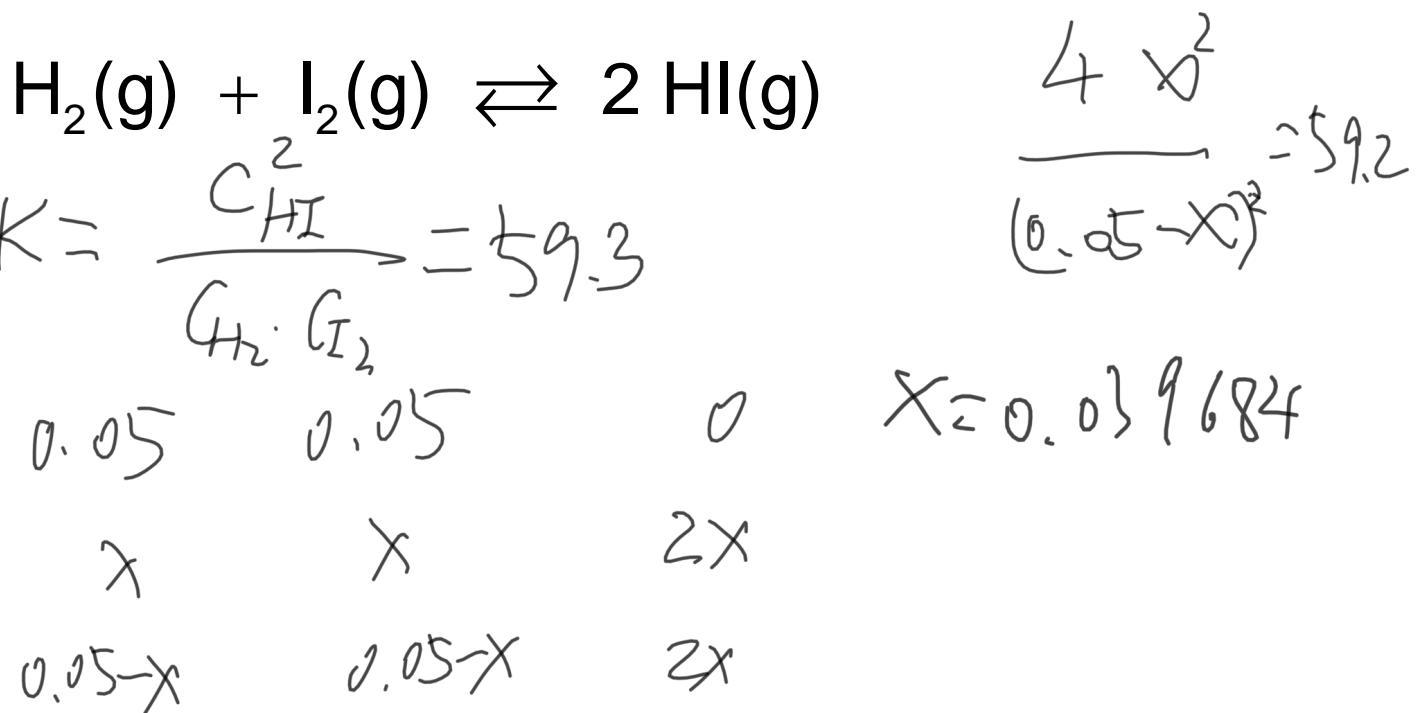


- Equilibrium concentrations can be determined from initial concentrations by realizing:
  - The first row contains the initial concentrations
  - The second row contains the changes in the initial concentrations as the system comes to equilibrium
  - The third row contains the final equilibrium concentrations
- Equilibrium concentrations can be determined from initial concentrations by realizing the direction in which the reaction will shift to achieve equilibrium, expressing the concentration change in terms of a single variable, and solving for the equilibrium concentrations using the equilibrium expression

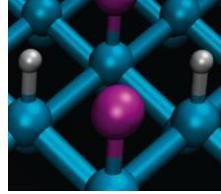
## Example Problem 12.6



- Calculate the equilibrium concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  if the initial concentrations are 0.050 M each for  $\text{H}_2$  and  $\text{I}_2$  and  $K = 59.3$  at 400°C



