

Chapter Thirteen

Physical Properties Of Solutions



Review: Solution Terms & Types

- Solvent:** Larger portion of a solution
- Solute:** Smaller portion of a solution
- Solution:** A homogeneous mixture of two or more elements or compounds
- Solubility:** Measure of max amount of solute in solution

TABLE 13.1		Types of Solutions		
Solute	Solvent	State of Resulting Solution		Example
Gas	Gas	Gas *		Air
Gas	Liquid	Liquid		Carbonated water
Gas	Solid	Solid		H ₂ gas in palladium
Liquid	Liquid	Liquid		Ethanol in water
Liquid	Solid	Solid		Mercury in silver
Solid	Liquid	Liquid		Saltwater
Solid	Solid	Solid		Brass (Cu/Zn)

More Solubility Terms

Saturated solution:

Maximum amount of solute that stays in solution
– Any additional solute will precipitate

Unsaturated solution:

Contains less solute than in saturated solution

Supersaturated solution:

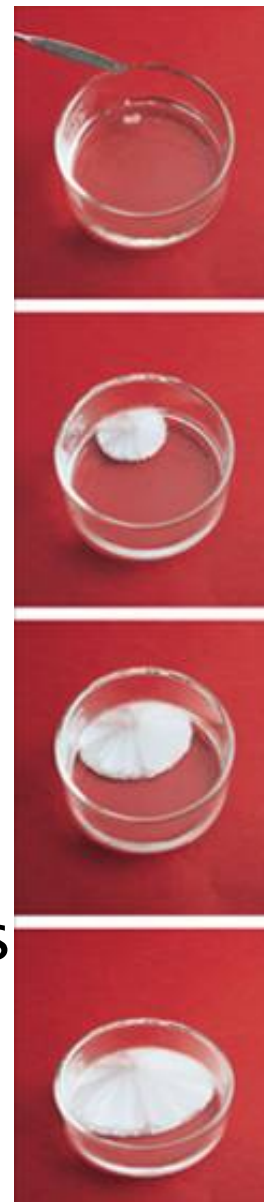
Contains more solute than in saturated solution
– Extremely unstable (easy to make extra precipitate)

Crystallization:

Extra solute in supersaturated solution precipitates & forms crystals

Precipitation:

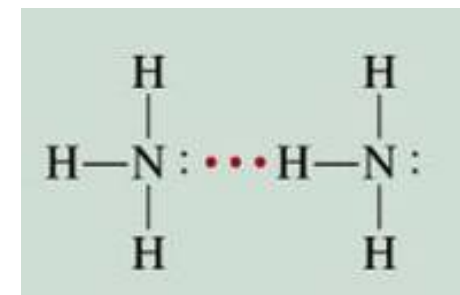
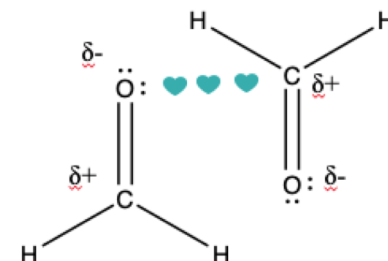
Solid comes out of solution, not always a crystal



Intermolecular Attractive Forces Review

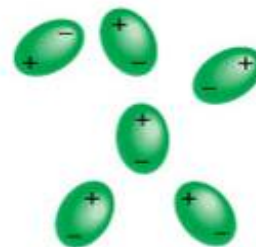
Polar molecules interact using:

- Dipole-dipole interactions – attraction between permanent partial charges
- Hydrogen bonding – dipole-dipole attraction involving H bonded to O, N, or F



Nonpolar molecules interact using:

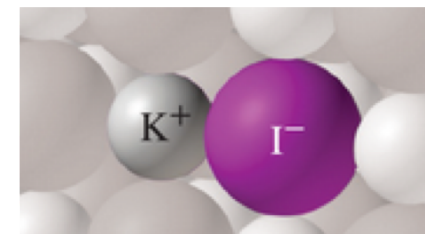
- Dispersion forces



Charges are temporary

Ions interact using:

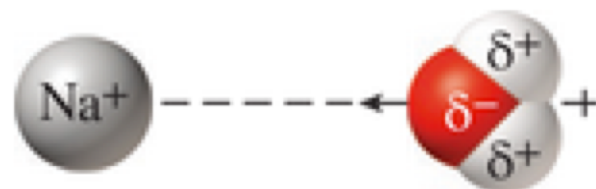
- The attraction between their positive and negative charges



Intermolecular Attractive Forces Review

In solutions, other important intermolecular forces include:

- **Ion–dipole attractions:** between an ion and the permanent dipole on a molecule
- **Dipole–induced dipole attractions:** a permanent dipole causes a temporary dipole in a nonpolar molecule or atom
- **Ion–induced dipole attractions:** the charge on an ion causes a temporary dipole in a nonpolar molecule or atom

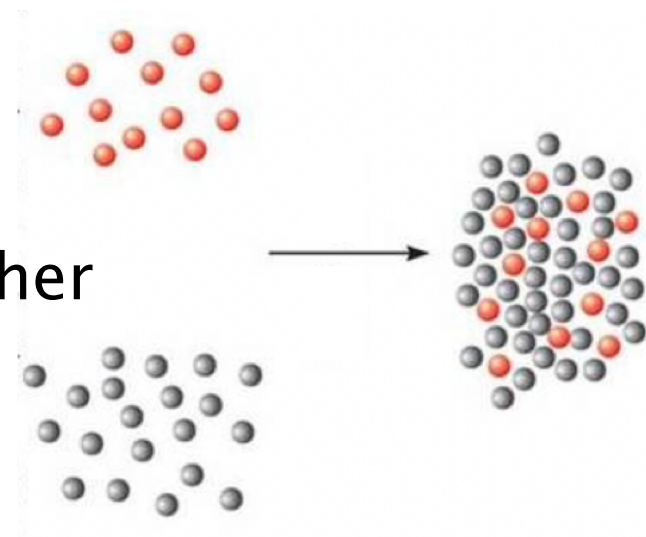


Solvent/Solute Intermolecular Forces & Solubility

Rule of thumb is that "like dissolves like."

Intermolecular forces are strongest for similar compounds

- Polar solvent/polar solute
- Nonpolar solvent/nonpolar solute
- Similar attractive forces lead to solvent and solute that are "miscible"
- **miscible** = fully dissolve in one another
 - resulting solution is stable



Examples:

- water/ethanol solutions
- Dissolution of ionic salts in H_2O
- CCl_4 in benzene (C_6H_6)

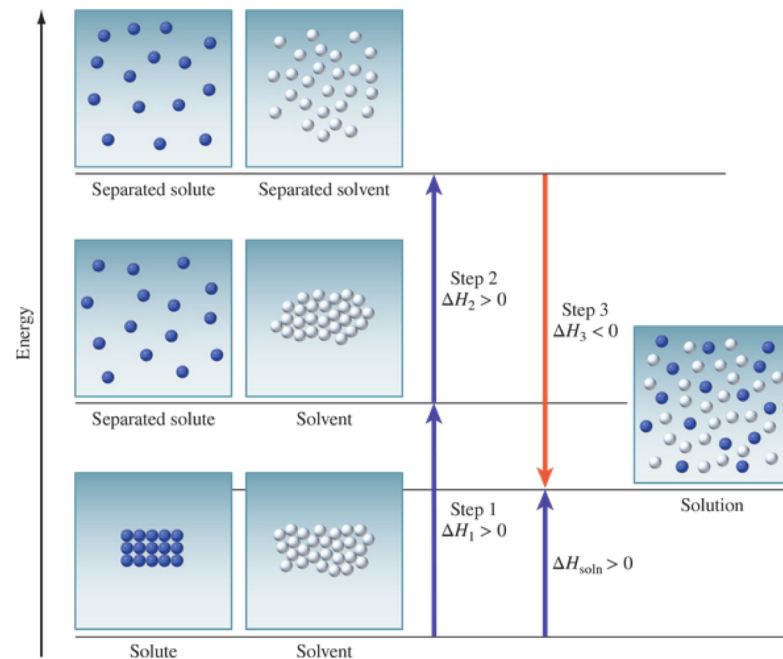
Energy & Entropy in Solution Formation

In order for something to dissolve:

- Solvent particles must separate (ΔH_1 , endothermic)
- Solute particles must separate (ΔH_2 , endothermic)
- Solute & solvent particles must mix (ΔH_3 , generally exothermic)
- Overall process is $\Delta H_{\text{solvation}} = \Delta H_1 + \Delta H_2 + \Delta H_3$
 - Hess's Law!

Energy required to separate <
Energy released by mixing =
Exothermic Process

Energy required to separate >
Energy released by mixing =
Endothermic Process



Energy & Entropy in Solution Formation

If overall process of dissolving is exothermic, resulting system (solution) has lower energy

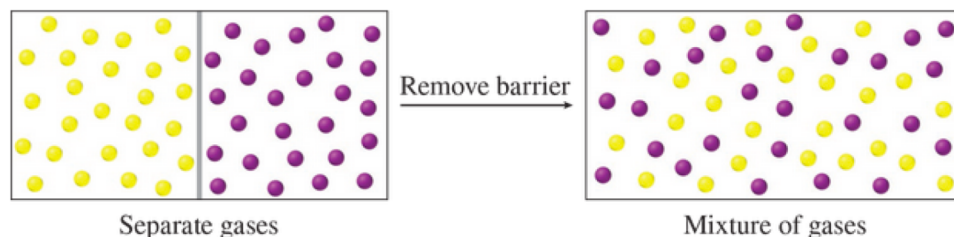
- The process is favored by enthalpy

If overall process of dissolving is endothermic, resulting system (solution) has higher energy

- The process is NOT favored by enthalpy
- The material is able to dissolve because the process is favored by ENTROPY

The **ENTROPY** of a system is a measure of how dispersed or spread out its energy is

- A measure of the DISORDER of a system
- Greater disorder = greater entropy
- Explains why gases mix spontaneously



The natural tendency is for entropy to increase

Concentration Units Review

$$\text{Molarity (M)} = \frac{\text{Moles Solute}}{\text{Liters of solution}} = \frac{\text{mol}}{\text{L}}$$

$$\text{Molality (m)} = \frac{\text{Moles Solute}}{\text{kg of solvent}} = \frac{\text{mol}}{\text{kg}}$$

Molarity is temperature dependent,
Molality is NOT temperature dependent

$$\text{Percent by mass} = \frac{\text{Mass solute (g)}}{\text{Mass of solution (g)}} \times 100$$

Grams cancel so no units, just % sign

ppm = part per million ($1\text{ g}/1 \times 10^6\text{ g}$)

How many grams of sodium hydroxide are present in 0.500 kg of water if the solution concentration is 0.500 m?

