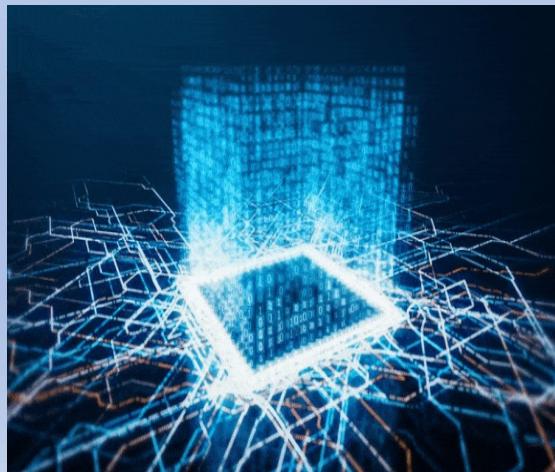
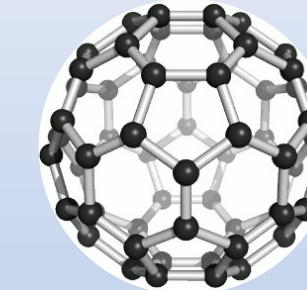
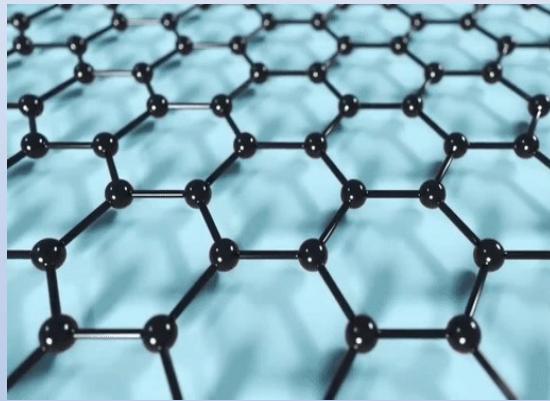


# CSE L-1/T-2: Chemistry

## CHEM 113



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# Chemistry

## *Course Contents*

1. Dual nature of electron and modern concept of chemical bonds
2. Properties and molecular structure
3. *Solutions and properties of dilute solutions*
4. *Introduction to colloids and nanochemistry*
5. *Phase rule*
6. *Phase diagram of monoclonponent systems*

# **Chemistry**

## ***Course Contents***

- 7. *Thermochemistry***
- 8. *Kirchhof's equation and experimental determination of calorific values of foods and fuels***
- 9. Chemistry of biodegradable and conductive polymer**
- 10. *Theory of electrolytic conduction, ionic mobility, transport number***
- 11. Chemistry of proteins, nucleic acids (DNA, RNA), carbohydrates, and lipids**
- 12. Introduction to computational chemistry**

# Chemistry

## Recommended Books

No.	Writer	Book
1	Darrell D. Ebbing and Steven D. Gammon	General Chemistry
2	Peter Atkins and Julio de Paula	Atkins' Physical Chemistry
3	Raymond Chang	Chemistry

# Chemistry

## *Evaluation of the Course*

*The theory course will be evaluated out of 300 marks, the distribution of which is given below:*

<i>Sl. No.</i>	<i>Items</i>	<i>Marks</i>
01	Class Participation	10%
02	Homework, Assignment and Quizzes	20%
03	Final Examination (3 hours)	70%
<b>Total</b>		<b>100%</b>

# Chemistry

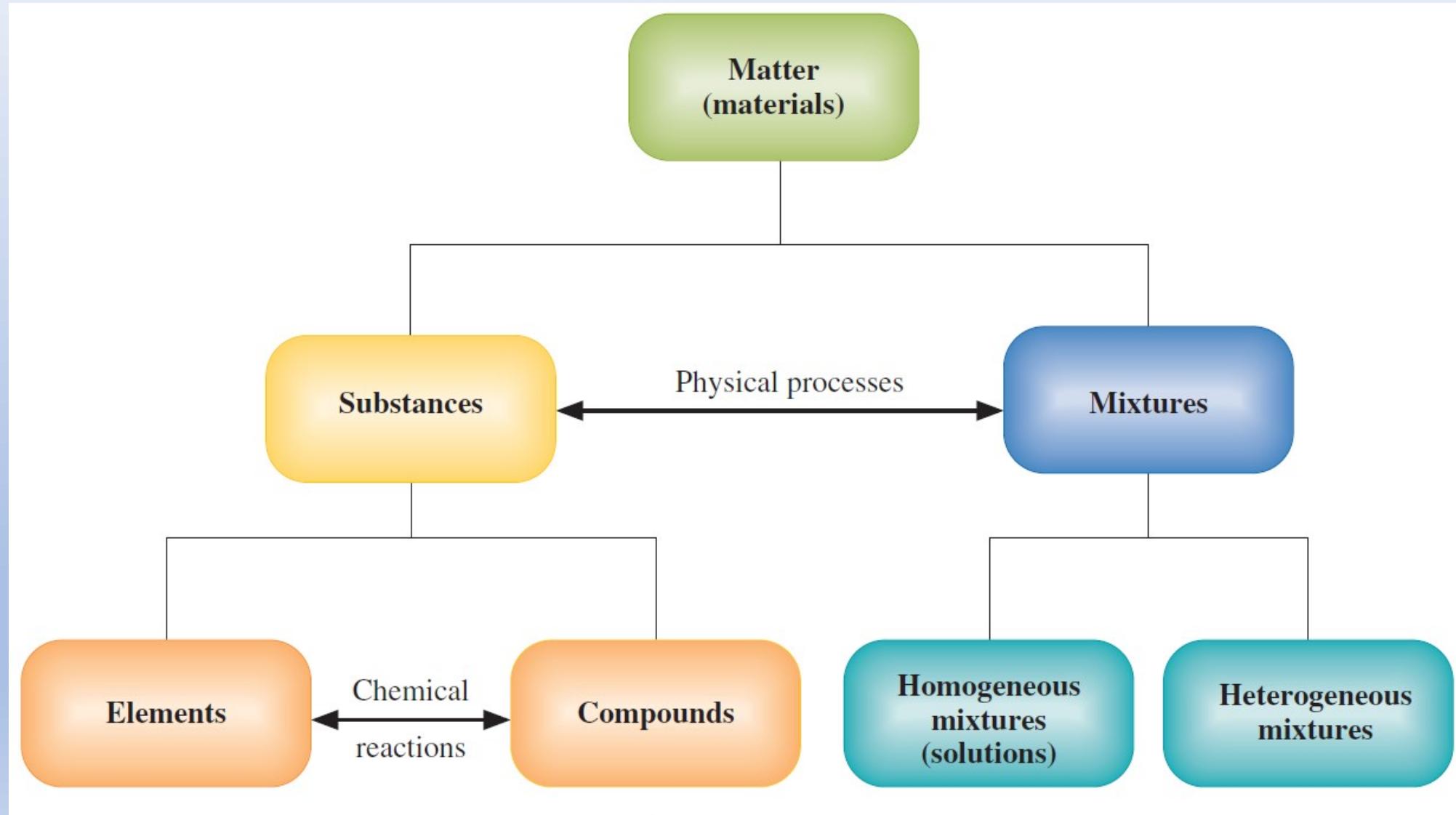
## *Attendance and Participation*

Attendance and Participation	Marks
<b>90% or above</b>	<b>10%</b>
<b>85 to below 90%</b>	<b>9%</b>
<b>80 to below 85%</b>	<b>8%</b>
<b>75 to below 80%</b>	<b>7%</b>
<b>70 to below 75%</b>	<b>6%</b>
<b>65 to below 70%</b>	<b>5%</b>
<b>60 to below 65%</b>	<b>4%</b>
<b>Below 60%</b>	<b>0%</b>

**THANK YOU**

# SOLUTION

# Matter: Physical State and Chemical Constitution

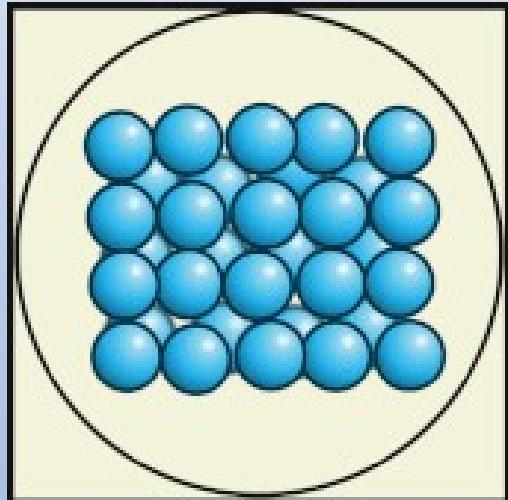


# Matter: Physical State and Chemical Constitution

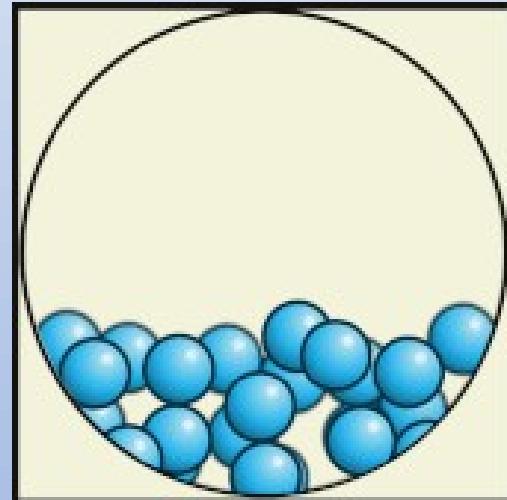
- ❖ A *physical change* is a change in the form of matter but not in its chemical identity.
- ❖ A *chemical change, or chemical reaction*, is a change in which one or more kinds of matter are transformed into a new kind of matter or several new kinds of matter.

# Matter: Physical State and Chemical Constitution

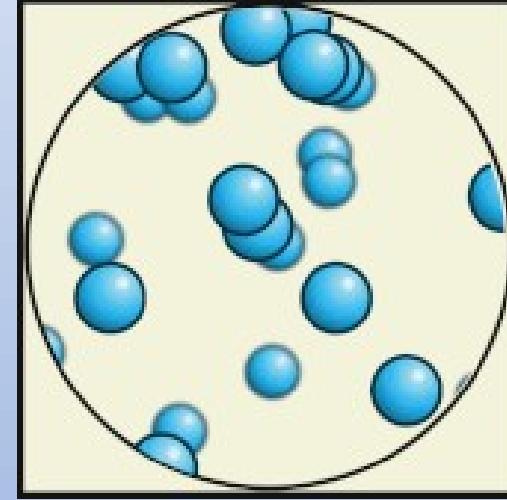
## *States of Matter: Four Fundamental States*