# Equilibrium Concentrations from Initial Concentrations



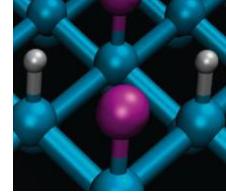
- The concentration of HI = 0 initially, so the reaction will shift to the right to achieve equilibrium

	H <sub>2</sub>	I <sub>2</sub>	HI
Initial concentration	0.050M	0.050M	0M
Change in concentration			
Final concentration			

- For every  $x$  moles of H<sub>2</sub> and I<sub>2</sub> consumed,  $2x$  moles of HI are produced

	H <sub>2</sub>	I <sub>2</sub>	HI
Initial concentration	0.050M	0.050M	0M
Change in concentration	- $x$	- $x$	+ $2x$
Final concentration			

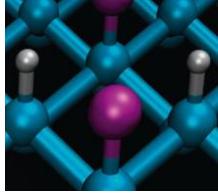
# Equilibrium Concentrations from Initial Concentrations



	$\text{H}_2$	$\text{I}_2$	$\text{HI}$
Initial concentration	0.050M	0.050M	0 M
Change in concentration	$-x$	$-x$	$+2x$
Final concentration	$0.050-x$	$0.050-x$	$2x$

- The final concentrations are expressed in terms of the initial concentration minus  $x$  for the reactants and initial concentration plus  $2x$  for the products
- Substitute the algebraic final concentration terms into the equilibrium concentration and solve for  $x$

# Equilibrium Concentrations from Initial Concentrations



$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(0.050 - x)(0.050 - x)} = 59.3$$

$$\sqrt{\frac{(2x)^2}{(0.050 - x)(0.050 - x)}} = \sqrt{59.3}$$

$$\frac{2x}{0.050 - x} = 7.70$$

$$0.39 = 9.70x$$

$$x = 0.040$$

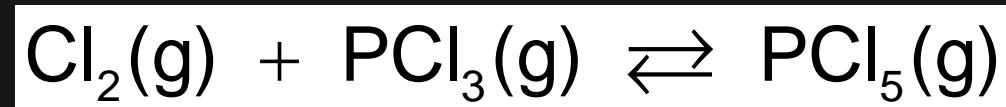
$$[H_2] = [I_2] = 0.050 - x$$

$$[H_2] = [I_2] = 0.050 - 0.040 = 0.010 \text{ M}$$

$$[HI] = 2x = 0.080 \text{ M}$$

## Example Problem 12.7

- The equilibrium constant for the reaction of chlorine gas with phosphorous trichloride to form phosphorus pentachloride is 33 at 250°C. If an experiment is initiated with concentrations of 0.050 M  $\text{PCl}_3$  and 0.015 M  $\text{Cl}_2$ , what are the equilibrium concentrations of all three gases?

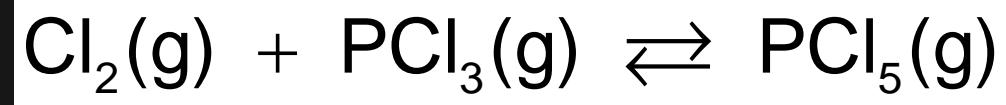


$$\begin{array}{ccc} 0.015 & 0.05 & 0 \\ -x & -x & x \end{array}$$

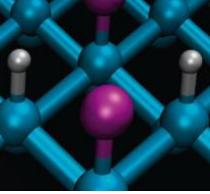
$$\begin{array}{ccc} 0.015-x & 0.05-x & x \end{array}$$

$$33 = \frac{x}{(0.015-x)(0.05-x)} \Rightarrow x = 0.0086$$

## Example Problem 12.7

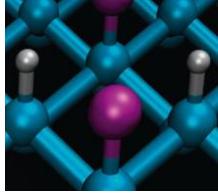


# LeChatelier's Principle



- **LeChatelier's principle:** When a system at equilibrium is stressed, it responds by reestablishing equilibrium to reduce the stress
- There are three common means to introduce a stress in a chemical equilibrium
  - Changes in concentration
  - Changes in pressure
  - Changes in temperature