A: 10.0 g

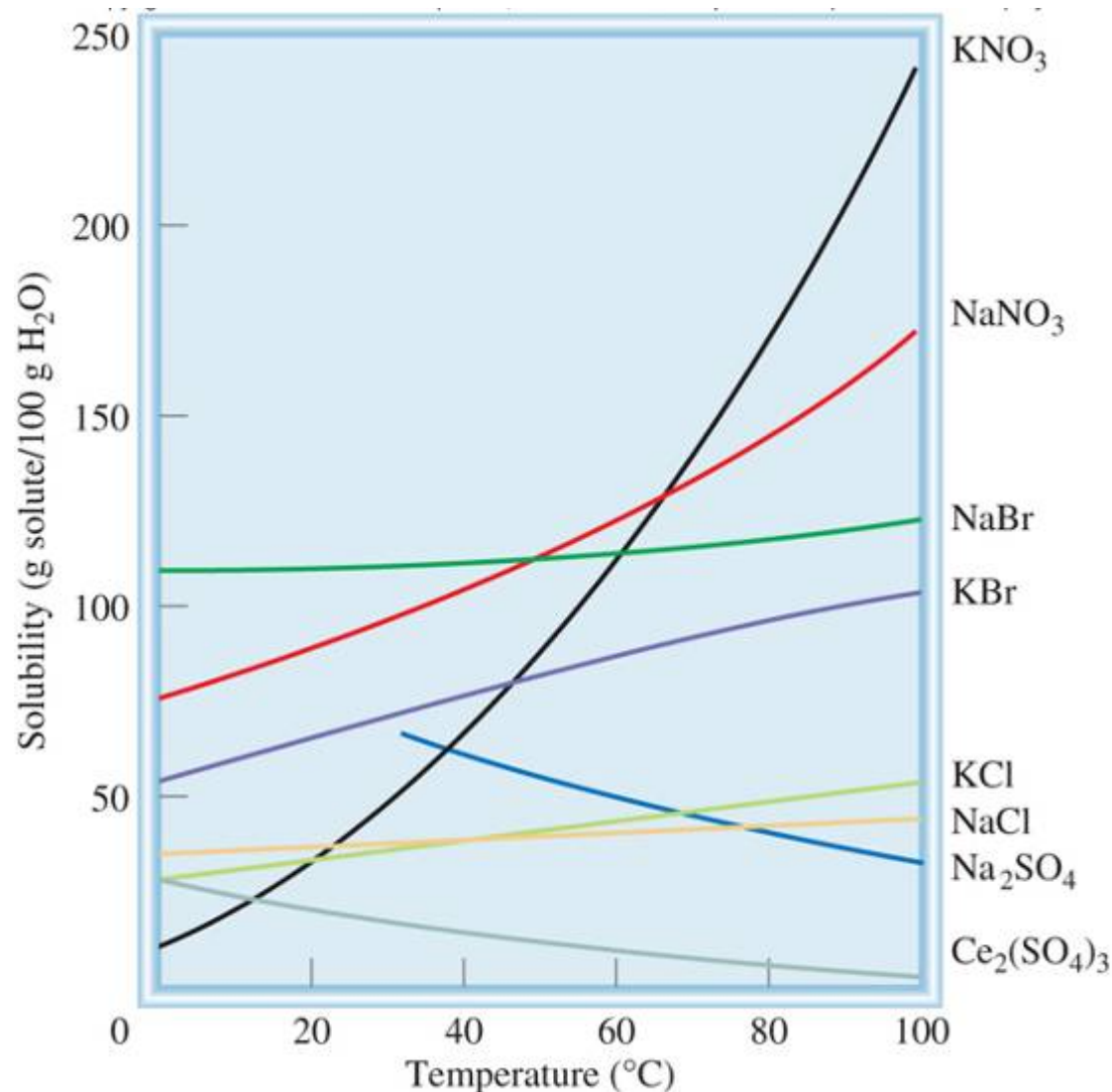
What mass of sodium hydroxide would be needed to make a 0.300 m solution with 4.00L of water at 20°C? (density of water is 0.998 g/mL at 20°C)

A: 47.9 g

A 14.0% by mass acetic acid (CH_3COOH) solution has a density of 1.02 g/mL. What is its molality?
What is its molarity?

Molality = 2.71 m
Molarity = 2.38 M

Solubility of Solids As A Function Of Temperature



For most solids, as temp increases, solubility **increases**.