**Solid**



**Liquid**

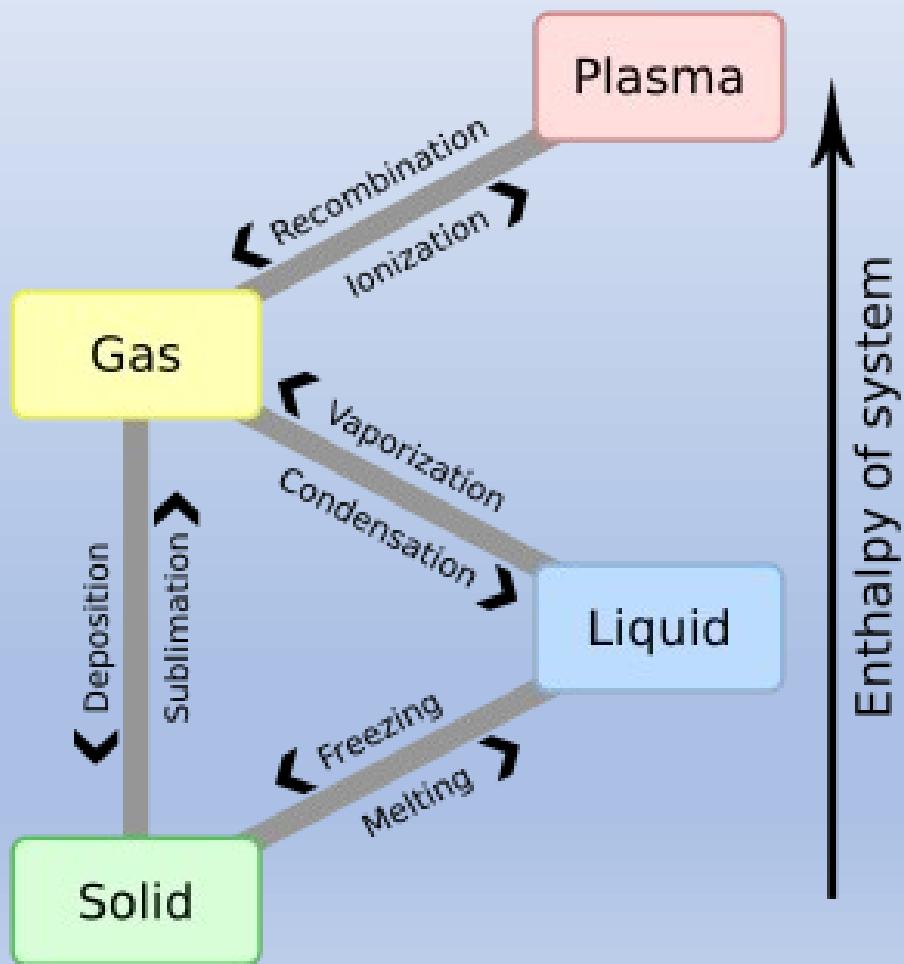


**Gas**



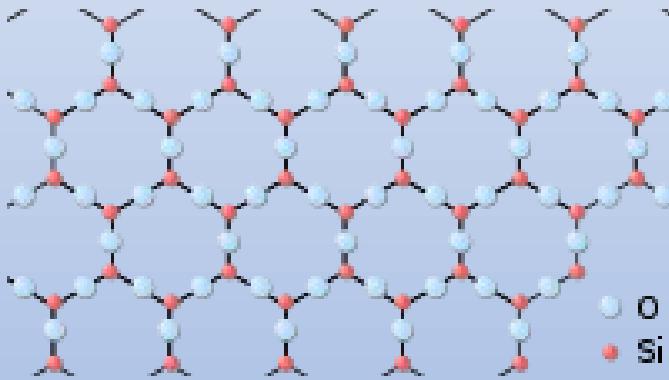
**Plasma**

# Matter: Physical State and Chemical Constitution

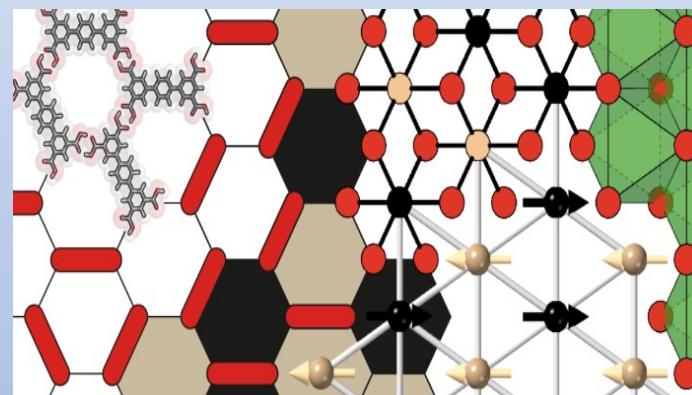


# Matter: Physical State and Chemical Constitution

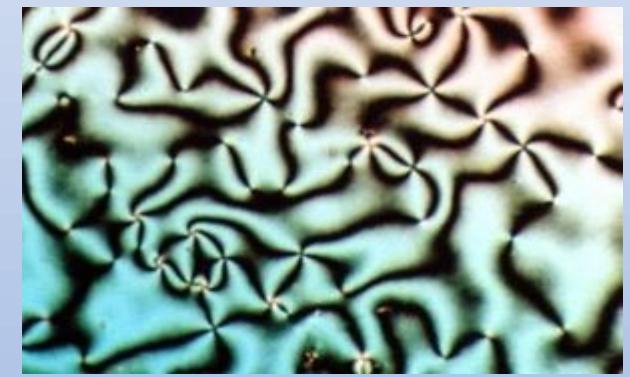
## *States of Matter : Non-classical States*



Glass



Crystals with some Disorders



Liquid Crystals

# Matter: Physical State and Chemical Constitution



# Matter: Physical State and Chemical Constitution

- ❖ A *substance* is a kind of matter that cannot be separated into other kinds of matter by any physical process.
- ❖ A *compound* is a substance composed of two or more elements chemically combined.
- ❖ A *mixture* is a material that can be separated by physical means into two or more substances.
- ❖ A *heterogeneous mixture* is a mixture that consists of physically distinct parts, each with different properties.

# Matter: Physical State and Chemical Constitution

- ❖ A **homogeneous mixture** (also known as a **solution**) is a mixture that is uniform in its properties throughout the given samples.
- ❖ A **phase** is one of several different homogeneous materials present in the portion of matter under study.

# Types of Solutions

A **solution** is a homogeneous mixture of two or more substances.

**TABLE 13.1** Types of Solutions

Solute	Solvent	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water ( $\text{CO}_2$ in water)
Gas	Solid	Solid	$\text{H}_2$ gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	$\text{NaCl}$ in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

# Types of Solutions

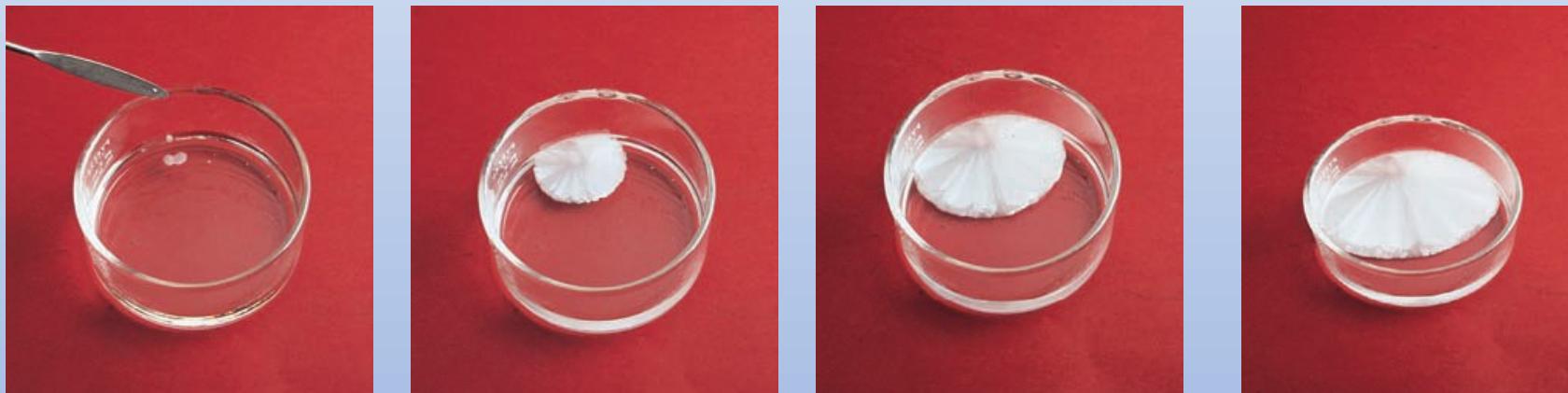
A **solution** is a homogeneous mixture of two or more substances.

- ❖ A solution that contains the maximum amount of a solute in a given solvent, at a specific temperature, is called a ***saturated solution***.
- ❖ Before the saturation point is reached, the solution is said to be ***unsaturated***; it contains less solute than it has the capacity to dissolve.
- ❖ A third type, a ***supersaturated solution***, contains more solute than is present in a saturated solution.

# Supersaturated Solution

Supersaturated solutions are not very stable. In time, some of the solute will come out of a supersaturated solution as crystals.

- ❖ The process in which dissolved solute comes out of solution and forms crystals is called ***crystallization***.



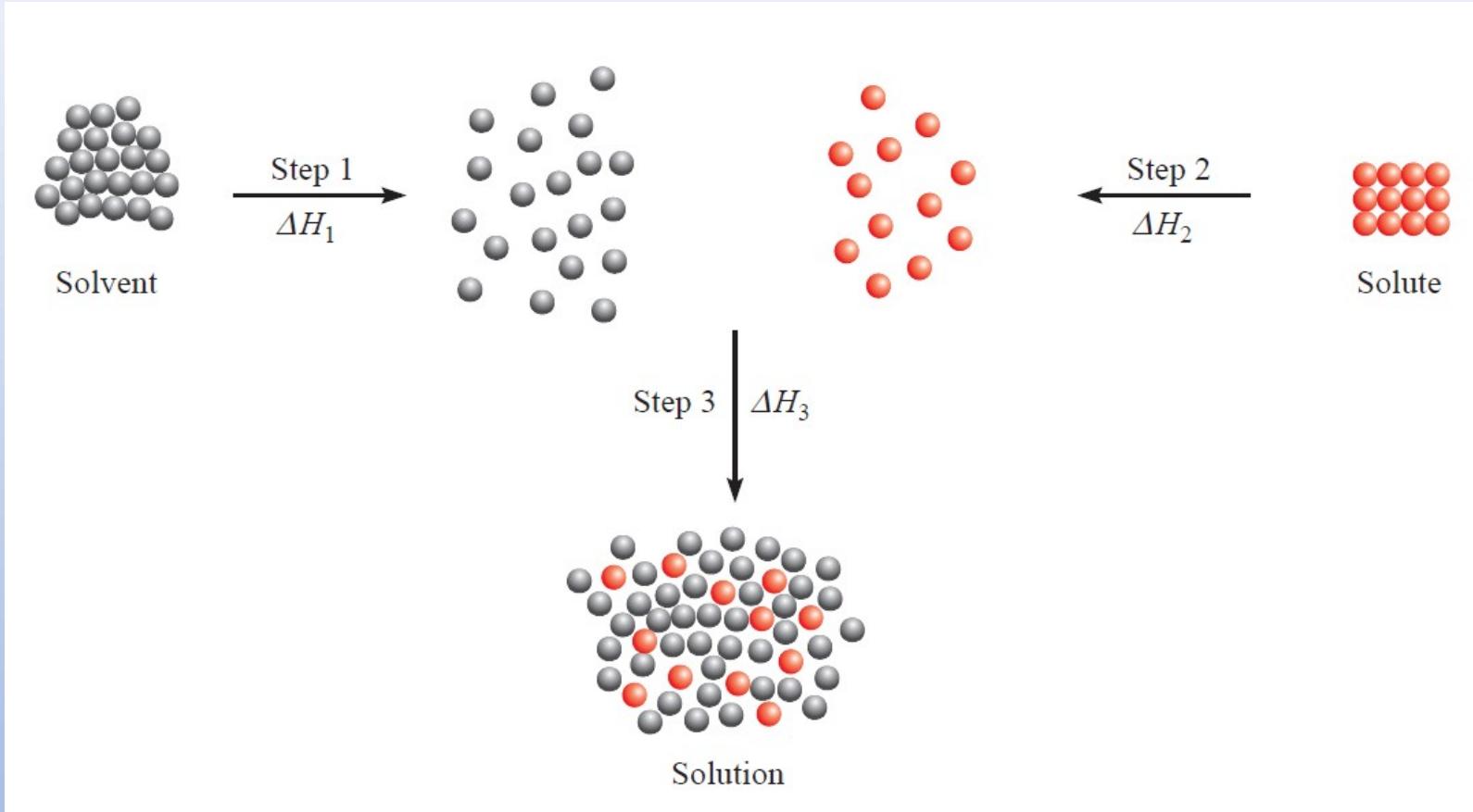
**Fig.** In a supersaturated sodium acetate solution (top), sodium acetate crystals rapidly form when a small seed crystal is added.

# Molecular View of the Solution Process

In liquids and solids, molecules are held together by intermolecular attractions. These forces also play a central role in solution formation.

- ❖ solvent-solvent interaction
- ❖ solute-solute interaction
- ❖ solvent-solute interaction

# Molecular View of the Solution Process



**Fig.** A molecular view of the solution process portrayed as taking place in three steps: First the solvent and solute molecules are separated (steps 1 and 2). Then the solvent and solute molecules mix (step 3).

# Molecular View of the Solution Process

- ❖ Step 1 is the separation of solvent molecules, and step 2 entails the separation of solute molecules.
- ❖ These steps require energy input to break attractive intermolecular forces; therefore, they are endothermic.
- ❖ In step 3, the solvent and solute molecules mix. This step may be exothermic or endothermic.

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

- ❖ If the solute-solvent attraction is stronger than the solvent-solvent attraction and solute-solute attraction, the solution process is favorable: that is, it is exothermic ( $\Delta H_{\text{soln}} < 0$ ).

