

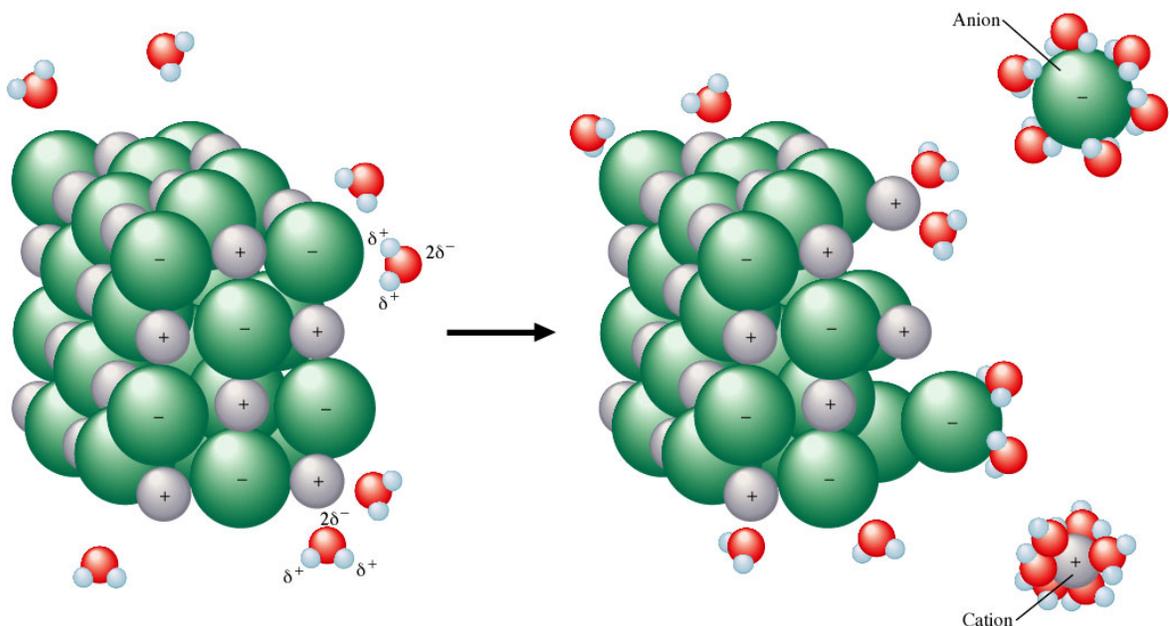
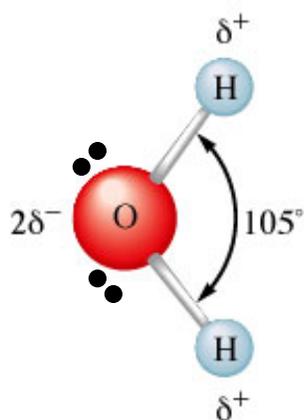
AP* Chemistry

TYPES OF CHEMICAL REACTIONS & SOLUTION STOICHIOMETRY

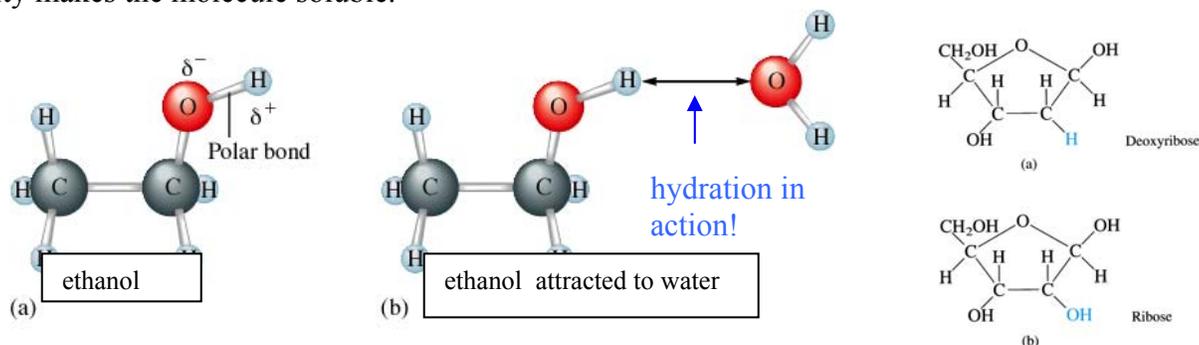
Chemists have used reactions to produce the materials Teflon, nylon, Dacron, Kevlar, polystyrene, and PVC among many others!

