

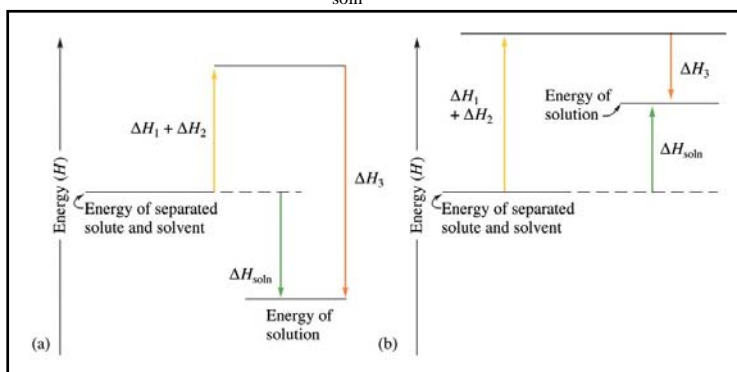
Chapter 13 – Properties of Solutions

• Solution Composition – a Review

- most of this section should be a review
- solute vs. solvent
 - solute is the species that is added to the solution – the more dilute/less concentrated component of a solution
 - solvent is the species that is in abundance – the more concentrated component
 - when solute is added to solvent – a solution is born

• 13.1 The Solutions Process

- Natural Tendency toward Mixing
 - the universal rule is “like dissolves like”
 - polar solvent will dissolve polar/ionic species
 - nonpolar solvent will solvate/dissolve nonpolar compounds
 - also in play are some thermodynamics which we will talk about later in the semester
- The Effect of Intermolecular Forces on Solution Formation
 - in order to form a solution we have to break apart the forces present in the solute and solvent
 - once we separate the like molecules apart enough new intermolecular forces can be formed btwn the two thereby resulting in solution formation
- Energetics of Solution
 - next, we assume that the formation of solution takes place thru the following steps:
 - 1 -- solute is separated into its individual components – endothermic
 - 2 -- the intermolecular forces btwn solvent molecules are overcome to accommodate the solute components - endothermic
 - 3 -- solvent and solute interact thru intermolecular forces – exothermic
 - overall: $\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$
 - there are two possible scenarios for our ΔH_{soln}



- (a) shows an $\Delta H_{\text{soln}} < 0$
 - this means that when the solute is added to the solvent it is easily dissolved and so the solution is generated without the addition of heat
 - in other words the solute is soluble in the solvent
 - e.g. NaCl into water
- (b) shows $\Delta H_{\text{soln}} > 0$

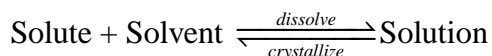
- in this case heat is needed to force the solute into the solvent
- this is an example of an initially insoluble situation
- e.g. CaSO_4 into water

- Solution formation & Chemical Reactions

- Keep in mind that solution formation doesn't chemically change the players involved
- A chemical reaction is more advanced than a simple formation of a solution as they result in brand new products

• **13.2 Saturated Solutions & Solubility**

- the opposite process to dissolution is crystallization in which the solvated solute finds its brothers and breaks out of the solution to form precipitate.



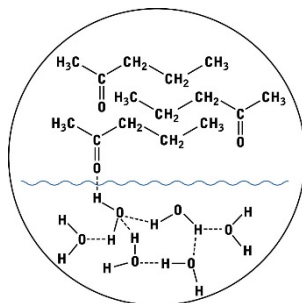
- when the rate of dissolution matches that of crystallization we have another example of equilibrium
- A saturated solution is one that has as much solute as can be dissolved in a given amount of solvent
- The solubility of a solute in solvent is equal to this amount and will typically be given in either g/L or mol/L.
- any amount that is less than the maximum is considered to be an unsaturated solution
- if heat is added and more solute is dissolved than this maximum a supersaturated solution is produced

