Chem 1045
Lecture Notes

Chemistry & Chemical Reactivity
Kotz/Treichel/Townsend, 8th Ed

These Notes are to <u>SUPPLEMENT </u>the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, <u>READ THE CHAPTER</u> prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test! The author is not responsible for typos in these notes.

## <u>Chapter 4, Stoichiometry:</u> Quantitative Information about Chemical Reactions

Sparkler, powdered iron reacts with oxygen $4 \, Fe \downarrow + 3 \, O_2 \uparrow \rightarrow 2 \, Fe_2O_3 \downarrow$

Thermite, reduction of iron III, very exothermic: $Fe_2O_5 \downarrow + 2 \, Al \downarrow \rightarrow 2 \, Fe \, (l) + Al_2O_3 \downarrow$

4.1 Mass Relationships in Chemical Reactions: Stoichiometry

A balanced chemical equation shows:
- The quantitative relationship between reactants and products in a chemical reaction
- The number of moles of each reactant and product
- The coefficients relate the number of moles of each substance to each other

$P_4 \downarrow$	$+$ $6 \, Cl_2 \uparrow$	$\rightarrow$	$4 \, PCl_{3 \, (l)}$
1 mole	6 mole		4 mole
124. g	425. g		549. g
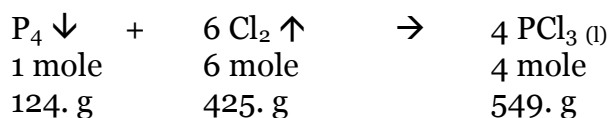
One mole of P_4 reacts with 6 moles of Cl_2 to produce 4 moles PCl_3

What if we only had 1.45 g of P_4, how much PCl_3 in grams is formed?

<u>METHOD #1   The Old Fashion Way (taught it this way up to this year)</u>

Step 1: Write the balanced equation – see above

Step 2: Calculate the amount (moles) from mass (grams)

1.45 g P_4 * (1 mole P_4 / 123.9 g P_4) = 0.0117 mole P_4

⎣————————→ P = 30.97 g/mole   4P =123.88 g/4 mole

Step 3: Use a stoichiometric factor , **put in a conversion factor so the units cancel out**

0.0117 ***mole P₄*** * (6 mole Cl_2 / ***1 mole P₄***) = 0.0702 mole Cl_2

1 mole P₄ cancels out

Step 4: Calculate mass from amount

0.0702 ***mole Cl₂*** * (70.91 g Cl_2 / 1 ***mole Cl₂***) = <u>**4.98 g Cl₂**</u> Always box in your answer

mole Cl₂ cancels out   ⎣————————→ Cl = 35.45 g/mole Cl_2 = 70.90 g/mole
Note: Book has a rounding error 70.91 instead of 70.91

Now calculate the amount of $PCl_{3 \, (l)}$ produced

Since there is mass conservation, total wt of reactants = total weight of products

Total wt of products = 1.45 g P_4 + 4.08 g Cl_2 = **6.43 g $PCl_{3 \, (l)}$**

You could also calculate it from

$$0.0117 \text{ mole } P_4 * (4 \text{ PCl}_{3\,(l)}/ 1 \text{ mole } P_4) = 0.0468 \text{ mole } \textbf{PCl}_3$$

Mw Calculation: 1 P   1 * 30.97 g/mole   30.97 g/mole
                           3 Cl   3 * 35.56 g/mole   <u>106.35 g/mole</u>
   **Mw PCl$_3$**   **137.32 g/mole**

$$0.0468 \text{ mole } \textbf{PCl}_3 * (137.3 \text{ g PCl}_{3\,(l)} / 1 \text{ mole PCl}_{3\,(l)}) = \textbf{6.43 g PCl}_{3\,(l)}$$

<u>**METHOD #2**</u>   **The Amounts Table** (New Method, Currently used in Chem II)

Initial Amount in moles   Starting amount of each reactant and product
Change   Change that occurs during the reaction
Final Amount in moles   Final amount of each reactant and product after the reaction

<u>**Equation**</u>	**P4 ↓ +**	**6 Cl₂ ↑** →	**4 PCl₃ (l)**
Initial Amount		**2.** 6 * 0.0117 mol	
	1. 0.0117 mole	**2.** 0.0702 mole	**3.** 0 mole
	1. (1.45 g)	**2.** (4.98 g)	**3.** (0 g)
Change in Amount	- 0.0117 mole	- 0.0702 mole	+(4 * 0.0117 mol)
			+ 0.0468 mole
Amount after Rx	0 mol	0 mol	**0.0468 mol**
	(0 g)	(0 g)	**(6.43 g)**

<u>**METHOD #3**</u>   **My Way** Calculate the Molecular Weight of the "Whole Entity" and then set up a ratio table. This is similar to Amounts Table; we do it like this in Grad School and in Industry!

<u>**Equation**</u>   **P4 ↓ +**   **6 Cl₂ ↑**   →   **4 PCl₃ (l)**
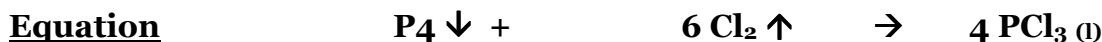
    Calculate the Mw's:

    P = 30.97 g/mole   **P4** =4 * 30.97 g/mole = 123.88 g/ "Mole P$_4$"

Minor Changes in notes from here on

    4 PCl$_3$ 4 P = 4 * 30.97 g/mole P =   123.88 g/mole P4
                        12 Cl = 12 * 35.45 g/mole Cl =   <u>425.40</u> g/mole 12 Cl (or 4 Cl$_3$)
   **Mw 4 PCl$_3$ =**   549.28 = **549.28 g / "Mole 4 PCl$_3$"**

Equation	**P4 ↓ +**	**6 Cl₂ ↑**	→ **4 PCl₃ (l)**
Amount	1.45 g	?	?
Moles of Whole Entity	123.88 g/mole P4		**549.28 g / "Mole 4 PCl₃"**

    Now set up a ratio equivalence of the weight of starting material (1.45 g) to molecular weight of the entire starting material (123.88 g/ "Mole P$_4$") equals X (the amount of product to be determined) to the molecular weight of the product (549.3 g / "Mole 4 PCl$_3$")

$$\frac{1.45 \text{ g}}{123.88 \text{ g/ "Mole P}_4\text{"}} = \frac{X}{549.28 \text{ g / "Mole 4 PCl}_3\text{"}}$$

    Solve for X: **X** = 6.429254 = **6.43 g 4 PCl$_3$**

Example 4.1 25.0 g glucose ($C_6H_{12}O_6$) reacts with O_2 to give CO_2 & H_2O. How much O_2 is needed?
       Remember – you must start with a Balanced Equation!

