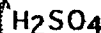
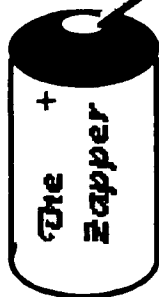


Solution Chemistry



Riddle: What did the saturated solution say to the traveling solute salesman?

Electrochemistry....
shocking, isn't it!!!



Solution: No thanks, I'm already full.

Eureka!!! I finally
understand chemistry!!



Unit 11

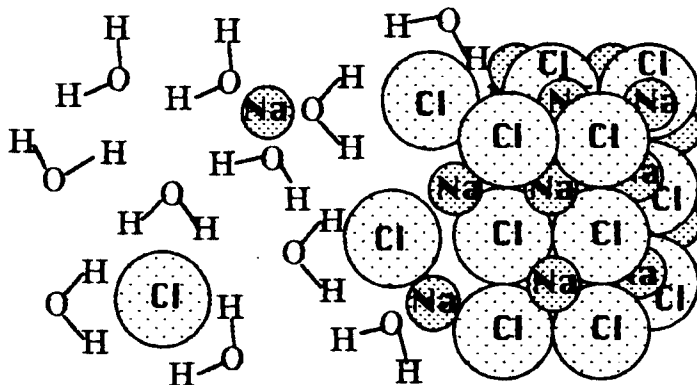
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Unit 11: Solution Chemistry

I. The Dissolving Process Making Solutions

When two materials that have similar attractive forces are combined, they will mix together to form a solution. *Remember:* "Like dissolves like." The substance present in the greater quantity is called the **solvent**. The substance present in the lesser quantity is called the **solute**.

When a polar or ionic solid is added to water, the forces of attraction between the solute and solvent break the solid down piece by piece. Each positive and negative ion becomes completely surrounded by the water molecules. The rate of dissolving can be increased by stirring, reducing the particle size of the solute or heating the mixture.



The dissolving process, like most other physical and chemical changes, is much more complex than it appears to be based on the balanced chemical equations. Usually, a series of steps, called a **reaction mechanism**, is required to convert the reactants into the products. Consider the dissolving of the NaCl above. First of all, energy is required to break the strong ionic bonds between the Na^{1+} ions and the Cl^{1-} ions in the solid crystal. Energy is also needed to break the extensive hydrogen bonding that occurs between the water molecules. Finally, energy is released when the ion-dipole attractions form between the $\text{Na}^{1+}/\text{Cl}^{1-}$ ions with the water molecules to make the final solution. How fast the overall reaction occurs is limited by the slowest individual reaction, called the **rate-determining step**.

Factors Affecting Reaction Rates

1. *Nature of the Reactants* - particles in the reactants must collide together at the proper orientation and with sufficient energy in order to react. The nature of the reactants determines the effectiveness of the collisions in producing the products.
2. *Temperature*- as the temperature increases, the particles move faster, resulting in more collisions that are effective in producing products. As a general rule, for every 10°C increase in temperature, the reaction rate approximately doubles.
3. *Concentration* - increasing the concentrations of the reactants results in more collisions between the particles, which increases the probability of forming products.
4. *Surface Area*- a larger surface area produces more contact between the solute and solvent particles, resulting in a higher frequency of collisions.
5. *Adding a Catalyst* - a catalyst is a substance that increases the rate of the reaction without itself being consumed by the reaction. They combine with the reactants to produce a more reactive intermediate product, which provides a different reaction mechanism requiring less activation energy to occur. For example, your car's catalytic converter contains rhodium and platinum metals, which speed up the conversion of harmful $\text{CO}(\text{g})$ into $\text{CO}_2(\text{g})$ and helps break down nitrogen oxide pollutants into their elements.

Problem:

You have just been hired by a large food production company to make the base mixture for gravy by dissolving corn starch (a polymer made of glucose molecules) in distilled water. Describe the procedures you would use to make as much of the mixture as possible in the least amount of time, given a silo filled with corn on the cob.

II. Solutions, Suspensions, and Colloids

Not all substances will form a true solution with water. For example, after a heavy rain, dirt and silt will mix with the water in a stream to form a muddy, temporary **suspension** of particles. The suspended particles are much larger than the water molecules, and quickly settle out to form a heterogeneous mixture. When the particle size of the solute has a range from 10^{-7} cm to 10^{-4} cm, the particles are too large to completely disappear, like in a true solution, but too small to settle out. Instead, they remain permanently suspended by the constant bombardment of the water molecules, forming a mixture called a **colloid**. The surface charges on the colloidal particles keep them apart and prevent the particles from settling out.

Colloids can be produced by mixtures of the same phase of solute and solvent, or different phase materials. *Fog* and *smoke* (sometimes called aerosols) consist of colloidal-sized liquid droplets or solid particles suspended in air. *Foams* are a dispersion of gas bubbles in a solid or liquid, such as in shaving cream. Usually a substance called a **surfactant** is added to foams to coat the surface of the gas bubbles and make them stable in their surrounding environment. Colloidal solids dispersed in a liquid, as in toothpaste or paints, form *sols*. Solid-in-solid photographic film and liquid-in-liquid mayonnaise are examples of *emulsions*. The mayonnaise actually contains a mixture of oil, water and vinegar that is stabilized by adding egg white. Semi-rigid materials that are mostly solid with some liquid molecules dispersed throughout are called *gels*.

