

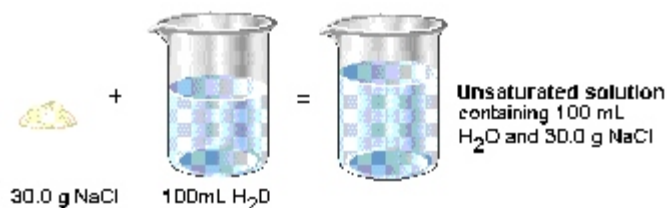
Chapter 12 – Solutions

SOLUTIONS are homogeneous mixtures of one substance -- the SOLUTE -- dispersed in another substance -- the SOLVENT. Solutions have continuously variable compositions.

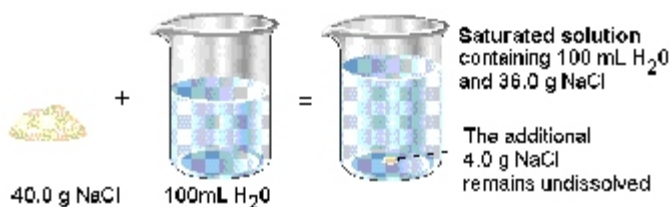
We will deal mostly with liquid solutions where the solvent is a liquid and the solute is either a gas, liquid or solid, although examples of gaseous and solid solutions are very common.

Solubility and Dissolution

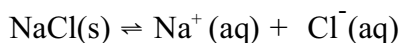
Suppose we add 30.0 g of NaCl to 100. mL of water at 20°C and stir it up. We would find that all of the NaCl eventually dissolves.



Now suppose we add 40.0 g of NaCl to a separate 100. mL of water at 20°C. We start to stir and most of the NaCl dissolves. However, no matter how long we stir, some of the NaCl will remain undissolved.



This is an example of a SATURATED SOLUTION, a solution which has dissolved in it the maximum amount of solute. A saturated solution is an example of a dynamic equilibrium, where the rate of dissolution equals the rate of crystallization.



Both processes occur simultaneously, as emphasized by the double arrows.

The SOLUBILITY of a substance in a particular solvent is the amount that dissolves in a particular amount of solvent at a particular temperature to give a saturated solution.

A solution that contains less solute than a saturated solution is said to be UNSATURATED, while a solution that contains more solute than a saturated solution is said to be SUPERSATURATED.

In qualitative terms, we talk about concentrated and dilute solutions. A concentrated solution has a relatively large amount of solute in a given volume of solvent or solution, while a dilute solution has less.

Factors Governing Solubility

Generally, LIKE DISSOLVES LIKE. That is, substances with similar molecular structures tend to dissolve in one another. Polar solutes are generally more soluble in polar solvents, while non-polar solutes are generally more soluble in non-polar solvents. Hydrogen bonding capability often affects the solubility of a solute in a given solvent.

The two factors that govern solubility are:

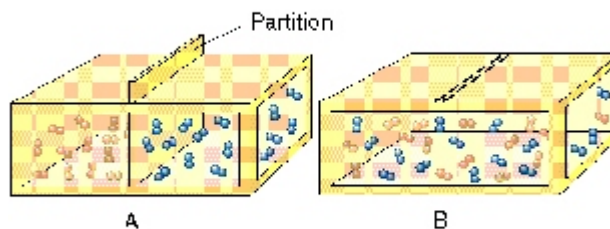
- 1) The natural tendency toward more randomness or disorder or increasing *ENTROPY*.
- 2) The natural tendency toward lower energy.

When one gas mixes with another, the disorder or entropy increases. Intermolecular forces in gases are generally negligible, so the only factor of consequence is entropy.

Substances in which intermolecular forces are of the same type are often miscible.

Octane and heptane are miscible because the IMFs are relatively weak London forces. Water and ethanol are also miscible because the dominant IMFs are hydrogen bonds.

Octane and water are **not** miscible because, for octane to dissolve in water, the network of strong hydrogen bonds must be broken up. The interaction between octane and water molecules cannot make up for this, so octane and water are immiscible.



Solutions of Ionic Solutes

Solubilities of ionic solutes in water differ markedly. Here we need to consider the interaction between cations and anions in the solid (lattice energy) and the ion-dipole forces between water molecules and the ions in solution. Water molecules are polar, with a positive and negative end. The water molecules surround the solute ions so that the negative end of the water molecule is closest to cations and the positive end is closest to anions.

The process of water molecules surrounding solute particles is called hydration. (A more general term -- solvation -- corresponds to any arbitrary solvent.)

