GENERAL CHEMISTRY

Chapter 13

Properties of Solutions

Objectives

- Define **entropy** and understand its contribution to spontaneous processes
- Define the following terms: **solute, solvent, miscible,** and **immiscible**
- Predict whether certain solutes and solvents will be **miscible** or **immiscible**
- Understand the **crystallization** of **saturated solution**
- Use **Henry's Law** to interrelate concentration and pressure

Contents

13-1 The Solution Process

- **A solution** is formed when one substance disperses uniformly throughout another

Nearly all systems have the tendency to spontaneously become more disorder.

Entropy is a measure of the disorder *of the universe, on both a macro and a microscopic level*

➔ *Systems spontaneously drift toward high entropy (increased disorder)*

Entropy is denoted as S

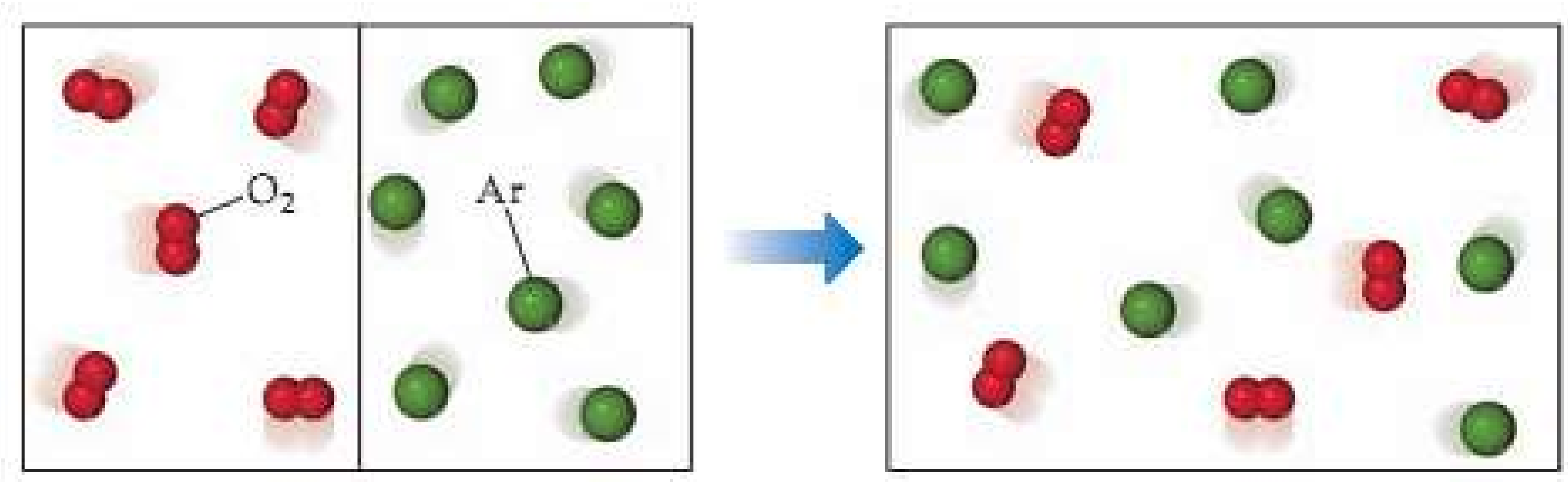
13-1 The Solution Process

- **Solvent:** the component that is present in a **greater** amount in a solution
  - It is not necessarily be a liquid (can be a liquid or solid)
- **Solute:** the component that is present in a **lesser** amount in a solution
- **Solvation:** the interaction(s) between solvent and solutes in solution. Solvate something means to dissolve it
- **Miscible:** When two liquids dissolve completely in each other, we say they are miscible. Two liquids that do not dissolve in each other, like oil and water, are immiscible
- **Mixing** leads to an increase in the **entropy** of the system

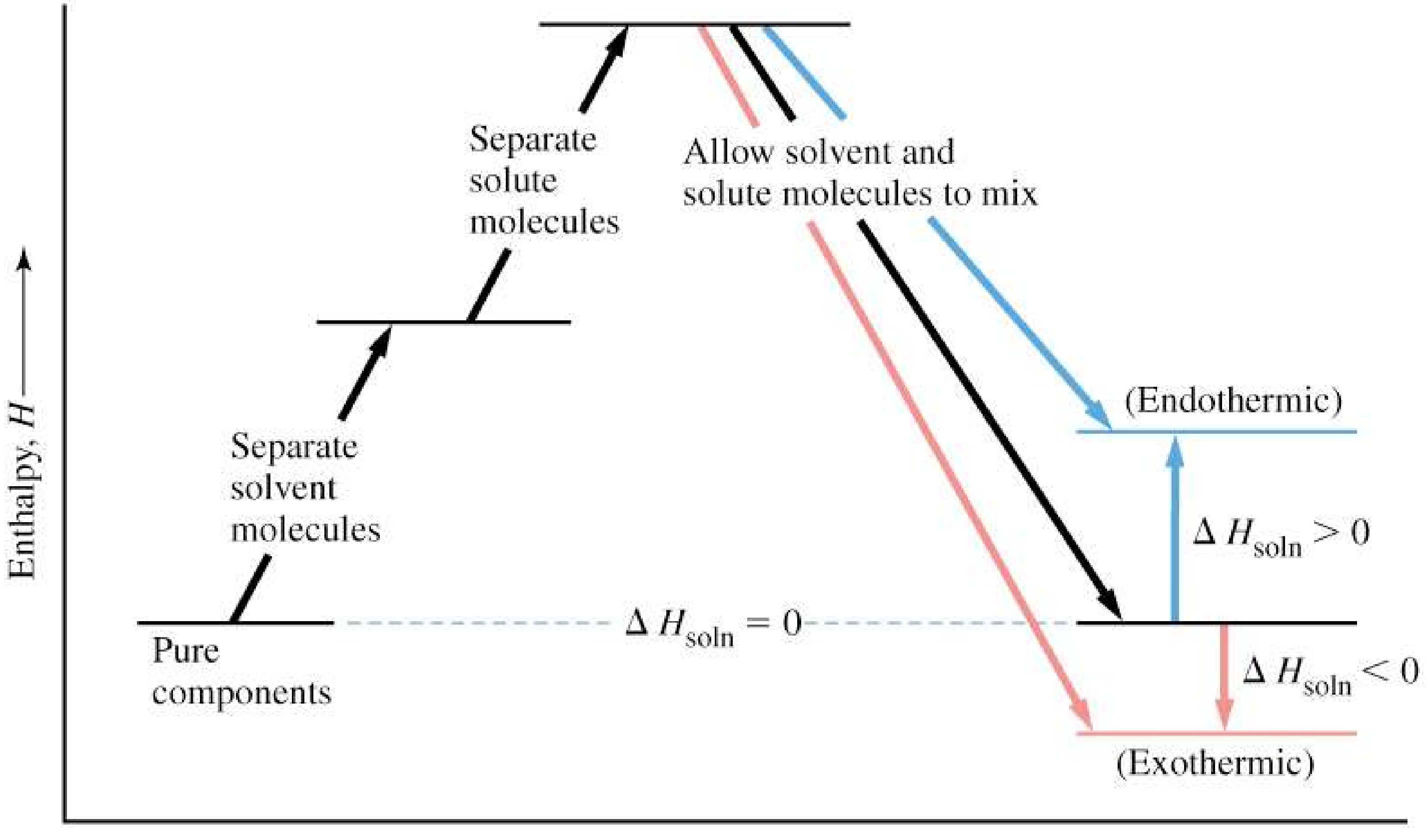
Solution	Components
Gaseous solutions	
Air	N_2, O_2, and several others
Natural gas	CH_4, C_2H_6, and several others
Liquid solutions	
Seawater	H_2O, NaCl, and many others
Vinegar mL of	H_2O, $HC_2H_3O_2$ (acetic acid)
Soda pop	H_2O, CO_2, $C_{12}H_{22}O_{11}$ (sucrose), and several others
Solid solutions	
Yellow brass	Cu, Zn
Palladium–hydrogen	Pd, H_2

