Chap 9: Properties of Mixtures

- Intermolecular Forces & Solubility
  - (Intramolecular) (Bonding)
    - Ionic
    - Covalent
    - Metallic
  - Intermolecular
    - Ion-Dipole (strongest)
    - Hydrogen bonding
    - Dipole-Dipole
    - Ion-Induced Dipole
    - Dipole-Induced Dipole
    - Dispersion (London) (weakest

Chap 13: Properties of Mixtures

- Types of Solutions
  - Liquid Solutions
  - Gas Solutions
  - Solid Solutions
- The Solution Process
  - Solvation /Hydration
  - Solute
  - Solvent
  - Mixing

Chap 9: Properties of Mixtures

- Solution as an Equilibrium Process
  - Effect of Temperature
  - Effect of Pressure
- Concentration
  - Molarity & Molality
  - Parts of Solute by Parts of Solution
  - Interconversion of Concentration Terms
- Colligative Properties of Solutions
  - Vapor Pressure
  - Boiling Point Elevation
  - Freezing Point Depression
  - Osmotic Pressure
- Structure and Properties of Colloids

Intermolecular Forces & Solubility

- Solutions – Homogeneous mixtures consisting of a **solute** dissolved in a **solvent** through the actions of **intermolecular forces**

- Solute dissolves in Solvent

- Distinction between Solute & Solvent not always clear

- Solubility – Maximum amount of solute that dissolves in a fixed quantity of solvent at a specified temperature

- "Dilute" & "Concentrated" are qualitative (relative) terms

Intermolecular Forces & Solubility

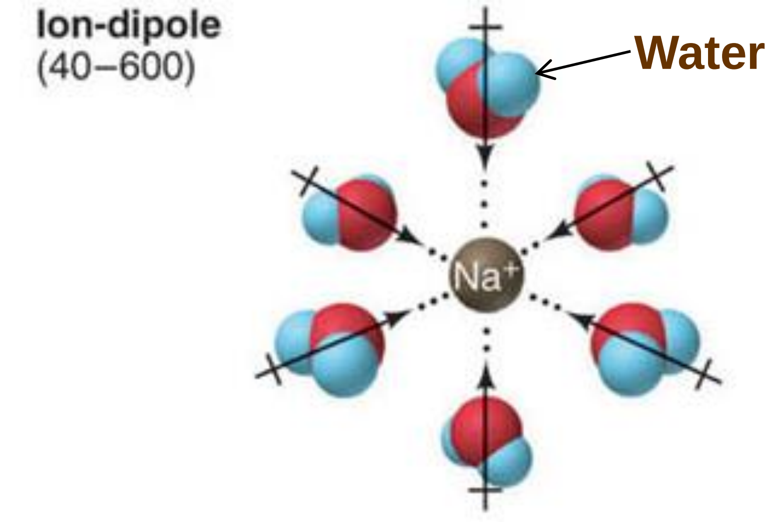
- Substances with similar types of intermolecular forces (IMFs) dissolve in each other

“Like Dissolves Like”

- Nonpolar substances (e.g., hydrocarbons) are dominated by dispersion force IMFs and are soluble in other nonpolar substances
- Polar substances have Hydrogen Bonding, ionic, and dipole driven IMFs (e.g., Water, Alcohols) and would be soluble in polar substances (solvents)

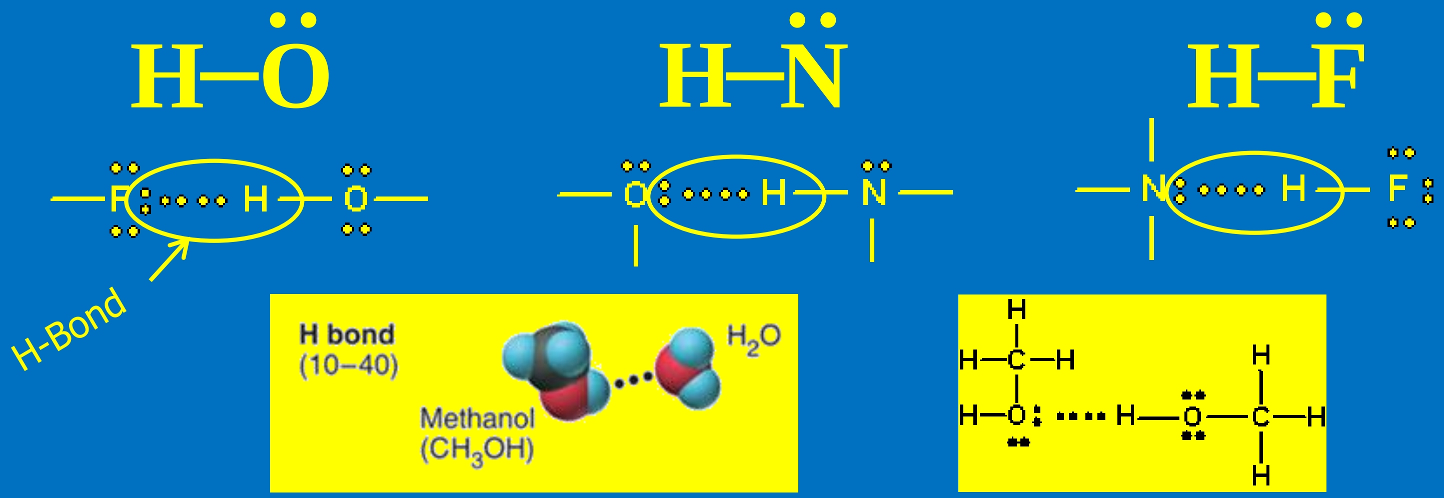
Intermolecular Forces & Solubility

- Intermolecular Forces
  - Ion-Dipole forces
    - Principal forces involved in solubility of **ionic** compounds in water
    - Each ion on crystal surface attracts oppositely charged end of Water dipole
    - These attractive forces overcome attractive forces between crystal ions leading to breakdown of crystal structure



Intermolecular Forces & Solubility

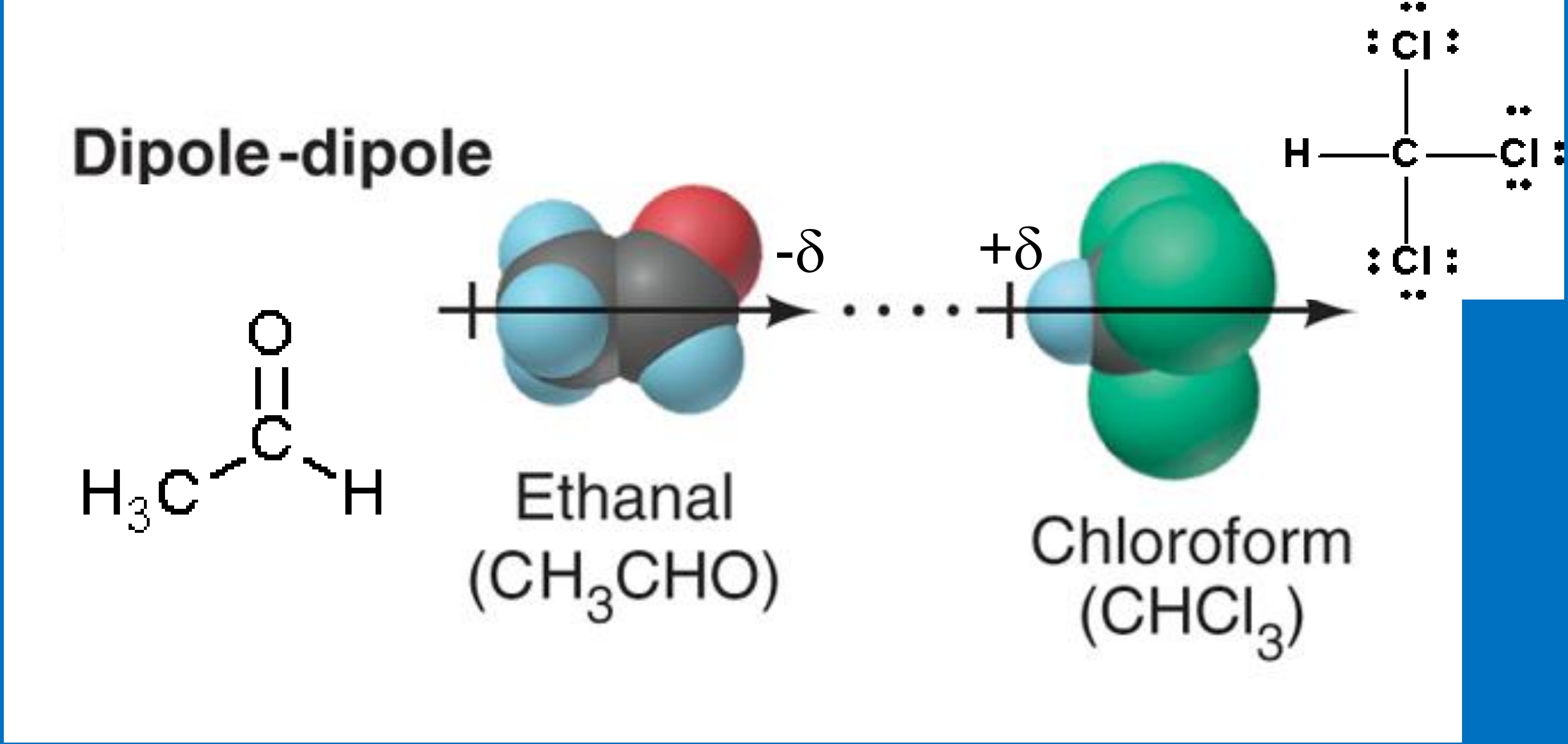
- Intermolecular Forces
  - Hydrogen Bonding – Dipole-Dipole force that arises between molecules that have an H atom bonded to a small highly electronegative atom with lone electrons pairs (N, O, F)



