Lecture Presentation

Chapter 12

Solutions and Their Properties

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Solutions

Solution: A homogeneous mixture

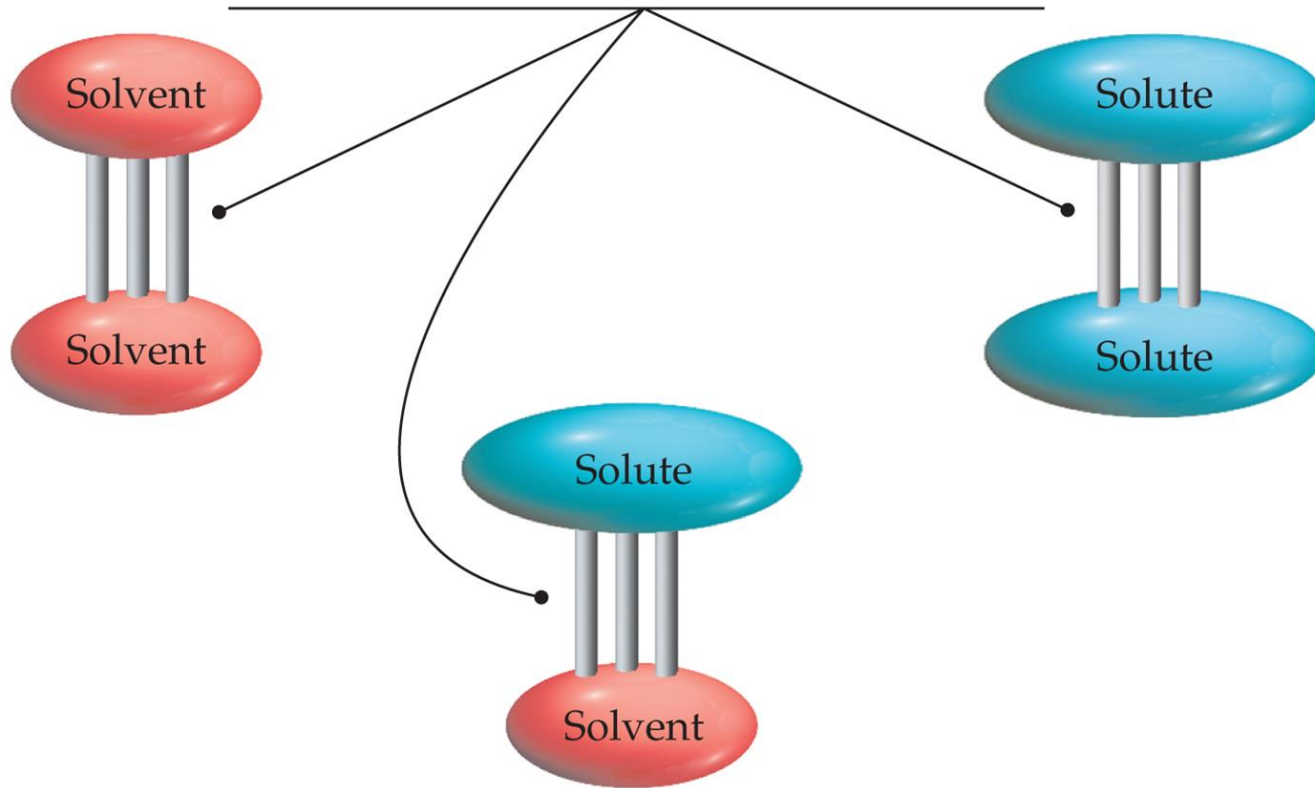**Solvent**: The major component

Solute: A minor component

TABLE 12.1 Some Different Kinds of Solutions

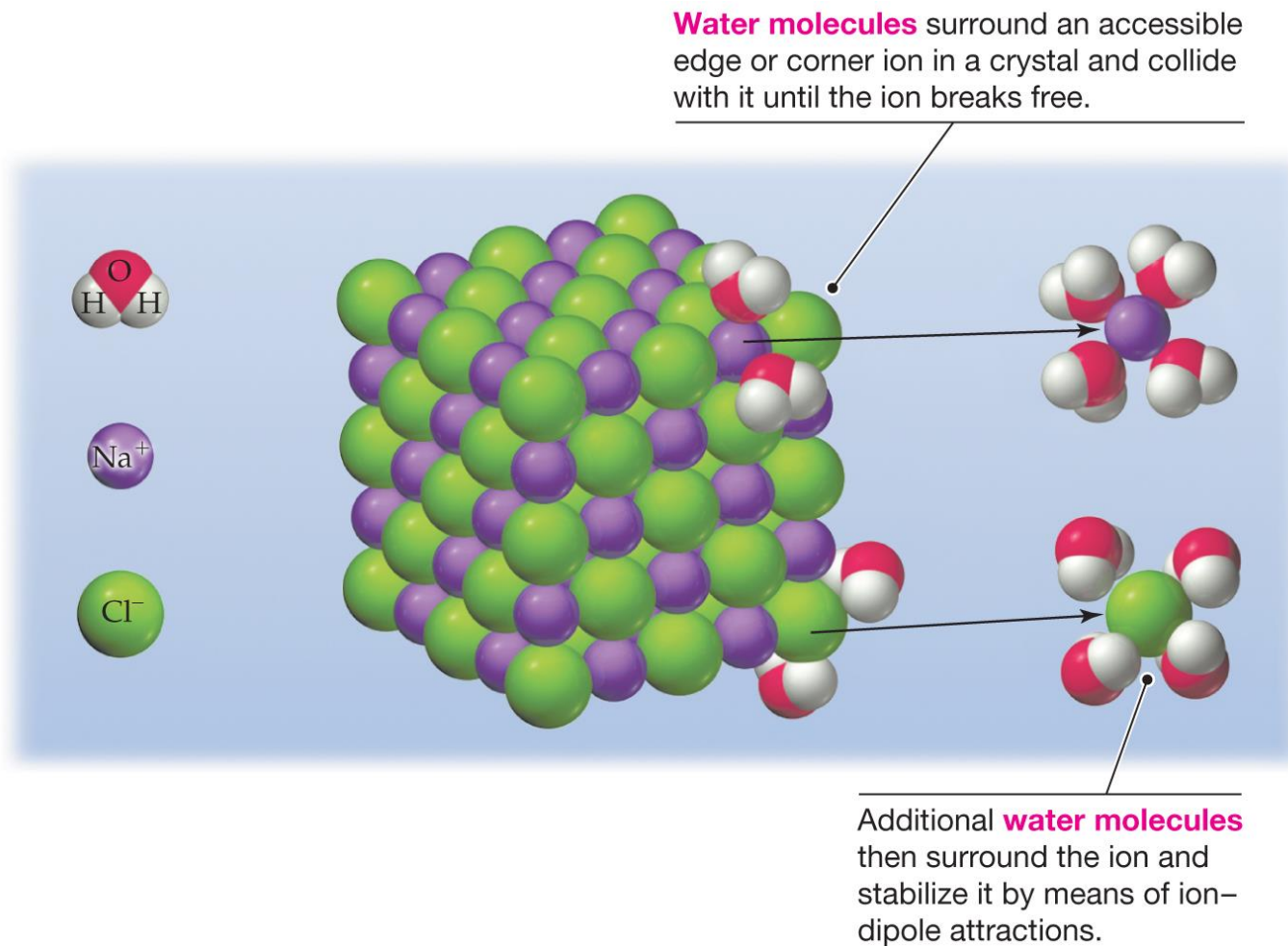| Kind of Solution	Example
Gas in gas	Air (O_2, N_2, Ar, and other gases)
Gas in liquid	Carbonated water (CO_2 in water)
Gas in solid	H_2 in palladium metal
Liquid in liquid	Gasoline (mixture of hydrocarbons)
Liquid in solid	Dental amalgam (mercury in silver)
Solid in liquid	Seawater (NaCl and other salts in water)
Solid in solid	Metal alloys, such as sterling silver (92.5% Ag, 7.5% Cu)

Energy Changes and the Solution Process

Like dissolves like. Solutions form when the intermolecular forces involved in these three kinds of interactions are similar.