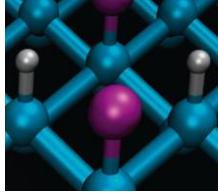
# Effect of a Change in Concentration



- For a reaction at equilibrium, a change in concentration for one or more of the reactants and/or products will disturb the equilibrium
  - The system will react to reestablish equilibrium
- For a reaction at equilibrium, increasing the concentration of one of the reactants will shift the equilibrium toward the products
  - The reactant concentration will decrease as reactant is converted to product, and the product concentration will increase until equilibrium is reestablished
  - For a reaction at equilibrium,  $Q = K$

$$Q = \frac{[\text{products}]}{[\text{reactants}]}$$

# Effect of a Change in Concentration



**Table 12.2** Equilibrium shifts driven by concentration changes

The effects of concentration changes on equilibrium can be rationalized by considering the reaction quotient,  $Q$ , and comparing it to the equilibrium constant,  $K$ .

Type of Concentration Change	Resulting Change in $Q$	Response of System
[Products] increased	$Q > K$	More reactants formed
[Products] decreased	$Q < K$	More products formed
[Reactants] increased	$Q < K$	More products formed
[Reactants] decreased	$Q > K$	More reactants formed

## Example Problem 12.8

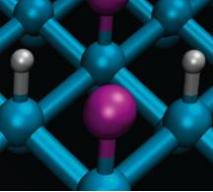
- Predict the change in the reaction quotient, Q, when:



Then, explain how the equilibrium shifts in response to each stress

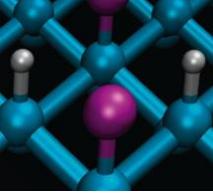
- Sodium acetate is added
- Additional acetic acid is added
- Sodium hydroxide is added

# Effect of a Change in Pressure



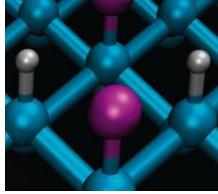
- For reactions involving gases, if the number of moles of gas differs between reactants and products, a shift in pressure (due to a volume change) will result in a change in equilibrium position
  - For an increase in pressure, the equilibrium will shift toward the side of the equation with fewer moles of gas
  - For a decrease in pressure, the equilibrium will shift toward the side of the equation with more moles of gas

# Effect of a Change in Temperature on Equilibrium



- During a temperature change, heat flows in or out of the reacting system
  - Heat is treated as a product for an exothermic reaction
$$\text{reactants} \rightleftharpoons \text{products} + \text{heat}$$
  - Heat is treated as a reactant for an endothermic reaction
$$\text{reactants} + \text{heat} \rightleftharpoons \text{products}$$
- An increase in the temperature causes the equilibrium to shift away from the side with the heat
- A decrease in the temperature causes the equilibrium to shift toward the side with the heat

# Effect of a Change in Temperature on Equilibrium



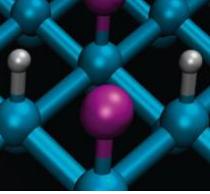
**Table 12.3** Equilibrium shifts driven by temperature changes

The effects of temperature changes on a chemical system at equilibrium depend on whether the reaction is exothermic or endothermic. Unlike concentration or pressure changes, temperature changes also alter the *value* of the equilibrium constant.

Type of Reaction	Type of Temperature Change	Response of System
Exothermic	$T$ increase	More reactants formed
Exothermic	$T$ decrease	More products formed
Endothermic	$T$ increase	More products formed
Endothermic	$T$ decrease	More reactants formed

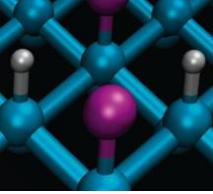
Summary of the effects a temperature change will have on exothermic and endothermic reactions at equilibrium

# Effect of a Catalyst on Equilibrium

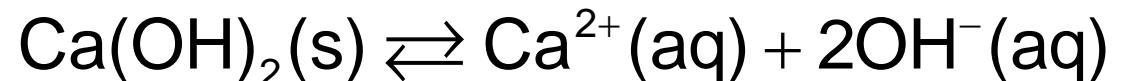


- When a catalyst is added to a system at equilibrium, there is no impact on the equilibrium position
  - Catalysts speed up the rate of the forward and reverse reactions **to the same extent**
  - The equilibrium concentrations of products and reactants do not change