The Natural Tendency toward Mixing

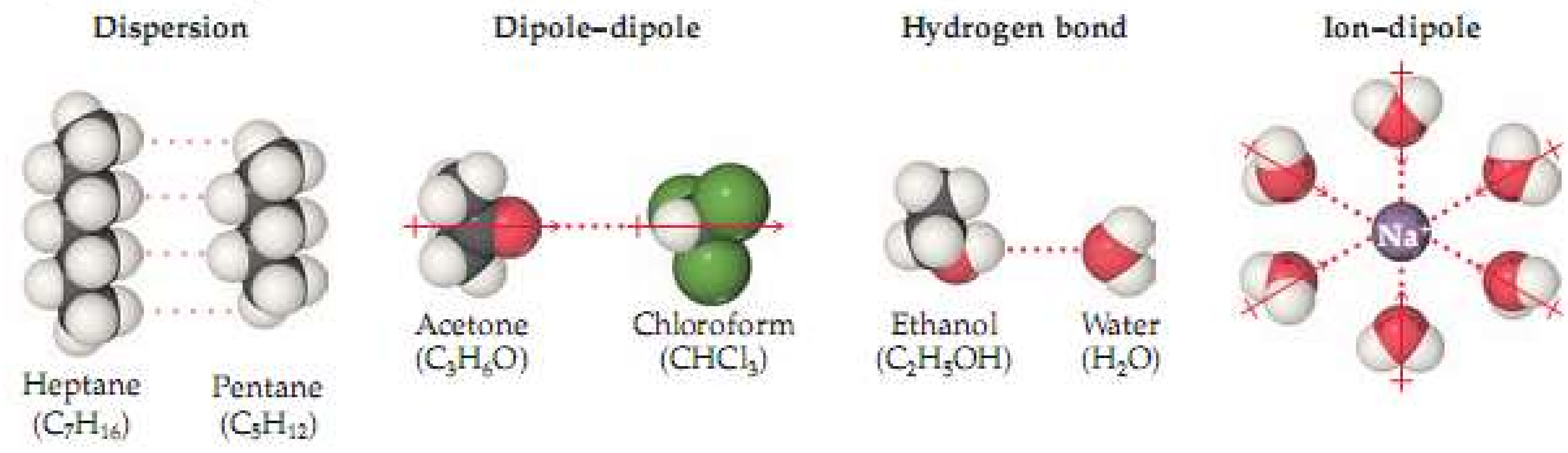
- **Mixing** leads to an increase in the entropy of the system
- Gases spontaneously mix unless restrained by their containers because with gases intermolecular forces are too weak
- When the solvent or solute is a solid or liquid, intermolecular forces become important in determining whether a solution forms



The Effect of Intermolecular Forces on Solution Formation



The Effect of Intermolecular Forces on Solution Formation



Solutions form when the magnitudes of the solvent–solute interactions are either comparable to or greater than the solute– solute and solvent–solvent interactions

Hydration Energy

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ $\Delta H_{lattice} > 0$

$Na^+(g) + n\,H_2O(l) \rightarrow Na^+(aq)$ $\Delta H_{hydration} < 0$

$Cl^-(g) + n\,H_2O(l) \rightarrow Cl^-(aq)$ $\Delta H_{hydration} < 0$

$NaCl(s) + 2n\,H_2O\,(l) \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta H_{soln} > 0$

$\Delta H_{soln} > 0$ Enthalpy	$\Delta S_{soln} > 0$ Entropy	but	$\Delta G_{solution} < 0$ Free energy

We will take an insight look at H, S and G in Chapter 19

Energetics of Solution Formation

Three kinds of intermolecular interactions are involved in solution formation:

1. **Solute–solute interactions** between solute particles must be overcome to **disperse the solute particles** through the solvent.

$$(\text{solute})_n \rightleftharpoons n\ \text{solute} \qquad \Delta H_{\text{solute}}$$

2. **Solvent–solvent interactions** between solvent particles must be overcome to **make room for the solute particles** in the solvent.

$$(\text{solvent})_m \rightleftharpoons m\ \text{solvent} \qquad \Delta H_{\text{solvent}}$$

3. **Solvent–solute interactions** between the solvent and solute particles occur as the particles mix.

$$n\ \text{solute} + m\ \text{solvent} \rightleftharpoons \text{solution} \qquad \Delta H_{\text{mix}}$$

$$\boxed{\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}}$$

Energetics of Solution Formation

$$\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

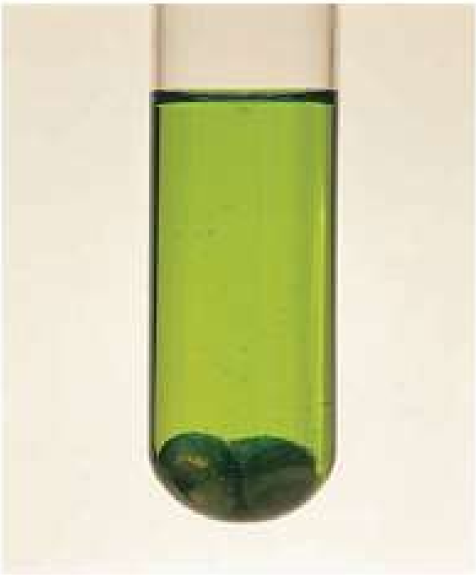
While breaking molecules apart always **consumes** energy, getting molecules together always **gives** off energy

1. $\Delta H_{\text{solute}} > 0$
2. $\Delta H_{\text{solvent}} > 0$
3. $\Delta H_{\text{mix}} < 0$
4. **ΔH_{soln} depends on the absolute values of ΔH_{solute} , $\Delta H_{\text{solvent}}$ and ΔH_{mix}**

Solution Formation and Chemical Reactions

!!! We must be careful to distinguish the physical process of solution formation from chemical reactions that lead to a solution

Nickel metal and hydrochloric acid



Nickel reacts with hydrochloric acid, forming $NiCl_2(aq)$ and $H_2(g)$. The solution is of $NiCl_2$, not Ni metal