Solvent

Solvent

Solute

Solute

Solute
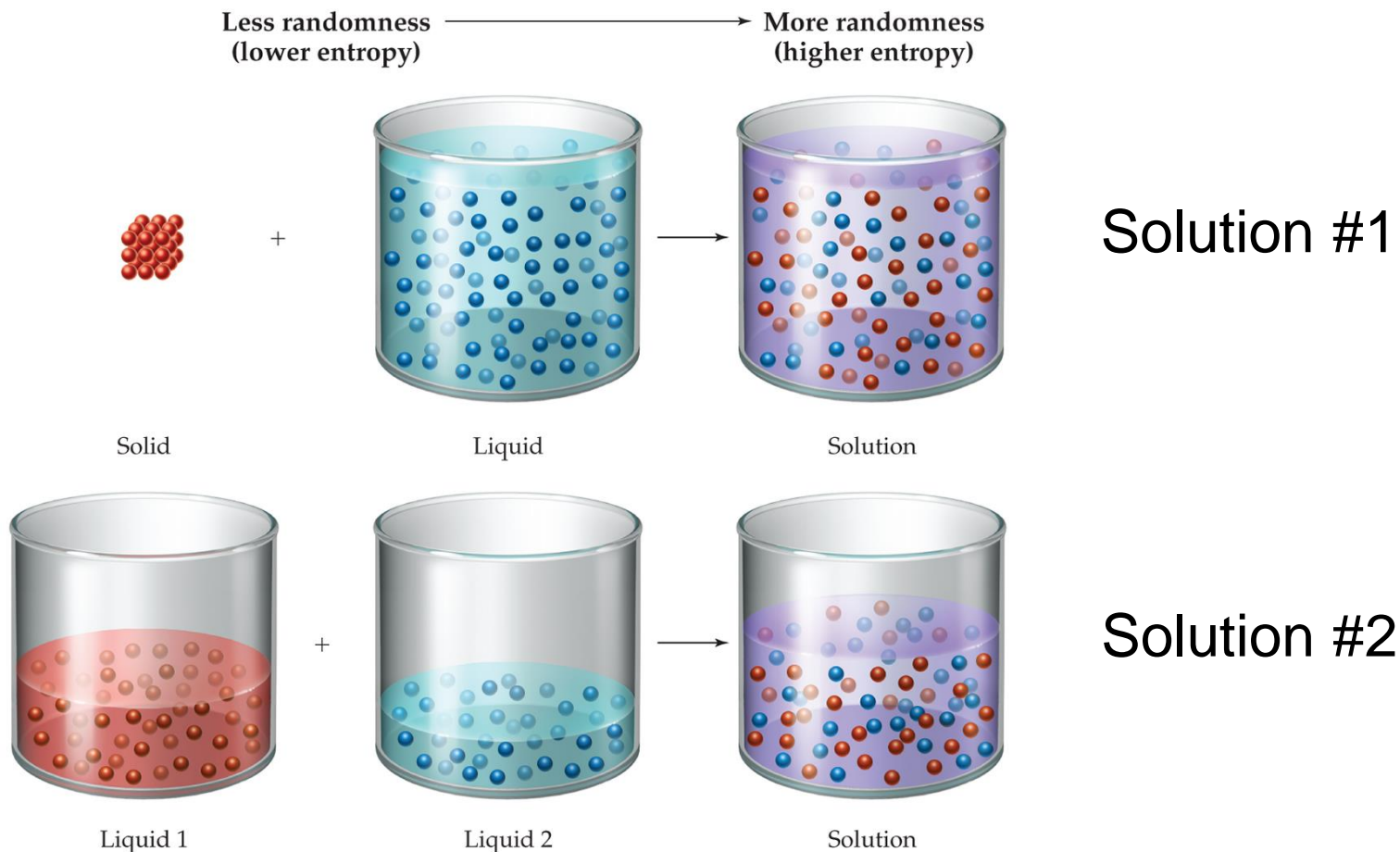
Solvent

Energy Changes and the Solution Process

The sodium and chloride ions are *hydrated*.

Water molecules surround an accessible edge or corner ion in a crystal and collide with it until the ion breaks free.

Additional water molecules then surround the ion and stabilize it by means of ion–dipole attractions.

Energy Changes and the Solution Process

There is an *entropy* change for the solution process.

Less randomness (lower entropy) → More randomness (higher entropy)

Solid + Liquid → Solution **Solution #1**

Liquid 1 + Liquid 2 → Solution **Solution #2**

Energy Changes and the Solution Process

$$\Delta G = \Delta H - T\Delta S$$

TABLE 12.2 Some Enthalpies and Entropies of Solution in Water at 25 °C

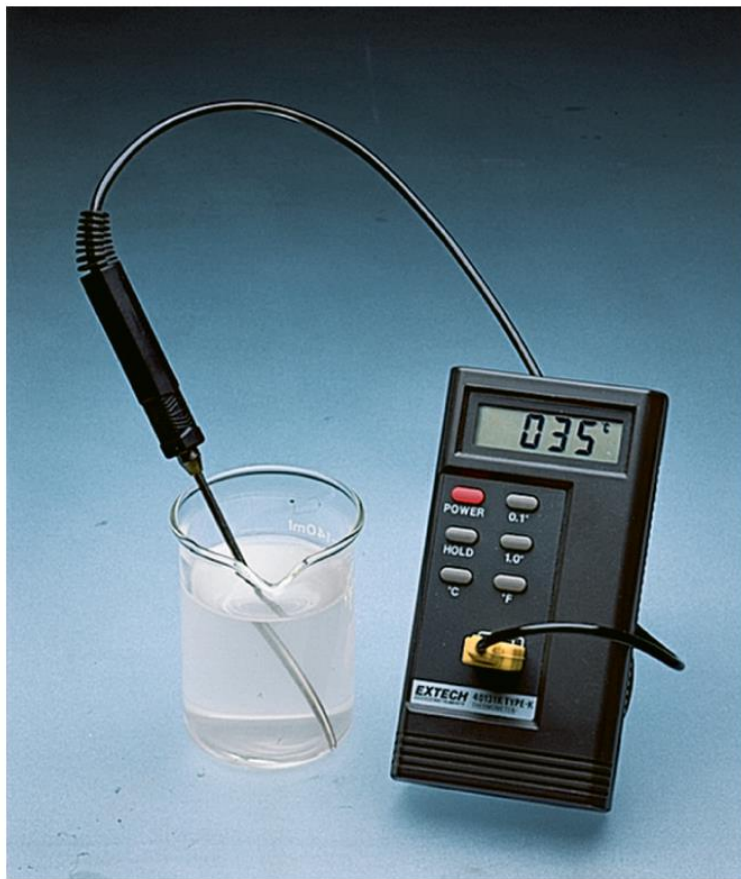| Substance	ΔH_{soln} (kJ/mol)	ΔS_{soln} [J/(K · mol)]
LiCl	−37.0	10.5
NaCl	3.9	43.4
KCl	17.2	75.0
LiBr	−48.8	21.5
NaBr	−0.6	54.6
KBr	19.9	89.0
KOH	−57.6	12.9

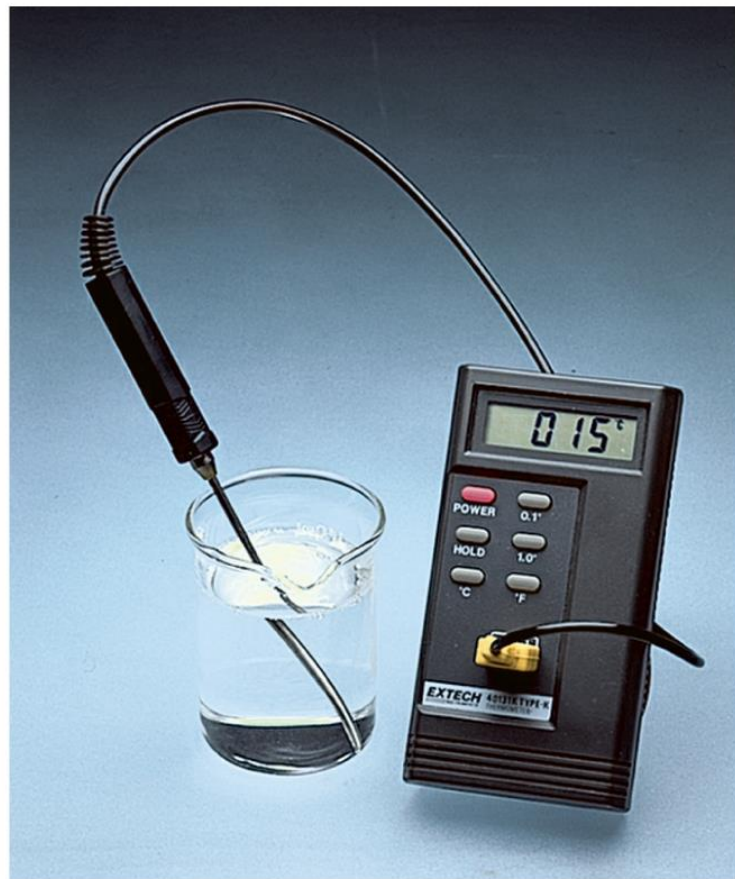**Endothermic**: $+\Delta H$ **Spontaneous**: $-\Delta G$
Exothermic: $-\Delta H$ **Nonspontaneous**: $+\Delta G$

Energy Changes and the Solution Process

Dissolution of $CaCl_2$ in water is **exothermic**, causing the temperature of the water to rise from its initial 25 °C value.