# Molecular View of the Solution Process

- ❖ Step 1 is the separation of solvent molecules, and step 2 entails the separation of solute molecules.
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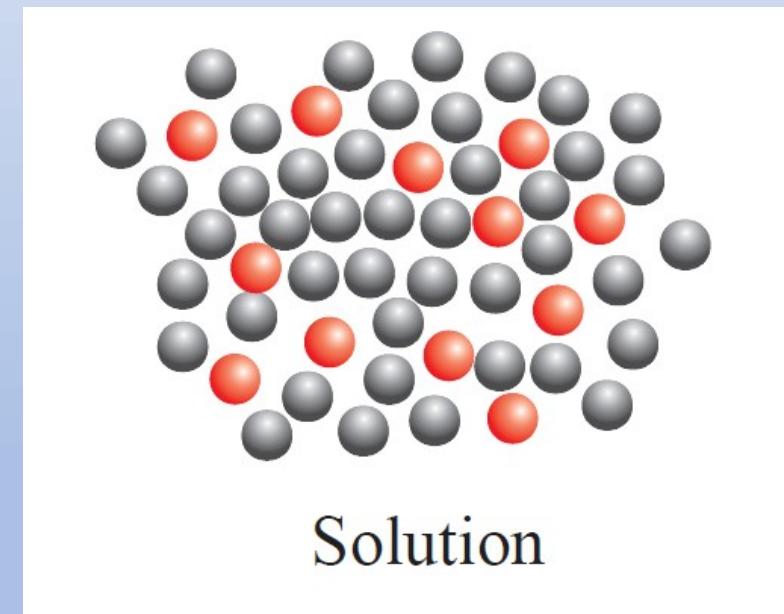
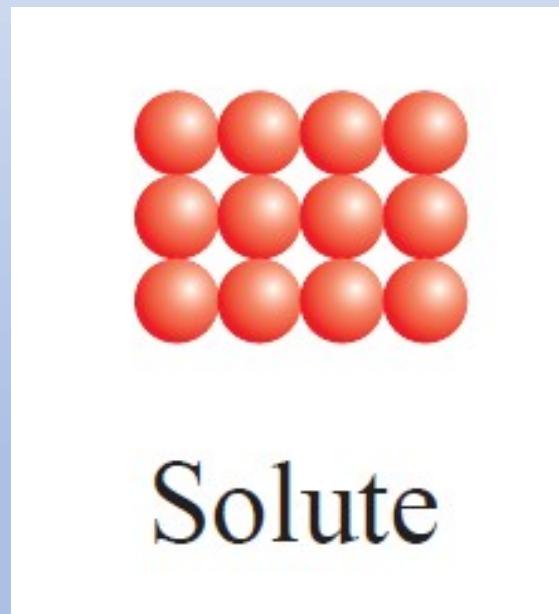
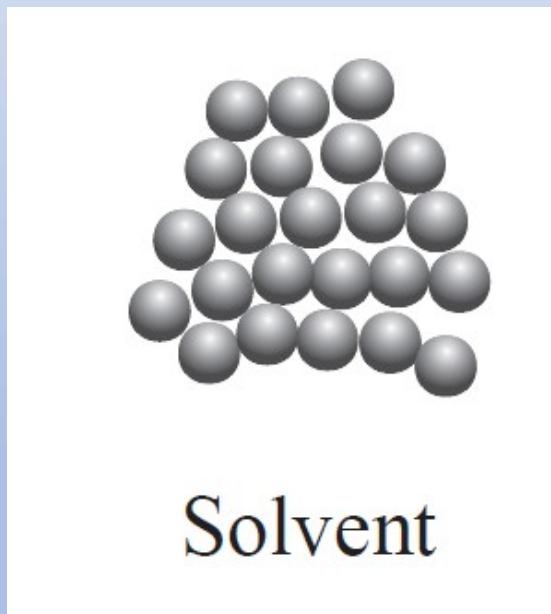
$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

- ❖ If the solute-solvent interaction is weaker than the solvent-solvent and solute-solute interactions, the solution process is endothermic ( $\Delta H_{\text{soln}} > 0$ ).

**Why a solute dissolves in a solvent at all if the attraction among its own molecules is stronger than that between its molecules and the solvent molecules?**

- ❖ The solution process, like all physical and chemical processes, is governed by two factors.
- ❖ One is energy, which determines whether a solution process is exothermic or endothermic.
- ❖ The second factor is an inherent tendency toward disorder in all natural events.
- ❖ When solute and solvent molecules mix to form a solution, there is an increase in randomness or disorder.

Why a solute dissolves in a solvent at all if the attraction among its own molecules is stronger than that between its molecules and the solvent molecules?

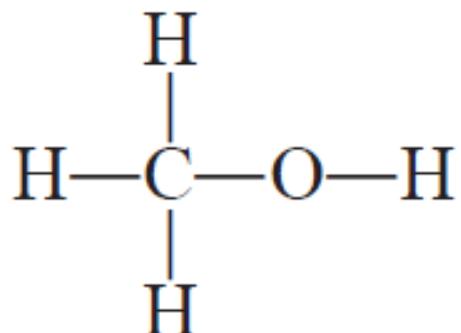


# Solubility

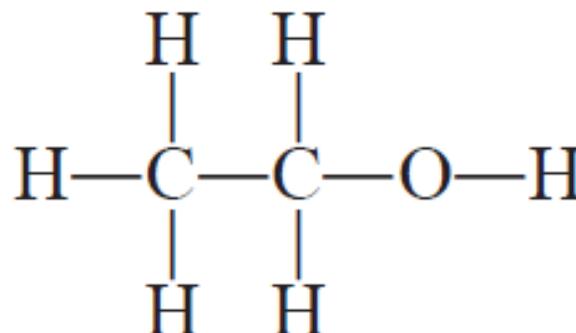
- ❖ Solubility is a measure of the amount of a solute that will dissolve in a solvent at a specific temperature.
- ❖ The saying “like dissolves like” helps in predicting the solubility of a substance in a solvent.
- ❖ What this expression means is that two substances with intermolecular forces of a similar type and magnitude are likely to be soluble in each other.
- ❖ For example, both carbon tetrachloride ( $\text{CCl}_4$ ) and benzene ( $\text{C}_6\text{H}_6$ ) are nonpolar liquids. The only intermolecular forces present in these substances are dispersion forces.

# Solubility

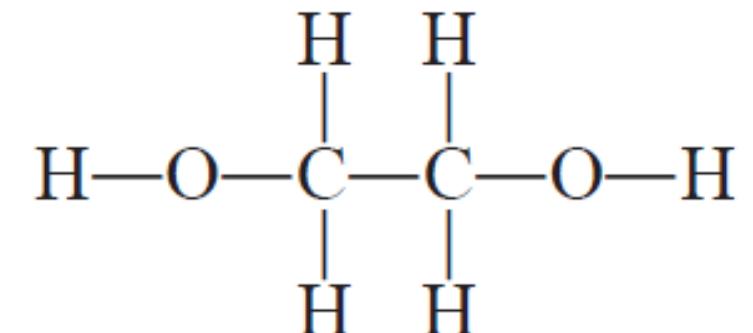
- ❖ When two liquids are completely soluble in each other in all proportions, as in this case, they are said to be ***miscible***.
- ❖ Alcohols such as methanol, ethanol, and ethylene glycol are miscible with water because of their ability to form hydrogen bonds with water molecules.



methanol



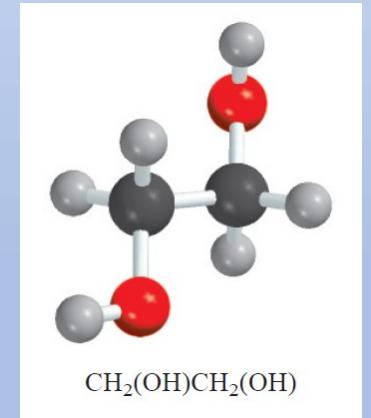
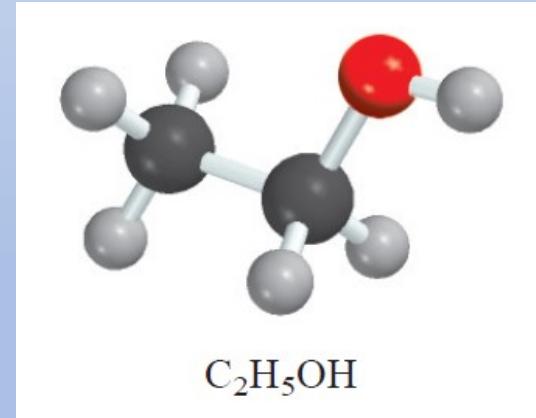
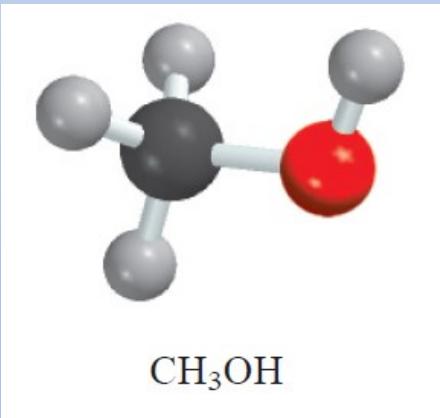
ethanol



1,2-ethylene glycol

# Solubility

- ❖ When two liquids are completely soluble in each other in all proportions, as in this case, they are said to be ***miscible***.
- ❖ Alcohols such as methanol, ethanol, and ethylene glycol are miscible with water because of their ability to form hydrogen bonds with water molecules.



# Solubility

- ❖ When sodium chloride dissolves in water, the ions are stabilized in solution by hydration, which involves ion-dipole interaction.
- ❖ In general, we predict that ionic compounds should be much more soluble in polar solvents, such as water, liquid ammonia, and liquid hydrogen fluoride, than in nonpolar solvents, such as benzene and carbon tetrachloride.
- ❖ Because the molecules of nonpolar solvents lack a dipole moment, they cannot effectively solvate the  $\text{Na}^+$  and  $\text{Cl}^-$  ions.
- ❖ *Solvation* is the process in which an ion or a molecule is surrounded by solvent molecules arranged in a specific manner.
- ❖ When the solvent is water, the process is called *hydration*.

# Solubility

- ❖ The predominant intermolecular interaction between ions and nonpolar compounds is the ion-induced dipole interaction, which is much weaker than the ion-dipole interaction.
- ❖ Consequently, ionic compounds usually have extremely low solubility in nonpolar solvents.

Predict the relative solubilities in the following cases: (a) Bromine ( $\text{Br}_2$ ) in benzene ( $\text{C}_6\text{H}_6$ ,  $\mu = 0$  D) and in water ( $\mu = 1.87$  D), (b) KCl in carbon tetrachloride ( $\text{CCl}_4$ ,  $\mu = 0$  D) and in liquid ammonia ( $\text{NH}_3$ ,  $\mu = 1.46$  D), (c) formaldehyde ( $\text{CH}_2\text{O}$ ) in carbon disulfide ( $\text{CS}_2$ ,  $\mu = 0$ ) and in water.

## *Units for Expressing Concentration*

**Concentration** is a general measurement unit stating the amount of solute present in a known amount of solution.

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}}$$

- ❖ Although the terms “*solute*” and “*solution*” are often associated with *liquid samples*, they can be extended to **gas-phase** and **solid-phase** samples as well.
- ❖ The actual *units* for reporting concentration depend on **how the amounts of solute and solution are measured**.

## *Units for Expressing Concentration*

**Table 2.4** Common Units for Reporting Concentration

Name	Units <sup>a</sup>	Symbol
molarity	$\frac{\text{moles solute}}{\text{liters solution}}$	M
formality	$\frac{\text{number FWs solute}}{\text{liters solution}}$	F
normality	$\frac{\text{number EWs solute}}{\text{liters solution}}$	N
molality	$\frac{\text{moles solute}}{\text{kg solvent}}$	m
weight %	$\frac{\text{g solute}}{100 \text{ g solution}}$	% w/w
volume %	$\frac{\text{mL solute}}{100 \text{ mL solution}}$	% v/v
weight-to-volume %	$\frac{\text{g solute}}{100 \text{ mL solution}}$	% w/v
parts per million	$\frac{\text{g solute}}{10^6 \text{ g solution}}$	ppm
parts per billion	$\frac{\text{g solute}}{10^9 \text{ g solution}}$	ppb

<sup>a</sup>FW = formula weight; EW = equivalent weight.

