

Name: _____ Date: _____

Chemistry 12	UNIT ONE	RATES OF REACTIONS
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REVIEW READING:

Chapter 1	Chapter 5
Types of reactions SIG FIGS **The mole Solution concentrations Ideal Gas Equation **Stoichiometry	Thermochemistry Enthalpy

ENERGY EFFECTS IN CHEMICAL REACTIONS

Molecules possess both kinetic and potential energy.

There are three modes of kinetic energy in molecules:

- 1) Rotation: molecule can rotate on an imaginary axis i.e. tumble
- 2) Vibration: stretching of bonds and bending of bonds eg. H₂O
- 3) Translation: motion between two points

Two types of potential energy that molecules can have:

- 1) Nuclear binding energy: energy which holds the nucleus together
- 2) Bond energy (electronic energy):
 - whenever bonds are formed, energy is released. The molecule is at a lower potential energy or more stable configuration.
 - whenever bonds are broken, energy is absorbed. The resulting species are at a higher potential energy.

Most of the energy absorbed or lost in ordinary chemical reactions is due to the making and breaking of bonds.

The energy absorbed or lost is usually in the form of heat (very seldom light or electrical energy). This heat of reaction is referred to as the enthalpy of reaction. Given the symbol, H.

ΔH_r = the change in enthalpy for a reaction or the Heat of reaction

ΔH_r is the amount of heat gained or lost in a chemical reaction. Units are kJ.

Name: _____ Date: _____

If heat is liberated in a reaction it is an exothermic reaction and ΔH_r is negative.
If heat is absorbed overall in a reaction it is an endothermic reaction
and ΔH_r is positive.

Since the amount of energy a molecule possesses depends upon temperature and possibly pressure, it is important to specify the temperature and pressure in which the reaction is carried. If ΔH_r values are to be calculated and compared, then some standard temperature and pressure should be chosen.

The standard chosen was 25°C and 101.3 kPa which = 1 atm = 765 mmHg

ΔH_r° - the $^\circ$ means that the heat of reaction was determined at standard state conditions (in the box, above)

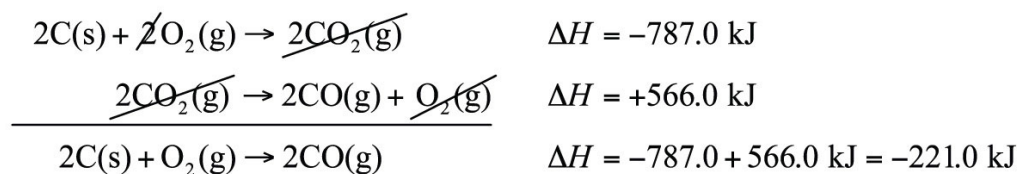
NOTE: only gas reactions are dependent upon pressure
(that is, at least one of the reactants is a gas in the reaction)

Thermochemistry:

Hess' Law of Heat Summation

When a reaction can be expressed as the algebraic sum of two or more other reactions, the heat of the overall reaction is the algebraic sum of the heats of these reactions.

example:

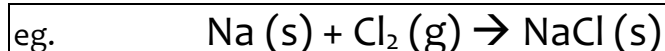


Name: _____ Date: _____

6.1 THE IMPORTANCE OF REACTION RATES

Spontaneous Chemical Reactions

If a chemical reaction occurs at all, it is called spontaneous.



The reverse reaction is NOT spontaneous because you need to supply energy to breakdown the NaCl into its constituent elements.

Two driving forces in any chemical reaction:

- 1) a drive to minimum enthalpy, H
 - 2) a drive to maximum entropy, S
- (the spontaneity of a reaction depends on these two)

Entropy can be defined as the measure of the randomness of a chemical system. A large value for entropy means very random. If entropy increases during a chemical reaction, it means the system is becoming more random or disordered.

These two variables are related in the Gibb's free energy equation which says:

$$\Delta G = \Delta H - T \Delta S$$

where ΔG is a measure of the energy available (per mole) to do useful work from a chemical reaction.

