Chem 0103

Part 3: aqueous solutions

Solutions Are Mixtures

- A homogeneous mixture is called a solution.
  - mixture: means that concentrations can be changed (different from compounds which have fixed ratios of atoms)
  - homogeneous: means that particles are evenly distributed. You can take a sample, and it will be representative of the entire solution (not like vegetable soup)
  - solutions are transparent (not milky)
  - components do not separate by density (not like oil and vinegar)
- Example: glass of tea
  - Solvent: water
  - Solutes: flavor, sugar, colored substances

Ionic and molecular compounds in solution

- Molecules don't break apart when they dissolve, and they stay neutral

  e.g. $C_6H_{12}O_6\,(s) \longrightarrow C_6H_{12}O_6\,(aq)$
- Ionic compounds in aqueous solutions produce separate ions

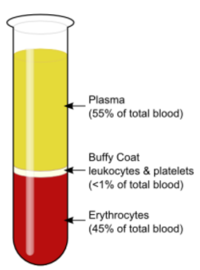
  e.g. $Mg(NO_3)_2\,(s) \longrightarrow Mg^{2+}\,(aq) + 2\,NO_3{}^-\,(aq)$
  - Ions conduct electricity
  - Named after moving to anode and cathode
  - Ionic compounds are also called **electrolytes**

Colloids and suspensions

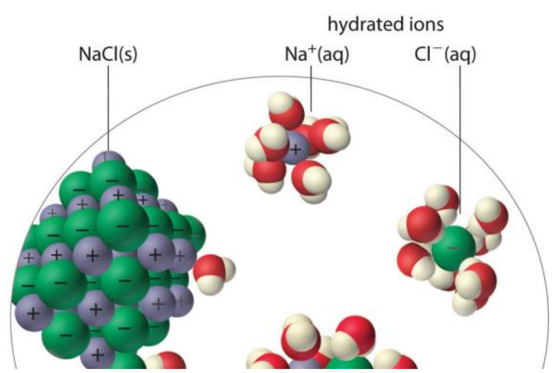
- Some solutions appear to be solutions, but are not (you know because they are not transparent liquids).
- Colloids are solutions of undissolved particles that do not separate over time. Milk is a colloidal mixture because it contains proteins and fats that stick to each other as undissolved particles.
- Blood is considered a suspension. Blood cells will settle in a tube upon standing.
- Particles in a suspension are larger than particles in a colloid.

Suspensions settle

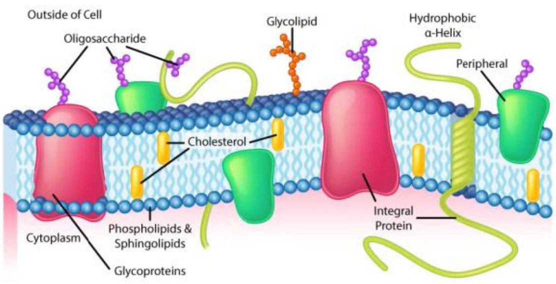
Blood cells can be separated by centrifugation, a spinning process that accelerates settling.



Why does NaCl dissolve in water?



What holds a cell membrane together?



Acids and Bases

- Everyday life includes contact with many acids and bases

- Basic spring in Yellowstone Natl Park

- Stomach is acidic (HCl)

Connections to acid/base topic

- pH refers to the acidity of a solution.

- Amino acids, which are the building blocks of proteins, will change form if the acidity of a solution changes. Proteins change their shape and functionality if the pH of a solution is changed.

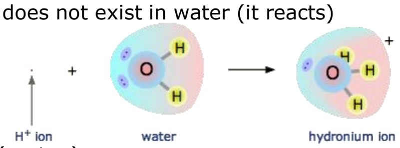
- Our bodily fluids contain compounds that maintain pH. These compounds are called buffers.