Dissolution of NH_4NO_3 is **endothermic**, causing the temperature of the water to fall from its initial 25 °C value.

Energy Changes and the Solution Process

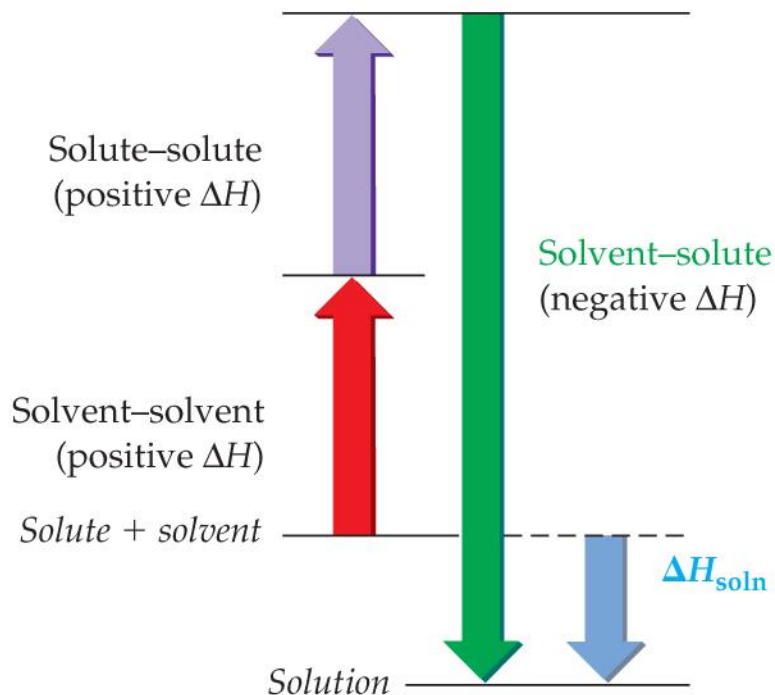**Solvent–Solvent Interactions**: Energy is absorbed (positive ΔH) to overcome intermolecular forces between solvent molecules.

Solute–Solute Interactions: Energy is absorbed (positive ΔH) to overcome intermolecular forces holding solute particles together in a crystal.

Solvent–Solute Interactions: Energy is released (negative ΔH) when solvent molecules cluster around solute particles and solvate them.
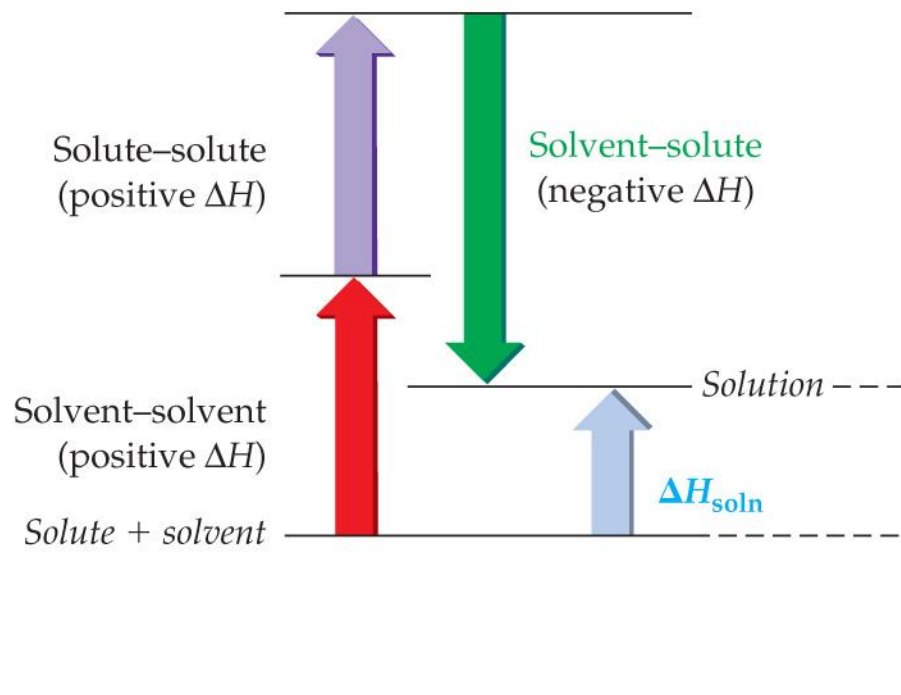
Energy Changes and the Solution Process

Solute–solute (positive ΔH)

Solvent–solute (negative ΔH)

Solvent–solvent (positive ΔH)

Solute + solvent

ΔH_{soln}

Solution

$\Delta H_{soln} < 0$

ΔH_{soln} is negative if solvent–solute interactions are dominant.

Solute–solute (positive ΔH)

Solvent–solute (negative ΔH)

Solvent–solvent (positive ΔH)

Solute + solvent

Solution – – –

ΔH_{soln}

$\Delta H_{soln} > 0$

ΔH_{soln} is positive if solvent–solute interactions are not dominant.

Concentration Units for Solutions

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

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

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

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

Concentration Units for Solutions

Assuming that seawater is an aqueous solution of NaCl, what is its molarity? The density of seawater is 1.025 g/mL at 20 °C, and the NaCl concentration is 3.50 mass percent.

Assuming 100.00 g of solution, calculate the volume:

$$100.00 \text{ g solution} \times \frac{1 \text{ mL}}{1.025 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.09756 \text{ L}$$

Convert the mass of NaCl to moles:

$$3.50 \text{ g NaCl} \times \frac{1 \text{ mol}}{58.4 \text{ g}} = 0.0599 \text{ mol}$$

Concentration Units for Solutions

Calculate the molarity of the solution:

$$\frac{0.0599 \text{ mol}}{0.09756 \text{ L}} = 0.614 \text{ M}$$

Concentration Units for Solutions

What is the molality of a solution prepared by dissolving 0.385 g of cholesterol, $C_{27}H_{46}O$, in 40.0 g chloroform, $CHCl_3$?

Convert the mass of cholesterol to moles:

$$0.385 \text{ g} \times \frac{1 \text{ mol}}{386.0 \text{ g}} = 0.000\ 997 \text{ mol}$$

Calculate the mass of chloroform in kilograms:

$$40.0 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0400 \text{ kg}$$

Concentration Units for Solutions

Calculate the molality of the solution:

$$\frac{0.000\ 997\ \text{mol}}{0.0400\ \text{kg}} = 0.0249\ m$$

Concentration Units for Solutions

| Name	Units	Advantages	Disadvantages
TABLE 12.3 A Comparison of Various Concentration Units			
Molarity (M)	$\dfrac{\text{mol solute}}{\text{L solution}}$	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 (m)	$\dfrac{\text{mol solute}}{\text{kg solvent}}$	Temperature-independent; useful in special applications	Measure by mass; must know density to convert to molarity