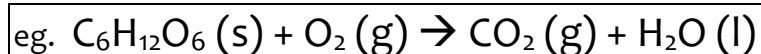
ΔH has units of Joules (J). T is temperature in Kelvin (K), S is the entropy in Joules per Kelvin.

If ΔG is negative, the reaction is spontaneous to the right and useful work can be done.

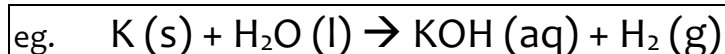
If ΔG is positive, the reaction as written is not spontaneous to the right but the reverse reaction would be spontaneous.

If $\Delta G = 0$ then the chemical system is at equilibrium. (the rate of the forward rxn equals the rate of the reverse rxn so no useful work can be obtained from this system).

Spontaneous reactions may occur very slowly,



or very quickly,



Hence the importance of reaction rates for chemists is how to control them, i.e. how to speed them up or slow them down.

eg. slower rusting metal or

Name: _____ Date: _____

faster acting "beano"

EVERYDAY SITUATIONS REQUIRING THE CONTROL OF REACTION RATES:

1. Body chemistry requires exact temp. to ensure rxns of life occur at appropriate rate.
2. Fuels burn quickly in air and may explode in pure oxygen. As the oxygen concentration is lowered, the rate of burning drops to zero, which is why "smothering" a fire is effective.
3. Food preservation to slow reactions in which bacteria grows.
4. Protectants in car paints that are used to prevent oxygen from reacting with the iron in the car to produce rust.
5. Enzymes that catalyze our body chemistry.

Can you add to this list?

Name: _____ Date: _____

6.2 AVERAGE RATE OF A CHEMICAL REACTION

Reaction rate: a positive quantity indicating how the amount of reactant, product, (or energy) changes with time

Average reaction rate: relates the speed at which the whole transformation occurred. Reflects the overall process.

AVERAGE RATE = $\frac{\text{change in concentration of product}}{\text{time elapsed}}$
= $\frac{\text{mol / L}}{\text{min.}}$ = $\text{mol L}^{-1} \text{ min}^{-1}$ = M / min = $\frac{\Delta C}{\Delta t}$

OR = $\frac{\text{change in concentration of reactant}}{\text{time elapsed}}$

since C_1 (reactant) > C_2 (reactant) as the reaction proceeds, then ΔC will be negative. Therefore always assume a positive ΔC (or absolute value)

Consider: $\text{H}_2\text{O (g)} + \text{C (s)} \rightarrow \text{CO (g)} + \text{H}_2 \text{ (g)}$

The average rate of production of CO (g) or $\text{H}_2 \text{ (g)}$ EQUALS
the average rate of LOSS of $\text{H}_2\text{O (g)}$ or C (s) over the same time period

HOWEVER Consider: $2\text{H}_2 \text{ (g)} + \text{O}_2 \text{ (g)} \rightarrow 2\text{H}_2\text{O (g)}$

The average rate of LOSS of $\text{H}_2 \text{ (g)}$ DOES NOT EQUAL
the average rate of LOSS of $\text{O}_2 \text{ (g)}$ BECAUSE THE MOLE RATIO IS 2:1

Sample questions in the textbook: p. 240

Consider: $\text{X} + 2\text{Y} \rightarrow \text{Z}$

$$\text{Rate} = \frac{\Delta Z}{\Delta t} = \frac{\Delta X}{\Delta t} = \frac{1}{2} \frac{\Delta Y}{\Delta t}$$

All of these are valid units for rate:

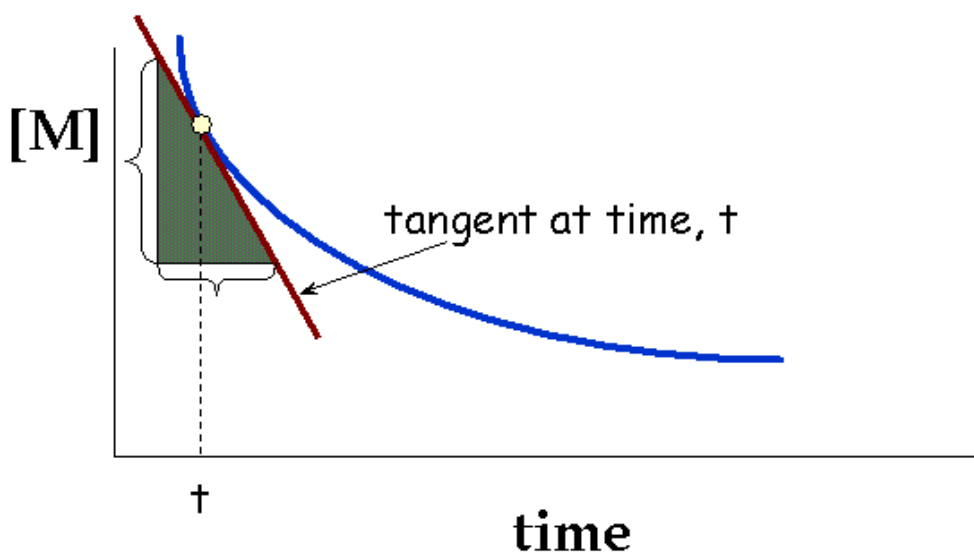
moles / s, g / min, L / hr, [] / s, kJ / s, kCal / s, kPa / s, mmHg / s, etc.

Most calculations involving rate are "Average Rate" problems. (eg. word problems, stoichiometry)

Name: _____ Date: _____

Instantaneous reaction rate: relates the speed of a transformation at a particular point in time (note: instantaneous rate must be identified and linked to a specific time)

Instantaneous Rate_{time, t} = slope of the tangent at time = t



Name: _____ Date: _____

6.3 HOW RATES ARE MEASURED

LIQUIDS:

1. Sampling: small sample withdrawn from solution then analysis of concentration by titration. (change in acidity or pH) $[\text{conc}] / \text{time}$
2. Colour change: instrument (spectrometer) measures colour and relates to concentration of coloured substance colour $\rightarrow [\text{conc}] / \text{time}$
3. Density: density changes as concentration of a product or reactant changes density $\rightarrow [\text{conc}] / \text{time}$
4. Electric conductivity: conductivity changes as concentration of product or reactant changes electric conductivity $\rightarrow [\text{conc}] / \text{time}$

GASES:

5. Gas volume produced at constant pressure pressure $\rightarrow [\text{conc}] / \text{time}$
6. Absorption spectrographs
7. Gas chromatography

SOLIDS:

Reactions are too slow

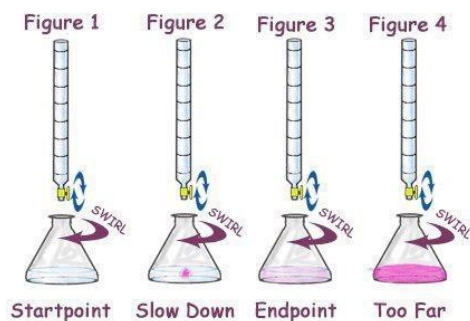
Sample questions in the textbook: p. 243

