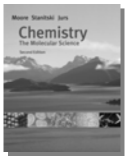

Chemistry: The Molecular Science

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Chapter 15: The Chemistry of Solutes and Solutions

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Solubility & Intermolecular Forces

A solution is a homogeneous mixture of two or more substances. It consists of:

solvent - component in the greatest amount.
solute - all other components (may be >1)

Solvent-solute interactions determine if a substance will dissolve in a particular solvent.

Solutions

Solutions can exist in all 3 physical states, and can be mixtures of solids, liquids and gases:

Type of Solution	**Examples**
Gas in gas	Air
Gas in liquid	Carbonated drinks.
Gas in solid	Hydrogen in palladium metal.
Liquid in liquid	Motor oil, vinegar.
Solid in liquid	Ocean water, sugar-water.
Solid in solid	Bronze, pewter, 14K gold.

Solubility & Intermolecular Forces

Like dissolves like

- Materials with similar intermolecular forces are soluble in each other.
- Dissimilar ones are not.
- Substances dissolve when solvent~solute attraction is stronger than solvent~solvent or solute~solute forces.

Miscible liquids are soluble in each other in all proportions.
e.g. ethanol and water (both are H-bonded polar liquids).

Immiscible liquids are not soluble in each other.

- but may have very low solubility.
e.g. gasoline (non-polar) and water (polar).

Alcohols and Water

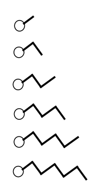
Name	Formula	Solubility (g/100g H_2O @20°C)	
methanol	CH_3OH	miscible	
ethanol	C_2H_5OH	miscible	London
1-propanol	C_3H_7OH	miscible	forces
1-butanol	C_4H_9OH	7.9	increasing
1-pentanol	$C_5H_{11}OH$	2.7	
1-hexanol	$C_6H_{13}OH$	0.6	

Solubility in water decreases as alcohols grow larger because:

- Solute~solute attraction grows
- Solute~solvent attraction stays ≈ constant.

Alcohols and Water

Alternate view
Alcohols have a polar –OH head attached to a non-polar hydrocarbon tail.



The head is hydrophilic ("water loving")

The tail is hydrophobic ("water hating")

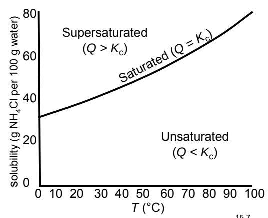
As the tail gets bigger, it is harder and harder to dissolve.

Saturation

A solution may be unsaturated, saturated or supersaturated.

Unsaturated

- [Solute] is less then its solubility.
- All added solid is dissolved
- The solution can still dissolve more solute.



 15.7

Saturation

Saturated

- No more solute will dissolve.
- Undissolved solid solute is usually present.

Supersaturated

- Certain solutions can form that have more than the equilibrium amount dissolved.
  - A saturated solution can be prepared at high T (solubility usually increases with T).
  - When T is lowered the solute may stay in solution – the solution can temporarily have too much dissolved.

 15.8

Saturated Solutions

At saturation, the concentration remains constant, but the solute is in dynamic equilibrium:

$$\text{solute} + \text{solvent} \rightleftharpoons \text{solution}$$

Solute species constantly move in and out of solution.

 15.9

Dissolving Ionic Solids in Liquids

When an ionic compound dissolves in water, the ions

- must overcome the force holding them in the crystal lattice.
- become hydrated.

Lattice energy

Energy holding the ions together in a crystal (positive)

Energy must be added to break up a crystal.

Enthalpy of hydration ($\Delta H_{hydration}$)

Energy released when an ion becomes hydrated (surrounded by water).

 15.10

Solubilities of Solids

$\Delta H_{solution}$= Lattice E + ΔH_{hyd}(cations) + ΔH_{hyd}(anions)

$\Delta H_{solution}$ may be:

- positive (endothermic) – cold packs (NH_4NO_3)
- negative (exothermic) – hot packs ($CaCl_2$)

Ionic solids are insoluble in nonpolar solvents

- Ionic compound lattice energies are large.
  - need energy to break them apart.
- Nonpolar solvents (e.g. hexane, benzene, …) cannot hydrate the ions.
  - do not release energy to offset the lattice energy.

 15.11

Temperature and Solubility

Gases

Le Chatelier's principle can be used:

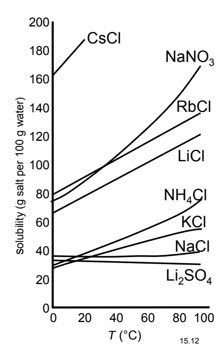
$$\text{Gas} + \text{solvent} \rightleftharpoons \text{sat. solution}$$

Gas: $\Delta H_{soln} < 0$

Gas solubility almost always decreases as T increases.

Solids

Solubility usually increases as T increases.



 15.12

Pressure and Dissolving Gases

Increasing the P of a gas above a liquid increases the concentration of the gas.