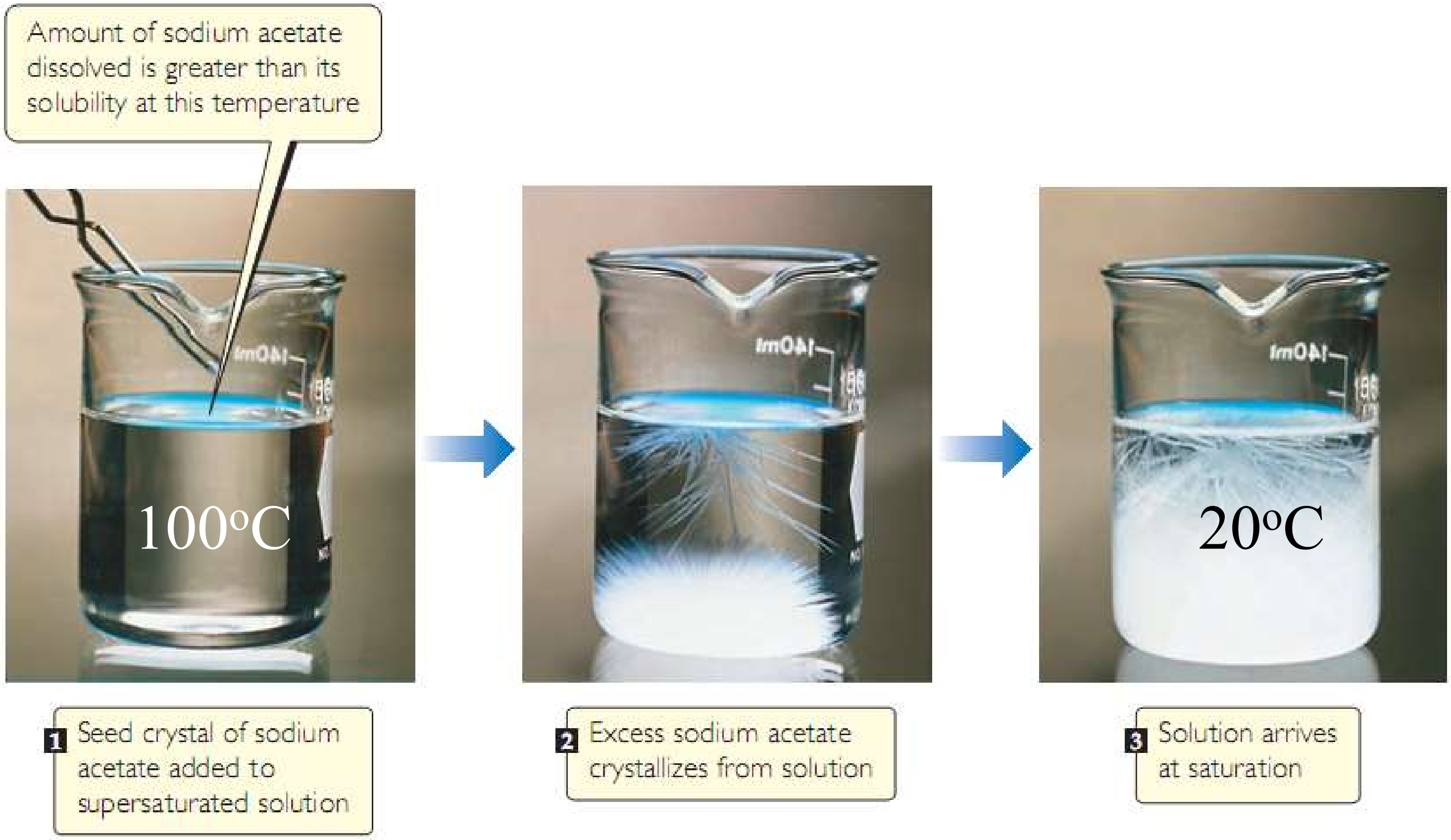
$NiCl_2 \cdot 6\,H_2O(s)$ remains when solvent evaporated

$$Ni(s) + 2\,HCl(aq) \longrightarrow NiCl_2(aq) + H_2(g)$$

13.2 Saturated Solutions and Solubility

$$\text{Solute} + \text{solvent} \underset{\text{crystallize}}{\overset{\text{dissolve}}{\rightleftharpoons}} \text{solution}$$

A solution that is in equilibrium with undissolved solute is **saturated**



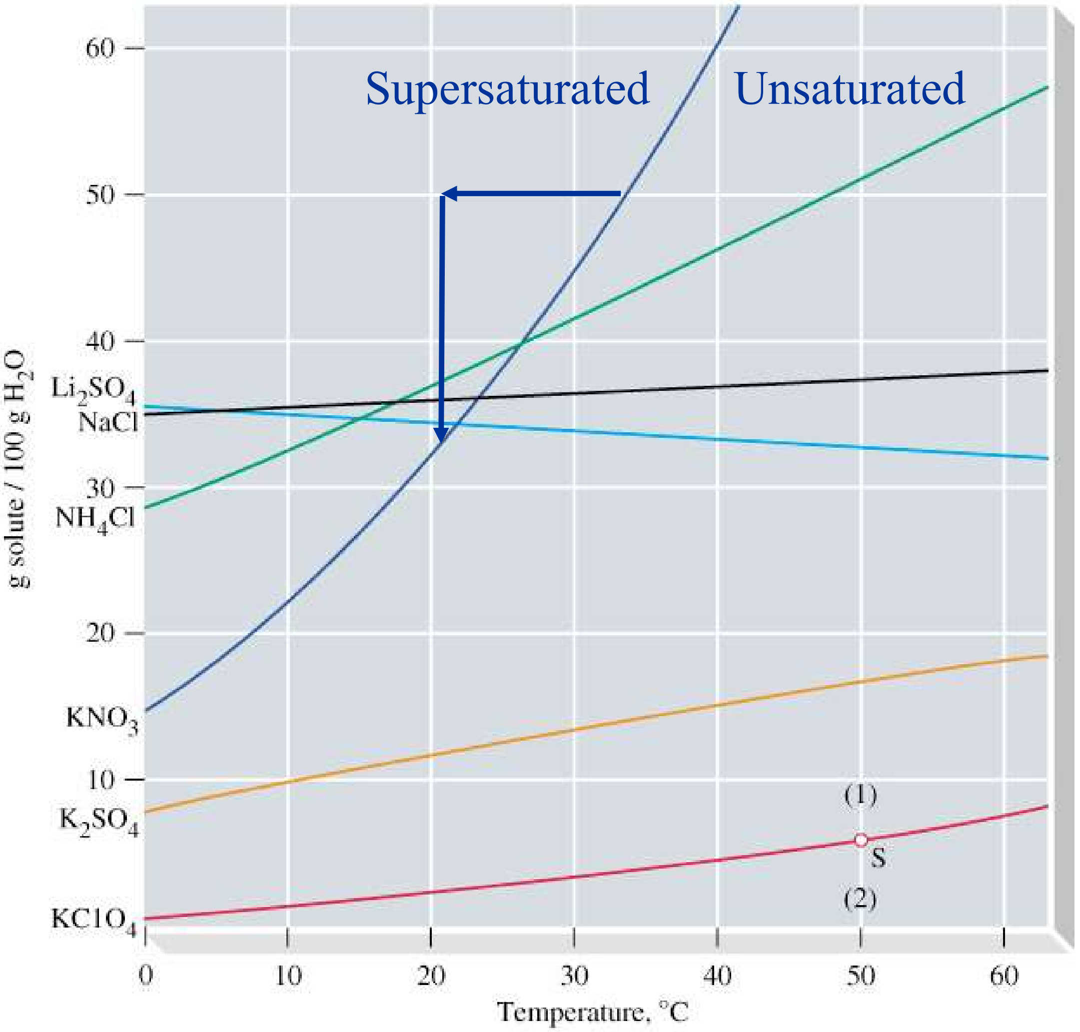
Amount of sodium acetate dissolved is greater than its solubility at this temperature

1 Seed crystal of sodium acetate added to supersaturated solution

2 Excess sodium acetate crystallizes from solution

3 Solution arrives at saturation

Solubility Curves



13.3 Factors affecting Solubility

- Solute–Solvent Interactions

The stronger the attractions between solute and solvent molecules, the greater the solubility of the solute in that solvent

- **Polar** liquids tend to **dissolve** in **polar** solvents.
  - acetone, a polar molecule, mixes in all proportions with water
- **Nonpolar** liquids tend to be **insoluble** in **polar** liquids
  - Hexane, a nonpolar molecule, is insoluble in water
- Substances with **similar intermolecular attractive forces** tend to be **soluble** in one another
- **Nonpolar** substances are more likely to be **soluble** in **nonpolar** solvents;
- **Ionic polar solutes** are more likely to be **soluble** in **polar solvents**.
- **Network solids** such as diamond and quartz are **not soluble** in **either polar or nonpolar** solvents because of the strong bonding within the solid.