Name: _____ Date: _____

6.3 How rates are measured

TITRATION / SAMPLING

Titration of an Acid with a Base using phenolphthalein indicator

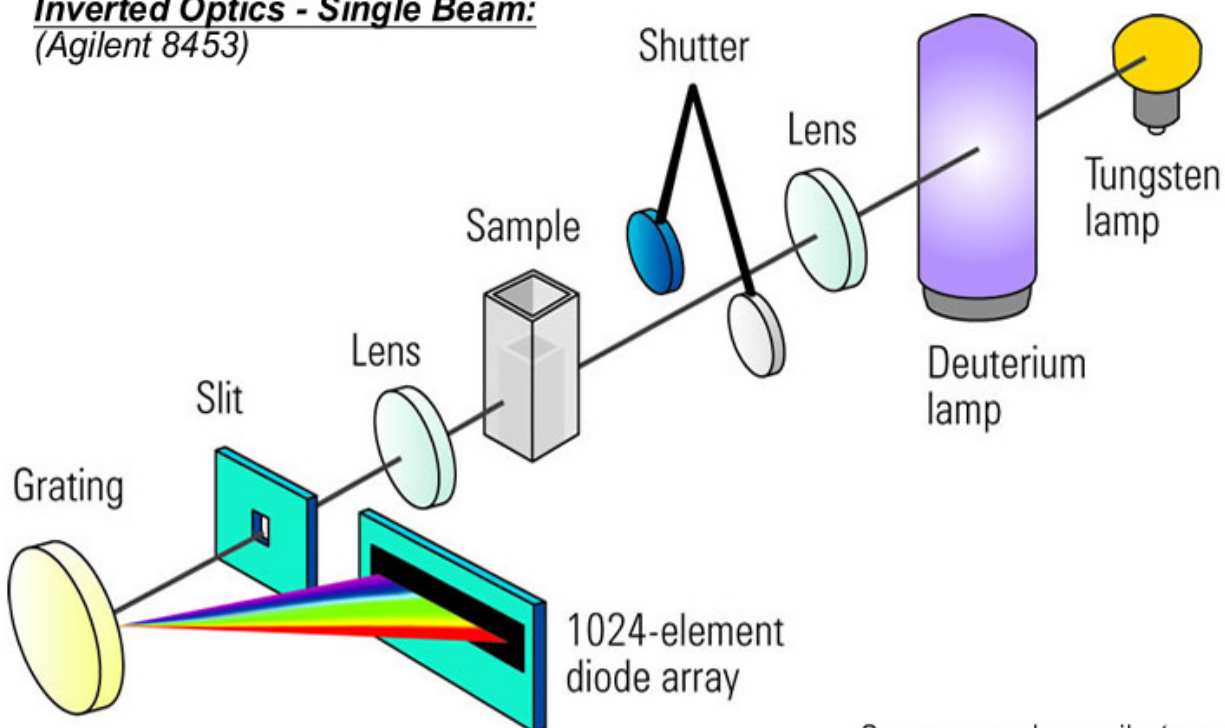


Name: _____ Date: _____

SPECTROMETER



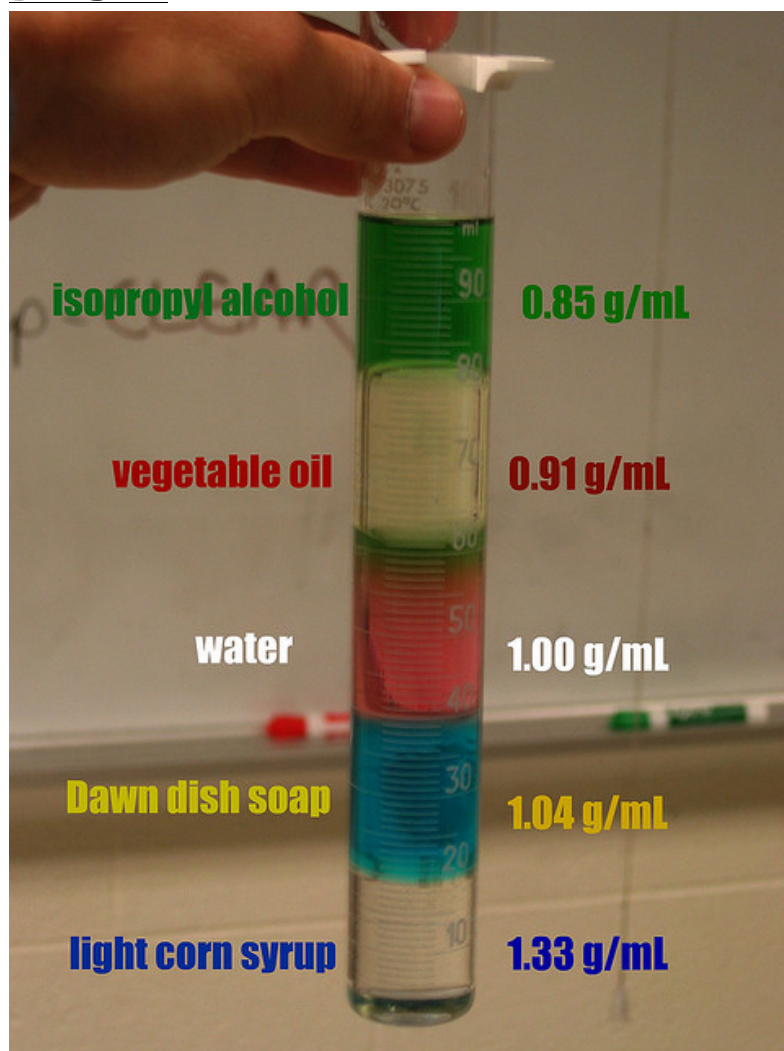
Inverted Optics - Single Beam: (Agilent 8453)