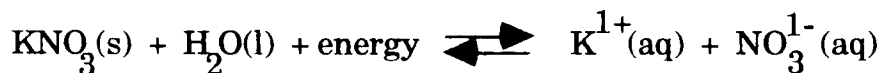
There are 2 experimental methods that can be used to determine if a mixture is a colloid or not. If a beam of light is passed through a colloid, the light will be scattered by the larger particle size (this is known as the *Tyndall Effect*), such as when your car's headlight beams are scattered by water droplets in fog. In a solution, the particles are so small that the light passes directly through it with little or no deflection. As a second test, filter the mixture using a membrane with very small pores, such as a plastic sandwich bag or dialysis tubing. The atomic or ionic particles of the solution will slowly diffuse through the membrane and out of the baggie, but the larger colloidal particles will remain trapped inside the membrane walls.

Problems:

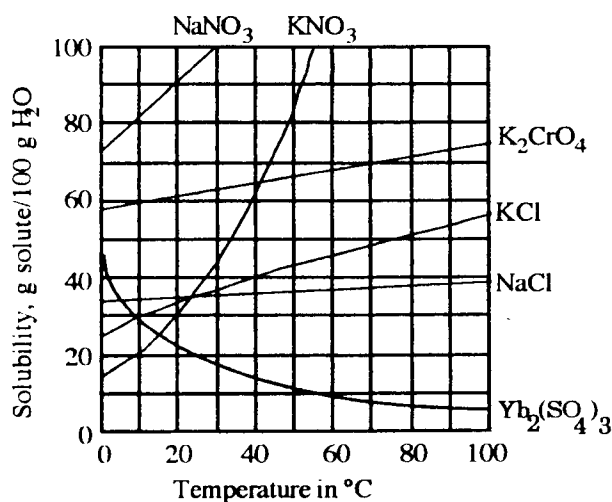
1. Explain how you could determine whether a solution, a suspension or a colloid is produced after mixing a solute and a solvent together in the lab.
2. Describe how you could separate and recover the components in a mixture consisting of a suspension of clay particles, a solution of NaCl and a colloidal dispersion of starch.

III. Solution Equilibrium

The most common type of solutions involve a solid solute dissolving in water as the solvent. Energy is required to separate both the solute particles and water molecules from each other, then energy is released when bonds are reformed between the solute and solvent particles. In most cases, the net process is an endothermic reaction which can be written as an equilibrium equation. For saturated $\text{KNO}_3(\text{aq})$, the equation is:



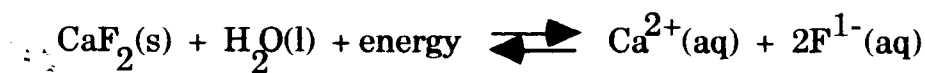
A solubility curve provides a summary of the maximum amount of solid that will dissolve in a given amount of water at various temperatures. For example, a maximum of 90 g of sodium nitrate will dissolve in 100 g of water at 20°C . This solution is said to be **saturated** because the rate of dissolving is equal to the rate of crystallization. If the temperature is increased to 30°C , the solution becomes **unsaturated** since an additional 10 g of NaNO_3 can be dissolved at this higher temperature. If the temperature is cooled down to 0°C , then only 73 g will remain dissolved. The 17 g of excess solute will usually crystallize and precipitate out. Sometimes the excess remains dissolved, forming an unstable, **supersaturated** solution. Any disturbance or addition of a "seed crystal" of the solute will cause the excess to precipitate out of this type of solution.



Problems:

- State whether the following solutions would be saturated, unsaturated or supersaturated.
 - 75 g of K_2CrO_4 dissolved in 100 g of water at 70°C
 - 100 g of KNO_3 dissolved in 100 g of water at 55°C
 - 10 g of NaCl dissolved in 25 g of water at 40°C
- Which compound is *least* soluble in water at 0°C ? at 100°C ?
- How many grams of KCl will precipitate out if a saturated solution is cooled from 100°C to 0°C ?
- How much additional KNO_3 can be dissolved if a saturated solution at 10°C is heated to 50°C ?
- What happens when a saturated solution of $\text{Yb}_2(\text{SO}_4)_3$ at 0°C is heated to 60°C ?

For compounds that are only slightly soluble in water (less than 1 g dissolves per 100 g of water), a different method is used to determine the amount of solute that will dissolve. There is a definite ratio between the concentrations of the ions produced and the concentrations of the solute and solvent reactants. This ratio is called the **equilibrium constant, K_{eq}** , and its value is mathematically calculated by multiplying together the molar concentrations of the products, each concentration being raised to a power equal to its coefficient in the balanced equation, then dividing by the concentrations of the reactants raised to their appropriate exponents. For saturated calcium fluoride:



$$K_{\text{eq}} = \frac{[\text{Ca}^{2+}(\text{aq})][\text{F}^{1-}(\text{aq})]^2}{[\text{CaF}_2(\text{s})][\text{H}_2\text{O}(\text{l})]}, \text{ where the } [] \text{ indicate molarity}$$

Since the concentration of a pure solid or liquid is based only on the density of the substance and remains relatively constant, the concentrations of the $[\text{CaF}_2(\text{s})]$ and $[\text{H}_2\text{O}(\text{l})]$ will not change. These values are combined with the K_{eq} value to obtain a unified constant called the **solubility-product constant, K_{sp}** .

