

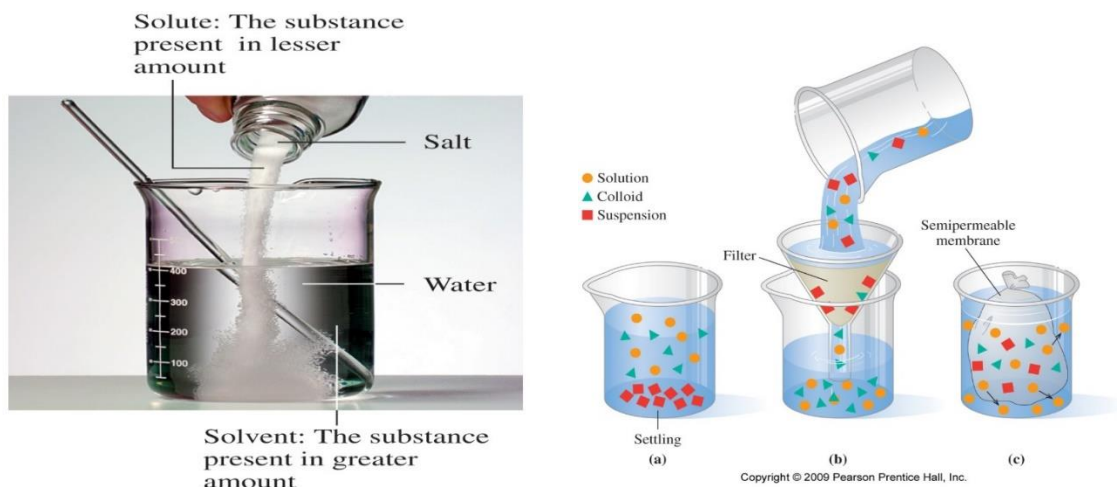
## 13.1 – Solutions

Homogeneous mixtures can be classified according to the size of their particles as either solution or colloids

Solution is the common class of homogenous mixture. They are transparent, may be colored and can't be physically separated.

Colloids are often murky or opaque to light. (E.g: milk or fog)

Suspensions have larger particles than colloids. Their particles separate out on standing and are visible



**Table 13.1** Some Different Kinds of Solutions

Gas in gas	Air (O <sub>2</sub> , N <sub>2</sub> , Ar, and other gases)
Gas in liquid	Carbonated water (CO <sub>2</sub> in water)
Gas in solid	H <sub>2</sub> in palladium metal
Liquid in liquid	Gasoline (mixture of hydrocarbons)
Liquid in solid	Dental amalgam (mercury in silver)
Solid in liquid	Seawater (NaCl and other salts in water)
Solid in solid	Metal alloys, such as sterling silver (92.5% Ag, 7.5% Cu)

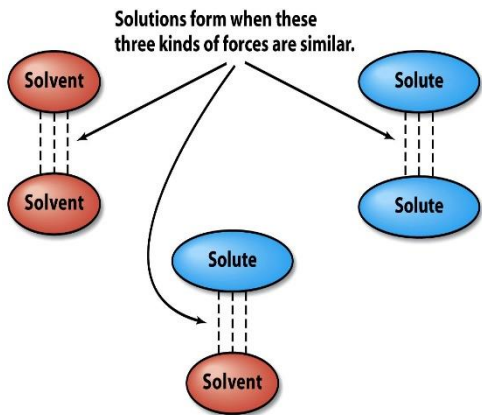
## 13.2 Enthalpy Changes and the Solution Process

### A good rule of thumb, “like dissolves like”

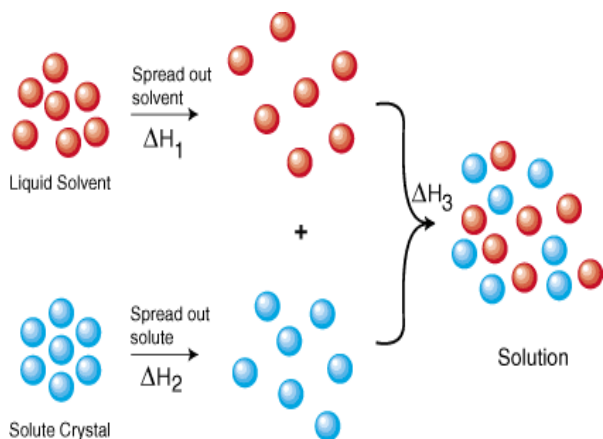
Solution will form when the three types of intermolecular interactions are similar in kind and magnitude

