Chapter 12 Physical Properties of Solutions

Chemistry by Chang and Goldsby

Chapter 12: Physical Properties of Solutions
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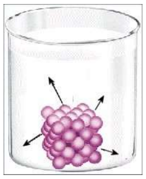
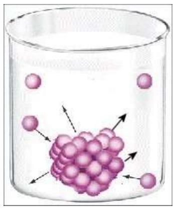
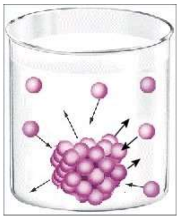
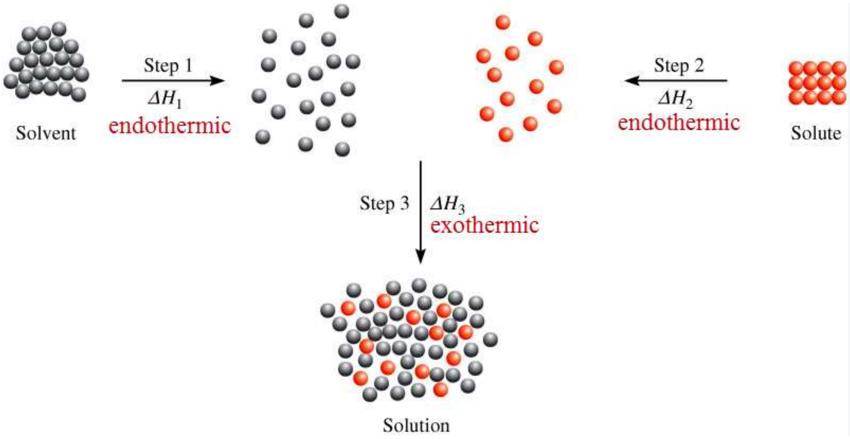
12.1 Types of Solutions

<table>
<tr><td colspan="2">An unsaturated solution contains less solute than it has the capacity to dissolve.</td><td>A saturated solution contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td><i>Salt is put into solvent and starts to dissolve</i>
4 particles dissolving
0 precipitating</td><td><i>Salt is still dissolving but some ions are precipitating</i>
4 particles dissolving
2 precipitating</td><td><i>Rate dissolving equals rate precipitating. (Saturated)</i>
4 particles dissolving
4 precipitating</td></tr>
</table>

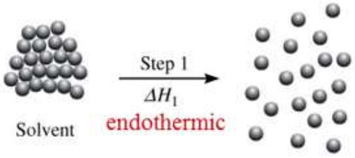
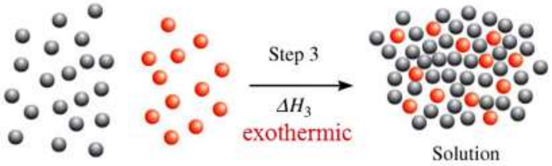
Supersaturated solutions are not part of AP Chemistry.

12.2 Molecular View of the Solution Process in terms of particles and energy.

Important three-step diagram for making a solution that is often seen on AP Chem Exams:



Remember and understand the thermodynamics of each step.

Step 1	Endothermic breaking bonds Solvent intermolecular attractions are broken to separate solvent molecules.	
Step 2	Endothermic breaking bonds Solute intermolecular attractions are broken to separate solute molecules or ions.	
Step 3	Exothermic formation of new bonds Creating the solution by forming **solvent-solute intermolecular bonds.**	

The sum of the three steps will result in either an endothermic or exothermic solution reaction.

If $\Delta H_1 + \Delta H_2 > |\Delta H_3|$ then the enthalpy of solution, **$\Delta H_{solution}$ is +, endothermic**

The endothermic processes require more energy to break the solvent intermolecular bonds and solute intermolecular bonds than the energy that is released by the exothermic formation of the solution's intermolecular bonds.

Generally, endothermic processes are not favored, but if the solution has a greater amount of disorder, entropy, the drive to greater "disorder" can drive the reaction forward.