METHOD #1   The Old Fashion Way

$$C_6H_{12}O_6 \; + \; 6\,O_2 \; \rightarrow \; 6\,CO_2 \; + \; 6\,H_2O$$
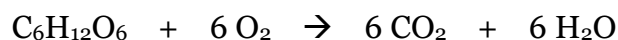
6 C   6 * 12.01   72.06 g/mole   **You must show all calculations** including calculation
12 H   12 * 1.007   12.084 g/mole   **of molecular weight and Sig Digit (SD) rounding**
6 O   6 * 16.00   96.00   g/mole
                      180.144 g/mole = **180.14 g/mole**

Determine the amount of O2
   1. Determine moles of glucose: Moles = Wt / Mw
                                       25.0 g / 180.14 g/mole = 0.13878 = **0.139 mole glucose**

   2. Use stoichiometric factor to determine the number of moles of O2

               0.139 mole glucose * 6 mole O2   = **0.834 mole O_2**
                                     1 mole glucose

   3. Determine amount (wt in g) of O_2 Moles = Wt / Mw   →   Wt = Moles * Mw

               0.834 mole O_2 * 32.00 g/mole O_2 = 26.688 = **26.7 g O_2**

Determine the amount of CO_2 produced:

   4. Use stoichiometric factors

       0.139 mole glucose *   6 mole CO_2 *   44.01 g CO_2 = 36.70 = **36.7 g CO_2**
                                 1 mole glucose   1 mole CO_2

                        ←Stoichiometric→   ←Convt Moles→
                              Factor   to Grams

Determine the amount of H2O produced by adding wt of reactants and subtracting wt of CO_2

   5. 25.0 g glucose + 26.7 g O2 - 36.7 g CO2 = **15.0 g H2O**
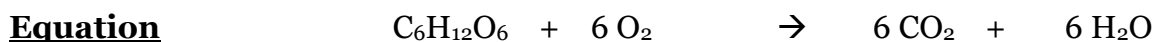
METHOD #2   Amounts Table

Equation	$C_6H_{12}O_6$ +	6 O_2	→	6 CO_2 +	6 H_2O
Initial Amount	0.139 mole	6 * 0.139 mole = 0.834 mole (Note math error in book, book says 0.832)		0	0
Change in Amount	- 0.139 mole	- 0.834 mole		6 * 0.139 mole +0.834 mole	6 * 0.139 mole +0.834 mole
Amount after Rx	**0**	**0**		0.834 mole	0.834 mole

       Now determine the wt of H_2O formed. **From:** Moles = Wt/Mw **Derive**:   Wt = Moles * Mw
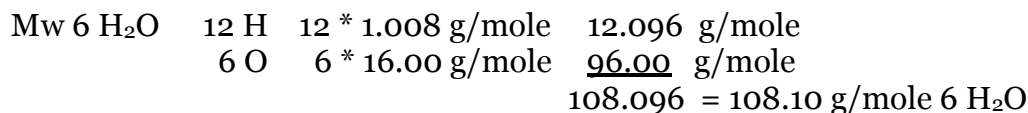
       Mw H_2O 2 H   2 * 1.008 g/mole   2.016 g/mole
                     1 O   1 * 16.00 g/mole   16.00 g/mole
                                                  18.016 = **18.02 g/mole H_2O**

       Wt = Moles * Mw = 0.834 moles * 18.02 g/mole H_2O = 15.02868 = **15.0 g H_2O**

METHOD #3   My Way

Equation $C_6H_{12}O_6$ + 6 O_2 →   6 CO_2 + 6 H_2O

    Mw of $C_6H_{12}O_6$ is 180.14 g/mole from above

    Mw 6 H_2O 12 H 12 * 1.008 g/mole 12.096 g/mole
             6 O   6 * 16.00 g/mole <u>96.00</u> g/mole
                                 108.096 = 108.10 g/mole 6 H_2O

So, we can re-write the above equation as below. Amount is above the reaction, Mw below:

    25.0 g   18.0 g
    $C_6H_{12}O_6$ +   6 O_2 →   6 CO_2 + 6 H_2O
    180.14 g/mole   108.10 g/mole
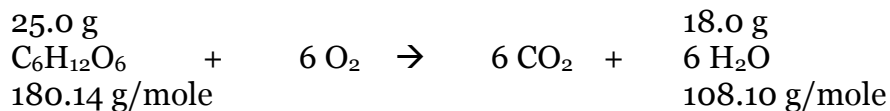
    Now set up a ratio of grams over Mw = grams over mw

$$\frac{25.0 \text{ g } C_6H_{12}O_6}{180.14 \text{ g/mole } C_6H_{12}O_6} = \frac{X}{6 * 18.02 \text{ g/mole } H_2O}$$

        X = 15.0 g H_2O

4.2 Limited Supply

Limiting reactant is one where its amount determines or limits the amount of product formed. One reactant is in excess and one is the limiting reactant. **You can tell that a reaction is a Limiting Reactant** if the amount (wt or moles) of at least 2 of the starting materials is given, one is probably in excess!

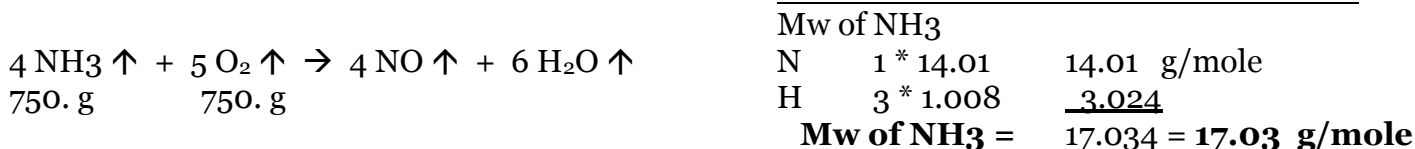**Toy Sparkler:** the amount of Al and KNO3 determine the amount of product, because there is an excess amount of oxygen available: 4 Al ↓ + 3 O2 ↑ → 2 Al2O3 ↓
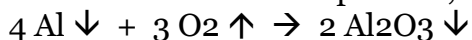
Converting CO to CO2 you use excess O2   2 CO ↑ + O2 ↑ → 2 CO2 ↑
Oxygen in the air is in excess in both cases
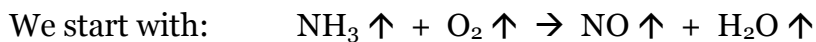
Stoichiometry Calculation with a limiting reactant

What if you have 750. g of each starting material, how much product is formed?

                                            <u>**You must show all Mw Calculations**</u>
                                            Mw of NH3
4 NH3 ↑ + 5 O_2 ↑ → 4 NO ↑ + 6 H_2O ↑   N   1 * 14.01   14.01 g/mole
750. g   750. g   H   3 * 1.008   <u>3.024</u>
                                        Mw of NH3 =   17.034 = **17.03 g/mole**

Just for fun, let's work out the balancing of the above REDOX equation:

We start with: NH_3 ↑ + O_2 ↑ → NO ↑ + H_2O ↑
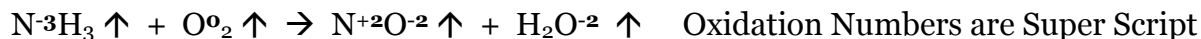
Nitrogen (N) in NH_3 ↑ has an Oxidation Number of -3 (Each H is +1, it's not a hydride where it
                                      would be -1 each)

Nitrogen (N) in NO has an Oxidation Number of +2 (Oxygen is always -2, except in Peroxides)

Oxygen in O_2 is a pure element, so it has an Oxidation Number of 0 (Zero)

Oxygen (O) in NO has an Oxidation Number of -2

    $N^{-3}H_3$ ↑ + O^o_2 ↑ → $N^{+2}O^{-2}$ ↑ + H_2O^{-2} ↑   Oxidation Numbers are Super Script

Break this down to half reactions:
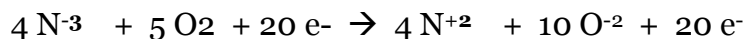$$N^{-3} \rightarrow N^{+2} + 5\,e^-$$
$$O^0_2 + 4\,e^- \rightarrow O^{-2} + O^{-2}$$