# Units for Expressing Concentration

## *Molarity and Formality*

**Both** molarity and formality express concentration as *moles of solute per liter of solution*.

There is, however, a **subtle difference** between molarity and formality.

**Molarity** is the concentration of a particular chemical species in solution.

**Formality**, on the other hand, is a substance's total concentration in solution without regard to its specific chemical form.

**Molarity:** The number of moles of solute per liter of solution (**M**)

**Formality:** The number of moles of solute, regardless of chemical form, per liter of solution (**F**)

# Units for Expressing Concentration

## *Molarity and Formality*

### Molarity and Formality of NaCl

Dissolving 0.1 mol of NaCl in 1 L of water gives a solution containing 0.1 mol of  $\text{Na}^+$  and 0.1 mol of  $\text{Cl}^-$ .

The *molarity* of NaCl, therefore, is *zero* since there is essentially no undissociated NaCl in solution.

The solution, instead, is 0.1 M in  $\text{Na}^+$  and 0.1 M in  $\text{Cl}^-$ .

The *formality* of NaCl, however, is *0.1 F* because it represents the total amount of NaCl in solution.

*When we state that a solution is 0.1 M NaCl we understand it to consist of  $\text{Na}^+$  and  $\text{Cl}^-$  ions.*

# Units for Expressing Concentration

## *Molarity and Formality*

### Molarity and Formality of NaCl and Glucose

Dissolve 1 mole of glucose in 1L water.

Molarity: 1 M

Formality: 1 F

Dissolve 1 mole of NaCl in 1L water.

Molarity: 0 M

Formality: 1 F

Molarity of Na<sup>+</sup>: 1 M

Molarity of Cl<sup>-</sup>: 1M

## Units for Expressing Concentration

### *Normality*

**Normality** uses the *chemical equivalent*, which is the amount of one chemical species reacting stoichiometrically with another chemical species.

Normality is *a function of the chemical reaction* in which the species participates.

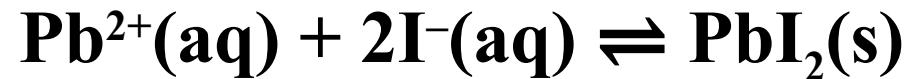
Although a solution of  $\text{H}_2\text{SO}_4$  has a *fixed molarity*, its *normality depends on how it reacts*.

The number of *equivalents, n*, is based on a reaction unit, which is that *part of a chemical species* involved in a reaction.

## Units for Expressing Concentration

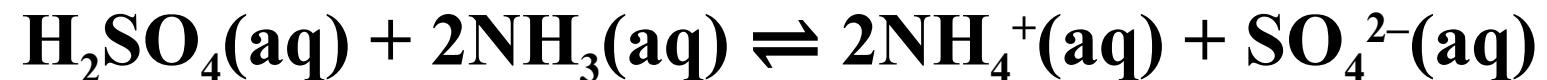
### *Normality*

The number of *equivalents*, *n*, is based on a reaction unit, which is that *part of a chemical species* involved in a reaction.



*n* = 2 for  $\text{Pb}^{2+}$ , and *n* = 1 for  $\text{I}^-$

In an *acid–base reaction*, the reaction unit is the *number of  $\text{H}^+$  ions* donated by an acid or accepted by a base.



*n* = 2 for  $\text{H}_2\text{SO}_4$  and *n* = 1 for  $\text{NH}_3$

## Units for Expressing Concentration

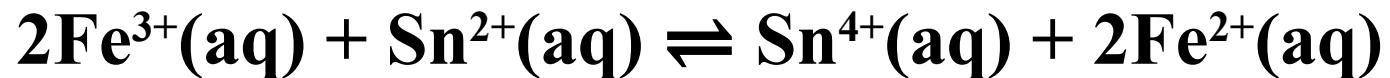
### *Normality*

For a *complexation reaction*, the reaction unit is the *number of electron pairs* that can be accepted by the metal or donated by the ligand.



$n = 2$  for  $\text{Ag}^+$  and  $n = 1$  for  $\text{NH}_3$

In an *oxidation-reduction reaction*, the reaction unit is the *number of electrons* released by the reducing agent or accepted by the oxidizing agent.



$n = 1$  for  $\text{Fe}^{3+}$  and  $n = 2$  for  $\text{Sn}^{2+}$

## Units for Expressing Concentration

### Normality

**Normality** is the number of *equivalent weights (EW) per unit volume* and, like formality, is independent of speciation.

An *equivalent weight* is defined as the *ratio of a chemical species' formula weight (FW) to the number of its equivalents*.

$$EW = \frac{FW}{n}$$

Consequently, the following simple relationship exists between normality and molarity.

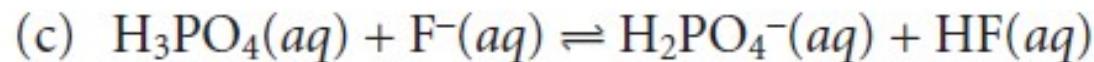
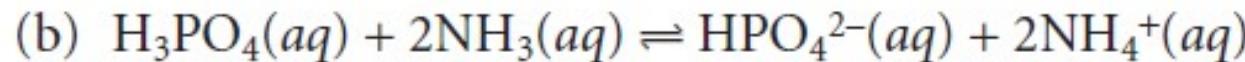
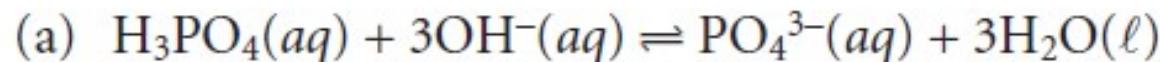
$$N = n \times M$$

## Units for Expressing Concentration

### *Normality*

#### EXAMPLE 2.I

- Calculate the equivalent weight and normality for a solution of 6.0 M H<sub>3</sub>PO<sub>4</sub> given the following reactions:



#### SOLUTION

For phosphoric acid, the number of equivalents is the number of H<sup>+</sup> ions donated to the base. For the reactions in (a), (b), and (c) the number of equivalents are 3, 2, and 1, respectively. Thus, the calculated equivalent weights and normalities are

## Units for Expressing Concentration

### Normality

#### EXAMPLE 2.1

- Calculate the equivalent weight and normality for a solution of 6.0 M H<sub>3</sub>PO<sub>4</sub> given the following reactions:
  - H<sub>3</sub>PO<sub>4</sub>(aq) + 3OH<sup>-</sup>(aq) ⇌ PO<sub>4</sub><sup>3-</sup>(aq) + 3H<sub>2</sub>O(l)
  - H<sub>3</sub>PO<sub>4</sub>(aq) + 2NH<sub>3</sub>(aq) ⇌ HPO<sub>4</sub><sup>2-</sup>(aq) + 2NH<sub>4</sub><sup>+</sup>(aq)
  - H<sub>3</sub>PO<sub>4</sub>(aq) + F<sup>-</sup>(aq) ⇌ H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq) + HF(aq)

$$(a) \text{ EW} = \frac{\text{FW}}{n} = \frac{97.994}{3} = 32.665 \quad N = n \times M = 3 \times 6.0 = 18 \text{ N}$$

$$(b) \text{ EW} = \frac{\text{FW}}{n} = \frac{97.994}{2} = 48.997 \quad N = n \times M = 2 \times 6.0 = 12 \text{ N}$$

$$(c) \text{ EW} = \frac{\text{FW}}{n} = \frac{97.994}{1} = 97.994 \quad N = n \times M = 1 \times 6.0 = 6.0 \text{ N}$$

## Units for Expressing Concentration

### *Molality*

***Molality***: The number of moles of solute per kilogram of solvent (m).

***Molality*** is used in thermodynamic calculations where a ***temperature-independent*** unit of concentration is needed.

Molarity, formality, and normality are ***based on the volume*** of the solution in which the solute is dissolved.

Since ***density*** is a temperature-dependent property a solution's volume, and thus its molar, formal, and normal concentrations, ***will change as a function of its temperature***.

## Units for Expressing Concentration

### Molality

By using the *solvent's mass* in place of its *volume*, the resulting concentration becomes *independent of temperature*.

Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water. The molar mass of sulfuric acid is 98.08 g.

The density of a 2.45 M aqueous solution of methanol ( $\text{CH}_3\text{OH}$ ) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid ( $\text{H}_3\text{PO}_4$ ). The molar mass of phosphoric acid is 98.00 g.

## Units for Expressing Concentration

### *Weight, Volume, and Weight-to-Volume Ratios*

***Weight percent:*** Grams of solute per 100 g of solution, (% w/w).

***Volume percent:*** Milliliters of solute per 100 mL of solution, (% v/v).

***Weight-to-volume percent:*** Grams of solute per 100 mL of solution, (% w/v).

## Units for Expressing Concentration

### *Weight, Volume, and Weight-to-Volume Ratios*

***Parts per million:*** *Micrograms of solute per gram of solution;* for aqueous solutions, the units are often expressed as *milligrams of solute per liter of solution* (ppm).

$$\text{ppm} = \frac{\text{mg}}{\text{Liter}} = \frac{\mu\text{g}}{\text{mL}}$$

***Parts per billion:*** *Nanograms of solute per gram of solution;* for aqueous solutions, the units are often expressed as *micrograms of solute per liter* of solution (ppb).

$$\text{ppb} = \frac{\mu\text{g}}{\text{Liter}} = \frac{\text{ng}}{\text{mL}}$$

## Units for Expressing Concentration

### *Converting Between Concentration Units*

The units of concentration most frequently encountered in analytical chemistry are *molarity*, *weight percent*, *volume percent*, *weight-to-volume percent*, *parts per million*, and *parts per billion*.

By recognizing the general definition of concentration given in the following equation, it is easy to convert between concentration units.

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}}$$

## Units for Expressing Concentration

### *Converting Between Concentration Units*

#### **EXAMPLE 2.2**

- A concentrated solution of aqueous ammonia is 28.0% w/w NH<sub>3</sub> and has a density of 0.899 g/mL. What is the molar concentration of NH<sub>3</sub> in this solution?

#### **SOLUTION**

$$\frac{28.0 \text{ g NH}_3}{100 \text{ g solution}} \times \frac{0.899 \text{ g solution}}{\text{mL solution}} \times \frac{1 \text{ mole NH}_3}{17.04 \text{ g NH}_3} \times \frac{1000 \text{ mL}}{\text{liter}} = 14.8 \text{ M}$$

#### **EXAMPLE 2.3**

- The maximum allowed concentration of chloride in a municipal drinking water supply is  $2.50 \times 10^2$  ppm Cl<sup>-</sup>. When the supply of water exceeds this limit, it often has a distinctive salty taste. What is this concentration in moles Cl<sup>-</sup>/liter?