Common intermolecular forces that can be used to predict the formation of a solution:

- Ion-ion interaction (Na<sup>+</sup> Cl<sup>-</sup>)
- Ion-dipoles (Na<sup>+</sup> H<sub>2</sub>O, Cl<sup>-</sup> H<sub>2</sub>O)
- Hydrogen bonding (OH, NH, HF) (polar interaction)
- Dipole-dipole (polar interaction)
- London dispersion (nonpolar molecules)



Solute-to-Solvent	>	Solute-to-Solute + Solvent-to-Solvent	Solution Forms
Solute-to-Solvent	=	Solute-to-Solute + Solvent-to-Solvent	Solution Forms
Solute-to-Solvent	<	Solute-to-Solute + Solvent-to-Solvent	Solution May or May Not Form

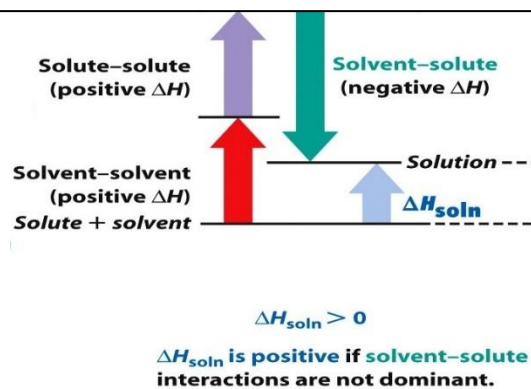
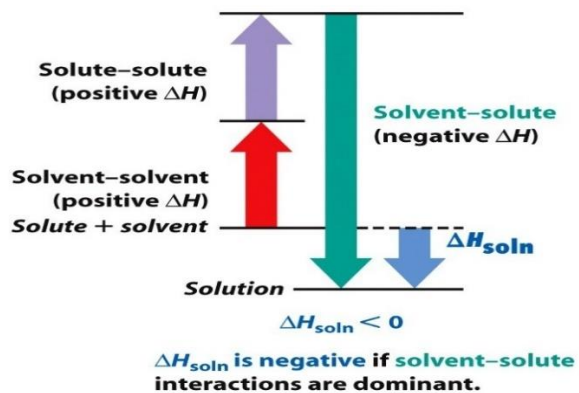


Simply put, three processes affect the energetics of the process:

- \_ Separation of solute particles  $\Delta H_1$  (this is always endothermic)
- \_ Separation of solvent particles  $\Delta H_2$  (this too is always endothermic)
- \_ New interactions between solute and solvent  $\Delta H_3$  (this is always exothermic)

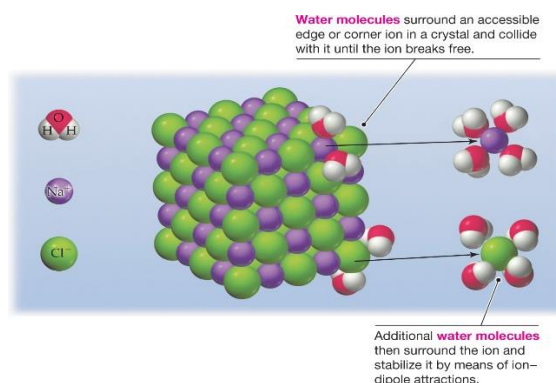
The overall enthalpy change associated with these three processes :

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3 \quad (\text{Hess's Law})$$



The *solute-solvent* interactions are **greater** than the sum of the *solute-solute* and *solvent-solvent* interactions.

The *solute-solvent* interactions are **less** than the sum of the *solute-solute* and *solvent-solvent* interactions.