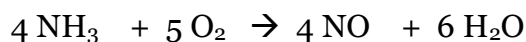Now to balance he electrons, you multiply the top equation by 4 and the bottom by 5

$$4 * [\; N^{-3} \rightarrow N^{+2} + 5\,e^- \;]$$
$$5 * [\; O^0_2 + 4\,e^- \rightarrow O^{-2} + O^{-2} \;]$$

Combine them and get:

$$4\,N^{-3} + 5\,O2 + 20\,e^- \rightarrow 4\,N^{+2} + 10\,O^{-2} + 20\,e^-$$

Canceling out the 20 electrons on both sides and adding in the Spectator Ions (12 H) we get:

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$$

METHOD #1   The Old Fashion Way

Step 1: Find the amount of each reactant in moles

750. g NH3 / 17.03 g/mole NH_3 = 44.0399 = **44.0 mole NH_3**

750. g O2 / 32.00 g/mole O_2 = 23.437 = **23.4 mole O_2**

Step 2: What is the limiting reactant

Stoichiometric ratio = 5 mole O2 / 4 mole NH_3 = 1.25 mole O_2/NH_3 **Theoretical**

Ratio available = 23.4 mole O2 / 44.0 mole NH_3 = 0.532 mole O_2/NH_3 **Actual**

The available ratio is smaller (0.532 moles < 1.25 moles) **so there is not enough O_2**

O2 is the limiting reagent and used for all calculations.   **NH_3 is in excess.**

Step 3: Calculate the mass of product

23.4 mole O_2 * (4 mole NO / 5 mole O_2) * 30.01 g NO/mole NO   = **562. g NO**
　　　　　　←Stoichiometric Factor→   ← Cnvt g to moles →

Note: you arranged ratios above so units cancel out and give your answer in grams of NO

Step 4: Calculate the mass of excess reactant

23.4 mole O_2 * (4 mole NH_3/5 mole O_2) = 18.8 mole NH3 is required
　　　　　　←Stoichiometric Factor→

Note: you arranged Stoich Factor above so units cancel out and give your answer in moles NH3

Excess moles NH_3 = 44.0 mole NH_3 available – 18.8 mole required = 25.2 mole NH_3 excess

Excess g NH_3 = 25.2 mole NH_3 * 17.03 g/mole NH_3 = **429 g NH_3 in excess**

METHOD #2   The Amounts Table

Equation	4 NH3 ↑ +	5 O2 ↑ →	4 NO ↑ +	6 H2O ↑
Initial Amount	44.0 mole	23.4 mole	0	0
Change in Amount	-(4/5)*23.4 mole[*1] - 18.8 mole	-23.4 mole	+(4/5)*23.4 mole + 18.8 mole	+(6/5)* 23.4 mole +28.1 mole
Amount after Rx	25.2 mole	0 mole	18.8 mole	28.1 mole

　　　　*1 from above: -(4 NH_3/5 O_2) * 23.4 mole O_2 = (4 NH_3 / 5) * 23.4 mole
　　　　　　　　　　|→ Stoichiometric coefficient to convert amount of O_2 to NH_3

All of the O_2 is used up (0 moles remain), 25.2 moles of the 44.0 moles of NH_3 are used, 18.8 moles of NO is generated as well as 28.1 moles of H_2O. The weights can be determined as above.

METHOD #3, My way using "Whole Entity" Moles (also PS Tip 4.2)

Calculate the "Whole Entity" $4 NH_3$ = 4 * 17.04 = 68.16 g/Mole "4 NH_3"

$5 O_2$ = 10 * 16.00 = 160.00 g/Mole "5 O_2"

Equation $4 NH_3 \uparrow$ + $5 O_2 \uparrow \rightarrow$ $4 NO \uparrow$ + $6 H_2O \uparrow$

Weight 750. g 750. g

"Moles" 11.0 "Moles" 4.68 "Moles"

The 5 O_2 at 4.68 "Moles" is the smallest amount, so it is the limiting reagent.

Amount of $4 NH_3$ = 4.68 "Moles" = 4.68 * 68.16 g/"Mole" = 318.988 = **319 g NH_3 used**

Excess NH_3 = 750. g − 319. g = **431. g NH_3 in excess**

Interactive Example 4.2 Student should know how to do this problem!
How much methanol is formed? Which compound is in excess and by how much?

$$CO \uparrow + 2 H_2 \uparrow \rightarrow CH_3OH_{(l)}$$

356 g 65.0 g ??
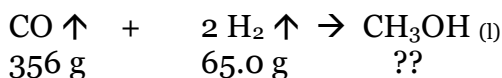
METHOD #3 Moles of Reaction –"Moles"

For the reaction: $2 CO \uparrow + O_2 \uparrow \rightarrow 2 CO_2 \uparrow$ we have 9.5 g CO and xcs O2 determine amt CO2

Mw CO = 12.00 g/mole C **Mw CO2** = 12.00 g/mole C

16.00 g/mole O 32.00 g/mole 2 O

28.00 g/mole CO 44.00 g/mole CO_2

Starting with 9.5 g CO, excess O2, how much CO2 in moles and g is produced

1 "Mole" of CO = 2 CO 1 "Mole" of O2 = O2 1 "Mole" of CO2 = 2 CO2

The "Mole of 2 CO" equals 2 CO = 2 * 28.00 g/mole CO = 56.00 g/mole**"Mole of 2 CO"**

The "Mole of 2 CO_2" equals 2 CO_2 = 2 * 44.00 g/mole CO = 88.00 g/mole**"Mole of 2 CO_2"**

9.5 g Xcs ?

$2 CO \uparrow$ + $O_2 \uparrow \rightarrow$ $2 CO_2 \uparrow$

56.00 g/mole 88.00 g/mole
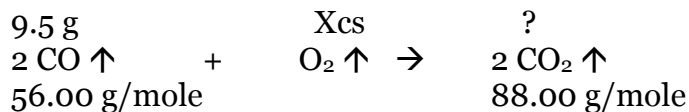
Set up the relationship: $\dfrac{9.5\ g}{56.00\ g/mole}$ = $\dfrac{X}{88.00\ g/mole}$
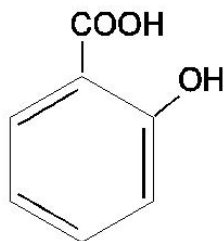
X = 14.928 = **15. g CO_2**

4.3 Percent Yield

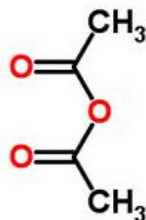**Theoretical yield** is the maximum mass of product that can be obtained from a chemical reaction

Actual yield is the mass of material actually obtained in the laboratory

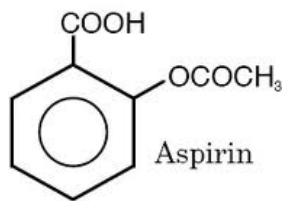**Percent yield** specifies how much of the theoretical yield was obtained

% Yield = 100% * Actual Yield / Theoretical Yield

$C_7H_6O_3 \downarrow$ + $C_4H_6O_{3\ (l)}$ $C_9H_8O_4 \downarrow$ $+ CH_3COOH$

Salicylic Acid   Acetic Anhydride   Aspirin   Acetic Acid

Problem: 14.4 g Salicylic Acid + Xcs Acetic Anhydride → 6.26 g Aspirin + some acetic acid
What is the Percent Yield?