$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{F}^{1-}(\text{aq})]^2$$

When a specific volume of saturated $\text{CaF}_2(\text{aq})$ is evaporated to dryness, the molarity of the solution can be calculated, knowing the mass of solid remaining. At 25°C , 2.14×10^{-4} moles of $\text{CaF}_2(\text{s})$ will dissolve per liter of water. Based on the balanced chemical equation for the dissolving process, the molarity of Ca^{2+} ions will also be $2.14 \times 10^{-4} \text{ M}$ and the molarity of the F^{1-} ions will be double this amount, with a value of $4.28 \times 10^{-4} \text{ M}$. Therefore, the K_{sp} value equals.....

$$[2.14 \times 10^{-4} \text{ M Ca}^{2+}][4.28 \times 10^{-4} \text{ M F}^{1-}]^2 = 3.92 \times 10^{-11}$$

If the ion product of $[\text{Ca}^{2+}][\text{F}^{1-}]^2$ in an experiment has a value *less than* this K_{sp} value, then the solution will be unsaturated. If the ion product is *greater than* the K_{sp} value, then a precipitate will form from the excess CaF_2 .

When comparing compounds that dissolve to form the same number of moles of ions, the greater the K_{sp} value the more soluble the solid will be. For example, one mole of the CaF_2 breaks down to form a total of 3 moles of ions. Barium fluoride, BaF_2 , also forms 3 moles of ions, but since its K_{sp} value of 1.7×10^{-6} is larger, more moles of BaF_2 will dissolve. On the other hand, Ag_2S with a K_{sp} value of 1.6×10^{-49} is much less soluble than either the CaF_2 or BaF_2 .

Problems:

1. Calculate the experimental K_{sp} value for PbI_2 , if 1.28 g of the solid remains after a liter of saturated solution is evaporated to dryness.

ANS: 8.5×10^{-8}

2. The K_{sp} value for BaCO_3 is 4.9×10^{-9} at 25°C . How many grams of BaCO_3 will be dissolved in a liter of this solution?

ANS: 0.014 g BaCO_3

3. Will a precipitate form when 20.0 mL of 0.010 M $\text{BaCl}_2(\text{aq})$ are mixed with 20.0 mL of 0.0050 M $\text{Na}_2\text{SO}_4(\text{aq})$, if the K_{sp} value for $\text{BaSO}_4(\text{s})$ is 1.6×10^{-9} ?

ANS: yes, the experimental $K_{\text{sp}} = 1.25 \times 10^{-5}$
which is > the accepted K_{sp} value

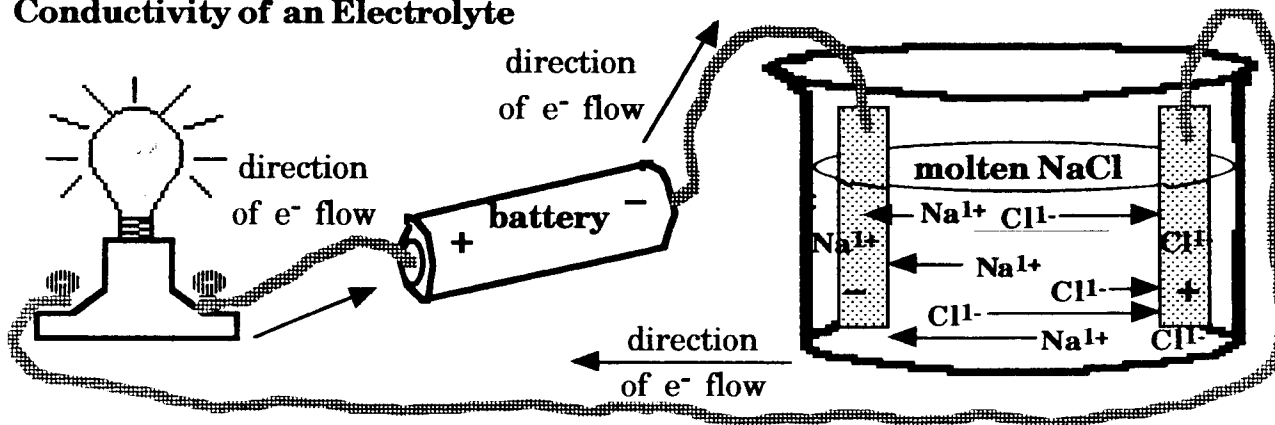
IV. Colligative Properties

You may have noticed on the vapor pressure curve in the last study guide that the 5 molal (5 *m*) solution of NaCl(aq) caused an elevation in the boiling point of pure water as the solvent. This is due to the increased attractive forces resulting from ion-dipole attractions between the Na¹⁺ ions and Cl¹⁻ ions with the polar water molecules. The presence of these ions at the surface of the solution also reduces the number of water molecules at the surface, thereby slowing the evaporation rate. This elevation of the boiling point of water by the addition of a solute is called a **colligative property** of the solution. The greater the concentration of particles of a nonvolatile solute in the solution, the greater the reduction in the solvent's vapor pressure, and the higher the temperature needed to boil the solution.