  - Especially important in aqueous (water) solutions.
    - Oxygen- and nitrogen-containing organic and biological compounds, such as alcohols, sugars, amines, amino acids.
    - O & N are small and electronegative, so their bound H atoms are partially positive and can get close to negative O in the dipole water (H_2O) molecule

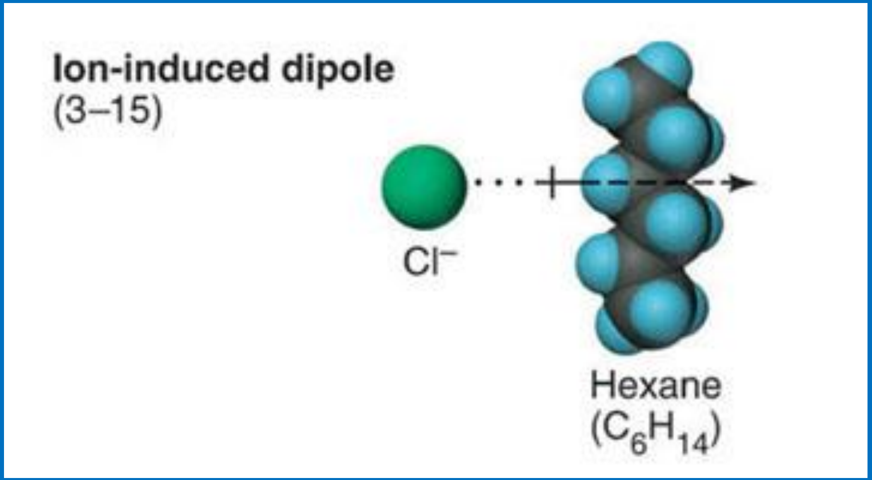
Intermolecular Forces & Solubility

- Intermolecular Forces
  - Dipole-Dipole forces
    - In the absence of H bonding, Dipole-Dipole forces account for the solubility of polar organic molecules, such as Aldehydes (R-CHO) in polar solvents such as chloroform ($CHCl_3$)



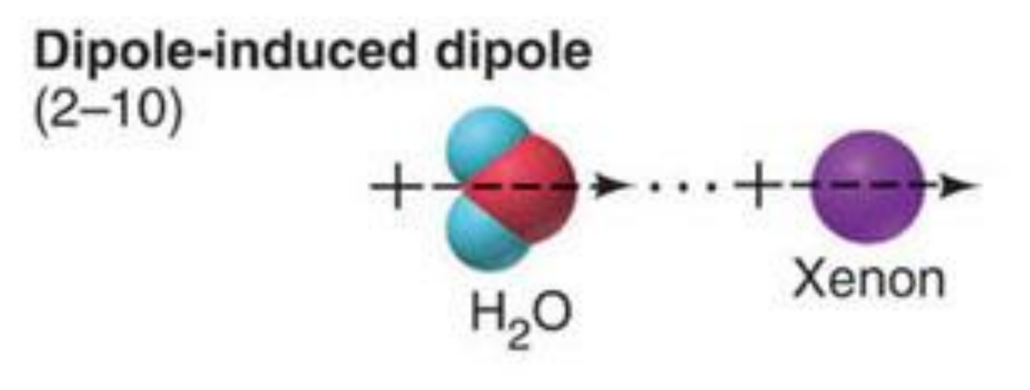
Intermolecular Forces & Solubility

- Intermolecular Forces
  - Ion-induced Dipole forces
    - One of 2 types of charged-induced dipole forces (see – dipole-induced dipole on next slide)
    - Rely on polarizability of components
    - Ion's charge distorts electron cloud of nearby nonpolar molecule
    - Ion increases magnitude of any nearby dipole; thus contributes to solubility of salts in less polar solvents Ex. LiCl in Ethanol



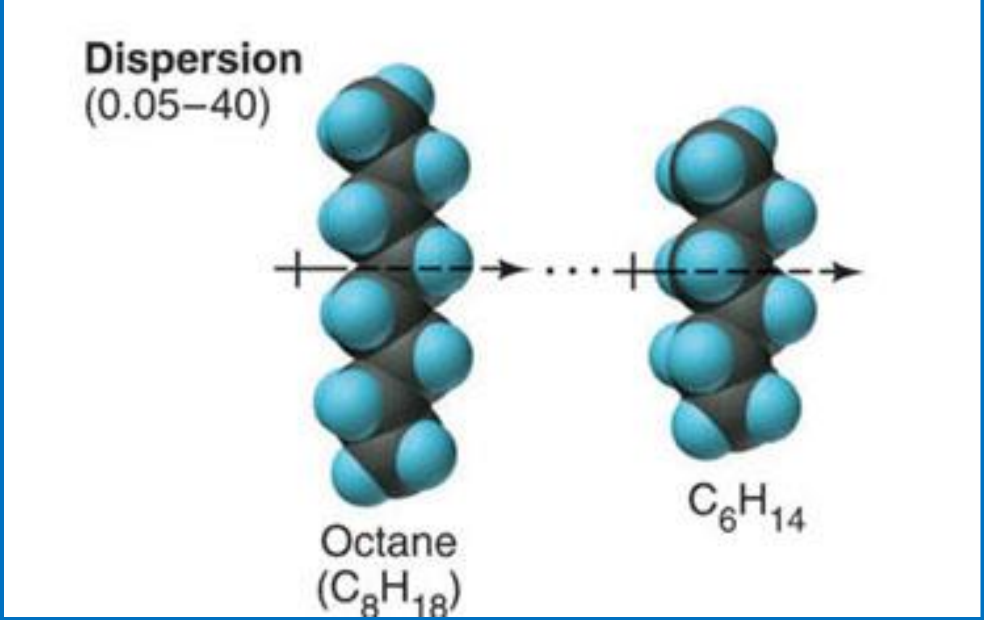
Intermolecular Forces & Solubility

- Intermolecular Forces
  - Dipole-Induced Dipole forces
    - Intermolecular attraction between a polar molecule and the oppositely charged pole it induces in a nearby molecule
    - Also based on polarizability, but are weaker than ion-induced dipole forces because the magnitude of charge is smaller – ions vs dipoles (coulombs law)
    - Solubility of atmospheric gases (O_2, N_2, noble gases) have limited solubility in water because of these forces



Intermolecular Forces & Solubility

- Intermolecular Forces
  - Dispersion forces (Instantaneous Dipoles)
    - Contribute to solubility of all solutes in all solvents
    - Principal type of intermolecular force in solutions of nonpolar substances, such as petroleum and gasoline
    - Keep cellular macromolecules in their biologically active shapes



Liquid Solutions

- Solutions can be:

  Liquid Gaseous Solid

- Physical state of Solvent determines physical state of solution
- Liquid solutions – forces created between solute and solvent comparable in strength (“like” dissolves “like”)
  - Liquid – Liquid
    - Alcohol/water – H bonds between OH & H_2O
    - Oil/Hexane – Dispersion forces
  - Solid – Liquid
    - Salts/Water – Ionic forces
  - Gas – Liquid
    - (O/H_2O) – Weak intermolecular forces (low solubility, but biologically important)

Liquid Solutions

- Gas Solutions
  - Gas – Gas Solutions – All gases are infinitely soluble in one another
  - Gas – Solid Solutions – Gases dissolve into solids by occupying the spaces between the closely packed particles
    - Utility – Hydrogen (small size) can be purified by passing an impure sample through a solid metal like palladium (forms Pd-H covalent bonds)
    - Disadvantage – Conductivity of Copper is reduced by the presence of Oxygen in crystal structure (copper metal is transformed to $Cu(I)_2O$

Liquid Solutions

- Solid Solutions
  - Solid – Solid Solutions
    - Alloys – A mixture with metallic properties that consists of solid phases of two or more pure elements, solid-solid solution, or distinct intermediate (heterogeneous) phases
    - Alloys Types
      - Substitutional alloys – Brass (copper & zinc), Sterling Silver(silver & copper), etc. substitute for some of main element atoms
      - Interstitial alloys – atoms of another elements (usually a nonmetal) fill interstitial spaces between atoms of main element, e.g., carbon steel (C & Fe)

Practice Problem

- A solution is ______________

a. A heterogeneous mixture of 2 or more substances
b. A homogeneous mixture of 2 or more substances
c. Any two liquids mixed together
d. very unstable
e. the answer to a complex problem

