5.111 Lecture Summary #20 Monday October 27, 2014

Reading for Today: Sections 9.8 - 9.13 (8.8-8.13 same in 4th ed.) on solubility; Sections 11.1 – 11.2, 11.4-11.6 (10.1-10.2, 10.4-10.6 in 4th ed.) on acids and bases.
Reading for Lecture #21: Sections 11.7-11.9, 11.11-11.13 (10.7 -10.9, 10.11 – 10.13 in 4th ed).

Topics: I. Solutions and Solubility
II. Classification of Acids and Bases

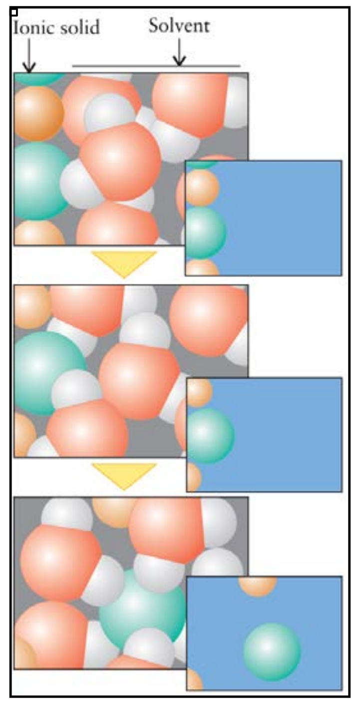
I. SOLUTIONS AND SOLUBILITY

So far, we've been discussing pure compounds. However, most substances are __________.

Solutions are homogeneous mixtures.
Solvent: the substance that does the dissolving (i.e. water)
Solute: any dissolved substance in a solution

MOLAR SOLUBILITY

Ionic solids. Consider NaCl dissolving in water.



Polar water molecules ____________ ions at the surface of the salt's crystal lattice, prying some of the Na^+ and Cl^- ions away.

Stirring can ____________________ the process by bringing more free water molecules to the surface of the solid, and taking more hydrated ions away.

Solubility equilibrium: $NaCl\ (s) \rightleftharpoons Na^+\ (aq) + Cl^-\ (aq)$

$K_{sp} = [Na^+][Cl^-]$ where sp stands for "solubility product"

is a measure of the dissolution of an ionic solid in water.

Note NaCl does not appear in the expression since it is a solid.

Organic solids. Consider glucose dissolving in water.

Water molecules form **hydrogen bonds** to the glucose molecules near the surface of a glucose crystal. Some glucose molecules are pulled away by the surrounding water (are solubilized), other molecules are not.

Glucose is a hydrogen bond ____.

A solution is ________________ when the solvent has dissolved all the solute that it can and some undissolved solute remains.

The dissolved and undissolved solute are in _______________________________________ with each other.

The amount that dissolves depends on the **molar solubility (s)** of the substance.

Molar solubility (s) of a substance is its molar concentration in a **saturated** solution, and represents the limit of its ability to dissolve in a given solvent. (units: ________________)

Note: molar solubility (s) and K_{sp} are not the same, but they can be calculated from each other. $[Na^+] = [Cl^-] = s$ (is the molar solubility of either ion at equilibrium), thus

$K_{sp} = [Na^+][Cl^-] = s^2$ for this particular ionic compound.

Like-Dissolves-Like Rule

A polar liquid like water is generally the best solvent for ionic and _______________ compounds.

Conversely, nonpolar liquids, including hexane and tetrachloroethane (used in dry cleaning), are better for nonpolar (hydrophobic) compounds.

Applications of this rule:

pharmaceutical drug design -- solubility of nonpolar enzyme inhibitors in aqueous solutions.

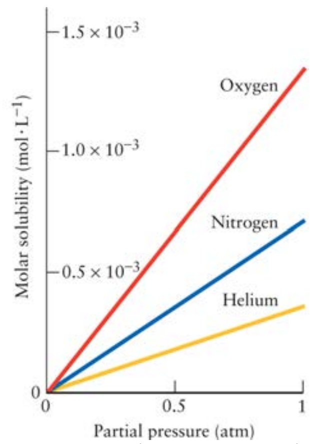
cleaning products -- want to dissolve polar and nonpolar stains

IMPACT OF PRESSURE AND TEMPERATURE ON SOLUBILITY

Pressure and Gas Solubility

Henry's Law: the solubility of a gas (s) is directly proportional to its partial pressure (P).

$s = k_H P$ where k_H is Henry's constant, and depends on the gas, the solvent, and the temperature.



The solubility of a gas is __________________to its partial pressure, because an increase in pressure corresponds to an ________________ in the rate at which gas molecules strike the surface of the solvent.

In Their Own Words

Former MIT postdoctoral scholar Dr. Hector Hernandez discusses how gas solubility and Le Chatelier's principle relate to his research on CO_2 capture and storage in the lab of MIT Professor Janelle Thompson.

Hector's s video can be found at: http://chemvideos.mit.edu/all-videos/.

Courtesy of Hector Hernandez. Used with permission.

