

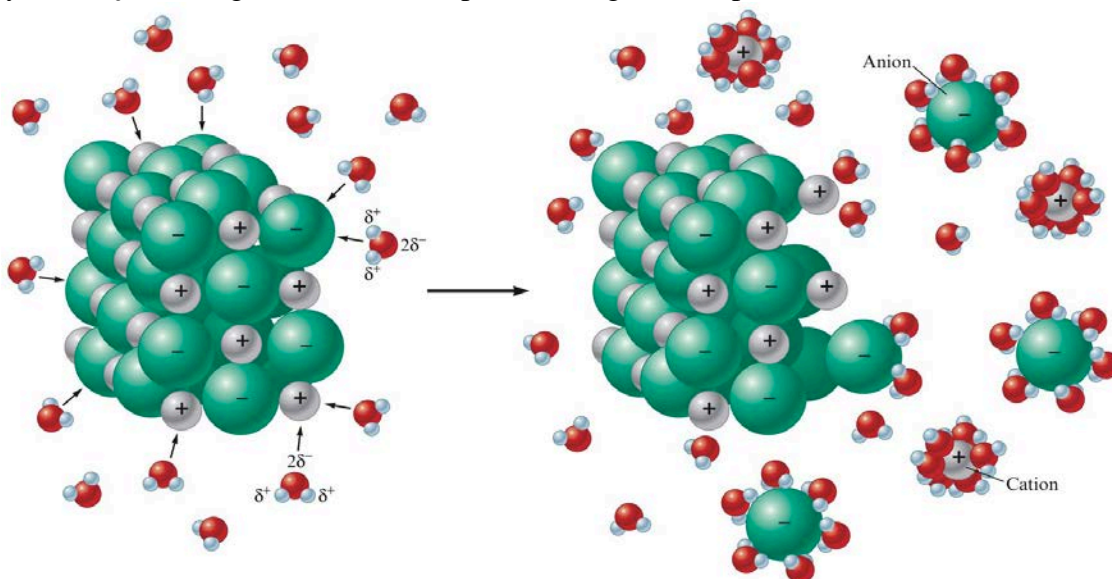
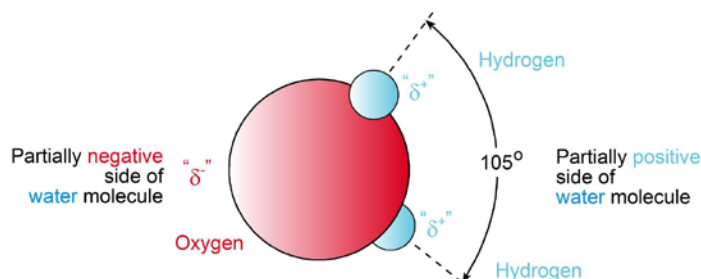
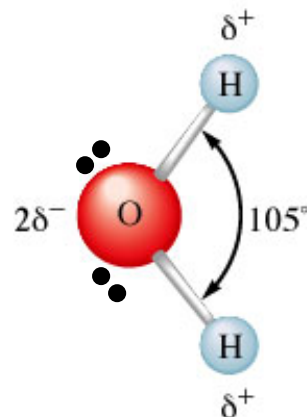
AP* Chemistry

TYPES OF CHEMICAL REACTIONS & SOLUTION STOICHIOMETRY

Chemists have used reactions to produce the materials Teflon, nylon, Dacron, Kevlar, polystyrene, and PVC among many others!

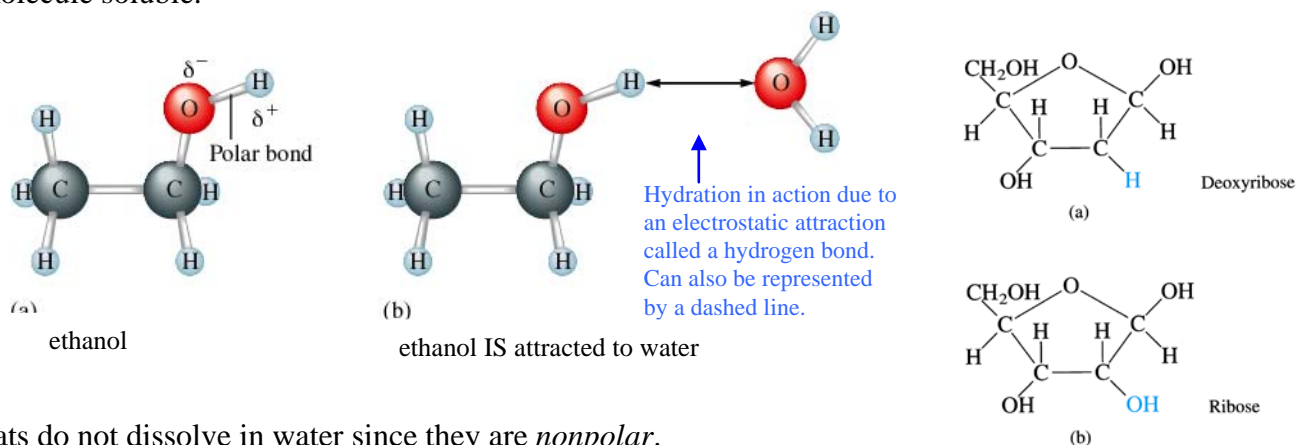
WATER, THE COMMON SOLVENT

- **Properties** – Water has a high specific heat, high heat of vaporization, high cohesive and adhesive forces. *All* of these properties contribute to life on this planet!
- **The H₂O** – the two O—H bonds are polar covalent since oxygen has a higher electronegativity and thus the electrons are more attracted to the oxygen and spend more time there. This creates a *partial* charge indicated by the Greek lower case letter delta, δ
 - This unequal charge distribution makes the molecule **polar**. Also notice the 105° bond angle, the two unshared electron pairs are “hogs” and require more space than shared pairs thus the usual 109.5° bond angle is squished to about 105°
 - There are TWO unshared electron pairs associated with the oxygen atom that make the partial negative charge -2δ
- **hydration** – Since opposites attract, the positive ends of water are greatly attracted to the negative ions in a crystal structure while the converse is also true.
- **solubility** – NaCl is highly soluble while AgCl is classified as insoluble. When the hydration attractions are *greater* than the crystal lattice [ion-ion] attractions, the compound is soluble.
 - Also note that the particles are charged IONS.
 - They have a *full* charge rather than the partial charge on the poles of the water molecule.