Best method to calculate the Molecular Weight:

	Salicylic Acid		**Aspirin**	**You must show this calculation**
C	7 * 12.01	84.07	9 * 12.01	108.09
H	6 * 1.008	6.036	8 * 1.008	8.064
O	3 * 16.00	48.00	4 * 16.00	64.00
	TOTAL	138.106		180.159

Sig Digits TOTAL 138.11 g/mole   **180.16 g/mole**

Calculate the number of moles of Salicylic Acid
14.4 g Salicylic Acid * [1 mole Salicylic Acid / 138.11 g Salicylic Acid] = **0.104 mole Salicylic Acid**
     Note: Arrange conversion so g Salicylic Acid cancels out

Calculate the moles of Aspirin from the moles of starting material and Stoich Conv Factor
0.104 mole Salicylic Acid * [1 mole Aspirin / 1 mole Salicylic Acid] = **0.104 mole Aspirin**
     Note: Arrange conversion so mole Salicylic Acid cancels out

Convert moles of Aspirin to grams of Aspirin
0.104 mol Aspirin * 180.16 g Aspirin / 1 mole Aspirin = **18.8 g Aspirin**
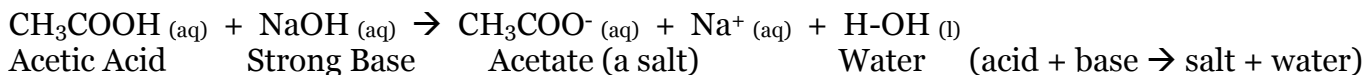   Note: mole Aspirin cancels out
     This is the Max you can get or the Theoretical 100% Yield

% Yield = 100% * Actual Yield / Theoretical Yield = 100% * 6.26 g / 18.8 g = **33.3 % yield**

4.4 Chemical Equations and Chemical Analysis
Quantitative Analysis of a mixture determines the amount of one compound in a mixture

Vinegar is an aqueous solution of acetic acid. You can titrate the acid with a base to determine the amount of acetic acid in vinegar:

$CH_3COOH_{(aq)}$ + $NaOH_{(aq)}$ → $CH_3COO^-_{(aq)}$ + $Na^+_{(aq)}$ + $H\text{-}OH_{(l)}$
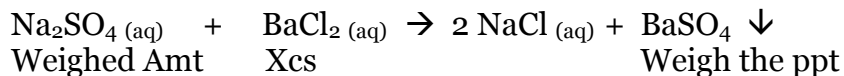Acetic Acid   Strong Base   Acetate (a salt)   Water   (acid + base → salt + water)

This is performed using a titration with an indicator solution to determine the endpoint (when all of the acid is neutralized by the base). Knowing how much base you used, you can determine the amount of acetic acid in the vinegar solution. This analysis is performed in most Chem I and II lab experiments. See the following on my Chemistry web pages:

     Titration Notes 19-Oct-2009.pdf
     --- and ---
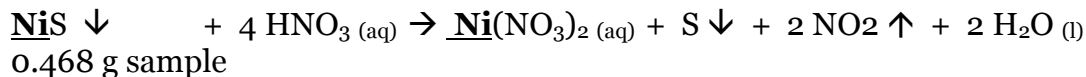   Notes Titration Notes Standardizing NaOH against KHP 28-Oct-2009.pdf

Problem: The mineral Thenardite is mostly Sodium Sulfate, Na_2SO_4. If you react a weighted amount of the mineral with Barium Chloride, Barium Sulfate will precipitate out. You dry and weigh the $BaSO_4$ and then can back calculate the amount of Na_2SO_4 in the sample.

$$Na_2SO_{4\ (aq)} \quad + \quad BaCl_{2\ (aq)} \rightarrow 2\ NaCl_{\ (aq)} + BaSO_4 \downarrow$$
Weighed Amt   Xcs   Weigh the ppt
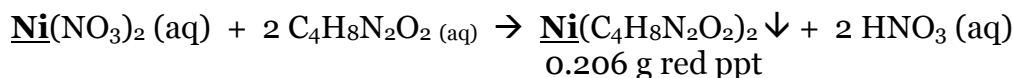
1 mole of $BaSO_4$ precipitated out represents 1 mole of Na_2SO_4 in the sample.

Example 4.3 Mineral Analysis for Nickel (II) Sulfide, NiS. 0.468 g of the mineral sample produces 0.206 g of $Ni(C_4H_7O_2)_2$. How much NiS is in the sample?

React the sample with Nitric Acid to dissolve it:

      NiS $\downarrow$ + 4 $HNO_{3\ (aq)}$ → **Ni**$(NO_3)_{2\ (aq)}$ + S $\downarrow$ + 2 NO2 $\uparrow$ + 2 $H_2O_{\ (l)}$
      0.468 g sample

React the resulting solution with dimethylglyoxime, $C_4H_8N_2O_2$ to form the ppt:

      Ni$(NO_3)_2$ (aq) + 2 $C_4H_8N_2O_{2\ (aq)}$ → **Ni**$(C_4H_8N_2O_2)_2 \downarrow$ + 2 HNO_3 (aq)
                                0.206 g red ppt

1 mole of Nickel (II) Sulfide, **NiS** results in 1 mole of **Ni**$(C_4H_8N_2O_2)_2 \downarrow$

Calculate the Mw $Ni(C_4H_8N_2O_2)_2$ NiS

1 Ni	1 * 58.69	58.69	1 Ni	1 * 58.69	58.69
8 C	8 * 12.01	96.08	1 S	1 * 32.07	32.07
16 H	16 * 1.008	16.128			90.76
4 N	4 * 14.01	56.04	Correct Sig Digits		90.76 g/mole NiS
4 O	4 * 16.00	64.00			

                  Total 290.938
      Correct Sig Digits   290.94 g/mole $Ni(C_4H_8N_2O_2)_2$ NOTE BOOK VALUE DIFFERS!

Moles of $Ni(C_4H_8N_2O_2)_2$ = 0.206 g of $Ni(C_4H_7O_2)_2$ * 288.9 g/mole $Ni(C_4H_8N_2O_2)_2$ = 7.13 x 10^{-4} moles

g of NiS = 7.13 x 10^{-4} moles $Ni(C_4H_8N_2O_2)_2$ * (1 mole NiS / 1 mole $Ni(C_4H_8N_2O_2)_2$) *
      (90.75 g NiS / mole Nis) = **0.0647 g Nis**

% Nis = 100% * Actual Yield / Theoretical Yield = 100% * 0.0647 g Nis / 0.468 g sample =
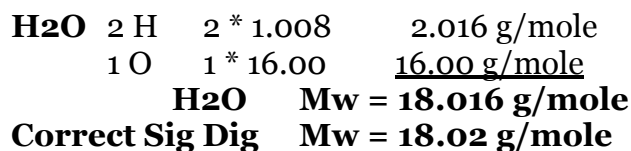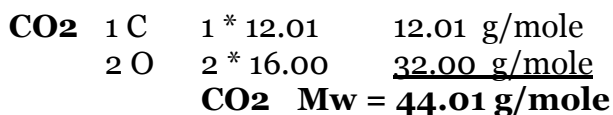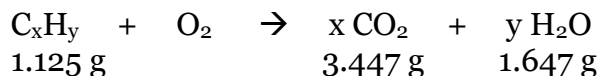   **13.8 % NiS**

Determining the Formula of a Compound by Combustion
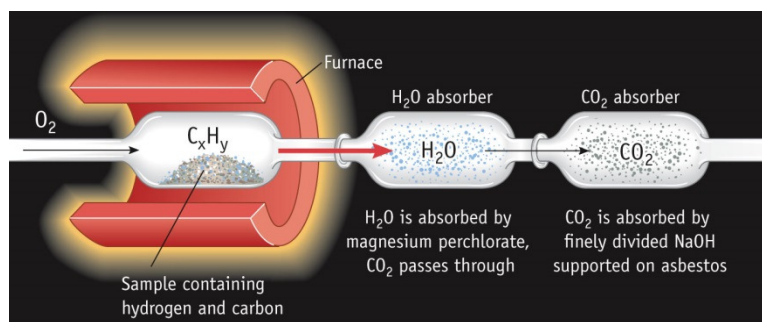
Burning an organic compound (contains C, H, N, and O) with excess oxygen will produce CO2 and H2O and Nitrogen is determined by a separate analysis. The amount of these materials can be determined (see above). From this data you can calculate the empirical formulae of the organic compound. Note: Nitrogen and Oxygen cannot be determined by this method!