# Solubility Equilibria

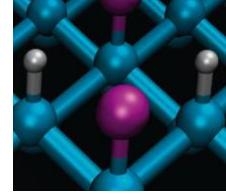


- The insoluble solutes predicted by the solubility guidelines are also referred to as sparingly soluble
  - Given enough fresh solvent, an insoluble salt will completely dissolve
- The equilibrium describing the solubility of an insoluble salt is heterogeneous
  - The insoluble salt is not included in the equilibrium expression
  - The chemical reaction representing the dynamic equilibrium between the insoluble salt and the dissolved ions is written with the dissolved ions as products



$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = 7.9 \times 10^{-6}$$

# Defining the Solubility Product Constant



- **Solubility product constant ( $K_{sp}$ ):** Special name for the equilibrium constant for solubility equilibria
  - $K_{sp}$  values can vary over a wide range
- **Molar solubility:** Concentration of a dissolved salt present in a saturated solution, expressed in molarity
  - Molar solubility is determined from  $K_{sp}$

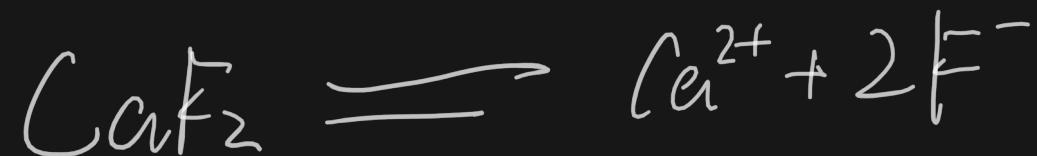
**Table 12.4  $K_{sp}$  values**

Values for a few compounds illustrate the wide range over which solubility product constants can vary.

Salt	$K_{sp}$
$\text{Ag}_2\text{CO}_3$	$8.1 \times 10^{-12}$
$\text{Ag}_3\text{PO}_4$	$1.3 \times 10^{-20}$
$\text{AgBr}$	$5.3 \times 10^{-13}$
$\text{AgCl}$	$1.8 \times 10^{-10}$
$\text{AgCN}$	$6.0 \times 10^{-17}$
$\text{Ca}_3(\text{PO}_4)_2$	$2.0 \times 10^{-33}$
$\text{CaCO}_3$	$4.8 \times 10^{-9}$
$\text{FeCO}_3$	$3.5 \times 10^{-11}$
$\text{Mg}_3(\text{PO}_4)_2$	$9.9 \times 10^{-25}$
$\text{PbCO}_3$	$1.5 \times 10^{-13}$
$\text{PtS}$	$9.9 \times 10^{-74}$
$\text{ZnS}$	$1.1 \times 10^{-21}$

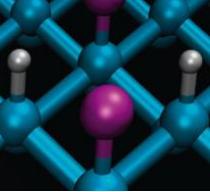
## Example Problem 12.10

- Write the solubility product constant expression for calcium fluoride



$$K_{sp} = [\text{Ca}^{2+}] [\text{F}^-]^2$$

## Example Problem 12.11



- What is the molar solubility of calcium phosphate, given that  $k_{sp} = 2.0 \times 10^{-33}$ ?



$$3x \quad 2x$$

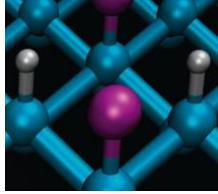
$$(3x)^2 \cdot (2x)^3 = 2 \times 10^{-33}$$

$$72x^5 = 2 \times 10^{-33}$$

$$x = 5.27 \times 10^{-18}$$

typical  
fault

# Relationship Between $K_{sp}$ and Molar Solubility



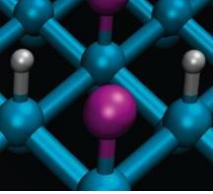
	$\text{Ca}_3(\text{PO}_4)_2(s)$	$\text{Ca}^{2+}(\text{aq})$	$\text{PO}_4^{3-}(\text{aq})$
Initial concentration	Solid	0 M	0 M
Change in concentration	Solid	$+3x$	$+2x$
Final concentration	Solid	$3x$	$2x$