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Water can also dissolve nonionic substances such as alcohols and sugars among others. Alcohols and sugars contain O—H bonds that are polar just as the O—H bond in water. This polarity makes the molecule soluble.

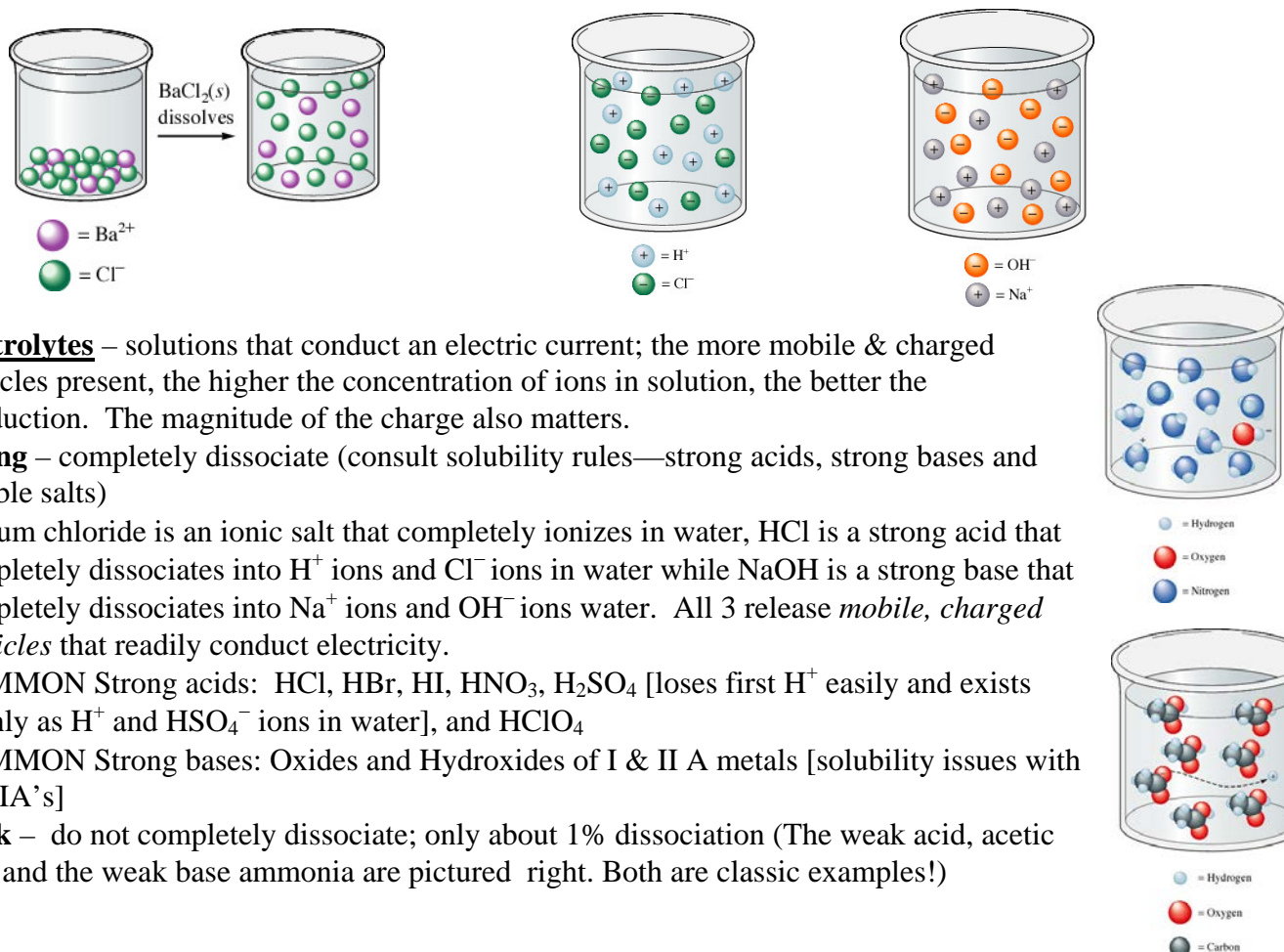


- Fats do not dissolve in water since they are *nonpolar*.
- “Like dissolves like”** is a useful guideline for predicting solubility, BUT it is not an explanation! You must address the electrostatic (“opposites attract”) aspects of solute-solvent interactions.

THE NATURE OF AQUEOUS SOLUTIONS: STRONG AND WEAK ELECTROLYTES

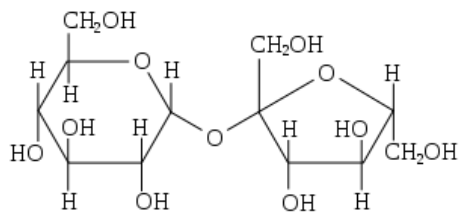
Remember a **solution** is a homogeneous mixture where a **solute** is dissolved in a **solvent**. **Aqueous** solutions are solutions where the solvent is *water*.