• **13.3 Factors Affecting Solubility**

- *Structure (Solute-Solvent Interactions)*

- recall covalent bond is one in which the electrons are evenly shared - e.g. btwn C and H
- an example would be oil which is composed primarily of C&H
- solubility is related to how well two substances mix together or their miscibility
- when two substance mix to form a homogeneous soln they are miscible - e.g. alcohol and water
- immiscibility is when two substances do not mix together - e.g. oil and water

Figure 9.8 from *Chemistry the Science in Context*



- recall the universal rule for solubility is that "like dissolves like"
 - a polar solvent like water can dissolve and solvate polar molecules
 - these molecules are hydrophilic "water loving"
 - a polar solvent cannot dissolve non-polar molecules like oil
 - these compounds are referred to as hydrophobic "water fearing"
 - the more hydrocarbon chains a substance contains the more hydrophobic the substance is
 - such species are only slightly soluble in water
 - this small solubility arises from dipole-induced-dipole interactions
- Ex: Which compound will be more soluble in water?
 - a.) CCl_4 or CHCl_3
 - b.) CH_3OH or $\text{C}_6\text{H}_{11}\text{OH}$
 - c.) NaF or MgO

- *Pressure Effects*

- primarily important for gas solubility

- **Henry's Law:** gas solubility $\propto P_{\text{gas}}$ or $C_{\text{gas}} = k_{\text{H}}P_{\text{gas}}$ where C_{gas} is concentration of gas in solution and k_{H} is Henry's constant for this gas in a particular solution
 - as we increase the pressure we increase the number of gaseous moles we can push into solution
 - the opposite is also true
- Example: Calculate the solubility of oxygen in water at 20°C and an atmospheric pressure of 0.35 atm. The mole fraction of O₂ in the air is 0.209 and $k_{\text{O}_2} = 1.3 \times 10^{-3} \text{ mol/L*atm}$.

What do we know? $T = 20^\circ\text{C} + 273.15 = 293.15\text{K}$, $P_{\text{total}} = 0.35 \text{ atm}$, $X_{\text{O}_2} = 0.209$

$$k_{\text{O}_2} = 1.3 \times 10^{-3} \text{ mol/L*atm}$$

What do we want to know? C_{O_2}

What relationships do we know? $P_{\text{O}_2} = P_{\text{total}} X_{\text{O}_2}$, $C_{\text{O}_2} = k_{\text{H}}P_{\text{O}_2}$

$$P_{\text{O}_2} = 0.35 \text{ atm} * 0.209 = 0.07315 \text{ atm}$$

$$C_{\text{O}_2} = 1.3 \times 10^{-3} \text{ mol/L*atm} * 0.07315 \text{ atm} = 9.5 \times 10^{-5} \text{ mol/L}$$

- Temperature

- we have already mentioned that we can increase T to force compounds together
- I should point out that if we are trying to mix polar and nonpolar species no amount of heat increase will ever cause miscibility
- previously, I eluded to the idea that the sign of ΔH_{soln} is a predictor as to the solubility of two species
 - while it is true to some extent there are many other factor which must also be considered
 - to be technically correct we must perform experiments to truly determine the extent of miscibility or immiscibility of two species

• 13.4 Expressing Solution Concentration

- ways we can relate solute and solution
 - Molarity, M: moles of solute per L of solvent

$$M = \frac{\text{moles of solute}}{\text{L of solvent}}$$

- mass percent/percent by weight

$$\text{Mass percent} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) \times 100\%$$

- mole fraction – which we just did in the last chapter

$$\chi_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{n_{\text{tot}}}$$

- molality, m: moles of solute per kg of solvent

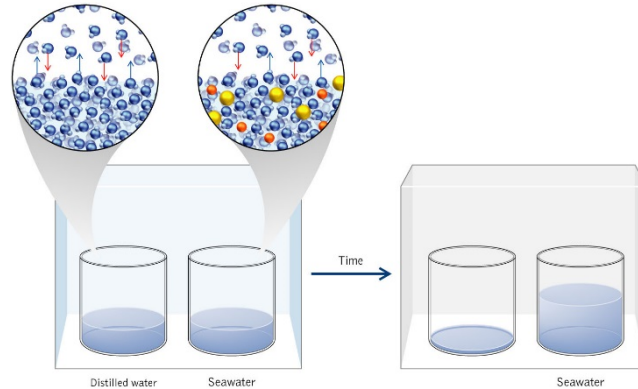
$$m = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