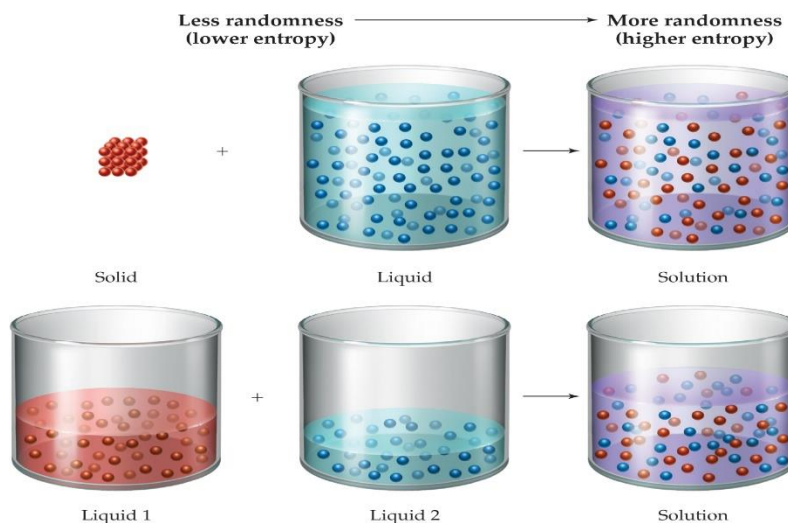
The sodium and chloride ions are **hydrated**.

### 13.3 – Predicting Solubilities

Like all chemical and physical processes, the dissolution of a solute in a solvent has associated with it a Gibbs free-energy change,  $\Delta G = H - TS$ , whose value describes its spontaneity. If  $\Delta G$  is negative, the process is spontaneous and the substance dissolves; if  $\Delta G$  is positive, the process is nonspontaneous and the substance does not dissolve.

If we defined the enthalpy of solution  $\Delta H_{\text{soln}}$  as the heat released or absorbed upon solution formation, and similarly the entropy of solution,  $\Delta S_{\text{sol}}$  is the entropy change that occurs when the solute dissolves in the solvent.

When one liquid dissolves in another, randomness increases as the different molecules intermingle



**Table 13.2** Some Enthalpies and Entropies of Solution in Water at

Substance	$\Delta H^{\circ}_{\text{soln}}(\text{kJ/mol})$	$\Delta S^{\circ}_{\text{soln}}[\text{J}/(\text{K} \cdot \text{mol})]$
LiCl	-37.0	10.5
NaCl	3.9	43.4
KCl	17.2	75.0
LiBr	-48.8	21.5
NaBr	-0.6	54.6
KBr	19.9	89.0
KOH	-57.6	12.9

Beside using intermolecular forces and polarity to predict the solubility, how can we predict if a solute will be soluble in a given solvent? Thermodynamics tells us that if the free-energy change of solution formation is negative, then the process will be spontaneous.

**Example:** Predict the solubilities of NaCl in water at 25°C.

### 13.4 Concentration Units for Solutions

In daily life, it's often sufficient to describe a solution as either dilute or concentrated. In scientific work, though, it's usually necessary to know the exact concentration of a solution—that is, to know the exact amount of solute dissolved in a certain amount of solvent. There are many ways of expressing concentration:

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Liters of solution}}$$

$$\text{Mole fraction (X)} = \frac{\text{Moles of component}}{\text{Total moles making up solution}}$$

$$\text{Mass percent} = \frac{\text{Mass of component}}{\text{Total mass of solution}} \times 100\%$$

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$$

A summary of the four most common units for expressing concentration, together with a comparison of their relative advantages and disadvantages

Name	Units	Advantages	Disadvantages
Molarity (M)	$\frac{\text{mol solute}}{\text{L solution}}$	Useful in stoichiometry; by volume	Temperature-dependent; must know density to find solvent mass
Mole fraction (X)	none	Temperature-independent; useful in special applications	Measure by mass; must know density to convert to molarity
Mass %	%	Temperature-independent; useful for small amounts	Measure by mass; must know density to convert to molarity
Molality ( <i>m</i> )	$\frac{\text{mol solute}}{\text{kg solvent}}$	Temperature-independent; useful in special applications	Measure by mass; must know density to convert to molarity

**Example:** What is the molality of a solution made by dissolving 1.45 g of table sugar (sucrose,  $C_{12}H_{22}O_{11}$ ) in 30.0 mL of water? The molar mass of sucrose is 342.3 g/mol, and the density of water is 1.00 g/mL.

**Example:** Nitrate,  $NO_3^-$  enters the water supply from fertilizer runoff or leaking septic tanks. The legal limit in drinking water is 10.0 ppm because infants who drink water exceeding this level can become seriously ill. What mass of nitrate (mg) is present in 1.5 L of water with a concentration of 10.0 ppm? (Assume the density of water is 1.0 g/mL.)

