Chemistry 12 - Notes on Unit 1 - Reaction Kinetics

Reaction Kinetics http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA0/MOVIES/NI3IOD.html

- study of **rates** of rx. and the **factors** which affect the rates.

    (note: "rx" = reaction(s))

Expressing Rates

rate = quantity of a **product** formed

                unit **time**

or **rate** = quantity of a **reactant** consumed

                    unit **time**

in general: **rate** = $\dfrac{\Delta\,\textbf{amount}\,(\text{a reactant or product})}{\Delta\,\textbf{time}}$

        Note: A **time unit** is always in the <u>denominator</u> of a rate equation.

eg.) $Zn_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + ZnCl_{2(aq)}$
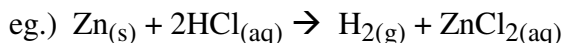
$r = \dfrac{\Delta \text{ mass of Zn}}{\Delta \text{ time}}$ $r = \dfrac{\Delta\,[\,HCl\,]}{\Delta \text{ time}}$ (note: [ ] = molar concentration)

$r = \dfrac{\Delta \text{ volume } H_2}{\Delta \text{ time}}$ Do ex. 1-5 p.2 S.W. (SW is Hebden's
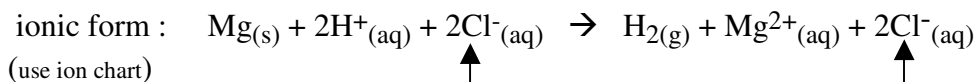
                                          Student Workbook)

<u>Note</u>

       - some rxs, when written in **ionic form** show that some ions don't
change concentration.

eg. $Mg_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + MgCl_{2(aq)}$
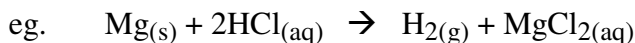
NOTE: To write an equation in IONIC FORM, dissociate all the aqueous (aq) compounds:

ionic form : $Mg_{(s)} + 2H^+_{(aq)} + 2Cl^-_{(aq)} \rightarrow H_{2(g)} + Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$

(use ion chart)

> **[Cl⁻] does not change as rx. proceeds (spectator ion)**

<u>Write</u> 4 possible equations which express rate.

Calculations Involving Reaction Rates

When doing calculations involving rate, amount (grams, moles, Litres etc.) use the general equation:

$$\text{Rate} = \frac{\Delta \text{ amount (g, mol, L)}}{\Delta \text{ time (s, min)}}$$

or

$$\Delta \text{ amount} = \text{Rate} \times \Delta \text{ time}$$

or

$$\Delta \text{ time} = \frac{\Delta \text{ amount}}{\text{Rate}}$$

WHEN YOU USE ONE OF THESE FORMULAS, MAKE SURE YOUR **UNITS** CAN CANCEL OUT PROPERLY!

to help solve for what you need.

ALWAYS use conversion factors to cancel units you don't want and replace them with ones you do want!

Eg.) $\quad 0.020 \dfrac{\text{mol}}{\text{min.}} = ? \dfrac{\text{mol}}{\text{s}}$

Solution: $\quad \dfrac{0.020 \text{ mol}}{1 \text{ min}} \times \dfrac{1 \text{ min}}{60 \text{ s}} = \dfrac{3.3 \times 10^{-4} \text{ mol}}{\text{s}}$

The 60 in 60 s/1min is an exact number by definition. Therefore, we don't consider it using significant digits. The 0.020 has 2 sig. digs., therefore the answer has 2.

You also must use molar mass to go grams ⇆ moles.