According to Coulomb's Law, the energy of attraction between two ions is proportional to the charges on the ions, and inversely proportional to the distance separating them. So, lattice energies increase with the charge on the ions and as the sizes of the ions decrease.

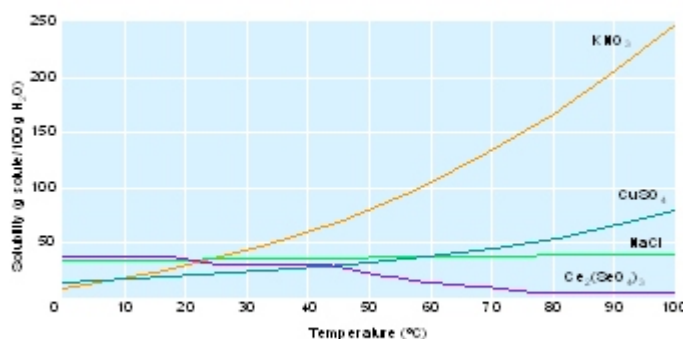
$$E \propto \frac{q_1 q_2}{d}$$

Hydration energies increase in the same manner. Generally speaking, the solubility of an ionic species increases as the size mismatch between the cation and anion increases.

LiClO_4 is about 10 times more soluble in water than NaClO_4 which is about 1000 times more soluble in water as KClO_4 .

Solubility and Temperature

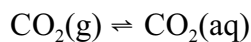
In general, gases become less soluble in a liquid as the temperature increases. Most (but certainly not all) ionic solids become more soluble as the temperature increases.



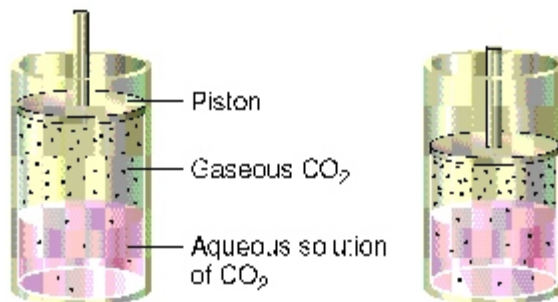
Solubility and Pressure

Pressure does not affect the solubility of solids in liquids or liquids in liquids to any appreciable extent. Gas solubility, however, is strongly affected by pressure.

LeChatelier's Principle says that *when a system in equilibrium is disturbed by a change in temperature, pressure or concentration, the position of the equilibrium shifts in such a way as to counteract the effect of the initial change.*



Consider gaseous CO_2 in a cylinder fitted with a movable piston over an aqueous solution of CO_2 . As the pressure of the CO_2 gas is increased, LeChatelier's Principle tells us the equilibrium will shift so as to counteract the pressure increase--more CO_2 dissolves.



All gases become more soluble at a given temperature when the partial pressure of the gas over the solution is increased.

Henry's Law: The solubility of a gas is directly proportional to the partial pressure of the gas above the solution.

$$S = k_H P$$

S is the solubility of the gas expressed in units that depend on the units of k_H .

k_H is the Henry's Law constant which depends on the gas, the liquid and the temperature. (g/L·atm or mol/L·atm)

P is the partial pressure of the gas over the liquid.

Example: What is the solubility of O₂ in pond water at 20°C if the partial pressure of O₂ is 0.21 atm? $k_H = 1.3$ mmol/L·atm

Note: Henry's Law does not hold when a chemical reaction takes place between the gas and the liquid.

Quantitative Measures of Concentration

1. Molarity (M)

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} = [X]$$

The units are moles per liter and the abbreviation is M (read "molar".) Square brackets around the symbol or formula of the solute are used to denote molarity. SI prefixes milli, micro etc. can be used in conjunction with M , giving mM , μM , etc.

Molarity serves as a conversion between volume of solution and number of moles of solute.

$$\# \text{ of moles of solute} = \text{volume (L)} \times \text{molarity}$$

Example: Suppose we have 25.00 mL of a 0.150 M aqueous NaOH solution. The number of moles of NaOH is therefore:

2. Mass Percentage of Solute

$$\text{mass percentage of solute} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

Example: Suppose we need 15.0 g of $\text{Cu}(\text{BF}_4)_2$ for a reaction. What mass of a 45.0% aqueous solution is required?

3. Molality (m)

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

The units are mol/kg and the symbol is m (read "molal").

Example: What mass of KNO_3 must be added to 250.0 g of water to prepare a 0.200 m KNO_3 solution?