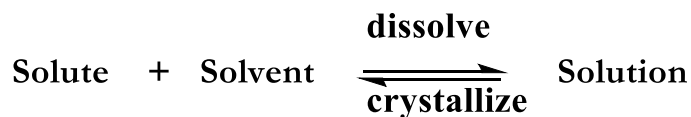
### 13.5- Factors that affects solubility

When there is an attraction between the particles of the solute and solvent.

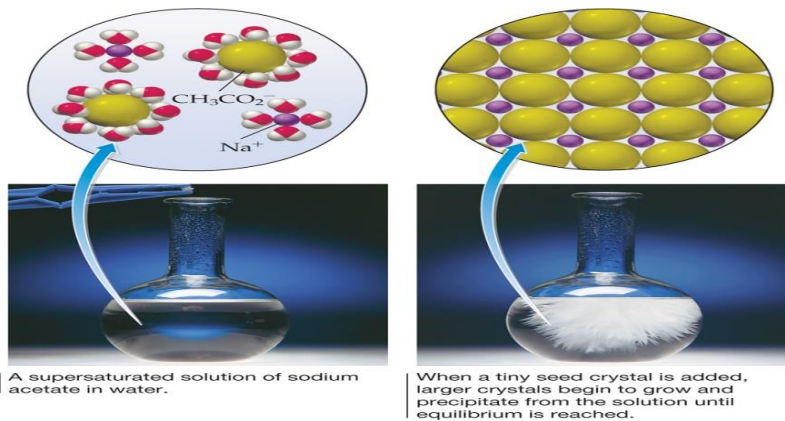
When a polar solvent such as water dissolves polar solutes such as sugar, and ionic solutes such as NaCl.

When a nonpolar solvent such as hexane ( $C_6H_{14}$ ) dissolves nonpolar solutes such as oil or grease.

- **Saturated solution:** A solution containing the maximum possible amount of dissolved solute at equilibrium.



- **Supersaturated Solution:** A solution containing a greater-than-equilibrium amount of solute.



- **Unsaturated solution:** a solution containing less than the equilibrium amount of solute

When there is an attraction between the particles of the solute and solvent.

When a polar solvent such as water dissolves polar solutes such as sugar, and ionic solutes such as NaCl.

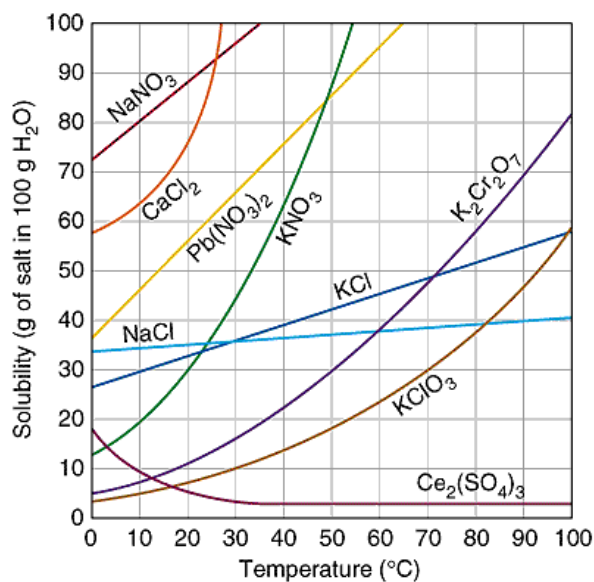
When a nonpolar solvent such as hexane ( $C_6H_{14}$ ) dissolves nonpolar solutes such as oil or grease.

### Effect of Temperature on Solubility

Solubility curves can be used to predict whether a solution with a particular amount of solute dissolved in water is saturated (on the line), unsaturated (below the line), or supersaturated (above the line)

#### Solubility

- depends on temperature
- most solids increases as temperature increases.
  - Hot tea dissolves more sugar than does cold tea because the solubility of sugar is much greater in higher temperature
- There is no obvious correlation between structure and solubility or between solubility and temperature.
- When a saturated solution is carefully cooled, it becomes a supersaturated solution because it contains more solute than the solubility allows.



**Example:** The solubility of KCl at 50°C is 42 g/100g . If 20.0 g of KCl was dissolved in 35.0 g water, would the solution be unsaturated, saturated or supersaturated?

## Effects of Pressure on Solubilities - Gases in Solution

• In general, the solubility of gases in water increases with increasing mass as the attraction between the gas and the solvent molecule is mainly dispersion forces.