Ans: b

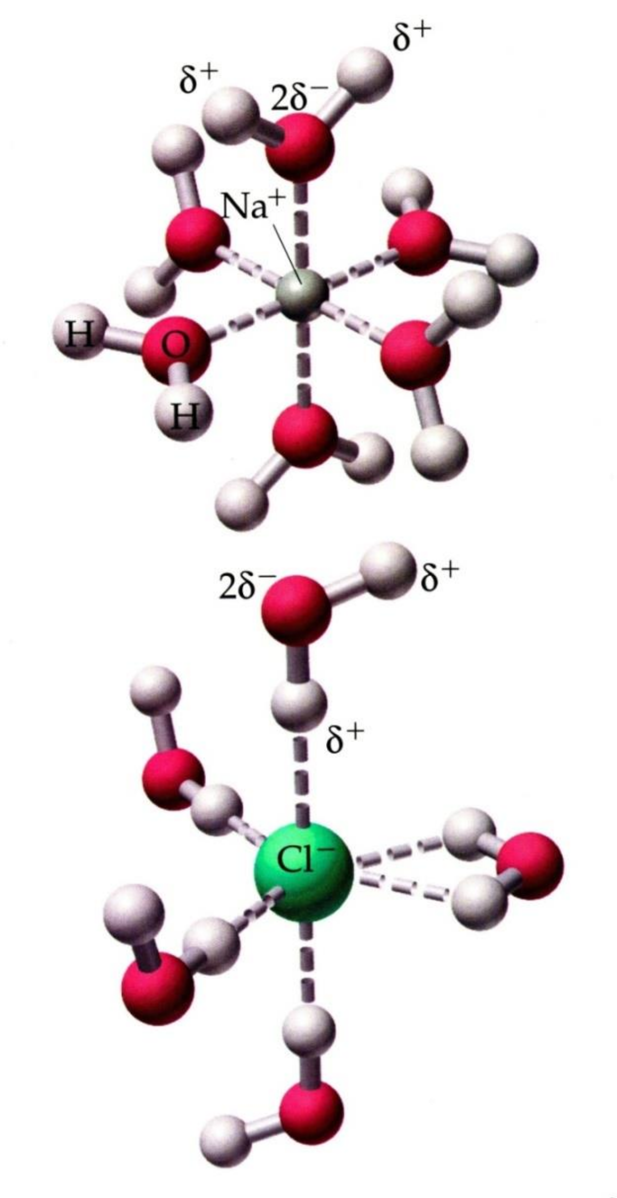
The Solution Process

- Elements of Solution Process
  - Solute particles must separate from each other
  - Some solvent particles must separate to make room for solute particles
  - Solute and Solvent particles must mix together
  - Energy must be absorbed to separate particles
  - Energy is released when particles mix and attract each other
  - Thus, the solution process is accompanied by changes in Enthalpy (ΔH), representing the *heat energy* tied up in chemical bonds and Entropy (S), the number of ways the energy of a system can be dispersed through motions of particles)

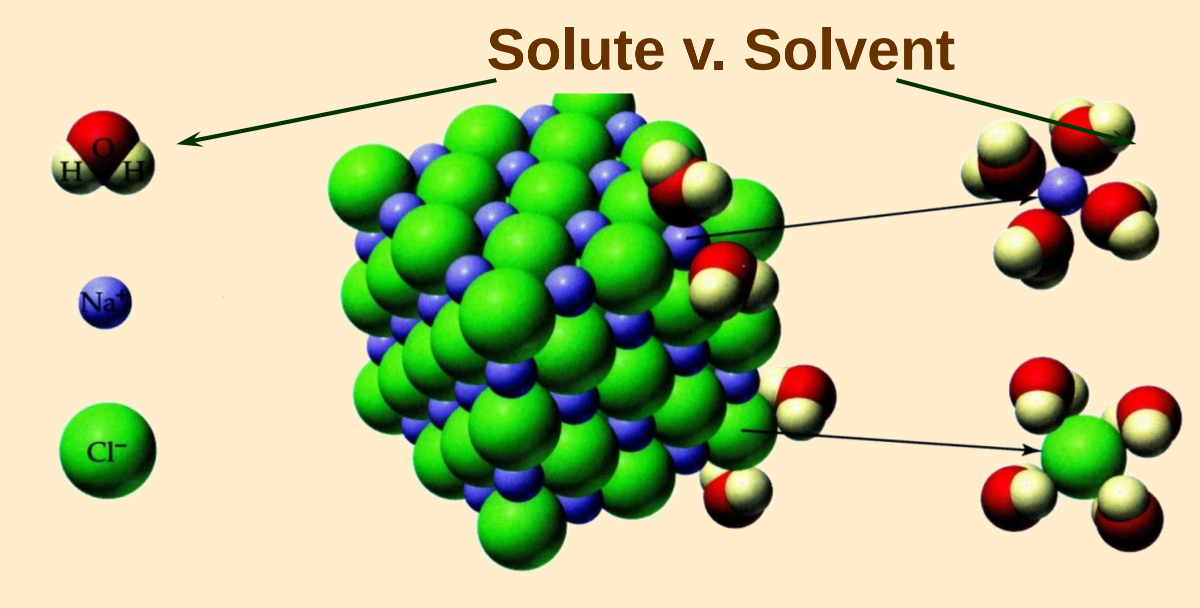
1. $\Delta H = \Delta E + P\Delta V$
2. **Entropy (S)**

Solution Process - Solvation

- Solvation – Process of surrounding a solute particle with solvent particles
- Hydrated ions in solution are surrounded by solvent molecules in defined geometric shapes
- Orientation of combined solute/solvent is different for solvated cations and anions
- *Cations attract the negative charge of the solvent*
- *Anions attract the positive charge of the solvent*



Solution Process



Coulombic - attraction of oppositely charged particles

van der Waals forces:
a. dispersion (London)
b. dipole-dipole
c. ion-dipole

Hydrogen-bonding **-** attractive interaction of a Hydrogen atom and a strongly electronegative Element:

Oxygen, Nitrogen or Fluorine

Hydration Energy

attraction between solvent and solute

Lattice Energy

solute-solute forces

Practice Problem

Predict which solvent will dissolve more of the given solute:

a. Sodium Chloride (solute) in Methanol or in 1-Propanol

Ans: Methanol

A solute tends to be more soluble in a solvent whose intermolecular forces are similar to those of the solute

NaCl is an ionic solid that dissolves through ion-dipole forces

Both Methanol & 1-Propanol contain a “Polar” -OH group

The Hydrocarbon group in 1-Propanol is longer and can form only weak dispersive forces with the ions; thus it is less effective at substituting for the ionic attractions in the solute

Practice Problem (con't)

Predict which solvent will dissolve more of the given solute:

b. Ethylene Glycol ($HOCH_2CH_20H$) in
Hexane ($CH_3(CH_2)_4CH_3$) or in Water (H_2O)

Ans: Very Soluble in Water

Ethylene Glycol molecules have two polar –OH groups and they interact with the Dipole water molecule through H-Bonding

The Water H-bonds can substitute for the Ethylene Glycol H-Bonds better than they can with the weaker dispersive forces in Hexane (no H-Bonds)

Practice Problem (con't)

Predict which solvent will dissolve more of the given solute:

c. Diethyl Ether ($CH_3CH_2OCH_2CH_3$) in

Water (H_2O) or in Ethanol (CH_3CH_2OH)

Ans: Ethanol

Diethyl Ether molecules interact with each other through dipole-dipole and dispersive forces and can form H-Bonds to both H_2O and Ethanol

The Ether is <u>more</u> soluble in Ethanol because Ethanol can form H-Bonds with the Ether Oxygen <u>and</u> the dispersion forces of the Hydrocarbon group (CH_3CH_2) are compatible with the dispersion forces of the Ether's Hydrocarbon group

Water, on the other hand, can form H bonds with the Ether, but it lacks any Hydrocarbon portion, so it forms much weaker dispersion forces with the Ether

The Solution Process

- Solute particles absorb heat (Endothermic) and separate from each other by overcoming intermolecular attractions

Solute (aggregated) + Heat → Solute (separated) $\Delta H_{solute} > 0$

- Solvent particles absorb heat (Endothermic) and separate from each other by overcoming intermolecular attractions

Solvent (aggregated) + Heat → Solvent (separated) $\Delta H_{solvent} > 0$

- Solute and Solvent particles mix (form a solution) by attraction and release of energy - an Exothermic process

Solute (separated) + Solvent (separated) → Solution + Heat $\Delta H_{mix} < 0$

Solution Process – Entropy Change

- Solids vs. Liquids vs. Gases
  - In a solid, particles are relatively fixed in their positions
  - In a liquid the particles are free to move around each other
    - This greater freedom of motion allows the particles to distribute their kinetic energy in more ways
  - Entropy increases with increased freedom of motion; thus, a material in its liquid phase will have a higher Entropy than when it is a solid

$$S_{liquid} > S_{solid}$$

A gas, in turn, would have a higher Entropy than its liquid phase

$$S_{gas} > S_{liquid} > S_{solid}$$

Solution Process – Entropy Change

- Relative change in Entropy (ΔS)
  - The change in Entropy from solid to liquid to gas is always positive

$$\Delta S_{gas} > \Delta S_{liquid} > \Delta S_{solid} > 0$$

  - The change from a liquid to a gas is called:

"Vaporization,"

thus, $\Delta S_{vap} > 0$

Solution Process – Entropy Change

- The change from a liquid to a solid is called:
  - "Fusion" (freezing)

thus, Entropy change would be negative

After the liquid has frozen there is less freedom of motion, thus the Entropy is less,

$$\Delta S_{fusion} < 0$$

Solution Process – Entropy Change

- Entropy and Solutions
  - There are far more interactions between particles in a solution than in either the pure solvent or the pure solute
  - Thus, the Entropy of a solution is higher than the sum of the solute and solvent Entropies

$$\mathbf{S_{soln} > (S_{solute} + S_{solvent}) \quad or \quad \Delta S > 0}$$

- The solution process involves the interplay between the:

  Change in Enthalpy (ΔH)

  Change in Entropy (ΔS)

- Systems tend toward

  "State of Lower Enthalpy (ΔH)"

  "State of Higher Entropy (ΔS)"

$$\mathbf{(Dissolution)}$$

Concentration

Definitions

Concentration Term	Ratio
Molarity (M)	$\frac{\text{amount (mol) of solute}}{\text{volume (L) of solution}}$
Molality (*m*)	$\frac{\text{amount (mol) of solute}}{\text{mass (kg) of solvent}}$
Parts by mass	$\frac{\text{mass of solute}}{\text{mass of solution}}$
Parts by volume	$\frac{\text{volume of solute}}{\text{volume of solution}}$
Mole Fraction (X)	$\frac{\text{amount (mol) of solute}}{\text{moles of solute + moles of solvent}}$

- Not useful in colligative properties because the exact amount of solvent is unknown.
- The following concentration units reflect the number of solute particles per solvent molecules and are useful with colligative properties.

$$\text{Weight \% of A} = \frac{\text{mass}_A}{\text{mass}_A + \text{mass}_B + \text{mass}_C + \cdots} \times 100$$

$$\text{Mole Fraction } (X_A) = \frac{n_A}{n_A + n_B + n_C + \cdots}$$

$$\text{Molality (m)} = \frac{\text{moles solute (mol)}}{\text{kilograms of solvent}}$$

$$\text{Molarity (M)} = \frac{\text{moles solute (mol)}}{\text{liters solution (L)}}$$

Practice Problem

The molality of a solution is defined as ________

a. moles of solute per liter of solution

b. grams of solute per liter of solution

c. moles of solute per kilogram of solution

d. moles of solute per kilogram of solvent

e. the gram molecular weight of solute per kilogram of solvent

Ans: d

Practice Problem

- What is the molality of a solution prepared by dissolving 32.0 g of $CaCl_2$ in 271 g of water

Ans:

$$\text{Molality} = \frac{\text{amount (mol) solute}}{\text{mass (kg) solvent}}$$

Step 1 - Convert Mass to Moles

$$\text{Moles } CaCl_2 = 32.0 \text{ g } CaCl_2 \times \frac{1 \text{ mol } CaCl_2}{110.98 \text{ g } CaCl_2} = 0.280 \text{ mol } CaCl_2$$

Step 2 – Compute Molality

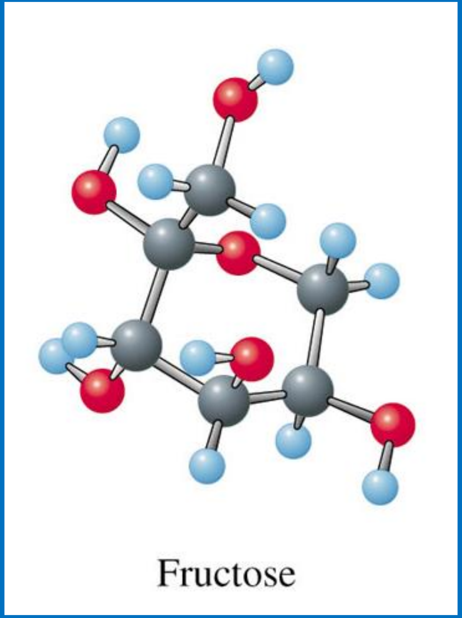
$$\text{Molality} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{0.288 \text{ mol } CaCl_2}{271 \text{ g} \times \frac{1 \text{ kg}}{10^3 \text{ g}}} = 1.06 \text{ m } CaCl_2$$

Practice Problem

Fructose, $C_6H_{12}O_6$ (FW = 180.16 g/mol, is a sugar occurring in honey and fruits. The sweetest sugar, it is nearly twice as sweet as sucrose (cane or beet sugar). How much water should be added to 1.75 g of fructose to give a 0.125 *m* solution?

$$\text{Molality(m)} = \left(\frac{\text{mol}_{\text{solute}}}{\text{kg}_{\text{solvent}}}\right)$$

$$\text{kg}_{\text{solvent}} = \left(\frac{\text{mol}_{\text{solute}}}{\text{m}}\right) = \left(\frac{1.75\ \text{g}_{\text{sucrose}} \times \dfrac{1\ \text{mol}_{\text{sucrose}}}{180.16\ \text{g}_{\text{sucrose}}}}{0.125\ \text{mol / kg}_{H_2O}}\right)$$



Fructose

$$\text{kg}_{\text{solvent}} = 0.0777\ \text{kg}_{H_2O} \times \frac{1000\ \text{g}}{1\ \text{kg}} = 77.7\ \text{g}_{H_2O}$$

Colligative Properties of Solutions

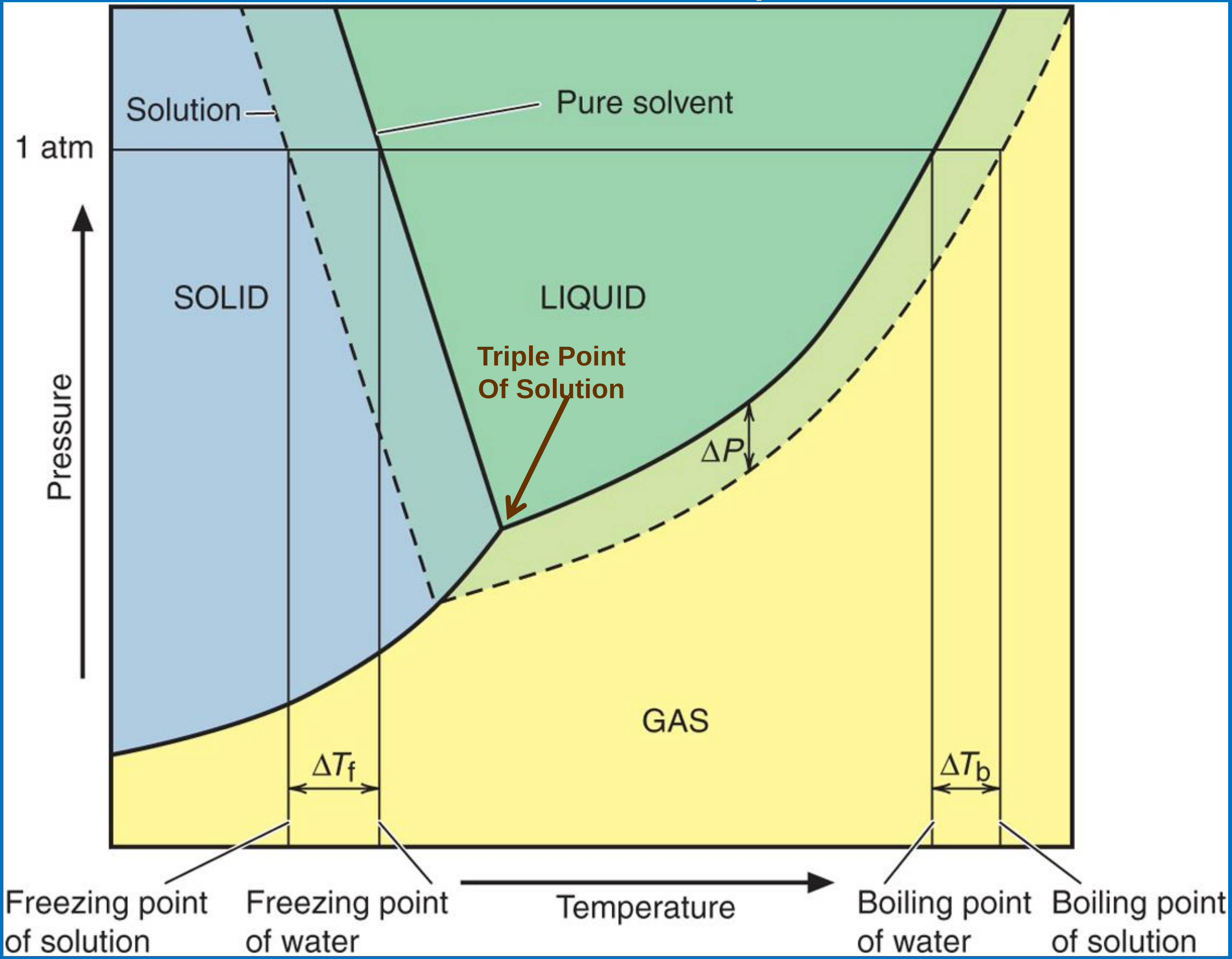
- Presence of Solute particles in a solution changes the physical properties of the solution
- The number of particles dissolved in a solvent also makes a difference in four (4) specific properties of the solution known as:

"Colligative Properties"

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

Colligative Properties of Solutions

Phase Diagram showing various phases of a substance and the conditions under which each phase exists