Some Factors That Affect Solubility

Saturated Solution: A solution containing the maximum possible amount of dissolved solute at equilibrium

$$\text{Solute + Solvent} \underset{\text{crystallize}}{\overset{\text{dissolve}}{\rightleftharpoons}} \text{Solution}$$
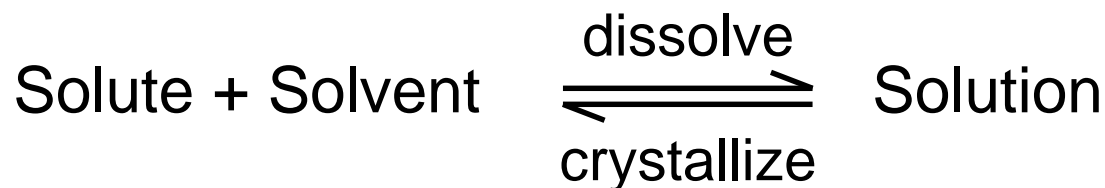
Supersaturated Solution: A solution containing a greater-than-equilibrium amount of solute
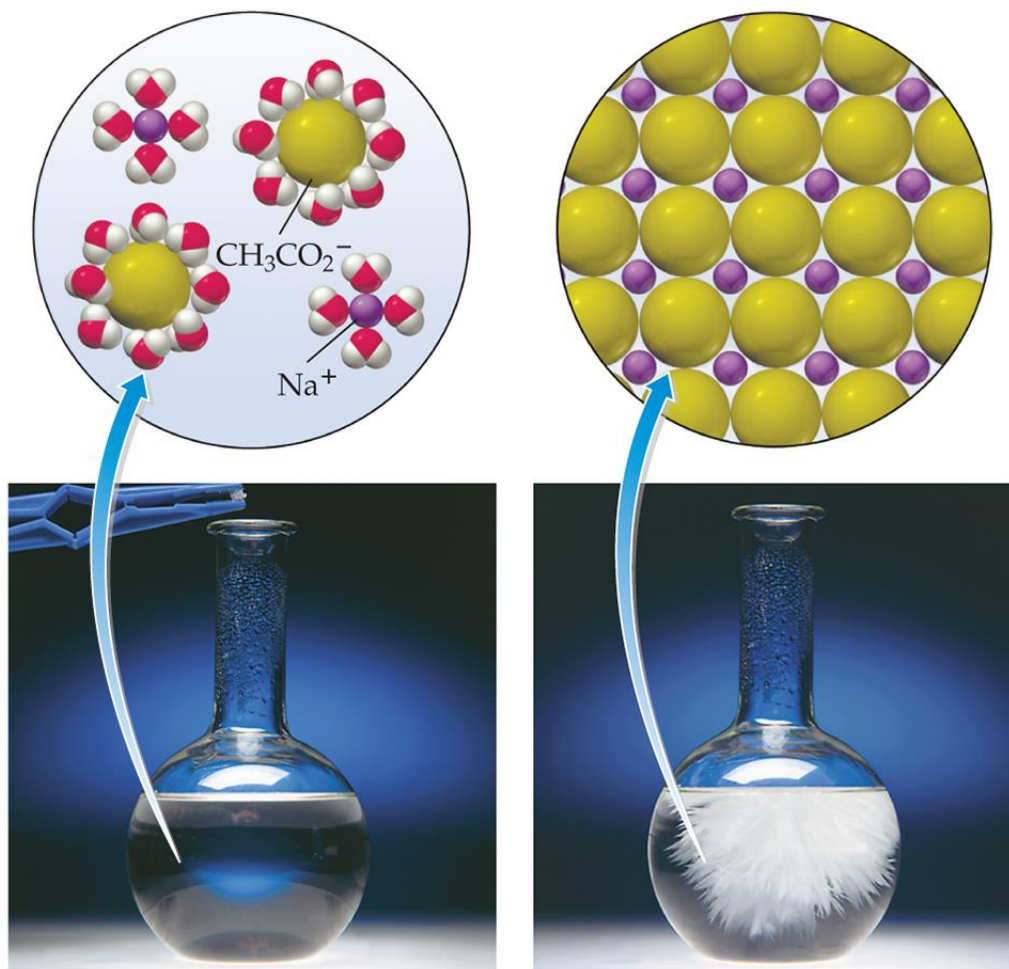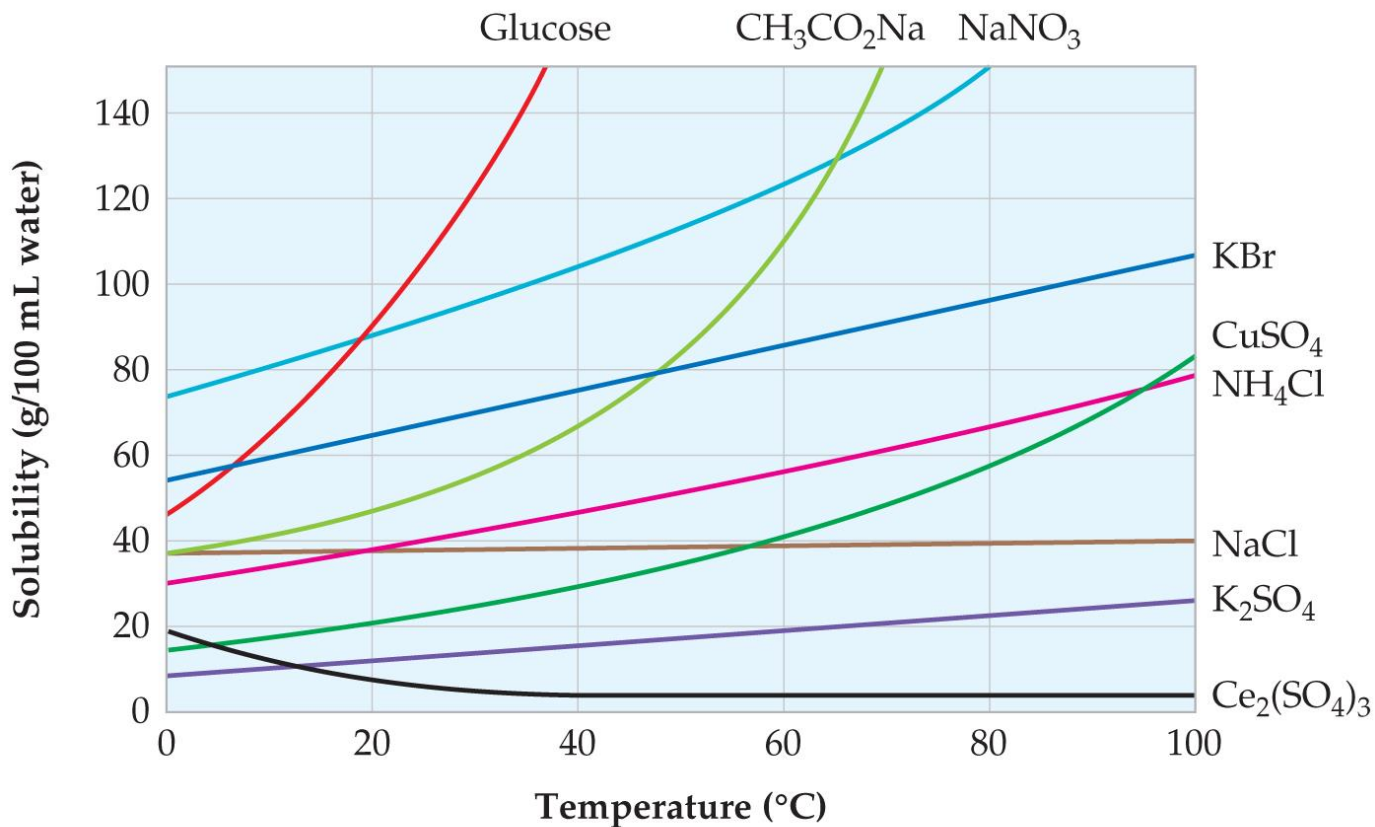
A supersaturated solution of sodium acetate in water.