Mathematically, the amount of boiling point elevation equals the molality of the solution (defined as the #moles of solute particles / #kg of solvent) times a constant, called the molal boiling point constant, K_b . For water, the K_b value is equal to 0.51°C / molal concentration of particles. $\Delta T_b = K_b m$

The 5 *m* NaCl(aq) actually contains 10 moles of ions / kg of water (5 moles of Na¹⁺ ions and 5 moles of Cl¹⁻ ions). $\Delta T_b = (0.51^\circ\text{C} / m) (10 \text{ molal ion concentration}) = 5.1^\circ\text{C}$ Water's normal boiling point of 100°C is elevated by 5.1°C (to 105.1°C) for the 5 *m* NaCl solution. If a 5 *m* AlCl₃(aq) solution is prepared, the boiling temperature would be elevated by 10.2°C. This is because the 5 moles of aluminum chloride ionizes in water to form twice as many ions as the sodium chloride does (5 moles of Al³⁺ ions and 15 moles of Cl¹⁻ ions). Both the NaCl and the AlCl₃ solutions are called **electrolytes**, because the ions in solution (or in molten form) allow it to be a conductor of electricity.

Conductivity of an Electrolyte



The battery in the diagram above produces a flow of electrons that travel from its negative terminal to the electrode inside of the molten NaCl. This electrode obtains a build-up of negative charge from these excess electrons, and the positive Na¹⁺ ions are attracted to it. The sodium ions will undergo reduction (gain electrons) in the presence of the excess electrons, and reform the metallic atoms: $\text{Na}^{1+} + e^- \rightarrow \text{Na}^0$

Due to the chemical reaction within the battery, the positive terminal acts like an electron vacuum cleaner, trying to suck up electrons from the other electrode inside of the molten NaCl. As electrons are lost from this electrode, it becomes positively charged and begins to attract the negative Cl¹⁻ ions. These chloride ions will be oxidized (lose electrons) to reform chlorine atoms, which quickly combine to make diatomic molecules: $2\text{Cl}^{1-} \rightarrow \text{Cl}_2^0 + 2e^-$. This also completes the electrical circuit making the light bulb glow brightly.

A molecular solute, such as sucrose(table sugar), $C_{12}H_{22}O_{11}$, will not break down into ions when it dissolves in water. Therefore, a 5 *m* sucrose solution will produce 5 moles of sucrose molecules / kg of water. The boiling point would only be elevated by 2.5°C, based on $\Delta T_b = (0.51^\circ C / m) (5 \text{ molal molecule concentration})$. Molecular solutes, such as sucrose, produce a solution that is a **nonelectrolyte**, because without the presence of charged ions in the solution, it is not capable of conducting electricity.

The solvent's freezing point is also effected by the addition of a solute, but the temperature is lowered. As an example, consider how an icy sidewalk in winter can be made passable by sprinkling salt on it to melt the ice. When a liquid begins to freeze, the particles in the solid arrange themselves in an orderly pattern. Any solute particles that are present in the solution disrupts this orderly pattern. Therefore, more kinetic energy must be removed from the solution before the pure solvent begins to solidify. This is called the molal freezing point depression, and for water, the K_f value is equal to $1.86^\circ C / \text{molal concentration of particles}$. $\Delta T_f = K_f m$

Problems:

1. What would be the normal boiling point of a 5.0 *m* solution of the strong electrolyte, potassium sulfate (K_2SO_4), at standard pressure conditions?

ANS: $107.65^\circ C$

2. 1,2-ethanediol(commonly called ethylene glycol) is the main component found in the antifreeze you add to your car's radiator. If a typical antifreeze mixture contains 1.5 kg of the nonelectrolyte, $C_2H_4(OH)_2$, with 1.5 kg of water, then what is the temperature range to which your car is protected from freezing or boiling over?

ANS: $-30^\circ C$ to $108^\circ C$

3. Acetic acid, $HC_2H_3O_2$, found in vinegar is said to be a weak electrolyte because it only partially ionizes to form H^{1+} and $C_2H_3O_2^{1-}$ in solution. What is the molality(*m*) of the solute particles if the freezing point of a brand of vinegar is $-0.248^\circ C$?