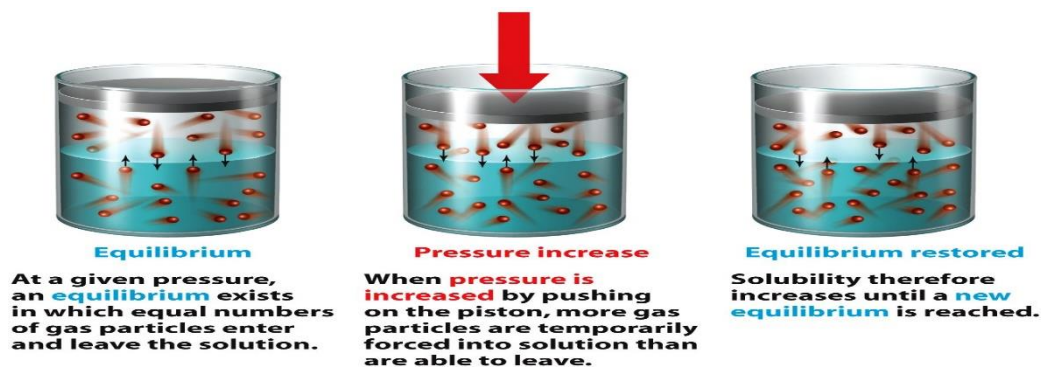
• Larger molecules have stronger dispersion forces.

Henry's law states

- the solubility of a gas in a liquid is directly related to the pressure of that gas above the liquid.
- at higher pressures, more gas molecules dissolve in the liquid.

$$\text{Solubility} = k \cdot P$$

- where
  - $k$  is the Henry's law constant for that gas in that solvent at that temperature
  - $P$  is the partial pressure of the gas above the liquid.



Henry's Law is what (in a manner of thinking) gives soda pop its fizz. The bubbling that occurs when a can of soda is opened results from the reduced pressure of carbon dioxide over the liquid. At lower pressure, the carbon dioxide is less soluble and bubbles of solution.

**Example:** Calculate the concentration of  $\text{CO}_2$  in a soft drink that is bottled with a partial pressure of  $\text{CO}_2$  of 4.0 atm over the liquid at  $25^\circ\text{C}$ . The Henry's law constant for  $\text{CO}_2$  in water at this temperature is  $3.1 \times 10^{-2} \text{ M/atm}$ .

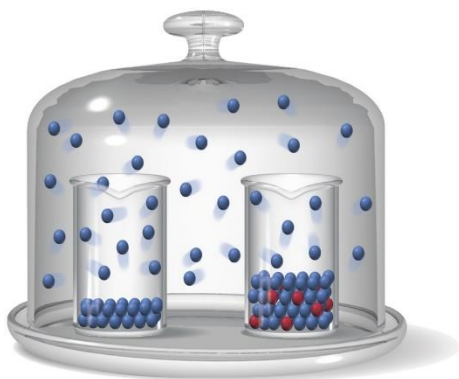
## 13.6 – Physical Behavior of Solutions: Colligative Properties

**Colligative Properties:** Properties that depend on the amount of a dissolved solute but not on its chemical identity.

- Vapor-Pressure Lowering
- Freezing-Point Depression
- Boiling-Point Elevation
- Osmotic Pressure

Solutions of ionic substances often have a vapor pressure significantly lower than predicted, because the ion-dipole forces between the dissolved ions and polar water molecules are so strong.

## 13.7 Vapor-Pressure Lowering of Solutions: Raoult's Law



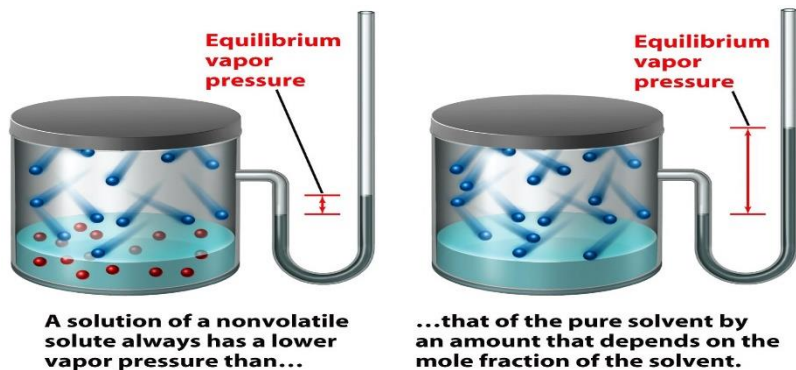
Beakers with equal liquid levels of pure solvent and a solution are placed in a bell jar. Solvent molecules evaporate from each one and fill the bell jar, establishing an equilibrium with the liquids in the beakers.