Acids and Bases—Definitions

- In the early twentieth century, Brønsted and Lowry redefined acids as a compound that donates a proton (i.e. H^+).

$$HCl\,(g) \xrightarrow{H_2O} H^+\,(aq) + Cl^-\,(aq)$$

- The Brønsted–Lowry definition of a base is a compound that accepts a proton.
- H^+ does not exist in water (it reacts)



(proton)

Acids

Strong acids

ionize completely

$HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$

- In a solution of 1.0 M HCl, there is 1M H^+ and 1M Cl^-
- No HCl is left un-ionized

Sulfuric acid H_2SO_4
Nitric acid HNO_3
Hydrochloric acid HCl

Weak acids

ionize only partially

$HF\ (aq) \rightleftharpoons H^+\ (aq) + F^-\ (aq)$

- You don't know how much HF, H^+ and F^- is present
- Commonly, weak acids are 5% ionized or less

The double arrow indicates that a reaction does not proceed completely to the right

Bases

Strong bases

ionize completely

$NaOH\ (s) \rightarrow Na^+\ (aq) + OH^-\ (aq)$
$Ca(OH)_2 \rightarrow Ca^{2+}\ (aq) + 2\ OH^-\ (aq)$

- In a solution of 1.0 M NaOH, there is 1M Na^+ and 1M OH^-
- No NaOH is left un-ionized

Weak bases

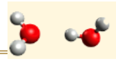
ionize only partially

$NH_{3(aq)} + H_2O \rightleftharpoons NH_4{}^+{}_{(aq)} + OH^-{}_{(aq)}$

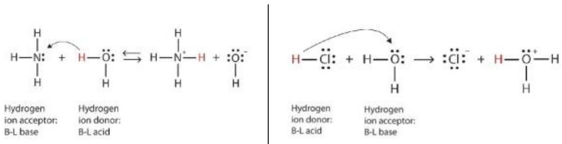
- Commonly, weak bases are 5% ionized or less

The double arrow indicates that a reaction does not proceed completely to the right

Water is both acid and base



- H_2O can gain or lose a proton:



Neutralization

- Strong acids and strong bases both completely dissociate to form ions in water.
- When HCl and NaOH are mixed, sodium ions and chloride ions are present, as well as hydroxide ions and hydronium ions.
- Hydronium and hydroxide ions react to form water molecules.
- Sodium and chloride ions do not react (spectator ions)
- The net equation is:

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2\,H_2O(l)$$

Antacids

- substances that neutralize excess stomach acid.
- Some antacids are bases that are not very soluble in water (slow release as necessary).
- E.g. Aluminum hydroxide and calcium carbonate are examples of antacids that are not very soluble in water.

Chemical Equilibrium

- Weak acids do not dissociate completely, but partially dissociate in an equilibrium reaction
- Here is an example of an equilibrium (not acid/base):

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

reactants equilibrium arrow products

Shifting the equilibrium

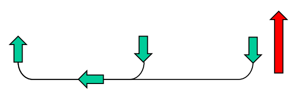
- Reconsider the production of ammonia.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) + \text{heat}$$

- What would happen if more nitrogen was injected in the reaction vessel? Adding or removing species changes the equilibrium.
  If one of the reactants, like H_2, is removed, the reverse reaction will increase faster than the forward reaction, allowing H_2 to be replenished. The equilibrium will shift to the left, forming more of the reactants.
- Changing temperature will change the equilibrium
  The reaction is known as an exothermic reaction (produces heat) as opposed to an endothermic reaction (absorbs heat from the surrounding). Raising the temperature is like adding product.

Le Chatelier's principle

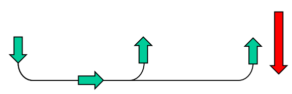
The equilibrium will shift to reverse changes imposed (like changing concentration, temperature etc).



$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Le Chatelier

...the stubborn toddler



$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Concentration

- In chemistry, the most common way to describe how much solute we have in solution is the concentration c

$$c_{solute} = n_{solute} / V_{total}$$

Example: A sodium chloride solution with a concentration of 1 mole / Liter contains 1 mole of NaCl for every liter of the finished solution.

