

Lecture Presentation

Chapter 12

Solutions and Their Properties

12.1, 12.3, 12.4, 12.7, 12.8,
12.9, 12.11, 12.13, 12.15,
12.17, 12.19, 12.21, 12.30,
12.44, 12.46, 12.48, 12.50,
12.54, 12.58, 12.62, 12.66,
12.68, 12.72, 12.74, 12.94,
12.106

John E. McMurry
Robert C. Fay

End 1/31 Friday
A section

Solutions

Solution: A homogeneous mixture

End 1/31/20
Friday C
section

Solvent: The major component

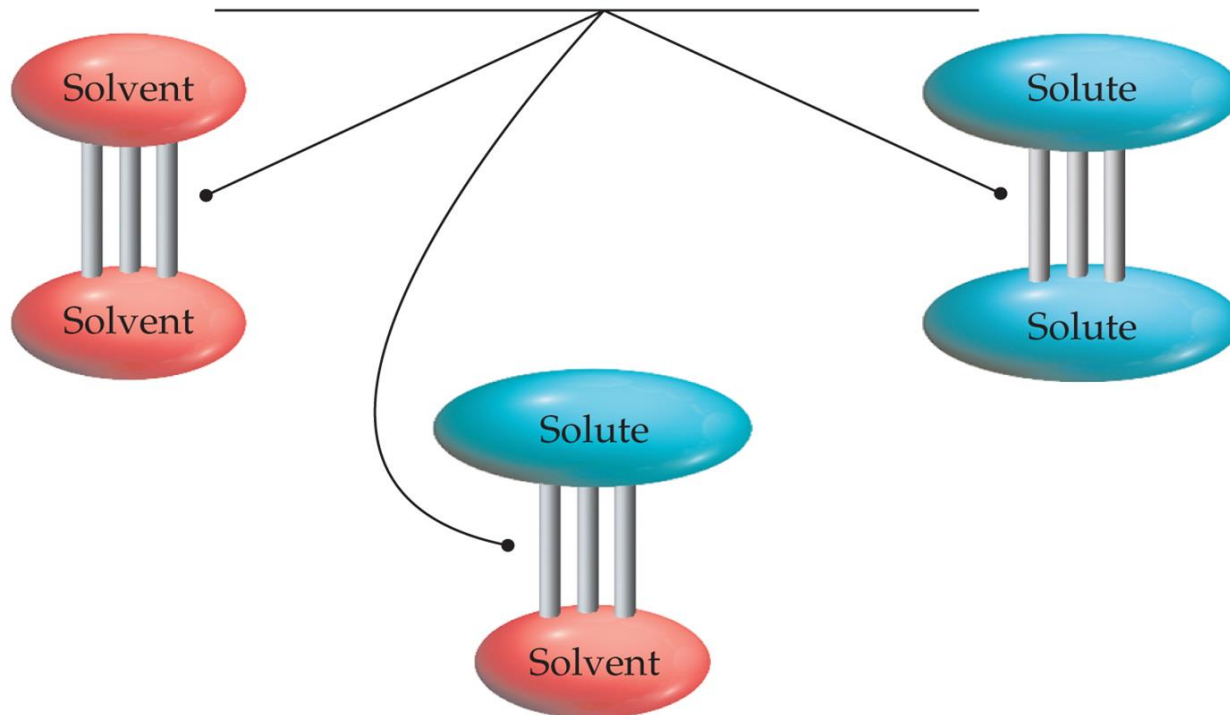
Solute: A minor component

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.



Soluble:

same intermolecular interactions

(a) salts in water

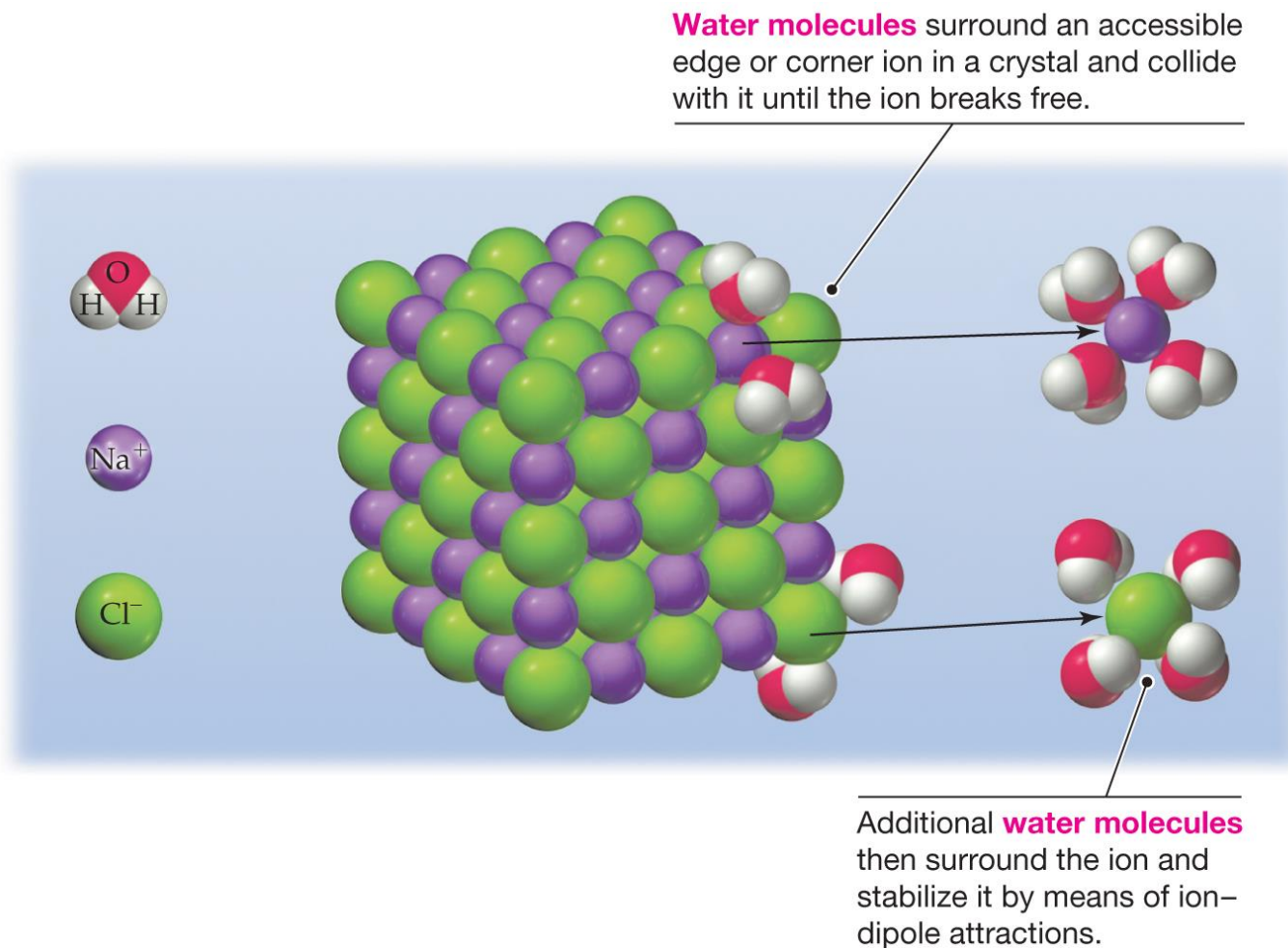
(b) H bonded with H bonded

(c) hydrocarbons in other hydrocarbons

(d) dipole dipole with dipole dipole

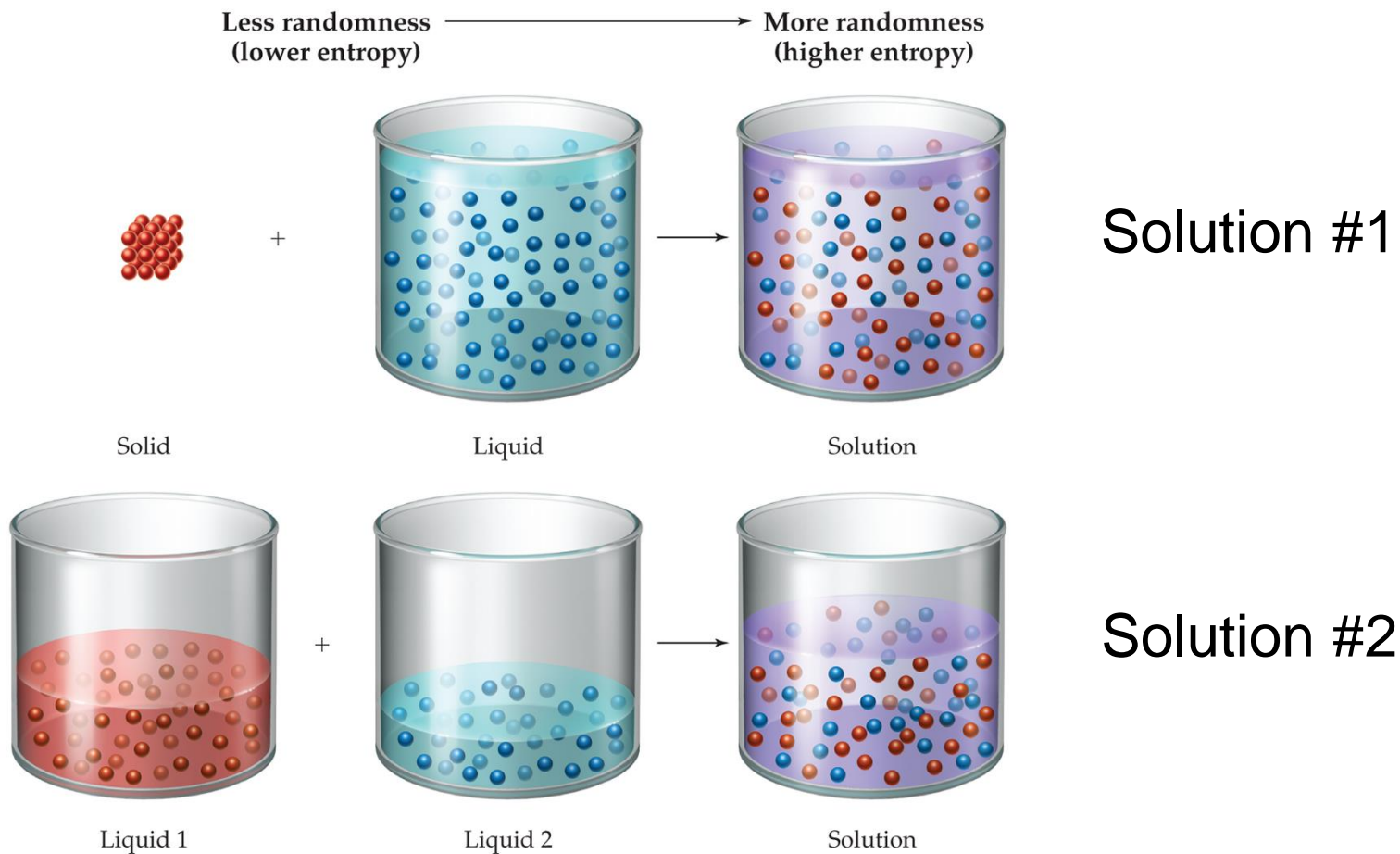
Energy Changes and the Solution Process

The sodium and chloride ions are *hydrated*.



Energy Changes and the Solution Process

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



Energy Changes and the Solution Process

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

ΔS solution is always + (because solution increases disorder)