The Solubilities Of Gases: Effect of Temperature

Gases are less soluble in liquids as temperature increases

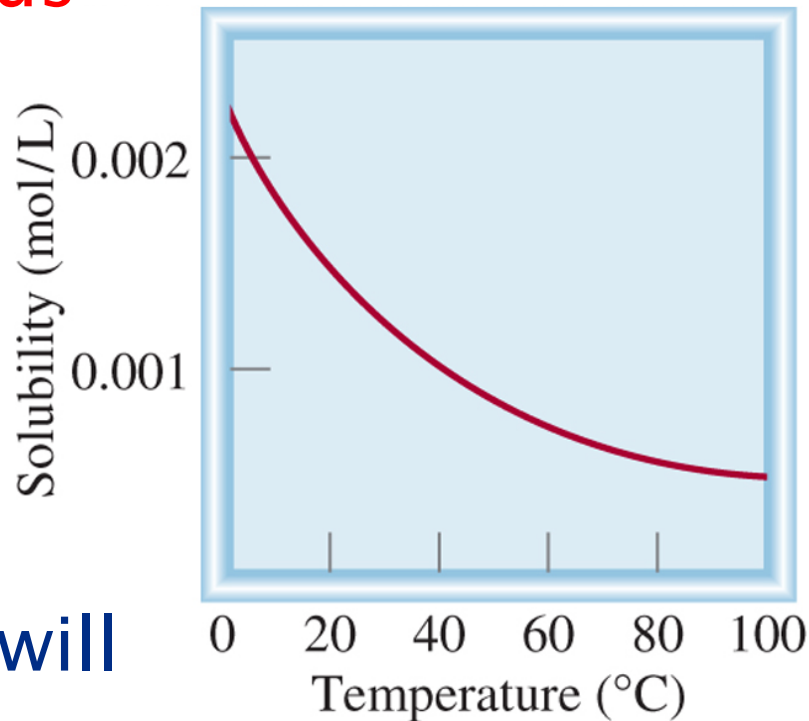
- Molecules move faster
- Disrupt intermolecular forces
- Gases escape the liquid
- Fewer gas molecules/atoms in liquid = Lower solubility

In sealed container, pressure will increase with increasing temp.

- More gas out of solution, moving faster, colliding more with container

Gas laws (Chapter 5!) govern gas phase and thus solubility

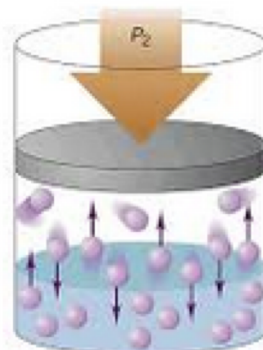
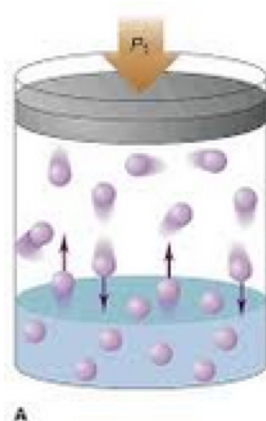
Solubility of O₂ in water



The Solubilities Of Gases: Effect of Pressure

Gas solubility in liquids increases as pressure increases

- Molecules pushed too close together so they are forced back into liquid



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If pressure is decreased.....



Henry's Law $c = kP$

c = solubility or concentration

P = pressure

k = proportionality constant

Common units for k : c = moles/L and P = atm

If you know the concentration at one pressure, k allows you to determine concentrations at different pressures

Solutions Of Electrolytes

Colligative properties:

- Physical properties of solutions that depend on the number of solute particles but NOT on the identity of the solute.
- Ex: Boiling Point, Freezing Point, Osmotic Pressure

van't Hoff factor, i

- Used in solution equations for colligative properties (ex. Boiling point elevation: $\Delta T_b = iK_b m$)
- Nonelectrolytic solutions: $i = 1$.
- Electrolyte solutions: i = the number of ions the solute will dissociate into

- Ex*: Hexane, $i = 1$
NaCl, $i = 2$
Pb(NO₃)₂, $i = 3$

*Note that these are the theoretical values. The experimental values are somewhat different due to formation of ion pairs.