Properties of Aqueous Solutions

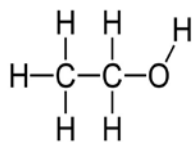


- electrolytes** – solutions that conduct an electric current; the more mobile & charged particles present, the higher the concentration of ions in solution, the better the conduction. The magnitude of the charge also matters.
- strong** – completely dissociate (consult solubility rules—strong acids, strong bases and soluble salts)
- Barium chloride is an ionic salt that completely ionizes in water, HCl is a strong acid that completely dissociates into H^+ ions and Cl^- ions in water while NaOH is a strong base that completely dissociates into Na^+ ions and OH^- ions water. All 3 release *mobile, charged particles* that readily conduct electricity.
- COMMON Strong acids: HCl, HBr, HI, HNO_3 , H_2SO_4 [loses first H^+ easily and exists mainly as H^+ and HSO_4^- ions in water], and HClO_4
- COMMON Strong bases: Oxides and Hydroxides of I & II A metals [solubility issues with the IIA's]
- weak** – do not completely dissociate; only about 1% dissociation (The weak acid, acetic acid and the weak base ammonia are pictured right. Both are classic examples!)

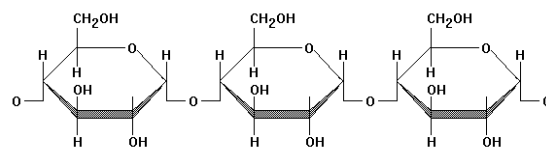
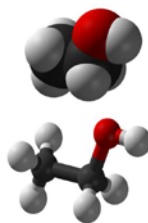
nonelectrolytes – solutions where dissolving has occurred but the solute *does not* make ions and therefore cannot conduct electricity. (*Pure water, sugar, alcohols, antifreeze, and starch*)



The Sucrose Molecule
1-Fructose + 1-Glucose



Ethanol



- Svante Arrhenius was the first to identify the conductive properties of solutions in the late 1890's. He correctly postulated that the extent to which a solution can conduct an electric current depends directly on the **number of ions present**.

THE COMPOSITION OF SOLUTIONS

Chemical reactions often take place when two solutions are mixed. To perform stoichiometric calculations in such cases two things must be known: (1) The nature of the reaction which depends on the exact substance and whether it exists as ions *or* molecules in solution AND (2) the amount of chemical (number of moles) present in the solution. Our favorite concentration unit is molarity:

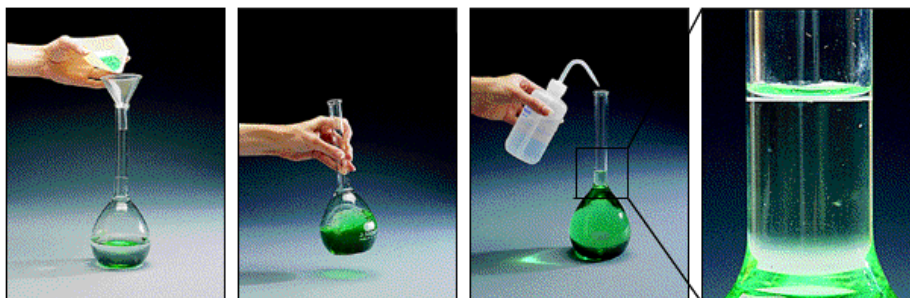
$$\text{Molarity } [M] = \frac{\text{moles of solute}}{\text{Liters of solution}}$$

- **Molarity** – is a concentration unit of moles per liter. $[\text{NaCl}] = 0.75 M$ means 0.75 moles of salt is contained in 1.00 L of **solution**. The square brackets indicate whatever is inside is a) in solution and b) its concentration is expressed in molarity. You may use *either* the square brackets or the unit M to express units of molarity on the AP exam.

$$M = \frac{\text{grams} / \text{MM}}{\text{Liters of solution}}$$

Preparing Solutions of KNOWN concentration

- Weigh out the solid as accurately as possible, place in a **volumetric flask**, add *only enough* distilled water to dissolve the solid and swirl to *completely* dissolve the solid THEN add a bit more water, filling to the mark on the flask. If you dump solid into 1.00 L of water you are neglecting the space the solid will occupy and your molar concentration will NOT be correct!



Exercise 1

Calculate the molarity of a solution prepared by dissolving 11.5 g of solid NaOH in enough water to make 1.50 L of solution.

0.192 M NaOH

Exercise 2

Calculate the molarity of a solution prepared by dissolving 1.56 g of gaseous HCl in enough water to make 26.8 mL of solution.

1.60 M HCl

Multiply the ions by their subscript if asked how many are present in a blah blah *M* sol'n of the whole compd.

Exercise 3

Give the concentration of each type of ion in the following solutions

- a. 0.50 *M* Co(NO₃)₂
- b. 1 *M* Fe(ClO₄)₃

a. 0.50 *M* Co²⁺ and (2 × 0.50) *M* NO₃⁻ or 1.0 *M* NO₃⁻
b. 1 *M* Fe³⁺ ions and 3 *M* ClO₄⁻ ions

ALWAYS REMEMBER AND NEVER EVER FORGET...

...Concentration (*M*) × Volume (in liters) = moles

or

Number of moles = *M* × L of solution

Exercise 4

Calculate the number of moles of Cl^- ions in 1.75 L of $1.0 \times 10^{-3} \text{ M ZnCl}_2$.