If $\Delta H_1 + \Delta H_2 < |\Delta H_3|$ then the enthalpy of solution, **$\Delta H_{solution}$ is - exothermic**

The exothermic process of forming solute-solvent bonds releases more kinetic energy than is used to dissociate the solute and solvent.

Solubility and the formation of solutions: The commonly used phrase “Like Dissolves Like” works to predict solubility because substances with similar intermolecular attractions will dissolve in one another.

HOWEVER! AP FRQ Explanation Warning! Do not use “like dissolves like” in your FRQ explanations!
Your FRQ explanation must specifically name the IMF’s involved in the dissolving process. The forbidden phrase “like dissolves like” is too simple in that it doesn’t identify the forces involved in solubility.

To explain the solubility of a solute in a solvent, your explanation must include IMF’s of the solute and solvent and their interactions. Use the following three parts in your explanation.

(1) Identify the primary intermolecular attraction of the solvent.
(2) Identify the primary intermolecular attraction of the solute.

The intermolecular attractions of the solvent keep the solvent molecules together and likewise for the solute.

(3a) If the solute has a high solubility:
State that the intermolecular attractions of the solute can compete with the solvent’s intermolecular attractions so the solute can mix with the solvent. Be sure to identify the type of intermolecular force of each component.

(3b) If the solute has a low solubility:
State that the intermolecular attractions of the solute cannot compete with the solvent’s intermolecular attractions so the two stay separate. Again, identify the type of intermolecular force of each component.

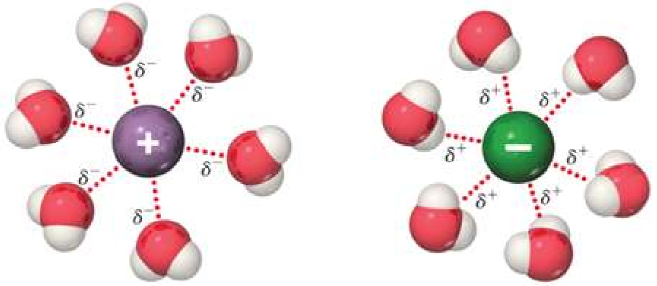
Solubility in terms of intermolecular forces.

Solvents with hydrogen bonding or strong dipoles can dissolve solutes with hydrogen bonding or strong dipoles.

Since the intermolecular attractions of the solvent are similar in size and strength to the solute, the solvent molecules can substitute their molecules for the solute’s molecules.

Solvents with hydrogen bonding or strong dipoles can dissolve ionic compounds.

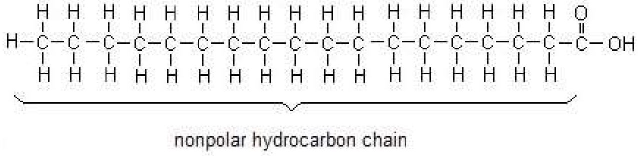
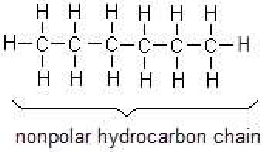
Hydrogen-bonded solvents are so polar that their dipoles are capable of dissolving ionic materials.

When dealing with soluble ionic compounds (sodium, potassium, ammonium, and nitrate) in water, you should reference **ion-dipole interactions.** The strong dipoles of water surround the ions of these salts to replace the ion-ion Coulombic attractions of the ionic solid. The hydrogen side dipole, δ⊕, will be attracted to the anions. The oxygen side dipole, δ-, will be attracted to the cations.	 In this diagram the cation and anion sizes are the same. However, on an exam question you may have to identify the ion by its size. To do this you will need to determine the electron configuration of each. Typically, on exams the cation is smaller than the anion.

Nonpolar solvents whose intermolecular attractions are London dispersion forces will dissolve solutes which are likewise bonded with London dispersion forces.