Colligative Properties of Solutions

- Colligative properties deal with the nature of a solute in aqueous solution and the extent of the dissociation into ions
- **Electrolyte** – Solute dissociates into ions and solution is capable of conducting an electric current
  - **Strong Electrolyte** – Soluble salts, strong acids, and strong bases dissociate completely; thus, the solution is a good conductor
  - **Weak Electrolyte** – polar covalent compounds, weak acids, weak bases dissociate weakly and are poor conductors
  - **Nonelectrolyte** – Compounds that do not dissociate at all into ions (sugar, alcohol, hydrocarbons, etc.) are nonconductors

Colligative Properties of Solutions

- Prediction of the magnitude of a colligative property
  - Solute Formula
    - Each mole of a nonelectrolyte yields 1 mole of particles in the solution

      Ex. 0.35 M glucose contains 0.35 moles of solute particles (glucose molecules) per liter
    - Each mole of strong electrolyte dissociates into the number of moles of ions in the formula unit

      Ex. 0.4 M Na_2SO_4 contains 0.8 mol of Na^+ ions and 0.4 mol of SO_4^{2-} ions (total 1.2 mol of particles) per liter of solution

Vapor Pressure

- ***Vapor pressure (Equilibrium Vapor Pressure)***:

  The pressure exerted by a vapor at equilibrium with its liquid in a closed system

- Vapor Pressure increases with increasing temperature
- nonvolatile nonelectrolyte (ex. sugar) & pure solvent
  - The vapor pressure of a solution of a nonvolatile nonelectrolyte (solute) is always lower than the vapor pressure of the pure solvent
  - Presence of solute particles reduces the number of solvent vapor particles at surface that can vaporize
  - At equilibrium, the number of solvent particles leaving solution are fewer than for pure solvent, thus, the vapor pressure is less

Vapor Pressure

- The vapor pressure of the solvent above the solution ($P_{solvent}$) equals the <u>Mole Fraction</u> of solvent in the solution ($X_{solvent}$) times the vapor pressure of the pure solvent ($P^{o}_{solvent}$)

  (Raoult's Law)

  $$P_{solvent} = X_{solvent} * P^{o}_{solvent}$$

  In a solution, the mole fraction of the solvent ($X_{solvent}$) is always <u>less than 1</u>; thus the partial pressure of the solvent above the solution ($P_{solvent}$) is always less than the partial pressure of the pure solvent $P^{o}_{solvent}$

  Ideal Solution – An ideal solution would follow Raoult's law for any solution concentration

  - Most gases in solution <u>deviate</u> from ideality
  - Dilute solutions give good approximation of Raoult's law

Vapor Pressure

- A solution consists of Solute & Solvent
- The sum of their mole fractions equals 1

$$X_{solvent} + X_{solute} = 1$$

$$X_{solvent} = 1 - X_{solute}$$

From Raoult's law

$$P_{solvent} = X_{solvent} P^{o}_{solvent} = (1 - X_{solute}) \times P^{o}_{solvent}$$

$$P_{solvent} = P^{o}_{solvent} - X_{solute} \times P^{o}_{solvent}$$

Rearranging

$$P^{o}_{solvent} - P_{solvent} = \Delta P = X_{solute} \times P^{o}_{solvent}$$

- The magnitude of ΔP (vapor pressure lowering) equals the mole fraction of the solute times the vapor pressure of the pure solvent

Vapor Pressure

- Vapor Pressure & Volatile Nonelectrolyte Solutions
- The vapor now contains particles of both a volatile solute and the volatile solvent

$$\mathbf{P_{solvent} = X_{solvent} \times P^o_{solvent} \quad and \quad P_{solute} = X_{solute} \times P^o_{solute}}$$

- From Dalton’s Law of Partial Pressures

$$\mathbf{P_{total} = P_{solvent} + P_{solute} = X_{solvent} \times P^o_{solvent} + X_{solute} \times P^o_{solute}}$$

- The presence of each volatile component lowers the vapor pressure of the other by making each mole fraction less than 1

Example Problem

- Given: Equi-molar solution of Benzene ($X_B = 0.5$) and Toluene ($X_T = 0.5$) (Both nonelectrolytes)

$$X_{ben} = 0.5 \qquad P^{o}_{ben} = 95.1\ \text{torr} \ @\ 25^{o}\text{C}$$

$$X_{tol} = 0.5 \qquad P^{o}_{tol} = 28.4\ \text{torr} \ @\ 25^{o}\text{C}$$

$$P_{ben} = X_{ben} \times P^{o}_{ben} = 0.5 \times 95.1\ \text{torr} = 47.6\ \text{torr}$$

$$P_{tol} = X_{tol} \times P_{tol} = 0.5 \times 28.4\ \text{torr} = 14.2\ \text{torr}$$

- Benzene lowers the vapor pressure of Toluene and Toluene lowers the vapor pressure of Benzene
- Compare Vapor composition vs Solution composition

$$X_{ben} = \frac{P_{ben}}{P_{tot}} = \frac{47.6\ \text{torr}}{47.6\text{torr} + 14.2\text{torr}} = 0.770\ \text{torr}$$

$$X_{tol} = \frac{P_{ben}}{P_{tot}} = \frac{14.2\ \text{torr}}{47.6\ \text{torr} + 14.2\ \text{torr}} = 0.230\ \text{torr}$$

Mole fractions in vapor are different

Boiling Point Elevation

- Boiling Point (T_b) of a liquid is the temperature at which its vapor pressure equals the external (atmospheric usually) pressure
- The vapor pressure of a solution (solvent + solute) is lower than that of the pure solvent at any temperature
- Thus, the difference between the external (atmospheric) pressure and the vapor pressure of the solution is greater than the difference between external pressure and the solvent vapor pressure - $\Delta P_{soln} > \Delta P_{solvent}$
- The boiling point of the solution will be higher than the solvent because additional energy must be added to the solution to raise the vapor pressure of the solvent (now lowered) to the point where it again matches the external pressure
- The boiling point of a concentrated solution is greater than the boiling point of a dilute solution

Boiling Point Elevation

- The magnitude of the boiling point elevation is proportional to the Molal concentration of the solute particles

$$\Delta T_b \propto m \quad \text{or} \quad \Delta T_b = K_b m$$

where : $\Delta T_b = T_{b_{solution}} - T_{b_{solvent}}$ = **boiling point elevation**

m = **solution molality** $(mol_{solute} / kg_{solvent})$

K_b = **molal boiling point elevation constant**

- Note the use of "Molality"
  - Molality is related to mole fraction, thus particles of solute
  - Molality also involves "Mass of Solvent"; thus, not affected by temperature

Freezing Point Depression

- Recall: The vapor pressure of a solution is lower than the vapor pressure of the pure solvent
- The lower vapor pressure of a solution is the result of fewer solvent molecules being able to leave the liquid phase because of the competition with solute molecules for space at the surface
- In solutions with nonvolatile solutes, only solvent molecules can vaporize; thus, only solvent molecules can solidify (freeze)
- The freezing point of a solution is the temperature at which solid solvent particles come out of solution
- The formation of solid solvent particles leaves the solution more concentrated in solute because there is less solvent particles available

Freezing Point Depression

- At the freezing point of a solution, there is an equilibrium established between solid solvent and liquid solvent
- There is also an equilibrium between the number of particles of solvent leaving the solution and the number of particles returning to the solution
- The freezing point is the temperature at which the vapor pressure of the pure solid in thermal contact with the solution is equal to the vapor pressure of the solution

Freezing Point Depression

- The vapor pressure of a solution is a function of the concentration of solute in the solvent
- As the concentration increases there are fewer solvent molecules left to escape to the vapor phase, thus the vapor pressure is lower
- Since vapor pressure is a function of temperature, a lower vapor pressure results in a lower temperature at which freezing occurs
- Thus, as the concentration of the solute in the solution increases, the freezing point of the solution is lowered