When equilibrium is established, the liquid level in the solution beaker is higher than the solution level in the pure solvent beaker – the thirsty solution grabs and holds solvent vapor more effectively

The vapor pressure of a volatile solvent above a solution is equal to its mole fraction of its normal vapor pressure,  $P^\circ$

- since the mole fraction is always less than 1, the vapor pressure of the solvent in solution will always be less than the vapor pressure of the pure solvent

$$P_{total} = P_A + P_B = (P_A^\circ X_A) + (P_B^\circ X_B)$$



### Raoult's Law

$$P_{soln} = P_{solv} X_{solv}$$

**Example:** The vapor pressure of pure water at 25°C is 23.8 atm. Determine the vapor pressure (torr) of water at 25°C above a solution prepared by dissolving 18.0 g glucose (MW = 180.0 g/mol) in 95.0 g of water?





**Van't Hoff Factors at 0.05 m Concentration in Aqueous Solution**

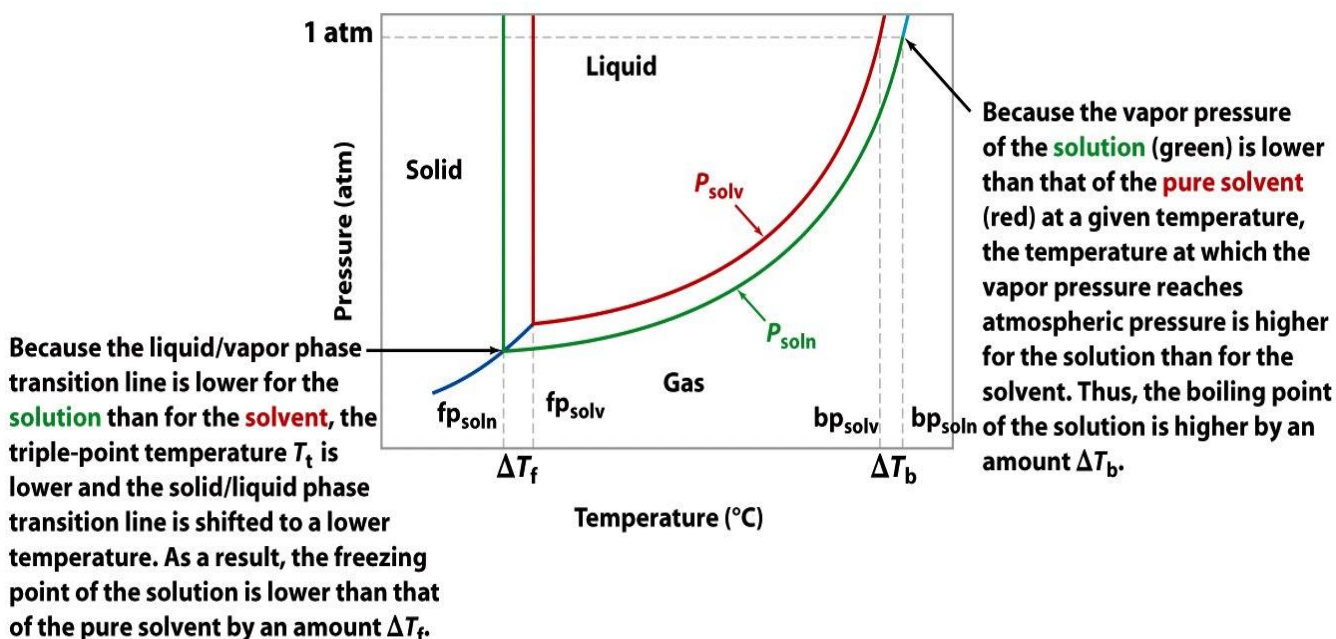
Solute	$i$ Expected	$i$ Measured
Nonelectrolyte	1	1
NaCl	2	1.9
MgSO <sub>4</sub>	2	1.3
MgCl <sub>2</sub>	3	2.7
K <sub>2</sub> SO <sub>4</sub>	3	2.6
FeCl <sub>3</sub>	4	3.4

- The smaller than expected value for  $i$  is due to incomplete dissociation of ionic compounds. As the concentration decreases, the experimental value for  $i$  increases until it reaches the theoretical maximum (decreased occurrence of ion-pairs in solution also plays a factor).

