

Chapter 11: Properties of Solutions

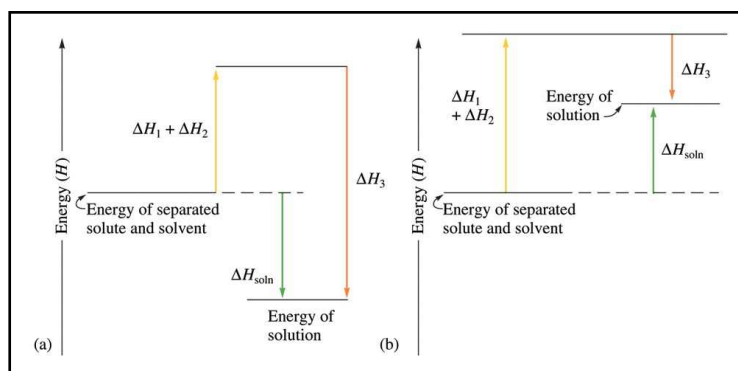
* 11.1 Solutions

- 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

* 11.2 Energy Changes & Solution Process

- we start our discussion with solubility – “like dissolves like”
 - polar solvent will dissolve polar/ionic compounds
 - nonpolar solvent for nonpolar compounds
- 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}

Figure 11.2 from text



-- (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. CaSO₄ into water

* 11.3 Units of Concentration

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

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

-- 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

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

-- parts per million, ppm

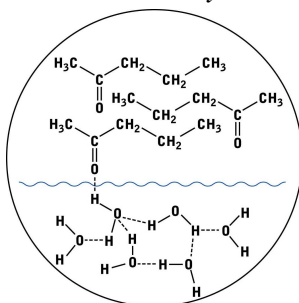
$$\text{ppm} = \frac{\text{mg of solute}}{\text{kg of solvent}} \text{ or } \frac{\text{g of solute}}{\text{g of solvent}} \times 10^6$$

* 11.4 Factors Affecting Solubility

Structure

- 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*



- 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 O_2 in the air is 0.209 and $k_{\text{O}_2} = 1.3 \times 10^{-3} \text{ mol/L}\cdot\text{atm}$.

What do we know? $T = 20^\circ\text{C} + 273.15 = 293.15\text{K}$, $P_{\text{total}} = 0.35 \text{ atm}$, $X_{\text{O}_2} = 0.209$
 $k_{\text{O}_2} = 1.3 \times 10^{-3} \text{ mol/L}\cdot\text{atm}$

What do we want to know? C_{O_2}

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

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

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

Temperature

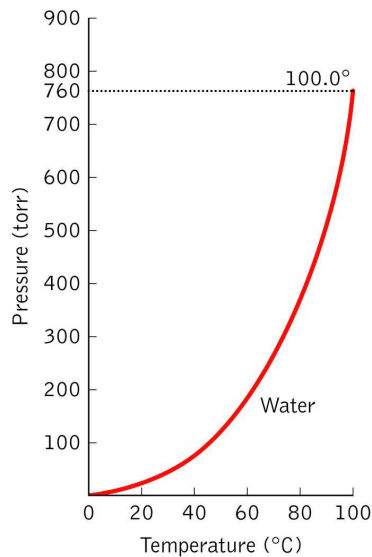
- we have already mentioned that we can increase T to force compounds together
- I should point out that if we are trying to mix polar and nonpolar species no amount of heat increase will ever cause miscibility
- previously, I eluded to the idea that the sign of ΔH_{soln} is a predictor as to the solubility 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

* 11.5 Physical Behavior of Solutions: Colligative Properties

* 11.6 The Vapor Pressures of Solutions - Raoult's Law

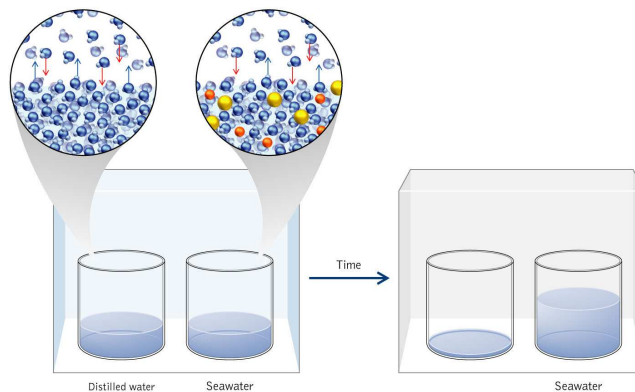
- vapor pressure increases with increasing temperature

Figure 9.11 *Chemistry: The Science in Context*



- when T increases so do the molecular motions and the ability for a molecule to escape from the liquid and go into the gas phase
- since the pressure of the atmosphere is lower at higher elevations - less temperature is required for water to boil
- 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*



- this figure is similar to Figure 11.9 in your text
- 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
 - $P_{\text{solution}} = X_{\text{solvent}} * P_{\text{solvent}}$
 - Ex. What is the vapor pressure of water in a 50:50 mixture of glycerol ($D_{C_3H_8O_3} = 1.261 \text{ g/mL}$) and water at 25°C ($P_{H_2O} = 23.8 \text{ torr}$)?