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: + ΔH

Spontaneous: - ΔG

Exothermic: - ΔH

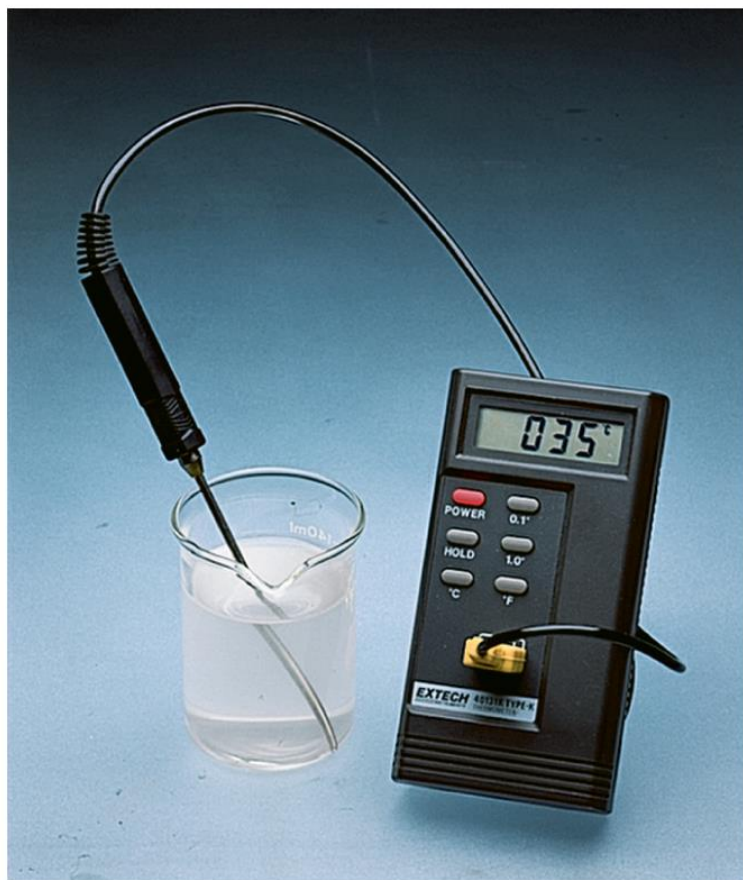
Nonspontaneous: + ΔG

Entropy always favors solution,

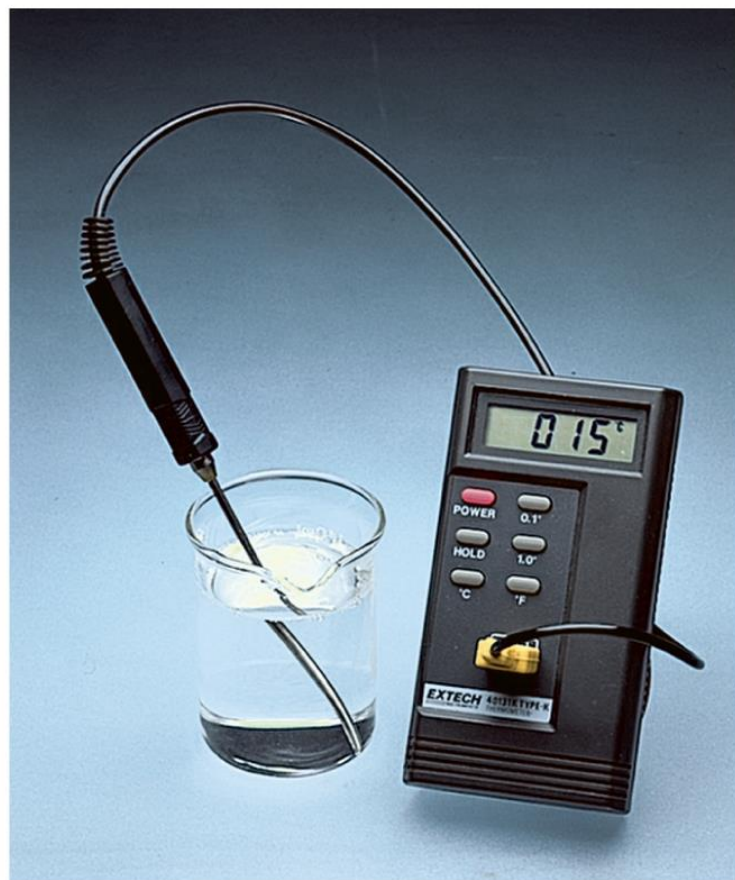
(a) **Enthalpy = negative** – always spontaneous

(b) **Enthalpy = positive** – spontaneous or not depends on size of terms & T

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.

Exothermic – system (solute) loses heat surrounding
(water) gains heat (always spontaneous)

Energy Changes and the Solution Process

To get solution:

break up solvent-solvent & solute-solute interactions

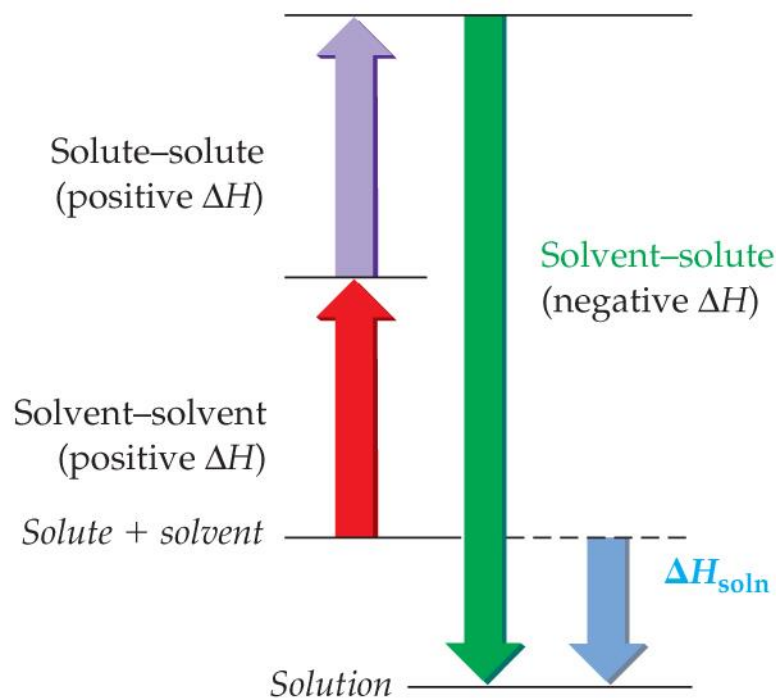
form – solvent-solute interaction

Solvent–Solvent Interactions: Energy is absorbed (**positive ΔH**) to break up intermolecular forces between solvent molecules. (**add energy**)

Solute–Solute Interactions: Energy is absorbed (**positive ΔH**) to break up intermolecular forces holding solute particles together in a crystal. (**add energy**)

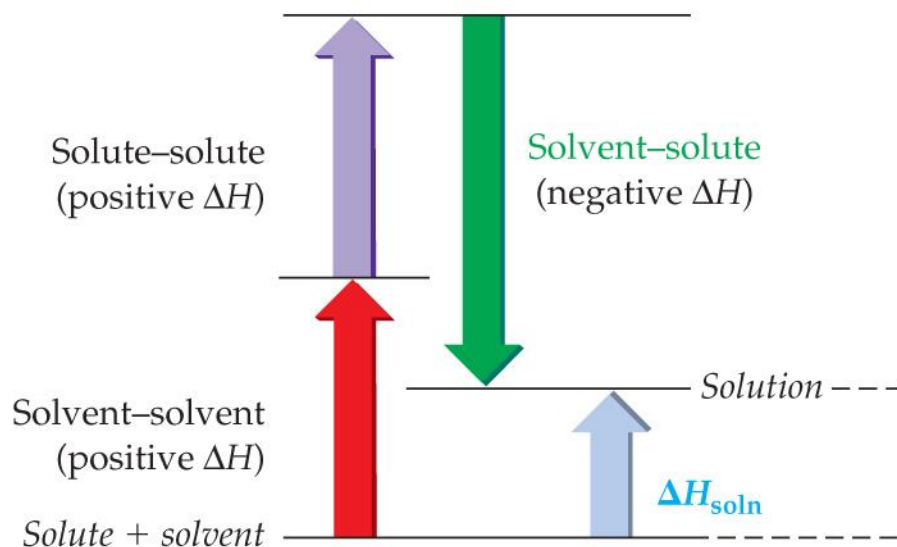
Solvent–Solute Interactions: Energy is released (**negative ΔH**) when solvent molecules cluster around solute particles and solvate them. (**get energy**)

Energy Changes and the Solution Process



$$\Delta H_{\text{soln}} < 0$$

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



$$\Delta H_{\text{soln}} > 0$$

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

overall ΔH_{soln} **negative** if more energy released during solution process than energy added to break up solute-solute and solvent solvent interactions. (ΔG negative, always spontaneous, system loses heat, surrounding get hot)

Concentration Units for Solutions

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

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

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

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

HW 12.2: Concentration Units for Solutions

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

Calculate the molarity of a solution made by dissolving 35.2 grams of NaCl (FM = 58.5 g/mol) into water to make up 235 mL of the solution.

HW 12.2: Concentration Units for Solutions

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

Calculate the molarity of a solution made by dissolving 35.2 grams of NaCl (FM = 58.5 g/mol) into water to make up 235 mL of the solution.

$$35.2 \text{ g NaCl} * \frac{1 \text{ mol NaCl}}{58.5 \text{ g NaCl}} = 0.602 \text{ mol NaCl}$$

$$235 \text{ mL solution} * \frac{1 \text{ L soln.}}{1000 \text{ mL soln.}} = 0.235 \text{ L solution}$$

$$\frac{0.602 \text{ mol NaCl}}{0.235 \text{ L solution}} = 2.56 \text{ M of Na Cl}$$

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, $CHCl_3$?

molality (m) = moles solute / kg solvent

Convert the mass of cholesterol (solute) 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 (solvent) to kilograms:

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

Calculate the molality of the solution:

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

HW12.3: Concentration Units for Solutions

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

What is the molality of a solution made by dissolving 35.2 grams of NaCl (FM = 58.5 g/mol) in 525 mL of water? The density of water is 1.00 g/mL under the conditions of the reaction.