When a tiny seed crystal is added, larger crystals begin to grow and precipitate from the solution until equilibrium is reached.
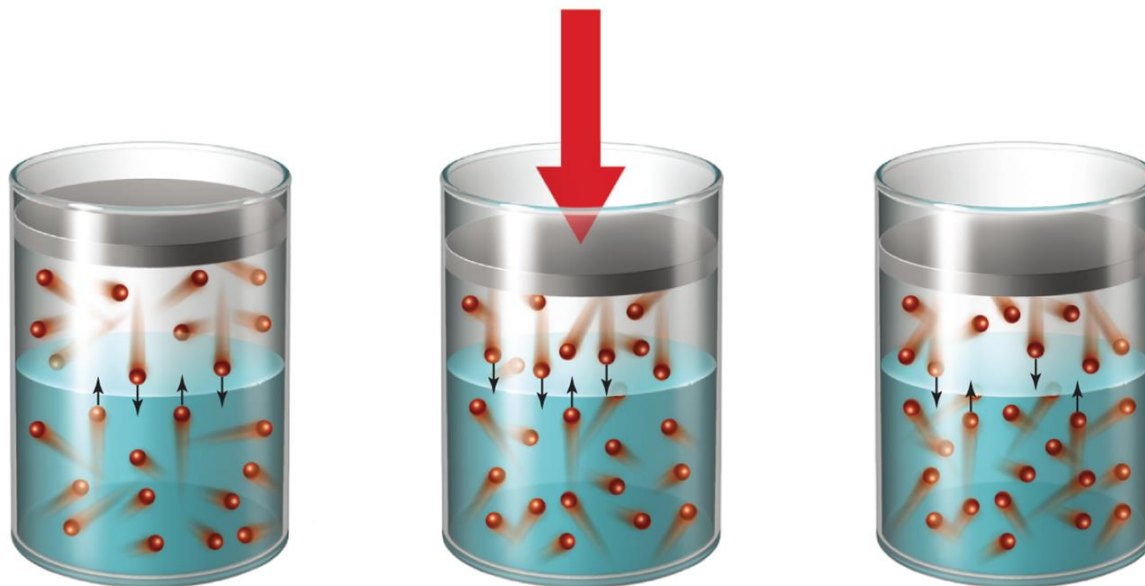
Some Factors That Affect Solubility

Most substances become more soluble as temperature rises, although the exact relationship is often complex and nonlinear.

Some Factors That Affect Solubility

Henry's Law

$$\text{Solubility} = kP$$

Equilibrium

At a given pressure, an **equilibrium** exists in which equal numbers of gas particles enter and leave the solution.

Pressure increase

When **pressure is increased** by pushing on the piston, more gas particles are temporarily forced into solution than are able to leave.

Equilibrium restored

Solubility therefore increases until a **new equilibrium** is reached.
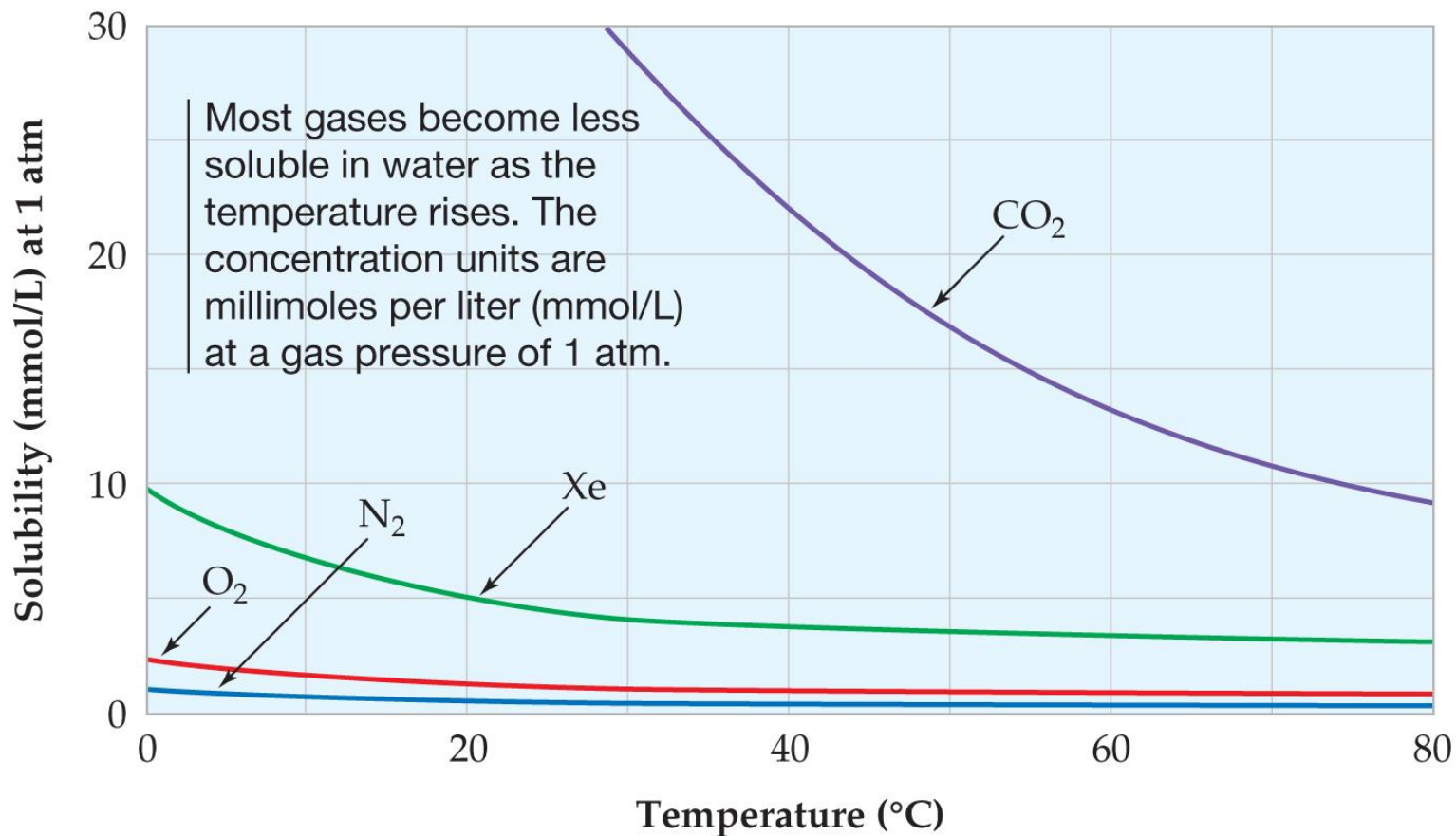
Some Factors That Affect Solubility

The solubility of CO_2 in water is 3.2×10^{-2} M at 25 °C and 1 atm pressure. What is the Henry's-law constant for CO_2 in mol/(L atm)?

$$\text{Solubility} = kP$$

$$k = \frac{\text{Solubility}}{P} = \frac{3.2 \times 10^{-2} \ \dfrac{\text{mol}}{\text{L}}}{1 \text{ atm}} = \boxed{3.2 \times 10^{-2} \text{ mol/(L atm)}}$$

Some Factors That Affect Solubility

Some Factors That Affect Solubility

# 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
- Boiling-point elevation
- Freezing-point depression
- Osmotic pressure

Vapor-Pressure Lowering of Solutions: Raoult's Law

Raoult's Law

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

Equilibrium vapor pressure

Equilibrium vapor pressure
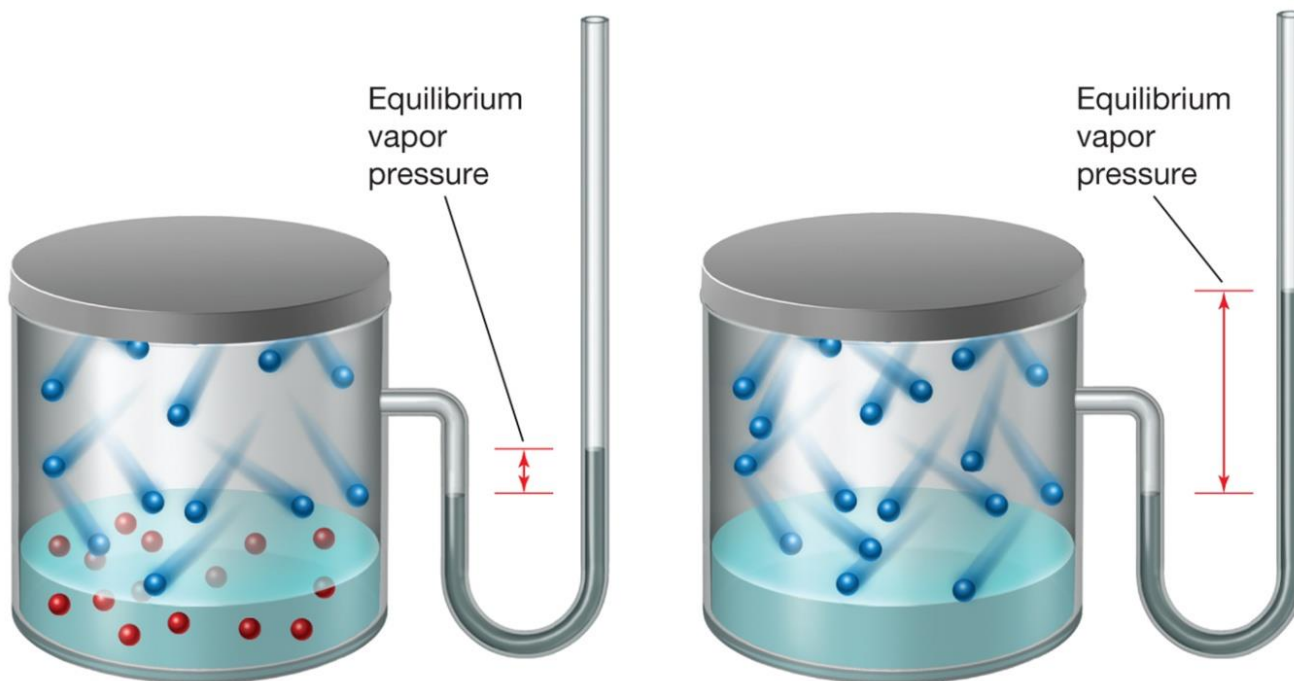
A solution of a **nonvolatile solute** always has a lower vapor pressure than …