Eg.) $\quad \dfrac{0.26 \text{ mol Zn}}{\text{min}} = ? \dfrac{\text{g of Zn}}{\text{s}}$

Solution: $\quad \dfrac{0.26 \text{ mol Zn}}{1 \text{ min}} \times \dfrac{65.4 \text{ g Zn}}{1 \text{ mol Zn}} \times \dfrac{1 \text{ min}}{60 \text{ s}} = \dfrac{0.28 \text{ g of Zn}}{\text{s}}$

You would use $\dfrac{22.4 \text{ L}}{1 \text{ mol}}$ for conversions moles ⇆ L (STP) for gases.

eg.) $0.030 \text{ mol } O_2 /s = $ _____ L/s (STP)

Solution: $\dfrac{0.030 \text{ mol } O_2}{1 \text{ s}} \times \dfrac{22.4 \text{ L}}{\text{mol}} = \dfrac{0.67 \text{ L } O_2}{\text{s}}$

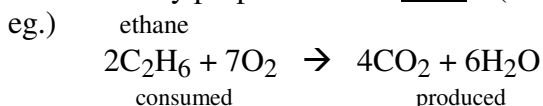(The 0.030 has 2 sig digs so the answer must have 2 sig. digs.)

NOTE: This conversion is only used for **gases** at STP!

Try this problem:

The rate of a reaction is 0.034 g of Mg per second. Calculate the number of moles of Mg used up in 6.0 minutes.

Comparing rates using balanced equations

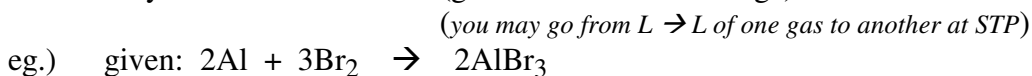-use **coefficient ratios** - only proportional to mol /s (not to g/s)

eg.)   ethane

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

consumed   produced

eg.) if ethane is consumed at a rate of 0.066 mol /s, calculate the rate of consumption of O_2 in mol /s

Solution: $\dfrac{0.066 \text{ mol } C_2H_6}{s}$ x $\dfrac{7 \text{ mol } O_2}{2 \text{ mol } C_2H_6}$ = $\dfrac{0.23 \text{ mol } O_2}{s}$

 if ethane is consumed at a rate of 0.066 mol /s calculate rate of <u>production</u> of CO_2

Solution: $\dfrac{0.066 \text{ mol } C_2H_6}{s}$ x $\dfrac{4 \text{ mol } CO_2}{2 \text{ mol } C_2H_6}$ = $\dfrac{0.13 \text{ mol } CO_2}{s}$

- when other units used – you must use **moles** to (go over the "mole" bridge)

(*you may go from L → L of one gas to another at STP*)

eg.)   given: $2Al + 3Br_2 \rightarrow 2AlBr_3$

if 67.5 g of Al are consumed per second - calculate the rate of consumption of Br_2 in g/s.

Solution: $\dfrac{67.5 \text{ g Al}}{s}$ x $\dfrac{1 \text{ mol Al}}{27.0 \text{ g Al}}$ x $\dfrac{3 \text{ mol } Br_2}{2 \text{ mol Al}}$ x $\dfrac{159.8 \text{ g } Br_2}{1 \text{ mol } Br_2}$ = **$\dfrac{599 \text{ g } Br_2}{s}$**

You may have to use a few conversions and the "rate equation" to arrive at an answer. As you did in Chem. 11, make a "plan" first and make sure your units all cancel the correct way!

Here's an example on the next page…

An experiment is done to determine the rate of the following reaction:

$$2Al_{(s)} + 6\ HCl_{(aq)} \rightarrow 3\ H_{2(g)} + 2\ AlCl_{3\ (aq)}$$
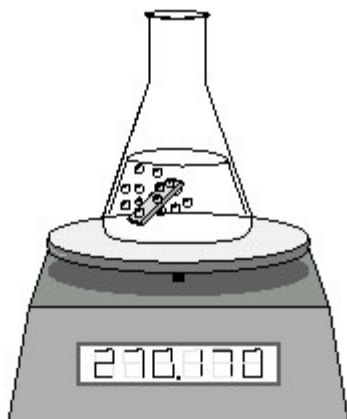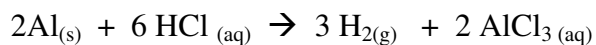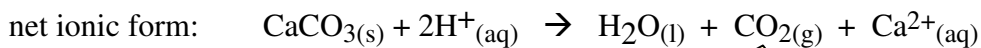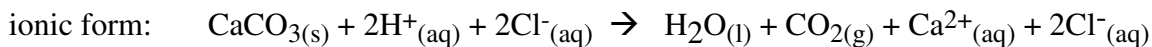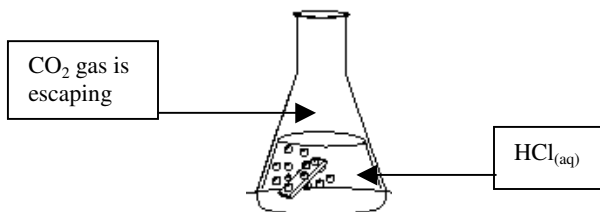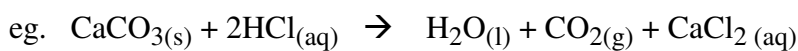
It is found that the rate of production of $H_{2(g)}$ is 0.060 g/s.