**Example:** What is the vapor pressure in mmHg of a solution made by dissolving 18.30 g of NaCl in 500.0 g of H<sub>2</sub>O at 70°C, assuming a van't Hoff factor of 1.9? The vapor pressure of water at 70°C is 233.7 mmHg.

### 13.8 Boiling-Point Elevation and Freezing-Point Depression

We saw in Section 11.3 that the vapor pressure of a liquid rises with increasing temperature and that the liquid boils when its vapor pressure equals atmospheric pressure. Because a solution of a nonvolatile solute has a lower vapor pressure than a pure solvent has at a given temperature, the solution must be heated to a higher temperature to cause it to boil. Figure 13.14 shows how the phase diagram for a solution is different than that of a pure solvent.



The change in boiling point  $T_b$  for a solution is proportional to the number of solute particles present and can be related to the molality of the solution

$$(\text{BP}_{\text{solution}} - \text{BP}_{\text{solvent}}) = \Delta T_b = m \cdot K_b$$

The freezing-point depression for a solution relative to that of a pure solvent depends on the concentration of solute particles, just as boiling-point elevation does.

$$(\text{FP}_{\text{solvent}} - \text{FP}_{\text{solution}}) = \Delta T_f = m \cdot K_f$$

$$\Delta T_f = K_f \cdot m$$

For ionic substances:

$$\Delta T_b = K_b \cdot m \cdot i$$

$$\Delta T_f = K_f \cdot m \cdot i$$

**Table 13.4** Molal Boiling-Point-Elevation Constants ( $K_b$ ), and Molal Freezing Point-Depression Constants ( $K_f$ )

Substance	$K_b$ [(°C · kg)/mol]	$K_f$ [(°C · kg)/mol]
Benzene (C <sub>6</sub> H <sub>6</sub> )	2.64	5.07
Camphor (C <sub>10</sub> H <sub>16</sub> O)	5.95	37.8
Chloroform (CHCl <sub>3</sub> )	3.63	4.70
Diethyl ether (C <sub>4</sub> H <sub>10</sub> O)	2.02	1.79
Ethyl alcohol (C <sub>2</sub> H <sub>6</sub> O)	1.22	1.99
Water (H <sub>2</sub> O)	0.51	1.86

**Example:** What is the normal boiling point in °C of an antifreeze solution prepared by dissolving 616.9 g of ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) in 500.0 g of water? The molal boiling point elevation constant for water is 0.51 °C·kg/mol and molar mass of ethylene glycol is 62.07 g/mol

**Example:** How many g of ethylene glycol, C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, must be added to 1.0 kg H<sub>2</sub>O to give a solution that boils at 105°C?  $K_b = 0.512$  (°C·kg)/mol.

**Example:** What is the freezing point in °C of a solution prepared by dissolving 7.40 g of MgCl<sub>2</sub> in 110 g of water. Assume MgCl<sub>2</sub> has completely ionized.

### 13.9 Osmosis and Osmotic Pressure

Certain materials, including those that make up the membranes around living cells, are semipermeable. That is, they allow water or other smaller molecules to pass through, but they block the passage of larger solute molecules or solvated ions.

**Osmosis:** The passage of solvent through a semipermeable membrane from the less concentrated side to the more concentrated side.

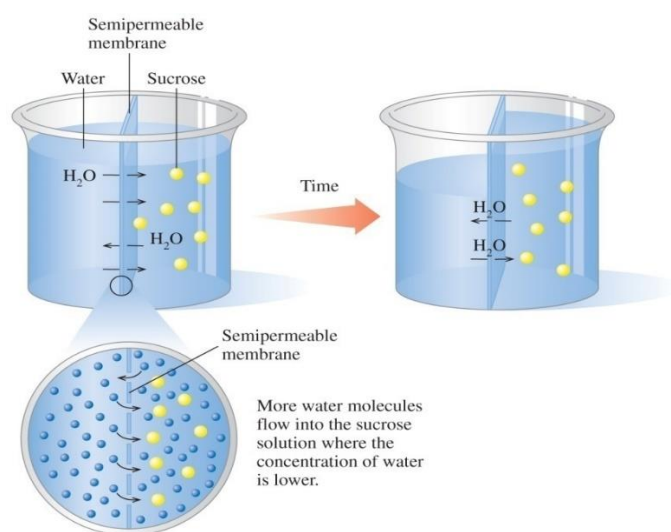
- Solvent flows from a **high solvent** concentration to a **low solvent** concentration. Or, solvent flows from a **low solute** concentration to a **high solute** concentration.
- the level of the solution with the higher solute concentration rises.
- the concentrations of the two solutions become equal with time.