- Initial concentration for dissolved solutes is zero. The equilibrium concentrations equal the change in concentration. Solving for  $x$  in the  $K_{sp}$  expression yields the molar solubility

$$K_{sp} = 2.0 \times 10^{-33} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3x)^3(2x)^2 = 108x^5$$

$$x = 1.1 \times 10^{-7}$$

# Common Ion Effect

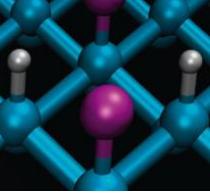


- For a sparingly soluble salt at equilibrium, the addition of a common ion from an outside source will depress the solubility of the salt
  - Ions found in both the sparingly soluble salt and the aqueous solution being added are said to be common ions
- The test tube on the left contains a saturated solution of silver acetate
  - Adding aqueous  $\text{AgNO}_3$  causes additional solid silver acetate to precipitate due to the **common ion effect**, as seen in the test tube on the right
  - This effect is an application of LeChatelier's principle



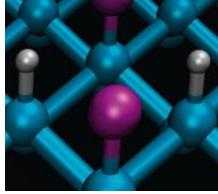
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# Acids and Bases

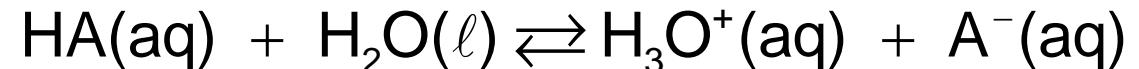


- Strong acids and strong bases completely dissociate in solution
- Weak acids and weak bases only partially dissociate in solution
  - Partial dissociation is due to an equilibrium for the weak acid or base
- Brønsted–Lowry theory
  - A Brønsted–Lowry acid is a proton donor
  - A Brønsted–Lowry base is a proton acceptor

# Role of Water in the Brønsted–Lowry Theory



- When an acid ionizes in water, the acid transfers a proton to water, creating a hydronium ion,  $\text{H}_3\text{O}^+$



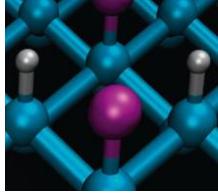
- When a base ionizes in water, water transfers a proton to the base, creating a hydroxide ion,  $\text{OH}^-$



- Amphoteric:** Term used to refer to a substance that can be either an acid or a base

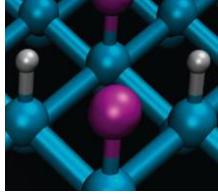


# Role of Water in the Brønsted–Lowry Theory

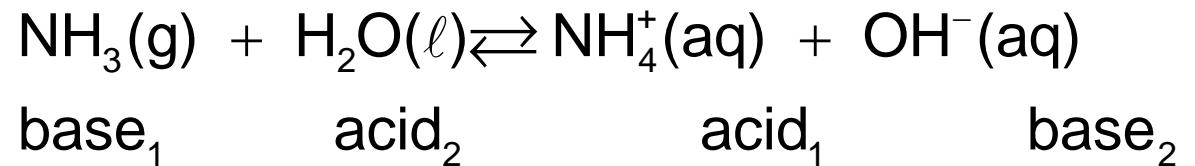


- The reaction between a weak acid or base and water is a dynamic equilibrium
  - The equilibrium is composed of two conjugate acid–base pairs
    - The conjugate acid of a base is the acid formed when the base accepts a proton
    - The conjugate base of an acid is the base formed when the acid donates a proton

# Role of Water in the Brønsted–Lowry Theory

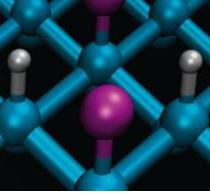


- For the equilibrium between ammonia and water



- NH<sub>3</sub> is the base, and NH<sub>4</sub><sup>+</sup> is the conjugate acid
- H<sub>2</sub>O is the acid, and OH<sup>-</sup> is the conjugate base

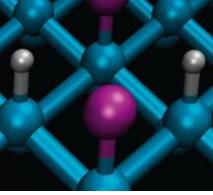
## Example Problem 12.13



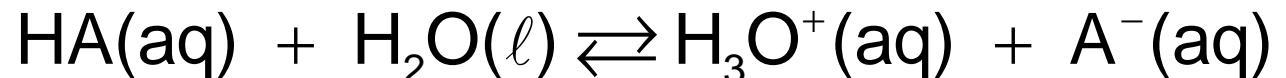
- When dissolved in water,  $\text{CH}_3\text{COOH}$  is called acetic acid. Write the equilibrium for its reaction in water and identify the conjugate acid–base pairs