Calculate the mass of Aluminum reacted in 3.0 minutes.

Measuring Reaction Rates

      - different methods for different reactions.
      - must look at subscripts & use common sense.

eg. $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)} + CaCl_{2\ (aq)}$

CO$_2$ gas is escaping

$HCl_{(aq)}$

ionic form: $CaCO_{3(s)} + 2H^+_{(aq)} + 2Cl^-_{(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)} + Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$

net ionic form: $CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)} + Ca^{2+}_{(aq)}$

in an open system $CO_{2(g)}$ escapes

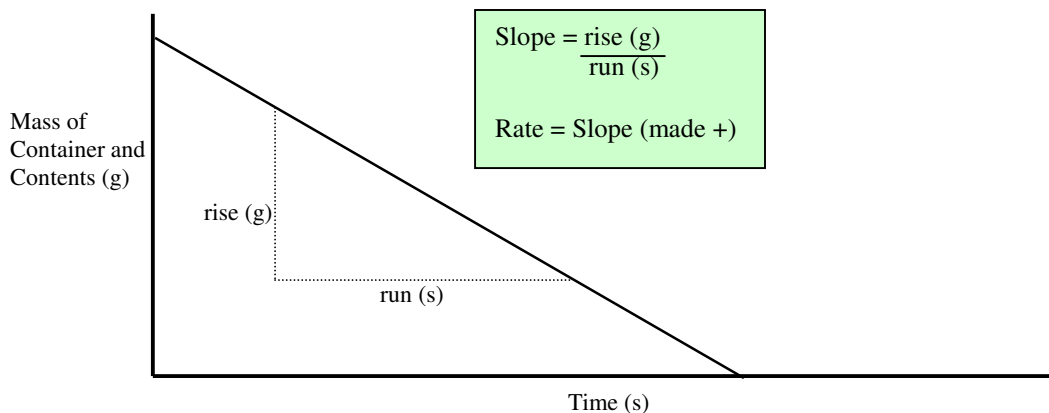- as CO_2 escapes, **mass** of the rest of the system will _____

- so rate could be expressed as..
.

$$r = \frac{\Delta \text{ mass of container and contents}}{\Delta \text{ time}} \quad \text{(open system)}$$
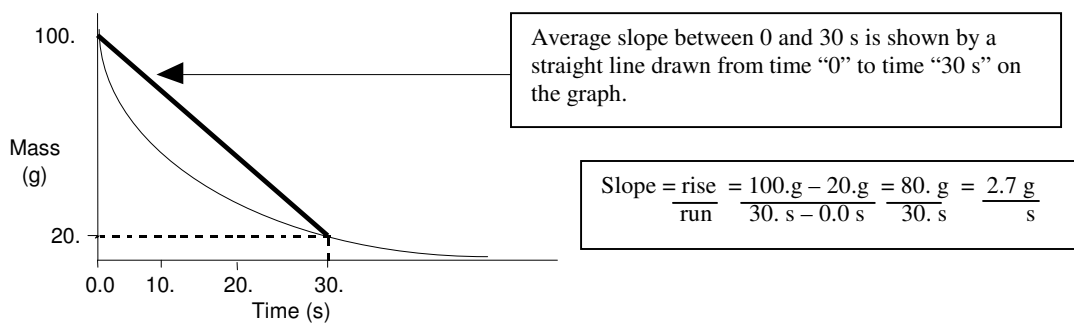
Note