$3.5 \times 10^{-3} \text{ mol Cl}^-$

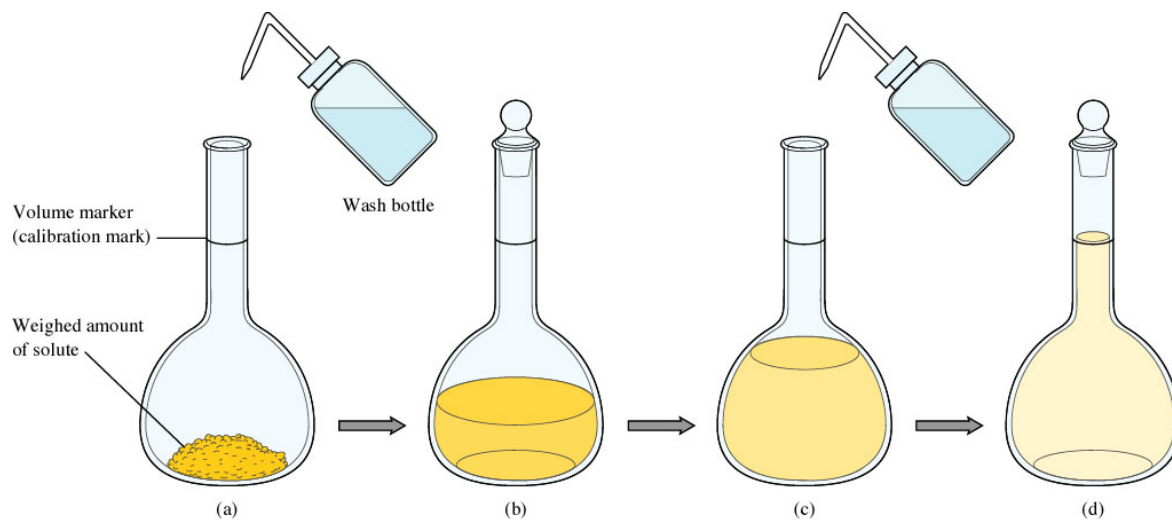
Exercise 5

Typical blood serum is about 0.14 M NaCl . What volume of blood contains 1.0 mg NaCl?

0.12 mL of blood contains $1.7 \times 10^{-5} \text{ mol NaCl}$ or 1.0 mg NaCl

Preparing a Standard solution – A “standard” solution is a solution whose *concentration is accurately known*. Once again, because this is IMPORTANT, use a volumetric flask that contains an exact total volume of solution.

1. A massed (weighed) amount of solute is placed into the volumetric flask (a), and a small quantity of distilled or deionized water is added.
2. The solid is dissolved in the water by gently swirling the flask with the stopper in place (b).
3. Additional water is added, until the level of the *solution* just reaches the mark etched on the neck of the flask (d).
4. Secure the stopper and invert the flask a few times to ensure even distribution of the solute throughout the



solution.

Exercise 6

To analyze the alcohol content of a certain wine, a chemist needs 1.00 L of an aqueous 0.200 M $\text{K}_2\text{Cr}_2\text{O}_7$ (potassium dichromate) solution. How much solid $\text{K}_2\text{Cr}_2\text{O}_7$ must be weighed out to make this solution? [FYI – this was initially the “stuff” used for breathalyzers!]

58.8 g $\text{K}_2\text{Cr}_2\text{O}_7$

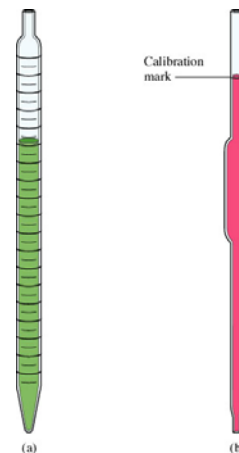
DILUTION FORMULA

$$M_1 V_1 = M_2 V_2 \quad \text{or} \quad M_{\text{stock}} V_{\text{stock}} = M_{\text{dilution}} V_{\text{dilution}}$$

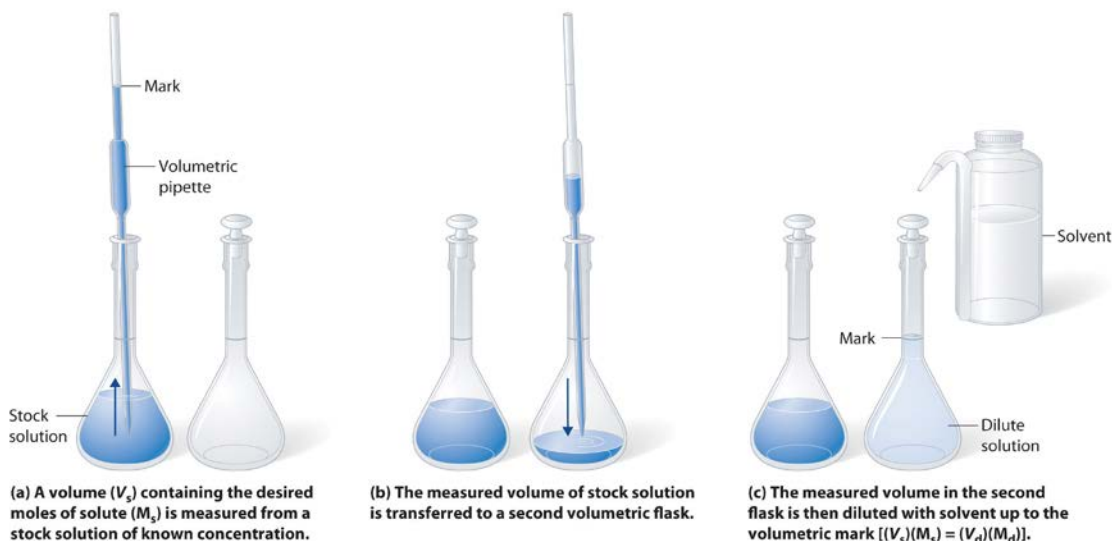
Preparing solutions from solutions by dilution is a common practice. Catchy, huh?

Often your sol'n involves diluting a more concentrated sol'n (commonly used when preparing acids and bases). The more concentrated solution is the **stock** solution. You will need the following:

- **Pipet** – a device for accurately measuring and transferring a given volume of solution; they come in several varieties but the most common are
 - **graduated measuring pipet** (a) – used to measure volumes for which a volumetric pipet is not available—has gradations
 - **volumetric or transfer pipet** (b) – gives one and only one measurement such as 5 mL or 10 mL, etc. but is mighty accurate



Generally, you would measure out the quantity of stock solution you determined from the dilution formula given above, and place it in a volumetric flask that would contain the volume of the diluted solution you needed to prepare. Next, you would fill the volumetric to the mark on the neck with deionized or distilled water until the meniscus reached the mark.