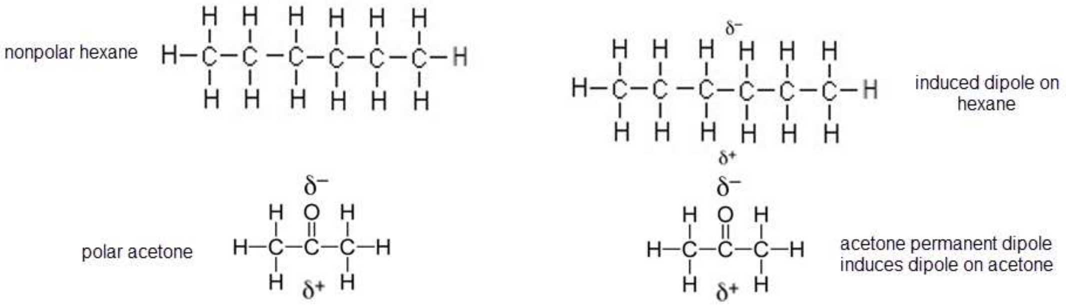
Because the LDF's of the solvent molecules are similar to the LDF's of the solute, the solvent can disrupt the intermolecular attractions of the solute and incorporate the solute into the solvent with similar intermolecular attractions.

LDF solvents are good at dissolving organic compounds with large aliphatic (nonpolar) segments.
The long nonpolar chain segments of fats (11 to 18 carbon atoms long) will dissolve in nonpolar solvents such as hexane.

	Solute: Solid stearic acid is a fatty acid found in many fats and oils. It is a soft, waxy solid at room temperature (melting temperature = 70°C). The primary intermolecular attraction for the 18-carbon substance is London dispersion forces. The hydrogen bonding of the carboxylic acid is not as significant as the long carbon chain. Only 0.003 g of stearic acid will dissolve in 1 liter of water. Fatty acids are the fats and oils you see floating on the surface of soups.
	Solvent: Hexane is a common nonpolar solvent. A liquid at room temperature, hexane's only intermolecular attraction is the London dispersion force. 200 g of stearic acid dissolves in 1 L of hexane. Stearic acid is over a hundred thousand times more soluble in hexane than in water

There is some slight solubility of nonpolar molecules in polar solvents. This can be explained by the formation of temporary dipoles produced by induction caused by polar solvents.

In this example the nonpolar hexane develops a temporary induced charge from the acetone.



A charge on the molecule with a permanent dipole attracts the opposite charge on a nonpolar molecule. This induction will produce a temporary dipole on the nonpolar molecule. This induced polarization of nonpolar molecules can result in some limited solubility of nonpolar substances in polar solvents.

This is a special case of solubility is mentioned in the AP Curriculum:

> *"Dipole-induced dipole interactions are present between a polar and nonpolar molecule. The strength of these forces increases with the magnitude of the dipole of the polar molecule and with the polarizability of the nonpolar molecule."*

AP exams often have "exception to the rule" items.

Dipole induced charges on nonpolar molecules explain why a small amount of stearic acid (0.003 g/L) that dissolves in water.

The term **miscible** applies to liquids whose intermolecular forces are so similar that they dissolve in one another in all proportions. In effect, the solubility is 100%. The best examples of miscible solvent-solute combinations are:

Small chain alcohols (methanol, ethanol, and propanol) which are miscible with water.

Nonpolar liquid hydrocarbons are miscible with nonpolar benzene.

12.3 Concentration Units

Mole Fraction, X_A (usually reported as a decimal value)

$$X_A = \frac{\text{moles of } A}{\text{total moles of components in the mixture}}$$

Molarity – you already know about this but review it because it is important!

Not AP: % by mass, but this is CLEP[1] material.

Percent by mass = mass of solute ÷ mass of solution × 100%

Note that the mass of solution = (mass of solute + mass of solvent)

Not AP: Molality but has been used on the CLEP Chemistry subject test.

Not AP: 12.4 The Effect of Temperature on Solubility

Not AP: 12.5 The Effect of Pressure on the solubility of Gases

The greater the pressure, the higher the solubility.

Uncapping a pressurized bottle will have its carbon dioxide undissolve, making a bubbly beverage. You do not need to know any of the equations in this section.