rate = slope of **amount. vs. time** graph

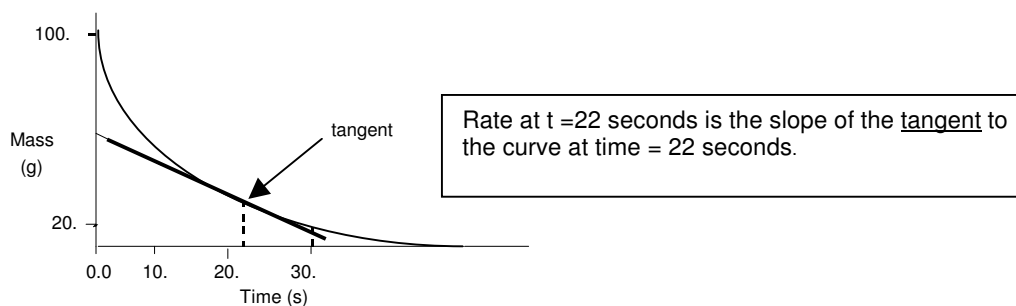(disregard sign of slope. Slope will be negative if something is being consumed and positive if something is being produced. Rate is just the Δamount/Δtime)

Slope = $\frac{\text{rise (g)}}{\text{run (s)}}$

Rate = Slope (made +)

Mass of Container and Contents (g)

rise (g)

run (s)

Time (s)

Note - for a changing rate (slope) –which is more realistic -rate could be expressed over a certain interval

Mass (g)

100.

20.

0.0   10.   20.   30.

Time (s)

Average slope between 0 and 30 s is shown by a straight line drawn from time "0" to time "30 s" on the graph.

Slope = $\frac{\text{rise}}{\text{run}} = \frac{100.g - 20.g}{30. s - 0.0 s} = \frac{80. g}{30. s} = \frac{2.7 g}{s}$

or rate at a certain point in time is the slope of the tangent at that point.

Mass (g)

100.

20.

0.0   10.   20.   30.

Time (s)

tangent

Rate at t =22 seconds is the slope of the <u>tangent</u> to the curve at time = 22 seconds.

[do ex.6 on page 3 of SW.] [Read page 11 and do ex. 18-19 on p. 11 SW.]
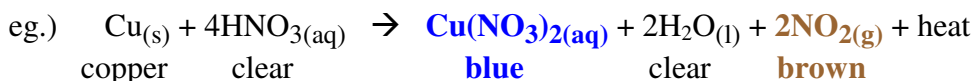[do <u>experiment</u> on measuring rx. rates]

Monitoring Reaction Rates

- properties which can be monitored (measured at specific time intervals) in
  order to determine rx. rate.

Note : Must consider -subscripts $_{(s)\ (l)\ (g)\ (aq)}$
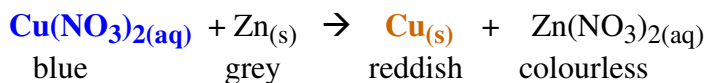   - coefficients of gases
          - heat (endo or exo?)

- Do demo with Cu & HNO_3
    discuss colour, mass, conc., pressure (volume) change

1.)   <u>**Colour changes**</u>
- only in reactions where coloured reactant is consumed or new coloured
product formed.

eg.) $Cu_{(s)}$ + $4HNO_{3(aq)}$ $\rightarrow$ **$Cu(NO_3)_{2(aq)}$** + $2H_2O_{(l)}$ + **$2NO_{2(g)}$** + heat
   copper   clear   **blue**   clear   **brown**
- in this case could measure - intensity of **blue**
            - intensity of **brown** gas

$Cu(NO_3)_{2(aq)}$ + $Zn_{(s)}$ $\rightarrow$ **$Cu_{(s)}$**   + $Zn(NO_3)_{2(aq)}$
  blue   grey   reddish   colourless
- as this reaction proceeds the blue colour fades

in ionic form: **$Cu^{2+}{}_{(aq)}$** + $2NO_3^-{}_{(aq)}$ + $Zn_{(s)}$ $\rightarrow$ $Cu_{(s)}$ + $Zn^{2+}{}_{(aq)}$ + $2NO_3^-{}_{(aq)}$
<u>net</u> ionic: **$Cu^{2+}{}_{(aq)}$** + $Zn_{(s)}$ $\rightarrow$ $Cu_{(s)}$ + $Zn^{2+}{}_{(aq)}$
     [**Cu^{2+} is blue!**]

- colour intensity can be measured quantitatively using a <u>**spectrophotometer**</u>
                  (see p. 4 S.W.)