WATER, THE COMMON SOLVENT

- **Properties**—high specific heat, high heat of vaporization, high cohesive and adhesive forces
All of these properties contribute to life on this planet!
- **H₂O**—the two O—H bonds are polar covalent [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.
 - Note that the particles are charged IONS.
- They have a **full** charge rather than the partial charge on the poles of the water molecule.



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.



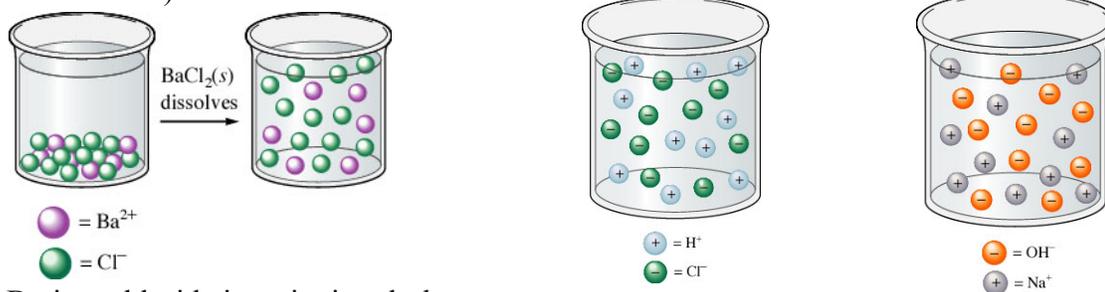
- Fats do not dissolve in water since they are *nonpolar*.
- **“Like dissolves like”** is a useful guideline for predicting solubility.

THE NATURE OF AQUEOUS SOLUTIONS: STRONG AND WEAK ELECTROLYTES

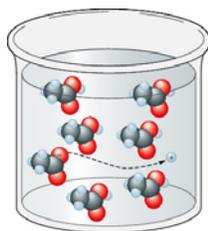
Remember a **solution** is a homogeneous mixture where a **solute** is dissolved in a **solvent**. **Aqueous** solutions are solutions where the solvent is *water*.

Properties of Aqueous Solutions

- **electrolytes**--solutions that conduct an electric current
- **strong** Λ completely dissociate (consult solubility rules—strong acids, strong bases and soluble salts)



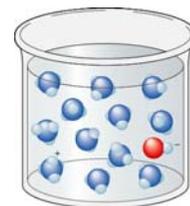
- Barium chloride is an ionic salt that completely ionizes in water, HCl is a strong acid that completely dissociates into ions in water while NaOH is a strong base that completely dissociates in water. All 3 release charged particles that readily conduct electricity.
- COMMON Strong acids: HCl, HBr, HI, HNO₃, H₂SO₄ [loses first H⁺ easily and exists mainly as H⁺ and HSO₄⁻ ions in water] AND HClO₄
- COMMON Strong bases: Oxides and Hydroxides of I & II A metals [solubility issues with the IIA's]



● = Hydrogen
● = Oxygen
● = Carbon

- **weak** ⇌ do not completely dissociate; only about 1% dissociation (weak acids and bases; ammonia, acetic acid)

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)



● = Hydrogen
● = Oxygen
● = Nitrogen

- 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 whether or not the substance exists as ions or molecules in solution AND (2) the amount of chemicals present in the solution.

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

- **Molarity**--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.

$$M = \frac{\text{g} / \text{FW}}{\text{Liters of solution}}$$

- Preparing Solutions of **KNOWN** concentration
- Weigh out the solid as accurately as possible, place in a **volumetric** flask, add enough distilled water to dissolve the solid THEN add 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 sol'n 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

- 0.50 *M* Co(NO₃)₂
- 1 *M* Fe(ClO₄)₃

- 0.50 *M* Co²⁺ and (2 x 0.50) *M* NO₃⁻ or 1.0 *M* NO₃⁻
- 1 *M* Fe³⁺ ions and 3 *M* ClO₄⁻ ions

ALWAYS REMEMBER AND NEVER EVER FORGET...