Example 4.4   1.125 g of a liquid hydrocarbon (C and H) was burned and produced 3.447 g of CO_2 and 1.647 g of H_2O. The Mw was found to be 86.2 g/mole. What are the empirical and molecular formulae of this compound?

$$C_xH_y \quad + \quad O_2 \quad \rightarrow \quad x\,CO_2 \quad + \quad y\,H_2O$$
1.125 g   3.447 g   1.647 g

CO2 1 C   1 * 12.01   12.01 g/mole   **H2O** 2 H   2 * 1.008   2.016 g/mole
       2 O   2 * 16.00   <u>32.00 g/mole</u>   1 O   1 * 16.00   <u>16.00 g/mole</u>
              CO2   Mw = 44.01 g/mole   **H2O   Mw = 18.016 g/mole**
                                                             Correct Sig Dig   Mw = 18.02 g/mole

Calculate the moles of each:
     3.447 g CO2 / 44.01 g/mole CO2 =   1.647 g H2O / 18.016 g/mole H2O =
            0.07832 mole CO2   **0.09142 mole H2O**

Convert to mole of C and H in the unknown

     0.07832 mole CO2 * (1 mole C in the unknown/ 1 mole CO2)   = 0.07832 mole C

     0.09142 mole H2O * (2 mole H in the unknown / 1 mole H2O)   = 0.18284 mole H
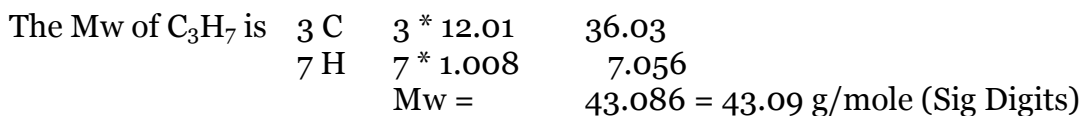
     The C/H mole ratio is (0.18284 mole H / 0.07832 mole C)   = 2.335 H/C

     2.335 is not a whole number – you can't have 2.3 parts of an atom, so multiply it by

          2 * 2.335 = 4.670, which also is not a whole number

          3 * 2.335 = 7.005 which is a whole number.

The Empirical Formulae is C_3H_7

The Mw of C_3H_7 is   3 C   3 * 12.01   36.03
                      7 H   7 * 1.008   7.056
                             Mw =   43.086 = 43.09 g/mole (Sig Digits)

The Molecular Formulae = Empirical Formulae * Multiplier

Multiplier = Mw of the compound / Mw of the Empirical Formulae = 86.2 / 43.09 = 2

Molecular Formulae = 2 * C_3H_7 = C_6H_{14}

This example is a little different; it has Oxygen which we cannot measure directly

Example 4.5 Carbon, Hydrogen and Oxygen analysis. **0.513 g of a compound** produces **5.01 g of CO2** and **0.103 g of H2O**. What are the empirical and molecular formulae of this compound? NOTE: The amount of Oxygen is not given – there may or may not be Oxygen in the compound!

$$C_xH_y \quad + \quad O_2 \quad \rightarrow \quad x\,CO_2 \quad + \quad y\,H_2O$$
0.513 g   5.01 g   0.103 g
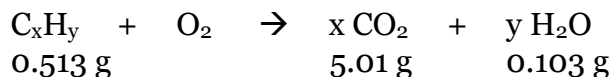
1. Determine the moles of Carbon and Hydrogen in the sample

     5.01 g CO2 * (1 mole CO2 / 44.01 g CO2) * (1 mole C)/(1 mole CO2)   = **0.0144 mole C**

     0.103 g H2O * (1 mole H2O / 18.02 g H2O) * (2 mole H)/(1 mole H2O)   = **0.0114 mole** H

2. Convert Moles to grams of each element in the original sample

     0.0144 mole C * (12.01 g C / mole C) = 0.137 g C in the original sample

     0.014 mole H * (1.008 g H / mole H) = 0.0115 g H in the original sample

Determine the amount of Oxygen in the sample

        0.513 g compound – 0.137 g C – 0.0115 g H = 0.364 g Oxygen in the original sample

3. Convert to moles

        0.365 g O * (1 mole O / 16.00 g O) = 0.0228 mole O in the original sample

4. Find the O / C ratio

0.0228 mole O / 0.0144 mole C = 2 O for every C

Above we determined that for every 0.0114 mole of C there is 0.0114 mole of H – a 1 to 1 ratio

5. So the empirical formulae = $C_1H_1O_2$ Mw =   1 C   1 * 12.01   12.01
                                                1 H   1 * 1.008   1.008
                                                2 O   2 * 16.00   <u>32.00</u>
                                      Mw $C_1H_1O_2$ = 45.018 = **45.02 g/mole**

6. The Mw of the compound is 86.2, but the Mw of $C_1H_1O_2$ = 45.02 g/mole
        Factor = 86.2 g/mole / 45.02 g/mole = 1.9147 = 2
        Molecular Formulae = 2 * Empirical Formulae = **$C_2H_2O_4$**

4.5 Measuring Concentrations of Compounds in Solution

Molarity = Moles of Solute / Liters of Solvent = Moles/L = **M**

See: Titration Notes 19-Oct-2009.pdf on my web pages

58.4 g of NaCl is added to water in a 1 liter volumetric flask and it is filled to the mark with water
    Mw NaCl = 22.99 + 35.45 = 58.44 g/mole
    Molarity = M = Moles/L = 58.4 g NaCl / (58.4 g/mole * 1.000 L) = **1.00 M NaCl**

Important Molarity is Moles per Liter, that means you fill a volumetric first with the solute and then fill to the 1.00 Liter mark with solvent. You DO NOT add 1.00 Liter of solvent to the solute!

Distilled water

250-mL volumetric flask   0.435 g KMnO$_4$

The KMnO$_4$ is first dissolved in a small amount of water.

Distilled water is added to fill the flask with solution just to the mark on the flask.

A mark on the neck of a volumetric flask indicates a volume of exactly 250. mL at 25 °C.

0.435 g KMnO4 is put into a 250 ml volumetric and it is filled to the mark with DI. What is it's M?

Mw KMnO4

	1 K	1 * 39.10	39.10
	1 Mn	1 * 54.94	54.94
	4 O	4 * 16.00	64.00
			158.04 g/mole

Moles of KMnO4 = 0.435 g KMnO4 / 158.04 g/mole = 0.0027524 = 2.75×10^{-3} Mole KMnO4

M KMnO4 = Moles/L = 2.75×10^{-3} Mole KMnO4 / 0.250 L = 0.0110096 = **1.10×10^{-2} M**
Note loss of SD in books answer!