Temperature and Solubility

Most substances dissolve more ________________ at higher temperatures, but that doesn't necessarily mean that they are more soluble (that is reach a higher final concentration of solute)

Most gases are _____________ soluble in warm water than in cold water.

Solids show a more varied behavior.

ENTHALPY, ENTROPY AND GIBBS FREE ENERGY OF SOLUTIONS

The change in molar enthalpy when a substance dissolves is called the enthalpy of solution $\mathbf{\Delta H_{sol}}$. The change can be measured calorimetrically from the heat released or absorbed when the substance dissolves at constant pressure.

A __________________ enthalpy of solution tells us that energy is **released** as heat when a substance dissolves.

A __________________ enthalpy of solution tells us that energy is **absorbed** as heat when a substance dissolves.

To predict whether dissolving of a substance is **spontaneous** at constant pressure and temperature, we need to consider ____________ .

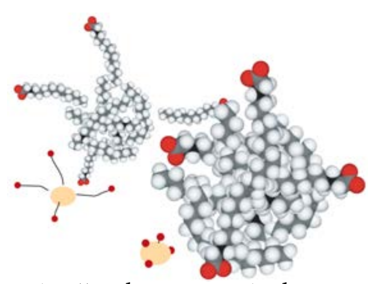
Since the **disorder** of a system typically increases when a solid dissolves, we expect the **entropy** of the system to ____________________*.

If ΔH_{sol} is negative, and the entropy of the system increases when the solute dissolves, then we expect the dissolving process to be ___________________.

* In some cases, the **entropy** of the system is lowered when a solution forms because the solvent molecules form a cage-like structure around the solute molecule.

Here even if ΔH_{sol} is negative, ΔG might be positive.

This cage-effect is why some hydrocarbons are insoluble in water even though they have weakly negative enthalpies of solution.



For gases, which enter a condensed state with much less freedom of movement when they dissolve in a liquid, the entropy of solution is __________________ and solubility ___________________ as the temperature rises.

What is the effect on the spontaneity of dissolving if ΔH_{sol} is positive?

II) CLASSIFICATION OF ACIDS AND BASES

1. Arrhenius - a narrow definition of acids and bases

An **acid** is a substance that when dissolved in water **increases** the concentration of hydrogen ions.
A **base** is a substance that **increases** the hydroxide concentration.

2. Brønsted-Lowry - a broader definition

A Brønsted-Lowry **acid** - a substance that can ________________ a hydrogen ion (H^+)

A Brønsted-Lowry **base** - a substance that can ________________ a hydrogen ion (H^+)

Example 1

CH_3COOH (aq) + H_2O (l) $\rightleftharpoons$ H_3O^+ (aq) + CH_3COO^- (aq)

Acid1 Base2 Acid2 Base1

(note: hydronium ion H_3O^+ (aq) is used instead of H^+ (aq) to represent the true nature of hydrogen ions in water)

Acid-bases occur as **conjugate acid-base pairs**.

CH_3COOH and CH_3COO^- are a pair. H_2O and H_3O^+ are a pair.

- The conjugate base of an acid is the base that is formed when the acid has donated a hydrogen ion (proton).
- The conjugate acid of a base is the acid that forms when base accepts a hydrogen ion (proton).

Example 2 Which are Brønsted-Lowry acids and which are Brønsted-Lowry bases?

(a) HCO_3^- (aq) + H_2O (l) $\rightleftharpoons$ H_3O^+ (aq) + CO_3^- (aq)

(b) HCO_3^- (aq) + H_2O (l) $\rightleftharpoons$ H_2CO_3 (aq) + OH^- (aq)

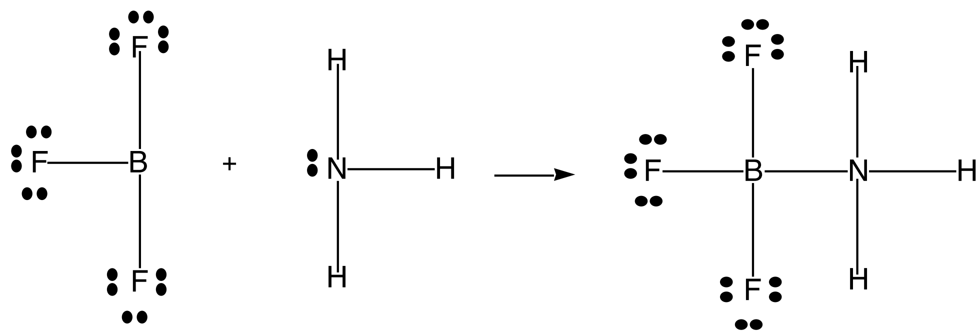
amphoteric - molecules that can function either as acids or bases depending on the reaction conditions (example H_2O).

3. Lewis Acid and Base - more general definition - applies to reactions that don't involve a hydrogen ion

Lewis **base** - species that ______________ lone-pair electrons

Lewis **acid** - species that_______________such electrons

Example 1



Ammonia is the Lewis base. It donates lone-pair electrons to BF_3, the Lewis acid and the electron acceptor.