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

Number of moles = *M* × L of solution

Exercise 4

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

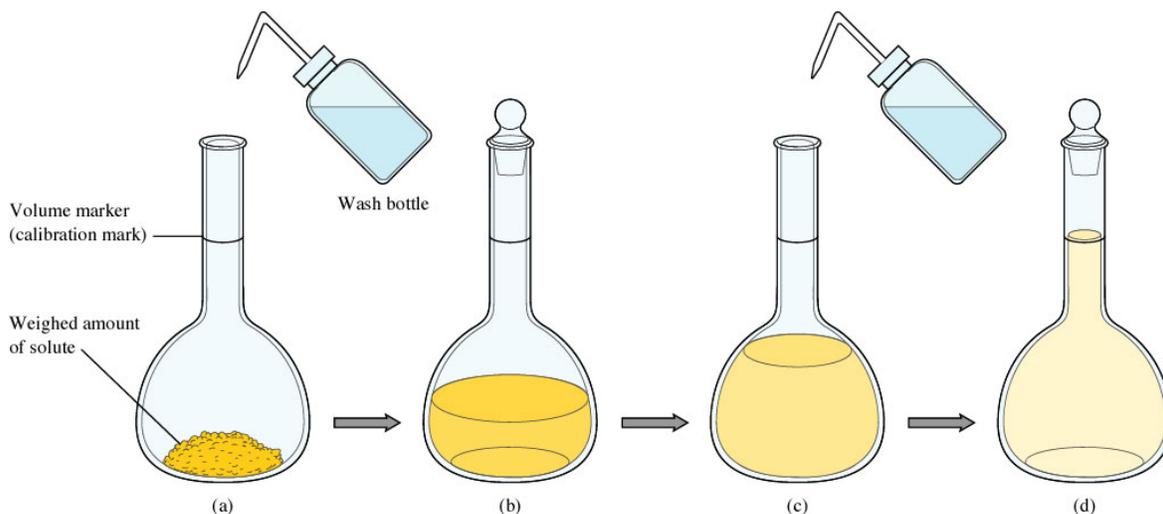
$3.5 \times 10^{-3} \text{ mol Cl}^-$

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

- **Standard solution**—is a solution whose *concentration is accurately known*
 - volumetric flask—contains an exact total volume of solution



Steps involved in the preparation of a standard solution. a) A weighed amount of a substance (the solute) is put into the volumetric flask, and a small quantity of water is added. (b) The solid is dissolved in the water by gently swirling the flask (with the stopper in place). (c) More water is added, until the level of the solution just reaches the mark etched on the neck of the flask (d).

Exercise 6

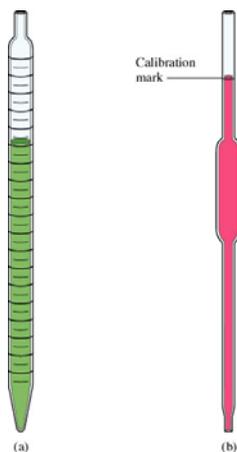
To analyze the alcohol content of a certain wine, a chemist needs 1.00 L of an aqueous 0.200 M $K_2Cr_2O_7$ (potassium dichromate) solution. How much solid $K_2Cr_2O_7$ must be weighed out to make this solution? [FYI—this was initially the “stuff” used for breathalyzers!]

58.8 g $K_2Cr_2O_7$

DILUTION

$$M_1V_1 = M_2V_2$$

- Preparing solutions by dilution. Often your soln involves diluting a more concentrated soln. (most common with acids). The more concentrated solution is the **stock** solution.



- **pipet**—a device for accurately measuring and transferring a given volume of solution
- **measuring pipet (a)**—used to measure volumes for which a volumetric pipet is not available—has gradations
- **volumetric or transfer pipet (b)**—gives only one measurement 5mL, 10mL, etc.

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.