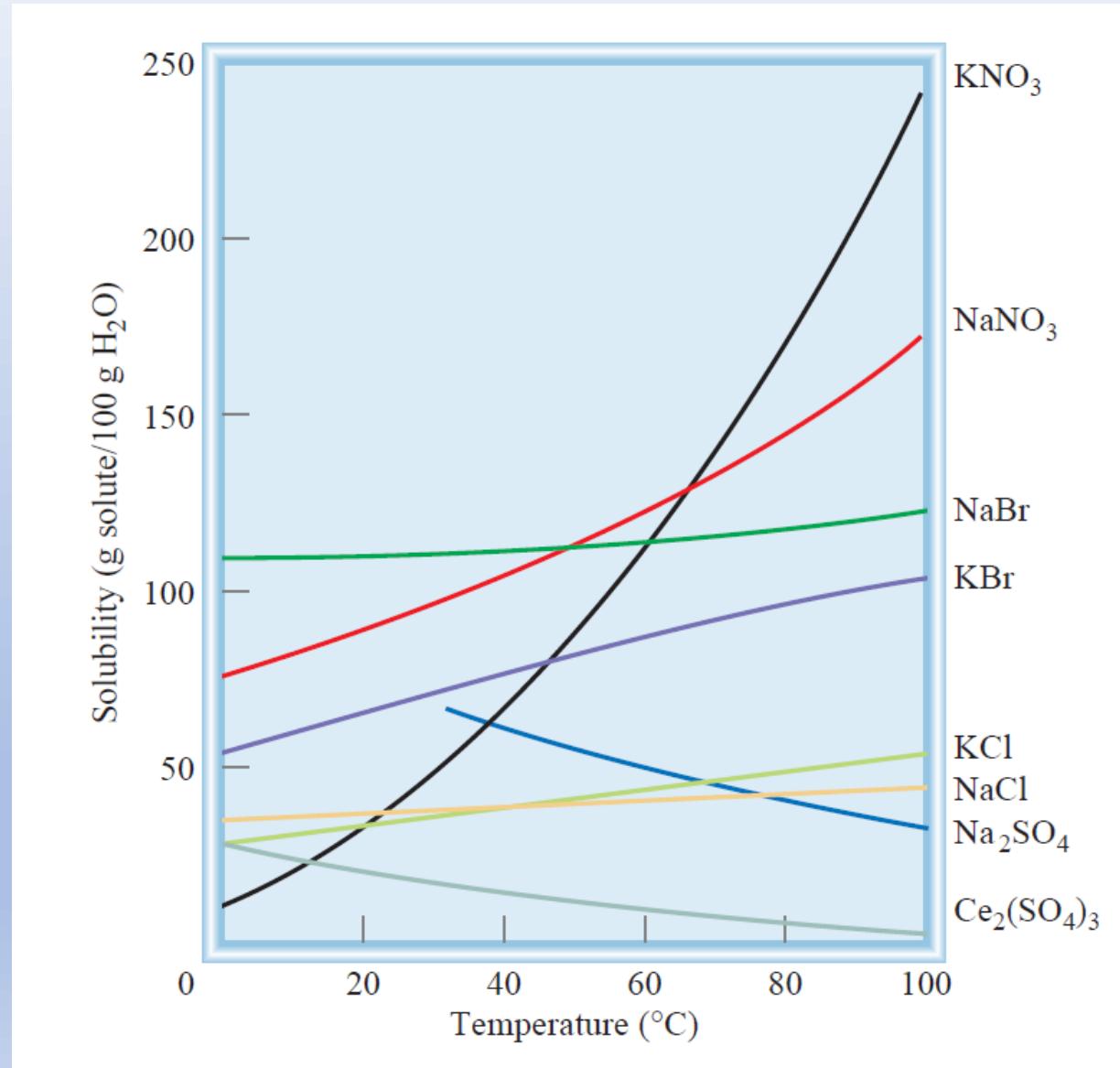
#### **SOLUTION**

$$\frac{2.50 \times 10^2 \text{ mg Cl}^-}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mole Cl}^-}{35.453 \text{ g Cl}^-} = 7.05 \times 10^{-3} \text{ M}$$

# Effect of Temperature on Solubility

- ❖ Solubility is defined as the maximum amount of a solute that will dissolve in a given quantity of solvent at a *specific temperature*.
- ❖ For most substances, temperature affects solubility.

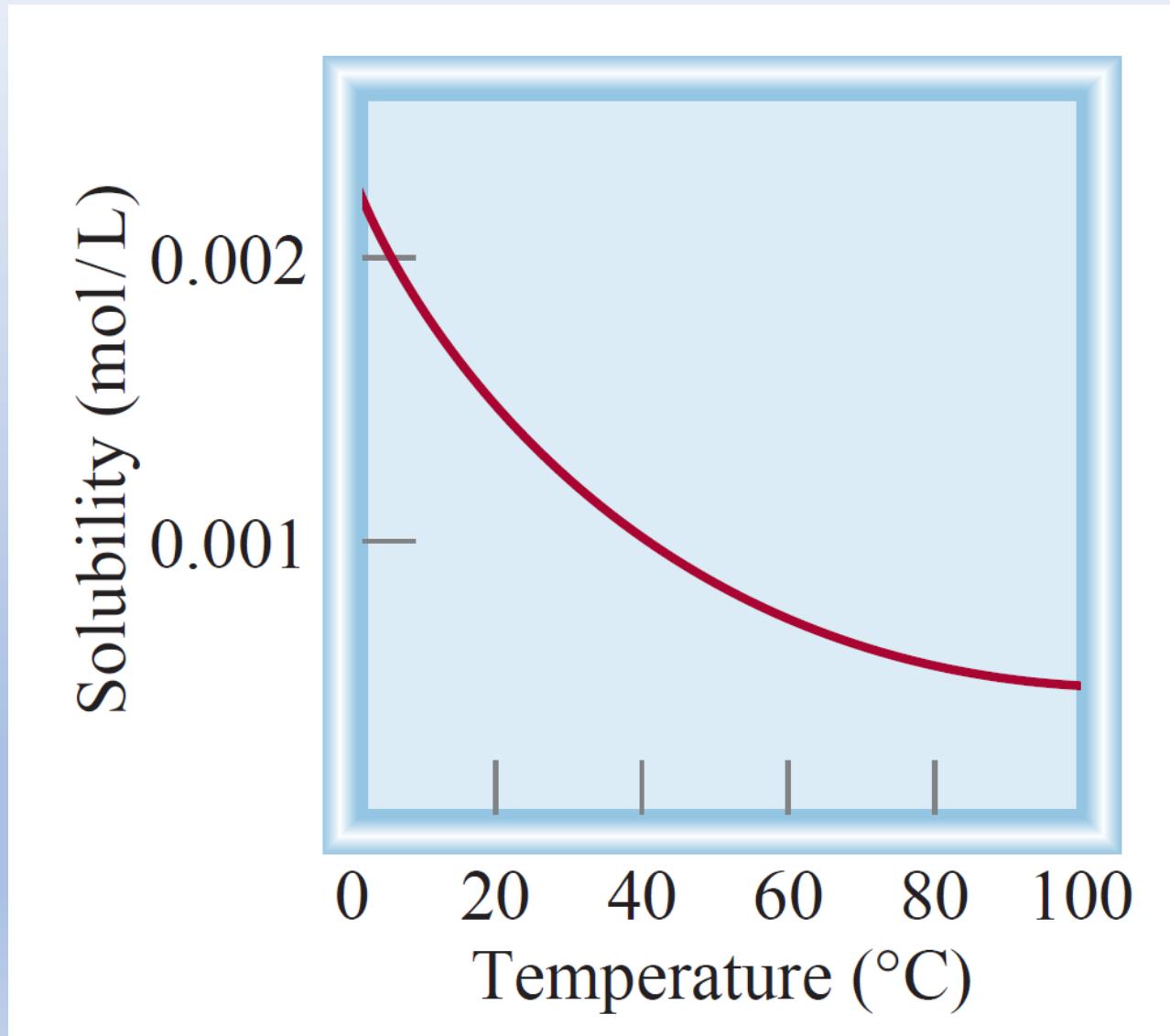
# Solid Solubility and Temperature



# Solid Solubility and Temperature

- ❖ In most but certainly not all cases, the solubility of a solid substance increases with temperature.
- ❖ However, there is no clear correlation between the sign of  $\Delta H_{soln}$  and the variation of solubility with temperature.
- ❖ For example, the solution process of  $\text{CaCl}_2$  is exothermic and that of  $\text{NH}_4\text{NO}_3$  is endothermic.
- ❖ But the solubility of both compounds increases with increasing temperature.
- ❖ In general, the effect of temperature on solubility is best determined experimentally.

# Gas Solubility and Temperature



# Gas Solubility and Temperature

- ❖ The solubility of gases in water usually decreases with increasing temperature.
- ❖ When water is heated in a beaker, you can see bubbles of air forming on the side of the glass before the water boils.
- ❖ As the temperature rises, the dissolved air molecules begin to “boil out” of the solution long before the water itself boils.
- ❖ The reduced solubility of molecular oxygen in hot water has a direct bearing on ***thermal pollution***, that is, *the heating of the environment—usually waterways—to temperatures that are harmful to its living inhabitants*.

# Gas Solubility and Temperature

- ❖ It is estimated that every year in the United States some 100,000 billion gallons of water are used for industrial cooling, mostly in electric power and nuclear power production.
- ❖ This process heats up the water, which is then returned to the rivers and lakes from which it was taken.
- ❖ Ecologists have become increasingly concerned about the effect of thermal pollution on aquatic life.
- ❖ Fish, like all other cold-blooded animals, have much more difficulty coping with rapid temperature fluctuation in the environment than humans do.

# Gas Solubility and Temperature

- ❖ An increase in water temperature accelerates their rate of metabolism, which generally doubles with each 10 °C rise.
- ❖ The speedup of metabolism increases the fish's need for oxygen at the same time that the supply of oxygen decreases because of its lower solubility in heated water.
- ❖ Effective ways to cool power plants while doing only minimal damage to the biological environment are being sought.

# Gas Solubility and Temperature

- ❖ On the lighter side, a knowledge of the variation of gas solubility with temperature can improve one's fishing.
- ❖ On a hot summer day, an experienced fisherman usually picks a deep spot in the river or lake to cast the bait.
- ❖ Because the oxygen content is greater in the deeper, cooler region, most fish will be found there.

# Effect of Pressure on the Solubility of Gases

- ❖ For all practical purposes, external pressure has no influence on the solubilities of liquids and solids, but it does greatly affect the solubility of gases.
- ❖ The quantitative relationship between gas solubility and pressure is given by *Henry's law*, which states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:

$$c \propto P$$

$$c = kP$$

Here,  $c$  is the molar concentration (moles per liter) of the dissolved gas;  $P$  is the pressure (in atmospheres) of the gas over the solution; and, for a given gas,  $k$  is a constant.

# Effect of Pressure on the Solubility of Gases

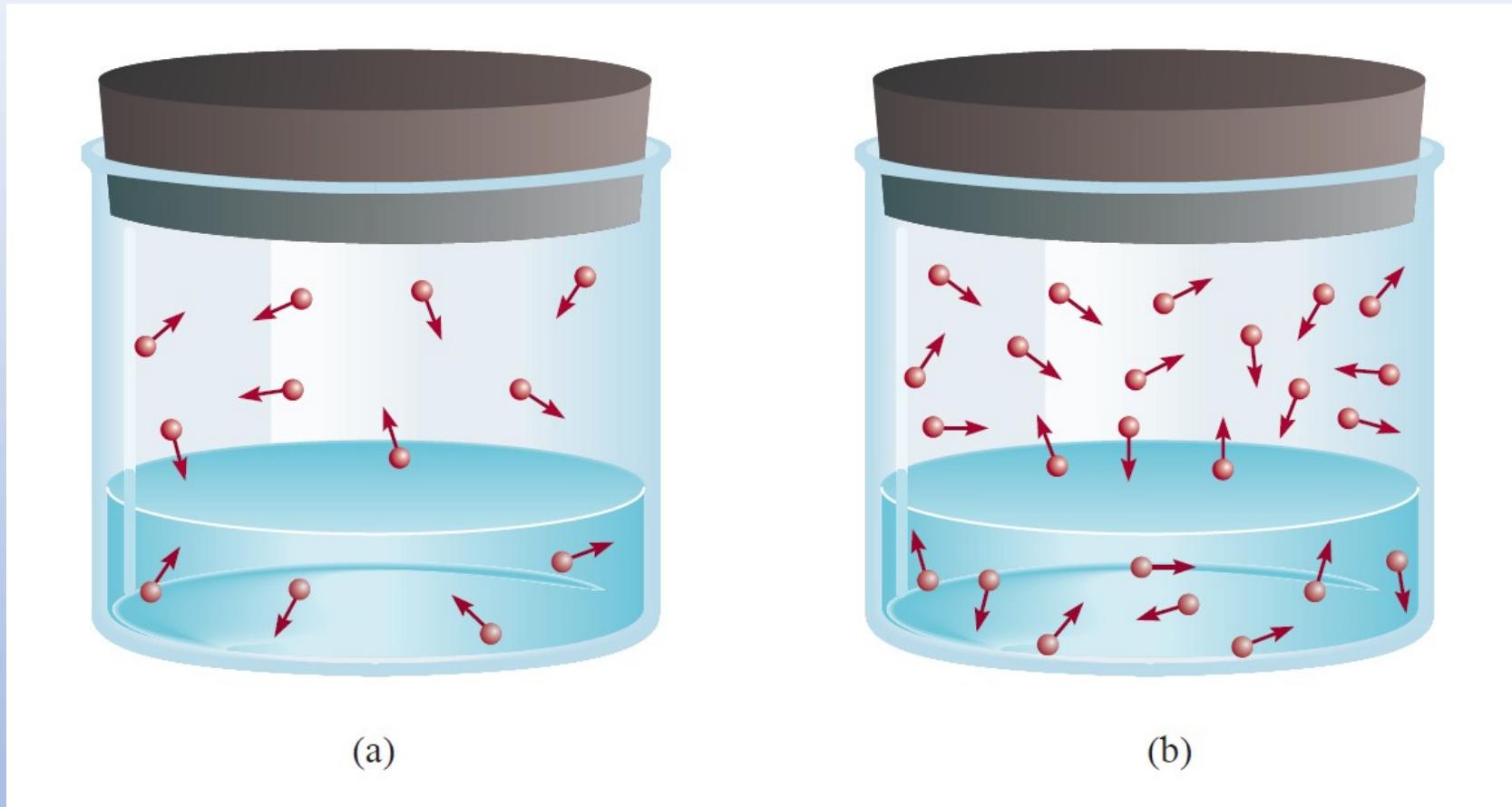


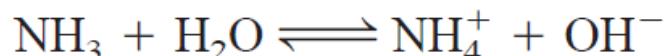
Fig. A molecular interpretation of Henry's law.