Vapor-Pressure Lowering

Raoult's Law:

$$P_a = X_a P_a^\circ$$

P_a : Vapor pressure of solvent “a” above a solution

P_a° : Vapor pressure of pure solvent “a”

x_a : Mole fraction of “a” in the solution

$$x_i = \frac{\text{moles}_i}{\text{Moles}_{\text{total solution}}} = \frac{n_i}{n_{\text{total moles}}}$$

Non-volatile solutes: Vapor pressure of the solution = vapor pressure of the solvent

- Vapor pressure will be lowered by presence of solute

Volatile solutes: Vapor pressure of the solution is sum of the partial pressures of the solute and the solvent

Works perfectly for ideal solutions; OK for dilute solutions

What is the vapor pressure of water in a 100.0g solution that contains 10.0g sucrose, $C_{12}H_{22}O_{11}$ at 40°C? The vapor pressure of pure water is 55.5 torr at 40°C.

MM: sucrose = 342.30 g/mol; water = 18.015 g/mol)

Step 1:Determine mole fraction of water

Step 2:Determine vapor pressure given $P^\circ = 55.5$ torr at 40°C

A: 55.2 torr

What mass (g) of ethanol (46.069 g/mol) must be added to 550.0 g water (18.015 g/mol) to give a solution with a vapor pressure of water 1.5 mmHg less than that of pure water at 30°C?

Vapor pressure of water at 30°C is 31.8 mmHg.

A: 69.6 g

Boiling Point Elevation

Vapor pressure above a solution is always less than vapor pressure above pure solvent.

1. Higher temperature needed for vapor pressure to hit 1 atm.
2. Boiling point of solution higher than boiling point of pure solvent
3. Boiling Point Elevation depends on:
 - Type of solvent
 - # of solute particles