Source: www.chem.agilent.com

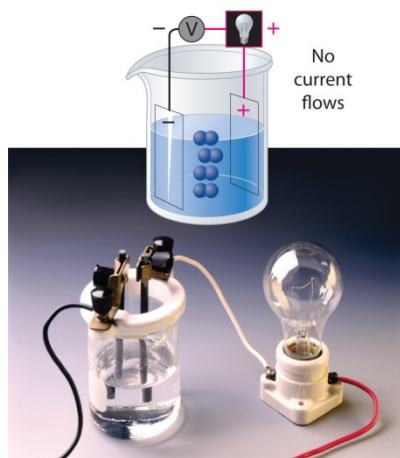
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DENSITY

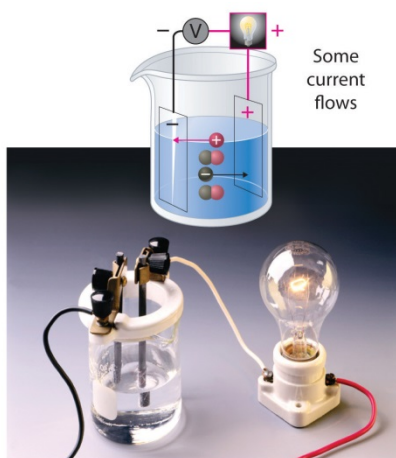


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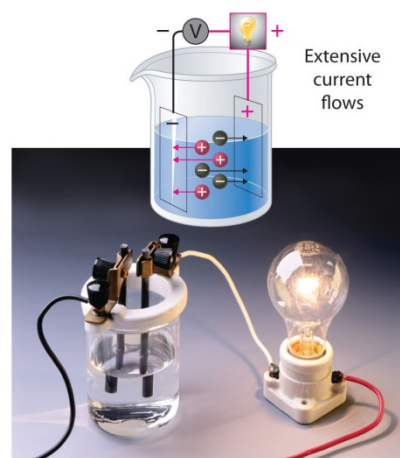
ELECTRIC CONDUCTIVITY