End 2/3 Monday

A section

End 2/4 Tuesday

C section

HW12.3: Concentration Units for Solutions

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

What is the molality of a solution made by dissolving 35.2 grams of NaCl (FM = 58.5 g/mol) in 525 mL of water? The density of water is 1.00 g/mL under the conditions of the reaction.

$$35.2 \text{ g NaCl} * \frac{1 \text{ mol NaCl}}{58.5 \text{ mol NaCl}} = 0.602 \text{ mol NaCl}$$

$$525 \text{ mL water} * \frac{1.00 \text{ g water}}{\text{mL water}} * \frac{1 \text{ Kg water}}{1000 \text{ g water}} = 0.525 \text{ Kg water}$$

$$\frac{0.602 \text{ mol NaCl}}{0.525 \text{ Kg}} = 1.15 \text{ m Na Cl in water}$$

HW 12.4: Concentration Units for Solutions

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

What is the mass percent of a solution made of 35.2 grams of sodium chloride dissolved in 92.5 grams of water ?

HW 12.4: Concentration Units for Solutions

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

What is the mass percent of a solution made of 35.2 grams of sodium chloride dissolved in 92.5 grams of water ?

Total mass of solution = 35.2 grams + 92.5 grams

$$\frac{35.2 \text{ grams}}{127.7 \text{ grams}} * 100 = 27.6 \%$$

HW 12.5: Concentration Units for Solutions

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

What is the mole fraction made by dissolving 7.25 moles of Na Cl in enough water to make up a solution consisting of 252.2 grams of water (FM water = 18.02 g/mol)?

HW 12.5: Concentration Units for Solutions

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

What is the mole fraction made by dissolving 7.25 moles of NaCl in enough water to make up a solution consisting of 252.2 grams of water (FM water = 18.02 g/mol)?

$$\text{Moles water} = \frac{252.2 \text{ grams water}}{18.02 \text{ grams water/mol water}} = 14.0 \text{ moles water}$$

$$\frac{7.25 \text{ moles NaCl}}{14.0 \text{ moles H}_2\text{O} + 7.25 \text{ moles NaCl}} = 0.341 \text{ mole fraction of NaCl in solution}$$

$$\frac{14.0 \text{ mol H}_2\text{O}}{14.0 \text{ mol H}_2\text{O} + 7.25 \text{ mol NaCl}} = 0.659 \text{ mol fraction of water in solution}$$

HW 12.6: Concentration Units for Solutions

Convert 3.50 mass percent of NaCl to Molarity. The density of the solution is 1.025 g/mL at 20 °C. (FM NaCl = 58.5 g/mol) (M = moles solute / liter solution) end A section

HW 12.6: Concentration Units for Solutions

Convert 3.50 mass percent of NaCl to Molarity. The density of the solution is 1.025 g/mL at 20 °C. (FM NaCl = 58.5 g/mol) (M = moles solute / liter solution)
[(mass solute/mass solution)*100 = mass %]

Assuming 100.00 g of solution, calculate the volume:

$$100.00 \text{ g solution} \times \frac{1 \text{ mL}}{1.025 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0976 \text{ L}$$

Convert the mass of NaCl to moles:

$$3.50 \text{ g NaCl} \times \frac{1 \text{ mol}}{58.5 \text{ g}} = 0.0598 \text{ mol}$$

End 2/5 W
A & C section

Calculate the molarity of the solution:

$$\frac{0.0598 \text{ mol}}{0.0976 \text{ L}} = 0.613 \text{ M}$$

Quiz 3 ends here
(given on 2/7/20 F)
both sections

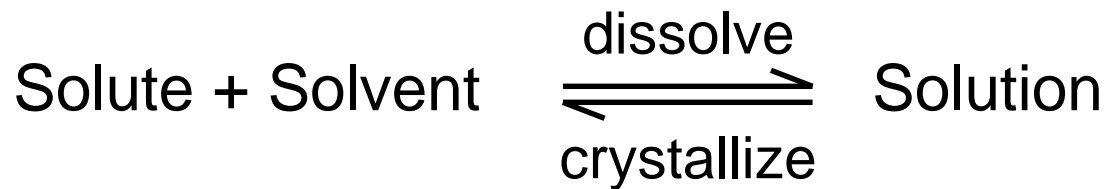
Concentration Units for Solutions

TABLE 12.3 A Comparison of Various Concentration Units

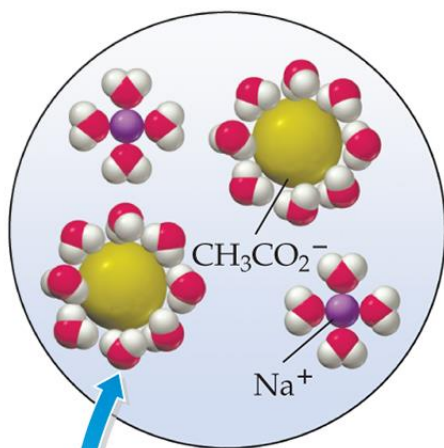
Name	Units	Advantages	Disadvantages
Molarity (M)	$\frac{\text{mol solute}}{\text{L solution}}$	Useful in stoichiometry; by volume	Temperature-dependent; must know density to find solvent mass
Mole fraction (X)	none	Temperature-independent; useful in special applications	Measure by mass; must know density 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

Some Factors That Affect Solubility

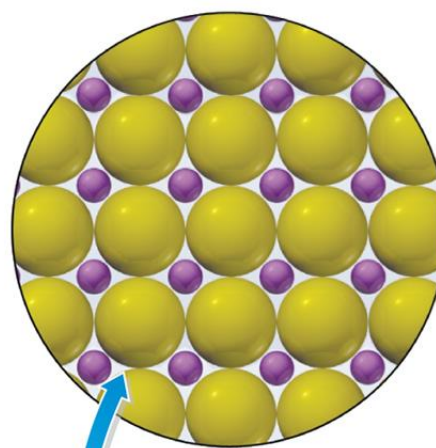
Saturated Solution: A solution containing the **maximum** possible amount of **dissolved solute** at equilibrium



Supersaturated Solution: A solution containing a **greater-than-equilibrium** amount of **solute** (usually get supersaturated solution by heating to dissolve solute and then cooling solution)