$$\Delta T_b = iK_b m$$

$$T_b = T_b^\circ + \Delta T_b$$

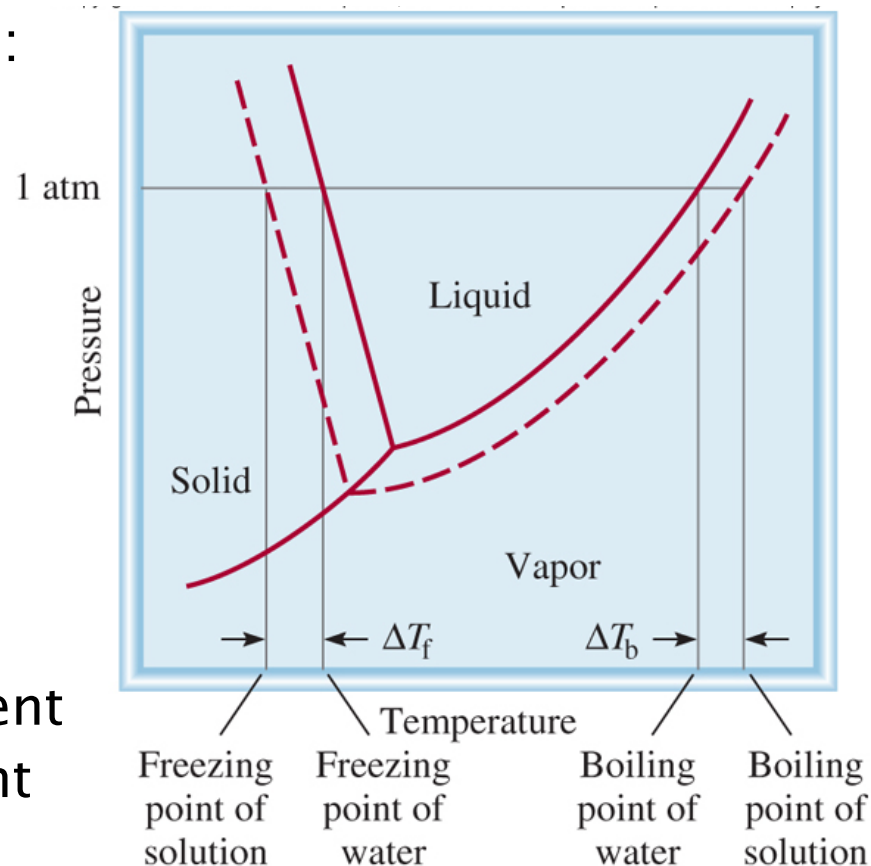
m = solute molality

T_b = boiling point of solution

T_b° = boiling point of pure solvent

K_b = constant – based on solvent

i = van't Hoff factor



Freezing Point Depression

Solution freezes at lower temperature than pure solvent

Freezing Point Depression depends on

- Type of solvent
- # of solute particles

$$\Delta T_f = iK_f m$$

$$T_f = T^\circ_f - \Delta T_f$$

m = solute molality

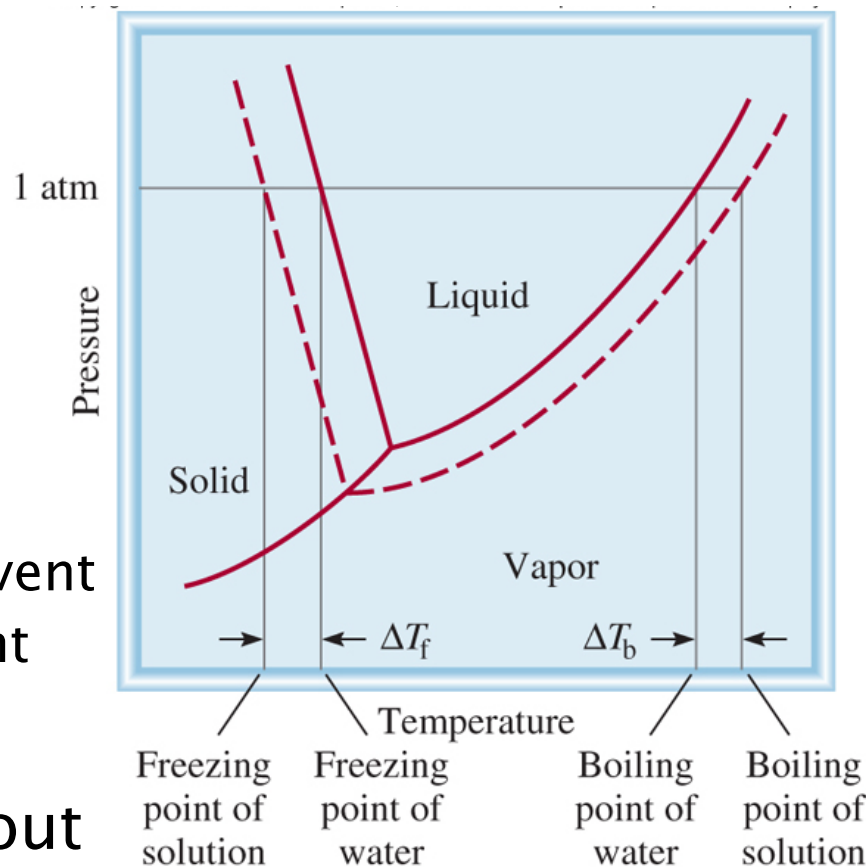
T_f = freezing point of solution

T°_f = freezing point of pure solvent

K_f = constant – based on solvent

i = van't Hoff factor

- Only the pure solvent freezes out
- Pure substances: "sharp" melting point
- Impure materials: broad melting point range



What is the boiling point of a 0.886 m solution of pentane in benzene? For benzene: bpt = 80.1°C , $K_b = 2.53^{\circ}\text{C/m}$

A: 82.3°C

What is the melting point of a 1.00 m solution of CaCl_2 in water? For water: mpt = 0.0°C , $K_f = 1.86^{\circ}\text{C/m}$

A: -5.6°C

A solution of 2.366 g solute in 82.10 g cyclohexane freezes at 2.65°C. Determine the molar mass of the solute.

For cyclohexane, $K_f = 20.0^\circ\text{C}/m$ and $T_f^\circ = 6.55^\circ\text{C}$.

Have freezing point of solution & pure solvent – can use $\Delta T_f = iK_fm$ to determine the **molality** of the solution

Use mass of solvent & molality to calculate moles solute

Given mass solute, so can calculate molar mass of solute

A: 148 g/mol

Constants

Will be provided on exams if needed

TABLE 13.2

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

Solvent	Normal Freezing Point (°C)*	K_f (°C/ <i>m</i>)	Normal Boiling Point (°C)*	K_b (°C/ <i>m</i>)
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

Osmotic Pressure

Semi-permeable membranes: Materials with tiny pores that only allow solvent molecules to pass

- solute cannot get through the membrane

Osmosis: Net flow of solvent molecules through a semi-permeable membrane from dilute to concentrated solution.