… that of the **pure solvent** by an amount that depends on the mole fraction of the solvent.

Vapor-Pressure Lowering of Solutions: Raoult's Law

The vapor pressure of pure water at 25 °C is 23.76 mm Hg. What is the vapor pressure of a solution made from 1.00 mol glucose in 15.0 mol of water at 25 °C? Glucose is a nonvolatile solute.

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

$$= 23.76 \text{ mm Hg} \times \frac{15.0 \text{ mol}}{1.00 \text{ mol} + 15.0 \text{ mol}} = 22.3 \text{ mm Hg}$$

Vapor-Pressure Lowering of Solutions: Raoult's Law

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.

Van't Hoff Factor: $\quad i = \dfrac{\text{Moles of particles in solution}}{\text{Moles of solute dissolved}}$

$$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$$

For sodium chloride, the predicted value of **i is 2**. For a 0.05 *m* solution of sodium chloride, the experimental value for **i is 1.9**.

Vapor-Pressure Lowering of Solutions: Raoult's Law

Because the entropy of the solvent in a solution is higher than that of pure solvent to begin with, ΔS_{vap} **is smaller for the solution** than for the **pure solvent**.

S_{vapor} _____

$[\Delta S_{vap}]_{soln}$ $[\Delta S_{vap}]_{solv}$

$S_{solution}$ _____
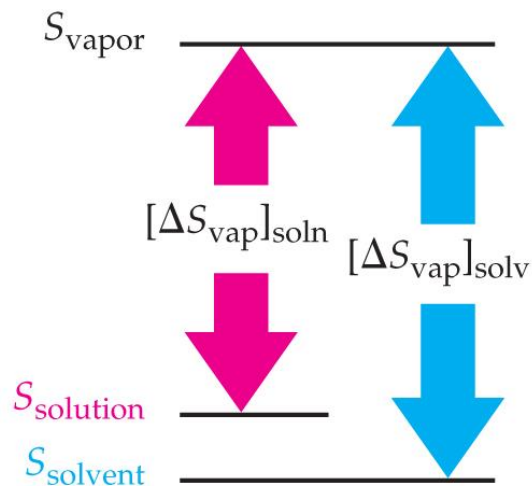
$S_{solvent}$ _____

As a result, vaporization of the solvent from the solution is less favored (less negative ΔG_{vap}), and the vapor pressure of the solution is lower.

If this is similar for the solvent and the solution . . .
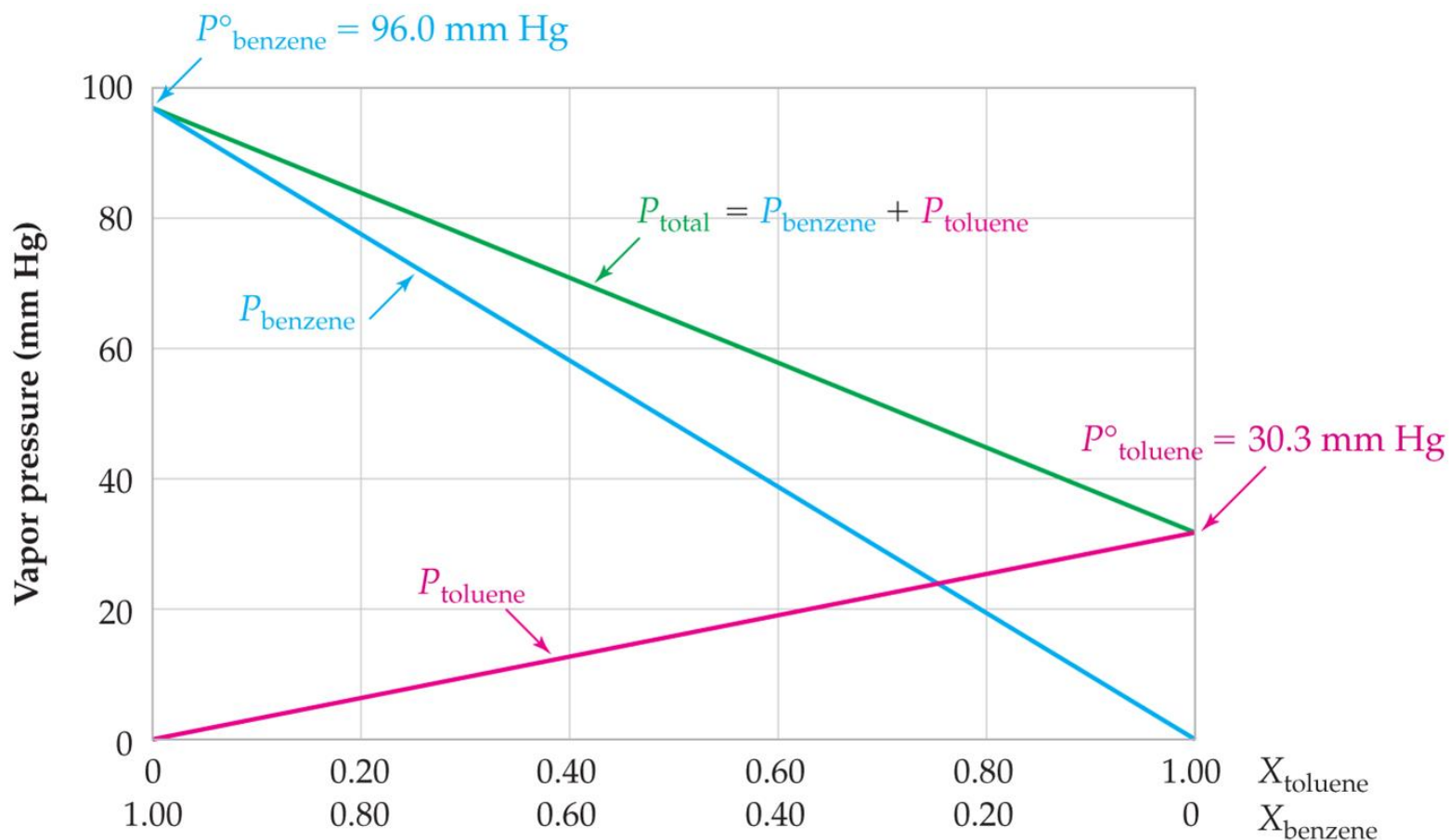
. . . and this is smaller for the solution . . .

$$\Delta H_{vap} - T\Delta S_{vap} = \Delta G_{vap}$$

. . . then this is less negative for the solution.