**Osmotic Pressure (P):** The amount of pressure necessary to cause osmosis to stop.

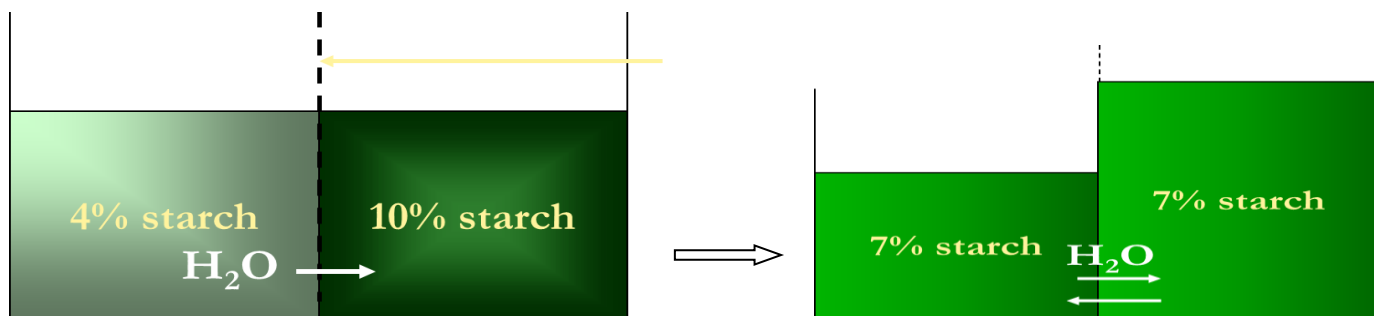
- Osmotic pressure can be calculated using molarity since it is calculated at a specific temperature and thus no need for temperature-independent units.

$$\Pi = MRT$$

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol}$$



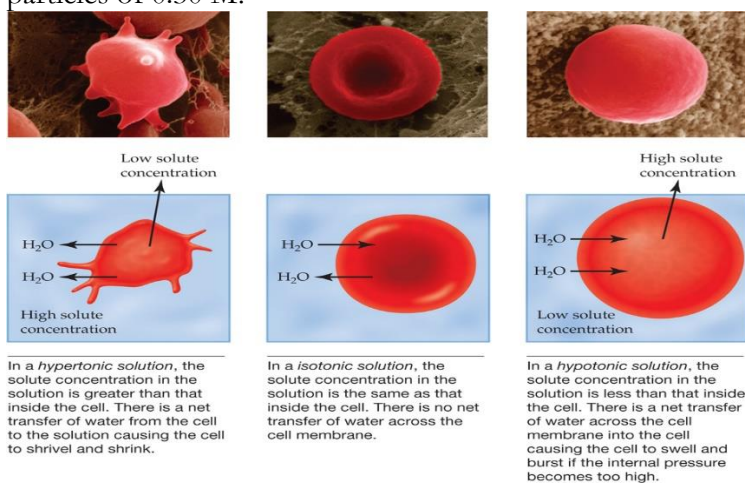
Suppose a semipermeable membrane separates a 4% starch solution from a 10% starch solution. Starch is a colloid and cannot pass through the membrane, but water can. What happens?



**Example:** The osmotic pressure of a solution containing 5.87 mg of an unknown protein per 10.0 mL of solution is 2.45 torr at 25°C. Find the molar mass of the unknown protein.

**Example:** Figure below shows the transport of solvent across the membrane of red blood cells in solutions of varying concentration.

(a) What is the osmotic pressure of a solution inside a red blood cell with a total concentration of dissolved particles of 0.30 M?



(b) Red blood cells rupture if the pressure differential across their membrane is 5 atm or higher. Would the blood cells rupture if they were placed in pure water?