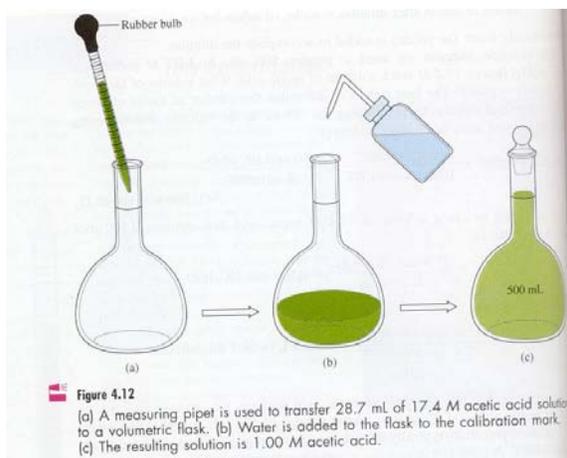


Figure 4.12
(a) A measuring pipet is used to transfer 28.7 mL of 17.4 M acetic acid solution to a volumetric flask. (b) Water is added to the flask to the calibration mark. (c) The resulting solution is 1.00 M acetic acid.

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**CHEMICAL EQUATIONS**

- **chemical reaction**--transforms elements and compounds into new substances
- **balanced chemical equation**--shows the relative amounts of reactants and products
- *s, l, g, aq*--solid, liquid, gas, aqueous solution
- NO ENERGY or TIME is alluded to
- Antoine Lavoisier (1743-1794)--law of conservation of matter: *matter can neither be created nor destroyed* ☞ this means “balancing equations” is all his fault!!

Not all reactions will fall neatly into just one category, but we have to start somewhere!
We will be starting AP Net Ionic Equations very soon where you will see several categories involved.

PRECIPITATION 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—expect quizzes on these throughout the year!

SOLUBILITY RULES: *memorize!!!*

1. Most alkali metal salts AND NH_4^+ salts ARE *soluble*
2. Cl^- , Br^- , I^- are *soluble*, *except for Ag^+ , Hg_2^{+2} , Pb^{+2}
3. F^- are *soluble*, *except for IIA metals
4. NO_3^- , ClO_3^- , ClO_4^- , and CH_3COO^- are *soluble*
5. SO_4^{-2} are *soluble*, *except for Ca^{+2} , Sr^{+2} , Ba^{+2} , Ag^+ , Pb^{+2} , Hg_2^{+2}
6. CO_3^{-2} , PO_4^{-3} , $\text{C}_2\text{O}_4^{-2}$, CrO_4^{-2} , S^{-2} , OH^- , and O^{-2} are **INSOLUBLE**
(rule 1 takes priority!)

Heavy metal
BAD GUYS!

It can be assumed that ionic cmpds. that dissolve in water are strong electrolytes and are therefore soluble.

Exercise 8

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

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

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

DESCRIBING REACTIONS IN SOLUTION

Three ways:

1. **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 chem.]
2. **complete ionic equation**—represents as IONS all reactants & products that are strong electrolytes
3. **net ionic equations**—includes only those solution components undergoing a change. Spectator ions are NOT included
 - **spectator ions**--not involved in the reaction process Λ started as an ion AND finished as an ion
 - THERE IS ALWAYS A CONSERVATION OF **CHARGE** IN NET IONIC EQN'S.

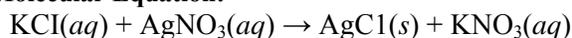
Exercise 9

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

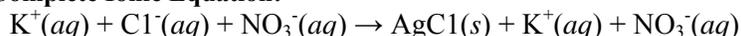
- Aqueous potassium chloride is added to aqueous silver nitrate to form a silver chloride precipitate plus aqueous potassium nitrate.
- Aqueous potassium hydroxide is mixed with aqueous iron(III) nitrate to form a precipitate of iron(III) hydroxide and aqueous potassium nitrate.

Answers:

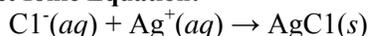
a. Molecular Equation:



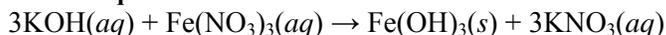
Complete Ionic Equation:



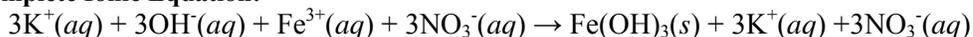
Net Ionic Equation:



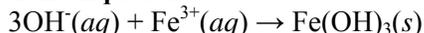
b. Molecular Equation:



Complete Ionic Equation:



Net Ionic Equation:



- Chemical analysis of mixtures by PRECIPITATION REACTIONS
- form an insoluble salt, filter the salt out and then dry to constant mass.
- use stoichiometry to determine the desired quantity.