Vapor-Pressure Lowering of Solutions: Raoult's Law

$$P_{total} = P_A + P_B = (P°_A X_A) + (P°_B X_B)$$

$P°_{benzene} = 96.0$ mm Hg

$P_{total} = P_{benzene} + P_{toluene}$

$P_{benzene}$

$P°_{toluene} = 30.3$ mm Hg

$P_{toluene}$

Vapor pressure (mm Hg)

$X_{toluene}$
$X_{benzene}$

Boiling-Point Elevation and Freezing-Point Depression of Solutions

Because the liquid/vapor phase transition line is lower for the **solution** than for the **pure solvent**, the triple-point temperature T_t is lower and the solid/liquid phase transition line is shifted to a lower temperature. As a result, the freezing point of the solution is lower than that of the pure solvent by an amount ΔT_f.
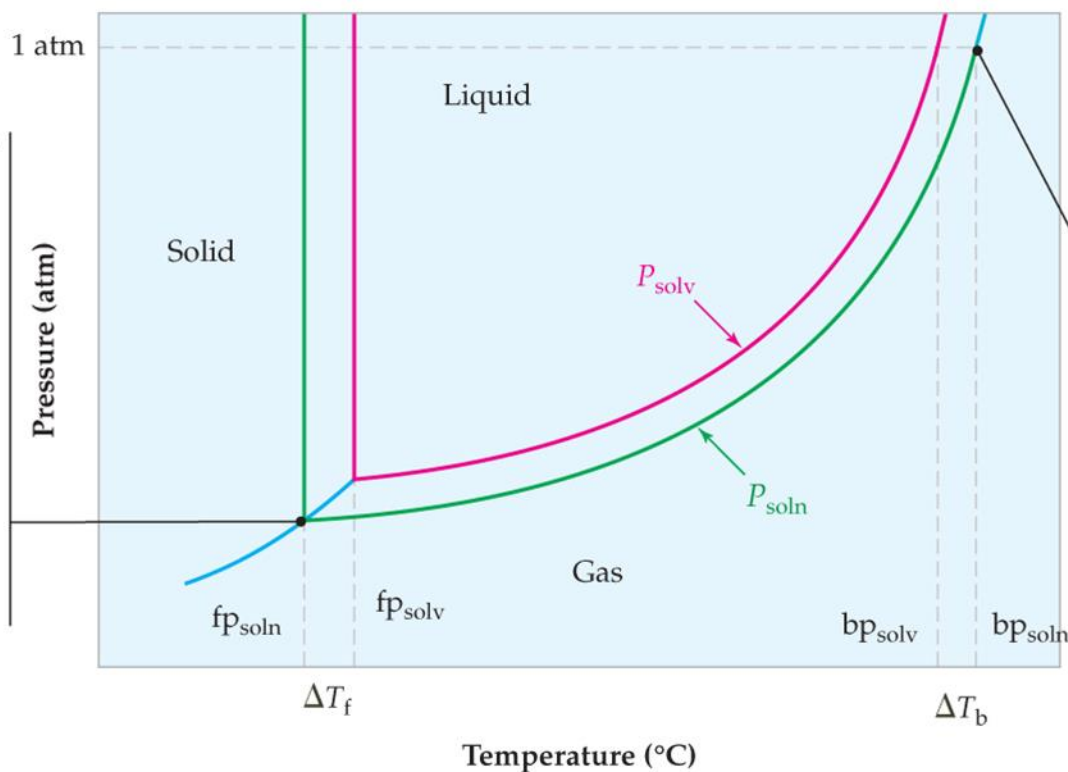
Because the vapor pressure of the **solution** is lower than that of the **pure solvent** at a given temperature, the temperature at which the vapor pressure reaches atmospheric pressure is higher for the solution than for the solvent. Thus, the boiling point of the solution is higher by an amount ΔT_b.

Boiling-Point Elevation and Freezing-Point Depression of Solutions

Nonelectrolytes

$$\Delta T_b = K_b m$$

$$\Delta T_f = K_f m$$

Electrolytes

$$\Delta T_b = K_b m i$$

$$\Delta T_f = K_f m i$$

TABLE 12.4 Molal Boiling-Point-Elevation Constants (K_b) and Molal Freezing-Point-Depression Constants (K_f) for Some Common Substances

Substance	$K_b[(°C \cdot kg)/mol]$	$K_f[(°C \cdot kg)/mol]$
Benzene (C_6H_6)	2.64	5.07
Camphor ($C_{10}H_{16}O$)	5.95	37.8
Chloroform ($CHCl_3$)	3.63	4.70
Diethyl ether ($C_4H_{10}O$)	2.02	1.79
Ethyl alcohol (C_2H_6O)	1.22	1.99
Water (H_2O)	0.51	1.86

Boiling-Point Elevation and Freezing-Point Depression of Solutions

Because the solvent in a solution has a higher entropy to begin with, ΔS_{vap} is **smaller for the solution** than for the **pure solvent**.

S_{vapor}

$[\Delta S_{vap}]_{soln}$ $[\Delta S_{vap}]_{solv}$

$S_{solution}$
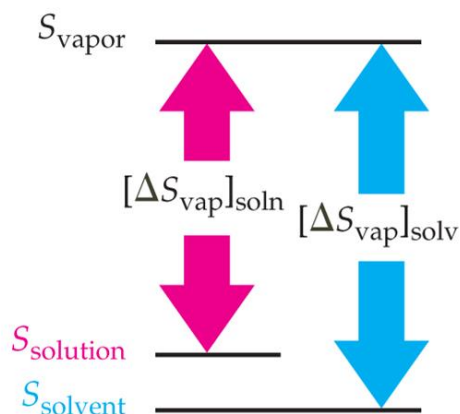
$S_{solvent}$

As a result, the boiling point of the solution T_b is higher than that of the pure solvent.

If this is similar for the solvent and the solution . . .

$$\frac{\Delta H_{vap}}{\Delta S_{vap}} = T_b$$

. . . and this is smaller for the solution, . . .

. . . then this is larger for the solution.

Boiling-Point Elevation and Freezing-Point Depression of Solutions

Because the solvent in a solution has a higher entropy level to begin with, ΔS_{fusion} **is larger for the solution** than for the **pure solvent**.

$S_{solution}$ ————————

$S_{solvent}$ ————————

$[\Delta S_{fusion}]_{solv}$ $[\Delta S_{fusion}]_{soln}$

S_{solid} ————————
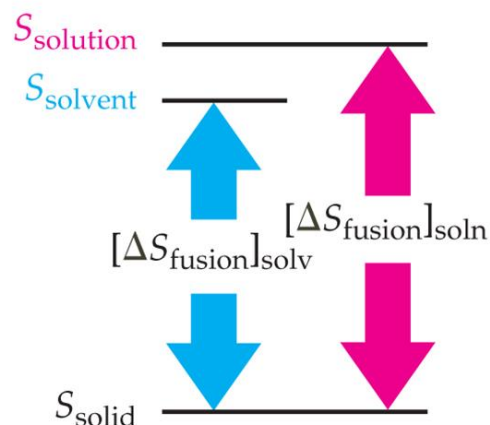
As a result, the freezing point of the solution T_f is lower than that of the pure solvent.

If this is similar for the solvent and the solution . . .

$$\frac{\Delta H_{fusion}}{\Delta S_{fusion}} = T_f$$

. . . and this is larger for the solution, . . .

. . . then this is smaller for the solution.
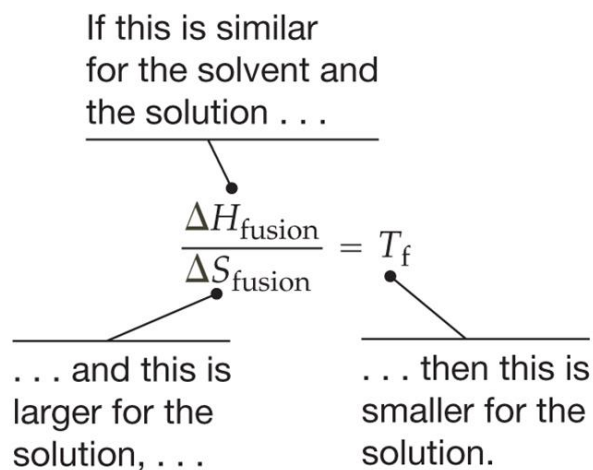
Boiling-Point Elevation and Freezing-Point Depression of Solutions

What is the freezing point (in Celsius) of a solution prepared by dissolving 7.40 g of $MgCl_2$ in 110 g of water? The van't Hoff factor for $MgCl_2$ is $i = 2.7$.

