

## Solutions

- A **solution** is a homogeneous mixture of two or more substances.
- The two main components of a solution are the **solute** and the **solvent**.
  - Solute is present in the smaller amount
  - The solvent is present in the larger amount.
- Any phase of matter can dissolve into any other phase.

## Types of solutions

### Types of solutions

- **Gases**
  - Gases dissolved in gases (air)
  - Liquids dissolved in gases (humid air)
  - Solids dissolved in gases (moth balls)
- **Liquids**
  - Gases in liquids (air dissolved in water)
  - Liquids in liquids (ethanol in water)
  - Solids in Liquids (salt in water)
- **Solids**
  - Gases in solids ( $H_2$  in Pt)
  - Liquids in solids (Hg/Ag amalgam)
  - Solids in solids (Cr in Fe alloy)

- **Solubility** – The maximum amount of solute that will dissolve in a solvent.
- **Saturated** – A solution is that is at the solubility limit.
- **Unsaturated** – Anything less than saturated.
- **Supersaturated** – A solution that contains more than the solubility limit.

## Terminology

- **Dilute** – A solution that contains relatively little solute.
- **Concentrated** – A solution that contains a relatively large amount of solute.
  - Can also mean a saturated solution, especially when applied to acids.
- **Aqueous solution** – A solution in which water is the solvent.

## Terminology

- For covalent compounds in liquid phase, the relative strengths of the intermolecular forces determines whether or not a solution forms.
- If the intermolecular forces are too dissimilar, like hydrogen bonding and London forces, the solution will not form. The liquids will remain essentially separated.

## Molecular Solutions

- If the intermolecular forces are very similar between the two substances, they will tend to be **miscible**.
- Miscible – substances that mix in all proportions. All solutions of gases in gases are miscible.

### Molecular solutions

If we look at a series of alcohols R-OH, where R is an organic group (C<sub>x</sub>H<sub>y</sub>) we can see how intermolecular forces affect solubility.

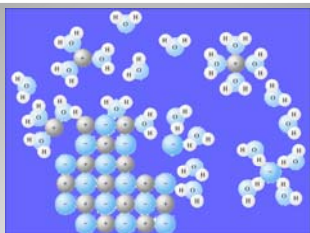
CH <sub>3</sub> OH	miscible
CH <sub>3</sub> CH <sub>2</sub> OH	miscible
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	miscible
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	7.9 g/100 mL
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH	2.7 g/100 mL
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> OH	0.6 g/100 mL

### Alcohols in water

### Ionic solids dissolving in water

- The polar water molecules are attracted to the ions in the solid. (ion-dipole interaction)
- The ions are attracted to each other (lattice energy) and the water molecules (hydration)
- If the attraction between the water molecules and the ions is greater than that between the ions the substance will dissolve.

### Ionic Solutions



### Solution formation

The two competing forces, hydration and lattice energy, determine solubility

Lattice energy – Holds ions together

- Increases with charge
- Decreases with radius of ion

Hydration energy – Pulls ions apart

- Increases with charge
- Decreases with radius of ion

For a series of compounds, if the lattice energy decreases faster than the hydration energy (smaller ions) the compounds become more soluble. If the hydration energy decreases faster (large ions) the compounds become less soluble.

### Ionic solutions

- For gases dissolved in liquid the solubility decreases with temperature
- Most ionic solids (some exceptions are CaSO<sub>4</sub>, Ca(OH)<sub>2</sub>, and Ce<sub>2</sub>(SeO<sub>4</sub>)<sub>3</sub>) are more soluble at higher temperatures
- The solution process can be exo- or endothermic. (NaOH – exothermic, NH<sub>4</sub>NO<sub>3</sub> – endothermic)

### Effects of temperature on solubility

- Pressure generally has no effect on the solubility of liquid or solids in liquids.
- For gases dissolved in liquids an equilibrium is established between the gas and the aqueous substance
  - Example:  $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$

### Effects of pressure on solubility

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- All equilibria are effected by Le Chatelier's principle
  - A system at equilibrium that is disturbed by a change will shift to relieve that change
- This means that the partial pressure of the gas above the solution affects the solubility of the gas.
  - Higher partial pressures – increased solubility
  - Henry's Law

### Gases dissolved in liquids

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- Henry's Law states that 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,  $k_H$  is the Henry's Law Constant (different for each gas) and P is the partial pressure of the gas.