ANS: 0.13 *m*

V. Acids and Bases An Equilibrium Between H^{1+} and OH^{1-} Ions in Solution

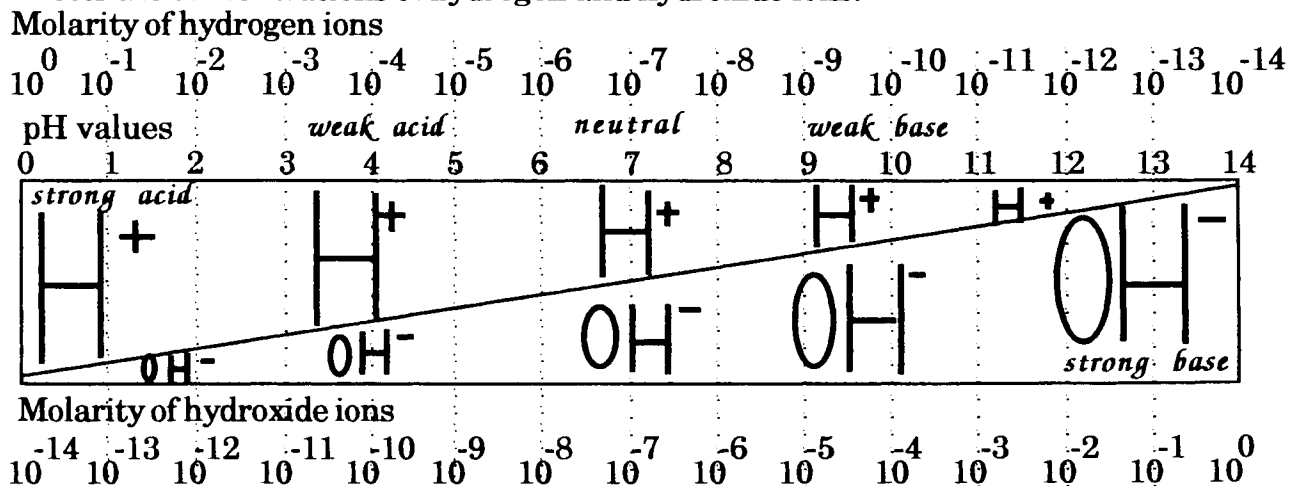
Based on electrical conductivity experiments, chemists have determined that in pure distilled water at room temperature($25^\circ C$), only 1 out of every 10,000,000 molecules breaks apart to form an H^{1+} ion and an OH^{1-} ion. Since water is a neutral solution, both ions have the same concentration of $1.0 \times 10^{-7} M$. This reaction is an equilibrium system and can be expressed as:

$$K_{eq} = \frac{[H^{1+}(aq)][OH^{1-}(aq)]}{[H_2O(l)]}$$

Since the concentration of water remains basically constant, the K_{eq} and $[H_2O]$ can be combined to form a new constant, K_w

$$K_w = [H^{1+}(aq)][OH^{1-}(aq)] = [1.0 \times 10^{-7} M H^{1+}(aq)][1.0 \times 10^{-7} M OH^{1-}(aq)] = 1.0 \times 10^{-14}$$

The **pH scale** indicates the concentration(molarity) of H^{1+} ions(or H_3O^{1+}) in solution. The H^{1+} ion will usually bond to a water molecule to form a hydronium ion, written as H_3O^{1+} . By definition, $pH = -\log[H^{1+}]$. In comparison, the $pOH = -\log[OH^{1-}]$. Therefore, the $pH + pOH = 14$. Another way of mathematically expressing the pH scale relationship is: $[H^{1+}] = 10^{-pH}$. The following chart summarizes how the pH scale reflects the concentrations of hydrogen and hydroxide ions:



An **acid** is a substance that will increase the concentration of H^{1+} ions in solution, so the pH is less than 7. As the concentration of the H^{1+} ions in solution increases when an acid dissolves, the concentration of the OH^{1-} ions decreases proportionately. Acids are usually a water(aqueous) solution of a compound that contains one or more hydrogen atoms that are bonded to either a nonmetal or a negatively charged, polyatomic ion, such as HCl, HNO_3 , and H_2SO_4 . **Acid rain** is caused by the reaction between water molecules in the atmosphere with $SO_2(g)$, $CO_2(g)$ and $NO_x(g)$ pollutants formed by the combustion of fossil fuels and internal combustion engines(automobiles). Nonmetal oxides combine with water to form acids.

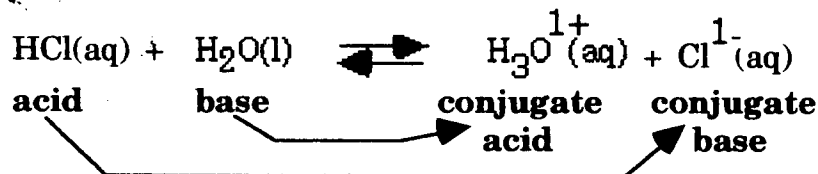
Characteristic properties of acid solutions include being conductors of electricity, having a sour taste, reacting with metals to release $H_2(g)$, reacting with carbonates to release $CO_2(g)$, neutralizing bases by forming a salt and water, and effecting the color of indicator dyes (turns litmus paper red and phenolphthalein colorless).

A **base** is a substance that can accept a proton, H^{1+} , from an acid. They increase the hydroxide(OH^{1-}) ion concentration in water solutions, and usually are compounds that contains one or more hydroxide ions that are bonded to a metal, such as NaOH and $Al(OH)_3$. However, not all basic substances will contain the hydroxide ion. As example, ammonia (NH_3) is classified as a base because it will chemically react with acids by accepting their proton to form the ammonium ion, NH_4^{1+} . Also, metal oxides will react with water to form basic solutions, such as $CaO + H_2O \rightarrow Ca(OH)_2$. For this reason, metal oxides are sometimes called *basic anhydrides*, meaning "bases without water".

Characteristic properties of basic solutions include conducting electricity, having a bitter taste, feeling slippery, reacting with fats and vegetable oils to make soap, neutralizing acids to form a salt and water, and effecting the color of indicator dyes (turns litmus paper blue and phenolphthalein pink).