Calculate the moles of $MgCl_2$:

$$7.40 \text{ g} \times \frac{1 \text{ mol}}{95.2 \text{ g}} = 0.0777 \text{ mol}$$

Calculate the molality of the solution:

$$\frac{0.0777 \text{ mol}}{110 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 0.71 \frac{\text{mol}}{\text{kg}}$$

Boiling-Point Elevation and Freezing-Point Depression of Solutions

Calculate the freezing point of the solution:

$$\Delta T_f = K_f m i = 1.86 \ \frac{°C \ kg}{mol} \times 0.71 \ \frac{mol}{kg} \times 2.7 = 3.6 \ °C$$

$$T_f = 0.0 \ °C - 3.6 \ °C = \boxed{-3.6 \ °C}$$

Osmosis and Osmotic Pressure

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

Osmotic Pressure (Π): The amount of pressure necessary to cause osmosis to stop, or the amount of pressure necessary to achieve an equilibrium passage of solvent molecules through a semipermeable membrane

Osmosis and Osmotic Pressure

$$\Pi = MRTi$$

A **solution** inside the bulb is separated from pure **solvent** in the beaker by a semipermeable membrane.

Net passage of **solvent** from the beaker through the membrane occurs, and the liquid in the tube rises until an equilibrium is reached.

More concentrated solution

Solvent

Less concentrated solution
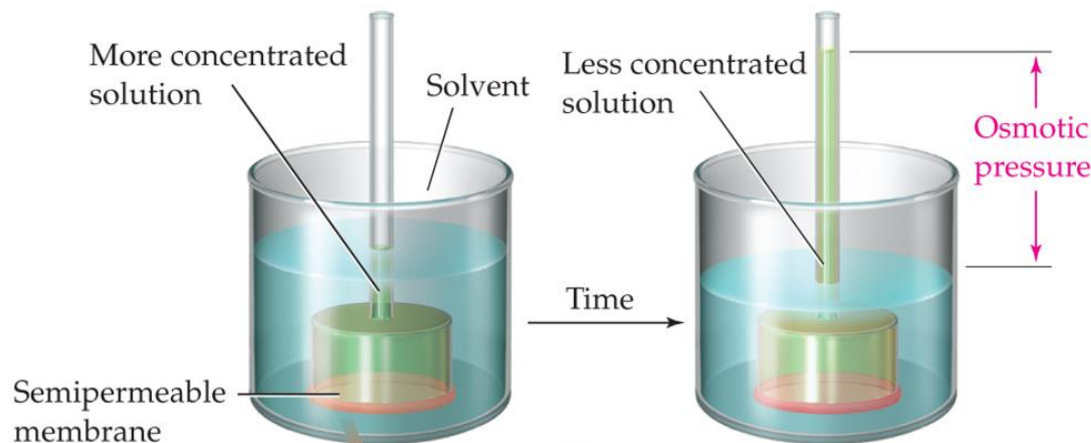
Osmotic pressure

At equilibrium, the **osmotic pressure** exerted by the column of liquid in the tube is sufficient to prevent further net passage of solvent.

Semipermeable membrane

Time
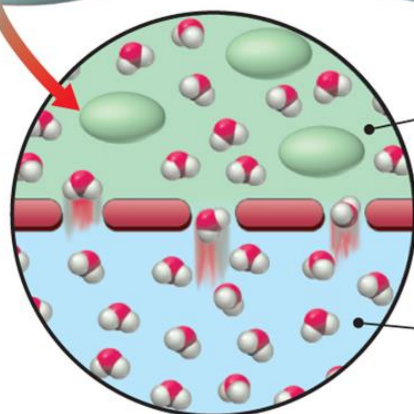
Solvent molecules on the **solution** side have a lower concentration and therefore pass through the **semipermeable membrane** less frequently.
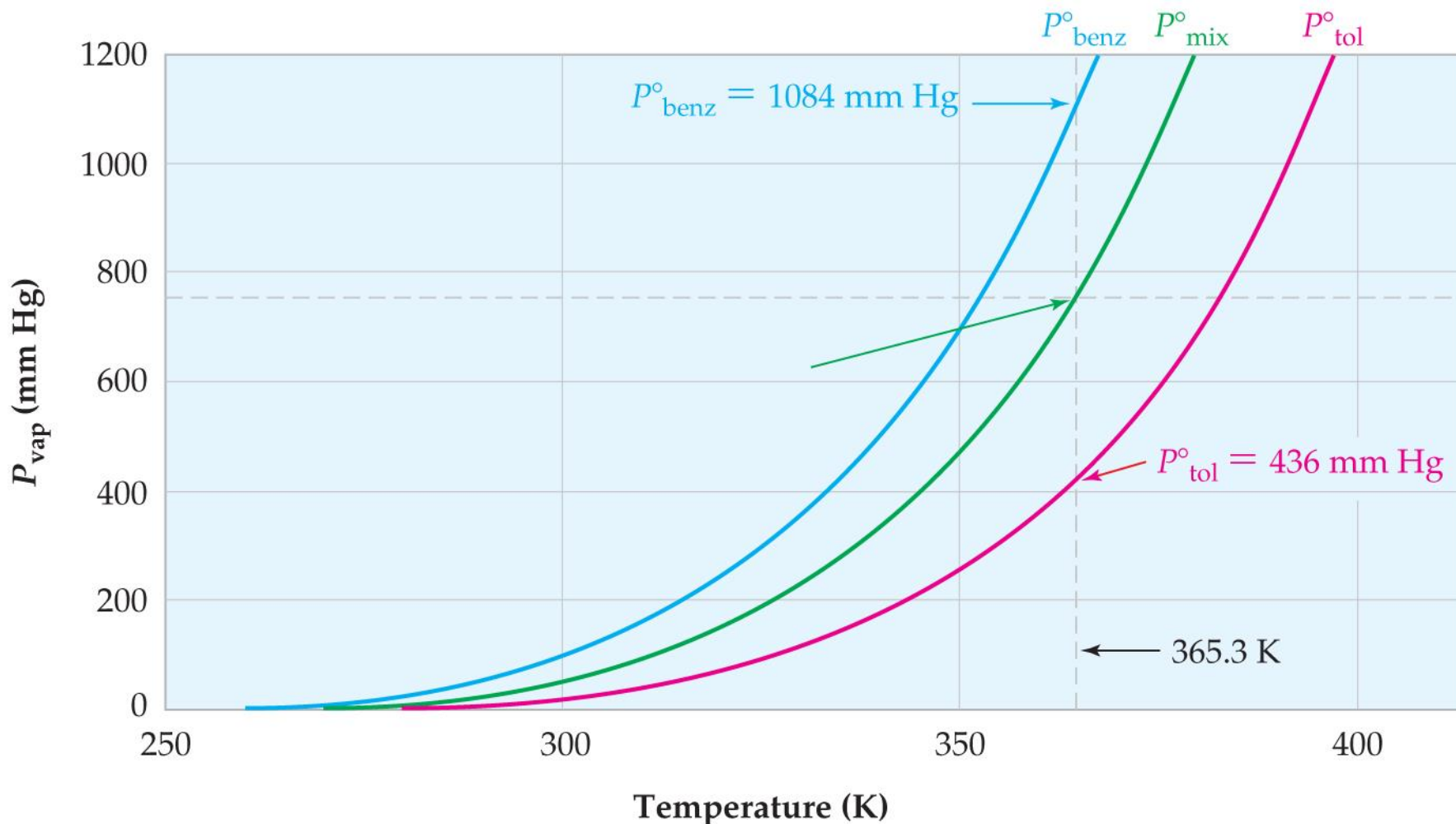
Semipermeable membrane

Solvent molecules on the **pure solvent** side have a higher concentration and therefore pass through the membrane more frequently.

Osmosis and Osmotic Pressure

Calculate the osmotic pressure of a 1.00 M glucose solution in water at 300 K.

$$P = MRTi = 1.00 \ \frac{mol}{L} \times 0.08206 \ \frac{L \ atm}{K \ mol} \times 300 \ K = 24.6 \ atm$$

Fractional Distillation of Liquid Mixtures

$P°_{benz}$ $P°_{mix}$ $P°_{tol}$

$P°_{benz} = 1084$ mm Hg

$P°_{tol} = 436$ mm Hg

365.3 K

P_{vap} (mm Hg)

Temperature (K)

The **mixture** of **benzene** and **toluene** boils at 92.2 °C (365.3 K) at atmospheric pressure, intermediate between the boiling points of the two pure liquids.

Fractional Distillation of Liquid Mixtures

Thermometer

The vapors from a boiling mixture of liquids rise inside the column, where they condense on contact with the cool column walls, drip back, and are reboiled by contact with more hot vapor.

Water out

Water in

Distillation column

Mixture to be separated

Receiver

Numerous boil/condense cycles occur before vapors finally pass out the top of the column, reach the water-cooled condenser, and drip into the receiver.