Not AP: 12.6 Colligative Properties of Nonelectrolyte Solutions but CLEP

Boiling Point Elevation and Freezing Point Depression

Solute particles in a solvent "interfere" with vaporization and freezing.

- Boiling Point Elevation
  Nonvolatile solutes raise the boiling temperatures of solvents.

- Freezing Point Depression

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[1] The College Board CLEP exams are administered in testing centers numerous times during the year. It is a digital test that some students take to prove that they are competent for college courses. The CLEP Chemistry exam has the lowest passing rate of all the CLEP subjects. You would be able to pass it easily with a little prep by the end of February.

Solutes lower the freezing temperatures of solvents

Not AP: 12.7 Colligative Properties of Electrolytes - Ion multiplication factor but CLEP

Because electrolytes (acids bases and ionic compounds) dissociate they have more particles per mole of solute. Thus, ionic compounds have a greater BPE and FPD per mol of solute than nonelectrolytes.

e.g. $MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2\ Cl^{-}(aq)$ will have 3 times the freezing temperature lowering effect than a nonelectrolyte such as ethanol.

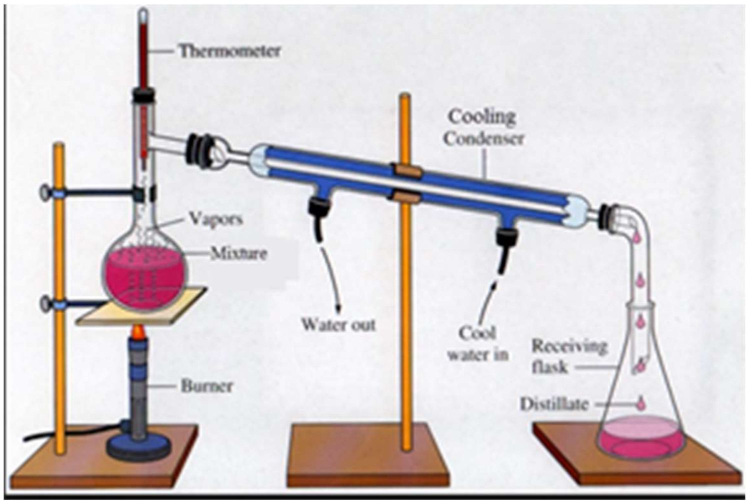
Not AP: 12.8 Colloids

I've separated out parts of Chang into this grouping because they are emphasized in the AP Chemistry exam curriculum.

The substances in a solution retain many of their physical and chemical properties. Therefore, they can be separated more easily than substances that have chemically reacted with one another and changed their physical and chemical properties.

The following laboratory techniques allow for the separation of mixtures based on this principle.

Vapor Pressure: Distillation



Distillation of a mixture is an effective method of separating large amounts of substances in a solution. The vapor pressure of each substance in the mixture will be dependent on each substance's original vapor pressure and mole fraction.

In the case of an ionic aqueous solution, since ionic compounds have no vapor pressure (are nonvolatile), only the water will vaporize (boil) leaving the salt behind. The distillate, liquid collected on condensation, will be just water.

In a mixture of water and a soluble molecular substance such as glucose or methanol, the substance with the weaker intermolecular attractions (higher vapor pressure and lower boiling point) will evaporate (boil) more quickly and condense in the distillate in higher concentrations.

In the glucose solution, water has smaller IMF's than glucose, and water with its lower boiling point will vaporize and then be condensed in the distillate.

In the methanol solution, the methanol has the lower IMF's and higher vapor pressure (boiling point 65°C), and methanol will be the primary substance in the distillate.

Intermolecular Attractions: Chromatography

Chromatography is a method of separating small quantities of components of a mixture. Chromatography relies on intermolecular attractions as a method of separating mixtures. There are many types of chromatography. You are expected to know two of them.

(a) Paper Chromatography

A simple type of chromatography uses a strip of paper that is suspended in a solution. A small sample of the mixture to be separated is placed on the chromatography medium (usually paper). Capillary action draws the solvent mixture up the paper. The degree of adhesion of each component of the mixture to the paper vs. each component's intermolecular attractions to the solvent is the differentiating factor in this method of separation.