Example: If I need 5 mmol of NaCl, I would dispense 5 ml of this solution.

Solutions in the lab

1) From scratch

Calculate chemical amount of solute you need

Calculate mass of solute you need

Weigh in the solute

Fill up with water to the correct final volume

2) From a more concentrated stock

Calculate volume of stock ($V_{stock} * c_{stock} = V_{dil} * c_{dil}$)

Measure volume of stock

Fill up with water to the final volume

Equilibrium constant

- The relation between reactant and product concentrations is described by the equilibrium constant K
- K is defined as: $K = \dfrac{[\text{products}]_{eq}}{[\text{reactants}]_{eq}}$
- The brackets, [ ], mean "concentration of."
- The expression for K for the generation of ammonia is:

$$K = \frac{{[NH_3]_{eq}}^2}{[N_2]_{eq} \cdot {[H_2]_{eq}}^2}$$

- Why squared and cubed?

Equilibrium constant expression K = ----

Only substances whose concentrations change, i.e. substances in the net reaction, appear in the equilibrium expression.

- Substances like **solids and pure liquids** have constant concentrations, so they do not appear in the expression.
- The **solvent** is assumed to have a constant concentration, so it also does not appear in the expression.

e.g. Water acting as acid and base:

$$H_2O\,(l) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + OH^-\,(aq)$$

pH Scale: how acidic or basic is the solution?

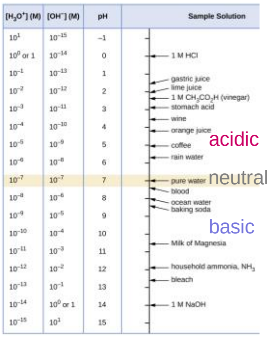
- A measure of the concentration of H+ in water:

$$pH = -\log\left(\frac{[H_3O^+]}{1\ \frac{mol}{L}}\right)$$

- Also a measure of the concentration of OH- in water:

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K = [H_3O^+] \cdot [OH^-] = 1 \times 10^{-14}$$



H^+ and OH^- concentrations at various pH

Solution is	pH	[H3O+]	[OH-]
Basic	> 7	< 10^{-7} M	> 10^{-7} M
Neutral	= 7	= 10^{-7} M	= 10^{-7} M
Acidic	< 7	> 10^{-7} M	< 10^{-7} M

Calculating pH: strong acids and bases

- Calculate the pH of a 0.01 M HCl solution. Because strong acids completely dissociate in solution, [HCl] = [H_3O^+]

- Calculate the pH of a 0.01 M NaOH solution

Weak Acids and Bases

- The principles of equilibrium apply to weak acids and bases because they only partially dissociate into ions.
- The dissociation of acetic acid into acetate ions and hydronium ions is shown as:

$$\mathrm{CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+\,(aq)}$$

- The equilibrium constant expression for this reaction would be:

$$K_A = \frac{[\mathrm{CH_3COO^-}]\cdot[\mathrm{H_3O^+}]}{[\mathrm{CH_3COOH}]}$$

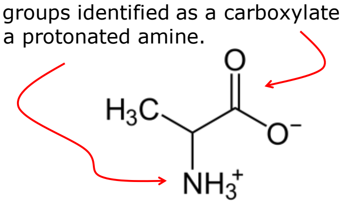
Equilibrium Constant, K_a

Substance or ion	Ka	pKa
Phosphoric acid H3PO4	7.6E-03	2.12
Hydrofluoric acid HF	3.5E-04	3.45
Formic acid HCOOH	1.8E-04	3.75
Lactic acid	1.4E-04	3.85
Acetic acid, CH3COOH	1.8E-05	4.75
Carbonic acid H2CO3	4.3E-07	6.37
Dihydrogen phosphate ion H2PO4-	6.2E-08	7.21
Boric acid	7.2E-10	9.14
Ammonium ion NH4+	5.6E-10	9.25
Phenol	1.3E-10	9.89
Bicarbonate ion HCO3-	5.6E-11	10.25
Hydrogen phosphate ion HPO4(2-)	2.2E-13	12.66

- Weak acids dissociate much less than 100% and have an equilibrium constant called an acid dissociation constant, Ka.
- The strength of a weak acid can be determined from the Ka value. The larger the Ka value, the stronger the acid (the more protons dissociated).