Freezing Point Depression

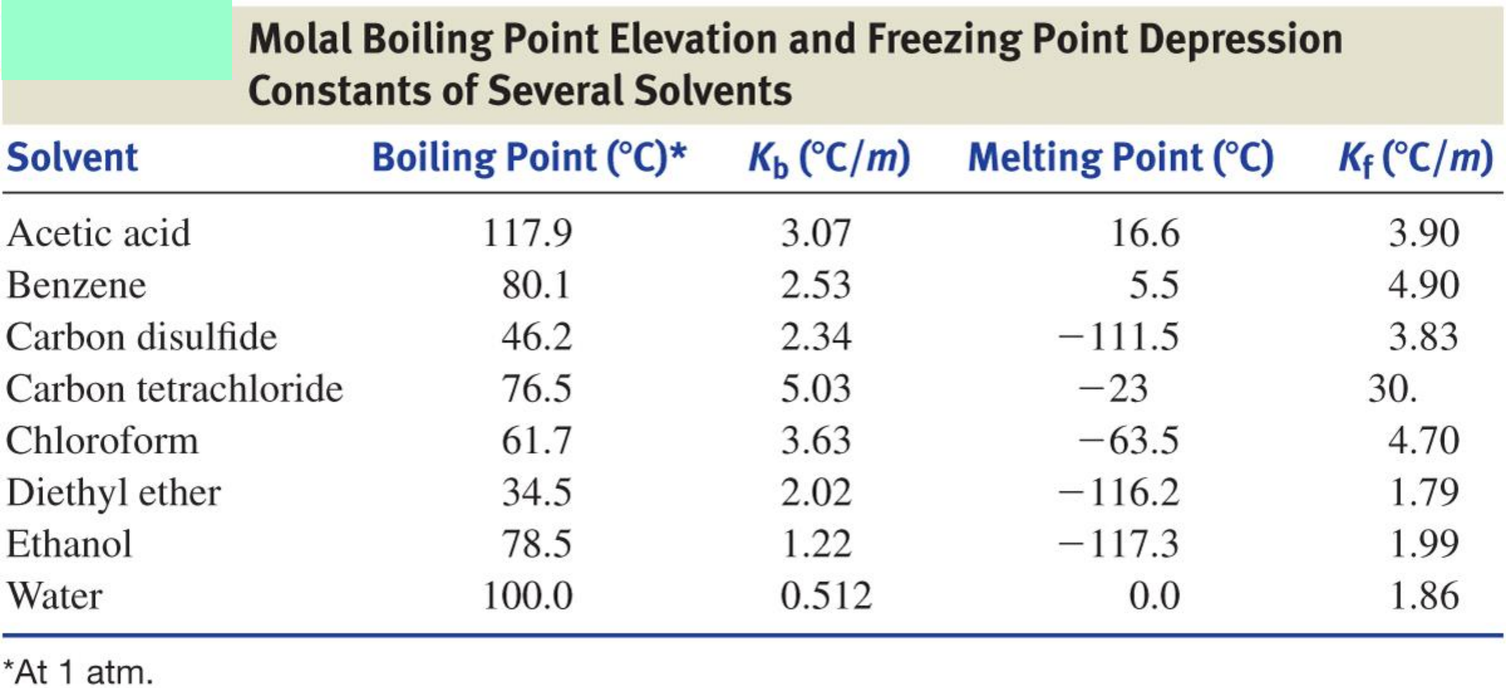
- The Freezing Point depression has the magnitude proportional to the Molal concentration of the solute

$$\Delta T_f \propto m \quad \text{or} \quad \Delta T_f = K_f m$$

$$\text{where:} \quad \Delta T_f = T_{f_{solvent}} - T_{f_{solution}} = \text{freezing point depression}$$

$$m = \text{solution molality } (mol_{solute} / kg_{solvent})$$

$$K_f = \text{molal freezing point depression constant}$$



Molal Boiling Point Elevation and Freezing Point Depression Constants of Several Solvents

Solvent	Boiling Point (°C)*	K_b (°C/m)	Melting Point (°C)	K_f (°C/m)
Acetic acid	117.9	3.07	16.6	3.90
Benzene	80.1	2.53	5.5	4.90
Carbon disulfide	46.2	2.34	−111.5	3.83
Carbon tetrachloride	76.5	5.03	−23	30.
Chloroform	61.7	3.63	−63.5	4.70
Diethyl ether	34.5	2.02	−116.2	1.79
Ethanol	78.5	1.22	−117.3	1.99
Water	100.0	0.512	0.0	1.86

*At 1 atm.

The van’t Hoff Factor

- Colligative properties depend on the relative number of solute to solvent “particles”
- In strong electrolytes solutions, the solute formula specifies the number of particles affecting the colligative property
- Ex. The BP elevation of a 0.5 m NaCl soln would be twice that of a 0.5 m glucose soln because NaCL dissociates into “2” particles per formula unit, where glucose produces “1” particle per formula unit
- The van’t Hoff factor (i) is the ratio of the measured value of the colligative property, e.g. BP elevation, in the electrolyte solution to the expected value for a nonelectrolyte solution

$$i = \frac{\text{measured value for electrolyte solution}}{\text{expected value for nonelectrolyte solution}}$$

The van’t Hoff Factor

- To calculate the colligative properties of strong electrolyte solutions, incorporate the van’t Hoff factor into the equati

$CH_3OH(l) \rightarrow CH_3OH(aq)$ 1:1, i = 1

$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$ 2:1, i = 2

$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^{-}(aq)$ 3:1, i = 3

$Ca_3(PO_4)_2(s) \rightarrow 3\ Ca^{2+}(aq) + 2\ PO_4^{3-}(aq)$ 5:1, i = 5

Ex. Freezing Point Depression with van’t Hoff factor for $Ca_3(PO_4)_2(s)$

$$\Delta T_f = iK_f c_m \qquad \Delta T_f = 5K_f c_m$$

Colligative Properties of Solutions

Colligative Property	Mathematical Relation
1. Vapor Pressure (Raoult's Law)	$P_{solvent} = i\left(P^o_{solvent} X_{solute}\right)$
2. Freezing Point Depression	$\Delta T_f = i\left(K_f m\right)$
3. Boiling Point Elevation	$\Delta T_b = i\left(K_b m\right)$
4. Osmotic Pressure	$\Pi = i\left(MRT\right)$

Practice Problem

What is the boiling point of 0.0075 *m* aqueous calcium chloride, $CaCl_2$?

$$\Delta T_b \propto \text{ or } \Delta T_b = iK_b m \qquad (i = 3)$$

$$\text{where: } \Delta T_b = T_{b_{solution}} - T_{b_{solvent}} = \text{boiling point elevation}$$

$$T_{b_{solution}} - T_{b_{solvent}} = 3 \times K_b m$$

$$T_{b_{CaCl_2}} = 3 \times K_b m + T_{b_{H_2O}}$$

$$T_{b_{CaCl_2}} = 3 \times 0.512 \frac{^{o}C}{m} \times 0.0075\,m + 100.0^{o}C$$

$$T_{b_{CaCl_2}} = 100.1^{o}C$$

Practice Problem

What is the freezing point of a 0.25 m solution of glucose in water (K_f for water is 1.86°C/m.)?

a. 0.93°C b. –0.93°C c. 0.46°C d. –0.46°C e. 0.23°C

Ans: d

$$\Delta T_f = T_{f_{solvent}} - T_{f_{solution}} = iK_fm \qquad (i = 1)$$

$$-T_{f_{solution}} = K_fm - T_{f_{solvent}}$$

$$T_{f_{solution}} = T_{f_{solvent}} - K_fm$$

$$T_{f_{solution}} = 0.0^{o}C - 1.86\left(\frac{^{o}C}{m}\right) \times 0.25\,m$$

$$T_{f_{solution}} = -0.46^{o}C$$

Practice Problem

What is the freezing point of 0.150 g of glycerol ($C_3H_8O_3$) in 20.0 g of water?

$$\Delta T_f = T_{f_{solvent}} - T_{f_{solution}} = iK_f m \quad (i = 1)$$

$$-T_{f_{solution}} = K_f m - T_{f_{solvent}}$$

$$T_{f_{solution}} = T_{f_{solvent}} - K_f m$$

$$T_{f_{solution}} = 0.0^{o}C - 1.86\left(\frac{^{o}C}{m}\right) \times \frac{0.150g\left(\frac{1mol}{92.094g}\right)}{20.0g \times \left(\frac{1kg}{1000g}\right)}$$

$$T_{f_{solution}} = 0.0^{o}C - 1.86\left(\frac{^{o}C}{\frac{mol}{kg}}\right) \times 0.0814\frac{mol}{kg}$$

$$T_{f_{solution}} = -0.151^{o}C$$

Practice Problem

What is the molar mass (M_m) of Butylated Hydroxytoluene (BHT) if a solution of 2.500 g of BHT in 100.0 g of Benzene (K_f = 5.065 °C/m; T_f = 5.455 °C) had a freezing point of 4.880 °C?

$$\Delta T_f = T_{f_{solvent}} - T_{f_{solution}} = iK_f m \qquad (i = 1)$$

$$m = \left(\frac{T_{f_{solvent}} - T_{f_{solution}}}{iK_f} \right)$$

$$m = \left(\frac{5.455^{o}C - 4.880^{o}C}{1 \times 5.065^{o}C / m} \right) = 0.1135\, mol_{BHT} / kg_{Benzene}$$

$$M_{mBHT} = Molar\ Mass_{BHT}(g / mol)$$

$$m = 0.1135 \frac{mol_{BHT}}{kg_{Benzene}} = \left(\frac{2.500\,g \times \frac{1mol_{BHT}}{M_{mBHT}(g)}}{100\,g_{Benzene} \frac{1kg}{1000g}} \right) = \left(\frac{25.00\,g \times \frac{1mol_{BHT}}{M_{mBHT}(g)}}{1kg_{Benzene}} \right)$$

$$\frac{M_{mBHT}(g)}{1\,mol_{BHT}} = \frac{25.00\,g_{BHT}}{0.1135\,mol_{BHT}} = 220.3g / mol \qquad (Actual\ M_m = 220.3\,g / mol)$$