EXAMPLE

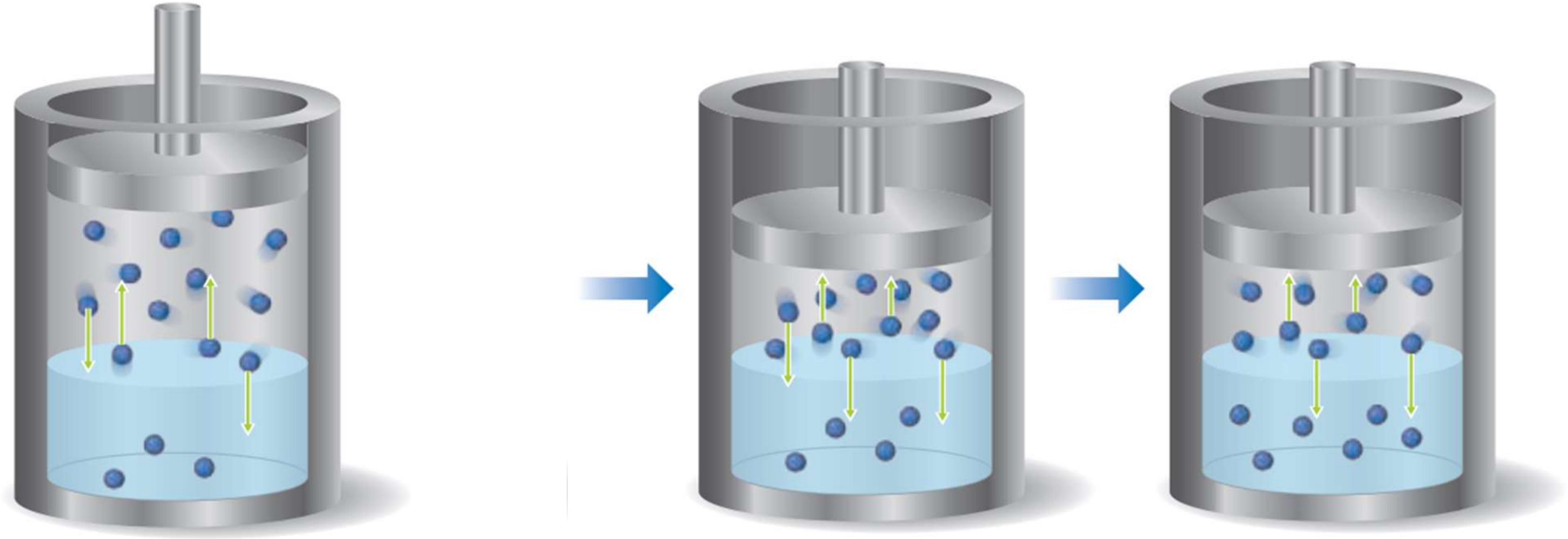
Predict whether each of the following substances is more likely to dissolve in the nonpolar solvent carbon tetrachloride (CCl_4) or in water: C_7H_{16}, Na_2SO_4, HCl, and I_2

- **C_7H_{16}** is a hydrocarbon, so it is molecular and **nonpolar**.
- **Na_2SO_4**, a compound containing a metal and nonmetals, is **ionic**.
- **HCl**, a diatomic molecule containing two nonmetals that differ in electronegativity, is **polar**.
- **I_2**, a diatomic molecule with atoms of equal electronegativity, is **nonpolar**.

➔ C_7H_{16} and I_2 (the nonpolar solutes) would be more soluble in the nonpolar CCl_4 than in polar H_2O,

➔ Water would be the better solvent for Na_2SO_4 and HCl (the ionic and polar covalent solutes)

13.3 Factors affecting Solubility



Equilibrium

Pressure is increased.
More CO_2 dissolves

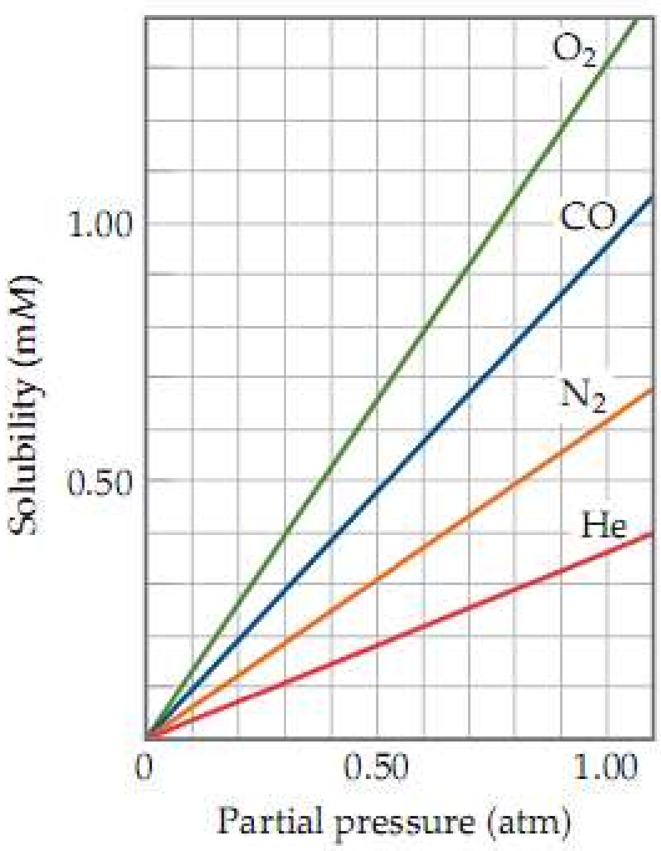
Equilibrium restored

Would pushing the piston down change the amount of gas molecules dissolved in the liquid?

13.3 Factors affecting Solubility

- Pressure
  - The solubilities of solids and liquids are not appreciably affected by pressure
  - The solubility of a gas in a liquid solvent increases in direct proportion to the partial pressure of the gas above the solution:

Henry's Law : $S_g = k P_g$



EXAMPLE

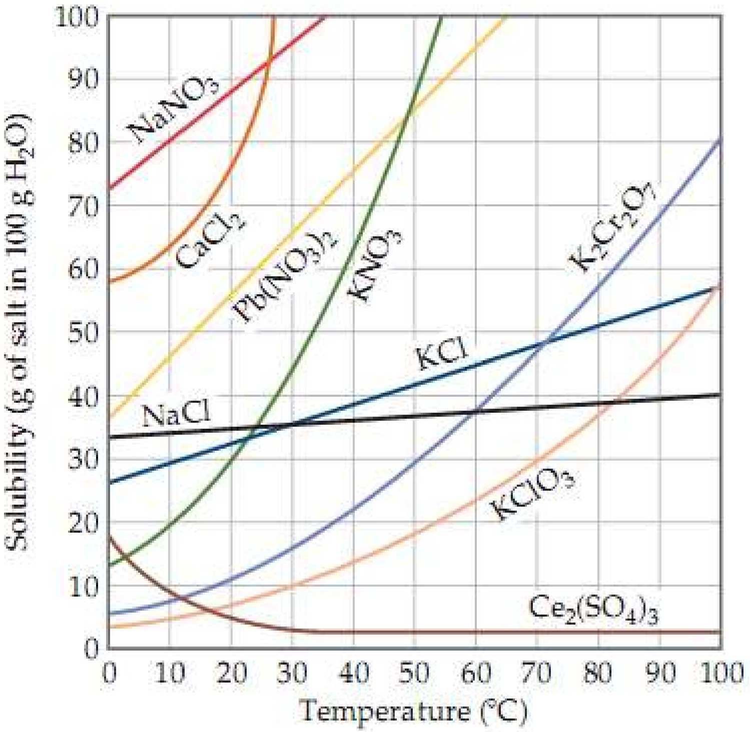
Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure of CO_2 of 4.0 atm over the liquid at 25 °C. The Henry's law constant for CO_2 in water at this temperature is $3.4 \text{ x } 10^{-2}$ mol/L.atm.

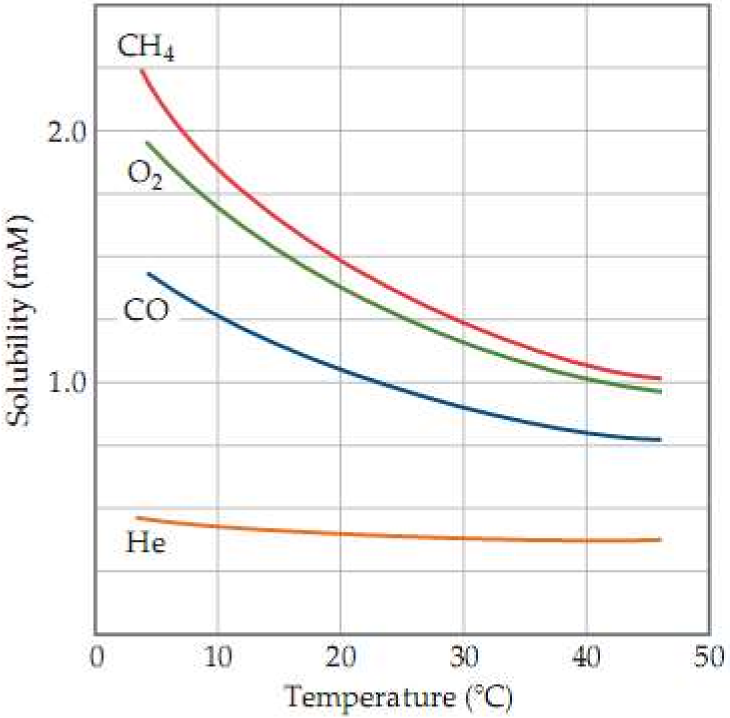
$$\begin{aligned} S_{CO_2} &= kP_{CO_2} \\ &= (3.4 \times 10^{-2} \text{ mol/L-atm})(4.0 \text{ atm}) \\ &= 0.14 \text{ mol/L} \\ &= 0.14\, M \end{aligned}$$

Calculate the concentration of CO_2 in a soft drink after the bottle is opened and the solution equilibrates at 25 °C under a CO_2 partial pressure of 30.4 Pa. The Henry's law constant for CO_2 in water at this temperature is $3.4 * 10^{-4}$ $mol/m^3.Pa$

13.3 Factors affecting Solubility

- Temperature
  - The solubility of most **solid** solutes in water **increases** as the solution temperature increases
  - The solubility of **gases** in water **decreases** with increasing temperature





13.4 Expressing Solution Concentration

- Mass percentage, ppm, and ppb
  - Mass percent

$$\text{Mass \% of component} = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 100$$

  - Parts per million (ppm)

$$\text{ppm of component} = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^6$$

  - Parts per billion (ppb)

13.4 Expressing Solution Concentration

- Mole Fraction, Molarity, and Molality
  - Mole Fraction

$$\text{Mole fraction of component} = \frac{\text{moles of component}}{\text{total moles of all components}}$$

  - Molarity

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of soln}}$$

  - Molality

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

EXAMPLE

A solution is made by dissolving 4.35 g of glucose ($C_6H_{12}O_6$) in 25.0 mL of water at 25 °C. Calculate the molality of glucose in the solution. Water has a density of 1.00 g/mL.

- Moles of solute

$$\text{Mol } C_6H_{12}O_6 = (4.35 \text{ g } C_6H_{12}O_6)\left(\frac{1 \text{ mol } C_6H_{12}O_6}{180.2 \text{ g } C_6H_{12}O_6}\right)$$