Amino acids: weak acid and base

- The molecule shown below is alanine, with functional groups identified as a carboxylate anion and a protonated amine.



- Alanine belongs to a class of molecules called amino acids, which are the building blocks of proteins.

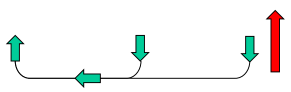
What happens when K_a = [H^+]?

$$K_A = \frac{[\mathrm{CH_3COO^-}]\cdot[\mathrm{H_3O^+}]}{[\mathrm{CH_3COOH}]}$$

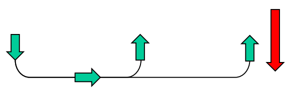
- What is the ratio of acetate to acetic acid?

First, let's see what the ratio is for pH = pKa

pH below or above the pKa

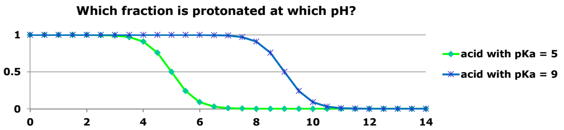


$$\mathrm{CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)}$$



$$\mathrm{CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)}$$

Which species at which pH?

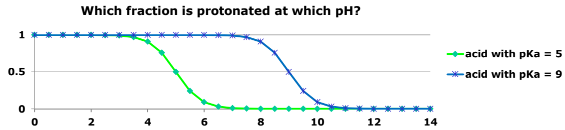


- Example 1: a drug molecule is administered at micromolar concentration. It contains a carboxylic acid group that undergoes the following acid-base equilibrium:

$$RCOOH \rightleftharpoons RCOO^- + H^+ \qquad pK_a = 5$$

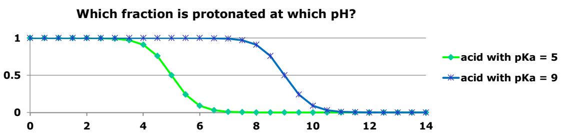
Is the compound charged at pH = 7? At pH = 4?

Weak acid/base as buffer



- Example 2: Equimolar amounts of acetic acid (pKa = 4.5) and its conjugate base, acetate, are mixed in water. What is the pH?

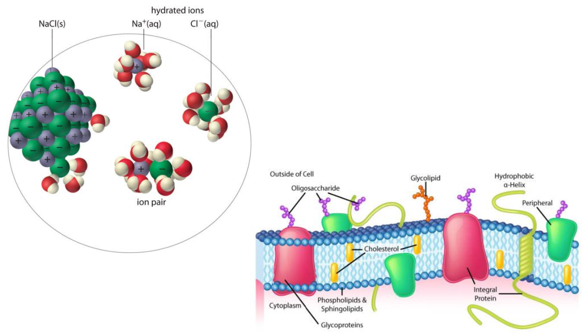
Weak acid/base as buffer



- Example 3: A buffer containing 100 mM acetic acid and 100 mM acetate has a pH of 4.5. What will the pH be if you add HCl to a concentration of 10 mM?

  Compare this to the pH of 10 mM HCl in pure water.

How do molecules and ions interact?