This solution contains 1.10×10^{-2} moles/Liter of K^+ and 1.10×10^{-2} moles/L of MNO_4^-

If we had a 0.10 M CuCl2, it would contain: $CuCl2 \rightarrow Cu^{2+}_{(aq)} + 2 Cl^-_{(aq)}$
Or 0.10 M Cu^{2+} and **0.20 M Cl⁻**

Preparing Solutions of Known Concentration

How do you prepare 2.00 L of 1.50 M Na2CO3?

Mw			
	2 Na	2 * 22.99	45.98
	1 C	1 * 12.01	12.01
	3 O	3 * 16.00	48.00

M = Moles / L = g/(Mw * L)   **Mw = 105.9**88.00 g/mole

9 g/mole

Rearrange: **g** = M * Mw * L = 1.50 M * 106.0 g/mole * 2.00 L = **318. g Na2CO3**

To prepare the solution: Take 318. g Na2CO3 place it in a 2.00 L volumetric. Fill the volumetric to the 2.00 L mark with DI.

Diluting a More Concentration Solution   **M1V1 = M2V2 =Moles = g / Mw**

Problem: You need 500. ml of 0.0010 M K2Cr2O7, you have 0.100 M K2Cr2O7

V2 = M1V1 / M2 = 500. ml * 0.0010 M / 0.100 M = 5.00 ml

To prepare the solution: Take 5.00 ml of 0.100 M K2Cr2O7 place it in a 500. ml volumetric, Fill to the mark with DI

Problem: What is the concentration of Fe^{3+} in a solution of diluting 1.00 ml of 0.236 M Fe^{3+} to 100.0 ml?
M1V1 = M2V2   Rearrange: M2 = M1V1/V2
M2 = 0.236 M * 1.00 ml / 100.0 ml = **2.36×10^{-3} M**

Serial Dilutions: dilute 10.0 ml of 0.550 mol/l of NaCl to 100.0 ml. Then dilute 5.00 ml to 100.0 ml. What is the final NaCl concentration?

1st dilution: M1V1 = M2V2
Rearrange: **M2** = M1V1/V2 = 0.550 M * 10.0 ml / 100.0 ml = **0.0550 M**
2nd dilution
M2 = M1V1/V2 = 0.0550 M * 5.00 ml / 100.0 ml = 0.00275 = **2.75×10^{-3} M**

See text book for more examples

4.6 pH, a Concentration Scale for Acids and Bases   pH = -log [H3O⁺]

pH of Vinegar	$= -\log (1.6 \times 10^{-3}$ M$)$	$= -(-2.80)$	$= 2.80$
pH of Pure Water	$= -\log (1.0 \times 10^{-7}$ M$)$	$= -(-7.00)$	$= 7.00$
pH of Blood	$= -\log (4.0 \times 10^{-8}$ M$)$	$= -(-7.40)$	$= 7.40$
pH of Ammonia Water	$= -\log (4.3 \times 10^{-12}$ M$)$	$= -(-11.37)$	$= 11.37$

For aqueous solutions at 25° C, pH values less than 7 are acidic, greater than 7 are basic, at 7 is neutral

Hydronium Ion concentration from pH   **$[H_3O^+] = 10^{-pH}$**

Diet Soda has a ph of 3.12, ? $[H3O^+]$ $[H3O^+] = 10^{-pH} = 10^{-3.12} =$ **7.6×10^{-4} M**
Students need to be able to perform this calculation on their calculators!

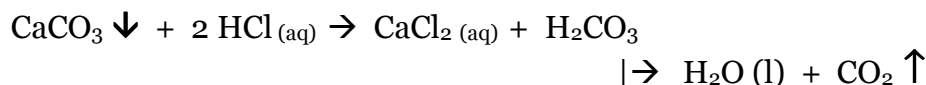pH is measured by a **pH meter**, it accurately measures $[H_3O^+]$

REMEMBER: **$M_1 V_1 = M_2 V_2 = $ Moles $= g / Mw$**

Example 4.8 – Students do these!

4.7 Stoichiometry of Reactions in Aqueous Solution

How much CaCO3 is required to react with 25 ml of 0.750 M HCl?

$CaCO_3 \downarrow + 2 HCl_{(aq)} \rightarrow CaCl_{2\,(aq)} + H_2CO_3$

                                        $| \rightarrow H_2O$ (l) $+ CO_2 \uparrow$

Moles of HCl   M = Moles / L   therefore: Moles = M * L
Moles HCl = M * L = 0.750 M * 25 ml * 1 L/ 1000. ml = 0.01875 moles HCl

Moles of $CaCO_3$ = 0.01875 moles HCl * (1 mole $CaCO_3$ / 2 mole HCl) = 0.009375 moles $CaCO_3$

Mw $CaCO_3$	1 Ca	1 * 40.08	40.08
	1 C	1 * 12.01	12.01
	3 O	3 * 16.00	48.00

                        Mw = 100.09 g / mole $CaCO_3$

g of $CaCO_3$ = 0.009375 moles $CaCO_3$ * 100.09 g / mole $CaCO_3$ = 0.93834 = **0.94 g $CaCO_3$**

OWL Example 4.9 Students need to work this problem

Titration: A method of Chemical Analysis

Titration involves quantitatively adding on solution to another using a accurate measuring device such as a burette. The point where the reaction of solution A is quantitatively completed against solution B is called the **end point or equivalence point** – equal molar amounts of acid and base have reacted. This is usually determined using an indication such as phenolphthalein.

OWL Example 4.10 1.034 g of oxalic acid is dissolved in water and an end point indicator added. This sample was titrated with 0.485 M NaOH and an end point reached when 34.47 ml of NaOH was added. What is the mass (wt) and mass % of oxalic acid in the original sample?
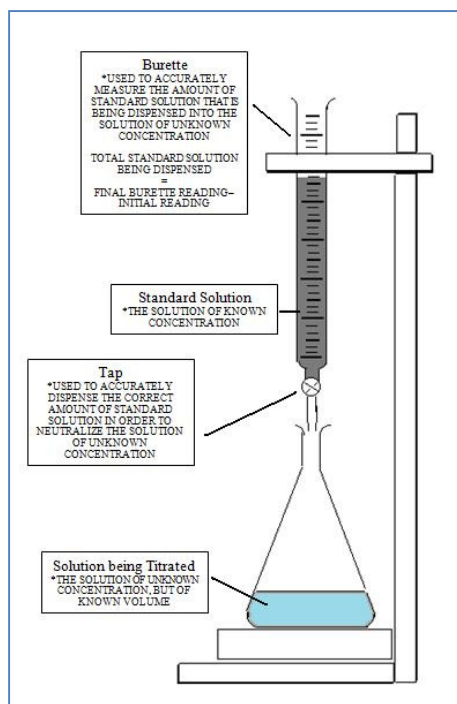

Oxalic Acid, $H_2C_2O_4$
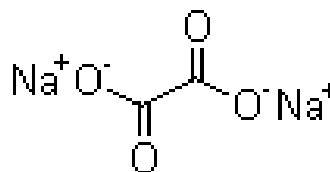
Write the equation: $H_2C_2O_{4\,(aq)} + 2\,NaOH \quad \rightarrow \quad Na_2C_2O_{4\,(aq)} + 2\,H_2O_{(l)}$
                        1.034 g   34.47 ml of 0.485 M