Colloids

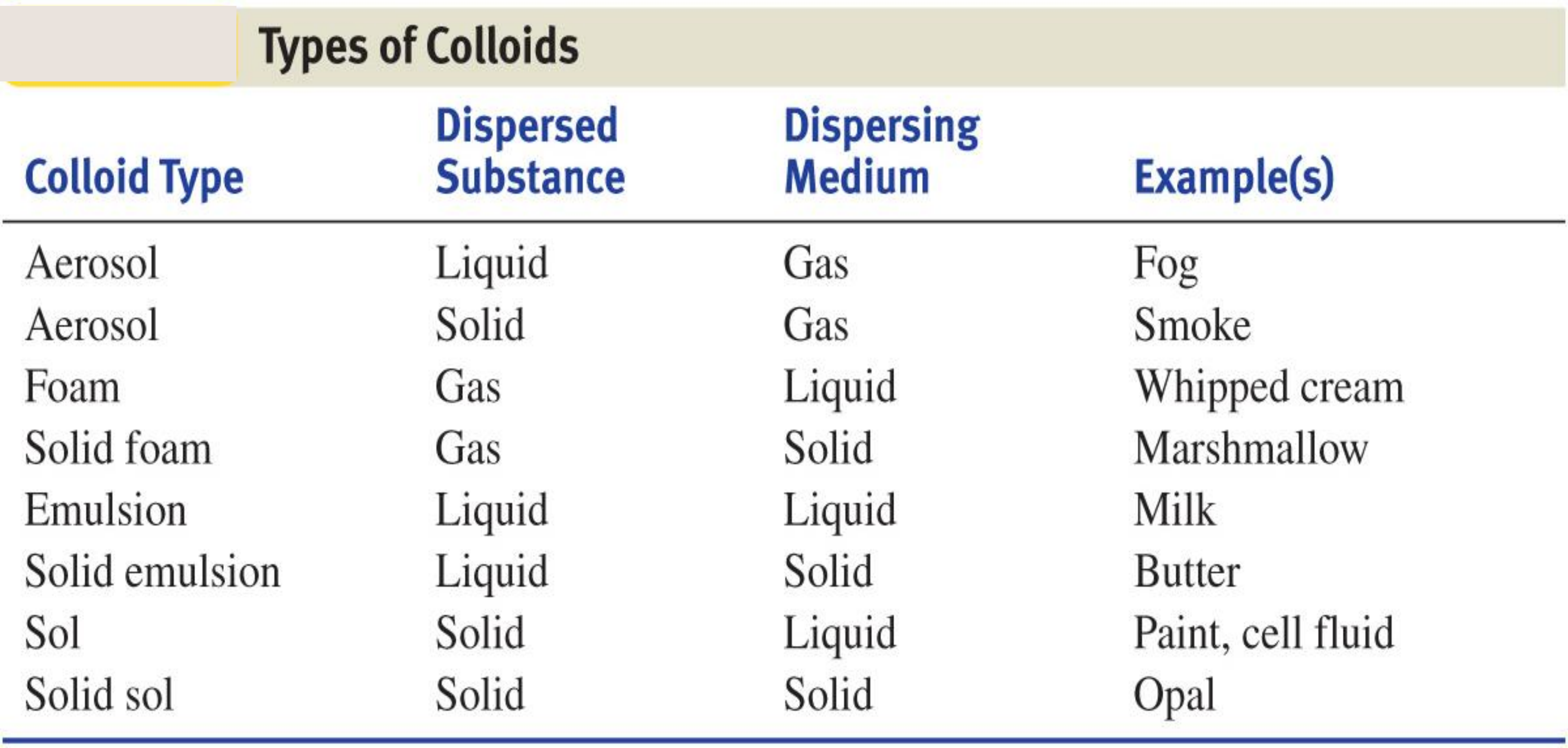
- Suspensions vs Mixtures vs Colloids
- A Heterogeneous mixture – fine sand suspended in water – consists of particles large enough to be seen by the naked eye, clearly distinct from surrounding fluid
- A Homogeneous mixture – sugar in water – forms a solution consisting of molecules distributed throughout and indistinguishable from the surrounding fluid
- Between these extremes is a large group of mixtures called colloidal dispersions – Colloids
- Colloid particles are larger than simple molecules, but small enough to remain in suspension and not settle out

Colloids

- Colloids have tremendous surface areas, which allows many more interactions to exert a large total adhesive force, which attracts other particles
  - Particle Size & Surface Area
    - Diameter – 1 to 1000 nm (10^{-9} to 10^{-6})
      - Single macromolecule or aggregate of many atoms, ions, or molecules
      - Very large surface area
      - Large surface area attracts other particles through various intermolecular forces (IMF)
    - Surface Area
      - A cube with 1 cm sides (SA – 6 cm^2) if divided into 10^{12} cubes (size of large colloidal particles) would have a total surface area of 60,000 cm^2

Colloids

- Colloid Classifications:
  - Colloids are classified according to whether the dispersed and dispersing substances are gases, liquids, or solids



Types of Colloids

Colloid Type	Dispersed Substance	Dispersing Medium	Example(s)
Aerosol	Liquid	Gas	Fog
Aerosol	Solid	Gas	Smoke
Foam	Gas	Liquid	Whipped cream
Solid foam	Gas	Solid	Marshmallow
Emulsion	Liquid	Liquid	Milk
Solid emulsion	Liquid	Solid	Butter
Sol	Solid	Liquid	Paint, cell fluid
Solid sol	Solid	Solid	Opal

Colloids

- Tyndall Effect
  - Light passing through a colloid is scattered randomly because the dispersed particles have sizes similar to wavelengths of visible light
  - The scattered light beams appears broader than one passing through a solution
- Brownian Motion
  - Observed erratic change of speed and direction resulting from collisions with molecules of the dispersing medium
  - Einstein’s explanation of Brownian motion further enhanced the concept of the molecular nature of matter

Osmosis

- Osmosis, a colligative property, is the movement of solvent particles through a semipermeable membrane separating a solution of one concentration from a solution of another concentration, while the solute particles stay within their respective solutions
- Many organisms have semipermeable membranes that regulate internal concentrations

Osmosis

- Water can be purified by “reverse osmosis”
- The direction of flow of the solvent is from the solution of lower concentration to the solution of higher concentration increasing its volume, decreasing concentation
- Osmotic pressure is defined as the amount of pressure that must be applied to the higher concentration solution to prevent the dilution and change in volume

Practice Problem

What is the osmotic pressure (mm Hg) associated with a 0.0075 M aqueous calcium chloride, $CaCl_2$, solution at 25 °C?

a. 419 mm Hg b. 140 mm Hg c. 89 mm Hg

d. 279 mm Hg e. 371 mm Hg

$$\Pi = i(\text{MRT}) \qquad i = 3$$

$$\Pi = 3 \times 0.0075 \frac{\text{mol}}{\text{L}} \times 0.0821 \frac{\text{L} \bullet \text{atm}}{\text{mol} \bullet {}^{\text{o}}\text{ K}} \times \left([25 + 273.15]^{\text{o}}\text{K}\right)$$

$$\Pi = 0.5507576\,\text{atm} \frac{760\text{ mm}}{1\text{ atm}} = 418.5758 = 419\text{ mm Hg}$$

Practice Problem

- Consider the following dilute NaCl(aq) solutions

  a. Which one will boil at a higher temperature?

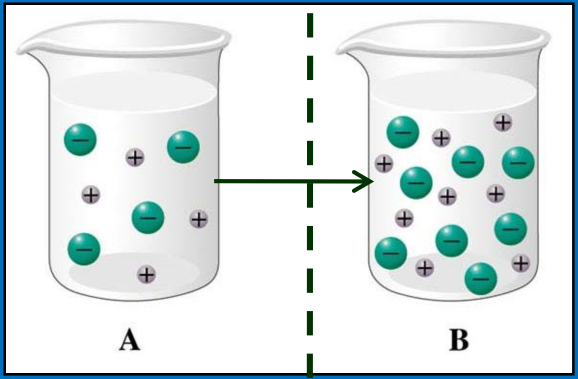
  b. Which one will freeze at a lower temperature?

  c. If the solutions were separated by a semi permeable membrane that allowed only water to pass, which solution would you expect to show an increase in the concentration of NaCl?

Ans: a. B (increase temperature (VP) to match atmospheric pressure

b. B (decrease temperature to reduce vapor pressure of solvent)

c. A (The movement of solvent between solutions is from the solution of lower concentration to the solution of higher concentration)

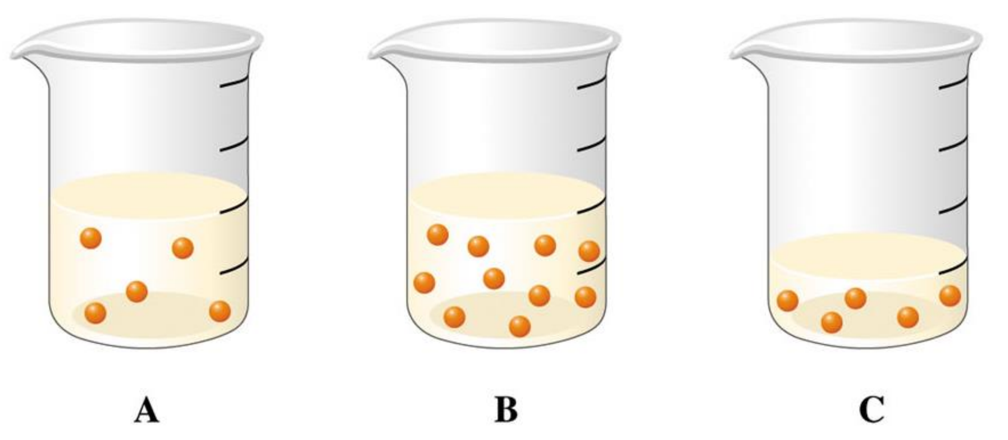


Practice Problem

Consider the following three beakers that contain water and a non-volatile solute. The solute is represented by the orange spheres.

a. Which solution would have the highest vapor pressure?
b. Which solution would have the lowest boiling point?
c. What could you do in the laboratory to make each solution have the same freezing point?