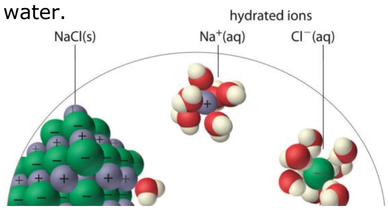


Types of non-covalent interactions

- Intermolecular forces hold two molecules together without forming a covalent bond.
- Ions interact with other ions and with molecules without forming covalent bonds
- Types, from strong to weak:
  - (ion-ion)
  - Ion-dipole
  - Hydrogen bond
  - Dipole-dipole
  - Van der Waals (London)

Ion–Dipole Attraction

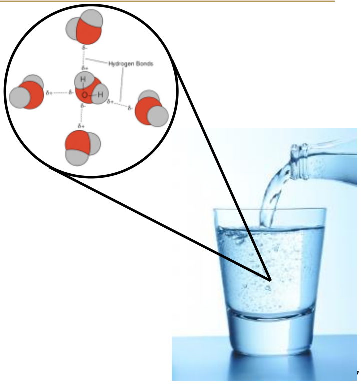
- An ion-dipole attraction is an attraction of an ion to the opposite partial charge on a polar molecule.
- This type of attraction occurs when table salt is dissolved in water. The sodium ion is attracted to the partial negative charge of water, and the chloride ion is attracted to the partial positive charge of water.



Hydrogen Bonding

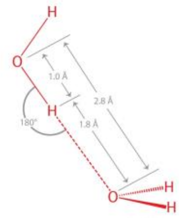
Donor

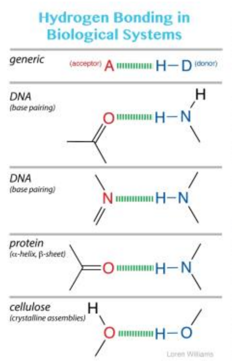
Acceptor



Hydrogen bonds are everywhere

Hydrogen bonding occurs between identical molecules (as seen in water), between two different polar molecules, or even between different parts of the same molecule.





https://ww2.chemistry.gatech.edu/~lw26/structure/molecular_interactions/mol_int.html

Polar molecules without H-bond donors

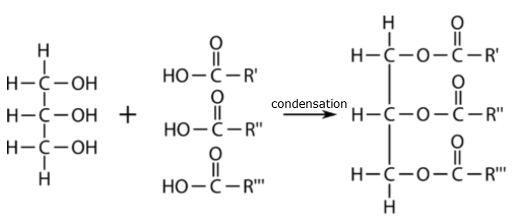
- Dipole–Dipole Attractions
- Dipole–dipole attractions occur between the dipoles of two polar molecules and are caused by the permanent, uneven distribution of electrons, which is caused by the electronegativity differences of atoms in the molecule.

Solubility - The Golden Rule

a.k.a
oil and water don't mix

- The golden rule of solubility—like dissolves like—means that molecules that are similar will dissolve each other.
- Molecules that have similar polarity and participate in the same types of intermolecular forces will dissolve each other.

Oils: Triglycerides of fatty acids

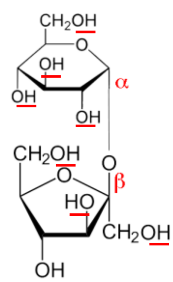


glycerol | 3 fatty acids | triglyceride (triester of glycerol)

polar | less polar | least polar

Solubility of polar compounds

- When table sugar is added to water, it will dissolve. The hydroxyl groups on the sugar molecule make it a polar molecule.
- The hydroxyl groups of sugar interact with water through hydrogen bonding.



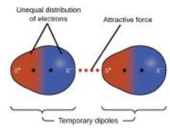
Sucrose

Solubility of ionic Compounds

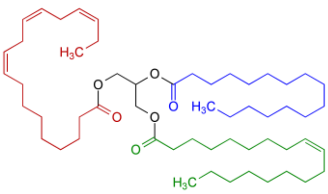
- The ion–dipole attractions between ions of an ionic compound and water are so strong that the ionic bond between ions is disrupted.
- When multiple water molecules interact with an ion, the sum of these attractive forces is greater than the strength of the ionic bonds.
- When an ionic compound, such as sodium chloride, interacts with water, a process known as hydration occurs, during which ions are surrounded by water molecules.