# Effect of Pressure on the Solubility of Gases

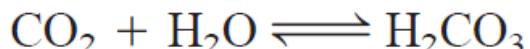
The solubility of nitrogen gas at 25°C and 1 atm is  $6.8 \times 10^{-4}$  mol/L. What is the concentration of nitrogen dissolved in water under atmospheric conditions? The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

# Effect of Pressure on the Solubility of Gases

Most gases obey Henry's law, but there are some important exceptions. For example, if the dissolved gas *reacts* with water, higher solubilities can result. The solubility of ammonia is much higher than expected because of the reaction



Carbon dioxide also reacts with water, as follows:



Another interesting example is the dissolution of molecular oxygen in blood. Normally, oxygen gas is only sparingly soluble in water (see the Practice Exercise in Example 13.5). However, its solubility in blood is dramatically greater because of the high content of hemoglobin (Hb) molecules. Each hemoglobin molecule can bind up to four oxygen molecules, which are eventually delivered to the tissues for use in metabolism:



This is the process that accounts for the high solubility of molecular oxygen in blood.

# Colligative Properties

- ❖ Several important *properties of solutions* depend on the *number of solute particles* in solution and **not on the nature of the solute particles**.
- ❖ These properties are called colligative properties (or *collective properties*) because they are *bound together* by a common origin; that is, they all depend on the number of solute particles present, whether these particles are atoms, ions, or molecules.

- Vapor-pressure lowering
- Boiling-point elevation
- Freezing-point depression
- Osmotic pressure

# Vapor-Pressure Lowering

- ❖ If a solute is ***nonvolatile*** (that is, it *does not have a measurable vapor pressure*), the vapor pressure of its solution is always **less than that of the pure solvent**.
- ❖ Thus, the relationship between solution vapor pressure and **solvent vapor pressure depends on the concentration of the solute in the solution**.
- ❖ This relationship is given by ***Raoult's law*** (after the French chemist Francois Raoult), which states that *the partial pressure of a solvent over a solution,  $P_1$ , is given by the vapor pressure of the pure solvent,  $P_1^0$ , times the mole fraction of the solvent in the solution,  $X_1$* :

$$P_1 = X_1 P_1^0$$

# Vapor-Pressure Lowering

- ❖ If a solute is ***nonvolatile*** (that is, it *does not have a measurable vapor pressure*), the vapor pressure of its solution is always **less than that of the pure solvent**.
- ❖ Thus, **the relationship between solution vapor pressure and solvent vapor pressure depends on the concentration of the solute in the solution.**
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# Vapor-Pressure Lowering

- ❖ In a solution containing only one solute,  $X_1 = 1 - X_2$

$$P_1 = (1 - X_2)P_1^\circ$$

$$P_1^\circ - P_1 = \Delta P = X_2 P_1^\circ$$

- ❖ The decrease in vapor pressure,  $\Delta P$ , is directly proportional to the concentration (measured in mole fraction) of the solute present.

TABLE 5.2

Pressure of Water  
Vapor at Various  
Temperatures

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00

# Vapor-Pressure Lowering

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30°C. What is the vapor-pressure lowering? The vapor pressure of pure water at 30°C is given in Table 5.2. Assume the density of the solution is 1.00 g/mL.

# Why is the vapor pressure of a solution less than that of its pure solvent?

- ❖ One driving force in physical and chemical processes is the increase in disorder—the greater the disorder created, the more favorable the process.
- ❖ Vaporization increases the disorder of a system because molecules in a vapor have less order than those in a liquid.
- ❖ Because a solution is more disordered than a pure solvent, the difference in disorder between a solution and a vapor is less than that between a pure solvent and a vapor.

# Vapor Pressure Lowering

❖ If both components of a solution are volatile (that is, have measurable vapor pressure), the vapor pressure of the solution is the sum of the individual partial pressures.

❖ Raoult's law holds equally well in this case:

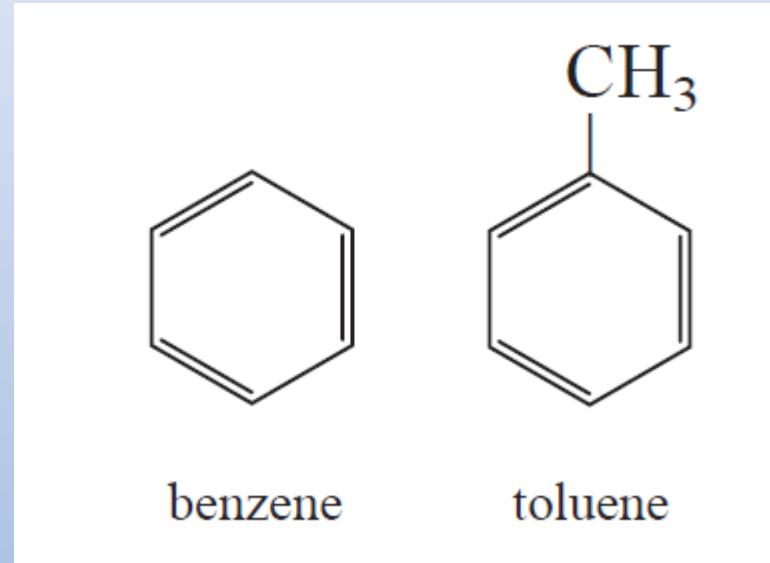
$$P_A = X_A P_A^\circ$$
$$P_B = X_B P_B^\circ$$

❖ The total pressure is given by Dalton's law of partial pressure.

$$P_T = P_A + P_B$$

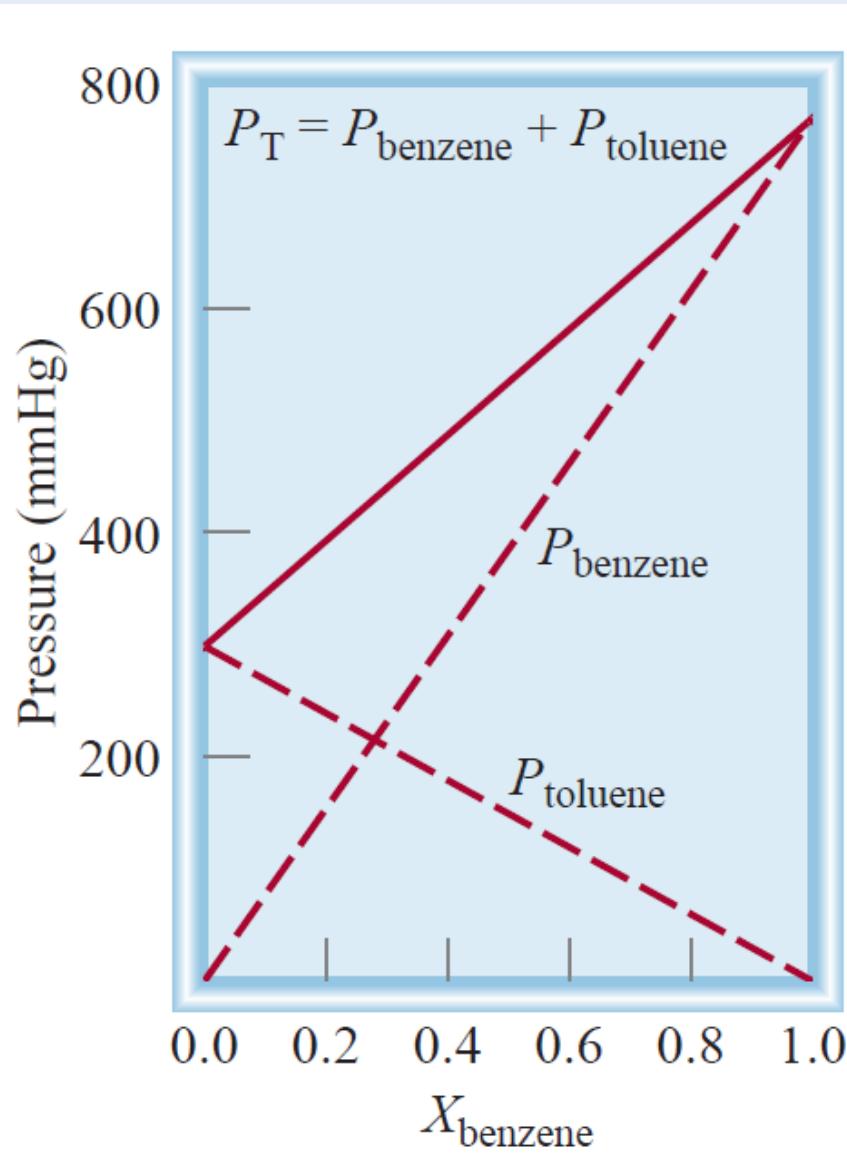
# Vapor Pressure Lowering

- ❖ Benzene and toluene have similar structures and therefore similar intermolecular forces:



- ❖ In a solution of benzene and toluene, the vapor pressure of each component obeys Raoult's law.

# Vapor Pressure Lowering

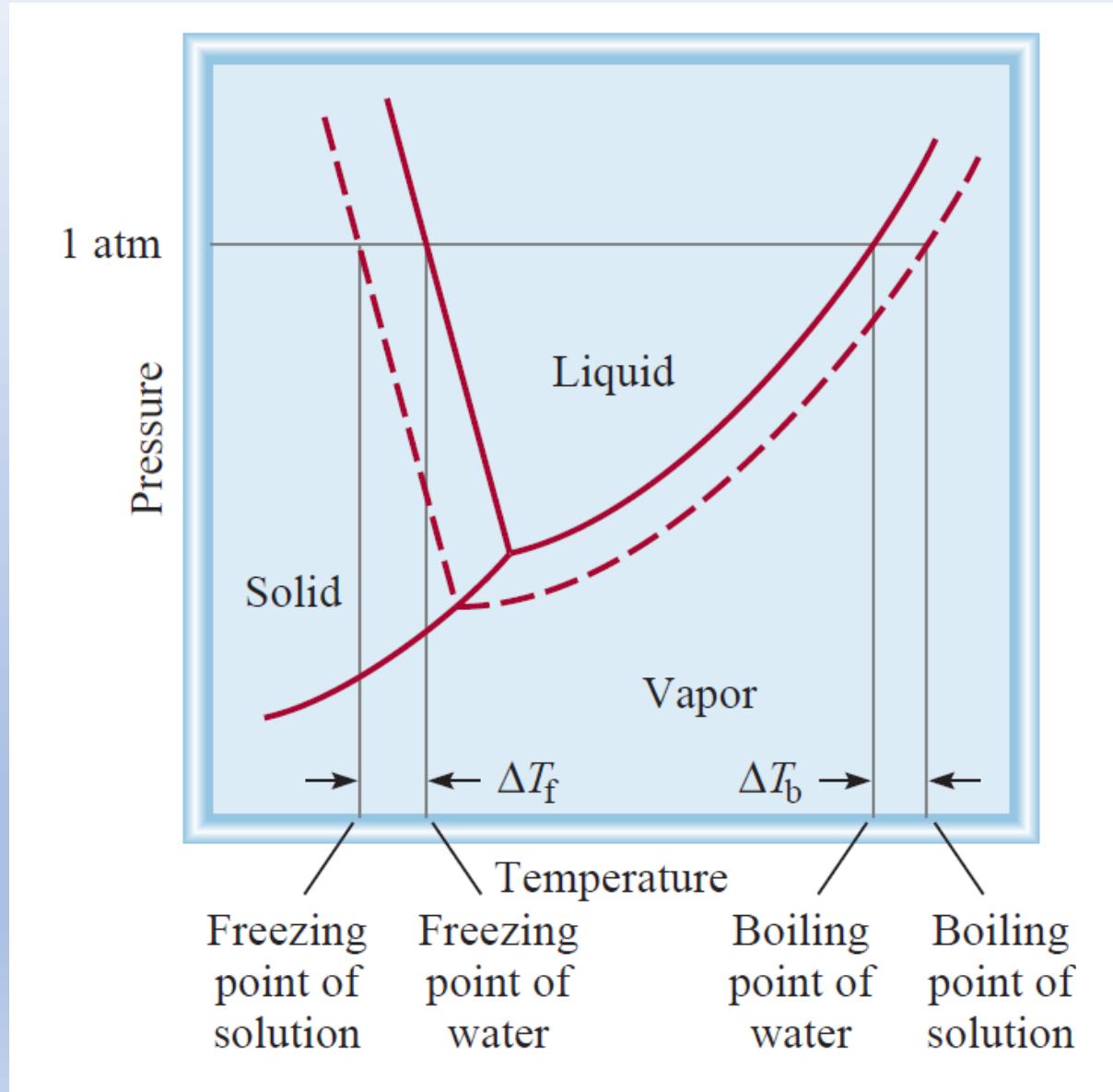


The dependence of the partial pressures of benzene and toluene on their mole fractions in a benzene-toluene solution at 80°C.