$$= 0.0241 \text{ mol } C_6H_{12}O_6$$

- Mass of the solvent

$$(25.0 \text{ mL})(1.00 \text{ g/mL}) = 25.0 \text{ g} = 0.0250 \text{ kg}$$

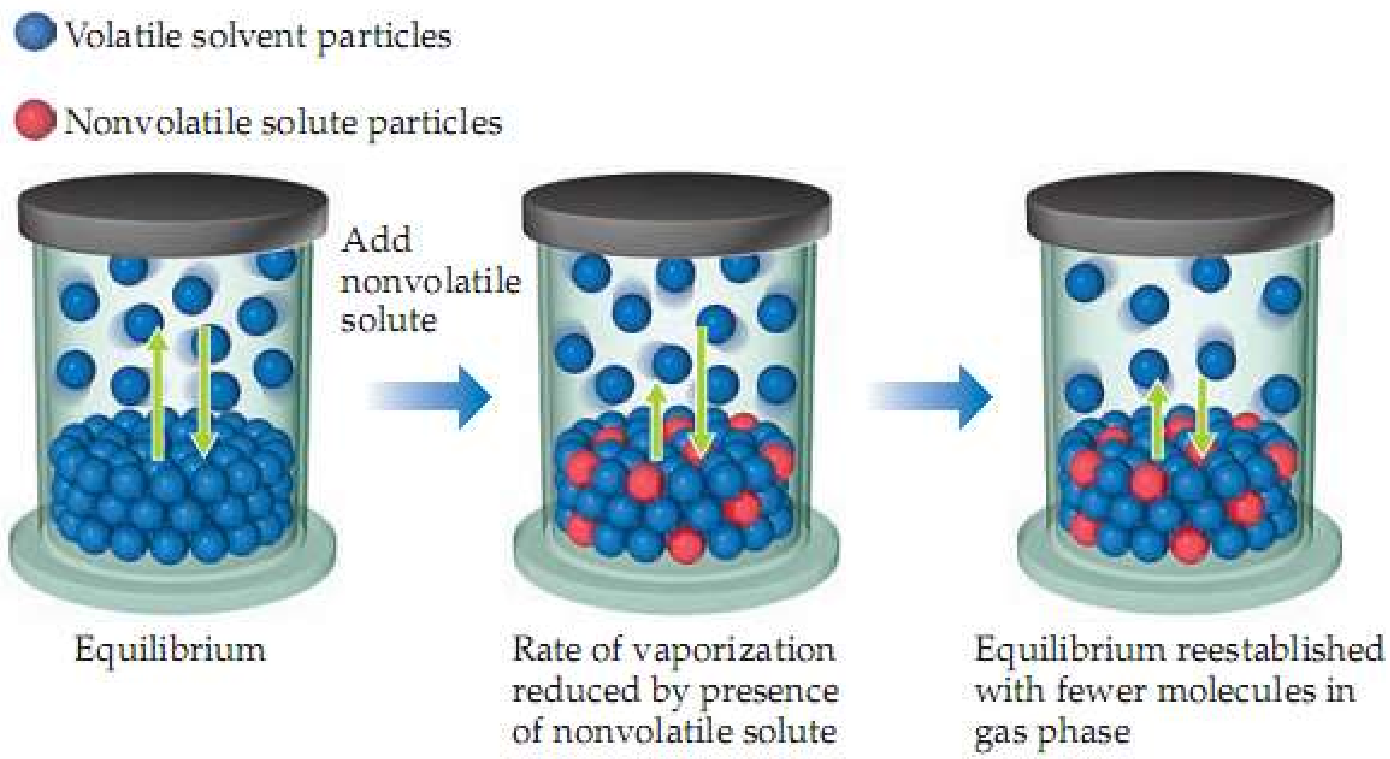
- Molality

$$\text{Molality of } C_6H_{12}O_6 = \frac{0.0241 \text{ mol } C_6H_{12}O_6}{0.0250 \text{ kg } H_2O} = 0.964\, m$$

13.5 Colligative Properties

- **4 Colligative Properties:** Boiling Point, Freezing Point, Vapor Pressure and Osmotic Pressure
- The **4 Colligative Properties** help to explain what happens to a pure solvent as solute is added to it.

Vapor-Pressure Lowering



Why?

Raoult’s Law

The difference between a solvent’s normal vapor pressure (P°_{solvent}) and a solution’s vapor pressure (P_{solution}) is presented by **Raoult’s law:**

$$P_{\text{solution}} = X_{\text{solvent}} P^\circ_{\text{solvent}}$$

Where P_{solution} is the partial pressure exerted by solvent vapor above the solution, X_{solvent} is the mole fraction of the solvent, and P°_{solvent} is the vapor pressure of the pure solvent,

EXAMPLE

Glycerin ($C_3H_8O_3$) is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25°C. Calculate the vapor pressure at 25 °C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25 °C is 23.8 torr (Appendix B), and its density is 1.00 g/mL.

$$\text{Moles } C_3H_8O_3 = (50.0 \text{ mL } C_3H_8O_3)\left(\frac{1.26 \text{ g } C_3H_8O_3}{1 \text{ mL } C_3H_8O_3}\right)\left(\frac{1 \text{ mol } C_3H_8O_3}{92.1 \text{ g } C_3H_8O_3}\right) = 0.684 \text{ mol}$$

$$\text{Moles } H_2O = (500.0 \text{ mL } H_2O)\left(\frac{1.00 \text{ g } H_2O}{1 \text{ mL } H_2O}\right)\left(\frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O}\right) = 27.8 \text{ mol}$$

$$X_{H_2O} = \frac{\text{mol } H_2O}{\text{mol } H_2O + \text{mol } C_3H_8O_3} = \frac{27.8}{27.8 + 0.684} = 0.976$$

$$P_{H_2O} = X_{H_2O} P^{\circ}_{H_2O} = (0.976)(23.8 \text{ torr}) = 23.2 \text{ torr}$$

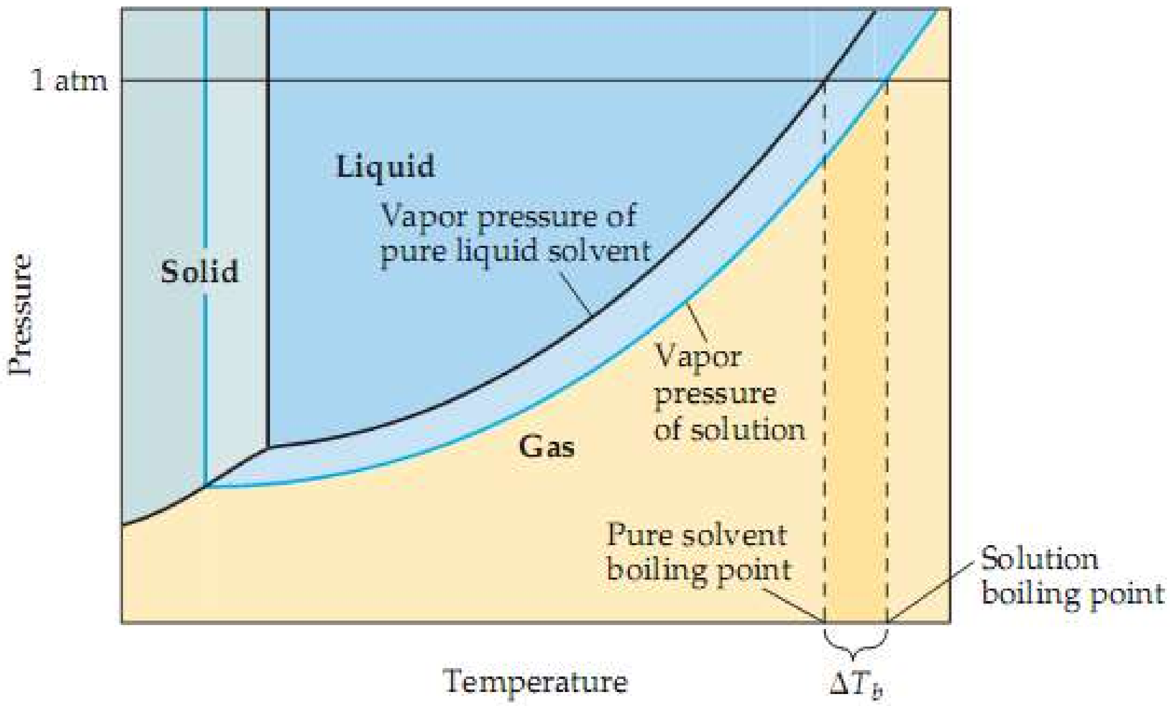
Boiling-Point Elevation

The boiling point of the solution is higher than that of the pure solvent.

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = iK_bm$$

i: van't Hoff factor

K_b: molal boiling point elevation constant



Freezing-Point Depression

De-icing salt

How?

The salt molecules gradually dissolve in the ice, get in between water molecules (separate the frozen water molecules from each other), converting them back into liquid. Hence salt molecules decrease water’s freezing point