Types of non-covalent interactions

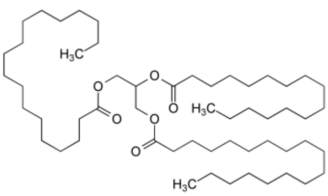
- Intermolecular forces hold two molecules together without forming a covalent bond.
- Ions interact with other ions and with molecules without forming covalent bonds
- Types, from strong to weak:
  - Ion-dipole
  - Hydrogen bond
  - Dipole-dipole
  - Van der Waals (or London or dispersion)



Fats, Oils, and Margarine



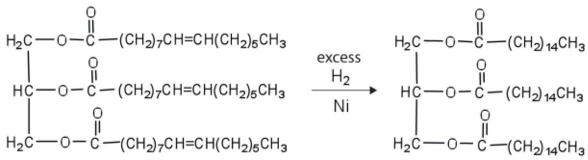
Oils: liquids
Shorter chains,
unsaturated



Fats: solids
Longer chains,
saturated

Fats, Oils, and Margarine—hydrogenation

- Hydrogenation: addition of hydrogen atoms to the double bond of an unsaturated compound.
- Hydrogenation progresses more rapidly if a catalyst is included in the reaction. A ***catalyst*** speeds up a reaction but remains unchanged at the completion of the reaction.



tripalmitin

Fats, Oils, and Margarine—partial hydrogenation

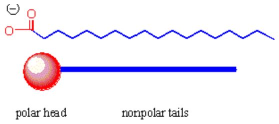
- This controlled process, known as ***partial hydrogenation***, allows production of margarines that are solid yet easier to spread than more solid butter.
- Partial hydrogenation produces margarines that are less saturated than butter, making them easier to spread.
- A consequence of partial hydrogenation is that some of the double bonds are incompletely hydrogenated.

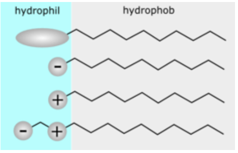
Fats, Oils, and Margarine—trans fats

- Incomplete hydrogenation of double bonds causes the favorable cis configuration of the double bonds to convert to the less favorable trans configuration, resulting in the compounds known as ***trans fats***.
- Some studies have shown that trans fats have deleterious health effects. This led to consideration of alternatives. Food labels must contain the amounts of trans fatty acids present in food.

The Unique Chemistry of Soap

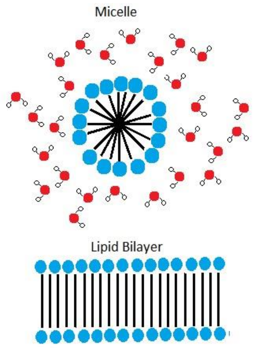
- Soaps ("detergents") are composed of fatty acid salts, which are ionic compounds.
- The charge on the carboxylate group makes this end of the molecule ionic and polar. The remaining part of the molecule is nonpolar.
- Molecules like soap have a polar and nonpolar end and are known as amphipathic compounds.



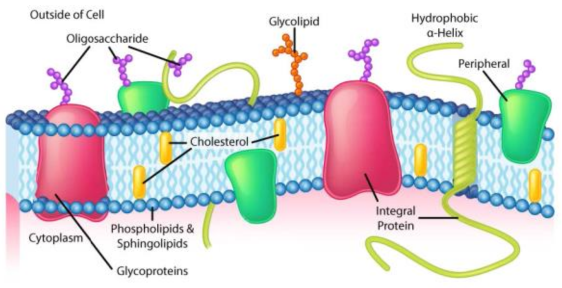


Does soap dissolve in water?

Soap works by trapping grease and dirt, which are nonpolar, in the inner core of the micelle, which then washes it away with water surrounding the outer shell.