Moles of NaOH = Molarity * Volume = 0.485 Moles/Liter * 34.47 ml * 1 L/1000. ml =
0.0167179 moles NaOH

***** ***** **Important Below** ***** *****

Oxalic Acid has 2 Acid Functions (-COOH), so it takes 2 moles of NaOH for each mole of Oxalic Acid

Moles of Oxalic Acid (OA) = moles NaOH * (1 mole oxalic acid / 2 moles NaOH) =
0.0167179 moles * (1 mole oxalic acid / 2 moles NaOH) = 0.0083589 moles OA

Mw Oxalic Acid   2 H   2 * 1.008   2.016
                        2 C   2 * 12.01   24.02
                        4 O   4 * 16.00   <u>64.00</u>
                                   Mw = 90.036 = **90.04 g OA/mole OA**

Moles of Oxalic Acid = Wt in g Oxalic Acid/ Mw Oxalic Acid   Then Rearrange:

Wt in g OA = Moles of OA * Mw OA = 0.0083589 moles OA * 90.04 g OA/mole OA =
0.7526353 = **0.753 g OA**

% of OA in the sample = 100% * amount of pure material found / wt of sample =
100% * 0.753 g OA / 1.034 g sample = **72.8 % Oxalic Acid**

***** ***** **Important Below** ***** *****

Standardizing an Acid or Base is the procedure in which the concentration of a compound in a solution is accurately determined by titration against a primary standard. A solid material that can be dried and accurately weighted is used for this standardization.
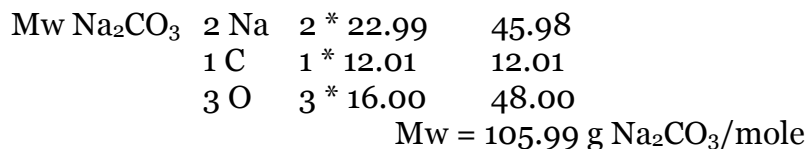
Sodium Carbonate, Na_2CO_3 is a weak base and can be used to standardize an acid such as HCl (l).

         Na_2CO_3 + 2 HCl → 2 NaCl + H_2CO_3
                                      |→ H_2O + CO_2 ↑

Potassium Acid Phthalate (KHP) is a weak acid and can be used to standardize a base such as NaOH $_{(l)}$

(KHP) $C_8H_5O_4^-K^+$ +   NaOH → $C_8H_4O_4^{2-}K^+Na^+$ + H-OH
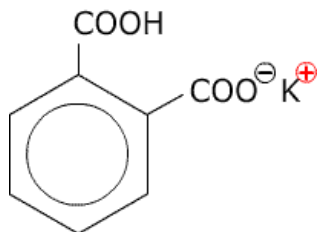
Example 4.11   0.263 g Na_2CO_3 requires 28.35 ml of HCl (aq) for the titration endpoint.
What is the molarity, M, of the HCl?

       Mw Na_2CO_3 2 Na   2 * 22.99   45.98
                      1 C   1 * 12.01   12.01
                      3 O   3 * 16.00   48.00
                                     Mw = 105.99 g Na_2CO_3/mole

M1V1 = M2V2 = Moles = g / Mw   Rearrange: M_1 = g / (Mw * V_1)

M1 = g Na2CO3 / Mw Na2CO3 * V1 HCl =

$\underline{0.263 \text{ g Na2CO3}}$ $\underline{\text{1 mole Na2CO3}}$ $\underline{\text{2 mole HCl}}$ $\underline{\hspace{1cm}1\hspace{1cm}}$ $\underline{\text{1000. ml}}$ = **0.175 M**
              *   106.0 g Na2CO3   *   1 mole Na2CO3   *   28.35 ml HCl   *   1 L

Determining Molar Mass by Titration
Using the following equation basic equation: **M1V1 = M2V2 = Moles = g * Mw,** with the proper input values, we can determine the Mw of a compound using titration.

OWL Example 4.12   1.056 g of an unknown acid, HA was titrated with 33.78 ml of 0.256 M NaOH according to the following equation: What is HA Mw?
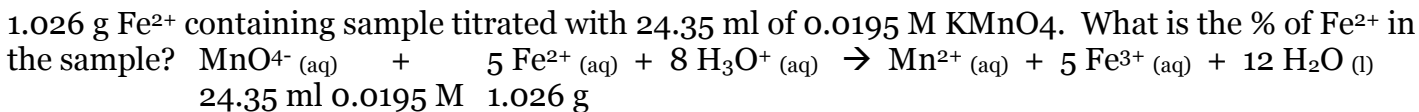
     HA $_{(aq)}$ +   NaOH $_{(aq)}$ →   NaA $_{(aq)}$ + H-OH $_{(l)}$
     1.056 g   33.78 ml of 0.256 M   ? Mw
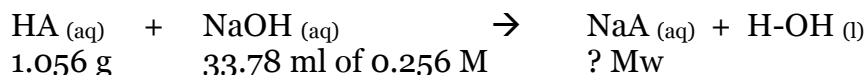
     Mw = g / M1V2   = 1.056 g / (0.256 **M NaOH** * 33.78 ml) * (1 L /1000. ml) =

         1.056 g / (0.256 **moles/L NaOH** * 33.78 ml) * (1 L /1000. ml) = 122.11 = **122. g/mole**

Titrations Using Oxidation-Reduction Reactions
Redox reactions concentrations can also be determined using titration, **<u>equation is given below</u>**

1.026 g Fe^{2+} containing sample titrated with 24.35 ml of 0.0195 M KMnO4. What is the % of Fe^{2+} in the sample? MnO_4^- $_{(aq)}$ +   5 Fe^{2+} $_{(aq)}$ + 8 H_3O^+ $_{(aq)}$ → Mn^{2+} $_{(aq)}$ + 5 Fe^{3+} $_{(aq)}$ + 12 H_2O $_{(l)}$
             24.35 ml 0.0195 M   1.026 g

Moles of Fe^{2+} = Moles MnO_4^- * (5 Fe^{2+} / 1 MnO_4^-) =   Remember Moles = M1V1

     (0.0195 moles/L * 24.35 ml * [1 L / 1000. Ml]) * (5 Fe^{2+} / 1 MnO_4^-) = 0.2374 moles of Fe^{2+}

Moles = wt / Mw   wt = moles * Mw = 0.2374 moles of Fe^{2+} * 55.85 g/mole = 0.13258 = **0.133 g Fe**

% Fe^{2+} = 100% * wt pure compound / wt of sample = 100% * 0.133 g Fe / 1.026 g sample = **12.9 % Fe**

4.8 Spectrophotometry is the quantative measure of the extent of light absorption by a sample. The extent of light absorption of spectrum of the sample is measured using a spectrophotometer:
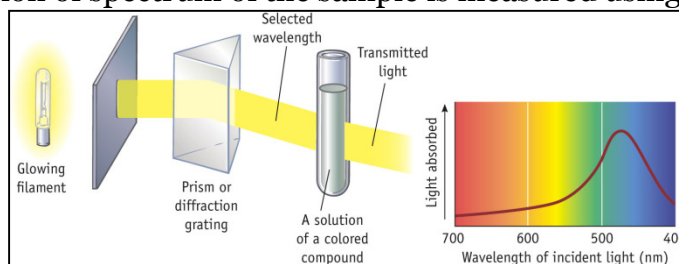
Transmittance, Absorbance and the Beer-Lambert Law

Transmittance or % Transmittance is the ratio of the amount of light that is transmitted (passes through or is not absorbed) to the amount of incident light (fell on the sample).
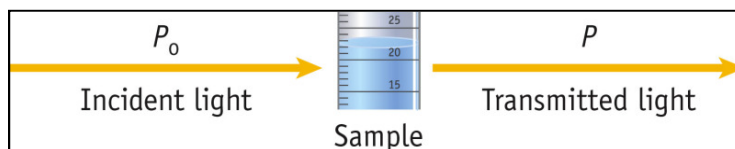
Transmittance (T) = P / Po

Absorbance (A) is the amount of light that is absorbed by the sample = **A = - log T = - log P/Po**
Absorbance is also related to the concentration of the sample by: **A = € * l * c**

   **€** = molar absorptivity = L / mole * cm
    l = the pathlength of the cell in cm
    c = the concentration in mole / L

The light absorbance of a sample is directly proportional to the concentration of the sample.