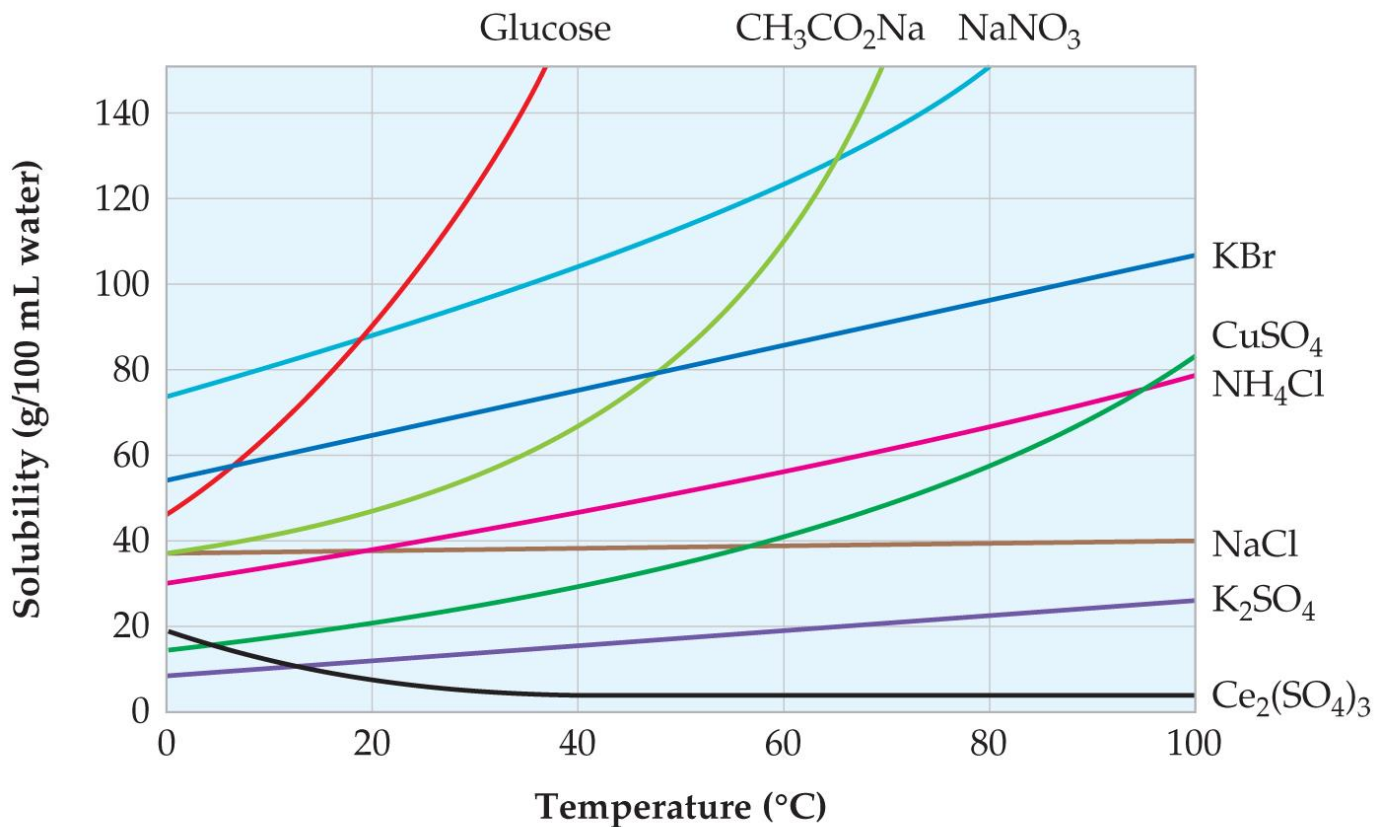
A supersaturated solution of sodium acetate in water.



