Chapter 13 Properties of Solutions

#### Solutions

•Solutions are homogeneous mixtures of two or more pure substances. •In a solution, the solute is dispersed uniformly throughout the solvent.

The intermolecular forces between solute and solvent particles must be strong enough to compete with those between solute particles and those between solvent particles.

#### How Does a Solution Form?

As a solution forms, the solvent pulls solute particles apart and surrounds, or solvates, them.

If an ionic salt is soluble in water, it is because the ion-dipole interactions are strong enough to overcome the lattice energy of the salt crystal.

## Energy Changes in Solution

•Simply put, three processes affect the energetics of the process:

Separation of solute particles

Separation of solvent particles

New interactions between solute and solvent

The enthalpy change of the overall process depends on  $\Delta H$  for each of these steps.

Why Do Endothermic Processes Occur?

Things do not tend to occur spontaneously (i.e., without outside intervention) unless the energy of the system is lowered.

Yet we know that in some processes, like the dissolution of  $NH_4NO_3$  in water, heat is absorbed, not released.

### Enthalpy Is Only Part of the Picture

The reason is that increasing the disorder or randomness (known as entropy) of a system tends to lower the energy of the system.

So even though enthalpy may increase, the overall energy of the system can still decrease if the system becomes more disordered.

### Student, Beware!

Just because a substance disappears when it comes in contact with a solvent, it doesn't mean the substance dissolved.

•

•Dissolution is a physical change—you can get back the original solute by evaporating the solvent.

•If you can't, the substance didn't dissolve, it reacted.

Types of Solutions

Saturated

Solvent holds as much solute as is possible at that temperature.
Dissolved solute is in dynamic equilibrium with solid solute particles.
Types of Solutions

•

•Unsaturated

Less than the maximum amount of solute for that temperature is dissolved in the solvent.

Supersaturated

Solvent holds more solute than is normally possible at that temperature.

These solutions are unstable; crystallization can usually be stimulated by adding a "seed crystal" or scratching the side of the flask.

Factors Affecting Solubility

•Chemists use the axiom "like dissolves like":

▶ Polar substances tend to dissolve in polar solvents.

Nonpolar substances tend to dissolve in nonpolar solvents.

The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.

Glucose (which has hydrogen bonding) is very soluble in water, while cyclohexane (which only has dispersion forces) is not.

•

•Vitamin A is soluble in nonpolar compounds (like fats).

•Vitamin C is soluble in water.

Gases in Solution

•In general, the solubility of gases in water increases with increasing mass.

•Larger molecules have stronger dispersion forces.

•

•The solubility of liquids and solids does not change appreciably with pressure.

•The solubility of a gas in a liquid is directly proportional to its pressure.

Henry's Law  $S_g = kP_g$ where • $S_g$  is the solubility of the gas;

•k is the Henry's law constant for that gas in that solvent;

 $\bullet P_g$  is the partial pressure of the gas above the liquid.

Temperature

Generally, the solubility of solid solutes in liquid solvents increases with increasing temperature.

•

•The opposite is true of gases:

Carbonated soft drinks are more "bubbly" if stored in the refrigerator.

 $\succ$ Warm lakes have less O<sub>2</sub> dissolved in them than cool lakes.

Ways of Expressing Concentrations of Solutions Mass Percentage Mass % of A = Parts per Million and Parts per Billion ppm =

Mole Fraction (X)

•In some applications, one needs the mole fraction of *solvent*, not solute—make sure you find the quantity you need!

Molarity (*M*)

•You will recall this concentration measure from Chapter 4.

•Because volume is temperature dependent, molarity can change with temperature.

### Molality (*m*)

Because both moles and mass do not change with temperature, molality (unlike molarity) is *not* temperature dependent.

Changing Molarity to Molality

If we know the density of the solution, we can calculate the molality from the molarity, and vice versa.

**Colligative Properties** 

•Changes in colligative properties depend only on the *number* of solute particles present, not on the *identity* of the solute particles.

•Among colligative properties are

► Vapor pressure lowering

► Boiling point elevation

Melting point depression

➢Osmotic pressure

Vapor Pressure

Because of solute-solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase.