Osmotic Pressure (π): Pressure needed to stop osmotic flow

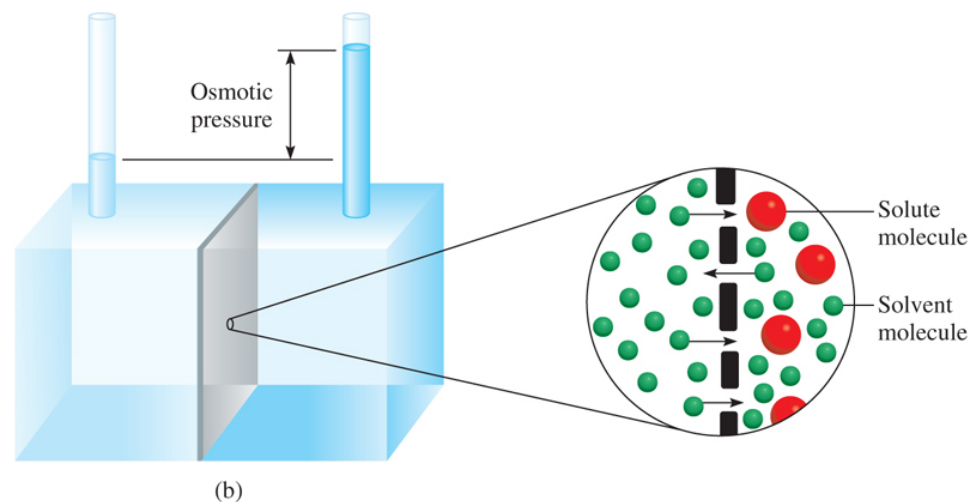
- π depends on:
 - concentration
 - temperature

$$\pi = iMRT$$

M = molarity

R = gas constant $\left(0.0821 \frac{\text{L atm}}{\text{mol K}}\right)$

T = temperature



What is the osmotic pressure of a 0.238 M aqueous sugar solution at 25°C?

A: 5.83 atm

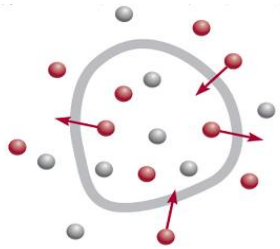
What is the molar mass of a solute if 397.2 g of the compound dissolved in water produces 592.4 mL of a solution that has an osmotic pressure of 1.98 atm at 35°C?

A: 8570 g/mol

Practical Applications Of Osmosis

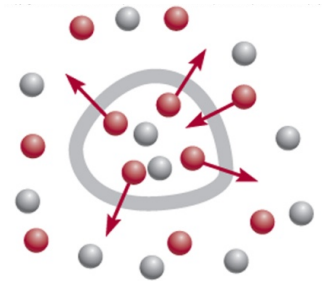
Isotonic Solution: Organ Transplants

- Same concentration on both sides of membrane
- Organs would burst if stored in water



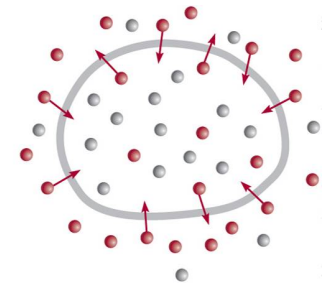
Hypertonic Solution: Food Preservation

- Higher concentration outside the membrane
- Salt pulls water from microbes and kills them



Hypotonic Solution: Tree Growth

- Lower concentration outside the membrane
- Water pulled through sap to top of trees



Reverse osmosis: Water Purification

- Reversing the net flow of solvent through a membrane by applying pressure greater than osmotic pressure.
- Obtain water with low solute concentration