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

Supersaturated solution

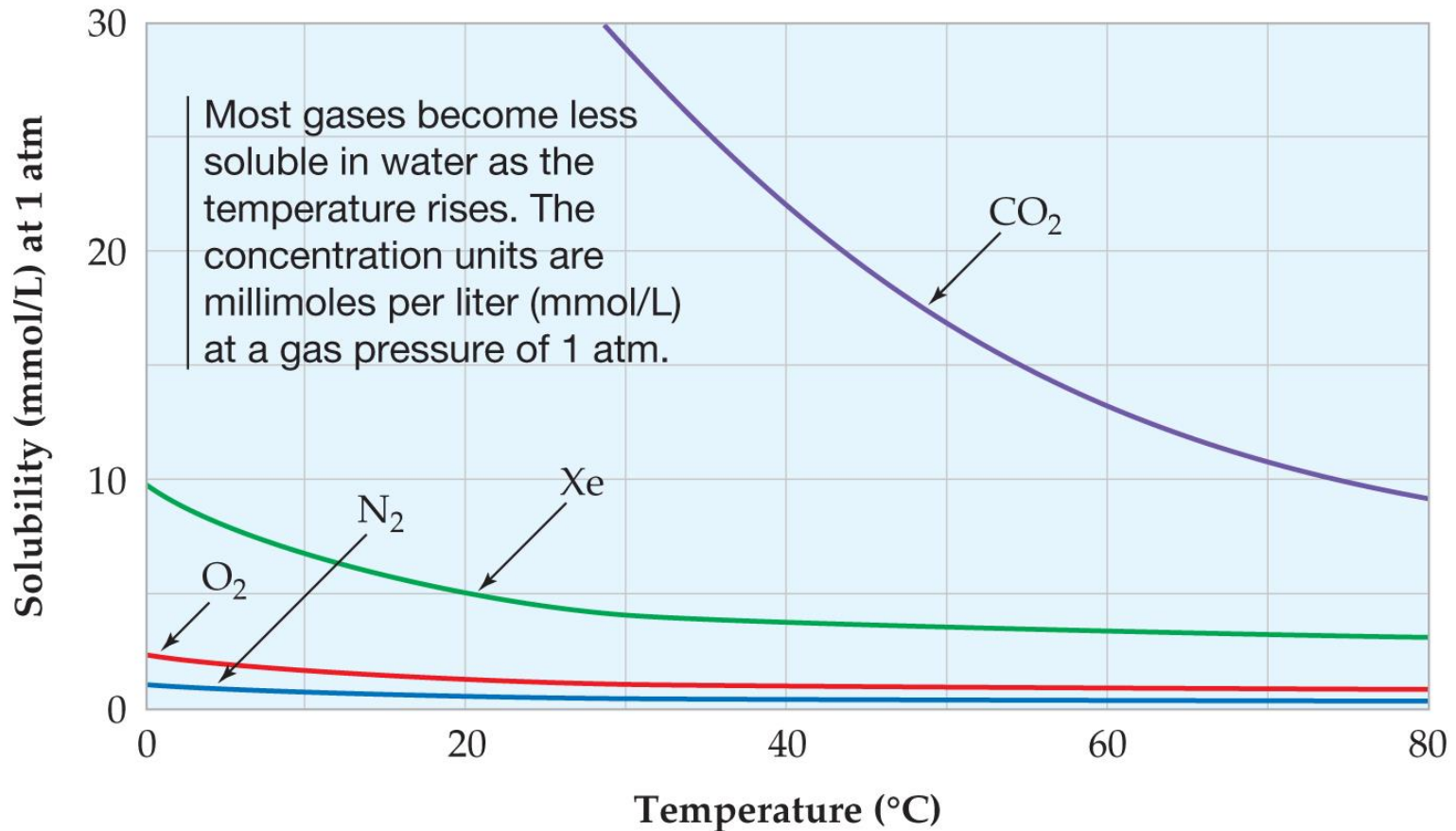
Some Factors That Affect Solubility



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

most solids more soluble – higher temperature of solvent

Some Factors That Affect Solubility

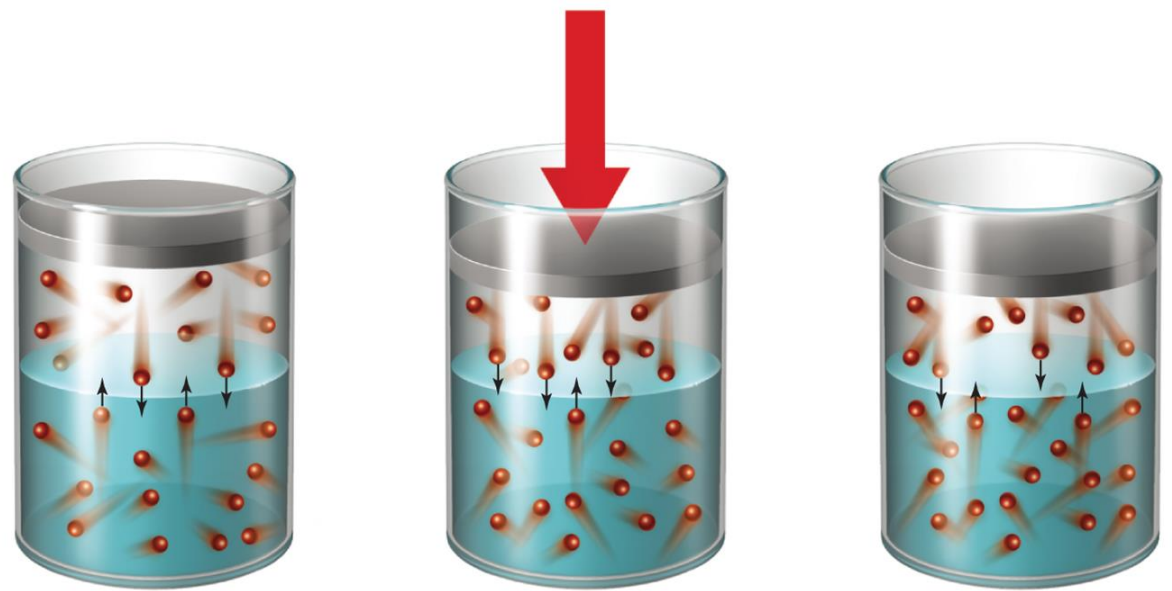


gases less soluble – higher temperature of solvent

Some Factors That Affect Solubility

Henry's Law
Solubility = kP

gases more soluble
at higher P



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 $3.2 \times 10^{-2} \text{ M}$ at 25°C and 1 atm pressure. What is the Henry's-law constant for CO_2 in $\text{mol}/(\text{L atm})$?

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

Solubility (M) (mol solute / L solution)

Henry's Law constant [$\text{mol}/(\text{L atm})$]

P (atm)

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

HW 12.7: Some Factors That Affect Solubility

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

Solubility (M)

Henry's Law constant [mol/(L atm)]

P (atm)

If the Henry's Law constant of CO₂ in water is 3.2 x 10⁻² mol / (L atm), what is the solubility of CO₂ in water at 2.5 atm ?

HW 12.7: Some Factors That Affect Solubility

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

Solubility (M)

Henry's Law constant [mol/(L atm)]

P (atm)

If the Henry's Law constant of CO₂ in water is 3.2 x 10⁻² mol / (L atm), what is the solubility of CO₂ in water at 2.5 atm ?

$$k = 3.2 \times 10^{-2} \text{ mol}/(\text{L atm}), P=2.5 \text{ atm}$$

$$\text{Solubility} = [3.2 \times 10^{-2} \text{ mol}/(\text{L atm})] * (2.5 \text{ atm})$$

$$\text{Solubility} = 0.080 \text{ M (or mol/L)}$$

Physical Behavior of Solutions: Colligative Properties

Colligative Properties: Properties that depend on the amount of a dissolved solute but not on its chemical identity (usually non volatile solute)

- Vapor-pressure lowering ($P_{\text{solution}} = i * P_{\text{solvent}} * X_{\text{solvent}}$) (Raoult's Law)
- Boiling-point elevation ($\Delta T_b = i * K_b * m$)
- Freezing-point depression ($\Delta T_f = - i * K_f * m$)
- Osmotic pressure ($\Pi = i * M * R * T$)

X = mole fraction

i = van't Hoff factor (=1 for nonelectrolytes) (= # of ions in solution per formula)

m = molality

K_b molal BP constant, K_f molal FP constant

M = molarity

R = gas constant = 0.08206 L atm / (mol K)

End 2/7 Friday A
section, C section

Vapor-Pressure Lowering of Solutions: Raoult's Law (colligative property)

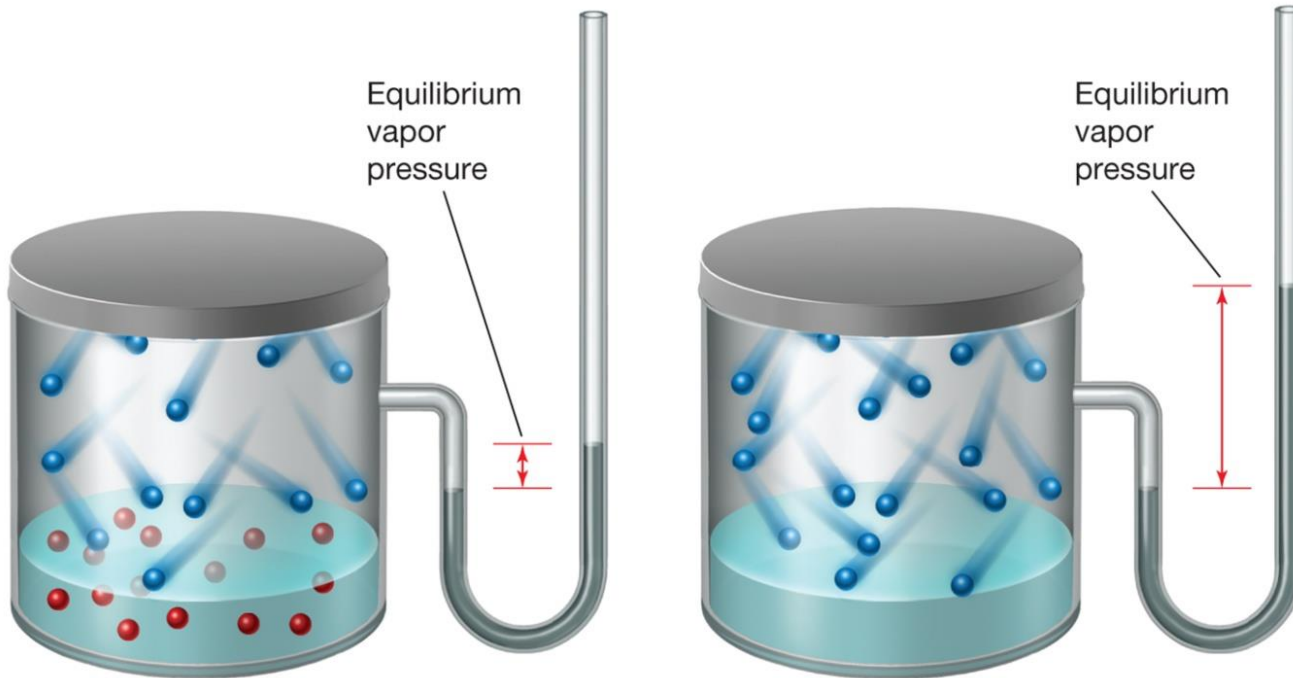
Raoult's Law

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

P_{soln} = Pressure of solution

P_{solv} = Pressure of solvent

X_{solv} = mole fraction of solvent



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 (colligative property)

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, non electrolyte solute.