Exercise 7

What volume of 16 M sulfuric acid must be used to prepare 1.5 L of a 0.10 M H₂SO₄ solution?

9.4 mL of acid

TYPES OF CHEMICAL REACTIONS

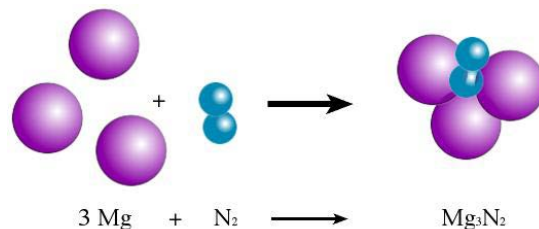
First, the semantics: Chemical REACTIONS vs. Chemical EQUATIONS

- **A chemical reaction** – transforms elements and compounds into new substances
- **A balanced chemical equation** – shows the relative amounts of reactants and products
- Phase symbols (*s*), (*l*), (*g*), (*aq*) – represent solid, liquid, gas, aqueous solution respectively
- NO ENERGY or TIME is ever alluded to with regard to the reaction
- Antoine Lavoisier (1743-1794)--Law of Conservation of Matter: *Matter can neither be created nor destroyed* ☞ this means you having to “balance equations” is his entire fault!!

Not all reactions will fall neatly into just one category, but we have to start somewhere! Let’s start with the “terminology” you most likely learned in a first-year chemistry or physical science type class.

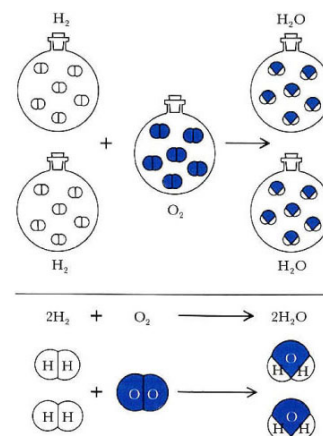
Synthesis or Composition Chemical Reactions

In a synthesis or composition reaction, two or more simple substances combine to form a more complex substance. These reactions are in the general form: $A + B \rightarrow AB$



Two or more reactants yielding a *single* product is another way to identify a synthesis reaction. One example of a synthesis reaction is the combination of magnesium and nitrogen to yield magnesium nitride as shown.

Another example is combining hydrogen gas with oxygen gas to produce a more complex substance, such as water shown right.

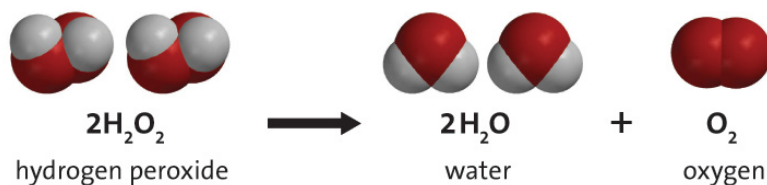


Decomposition Chemical Reactions

A decomposition reaction is the opposite of a synthesis reaction, where a more complex substance breaks down into its more simple parts. These reactions are in the general form: $AB \rightarrow A + B$



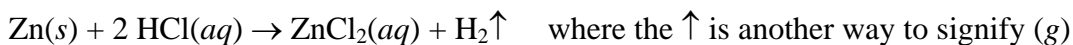
One example of a decomposition reaction is the decomposition of hydrogen peroxide. Why do we store it in a brown bottle anyway?



Single Replacement Chemical Reactions

In a single replacement reaction, a single uncombined element replaces another element within a compound; in other words, one element trades places with another element in a compound. These reactions come in the general form of: $A + BC \rightarrow AC + B$

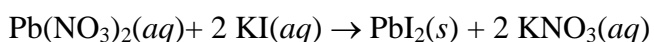
One example of a single displacement reaction is when zinc metal replaces hydrogen in hydrochloric acid to yield zinc chloride and hydrogen gas:



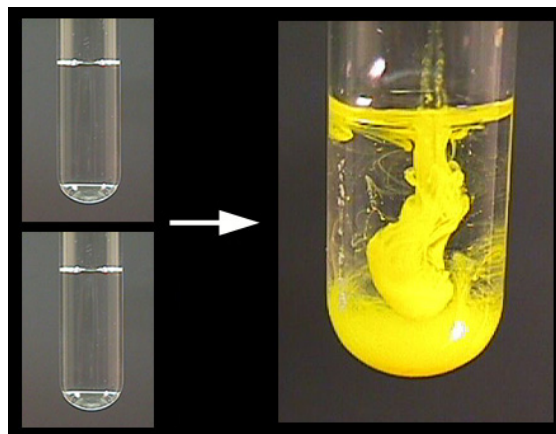
Double Replacement Chemical Reactions

In a double replacement reaction, the anions and cations of two compounds switch places and form two entirely different compounds. These reactions are in the general form: $AB + CD \rightarrow AD + CB$

For example, lead(II) nitrate reacts with potassium iodide to form lead(II) iodide and potassium nitrate:



Note that not all double replacement reactants result in a solid being formed!



Combustion Chemical Reactions

A combustion reaction involves a reaction between any combustible material and an *oxidizer* to form an oxidized product. The most famous “oxidizer” of all is oxygen. (Go, figure!) The products of such a reaction are simply oxides of that which is combusted.

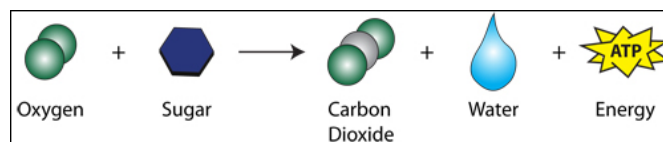
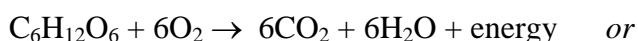
The unfortunate thing is that until now, most of the examples you’ve encountered have involved hydrocarbons like methane CH_4 , octane C_8H_{18} , etc. Why is that unfortunate? Because in the desperate search for an algorithm (Will it always work this way?) students often think the *only* products of combustion are the oxides of carbon either CO or CO_2 and the oxide of hydrogen, H_2O and thus write silly things on the AP Exam such as shown below:

Example: Write a balanced chemical equation for the burning of magnesium ribbon in air.