### Henry's Law

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- We'll usually use the two-point form of the equation which does not require knowing the constant
 
$$\frac{S_1}{S_2} = \frac{P_1}{P_2}$$
- The solubility at one pressure can be found from the solubility at another pressure as long as the temperature is constant.

### Henry's Law

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- Concentration is the amount of solute in a given amount of either solution or solvent
- Percentage units

$$\% \left( \frac{m}{m} \right) = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

### Concentration Units

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- Molarity
 
$$M = \frac{\text{mol solute}}{\text{L solution}}$$
- Molarity can be used as a conversion factor between number of moles of solute and volume of solution.

### Concentration Units

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- Molality (m)

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

- Used when we want a concentration unit that is temperature independent.

### Concentration Units

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- Mole fraction ( $X_A$ )

$$X_A = \frac{\text{mol solute A}}{\text{mol solution}}$$

- The sum of all mole fractions in a solution is equal to 1.

### Concentration Units

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- mole fraction to molality and back
- molality to molarity and back
  - requires the density of the solution
  - We will usually assume some value (usually the denominator of the given unit).

### Conversion between concentration units

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- A 0.594 M solution of Lithium nitrate has a density of  $1.14 \text{ g mL}^{-1}$ . What is the molality of the solution?

Assume 1 L of solution

$$0.594 \text{ mol LiNO}_3 \times \frac{68.944 \text{ g LiNO}_3}{1 \text{ mol LiNO}_3} = 40.95 \text{ g LiNO}_3$$

0.594 mol LiNO<sub>3</sub>

$$1 \text{ L} \times \frac{1 \text{ mL}}{10^{-3} \text{ L}} \times \frac{1.14 \text{ g}}{\text{mL}} = 1140 \text{ g solution}$$

$$1140 \text{ g solution} - 40.95 \text{ g LiNO}_3 = 1099 \text{ g solvent} = 1.099 \text{ kg solvent}$$

$$m = \frac{0.594 \text{ mol}}{1.099 \text{ kg}} = 0.540 \text{ m}$$

### Example

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- These are properties that depend on the concentration of the solute but not what the solute is.
  - vapor pressure lowering – Raoult's Law
  - freezing point depression
  - boiling point elevation
  - osmotic pressure

### Colligative properties of solutions

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- Vapor pressure lowering is the difference between the vapor pressure of the pure solvent and the vapor pressure of the solution.
- Vapor pressure of the solution with a nonvolatile solute – Raoult's Law

$$P_A = P_A^* X_A$$

v.p. of solution      v.p. of pure solvent      mole fraction of solvent

### Vapor pressure lowering

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- The v.p. lowering is then

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

Raoult's Law
definition of X
mole fraction of solute

### Vapor Pressure Lowering

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- Ideal solution – one in which both components follows Raoult's Law for all mole fractions.
- Occurs when the two substance are molecularly similar in terms of intermolecular forces (benzene and toluene)

### Vapor Pressure of a solution with a volatile solute

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- Calculation can be done with

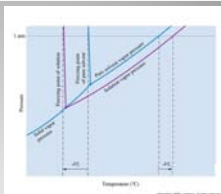
$$P = P_A^\circ X_A + P_B^\circ X_B$$

- The vapor pressure of the solution will be between the vapor pressures of the pure components
- The vapor will have a higher mole fraction of the more volatile component than the solution
  - fractional distillation

### Vapor Pressure of a solution with a volatile solute

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- Related to vapor pressure lowering
- Because the addition of a nonvolatile solute lowers the vapor pressure, the temperature must be increased beyond the normal b.p. to get the solution to boil.