# Boiling-Point Elevation

- ❖ The boiling point of a solution is the temperature at which its vapor pressure equals the external atmospheric pressure.
- ❖ Figure 13.7 shows the phase diagram of water and the changes that occur in an aqueous solution. Because at any temperature the vapor pressure of the solution is lower than that of the pure solvent, the liquid-vapor curve for the solution lies below that for the pure solvent.
- ❖ Consequently, the solution curve (dotted line) intersects the horizontal line that marks  $P = 1 \text{ atm}$  at a higher temperature than the normal boiling point of the pure solvent.

# Boiling-Point Elevation



# Boiling-Point Elevation

- ❖ This graphical analysis shows that the boiling point of the solution is higher than that of water.

$$\Delta T_b = T_b - T_b^{\circ}$$

- ❖ Because  $\Delta T_b$  is proportional to the vapor-pressure lowering, it is also proportional to the concentration (molality) of the solution. That is,

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

# Boiling-Point Elevation

- ❖ It is important to understand the choice of concentration unit here. We are dealing with a system (the solution) whose temperature is not kept constant, so we cannot express the concentration units in molarity because molarity changes with temperature.

# Boiling-Point Elevation

Table 13.2 lists the  $K_b$  values for several common solvents. Using the boiling-point elevation constant for water, if the molality of an aqueous solution is 1.00 m, the boiling point will be 100.52 °C.

TABLE 13.2

Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

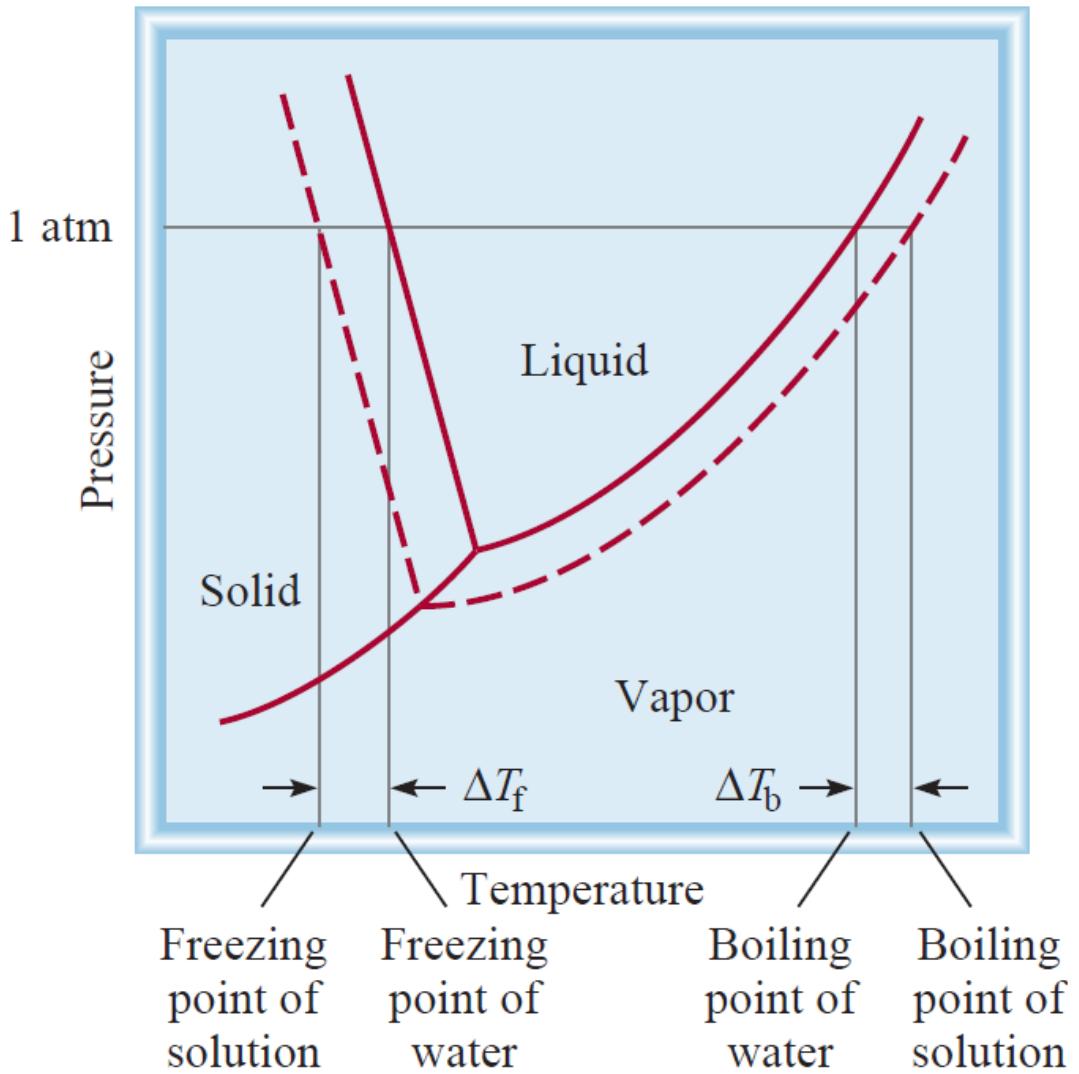
Solvent	Normal Freezing Point (°C)*	$K_f$ (°C/m)	Normal Boiling Point (°C)*	$K_b$ (°C/m)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	−117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

\*Measured at 1 atm.

# Freezing-Point Depression

- ❖ A nonscientist may remain forever unaware of the boiling-point elevation phenomenon, but a careful observer living in a cold climate is familiar with freezing-point depression.
- ❖ Ice on frozen roads and sidewalks melts when sprinkled with salts such as NaCl or CaCl<sub>2</sub>. This method of thawing succeeds because it depresses the freezing point of water.

# Freezing-Point Depression



- ❖ The figure shows that lowering the vapor pressure of the solution shifts the solid-liquid curve to the left.
- ❖ Consequently, this line intersects the horizontal line at a temperature lower than the freezing point of water.

# Freezing-Point Depression

- ❖ The freezing-point depression,  $\Delta T_f$ , is defined as

$$\Delta T_f = T_f^\circ - T_f$$

- ❖ Again,  $\Delta T_f$  is proportional to the concentration of the solution:

$$\Delta T_f \propto m$$

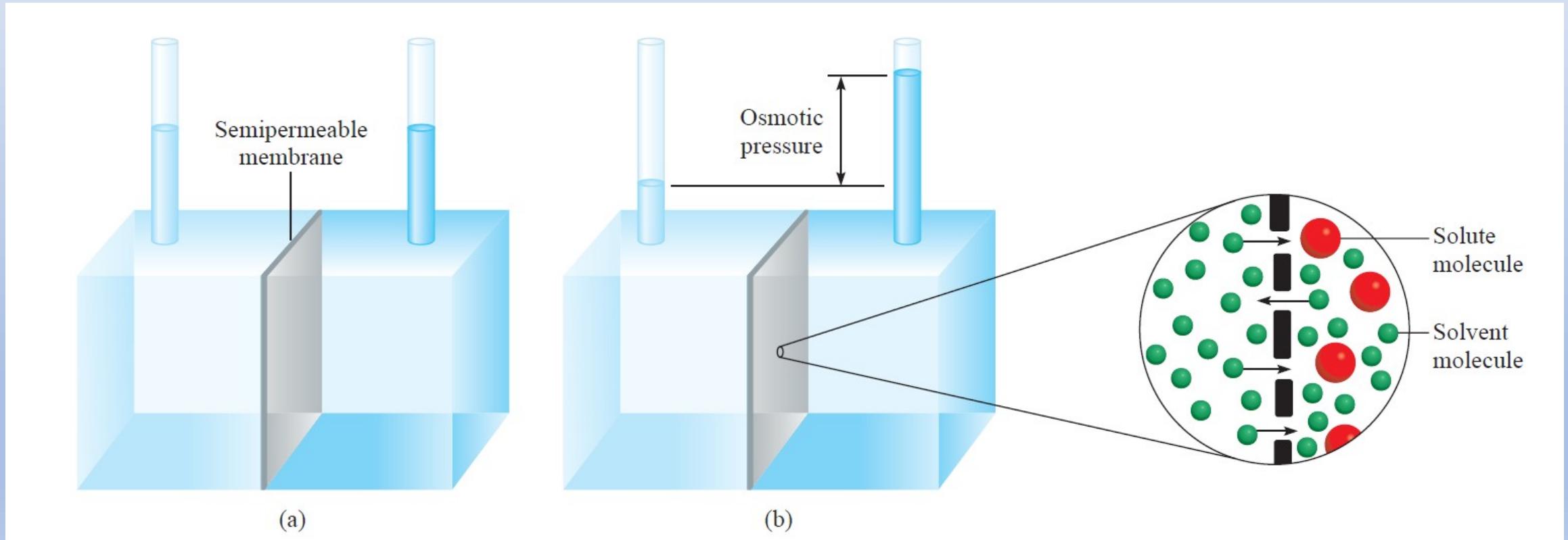
$$\Delta T_f = K_f m$$

# Freezing-Point Depression

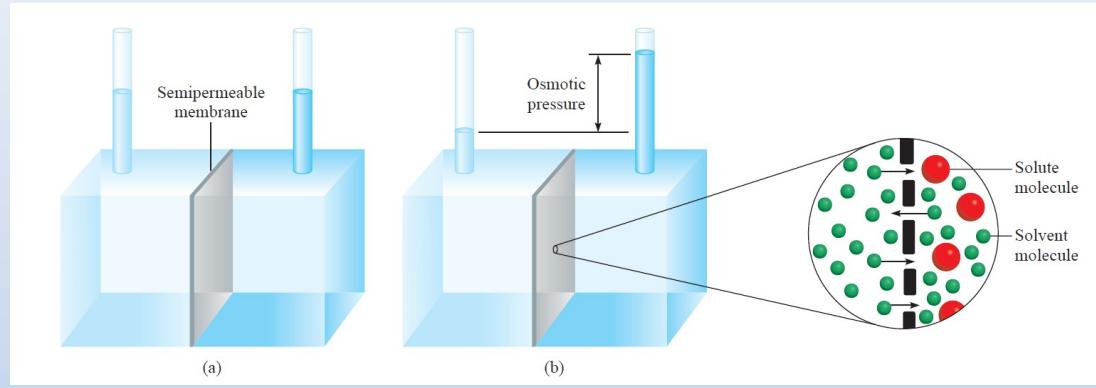
- ❖ A qualitative explanation of the freezing-point depression phenomenon is as follows.
- ❖ Freezing involves a transition from the disordered state to the ordered state.
- ❖ For this to happen, energy must be removed from the system.
- ❖ Because a solution has greater disorder than the solvent, more energy needs to be removed from it to create order than in the case of a pure solvent.
- ❖ Therefore, the solution has a lower freezing point than the solvent.
- ❖ Note that when a solution freezes, the solid that separates is the solvent component.
- ❖ Whereas the solute must be nonvolatile in the case of boiling-point elevation, no such restriction applies to freezing-point depression.

# Osmotic Pressure

- ❖ Many chemical and biological processes depend on the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.