Whenever an acid loses its proton, the substance remaining is called a conjugate base. The original reacting base that gains the proton forms a new conjugate acid. For

example, strong hydrochloric acid ionizes almost completely in water to form the hydronium and chloride ions show below:



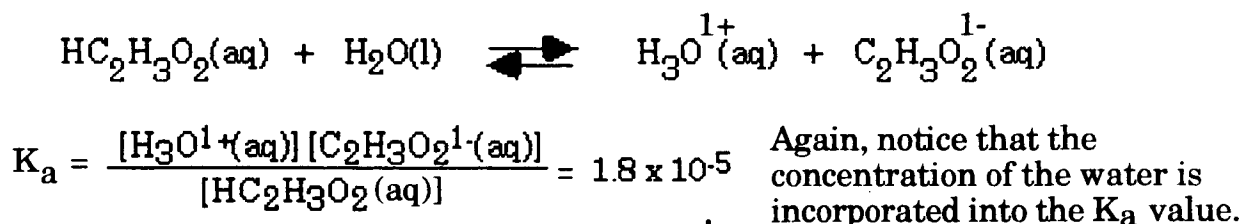
The $\text{Cl}^{1-}(\text{aq})$ formed is a very weak base because it is unlikely that it will regain a proton to form HCl. The stronger the reacting acid or base, the weaker its conjugate counterpart formed as a product. A **buffer** is a solution that consists of a weak acid and its conjugate base, so that it resists changes in pH even when other acids or bases are added. In your blood, the presence of the weak acid, H_2CO_3 , and its conjugate base, HCO_3^{1-} , work together to either donate or accept protons to help maintain the pH between 7.35 and 7.45. A pH outside of this range could cause illness or death.

Problems:

1. What is the hydrogen ion concentration in a 0.0001 M NaOH solution? What is the pH of this solution?
2. How many more hydrogen ions are present in a solution of hydrochloric acid with a pH of 1 as compared to the acetic acid(also known as ethanoic acid) in vinegar that has a pH of 3?

VI. Measuring the Strength of Acids and Bases

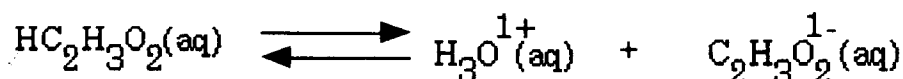
The pH scale is one indicator of the strength of acids and bases. A second gauge of strength is the degree of ionization of acids and bases, which determines how well they conduct electricity when dissolved in water. The better the conductivity, the stronger the acid or base. Strong acids, such as HCl, HNO_3 , and H_2SO_4 , ionize completely in water. Weak acids, such as organic acids containing the $-\text{COOH}$ group, only partially ionize and are considered to be weak electrolytes(semi-conductors). A third indicator is the K_a and K_b values represent the equilibrium constants for weak acids and bases. For example, the acetic acid in vinegar ionizes in water according to the following equation:



In general terms, the relative size of the K_a or K_b values can be used to rank order a list of acids / bases by relative strength. The acetic acid will be a stronger acid than carbonic acid, H_2CO_3 , with a K_a value of 4.4×10^{-7} when it donates one proton, but it is weaker than hydrofluoric acid, HF, which has a K_a value of 6.6×10^{-4} .

More specifically, the K_a or K_b value can be used to determine the approximate pH of a solution, such as the 1.0 M acetic acid used to make commercial vinegar sold in your local grocery store. Set up an "ICE" chart like the one on the next page to show the

Initial concentrations, Change in concentrations, and Equilibrium concentrations of the reactants and products used to calculate the K_a value.



Initial	1.0 M	0	0
Change	- x M	+ x M	+ x M
Equilibrium	(1.0 - x) M	x M	x M

Substitute the Equilibrium values into the K_a expression and solve for x .

For weak acids and bases, it can be assumed that the x value is small compared to the initial concentration of the solution. Therefore, only a small fraction of the 1.0 M acetic acid will ionize, and you can ignore subtracting the x value in the denominator.

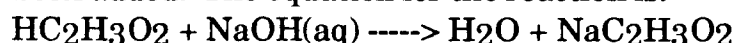
$$K_a \text{ of acetic acid} = 1.8 \times 10^{-5} = \frac{[x \text{ M}][x \text{ M}]}{[1.0 \text{ M}]}$$

$$x^2 = (1.0)(1.8 \times 10^{-5}) \quad \therefore x = \sqrt{1.8 \times 10^{-5}} = 4.2 \times 10^{-3} \text{ M}$$

The pH of the acid is between 2 and 3 ($\text{pH} = -\log[\text{H}_3\text{O}^{1+}(\text{aq})] = -\log(4.2 \times 10^{-3} \text{ M}) = 2.4$)

A fourth method to determine the strength of an acid or base is by **titration**. This experimental technique uses stoichiometry to determine the unknown concentration of a solution when mixed with a specific amount of another solution having a known concentration. When an acid reacts with a base, water and salt are formed as the products during what is called a *neutralization reaction*.