assuming 100mL of glycerol and 100mL of water:

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

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

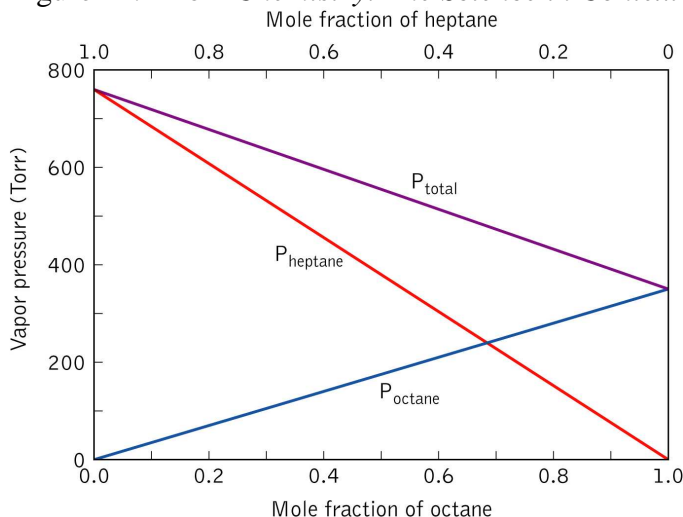
$$X_{\text{H}_2\text{O}} = \frac{5.55 \text{ mol of } \text{H}_2\text{O}}{5.55 \text{ mol of } \text{H}_2\text{O} + 1.37 \text{ mol of } \text{C}_3\text{H}_8\text{O}_3} = 0.802$$

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

- homogeneous mixtures and Raoult's law

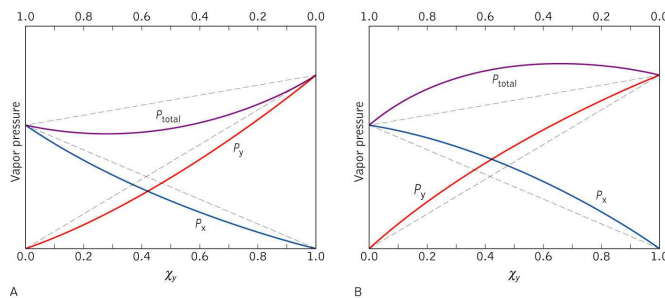
- an example such of a mixture occurs in the petroleum industry
- oil is composed of a number of different hydrocarbon such as octane and heptane, etc.
- these different compounds have similar but different bpts
- we can separate them by performing fractional distillation in which a mixture is boiled 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: $P_{\text{total}} = \Sigma(X_1 * P_1)$

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
- Ethanol & heptane

Figure 12.3 from *Chemistry: The Science in Context*



- positive deviations – the vp is lower than was expected
(e.g. water & ethanol – ethanol disrupts water’s ability to make 2 H-bonds)
- negative deviations – the vp is higher than was expected
(e.g. CHCl₃ & CH₃COCH₃ – H-bonds are formed between species making the intermolecular forces stronger than those of the pure liquids)

-- 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 75g of methanol and 25g of ethanol?

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

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

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

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

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

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

* 11.7 Boiling-Pt Elevation & Freezing-Pt Depression of Solutions

- 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:

$$\Delta T_b = K_b m_{\text{solute}}$$
 where ΔT_b is the change in bpt T, K_b is a const & m_{solute} 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? $K_{b,\text{water}} = 0.52^\circ\text{C} \cdot \text{kg} / \text{mol}$

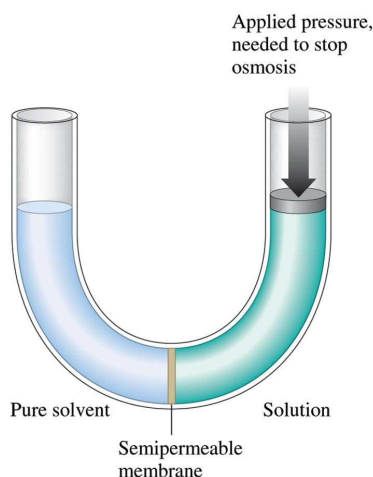
$$m = \frac{\Delta T_b}{K_b} = \frac{2.3^\circ\text{C}}{0.52^\circ\text{C}/m} = 4.4 \frac{\text{moles NaCl}}{1\text{kg H}_2\text{O}}$$

- 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: $\Delta T_f = K_f m_{\text{solute}}$

* 11.8 Osmosis & 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, $R = 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$ 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°C.

$$M = 1.14 - 0.31 = 0.83 \underline{M}$$

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

- 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 1.91×10^{-3} atm at 25 °C. Calculate the molar mass of hemoglobin.

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

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

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

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

* 11.7 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? $K_{f, \text{water}} = 1.86^\circ \text{C} \cdot \text{kg} / \text{mol}$

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