Intermolecular Forces and the Cell Membrane



Intermolecular Forces and the Cell Membrane

A Quick Look at Phospholipids

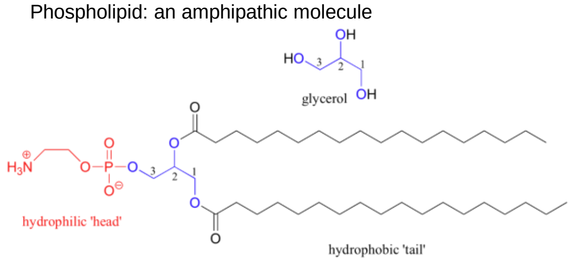
- ***Phospholipids*** are the primary structural components of cell membranes.
- Phospholipids have a glycerol backbone with two fatty acids linked to glycerol through an ester bond. The third OH group of glycerol is linked to a phosphate-containing group instead of a fatty acid.

Intermolecular Forces and the Cell Membrane

- The phosphate-containing group is ionic (polar), which is in contrast to the fatty acid tails (nonpolar).
- Because phospholipids have both a polar and nonpolar part, they are amphipathic.
- The fatty acid tails and phosphate-containing group are arranged as shown on the next slide.

Intermolecular Forces and the Cell Membrane

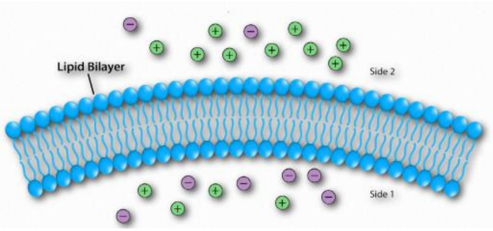
Phospholipid: an amphipathic molecule



cartoon drawing of a membrane lipid

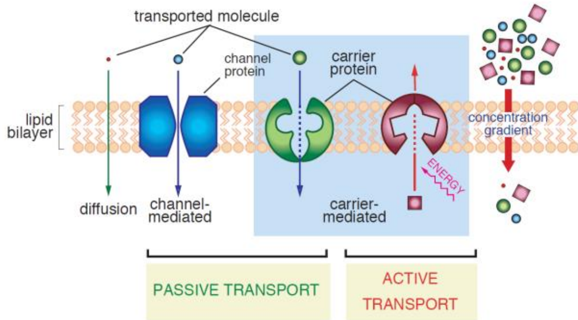
Intermolecular Forces and the Cell Membrane

- The nonpolar tails are oriented toward each other, creating a nonpolar interior region.



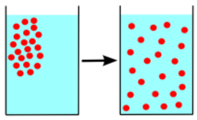
- The phospholipid bilayer is the foundation of the cell membrane.

Transport Across Cell Membranes



Diffusion in the kidneys

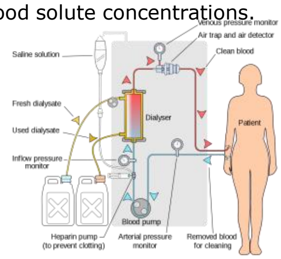
- Here, a drop of red food coloring is added to a beaker of water. Over time, the red dye molecules will diffuse throughout the water, and the resulting solution will have a uniform red color.



- Kidneys act to remove water molecules out of blood through diffusion across the membranes in the kidneys.
- Larger molecules, like proteins, are too large to pass the membrane and get reabsorbed in the blood.

Hemodialysis

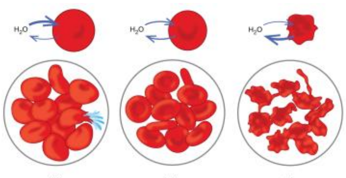
- A person whose kidneys have failed can undergo artificial dialysis called hemodialysis.
- Blood passes through one side of a semipermeable membrane in contact on the opposite side with a dialyzing solution that is isotonic with normal blood solute concentrations.



Osmosis in action

Food and fun:
Pickles, bears

Life and death:
IV fluids isotonic?



Reverse osmosis