• 13.5 Colligative Properties

- Vapor Pressures Lowering

- if we place a glass containing distilled water and one with seawater in a closed system after a bit of time we will see the volume in the distilled glass diminish as the volume in the seawater glass grows

Figure 9.10 from *Chemistry: The Science in Context*



- water escapes from the distilled beaker much faster
- since the system is enclosed, the distilled water liquefies back into the salt water beaker
- the driving force is that water wants to solvate the salt - this is also why we use dessicator packets of salt to keep water out of leather goods and other products
- Take Home Message: the presence of a nonvolatile solute lowers the vp of a solvent

-- we calculate the vp of a solution using Raoult's law

$$P_{\text{solution}} = X_{\text{solvent}} \cdot P_{\text{solvent}}$$

--- Ex. What is the vapor pressure of water in a 50:50 mixture of glycerol ($D_{\text{C}_3\text{H}_8\text{O}_3} = 1.261 \text{ g/mL}$) and water at 25°C ($P_{\text{H}_2\text{O}} = 23.8 \text{ torr}$)?

We assume 100mL of glycerol and 100mL of water:

$$100 \text{ mL of C}_3\text{H}_8\text{O}_3 \times \frac{1.261 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{92.097 \text{ g}} = 1.37 \text{ mol of C}_3\text{H}_8\text{O}_3$$

$$100 \text{ mL of H}_2\text{O} \times \frac{1.000 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{18.016 \text{ g}} = 5.55 \text{ mol of H}_2\text{O}$$

$$X_{\text{H}_2\text{O}} = \frac{5.55 \text{ mol of H}_2\text{O}}{5.55 \text{ mol of H}_2\text{O} + 1.37 \text{ mol of C}_3\text{H}_8\text{O}_3} = 0.802$$

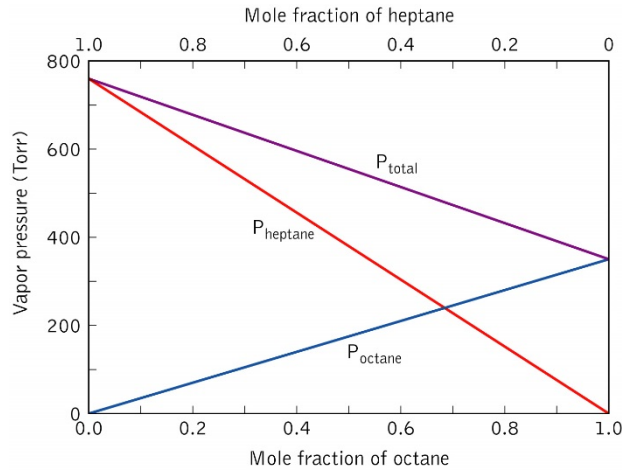
$$P_{\text{soln}} = 0.802 \times 23.8 \text{ torr} = 19.1 \text{ torr}$$

-- homogeneous mixtures and Raoult's law

- an example such of a mixture occurs in the petroleum industry
- oil is composed of a number of different hydrocarbon such as octane and heptane, etc.
- these different compounds have similar but different bpts
- we can separate them by performing fractional distillation in which a mixture is boiled and re-condensed into their various components
 - the compounds which are most volatile (most readily evaporated) have the lowest boiling points and they will go to the top of the tower since it is harder to re-condense them
 - those compounds with the highest boiling points are easy to condense and are collected in the lower portion of the tower