Silly answer: $\text{Mg} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ (Oh, my!)

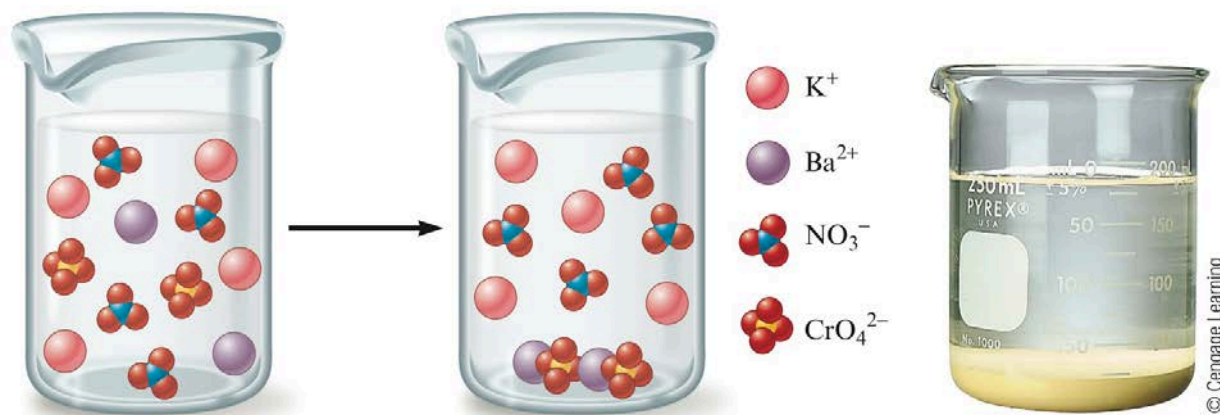
Correct answer: $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ (The correct chemical formula for the “oxide” of magnesium)

Additionally, most folks think of combustion in the literal “burning” sense, but cell respiration involves one of the most famous combustion reactions of all time!



The main difference for cellular respiration is that the energy release from glucose is performed in a very controlled manner using enzymes to *both* lower the activation energy of the reaction steps so that they can happen at body temperature and to spread out the energy release into small steps over a relatively long period of time. For combustion, the initial activation energy is high (a high temperature needed to start the burning, as seen by the high temperature needed for sugars to burn while cooking), and the energy release is very rapid, with all the chemical energy stored in the bonds released near-instantaneously, providing very large amounts of energy in a short period of time. It basically comes down to a controlled form of burning.

Precipitation Chemical Reactions (a subset of double replacement reactions)



The formation of a precipitate is a driving force for a chemical reaction. A **precipitate** is an insoluble solid that is formed when two aqueous solutions are mixed. We often separate the precipitate (ppt) from solution by filtration in what is called a **gravimetric analysis**.

To identify the precipitate, you **MUST** know your solubility rules. You'll find long lists of these in your textbook or on the web. For the AP Exam, just keep it simple and know these:

Disclaimer: It's WAY more fun if you name them! You are probably more creative than I. BUT, don't refer to the solubility rules this way when answering free response questions.

1. "Big Mamma": All nitrates are **soluble**.
2. "Big Daddy": All IA metals and ammonium salts are **soluble**.
3. "Halides": All are **soluble** except (the "heavy metal bad guys") silver, mercury or lead.
4. "Strong acids": **hydrochloric, hydrobromic, hydroiodic, nitric, perchloric, sulfuric**—WRITE THESE DISSOCIATED as $\text{H}^+ + \text{Cl}^-$ rather than HCl, etc.
5. "Strong bases": hydroxides [and oxides] of IA and IIA* metals—write these bases dissociated. If carbonic acid is formed as a product, it dissociates immediately so write $\rightarrow \text{CO}_2 + \text{H}_2\text{O}$. This also works for SO_2 .

Exercise 8

Using the solubility rules, predict what will happen when the following pairs of solutions are mixed.

- $\text{KNO}_3(aq)$ and $\text{BaCl}_2(aq)$
- $\text{Na}_2\text{SO}_4(aq)$ and $\text{Pb}(\text{NO}_3)_2(aq)$
- $\text{KOH}(aq)$ and $\text{Fe}(\text{NO}_3)_3(aq)$

- All the ions remain dissolved in solution. No chemical reaction occurs.
- The compound NaNO_3 is soluble, but PbSO_4 is insoluble. Mixed, PbSO_4 will precipitate from the solution.
- K^+ and NO_3^- salts are soluble. $\text{Fe}(\text{OH})_3$ is slightly soluble and will precipitate.

DESCRIBING REACTIONS IN AQUEOUS SOLUTION (Three ways!)

- COMPLETE balanced equation** – gives the overall reaction stoichiometry, but NOT the forms of the reactants & products as they exist in solution [the way we taught you in first-year chemistry]
- Complete ionic equation** – represents all reactants & products that are strong electrolytes as IONS
- Net ionic equations** – includes only those solution components undergoing a change. Spectator ions are NOT included.
 - Spectator ions** – not involved in the reaction process – started as an ion AND finishes as the *same ion*
 - THERE IS ALWAYS A CONSERVATION OF **MASS & CHARGE** IN NET IONIC EQN'S.

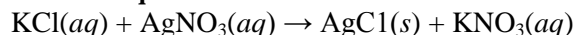
Exercise 9

For each of the following reactions, write the molecular equation, the complete ionic equation, and the net ionic equation.