<u>eg. of rate equation</u>
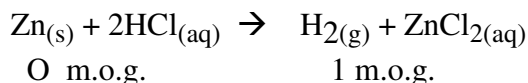   rate = <u>Δ colour intensity</u>
        Δ time

2.) <u>**Temp changes**</u>

- in exothermic reaction temperature of surroundings will _____
- in endothermic reaction temperature of surroundings will _____
      - measured in insulated container (calorimeter)

$$rate = \frac{\Delta\ temp}{\Delta\ time}$$

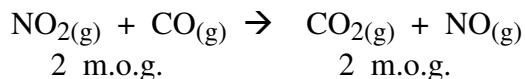**3.)** <u>**Pressure changes**</u>   (constant volume or sealed container)

    - if more **moles of gas** (coefficient) in **products** pressure will go <u>**up**</u>

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow H_2{}_{(g)} + ZnCl_2{}_{(aq)}$$
    O m.o.g.   1 m.o.g.
- If more MOG in reactants - pressure will _____

$$rate = \frac{\Delta\ pressure}{\Delta\ time}\ \ \ \ (constant\ volume)$$

- If <u>equal</u> MOG, pressure will **not** change:

$$NO_2{}_{(g)} + CO_{(g)} \rightarrow CO_2{}_{(g)} + NO_{(g)}$$
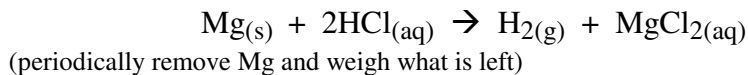   2 m.o.g.   2 m.o.g.

4.) <u>**Volume change**</u>   (constant pressure eg. balloon or manometer)

eg.) if more gas is produced, volume of balloon will increase

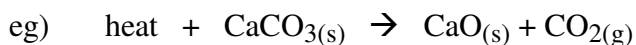$$rate = \frac{\Delta\ volume}{\Delta\ time}\ \ \ \ (constant\ pressure)$$

5.) <u>**Mass changes**</u>

    - if only one solid is used up
        - could remove periodically and weigh it:

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow H_2{}_{(g)} + MgCl_2{}_{(aq)}$$
(periodically remove Mg and weigh what is left)

  - if one gas is produced and escapes, measure mass of what's left in container
    (mass of container and contents)

eg)   heat + $CaCO_{3(s)}$ → $CaO_{(s)} + CO_{2(g)}$ ◁ Only CO_2 gas escapes. So as CO_2 escapes, the mass of the container and contents will decrease.

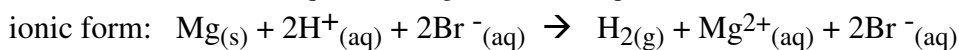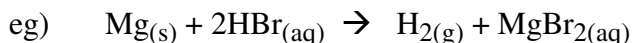   rate = $\dfrac{\Delta \text{ mass of container \& contents}}{\Delta \text{ time}}$

Note: it's <u>not practical</u> to measure <u>masses</u> of (aq) substances separately since they are mostly water.

   eg) $Ca_{(s)} + 2HNO_{3(aq)}$ → $H_{2(g)} + Ca(NO_3)_{2(aq)}$
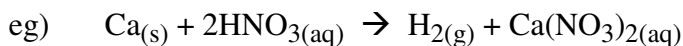
   $\dfrac{\cancel{\Delta \text{ mass of } HNO_{3}(aq)}}{\cancel{\Delta \text{ time}}}$ ◁ not acceptable

6.)   <u>Changes in molar concentration of specific ions</u>

   eg) $Mg_{(s)} + 2HBr_{(aq)}$ → $H_{2(g)} + MgBr_{2(aq)}$

   ionic form: $Mg_{(s)} + 2H^+{}_{(aq)} + 2Br^-{}_{(aq)}$ → $H_{2(g)} + Mg^{2+}{}_{(aq)} + 2Br^-{}_{(aq)}$

      - could monitor $[H^+]$ - it will _____crease

   eg.) rate = $\dfrac{\Delta [Mg^{2+}]}{\Delta \text{ time}}$ $[Mg^{2+}]$ - will _____crease

   Note: Does the $[Br^-]$ change? _____ Explain.