-- relationship btwn mixtures and Raoult's law: $P_{\text{total}} = \sum(X_1 \cdot P_1)$

Figure 12.2 from *Chemistry: The Science in Context*



---- solutions which have similar solute-solute, solute-solvent, and solvent-solvent interactions behave as an ideal solution

---- in other words they obey Raoult's law

---- solutions in which these interactions differ deviate from Raoult's law

--- Ex: At 20°C, the v.p. of ethanol is 45 torr and the v.p. of methanol is 92 torr. What is the v.p. at 20°C of a solution prepared by mixing 25g of methanol and 75g of ethanol?

$$25\text{g} \times \frac{1 \text{ mol } \text{C}_2\text{H}_5\text{OH}}{46.07\text{g}} = 0.5427 \text{ moles of } \text{C}_2\text{H}_5\text{OH}$$

$$75\text{g} \times \frac{1 \text{ mol } \text{CH}_3\text{OH}}{32.043\text{g}} = 2.3406 \text{ moles of } \text{CH}_3\text{OH}$$

$$X_{\text{C}_2\text{H}_5\text{OH}} = \frac{0.5427}{0.5427 + 2.3406} = 0.1882$$

$$X_{\text{CH}_3\text{OH}} = 1 - 0.1882 = 0.8118$$

$$P_{\text{total}} = X_{\text{C}_2\text{H}_5\text{OH}} P_{\text{C}_2\text{H}_5\text{OH}} + X_{\text{CH}_3\text{OH}} P_{\text{CH}_3\text{OH}} = 0.1882 * 45\text{torr} + 0.8118 * 92\text{torr}$$

$$P_{\text{total}} = 83\text{torr}$$

- Boiling Point Elevation & Freezing Point Depression

-- relationship btwn vp and bpt

--- a liquid boils when its vp equals the atmospheric pressure

--- in our saltwater example we raised the bpt by adding salt to water

--- in other words it also requires more atmospheric pressure than water to boil

-- as we said previously, the addition of a nonvolatile solute will raise the bpt of the solvent

--- in phase diagram terms – the liquid/vapor line is shifted to the right (toward a higher T)

--- the elevation of our bpt is dependent on the concentration of the solute:

$$\Delta T_b = K_b m_{\text{solute}} \text{ where } \Delta T_b \text{ is the change in bpt } T, K_b \text{ is a const \& } m_{\text{solute}} \text{ is the molality of the solute}$$

-- Ex: If the boiling point of a sample is 2.3 Celcius above the boiling point of pure water, what is the molality of NaCl in the sample? $K_{b,\text{water}} = 0.52^\circ\text{C} \cdot \text{kg} / \text{mol}$

$$m = \frac{\Delta T_b}{K_b} = \frac{2.3^\circ\text{C}}{0.52^\circ\text{C} / m} = 4.4 \frac{\text{moles NaCl}}{1\text{kg } \text{H}_2\text{O}}$$

-- we see a similar pattern with the freezing pt

--- if we add salt to ice in the winter – it melts

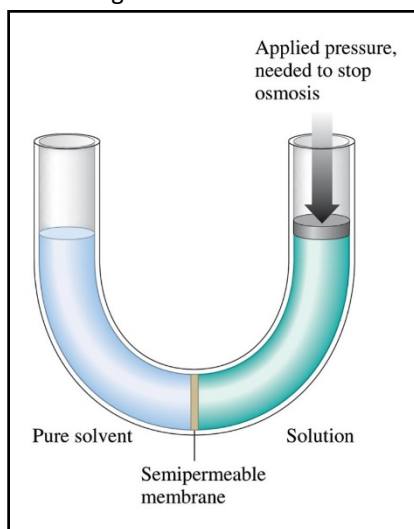
--- this occurs because addition of a nonvolatile solute results in lowering the vp of freezing and so the ice won't freeze until an even lower T than 0°C