4. Mole Fraction (X_A)

$$X_A = \frac{\text{moles of substance A}}{\text{total moles of all solution components}}$$

The sum of the mole fractions of all components of a solution is 1. Multiplying mole fraction by 100 gives mole percent.

Example: Calculate the mole fraction of sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in a solution prepared by dissolving 5.00 g sucrose in 100.0 g of water.

Conversion of Concentration Units

Conversion between concentration units is straightforward when the units are expressed in terms of mass or moles of solute and solvent. When conversions involve molarity it is necessary to know the density of the solution.

Example: What is the molality of a solution of benzene (b) in toluene (t) whose composition is reported as $X_b = 0.150$?

Example: An aqueous solution of HBr is 48.0% HBr by mass and has a density of 1.490 g/mL. What is the molar concentration of HBr?

COLLIGATIVE PROPERTIES

Colligative properties of solutions are properties that depend only on the concentration of solute particles (molecules or ions) but not on their chemical identity.

1. Vapor Pressure Lowering: The vapor pressure of a volatile solvent is lowered by the addition of a non-volatile solute.

Why is this? Vapor pressure arises from the fact that solvent molecules may leave the liquid phase and enter the gas phase. When a non-volatile solute is present, it can block the escape of solvent molecules from the liquid phase, but has no effect on the return of molecules to the liquid phase.

This effect was first observed by François Marie Raoult.

Raoult's Law: The partial pressure of a solvent, P_A , over a solution of a non-volatile solute equals the vapor pressure of the pure solvent, P_A° , times the mole fraction of the solvent, X_A , in the solution.

$$P_A = P_A^\circ X_A$$

Vapor pressure *lowering* is actually proportional to the mole fraction of solute, so it is the lowering of the vapor pressure that is a colligative property.

$$P_A^\circ - P_A = \Delta P = P_A^\circ - P_A^\circ X_A = P_A^\circ (1 - X_A) = P_A^\circ X_B$$

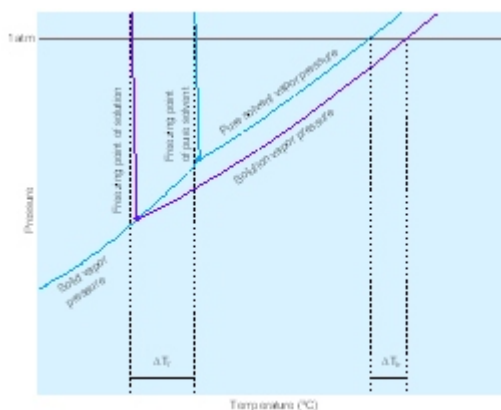
Therefore:

$$\Delta P = P_A^\circ X_B$$

Example: Calculate the vapor pressure at 100°C of a solution prepared by dissolving 5.00 g sucrose in 100. g of water.

Raoult's Law is reliable only at relatively low concentrations where there is large separation between solute particles. At low concentration, real solutions approximate ideal solutions.

The concept of vapor pressure lowering should give us a clue as to the effect of the addition of a non-volatile solute on the boiling point of a solvent.



2. Boiling Point Elevation

The normal boiling point of a liquid is the temperature at which its vapor pressure equals 1 atm. A non-volatile solute decreases the vapor pressure of a solvent, and therefore, it raises the temperature at which the vapor pressure is equal to 1 atm.

Addition of a non-volatile solute raises the boiling point of a solvent by an amount proportional to the molal concentration of the solute.

$$\Delta T_b = K_b c_m$$

Here, ΔT_b is the amount by which the boiling point is elevated (T_b of solution minus T_b of the pure solvent), K_b is the boiling point elevation constant ($^{\circ}\text{C}/\text{m}$) and c_m is the molal concentration of the solute.

K_b is a characteristic of the solvent, not the solute.

For water $K_b = 0.512 \text{ }^{\circ}\text{C}/\text{m}$. Values of K_b for other solvents are listed in Table 12.3

Example: What is the boiling point of a solution which is prepared by adding 20.0 g sucrose (342.3 g/mol) to 55.0 g of water?