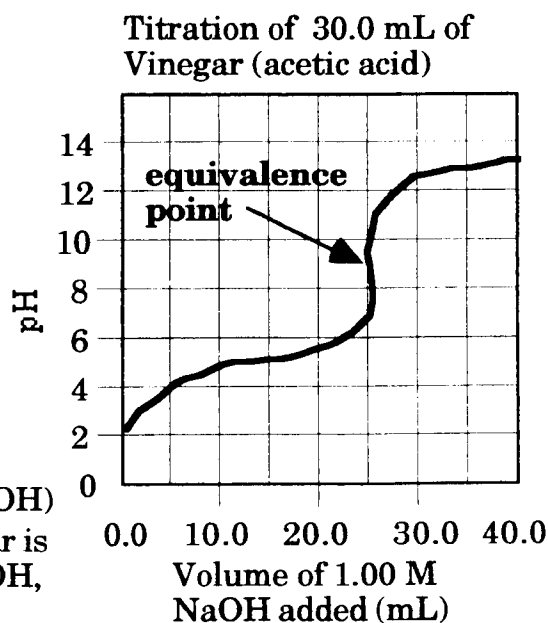
The graph at the right shows the results of the titration of 30.0 mL of the acetic acid in vinegar with a 1.00 M NaOH solution. The initial pH of the acetic acid is just above 2. It slowly rises as more NaOH is added, until a point where the correct stoichiometric proportions are achieved and the pH jumps dramatically. This is called the equivalence point, which occurs after 25 mL of NaOH has been added. The equation for the reaction is:



Since 1 mole of acid is needed to neutralize 1 mole of the base, $(M_{\text{acid}})(\text{mL}_{\text{acid}}) = (M_{\text{base}})(\text{mL}_{\text{base}})$.

$$(M_{\text{acid}})(30.0 \text{ mL acid}) = (1.00 \text{ M NaOH})(25 \text{ mL NaOH})$$

Therefore, the molarity of the acetic acid in vinegar is 0.83 M. In the presence of a strong base, like NaOH, the acetic acid ionizes almost completely.



Problems:

1. What is the K_a value of $\text{HClO}(\text{aq})$ if a 0.345 M solution has a pH of 4.0?

$$\text{ANS: } K_a = 2.9 \times 10^{-8}$$

2. How many mL of 0.00050 M NaOH would be needed to reach the neutralization point (equivalence point) when titrated with 25 mL of 0.0010 M H_2SO_4 ?

$$\text{ANS: } 100 \text{ mL}$$

VII. Electrochemistry.....Putting Electrons to Work

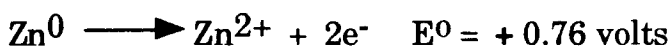
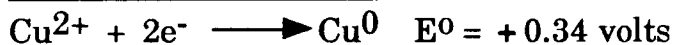
Any time that two chemicals are mixed together, there is a competition for electrons. One substance ultimately has a stronger attraction for the electrons than the other, and a transfer of electrons takes place to some degree. Chemists have developed a scale to compare the tendency of a substance to gain electrons relative to the H^{1+} ions in acids. This scale is called the **reduction potential**, symbolized by E^0 , which is measured in volts when using 1 M aqueous solutions at 25°C and 101.3 kPa. The reduction half-reactions and E^0 values for a few substances are listed below:

	Reduction Half-Reaction	E^0 (volts)
decreasing tendency to gain electrons ↓	$F_2(g) + 2e^- \longrightarrow 2F^{1-}$	+2.87
	$O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.23
	$Cu^{2+} + 2e^- \longrightarrow Cu^0$	+0.34
	$2H^{1+} + 2e^- \longrightarrow H_2(g)$	+0.00
	$Fe^{2+} + 2e^- \longrightarrow Fe^0$	-0.44
	$Zn^{2+} + 2e^- \longrightarrow Zn^0$	-0.76
	$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^{1-}$	-0.83
	$Li^{1+} + 1e^- \longrightarrow Li^0$	-3.00

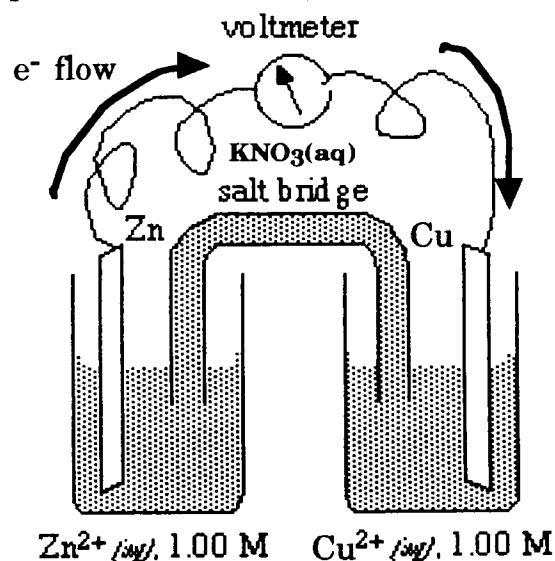
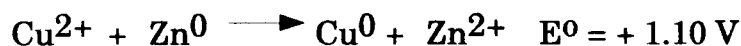
An electrochemical cell is a system that forces the transfer of electrons between an oxidized and reduced substance to travel through an external circuit and perform some useful work. It consists of two half-cells connected together by a semi-porous barrier, called a salt bridge, that is saturated with a strong electrolyte solution. Each half-cell consists of an electrode(usually a metal) and a solution of the metallic ions. The electrode at which oxidation occurs is called the *anode*, and reduction occurs at the *cathode*. The half-reaction with the lower reduction potential will undergo oxidation.