(a) Nonelectrolyte



(b) Weak electrolyte

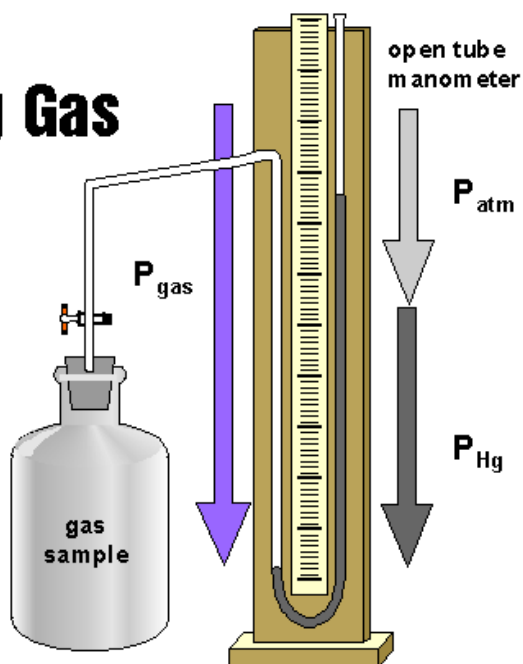


(c) Strong electrolyte

Name: _____ Date: _____

GAS VOLUME / PRESSURE

Measuring Gas Pressure



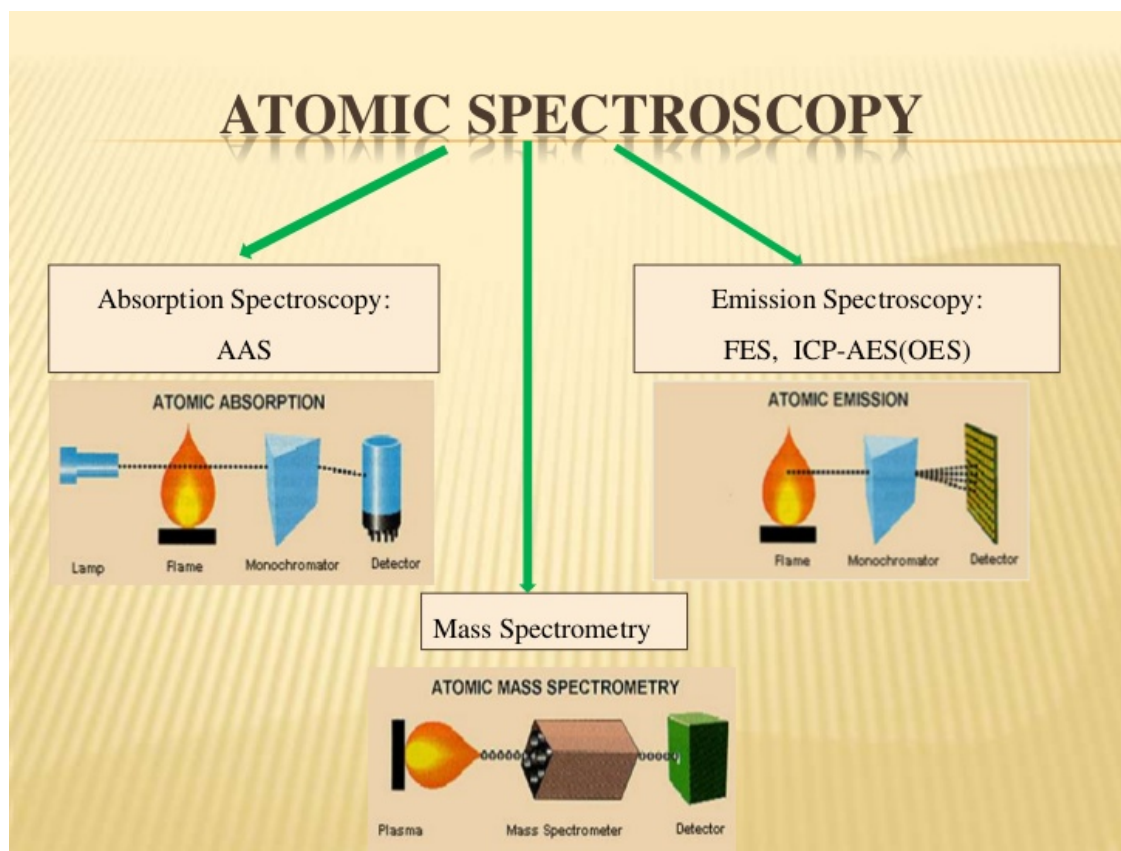
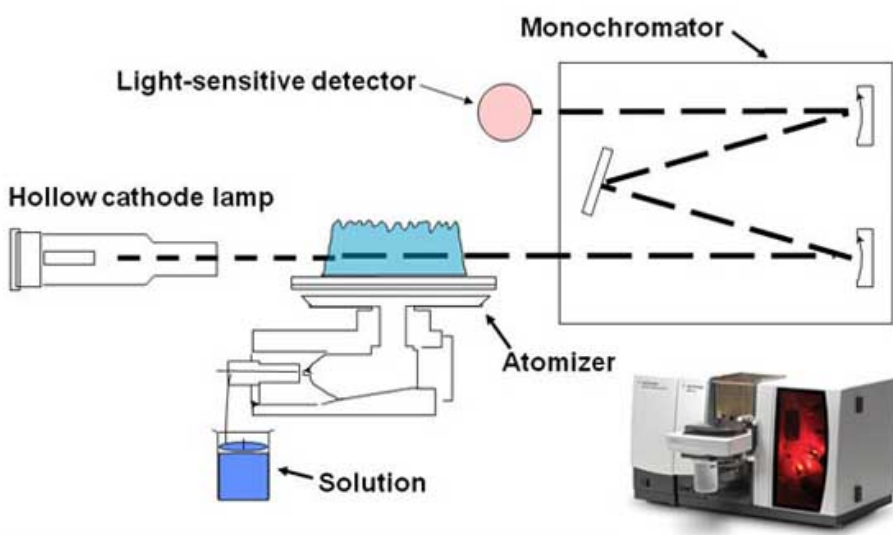