3. Freezing Point Depression

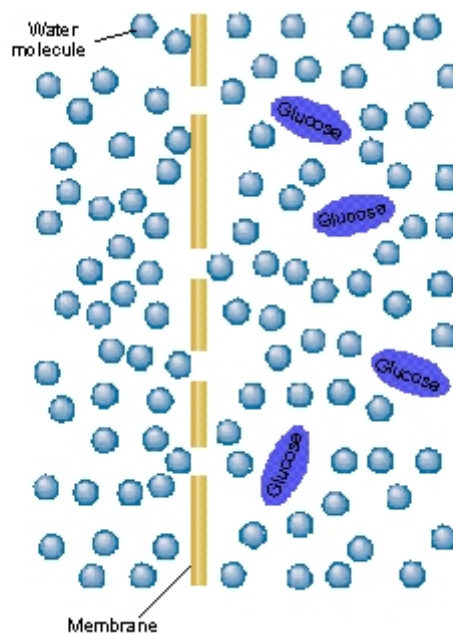
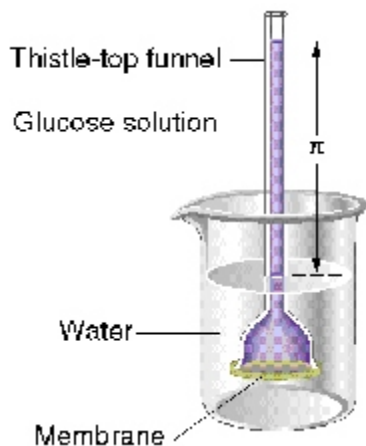
The presence of a solute lowers the freezing point of a solution below that of the pure solvent. This explains why solutions freeze over a range of temperatures rather than at a single, fixed temperature like a pure liquid does.

$$\Delta T_f = K_f c_m$$

Example: When 4.00 g of a certain non-electrolyte is dissolved in 55.0 g of benzene, the resulting solution freezes at 2.32°C. The normal freezing point of benzene is 5.48°C. What is the molar mass of the compound?
For benzene, $K_f = 5.12 \text{ }^\circ\text{C/m}$

4. Osmotic Pressure

Osmosis is the motion of solvent molecules through a semipermeable membrane from a solution of lower solute concentration to one of higher solute concentration.



$$\pi = MRT$$

π = osmotic pressure

M = molarity of solute

R = gas constant (0.08206 L · atm/mol · K)

T = absolute temperature (K)

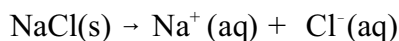
Example: What is the osmotic pressure of a 0.010 M aqueous solution of a non-electrolyte at 25°C?

Osmometry can be used to determine molar masses and is quite a bit more sensitive than the other colligative methods. For example, a 0.010 M solution of sucrose in water exhibits b.p. elevation of 0.005 K and a f.p. depression of 0.02 K, but produces an osmotic pressure equivalent to a 2 m column of water. These small ΔT s are difficult to measure, but an osmotic pressure of 2 m of water is huge.

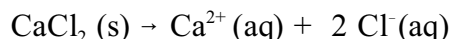
This is quite important in measuring very large molar masses. For example 0.10 g of hemoglobin (MW $\sim 66,500$ g/mol) in 100 mL of water has a concentration of 1.5×10^{-5} M and an immeasurably small f.p. depression, but an osmotic pressure of ~ 4 mm H₂O.

Colligative Properties of Ionic Solutions

Colligative properties depend on the total concentration of all ions in solution, and not on their identities. Thus, a solution prepared by dissolving 0.100 mol of NaCl in 1.00 kg of water is ideally 0.100 *m* in Na⁺ and 0.100 *m* in Cl⁻.



A solution prepared by dissolving 0.100 mol of CaCl₂ in 1.00 kg of water is ideally 0.100 *m* in Ca²⁺ and 0.200 *m* in Cl⁻.



When dealing with electrolyte solutions we can modify the equations for boiling point elevation, freezing point depression and osmotic pressure to include *i*, the van't Hoff factor. The van't Hoff factor indicates the number of particles resulting from each formula unit of a particular substance.

$$\Delta T_f = i K_f c_m$$

$$\Delta T_b = i K_b c_m$$

$$\pi = iMRT$$

The ideal value for *i* for NaCl is 2, since each formula unit of NaCl yields two ions. For CaCl₂ it is 3, etc. However, if the solution is not extremely dilute, cations and anions can form "ion-pairs," which act as a single particle. The degree of ion-pairing increases as the concentration of the ionic solute increases.

Therefore, as the concentration of solute increases, the value of i becomes smaller and smaller relative to its ideal value.

| | | |
|-----------|-------------|------------|
| For NaCl: | $m = 0.001$ | $i = 1.97$ |
| | $m = 0.01$ | $i = 1.94$ |
| | $m = 0.1$ | $i = 1.87$ |
| | $m = 1.0$ | $i = 1.81$ |