# Weak Acids and Bases



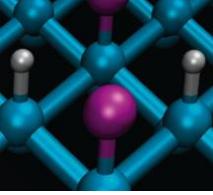
- Weak acids react with water to produce a conjugate acid–base system in which the acid and base in the products are stronger than their respective conjugate acid and base in the reactants
  - Weak acid equilibria favor reactants
  - Only a small percentage of acid molecules ionize



- The  $K$  for the dissociation of a weak acid is called the **acid ionization constant ( $K_a$ )**

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

# Weak Acids and Bases



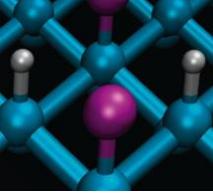
**Table 12.5** Acid ionization constant ( $K_a$ ) values

Acid ionization constants are shown for some common weak acids at 25°C. Larger values of  $K_a$  indicate stronger acids.

Name of Acid	Formula	$K_a$
<i>Organic Acids</i>		
Formic	HCOOH	$1.8 \times 10^{-4}$
Acetic	CH <sub>3</sub> COOH	$1.8 \times 10^{-5}$
Propanoic	CH <sub>3</sub> CH <sub>2</sub> COOH	$1.3 \times 10^{-5}$
Butanoic	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	$1.5 \times 10^{-5}$
Salicylic	C <sub>6</sub> H <sub>4</sub> (OH)COOH	$1.1 \times 10^{-3}$
Gluconic	HOCH <sub>2</sub> (CHOH) <sub>4</sub> COOH	$2.4 \times 10^{-4}$
Heptonic	HOCH <sub>2</sub> (CHOH) <sub>5</sub> COOH	$1.3 \times 10^{-5}$
<i>Inorganic Acids</i>		
Hydrofluoric	HF	$6.3 \times 10^{-4}$
Carbonic	H <sub>2</sub> CO <sub>3</sub>	$4.4 \times 10^{-7}$
Hydrocyanic	HCN	$6.2 \times 10^{-10}$

- Acid ionization constants for some common weak acids at 25°C
- Larger values of  $K_a$  indicate stronger acids

# Weak Acids and Bases



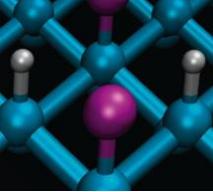
- For weak bases, an ionization equilibrium and the equilibrium expression can be written



- The  $K$  for the reaction of a weak base with water is called the **base ionization constant**,  $K_b$

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

# Weak Acids and Bases

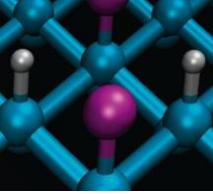


- The hydronium ion concentration for an aqueous solution can be reported as pH
  - pH is a logarithmic scale used to avoid dealing with small numbers in scientific notation

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

- $K_a$  and the initial concentration of a weak acid are required to calculate the hydronium concentration for a weak acid and the pH of the solution

# Weak Acids and Bases

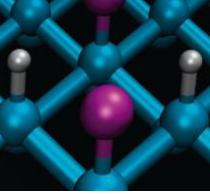


pH	$[H_3O^+]$ mol/L	Common substances in pH range
0	$10^0$	1.0 M HCl
1	$10^{-1}$	HCl in the human stomach
2	$10^{-2}$	
3	$10^{-3}$	Vinegar : $CH_3COOH(aq)$
4	$10^{-4}$	Soft drinks
5	$10^{-5}$	
6	$10^{-6}$	Milk
7	$10^{-7}$	Pure water, blood
8	$10^{-8}$	Seawater
9	$10^{-9}$	
10	$10^{-10}$	Milk of magnesia : $Mg(OH)_2(aq)$
11	$10^{-11}$	Household ammonia
12	$10^{-12}$	
13	$10^{-13}$	
14	$10^{-14}$	1.0 M NaOH