### Boiling point elevation

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- For dilute solutions the change in b.p. is proportional to the molal concentration

$$\Delta T_b = K_b m$$

### Boiling Point Elevation

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- Because of the vapor pressure lowering, the triple point moves to the left on the phase diagram.
- This means that the freezing point of a solution is lower than the f.p. of the pure solvent.

$$\Delta T_f = -K_f m$$

### Freezing point depression

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- Freezing point depression can be used
  - to melt ice on roads
  - addition of salt lowers the freezing point of the resulting solution. The water has to get to a lower temperature to freeze.
  - to determine the molar mass of solutes
    - If we know the f.p. of the pure solvent and the solution we can determine the molal concentration. This then tells us, with the mass of the solvent and mass of the solute, the molar mass of the solute.

### Applications

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- 6.234 g of a substance is dissolved into 500.0 g of benzene (a non-polar substance,  $K_f = 5.12^\circ\text{C m}^{-1}$ ). The freezing point drops by  $0.741^\circ\text{C}$ . What is the molar mass of the solute?

### Example

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- Find the molality

$$m = -\frac{\Delta T_f}{K_f} = -\frac{(-0.741^\circ\text{C})}{5.12^\circ\text{C m}^{-1}} = 0.1447\text{ m}$$

- Find the number of moles

$$m = \frac{\text{moles solute}}{\text{kg solvent}} \Rightarrow \text{moles} = 500.0\text{ g Benzene} \times \frac{1\text{ kg}}{10^3\text{ g}} \times \frac{0.1447\text{ mol}}{\text{kg}} = 0.07236\text{ mol}$$

- molar mass

$$\text{molar mass} = \frac{6.234\text{ g}}{0.07236\text{ mol}} = 86.1\text{ g mol}^{-1}$$

### Solution

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- Osmosis is the process of solvent molecules passing through a semi-permeable membrane due to a difference in concentration
- Osmotic pressure is the pressure that needs to be applied to a solution to just stop osmosis
- Ozzmosis is Ozzy Osbourne's 11<sup>th</sup> solo record

### Osmosis

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- Osmotic pressure is related to the molar concentration of the solute
- $$\Pi = MRT$$
- R is the gas constant and T is the absolute temperature.

### Osmotic pressure

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- Can be used to determine molar mass also.
- Used when the molarity of the solutions (and thus the molality) is very small and freezing point changes cannot be measured.
- This occurs with very large molecules
  - polymers (plastics)
  - proteins

### Osmotic pressure

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- Important in biology.
  - If the osmotic pressure of the solutions used is not correct (isotonic) the cells will be destroyed
    - crenellation
    - lysis (i.e. hemolysis)
- Reverse osmosis – purifying water
  - desalination

**Osmotic pressure**

- For ionic solutions the true concentration is higher than the apparent concentration
  - a 1.0 M NaCl solution is 2.0 M in ions
  - a 1.0 M CaI<sub>2</sub> solution is 3.0 M in ions
- The true concentration is taken into account by multiplying the equations by *i*.
  - *i* is the number of ions per formula unit.
  - *i* is called the van't Hoff factor.

**Colligative properties of ionic solutions**

- Equations for ionic solutions
 
$$\Delta P = iP_A X_B$$

$$\Delta T_b = iK_b m$$

$$\Delta T_f = -iK_f m$$

$$\Pi = iMRT$$

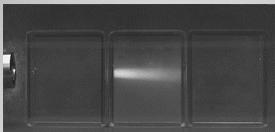
Works when the solutions are fairly dilute.  
Calculated values of *i* are often different from the values expected based on the ionic formula unit.

**Colligative properties of ionic solutions**

- Not a true solution (i.e. not homogeneous)
- Definition – a dispersion of particles of a substance throughout another substance.
  - examples:
    - fog
    - smoke
    - milk

**Colloids**

- Because the particles in a colloid are larger than in a solution they can scatter light.
- This is called the **Tyndall effect**.



**Tyndall effect**