Therefore, the vapor pressure of a solution is lower than that of the pure solvent.

Raoult's Law

•The partial pressure exerted by solvent vapor above the solution, PA, equals to the product of the mole fraction of the solvent in the solution, Xa, times the vapor pressure of the pure solvent.

 $P_{\rm A} = X_{\rm A} P^{\circ}_{\rm A}$ where

• $X_A$  is the mole fraction of compound A

 $\bullet P^{\circ}_{A}$  is the normal vapor pressure of A at that temperature

**NOTE:** This is one of those times when you want to make sure you have the vapor pressure of the *solvent*.

Boiling Point Elevation and Freezing Point Depression

Nonvolatile solute-solvent interactions also cause solutions to have higher boiling points and lower freezing points than the pure solvent.

•The boiling point of a liquid is the temperature at which its vapor pressure equals 1 atm. Boiling Point Elevation

The change in boiling point is proportional to the molality of the solution:  $\Delta T_b = K_b \cdot m$ 

where  $K_b$  is the molal boiling point elevation constant, a property of the solvent.

Freezing Point Depression

•The change in freezing point can be found similarly:  $\Delta T_f = K_f \cdot m$ 

•Here  $K_f$  is the molal freezing point depression constant of the solvent. Boiling Point Elevation and Freezing Point Depression

Note that in both equations,  $\Delta T$  does not depend on *what the solute is*, but only on *how many particles* are dissolved.

 $\Delta T_b = K_b \cdot m$ 

 $\Delta T_f = K_f \cdot m$ Colligative Properties of Electrolytes Since these properties depend on the number of particles dissolved, solutions of electrolytes (which dissociate in solution) should show greater changes than those of nonelectrolytes.

Colligative Properties of Electrolytes

However, a 1 M solution of NaCl does not show twice the change in freezing point that a 1 M solution of methanol does.

van't Hoff Factor

One mole of NaCl in water does not really give rise to two moles of ions. van't Hoff Factor

Some Na<sup>+</sup> and Cl<sup>-</sup> reassociate for a short time, so the true concentration of particles is somewhat less than two times the concentration of NaCl. The van't Hoff Factor

•

•Reassociation is more likely at higher concentration.

•Therefore, the number of particles present is concentration dependent.

The van't Hoff Factor

We modify the previous equations by multiplying by the van't Hoff factor, *i* 

$$\Delta T_f = K_f \cdot m \cdot i$$

• $i = \frac{\text{delta T f Measured}}{\text{Delta T f calculated}}$ 

•If the van't hoff factor is not given use the the ideal value in calculation Osmosis

•Some substances form semipermeable membranes, allowing some smaller particles to pass through, but blocking other larger particles.

•In biological systems, most semipermeable membranes allow water to pass through, but solutes are not free to do so.

## Osmosis

In osmosis, there is net movement of solvent from the area of **higher solvent concentration** (*lower solute concentration*) to the are of **lower solvent concentration** (*higher solute concentration*).

Osmotic Pressure

•The pressure required to stop osmosis, known as osmotic pressure,  $\pi$ , is

Osmosis in Blood Cells

•If the solute concentration outside the cell is greater than that inside the cell, the solution is hypertonic.

•Water will flow out of the cell, and crenation results.

Osmosis in Cells

•If the solute concentration outside the cell is less than that inside the cell, the solution is hypotonic.

•Water will flow into the cell, and hemolysis results.

Applications of osmosis

•Food preservation

•Dialysis

Dialysis works on the principles of the <u>diffusion</u> and osmosis of solutes and fluid across a <u>semi permeable membrane</u>

Molar Mass from

Colligative Properties

We can use the effects of a colligative property such as osmotic pressure to determine the molar mass of a compound.

Colloids:

Suspensions of particles larger than individual ions or molecules, but too small to be settled out by gravity.

# Tyndall Effect

- •Colloidal suspensions can scatter rays of light.
- •This phenomenon is known as the Tyndall effect.

# Colloids in Biological Systems

Some molecules have a polar, hydrophilic (*water-loving*) end and a nonpolar, hydrophobic (*water-hating*) end.

Sodium stearate is one example of such a molecule.

These molecules can aid in the emulsification of fats and oils in aqueous solutions.