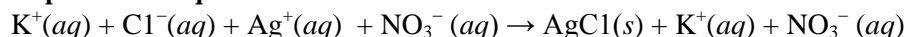
- Aqueous potassium chloride is added to aqueous silver nitrate to form a silver chloride precipitate plus aqueous potassium nitrate.
- Aqueous potassium hydroxide is mixed with aqueous iron(III) nitrate to form a precipitate of iron(III) hydroxide and aqueous potassium nitrate.

Answers:

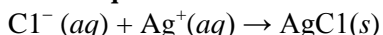
a. Molecular Equation:



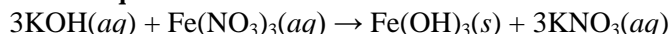
Complete Ionic Equation:



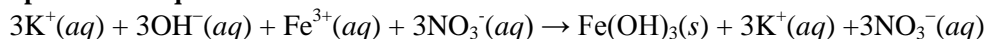
Net Ionic Equation:



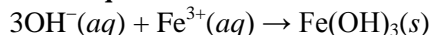
b. Molecular Equation:



Complete Ionic Equation:



Net Ionic Equation:



Chemical analysis of mixtures by PRECIPITATION REACTIONS

- Mix starting chemicals to form an insoluble salt, filter out the salt and then “dry to constant mass”.
- Use stoichiometry to determine any desired quantities.

Exercise 10

Calculate the mass of solid NaCl that must be added to 1.50 L of a 0.100 M AgNO₃ solution to precipitate all the Ag⁺ ions in the form of AgCl.

8.77 g NaCl

Exercise 11

When aqueous solutions of Na₂SO₄ and Pb(NO₃)₂ are mixed, PbSO₄ precipitates. Calculate the mass of PbSO₄ formed when 1.25 L of 0.0500 M Pb(NO₃)₂ and 2.00 L of 0.0250 M Na₂SO₄ are mixed.

15.2 g PbSO₄

ACIDS-BASES REACTIONS

- **Acid** --any compound (cmpd.) that, upon reaction with water, produces an ion called the **hydronium ion**, H₃O⁺ [or H⁺], and an anion (Arrhenius definition)
- **Base** – any cmpd. that provides a **hydroxide**, OH⁻, and a cation in water (Arrhenius definition)
**ammonia, NH₃ is an exception, so Bronsted-Lowry defined it as a proton acceptor!!
- **Neutralization** –When moles acid = moles base (and = moles salt formed!) each reactant is neutralized and the products formed are a salt [ask yourself if it is soluble] and water. Note: the pH is not necessarily 7.0 since it is the pH of the *salt formed* that determines the pH of the neutralized mixture and not all salts are neutral!

Exercise 12

What volume of a 0.100 M HCl solution is needed to neutralize 25.0 mL of 0.350 M NaOH ?

8.75×10^{-2} L (87.5 mL)

Another chance to practice limiting reactant!

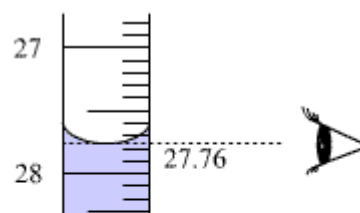
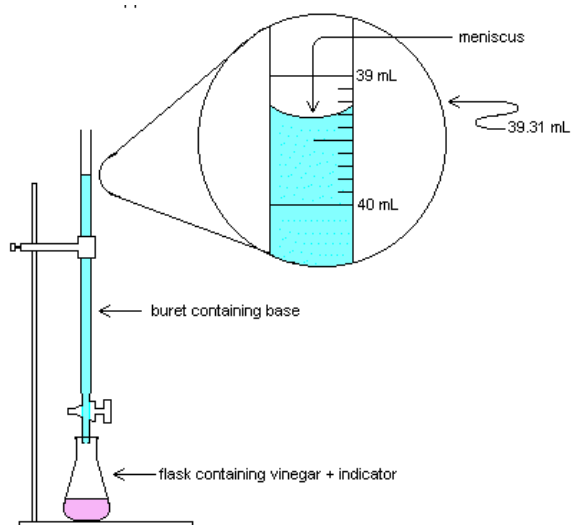
Exercise 13

In a certain experiment, 28.0 mL of 0.250 M HNO_3 and 53.0 mL of 0.320 M KOH are mixed. Calculate the number of moles of water formed in the resulting reaction. What is the concentration of H^+ or OH^- ions in excess after the reaction goes to completion?

0.123 M OH^-

Acid-Base Titrations

- o **Volumetric analysis** – a technique for determining the amount of a certain substance by doing a titration
- o **Titrant** – the substance delivered from a buret so that its volume is accurately known (base in the diagram below)
- o **Analyte** – the substance being analyzed; its mass or volume must also be accurately known (vinegar sample in the diagram below)
- o **Equivalence point** – # moles of OH^- equals (is equivalent to) # moles of H_3O^+ [acid-base titration; redox titrations also exist!]
- o **Indicator** – undergoes a color change at the end point (Phenolphthalein is not the only one in the world!)
- o **Standardization** – a procedure for establishing the *exact concentration* of a reagent



Move your eyes to the level of the liquid surface and read the value of the bottom of the meniscus with 1/10 of the smallest scale marked on the burette.

Exercise 14

A student carries out an experiment to standardize (determine the exact concentration of) a sodium hydroxide solution. To do this the student weighs out a 1.3009-g sample of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$, often abbreviated KHP). KHP (molar mass 204.22 g/mol) has one acidic hydrogen. The student dissolves the KHP in distilled water, adds phenolphthalein as an indicator, and titrates the resulting solution with the sodium hydroxide solution to the phenolphthalein endpoint. The difference between the final and initial buret readings indicates that 41.20 mL of the sodium hydroxide solution is required to react exactly with the 1.3009 g KHP. Calculate the concentration of the sodium hydroxide solution.

0.1546 M

Exercise 15

An environmental chemist analyzed the effluent (the released waste material) from an industrial process known to produce the compounds carbon tetrachloride (CCl_4) and benzoic acid ($\text{HC}_7\text{H}_5\text{O}_2$), a weak acid that has one acidic hydrogen atom per molecule. A sample of this effluent weighing 0.3518 g was shaken with water, and the resulting aqueous solution required 10.59 mL of 0.1546 M NaOH for neutralization. Calculate the mass percent of $\text{HC}_7\text{H}_5\text{O}_2$ in the original sample.