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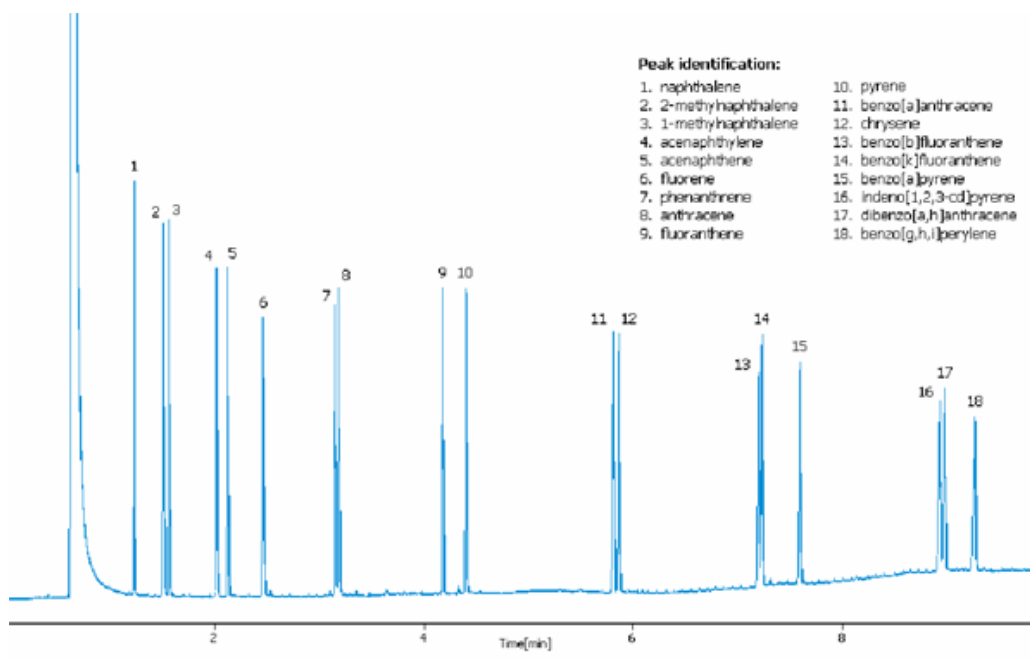
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ABSORPTION SPECTROGRAPH



Name: _____ Date: _____

GAS CHROMATOGRAPHY



Name: _____ Date: _____

SOLID REACTIONS



Name: _____ Date: _____

Sample Calculations of Average Reaction Rate:

1. A scientist collects the following data: 25g of S (s) produced in 5.0 min.
Calculate the Average Reaction rate :
2. Calculate the rate of O₂ needed and the rate of production of products.
$$\text{C}_2\text{H}_6 (\text{l}) + \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{g})$$

0.050 mol/s
3. Calculate the rate at which H₂ and N₂ must be supplied to maintain the production of 8.0 L/s of NH₃ at constant temp. and pressure.
$$\text{H}_2 (\text{g}) + \text{N}_2 (\text{g}) \rightarrow \text{NH}_3 (\text{g})$$
4. How fast is NO(g) produced when 2.0 mol/min of NH₃(g) are reacted with excess O₂(g)?
$$\text{NH}_3 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow \text{NO} (\text{g}) + \text{H}_2\text{O} (\text{g}) + 453 \text{ kJ}$$
5. At what rate must NH₃ (g) at STP be supplied to react at a rate of 3.0 mL / min of O₂ (g)?
$$\text{NH}_3 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow \text{NO} (\text{g}) + \text{H}_2\text{O} (\text{g}) + 453 \text{ kJ}$$
6. How long will it take to completely react 45.0 g of solid calcium carbonate with dilute hydrochloric acid if the reaction proceeds at an average rate of 2.35 g / min solid calcium carbonate under certain conditions?
7. A 5.0 g sample of magnesium reacts completely with a hydrochloric acid solution after 150 s. Express the average rate of consumption of magnesium, in units of g/min.

Name: _____ Date: _____

Wkst 1.1: Average Reaction Rate Calculations

- 1- Determine average reaction rates in mole/s for all chemicals involved if a camp stove burns propane (C_3H_8) at a rate of 3.00 mole/s.
- 2- If hydrogen gas is generated at 245 L/min at RTP in a reaction between HNO_3 and Al, find reaction rates for all reactants and products in mole/min.
- 3- If 176 g of NaOH reacts with H_2SO_4 in 15 seconds, find reaction rates for all participating chemicals in g/s.
- 4- Fluorine and ammonia gases react at STP to produce nitrogen and hydrogen fluoride gases. Find reaction rates in L/min if nitrogen is produced at 5.00 mole/min.
- 5- Determine reaction rates for all chemicals in g/s if a reaction between 450. g of HCl and 375 g of Fe_2S_3 yields FeCl_3 and H_2S during a 150. second interval.

Name: _____ Date: _____

Wkst 1.1: Average Reaction Rate Calculations



2- ? mol H_2 /min = (245 L/min) (1 mol/24.5 L) = 10.0 mol/min

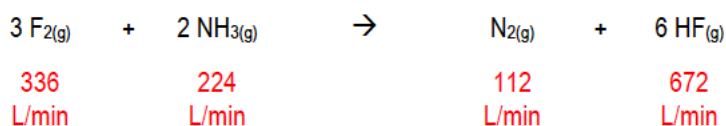
Al Rate = 6.66 mol/min
 HNO_3 Rate = 20.0 mol/min
 H_2 Rate = 10.0 mol/min
 $\text{Al}(\text{NO}_3)_3$ Rate = 6.66 mol/min

3- ? mol NaOH /s = (176 g / 15 s) (1 mol / 40.0 g) = 0.29 mol/s

NaOH Rate = 12 g/s
 H_2SO_4 Rate = 15 g/s
 Na_2SO_4 Rate = 21 g/s
 H_2O Rate = 5.2 g/s

4- ? L N_2 /min = (22.4 L/mol) (5.00 mol/min) = 112 L N_2 /min

Since all gases are at STP, Avogadro's hypothesis applies.



5- Watch for excess stoichiometry! Use only amounts of chemicals that have reacted!

Fe_2S_3 Rate = 2.50 g/s
 HCl Rate = 2.63 g/s
 FeCl_3 Rate = 3.89 g/s
 H_2S Rate = 1.23 g/s