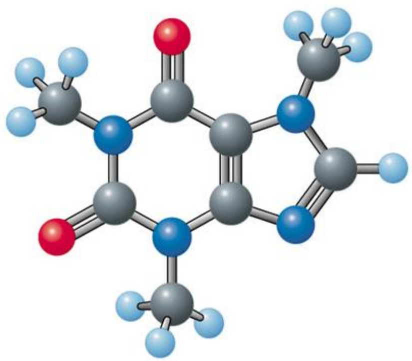
a. A
b. A
c. Condense “A” by ½



Practice Problem

Caffeine, $C_8H_{10}N_4O_2$ (FW = 194.14 g/mol), is a stimulant found in tea and coffee. A Sample of the substance was dissolved in 45.0 g of chloroform, $CHCl_3$, to give a 0.0946 *m* solution.

How many grams of caffeine were in the sample?



Caffeine

Ans:

$$\text{molality(m)} = \frac{\text{moles}_{\text{caffeine}}}{\text{kg}_{\text{CHCl}_3}}$$

$$\text{moles}_{\text{caffeine}} = \text{m} \times \text{kg}_{\text{CHCl}_3}$$

$$\text{moles}_{\text{caffeine}} = 0.0945\left(\frac{\text{mol}_{\text{caffeine}}}{\text{kg}_{\text{CHCl}_3}}\right) \times \left(45.0\text{g}_{\text{CHCl}_3}\right)\frac{1\text{kg}}{1000\text{g}}$$

$$\text{moles}_{\text{caffeine}} = 0.0042525\,\text{mol}_{\text{caffeine}}$$

$$\text{Mass}_{\text{caffeine}} = \text{mol}_{\text{caffeine}} \times \frac{194.14\text{g}}{\text{mol}_{\text{caffeine}}} = 0.826\text{g}$$

Practice Problem

A solution contains 0.0653 g of a molecular compound in 8.31 g of Ethanol. The molality of the solution is 0.0368 *m*. Calculate the molecular weight of the compound

$$\text{molality(m)} = \text{mol}_{\text{solute}} / \text{kg}_{\text{solvent}}$$

$$0.0368 = \frac{0.0653\text{g}\,\dfrac{1\text{mol}}{\text{Mm}}}{8.31\text{g}_{\text{ethanol}}\,\dfrac{1\text{kg}}{1000\text{g}}}$$

$$\text{Mm} = \frac{0.0653\text{g}}{0.0368\,\dfrac{\text{mol}}{\text{kg}} \times 8.31\text{g} \times \dfrac{1\text{kg}}{1000\text{g}}}$$

$$\text{Mm} = 213\text{g} / \text{mol} = \text{Molecular Weight}$$

Practice Problem

What is the vapor pressure (mm Hg) of a solution of 0.500 g of urea [$(NH_2)_2CO$, FW = 60.0 g/mol] in 3.00 g of water at 25 °C?

What is the vapor pressure lowering of the solution?

The vapor pressure of water at 25 °C is 23.8 mm Hg

$$\text{mol}_{\text{urea}} = 0.500\text{g}_{\text{urea}} \frac{1\text{mol}_{\text{urea}}}{60.0\text{g}_{\text{urea}}} = 0.00833\,\text{mol}_{\text{urea}} \qquad \text{mol}_{H_2O} = 3.00\,\text{g}_{H_2O} \frac{1\text{mol}_{H_2O}}{18.016\,\text{g}_{H_2O}} = 0.187\,\text{mol}_{H_2O}$$

$$\text{Mole Fraction Urea } (X_{\text{urea}}) = \frac{0.00833}{0.00833 + 0.187} = 0.0425$$

$$\text{Mole Fraction Water } (X_{H_2O}) = \frac{0.187}{0.00833 + 0.187} = 0.957$$

Partial Pressure of Solution, i.e., the solvent containing non-volatile electrolyte

$$P_{\text{solvent}} = i\left(P^o_{\text{solvent}} X_{\text{solvent}}\right) \qquad P_{\text{solvent}} = 1 \times (23.8\,\text{mmHg} \times 0.957) = 22.8\,\text{mmHg}$$

VaporPressure lowering

$$P^o_{\text{solvent}} - P_{\text{solvent}} = \Delta P = 23.8\,\text{mmHg} - 22.8\,\text{mmHg} = 1.00\,\text{mmHG}$$

$$P^o_{\text{solvent}} - P_{\text{solvent}} = \Delta P = X_{\text{urea}} \times P^o_{\text{solvent}} = 0.0425 \times 23.8\,\text{mmHg} = 1.01\,\text{mm Hg}$$

Practice Problem

What is the vapor pressure lowering in a solution formed by adding 25.7 g of NaCl (FW = 58.44 g/mol) to 100. g of water at 25 ^oC? (The vapor pressure of pure water at 25 ^oC is 23.8 mm Hg)

$$\mathrm{mol_{NaCl}} = 25.7\mathrm{g_{NaCl}} \frac{\mathrm{1mol_{NaCl}}}{\mathrm{58.44g_{NaCl}}} = 0.4398\ \mathrm{mol_{NaCl}}$$

$$\mathrm{mol_{H_2O}} = 100.\ \mathrm{g_{H_2O}} \frac{\mathrm{1mol_{H_2O}}}{\mathrm{18.016\ g_{H_2O}}} = 5.5506\ \mathrm{mol_{H_2O}}$$

$$\text{Mole Fraction NaCl } (X_{\mathrm{NaCl}}) = \frac{0.4398}{0.4398 + 5.5506} = 0.07342$$

Vapor Pressure lowering

$$\Delta P = i(X_{\mathrm{NaCl}} \times P^{o}_{\mathrm{solvent}}) = 2 \times 0.07432 \times 23.8\ \mathrm{mmHg} = 3.49\ \mathrm{mm\ Hg}$$

Practice Problem

A 0.0140-g sample of an ionic compound with the formula $Cr(NH_3)_5Cl_3$ (FW = 243.5 g/mol) was dissolved in water to give 25.0 mL of solution at 25 °C.

The osmotic pressure was determined to be 119 mm Hg. How many ions are obtained from each formula unit when the compound is dissolved in water?

$$\mathbf{\Pi = i(MRT)}$$

$$\text{Molarity(M)} = \frac{\text{mol}_{\text{solute}}}{\text{L}_{\text{soln}}} = \left(\frac{0.0140\ \text{g}\ \dfrac{1\text{mol}}{243.5\ \text{g}}}{25\ \text{ml}\ \dfrac{1\text{L}}{1000\ \text{mL}}} \right) = 0.0022998\ \text{M}$$

$$i = \left(\frac{\Pi}{MRT} \right) = \frac{119\text{mmHg}\ \dfrac{1\text{atm}}{760\ \text{mmHg}}}{0.0022998 \left(\dfrac{\text{mol}}{\text{L}} \right) \times 0.0821 \dfrac{\text{L} \bullet \text{atm}}{\text{mol} \bullet {}^{\text{o}}\ \text{K}} \times (273.15 + 25.0)^{\text{o}}\text{K}}$$

$$\mathbf{i = 2.78 = 3}$$

Equation Summary

- Component Enthalpies of Heat of Solution

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

$$\Delta H_{soln} = \Delta H_{\mathrm{solute}} + \Delta H_{\mathrm{hydration}}$$

- Component Enthalpies of Ionic Compound Heat of Soln

$$\Delta H_{soln} = \Delta H_{lattice} + \Delta H_{hydr\ of\ the\ ions}$$

- Relating Gas Solubility to its Partial Pressure (Henry’s Law)

$$\mathrm{S}_{\mathrm{gas}} = k_{H}\mathrm{P}_{\mathrm{gas}}$$

Equation Summary

- Relationship between vapor pressure & mole fraction

$$P_{solvent} = X_{solvent} \times P^{o}_{Solvent}$$

$$P_{solute} = X_{solute} \times P^{o}_{Solute}$$

$$P_{total} = P_{solvent} + P_{solute} = (X_{solvent} \times P^{o}_{Solvent}) + (X_{solute} \times P^{o}_{Solute})$$

- Vapor Pressure Lowering

$$P^{o}_{solvent} - P_{solvent} = \Delta P = i(X_{solute} \times P^{o}_{solvent})$$

- Boiling Point Elevation

$$\Delta T_b = T_{b_{solution}} - T_{b_{solvent}} = iK_b m$$

- Freezing Point Depression

$$\Delta T_f = T_{f_{solvent}} - T_{f_{solution}} = iK_f m$$

- Osmotic Pressure

$$\Pi = i \frac{n_{solute}}{V_{solution}} RT = iMRT$$

Equation Summary

Concentration Term	Ratio
Molarity (M)	$\frac{\text{amount (mol) of solute}}{\text{volume (L) of solution}}$
Molality (*m*)	$\frac{\text{amount (mol) of solute}}{\text{mass (kg) of solvent}}$
Parts by mass	$\frac{\text{mass of solute}}{\text{mass of solution}}$
Parts by volume	$\frac{\text{volume of solute}}{\text{volume of solution}}$
Mole Fraction (X)	$\frac{\text{amount (mol) of solute}}{\text{moles of solute + moles of solvent}}$