Spectrophotometric Analysis

1. Properly dilute the sample and record the spectrum, usually in the entire UV (350 nm -> 250 nm) or Visible (600 nm -> 350 nm). The maximum absorbance peak should be between 0.7 and 1.0 absorbance units. If not, redilute the sample and re-run the spectrum. Curve 2 below is not acceptable, Curve 1 is acceptable.
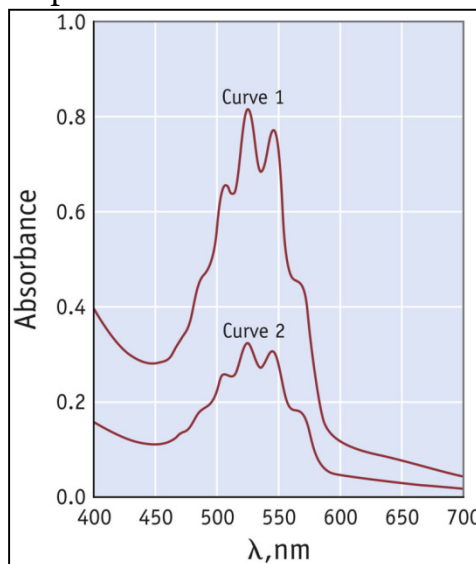

2. Choose a wavelength were the peak is widest and stongest.
3. Prepare a calibration plot of known concentration vs absorbance at a particular wavelength

4. Determine the concentration of the unknown by running it's curve and comparing its absorbance at the wavelength to the calibration curve.

Example 4.14 A solution of KMnO4 has an A of 0.539 at 540 nm in a 1 cm cell. What is it's concentration based on the following data:

| [KMnO4 (M)]	A		[KMnO4 (M)]	A
0.0300	0.162		0.120	0.670
0.0600	0.330		0.150	0.840
0.0900	0.499			
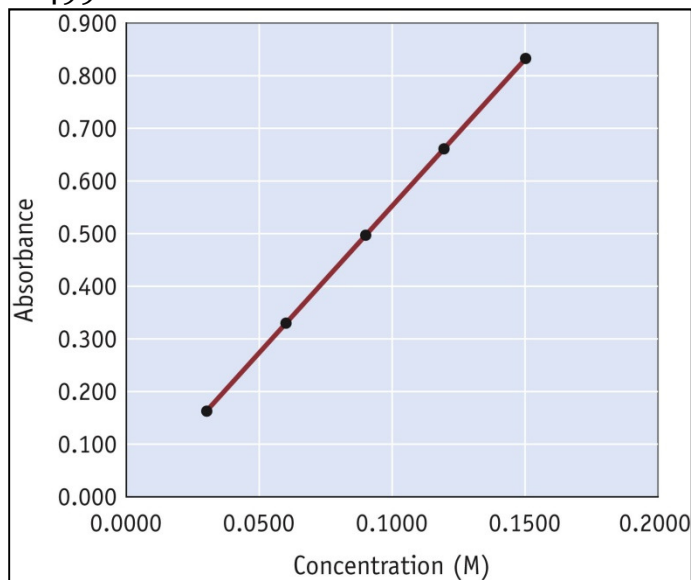
From the calibration curve, the sample has a concentration of 0.0969 M

Below is an actual analysis of a developer solution analysis that I developed at Eastman Kodak. The spectra were recorded directly to a computer. We first recorded the Ultra Violet spectra of a pure sample of each of the ingredients in the developer solution and stored it on the computer. We then recorded the spectrum of the actual developer and had the computer perform a mathematical fit of the components curves and accurately determine the concentration of each of the components. The analysis took about 10 minutes to perform and was accurate to 3 SD!
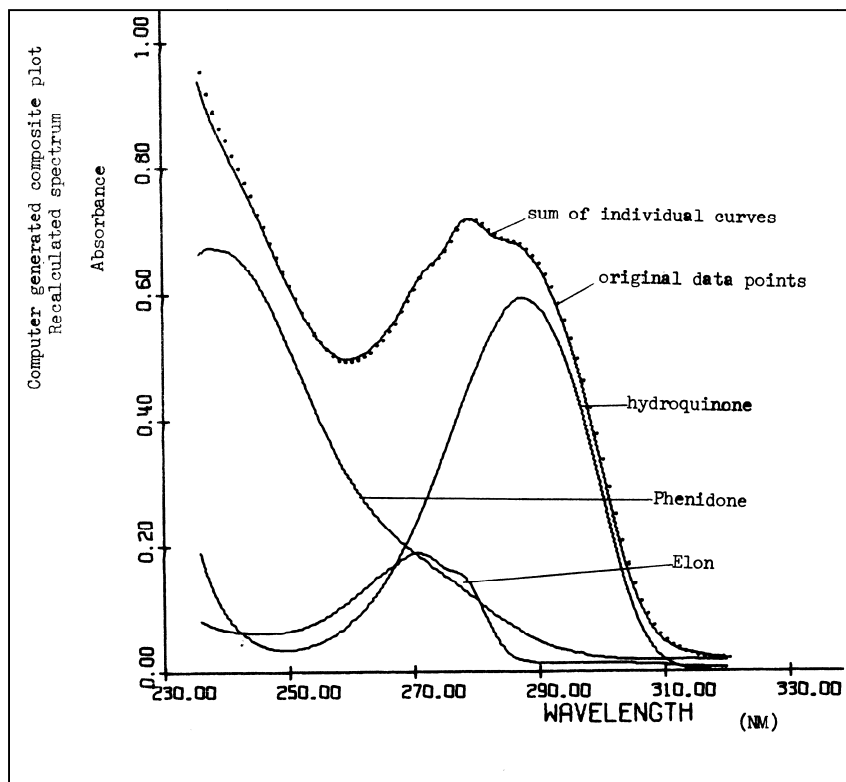
Antacids

NaHCO3, KHCO3, CaCO3, Mg(OH)2, and Al(OH)3 are antacids, they react with HCl in the stomach to neutralize it.

Write Balanced Complete, Ionic and Net Ionic equations for each reaction

Tums contains 500 mg of CaCO3, what volume of 0.500 M HCl (aq), also known as stomach acid will it neutralize? How much gas is given off (1 mole of a gas occupies 22.4 L).

Rolaids contains CaCO3 and Mg(OH)2. If 22.52 ml of 0.500 M HCl is neutralized by one tablet, and the one tablet contains 550. mg of CaCO3, how much Mg(OH)2 is in the tablet?