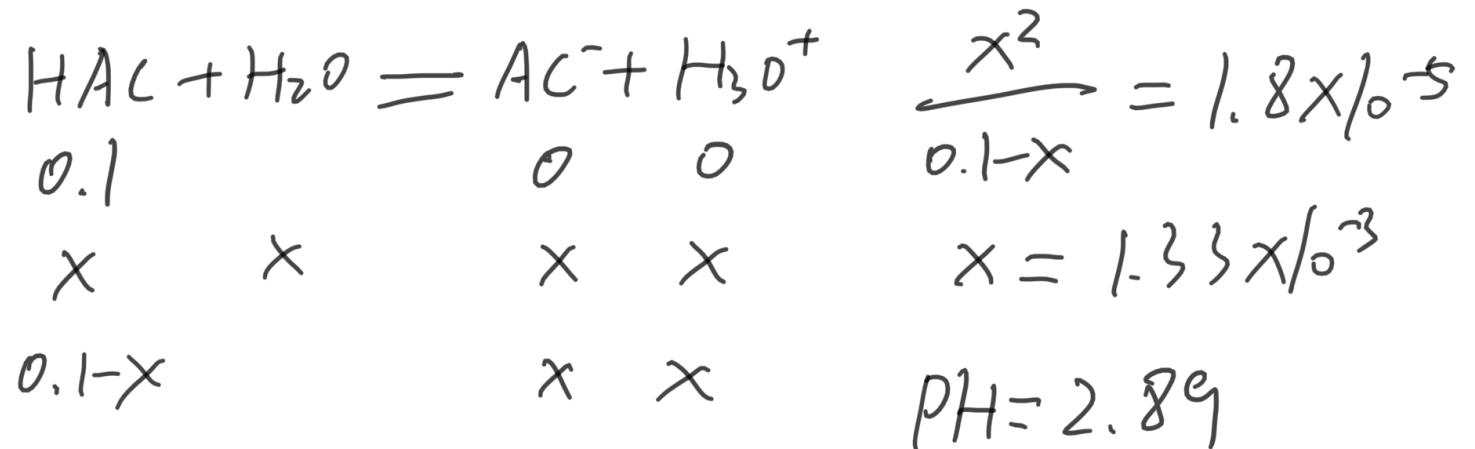
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- The pH scale provides an easy way to measure the relative acidity or basicity of aqueous solutions

## Example Problem 12.14

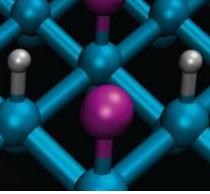


- The  $K_a$  of acetic acid is  $1.8 \times 10^{-5}$ . Calculate the pH of a 0.10 M acetic acid solution



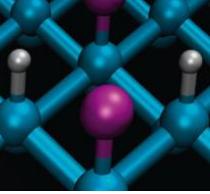
$$\frac{x^2}{0.1} = 1.8 \times 10^{-5} \Rightarrow x = 1.342 \times 10^{-3}$$
$$\text{pH} = 2.94$$

# Free Energy and Chemical Equilibrium



- Equilibrium is a state of minimum free energy
  - $\Delta G = 0$  at equilibrium
- A chemical system tends to move spontaneously toward equilibrium
  - When equilibrium is reached, the change in free energy is zero

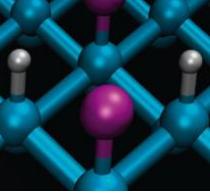
# Free Energy and Nonstandard Conditions



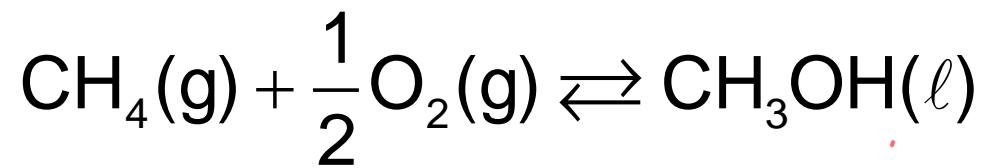
- For reactions with negative free energy changes, the equilibrium is product-favored, or the value of  $K$  is greater than 1
- For reactions with positive free energy changes, the equilibrium is reactant-favored, or the value of  $K$  is less than 1
- The value of the equilibrium constant can be calculated from the Gibbs free energy change or vice versa

$$\Delta G^\circ = -RT \ln K$$

# Example Problem 12.16



- Using tabulated thermodynamic data, calculate the equilibrium constant for the following reaction at 25°C



$$K = \frac{1}{[\text{CH}_4] \cdot [\text{O}_2]^{\frac{1}{2}}} =$$

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