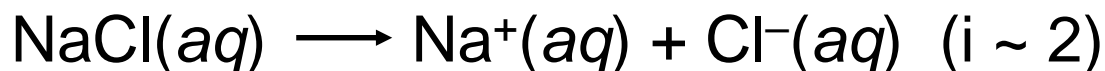
$$P_{\text{soln}} = P_{\text{solv}} X_{\text{solv}}$$

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

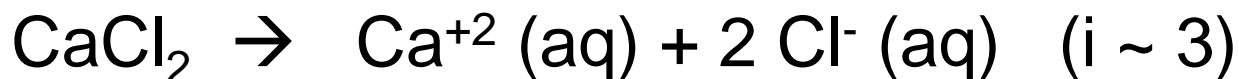
Van't Hoff Factor (colligative properties)

For all colligative properties, when a salt dissolves in water, dissociates and gives more # particles.

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



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**.



Colligative properties depend on # of particles.

BP Elevation (higher) & FP Depression (lower) of Solutions (colligative property)

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 · kg)/mol]	K_f [(°C · kg)/mol]
Benzene (C ₆ H 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 ₄ H ₁₀ O)	2.02	1.79
Ethyl alcohol (C ₂ H ₆ O)	1.22	1.99
Water (H ₂ O)	0.51	1.86

BP Elevation & FP Depression of Soln (colligative property)

What is the FP (in °C) of a solution prepared by dissolving 7.40 g of MgCl₂ in 110 g of water? [van't Hoff (MgCl₂) $i = 2.7$]

Calculate the moles of MgCl₂:

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

$$\Delta T_f = K_f m i$$

Calculate the molality of the solution:

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

$$K_f (\text{water}) = 1.86 \text{ }^\circ\text{C/m}$$
$$\text{FP}(\text{water}) = 0.0 \text{ }^\circ\text{C}$$

Calculate the freezing point of the solution:

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

$$T_f = 0.0 \text{ }^\circ\text{C} - 3.6 \text{ }^\circ\text{C} \text{ (FP depression)} = \boxed{-3.6 \text{ }^\circ\text{C}}$$

HW 12.8: BP Elevation & FP Depression of Soln (colligative prop.)

What is the BP (in Celsius) of a solution prepared by dissolving 10.0 g of LiCl in 150.0 g of water. Assume complete dissociation. (FM LiCl = 42.39 g /mol)

$$\Delta T_b = K_b m i$$

$$K_b \text{ (water)} = 0.51 \text{ }^\circ\text{C/m}$$
$$\text{BP(water)} = 100.0 \text{ }^\circ\text{C}$$

HW 12.8: BP Elevation & FP Depression of Soln (colligative prop.)

What is the BP (in Celsius) of a solution prepared by dissolving 10.0 g of LiCl in 150.0 g of water. Assume complete dissociation. (FM LiCl = 42.39 g/mol)

$$\Delta T_b = K_b m i$$

$$m = \frac{10.0 \text{ g LiCl}}{150.0 \text{ g H}_2\text{O}} * \frac{1 \text{ mol LiCl}}{42.39 \text{ g LiCl}} * \frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}} = 1.57 \text{ m LiCl}$$

$i = 2$ (complete dissociation)

$$K_b \text{ (water)} = 0.51 \text{ }^\circ\text{C/m}$$
$$\text{BP(water)} = 100.0 \text{ }^\circ\text{C}$$

$$\Delta T_b = K_b m i$$

$$\Delta T_b = (0.51 \text{ }^\circ\text{C/m}) * 1.57 \text{ m} * 2$$

$$\Delta T_b = 1.6 \text{ }^\circ\text{C} \text{ (BP elevation)}$$

$$\text{BP} = 100.0^\circ\text{C} + 1.6 \text{ }^\circ\text{C} = 101.6 \text{ }^\circ\text{C}$$

Osmosis and Osmotic Pressure

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

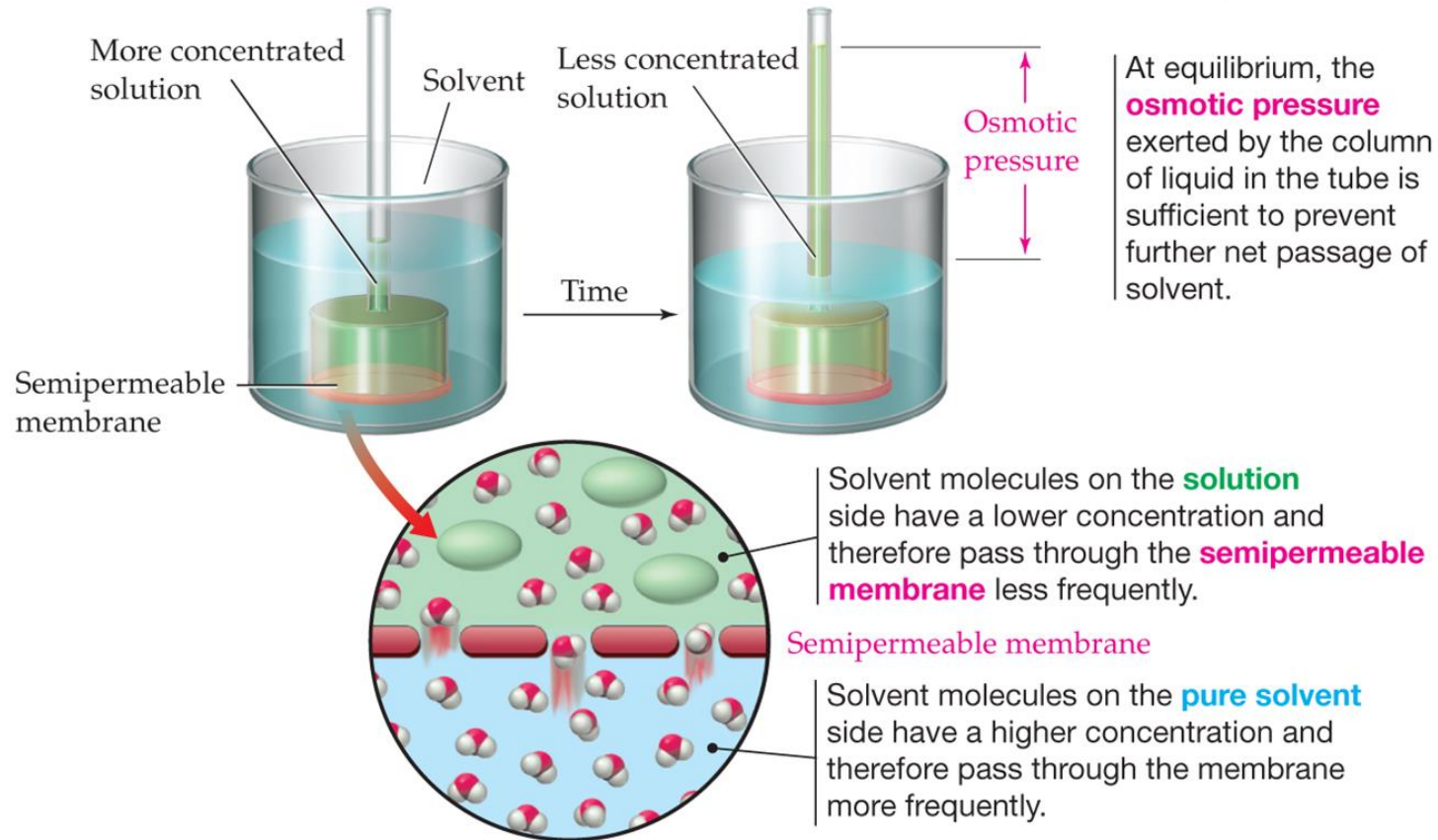
Osmotic Pressure (Π): The amount of pressure necessary to cause osmosis to stop, or the amount of pressure necessary to achieve an equilibrium passage of solvent molecules through a semipermeable membrane