Examine the diagram of the zinc-copper cell at the right. The Cu^{2+} will be reduced because it has a greater reduction potential. The zinc reaction should be reversed and the Zn^0 will be oxidized. Change the E^0 for the zinc to + 0.76 V.

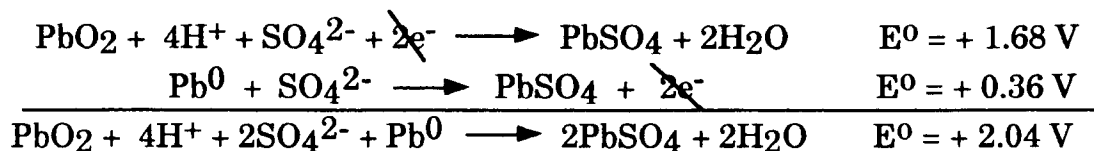
Half-Reaction Potentials



The net reaction will be:



The strength of an electrochemical cell is determined by the difference in the reduction potentials of the two half-cells, which is an intensive property. The voltage remains the same, regardless of the number of moles of reactants used. Based on the given half-reactions in the chart, the strongest cell would be made by combining fluorine gas and lithium metal to produce + 5.87 volts. A battery consists of two or more electrochemical cells which are connected together in series to produce a combined voltage output. The lead storage battery in your car is made of six of the cells below to generate 12 volts:



The direction of electron flow in any electrochemical cell can be reversed by adding a greater voltage input in the opposite direction. While driving, your car's electric generator (the alternator) temporarily recharges the battery by reversing the spontaneous reaction to reform the lead metal electrodes and replenish the PbO₂ and sulfuric acid ions. As soon as the car's engine is turned off, the battery starts to lose some of its energy again.

The use of electricity to cause a nonspontaneous reaction to occur is called **electrolysis**. Recharging the car's battery or forming elemental sodium and chlorine from molten NaCl are examples of this process. Chemists also use electrolysis to deposit a thin coating of a metal on top of an object during *electroplating*. This can be done for decorative purposes, as in silver plating of kitchen spoons, or to prevent corrosion (oxidation) of a metal, such as zinc-coated (galvanized) iron nails. An external power source is used to make the object to be coated the cathode with excess electrons. The object is then placed in an ionic solution of the metal to be used as the coating. The metallic ions in solution regain their electrons and are deposited onto the surface of the object.

Problems:

1. Write the half-reactions for a copper-lithium electrochemical cell and determine the voltage of the cell.

ANS: $E^\circ = + 3.34 \text{ V}$

2. Fuel cells are used on the space shuttle to provide both electricity and water. It is an electrochemical cell that is constantly being supplied with H₂(g) and O₂(g) in a basic solution of KOH. The reduction reaction is O₂(g) + 2H₂O + 4e⁻ → 4OH¹⁻(aq) with an E⁰ = + 0.40 V. The oxidation reaction is 2H₂(g) + 4OH¹⁻(aq) → 4H₂O + 4e⁻(aq) with an E⁰ = + 0.83 V. Write the net equation for the cell and calculate the voltage.

ANS: $E^\circ = + 1.23 \text{ V}$

3. When lithium metal reacts with water it forms hydrogen gas and a solution of lithium hydroxide. Write the oxidation and reduction half-reactions, the net equation for the cell, and calculate the voltage produced by the reaction.

ANS: $E^\circ = + 2.17 \text{ V}$

Unit 11 Objectives:

Having studied the unit notes and done the problems, you should be able to:

1. Describe the steps and energy changes involved when a solute dissolves in a solvent.
2. Explain what factors will effect the rate of dissolving of a solute.
3. Describe the differences between solutions, suspensions and colloids.
4. Interpret a solubility graph of the relationship between solubility and temperature to determine if a solution is unsaturated, saturated, or supersaturated.
5. Use the solubility product constant (K_{sp}) to determine ion concentrations and to predict if chemical precipitation occurs.
6. Describe the effects that a solute has on the properties of the solvent.
7. Distinguish between an electrolyte and a nonelectrolyte.
8. Express the concentrations of a solution in terms of molarity and molality.
9. Calculate the boiling point elevation and freezing point depression of a solution.
10. Identify substances as acids or bases and list the common properties of each.
11. Write an equation for the reaction of an acid and a base, and identify the conjugate acid and conjugate base pairs that are formed.
12. Describe how a buffer maintains a constant pH, even with the addition of strong acids or bases.
13. Determine the concentrations of the hydronium and hydroxide ions in solutions and use these values to calculate the pH and pOH of a solution.
14. Determine the strength of a weak acid or base from the K_a or K_b values.
15. From a titration experiment, determine the strength of an unknown acid or base.
16. Write equations for the neutralization reaction between acids and bases.
17. Describe and diagram the components of an electrochemical cell.
18. Calculate the voltage of an electrochemical cell from the half-cell reduction potentials.
19. Describe the processes of electrolysis and electroplating.