# Osmotic Pressure

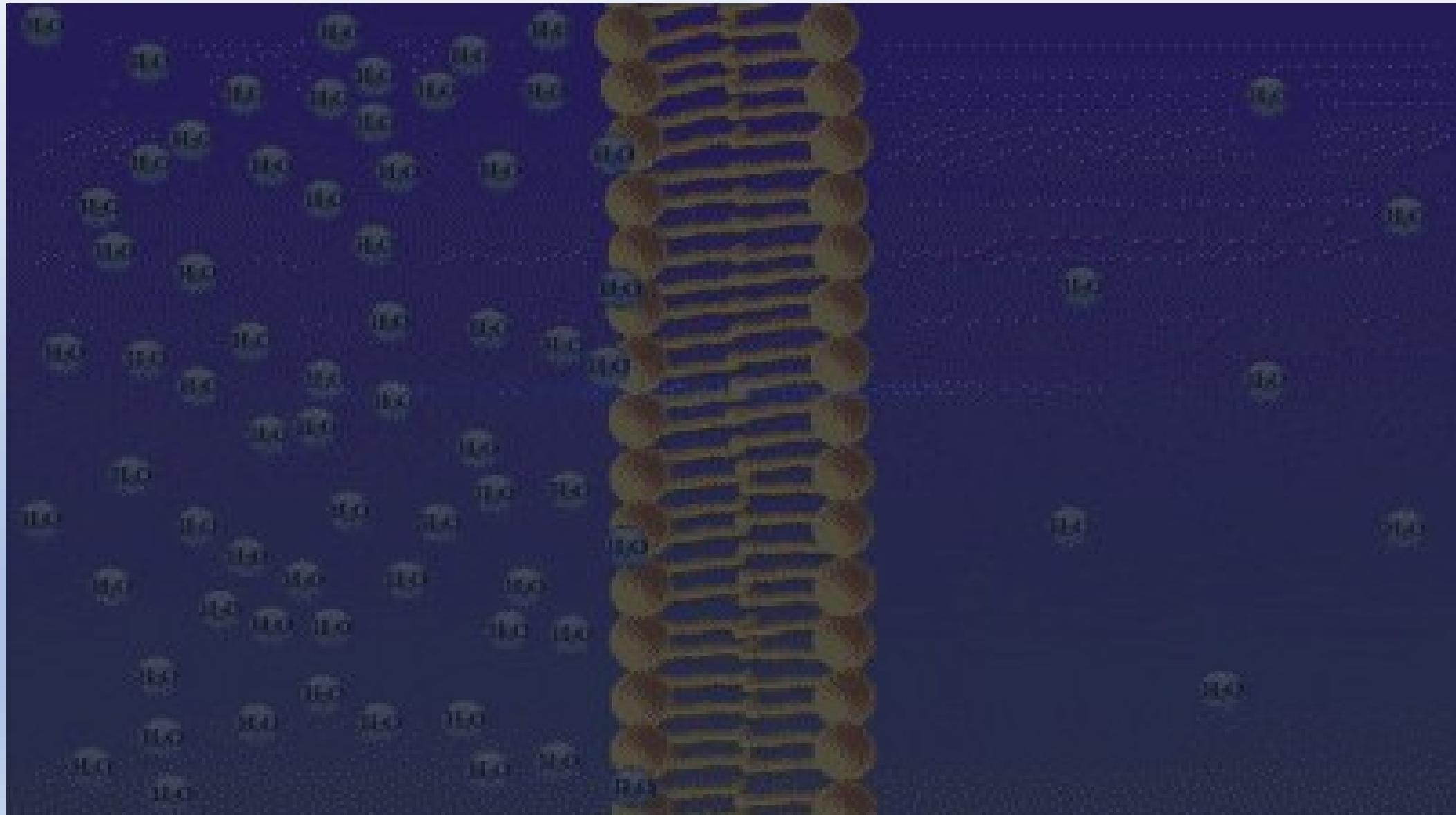


- ❖ The left compartment of the apparatus contains pure solvent; the right compartment contains a solution.
- ❖ The two compartments are separated by a semipermeable membrane, which allows solvent molecules to pass through but blocks the passage of solute molecules.
- ❖ At the start, the water levels in the two tubes are equal. After some time, the level in the right tube begins to rise; this continues until equilibrium is reached.

# Osmotic Pressure

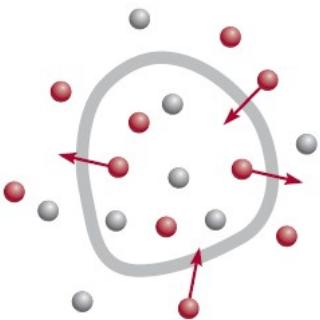
- ❖ The net movement of solvent molecules through a semipermeable membrane from a pure solvent or from a dilute solution to a more concentrated solution is called osmosis.
- ❖ The osmotic pressure ( $\Pi$ ) of a solution is the pressure required to stop osmosis.
- ❖ This pressure can be measured directly from the difference in the final fluid levels.

# Osmotic Pressure

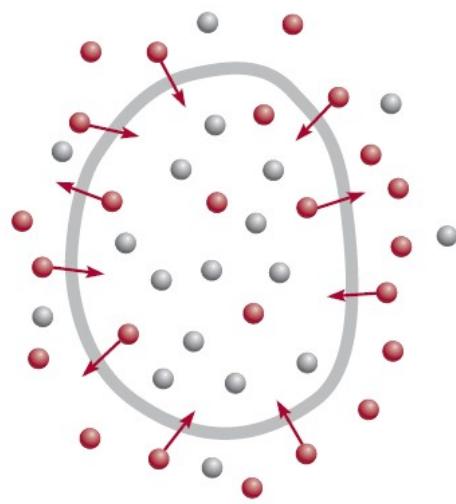


# Osmotic Pressure

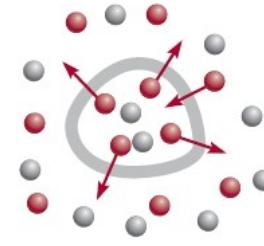
● Water molecules  
● Solute molecules



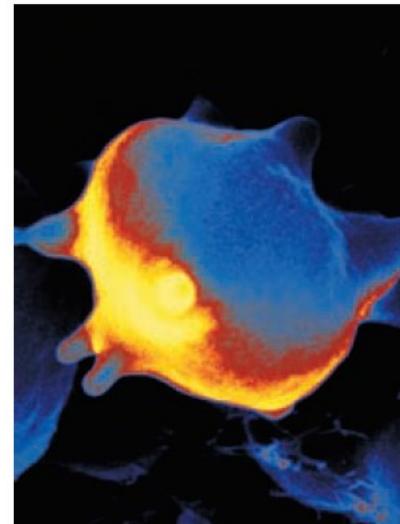
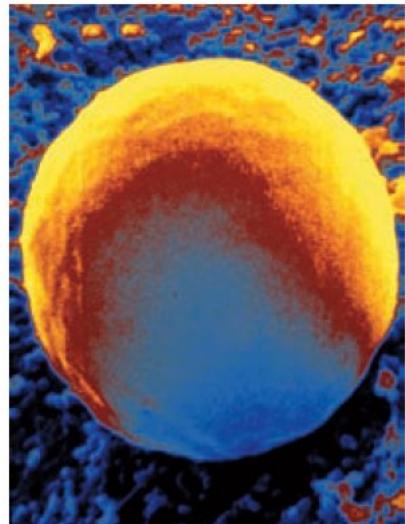
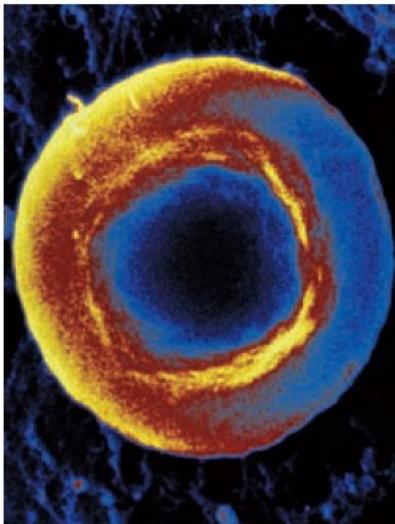
(a)



(b)



(c)



(d)

A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c).

(d) From left to right: a red blood cell in an isotonic solution, in a hypotonic solution, and in a hypertonic solution.

# Using Colligative Properties to Determine Molar Mass

- ❖ The colligative properties of nonelectrolyte solutions provide a means of determining the molar mass of a solute.
- ❖ Theoretically, any of the four colligative properties is suitable for this purpose.
- ❖ In practice, however, only freezing-point depression and osmotic pressure are used because they show the most pronounced changes.

## Example 13.9

A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume. If the osmotic pressure of the solution is found to be 10.0 mmHg at 25°C, calculate the molar mass of hemoglobin.

# Using Colligative Properties to Determine Molar Mass

**Solution** The sequence of conversions is as follows:

osmotic pressure  $\longrightarrow$  molarity  $\longrightarrow$  number of moles  $\longrightarrow$  molar mass

First we calculate the molarity using Equation (13.10)

$$\pi = MRT$$

$$M = \frac{\pi}{RT}$$

$$\begin{aligned} & 10.0 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \\ & = \frac{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} \\ & = 5.38 \times 10^{-4} \text{ M} \end{aligned}$$

The volume of the solution is 1 L, so it must contain  $5.38 \times 10^{-4}$  mole of Hb. We use this quantity to calculate the molar mass:

$$\text{moles of Hb} = \frac{\text{mass of Hb}}{\text{molar mass of Hb}}$$

$$\begin{aligned} \text{molar mass of Hb} & = \frac{\text{mass of Hb}}{\text{moles of Hb}} \\ & = \frac{35.0 \text{ g}}{5.38 \times 10^{-4} \text{ mol}} \\ & = 6.51 \times 10^4 \text{ g/mol} \end{aligned}$$

# Using Colligative Properties to Determine Molar Mass

- ❖ A pressure of 10.0 mmHg, as in Example 13.9, can be measured easily and accurately.
- ❖ For this reason, osmotic pressure measurements are very useful for determining the molar masses of large molecules, such as proteins.
- ❖ To see how much more practical the osmotic pressure technique is than freezing-point depression would be, let us estimate the change in freezing point of the same hemoglobin solution.
- ❖ If an aqueous solution is quite dilute, we can assume that molarity is roughly equal to molality.

$$\begin{aligned}\Delta T_f &= (1.86^\circ\text{C}/m)(5.38 \times 10^{-4} \text{ m}) \\ &= 1.00 \times 10^{-3}^\circ\text{C}\end{aligned}$$

# Using Colligative Properties to Determine Molar Mass

- ❖ The freezing-point depression of one-thousandth of a degree is too small a temperature change to measure accurately.
- ❖ For this reason, the freezing-point depression technique is more suitable for determining the molar mass of smaller and more soluble molecules, those having molar masses of 500 g or less, because the freezing-point depressions of their solutions are much greater.

# Colligative Properties of Electrolyte Solutions

- ❖ The colligative properties of electrolytes require a slightly different approach than the one used for the colligative properties of nonelectrolytes.
- ❖ The reason is that electrolytes dissociate into ions in solution, and so one unit of an electrolyte compound separates into two or more particles when it dissolves. (Remember, it is the number of solute particles that determines the colligative properties of a solution.)
- ❖ For example, each unit of NaCl dissociates into two ions— $\text{Na}^+$  and  $\text{Cl}^-$ .
- ❖ Thus, the colligative properties of a 0.1 m NaCl solution should be twice as great as those of a 0.1 m solution containing a nonelectrolyte, such as sucrose.

# Colligative Properties of Electrolyte Solutions

- ❖ Similarly, we would expect a 0.1 m  $\text{CaCl}_2$  solution to depress the freezing point by three times as much as a 0.1 m sucrose solution.
- ❖ To account for this effect, we must modify the equations for colligative properties as follows:

$$\Delta T_b = iK_b m \quad (13.11)$$

$$\Delta T_f = iK_f m \quad (13.12)$$

$$\pi = iMRT \quad (13.13)$$

# Colligative Properties of Electrolyte Solutions

- The variable  $i$  is the *van't Hoff factor*, which is defined as

$$i = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}} \quad (13.14)$$

TABLE 13.3

The van't Hoff Factor of 0.0500 M Electrolyte Solutions at 25°C

Electrolyte	$i$ (measured)	$i$ (calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
MgSO <sub>4</sub>	1.3	2.0
MgCl <sub>2</sub>	2.7	3.0
FeCl <sub>3</sub>	3.4	4.0

\*Sucrose is a nonelectrolyte. It is listed here for comparison only.