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.



Osmosis and Osmotic Pressure

Calculate the osmotic pressure of a 1.00 M glucose solution in water at 300 K. (glucose is non electrolyte – does not dissociate into ions, $i = 1$)

$$\Pi = MRT i = 1.00 \frac{\text{mol}}{\text{L}} \times 0.08206 \frac{\text{L atm}}{\text{K mol}} \times 300 \text{ K} = 24.6 \text{ atm}$$

HW 12.9: Osmosis and Osmotic Pressure

What is the osmotic pressure of an intravenous solution prepared by dissolving 50.0 g of dextrose ($C_6H_{12}O_6$) (FM dextrose = 180.18 g/mol) in enough water to make 1.00 L of solution. Body temperature is $37.0^\circ C$.

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

$$\Pi = M R T i$$

End class 2/10

Monday A section

End class 2/11

Tuesday C section

HW 12.9: Osmosis and Osmotic Pressure

What is the osmotic pressure of an intravenous solution prepared by dissolving 50.0 g of dextrose ($C_6H_{12}O_6$) (FM dextrose = 180.18 g/mol) in enough water to make 1.00 L of solution. Body temperature is 37.0°C.

$$\Pi = M R T i$$

$$M = \frac{50.0 \text{ g dextrose}}{1.00 \text{ L soln}} \times \frac{\text{mol dextrose}}{180.18 \text{ g dextrose}} = 0.278 \text{ M dextrose}$$

$$T = 37.0^\circ\text{C} + 273.15 = 310.15 \text{ K}$$

End class 2/10
Monday, A section

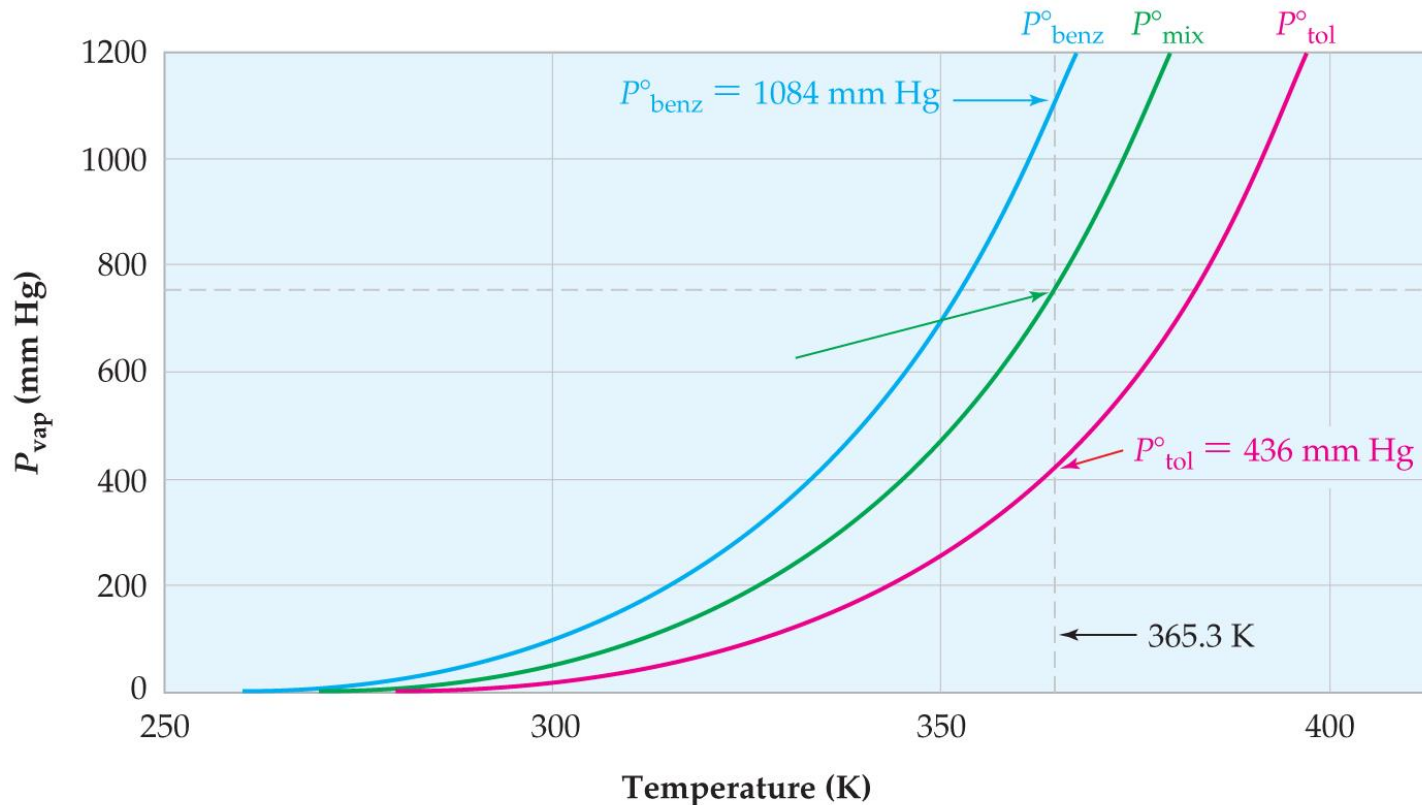
$i = 1$, dextrose is a non electrolyte

$$\Pi = \frac{0.278 \text{ M dextrose}}{\text{dextrose}} \times 0.08206 \frac{\text{L atm}}{\text{K mol}} \times 310.15 \text{ K} \times 1 =$$

$$\Pi = 7.08 \text{ atm}$$

Fractional Distillation of Liquid Mixtures

Syllabus: Leave out, NOT RESPONSIBLE on test



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.