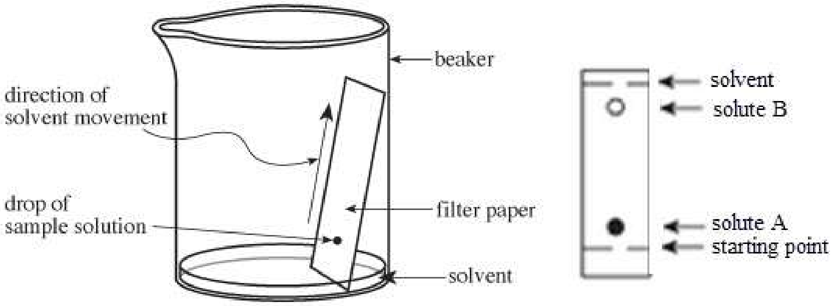
The ratio of the distance each component traveled compared to the solvent is called the retention (to the solvent) factor

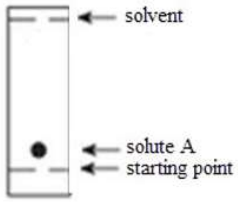
$$R_f = \frac{\text{component distance}}{\text{solvent distance}}$$

A low R_f ratio (close to zero) indicates that the intermolecular attractions of a component are closer to the stationary phase, in this case, paper.

A R_f ratio close to 1 indicates that the component adheres to the solvent rather than to the paper. This means that the component's intermolecular attractions are more similar to the solvent than to the stationary phase, the paper.

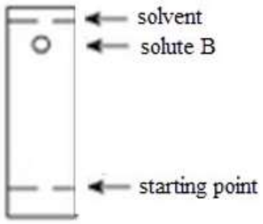
Chromatography experiment and resulting chromatogram.





Component A did not travel very far up the paper.

The R_f is a small ratio. Component A's IMF's to the paper must be greater than its attractions to the solvent.

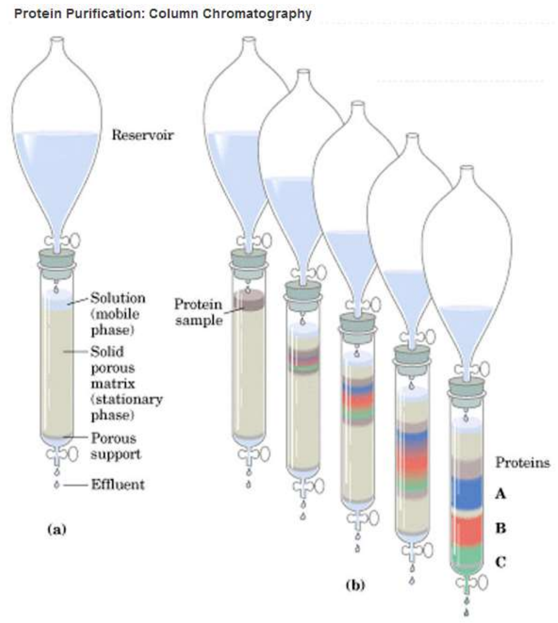


Component B traveled almost as far as the solvent front.

The R_f ratio is close to 1. Component B's IMF's must be closer to the solvent than to the paper.

Paper chromatography is an excellent method for separating very small samples. Only a tiny drop of substance is required.

(b) Column Chromatography



Another method of chromatography is column chromatography.

Column chromatography uses a column of porous material that a solution passes through.

Gravity causes the solution to go through the stationary phase (usually cellulose grains or silica gel).

However, **gravity plays NO part in separating** the components of a mixture.

The solutes are separated by their different intermolecular attractions to the stationary phase.

The fractions A, B, and C can be collected separately as they drip out of the burette.

Solubility: Separatory funnel

The solubility of substances in different solvents can be used to separate components in a mixture.

View the ChemAdvantage video on how to use a separatory funnel. This important organic chemistry lab equipment uses similar intermolecular forces between the solvent and solute to purify mixtures.