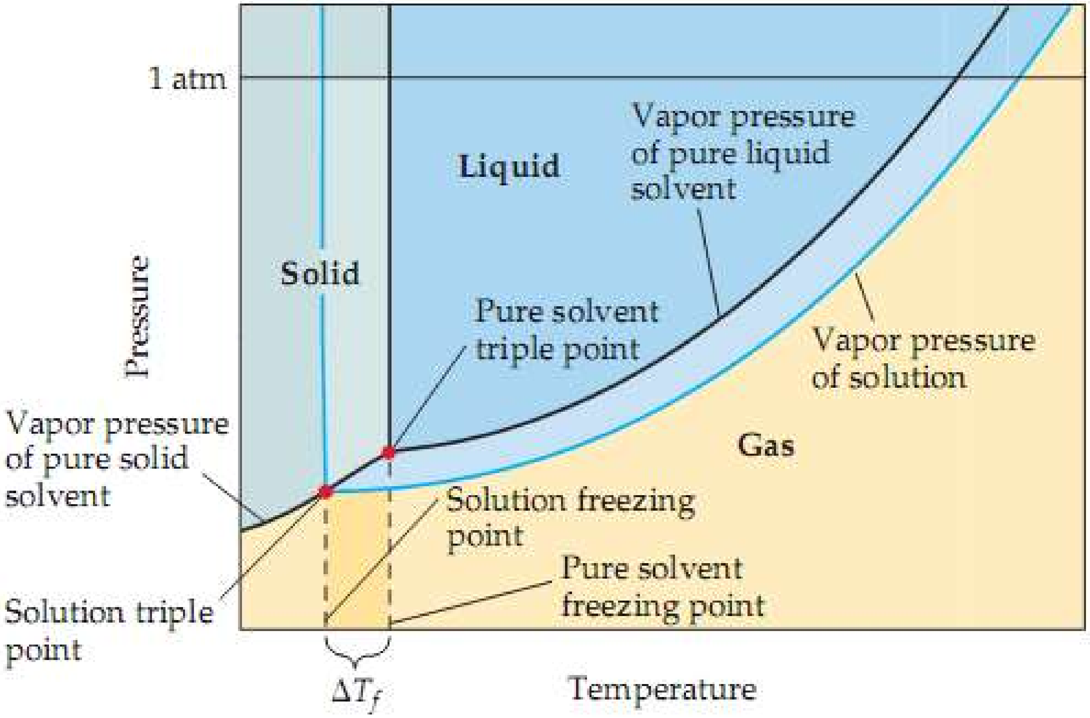
Freezing-Point Depression

The freezing point of the solution is lower than that of the pure liquid

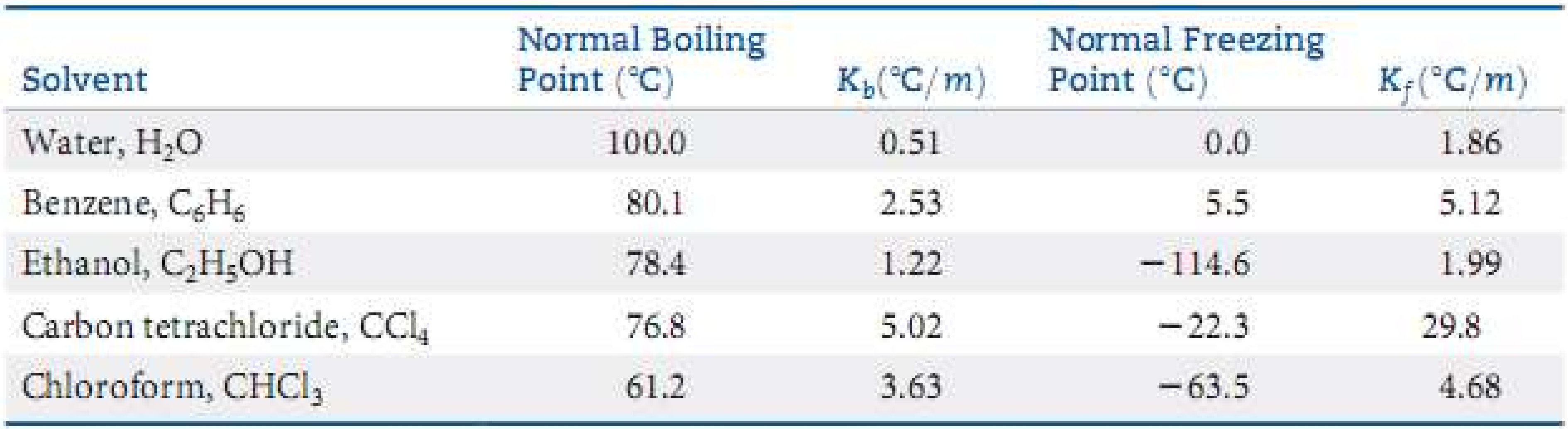
$$\Delta T_f = T_f(\text{solution}) - T_f(\text{solvent}) = -iK_f m$$

i: van't Hoff factor

K_f: molal freezing-point depression constant



Molal Boiling-Point-elevation and Freezing-Point-depression Constants



Solvent	Normal Boiling Point (°C)	K_b(°C/m)	Normal Freezing Point (°C)	K_f(°C/m)
Water, H_2O	100.0	0.51	0.0	1.86
Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, C_2H_5OH	78.4	1.22	−114.6	1.99
Carbon tetrachloride, CCl_4	76.8	5.02	−22.3	29.8
Chloroform, $CHCl_3$	61.2	3.63	−63.5	4.68

EXAMPLE

Automotive antifreeze contains ethylene glycol, $CH_2(OH)CH_2(OH)$, a nonvolatile nonelectrolyte, in water. Calculate the boiling point and freezing point of a 25.0% by mass solution of ethylene glycol in water.

$$\text{Molality} = \frac{\text{moles } C_2H_6O_2}{\text{kilograms } H_2O} = \left(\frac{250 \text{ g } C_2H_6O_2}{750 \text{ g } H_2O}\right)\left(\frac{1 \text{ mol } C_2H_6O_2}{62.1 \text{ g } C_2H_6O_2}\right)\left(\frac{1000 \text{ g } H_2O}{1 \text{ kg } H_2O}\right)$$

$$= 5.37\ m$$

$$\Delta T_b = iK_b m = (1)(0.51\ {}^\circ\text{C}/m)(5.37\ m) = 2.7\ {}^\circ\text{C}$$

$$\Delta T_f = -iK_f m = -(1)(1.86\ {}^\circ\text{C}/m)(5.37\ m) = -10.0\ {}^\circ\text{C}$$

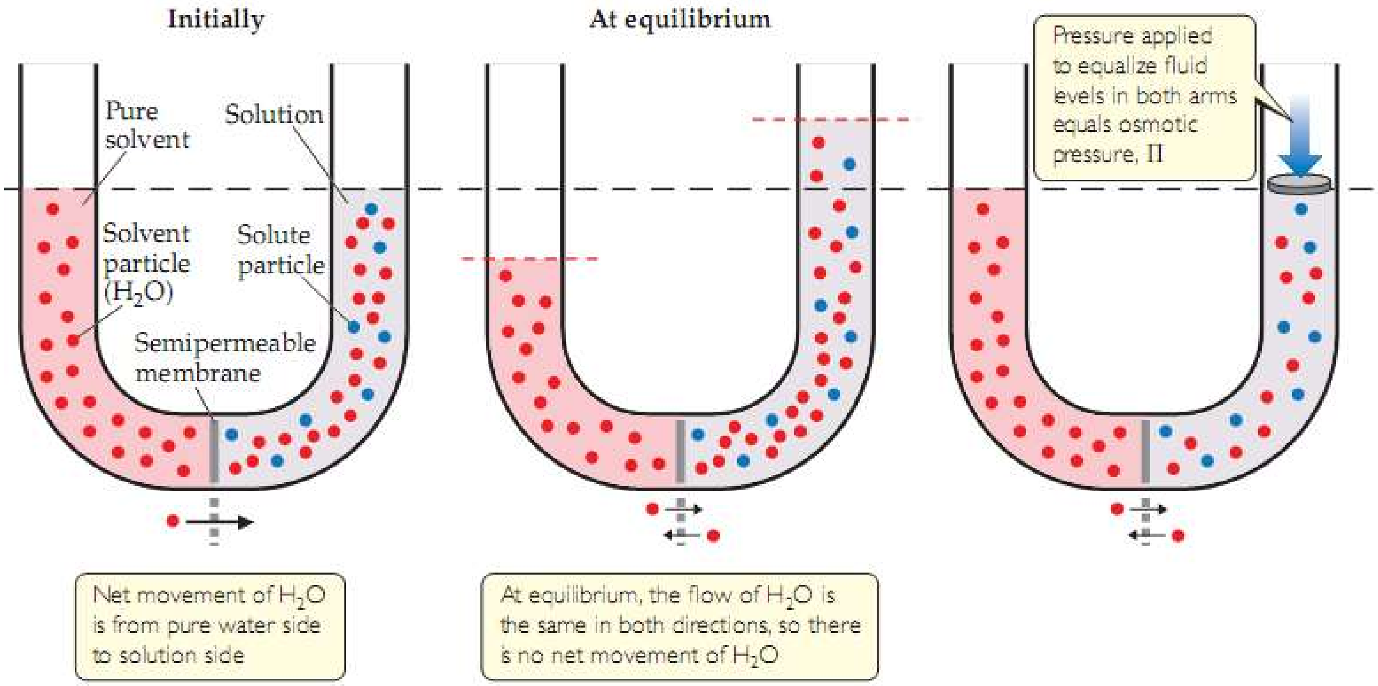
$$\begin{aligned} \Delta T_b &= T_b(\text{solution}) - T_b(\text{solvent}) \\ 2.7\ {}^\circ\text{C} &= T_b(\text{solution}) - 100.0\ {}^\circ\text{C} \\ T_b(\text{solution}) &= 102.7\ {}^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \Delta T_f &= T_f(\text{solution}) - T_f(\text{solvent}) \\ -10.0\ {}^\circ\text{C} &= T_f(\text{solution}) - 0.0\ {}^\circ\text{C} \\ T_f(\text{solution}) &= -10.0\ {}^\circ\text{C} \end{aligned}$$