--- the fpt depression is given by: $\Delta T_f = K_f m_{\text{solute}}$

- Osmotic Pressure

- osmosis: when solvent passes through a semipermeable membrane to balance the solute concentrations on each side of the membrane
- semipermeable membranes: allow only the solvent to pass through
- osmotic pressure: amount of pressure needed to stop the solvent from following to the more concentrated side of a semipermeable membrane

Figure 11.17 from text



-- mathematically: $\Pi = MRT$ where M is the molarity, $R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$ and T is in K

-- how red blood cells operate

-- Ex: Calculate the osmotic pressure across a semipermeable membrane separating seawater (1.14 M) from a solution of normal saline (0.31 M) at a $T = 20^\circ C$.

$$M = 1.14 - 0.31 = 0.83 M$$

$$\Pi = MRT = 0.83 M \times 0.0821 \frac{L \cdot atm}{mol \cdot K} \times (273.15 + 20) K = 20 atm$$

-- Ex: A solution was made by dissolving 5.00 mg of hemoglobin in water to give a final volume of 1.00 mL. The osmotic pressure of this solution was $1.91 \times 10^{-3} atm$ at $25^\circ C$. Calculate the molar mass of hemoglobin.

$$\pi = MRT \rightarrow M = \frac{\pi}{RT} = \frac{1.91 \times 10^{-3} atm}{0.0821 \frac{L \cdot atm}{mol \cdot K} \times (273.15 + 25) K} = 7.80 \times 10^{-5} \frac{\text{moles hemoglobin}}{L}$$

$$1.00 mL \times \frac{1 L}{1000 mL} \times \frac{7.80 \times 10^{-5} \text{ moles hemoglobin}}{L} = 7.80 \times 10^{-8} \text{ moles hemoglobin}$$

$$\text{molar mass hemoglobin} = \frac{5.00 mg \times \frac{1 g}{1000 mg}}{7.80 \times 10^{-8} \text{ moles hemoglobin}} = 6.41 \times 10^4 \frac{g}{mol}$$

- Reverse Osmosis

- defn: solvent is pumped through semi-impermeable membrane at a pressure greater than Π leaving behind solute particles
- we use this process to purify water

- Colligative Properties of Electrolyte Solutions - Why doesn't the ocean freeze?

- the actual number of ions in solution changes the bpt and fpt
- some ions will make a cluster with an oppositely charged ion and form an ion pair
 - when ion pairs are form they act like one particle and thereby reduce the number of solute particles in the solvent
 - this leads to a reduction in the previously mentioned colligative properties
- the van't Hoff factor, $i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$
- Incorporating this correction leads to the following equations:

$$\pi = iMRT \quad \Delta T_b = iK_b m \quad \Delta T_f = iK_f m$$
- Ex: The van't Hoff factor for a 0.05 m solution of magnesium sulfate is 1.3. What is the freezing point of the solution? $K_{f,water} = 1.86^\circ C \cdot kg / mol$

$$\Delta T_f = iK_f m = 1.3 \times 1.86 \frac{^\circ C}{m} \times 0.05 m = 0.12^\circ C$$

• 13.6 Colloids

- Colloids are species that are too large to form a solution while being too small to be generate a heterogenous mixture with a solvent

Table 13.5 Types of Colloids

Phase of Colloid	Dispersing (solvent-like) Substance	Dispersed (solute-like) Substance	Colloid Type	Example
Gas	Gas	Gas	—	None (all are solutions)
Gas	Gas	Liquid	Aerosol	Fog
Gas	Gas	Solid	Aerosol	Smoke
Liquid	Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Liquid	Emulsion	Milk
Liquid	Liquid	Solid	Sol	Paint
Solid	Solid	Gas	Solid foam	Marshmallow
Solid	Solid	Liquid	Solid emulsion	Butter
Solid	Solid	Solid	Solid sol	Ruby glass

- There are a number of cool and innovative ways in which these compounds are being utilized ranging from medicines to sewage disposal with a whole host of others in between.
- Below is a picture of colloidal silver