56.84%

OXIDATION-REDUCTION REACTIONS involve electron transfer

Terms to Know:

“OIL RIG” – oxidation is loss, reduction is gain (of electrons)

Oxidation – the loss of electrons, increase in charge

Reduction – the gain of electrons, reduction of charge

Oxidation number – the assigned charge on an atom (think formula writing)

Rules for Assigning Oxidation States—you know most of this already from your formula writing days!

1. The oxidation state of an atom in an element is ZERO including allotropes [i.e. N₂, P₄, S₈].
2. The oxidation state of a monatomic ion is the same as its charge.
3. In its compounds, fluorine is always assigned an oxidation state of -1.
4. Oxygen is usually assigned an oxidation state of -2 in its covalent compounds, such as CO, CO₂, SO₂, and SO₃. Exceptions to this rule include peroxides (compounds containing the O₂²⁻ group), where each oxygen is assigned an oxidation state of -1, as in hydrogen peroxide (H₂O₂), and OF₂ in which oxygen is assigned a +2 oxidation state.
5. In its covalent compounds with nonmetals, hydrogen is assigned an oxidation state of +1. Metal hydrides are an exception; H is at the end of the chemical formula since it has an oxidation state of -1.
6. The sum of the oxidation states must be zero for an electrically neutral compound. For a polyatomic ion, the sum of the oxidation states must equal the charge of the ion.

Exercise 16

Assign oxidation states to all atoms in the following:

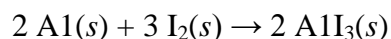
- a. CO₂
- b. SF₆
- c. NO₃⁻

- a. oxygen is -2 & carbon is +4
- b. fluorine is -1 & sulfur is +6
- c. oxygen is -2 & nitrogen is +5

BEWARE! There can be non-integer oxidation states like in Fe₃O₄. There's a -8 for the 4 oxygens divided across 3 iron ions, therefore Fe's charge is Fe^{8/3+}

Exercise 17

When powdered aluminum metal is mixed with pulverized iodine crystals and a drop of water is added to help the reaction get started, the resulting reaction produces a great deal of energy. The mixture bursts into flames, and a purple smoke of I_2 vapor is produced from the excess iodine. The equation for the reaction is



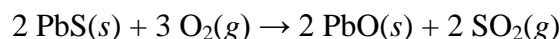
For this reaction, identify the atoms that are oxidized and reduced.



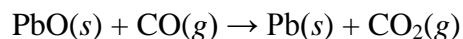
Aluminum is oxidized; Iodine is reduced

Exercise 18

Metallurgy, the process of producing a metal from its ore, always involves oxidation-reduction reactions. In the metallurgy of galena (PbS), the principal lead-containing ore, the first step is the conversion of lead sulfide to its oxide (a process called *roasting*):



The oxide is then treated with carbon monoxide to produce the free metal:



For each reaction, identify the atoms that are oxidized and reduced.

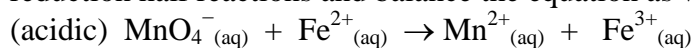
**First Reaction:
sulfur is oxidized; oxygen is reduced**

**Second Reaction:
carbon is oxidized; lead is reduced**

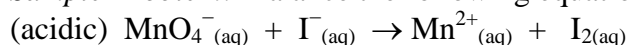
Balancing Redox Reactions by Half Reaction Method

1. Divide the equation into oxidation and reduction half reactions. [OILRIG]
2. Balance all elements *besides* hydrogen and oxygen.
3. Balance O's by adding H₂O's to the appropriate side of each equation.
4. Balance H's by adding H⁺
5. Balance the charge by adding electrons. [OILRIG again]
6. Multiply the half reactions to make the number of moles of electrons equal for *both* half-reactions. Why? So we can cancel out all electron and balance the charge.
7. Cancel out any common terms and recombine the two half reactions.
8. IF BASIC, neutralize any excess H⁺ by adding the *SAME NUMBER* of OH⁻ to EACH side of the balanced equation. [This creates some waters that will most likely cancel!]
9. CHECK!!

Sample Problem: Assign oxidation states to all atoms in the following equation, identify the oxidation and reduction half reactions and balance the equation as well.

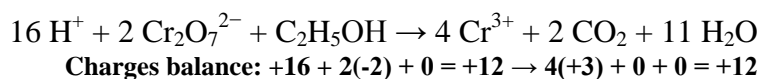
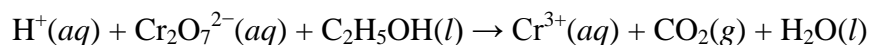
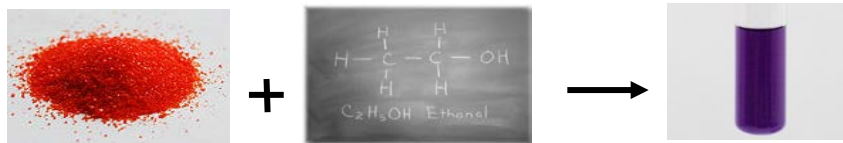


Sample Problem: Balance the following equation using the half-reaction method.



Exercise 19

Potassium dichromate ($K_2Cr_2O_7$) is a bright orange compound that can be reduced to a blue-violet solution of Cr^{3+} ions. Under certain conditions, $K_2Cr_2O_7$ reacts with ethyl alcohol (C_2H_5OH) as shown below. Balance this equation using the half-reaction method.



Exercise 20

Silver is sometimes found in nature as large nuggets; more often it is found mixed with other metals and their ores. An aqueous solution containing cyanide ion is often used to extract the silver using the following reaction that occurs in basic solution. Balance this equation using the half-reaction method.