Osmosis

Osmosis is the process of a **solvent moving** from one compartment to another, **across a semipermeable membrane**, toward higher solute concentration.

Osmotic pressure is generated at equilibrium due to the different heights of liquid on either side of the membrane and is equivalent to the pressure needed to equalize the fluid levels across the membrane.



Pressure applied to equalize fluid levels in both arms equals osmotic pressure, Π

Net movement of H_2O is from pure water side to solution side

At equilibrium, the flow of H_2O is the same in both directions, so there is no net movement of H_2O

Osmosis pressure, Π

↑ $\Delta T_b = i \times k_b \times m$

↓ $\Delta T_f = i \times k_f \times m$

↑ $\Pi = i \times M \times R \times T$

↓ $P_{solution} = X \times P^{o}{}_{solvent}$

$$\text{i = van 't Hoff factor} = \frac{\text{\# of particles that the solute breaks into}}{\text{\# of molecules dissolved}}$$

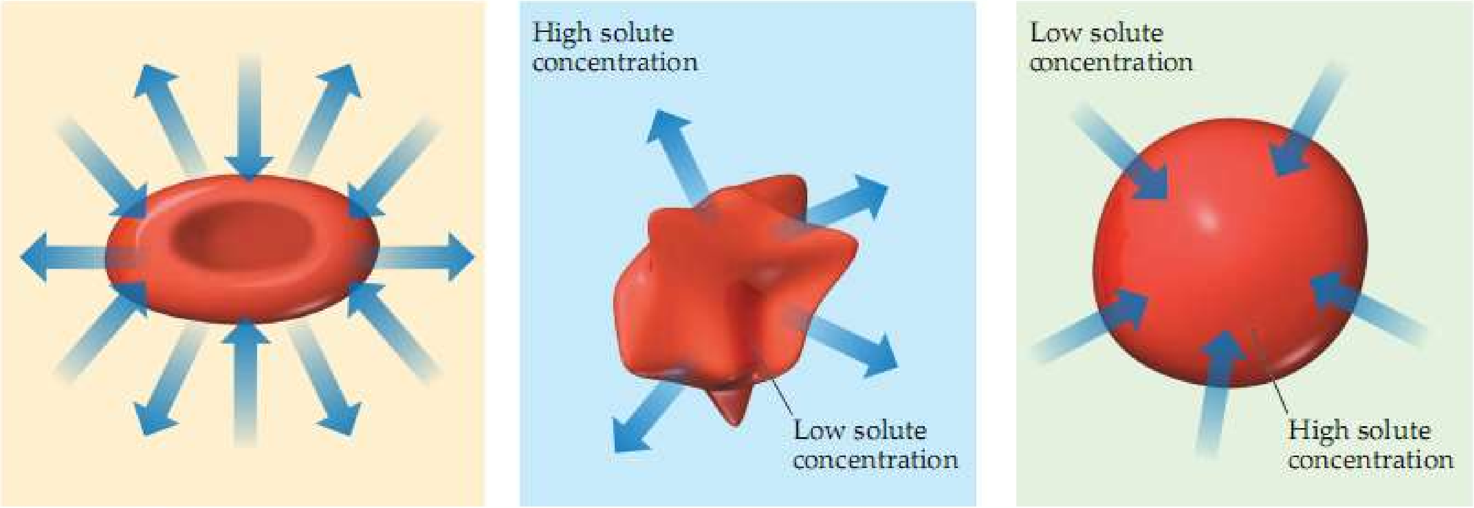
k_b = boiling point elevation constant, for water k_b = 0.512 ^{o}C/m
k_f = freezing point depression constant, for water k_b = 1.86 ^{o}C/m
M = molarity
m = molality
R = gas constant
T = temperature in Kelvin

$P_{solution}$ = vapor pressure of the solution
$P^{o}{}_{solvent}$ = vapor pressure of the pure solvent

Osmosis

If water moves out of the red blood cell, it shrivels (crenation);
If water moves into the red blood cell, it will swell and may burst (hemolysis).

The arrows represent the net movement of water molecules.



Red blood cell in isotonic medium neither swells nor shrinks.

Crenation of red blood cell placed in hypertonic environment

Hemolysis of red blood cell placed in hypotonic environment

People who need body fluids or nutrients replaced but cannot be fed orally are given solutions by intravenous (IV) infusion, which feeds nutrients directly into the veins. To prevent crenation or hemolysis of red blood cells, the IV solutions must be isotonic with the intracellular fluids of the blood cells

EXAMPLE

The average osmotic pressure of blood is 7.7 atm at 25 °C. What molarity of glucose ($C_6H_{12}O_6$) will be isotonic with blood?

$$\Pi = iMRT$$

$$M = \frac{\Pi}{iRT} = \frac{(7.7\ \text{atm})}{(1)\left(0.0821\frac{\text{L-atm}}{\text{mol-K}}\right)(298\ \text{K})} = 0.31\ M$$

EXAMPLE

A solution of an unknown nonvolatile nonelectrolyte was prepared by dissolving 0.250 g of the substance in 40.0 g of CCl_4. The boiling point of the resultant solution was 0.357 °C higher than that of the pure solvent. Calculate the molar mass of the solute.

Molality:

$$\text{Molality} = \frac{\Delta T_b}{iK_b} = \frac{0.357\ ^\circ\text{C}}{(1)5.02\ ^\circ\text{C}/m} = 0.0711\ m$$

The number of moles of solute in the solution

$$(0.0400\ \text{kg CCl}_4)\left(0.0711\ \frac{\text{mol solute}}{\text{kg CCl}_4}\right) = 2.84 \times 10^{-3}\ \text{mol solute}$$

The molar mass of the solute

$$\text{Molar mass} = \frac{0.250\ \text{g}}{2.84 \times 10^{-3}\ \text{mol}} = 88.0\ \text{g/mol}$$

13.6 Colloids

This is a self-read section