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 Na_2SO_4 and $\text{Pb}(\text{NO}_3)_2$ are mixed, PbSO_4 precipitates. Calculate the mass of PbSO_4 formed when 1.25 L of 0.0500 M $\text{Pb}(\text{NO}_3)_2$ and 2.00 L of 0.0250 M Na_2SO_4 are mixed.

15.2 g PbSO_4

ACIDS-BASES REACTIONS

- **acids**--any compd. that, on reaction with water, produces an ion called the **hydronium ion, H_3O^+** [or H^+], and an anion (Arrhenius definition)
- **base**--any compd. that provides a **hydroxide, OH^-** , and a cation in water (Arrhenius definition)
**ammonia, NH_3 is an exception, so Bronsted-Lowry defined it as a proton acceptor!!
- **neutralization**—when moles acid = moles base each is neutralized [pH is not necessarily 7.0].
The products formed are a salt [ask yourself if it is soluble] and water

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)

A chance to practice limiting reactant!

Exercise 13

In a certain experiment, 28.0 mL of 0.250 M HNO₃ and 53.0 mL of 0.320 M KOH are mixed. Calculate the amount 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
- o **analyte**—the substance being analyzed; its mass or volume must also be accurately known
- o More terms to know:
 - **equivalence point**--# moles of OH⁻ equals (is equivalent to) # moles of H₃O⁺ [acid-base titration; redox titrations also exist!]
 - **indicator**--undergoes a color change near the equivalence point.
 - **standardization**--a procedure for establishing the *exact concentration* of a reagent

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.

56.82%

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

Oxidizing agent (OA) – the species that is reduced and thus *causes* oxidation

Reducing agent (RA) – the species that is oxidized and thus *causes* reduction

Rules for Assigning Oxidation States—you know most of this already!

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.

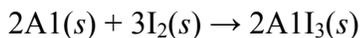
- a. CO₂
- b. SF₆
- c. NO₃⁻

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

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 I₂ vapor is produced from the excess iodine. The equation for the reaction is

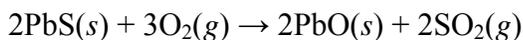


For this reaction, identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents.

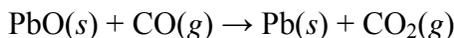
**Aluminum is oxidized; Iodine is reduced
Al is the reducing agent; I₂ is the oxidizing agent**

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:



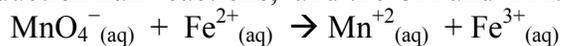
For each reaction, identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents.

**First Reaction:
sulfur is oxidized; oxygen is reduced
O₂ is the oxidizing agent; PbS is the reducing agent
Second Reaction:
carbon is oxidized; lead is reduced
PbO is the oxidizing agent; CO is the reducing agent**

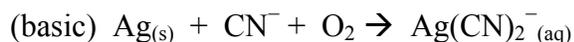
Balancing Redox Reactions by Half Reaction Method

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 electrons equal for both half-reactions.
7. Cancel out any common terms and recombine the two half reactions.
8. IF BASIC, neutralize any H⁺ by adding the SAME NUMBER of OH⁻ to EACH side of the balanced equation. [This creates some waters that will cancel!]
9. CHECK!!

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

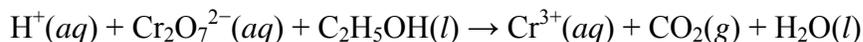


Sample Problem: Balance the following equation using the half-reaction method.



Exercise 19

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is a bright orange compound that can be reduced to a blue-violet solution of Cr^{3+} ions. Under certain conditions, $\text{K}_2\text{Cr}_2\text{O}_7$ reacts with ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) as follows:



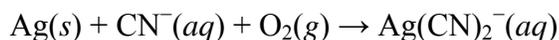
Balance this equation using the half-reaction method.

Elements balance: 22H, 4Cr, 15O, 2C \rightarrow 22H, 4Cr, 15O, 2C

Charges balance: +16 + 2(-2) + 0 = +12 \rightarrow 4(+3) + 0 + 0 = +12

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.

Elements balance: 8C, 8N, 4Ag, 4O, 4H \rightarrow 8C, 8N, 4Ag, 4O, 4H

Charges balance: 8(1-) + 0 + 0 + 0 = 8- \rightarrow 4(1-) + 4(1-) = 8-