Gas + solvent $\rightleftharpoons$ saturated solution

Le Chatelier: More gas on the reactant side shifts the equilibrium toward products (more gas in solution).

Henry's Law

"The solubility of a gas in a liquid is directly proportional to the pressure of the gas".

$$S_g = k_H P_g$$

Solubility

Henry's law constant

Solution Concentration: Units

$$\text{Mass fraction} = \frac{\text{Mass Solute}}{\text{Total Mass of Solution}}$$

Weight percent = Mass fraction x 100%

Example

Sterile saline solutions (NaCl in water) are often used in medicine. What is the weight percent of NaCl in a solution made by dissolving 4.6 g of NaCl in 500. g of pure water?

$$\text{mass fraction} = \frac{4.6\text{ g}}{500.\text{ g} + 4.6\text{ g}} = 0.0091$$

weight percent = 0.0091 x 100% = 0.91 %

Parts per Million, Billion…

Very dilute solutions have very low mass fractions.

Trace amounts in dilute solution are often listed as:

$$\text{Parts per million (ppm)} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6$$

$$\text{Parts per billion (ppb)} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9$$

$$\text{Parts per trillion (ppt)} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^{12}$$

PPM, PPB and PPT

1 ppm of solute in water = 1 mg / 1000 g of solution

Since 1L of water has a mass ≈ 1000 g.

1 ppm ≈ 1 mg/L

Similarly 1 ppb ≈ 1 µg/L

1 ppt ≈ 1 ng/L

Molarity and Molality

Molarity has been defined before:

$$\text{Molarity} = \text{M} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Molality is another concentration scale:

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

It is another mass-based unit.

- it uses the mass of solvent and not solution.
- its value is unaffected by temperature (molarity varies with T)

Vapor Pressure of Solutions

The vapor pressure of a pure solvent drops whenever non-volatile solute is added.

Raoult's law: $P_1 = X_1 P°_1$

vapor pressure of solvent over the solution

mole fraction of the solvent

vapor pressure of pure solvent

As the purity of the solvent decreases, its vapor pressure drops.

Vapor Pressure Lowering

Example

The vapor pressure of an aqueous solution of urea is 291.2 mmHg. The vapor pressure of pure water is 355.1 mmHg. Calculate the mole fraction of each component.

Urea is non-volatile, water will obey Raoult's law:

$P_{water} = X_{water} P°_{water}$

291.2 mmHg = X_{water}(355.1 mmHg)

X_{water}= 291.2/355.1 = 0.820

X_{urea} = 1 – 0.820 = 0.180

Colligative Properties

Vapor pressure lowering is a colligative property:

A property that depends upon the number of solute "particles" in solution.

- The chemical make-up of the particles is unimportant.
- 1 mol of sugar and 1 mol of urea have the same effect.
- 1 mol of NaCl will be different.
  - Each NaCl yields 2 particles in solution (1 Na^+ ion and 1 Cl^- ion).
  - Sugar does not dissociate in solution.

Boiling Point Elevation

Non-volatile solutes increase the boiling point of a solvent. Why?

- The vapor pressure of the solvent has been lowered.
- Higher *T* is needed to get the vapor *P* = external *P*.

Quantitatively $\Delta T_b = K_b \, m_{solute}$

Notice: the K_b value only depends on the solvent
the molality, *m* depends on the solute

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Freezing Point Lowering

A non-volatile solute lowers the freezing point of a solvent:

Quantitatively $\Delta T_f = K_f \, m_{solute}$

K_f is a constant for the solvent.

Ethylene glycol (antifreeze) is added to car radiators. It raises the boiling point of water (stops "boil over") and lowers the freezing point (stops freezing).

Freezing Point Lowering

Example

Calculate the freezing point of an aqueous 30.0% ethylene glycol mixture. For water K_f = 1.86°C kg mol^{-1}.

In a 100.0 g solution: 30.0 g of $C_2H_2(OH)_2$ + 70.0 g of H_2O

moles of $C_2H_2(OH)_2$ = 30.0 g / 62.07 g mol^{-1} = 0.4833 mol

molality = (0.4833 mol / 0.070 kg) = 6.904 molal

ΔT_f = 1.86°C kg mol^{-1}(6.904 mol/kg) = 12.8 °C

freezing point = 0.00°C – 12.8°C = -12.8°C

Remember: freezing points are lowered

Boiling Point Elevation

Example
A what temperature will 1.000 molal aqueous solutions of urea, sucrose and sodium chloride boil?

The boiling points of the urea and sucrose solutions should be the same – colligative properties only depend upon the number of particles in solution:

ΔT_b = 0.51°C kg mol^{-1}(1.000 mol/kg) = 0.51 °C
boiling point = 100.00°C + 0.51°C = 100.51°C

1.0 molal sodium chloride has a higher boiling point. Why…