   - <u>the concentration of a specific ion can be measured:</u>
         - using spectrophotometer
         - periodic samples taken and titrated to measure conc.

7.)   <u>Changes in Acidity</u> $[H^+]$

   - special case of #6
   rate = $\dfrac{\Delta [H^+]}{\Delta \text{ time}}$

   pH is a measure of **acidity**

   pH   <u>0</u>   <u>7</u>   <u>14</u>
         <----------------- ------------------>
         more acidic   more basic
         (less basic)   (less acidic)

if H^+ is a <u>reactant</u> (or any acid HCl, HNO_3 etc.)

$[H^+]$ will **decrease** so pH will <u>INCREASE</u>!
(less acidic)

rate = $\dfrac{\Delta\,pH}{\Delta\,time}$

> Measured with a pH meter

(read p. 4-5 SW. Ex. 7-9 page 5)

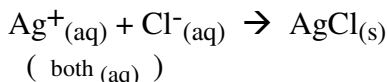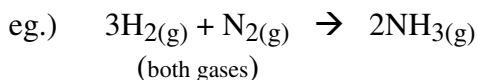- <u>Do Hand-In Assignment on Reaction Rates</u>

- <u>Do expt 18-B (or A)</u> To look at factors affecting rx rates.

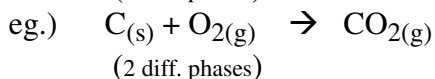- **<u>Factors affecting reaction rates</u>**
- <u>2 kinds of reactions:</u>
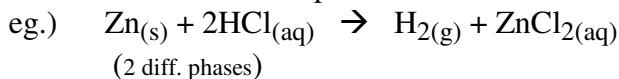
<u>Homogeneous</u> reactions
- all **reactants** are in the **same phase**
(don't consider products)

eg.) $3H_{2(g)} + N_{2(g)}$ → $2NH_{3(g)}$
(both gases)

$Ag^+_{(aq)} + Cl^-_{(aq)}$ → $AgCl_{(s)}$
(both $_{(aq)}$)

<u>Heterogeneous</u> Reactions
- more than one phase in reactants.
eg.) $Zn_{(s)} + 2HCl_{(aq)}$ → $H_{2(g)} + ZnCl_{2(aq)}$
(2 diff. phases)
eg.) $C_{(s)} + O_{2(g)}$ → $CO_{2(g)}$
(2 diff. phases)

<u>Factors that affect both homogeneous & heterogeneous. reactions</u>

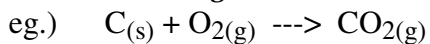**1.) Temperature** - as temperature increases, rate _____

2.) Concentration of reactants
- as cons. of one or more reactants increases, rate _____
- also **<u>partial pressure</u>** of a gas (partial pressure of a gas is the pressure exerted by
that gas in a mixture of gases - it's proportional to concentration)

**3.) Pressure**
- affects reactions with ***gases in reactants***.
eg.) $C_{(s)} + O_{2(g)}$ ---> $CO_{2(g)}$
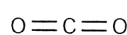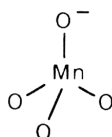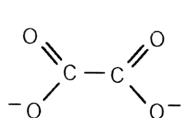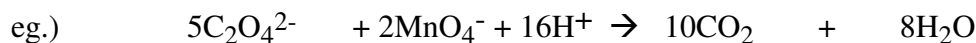- as pressure increases, rate _____
<u>Note</u>: a **decrease in the <u>volume</u>** of reaction container **increases the <u>pressure</u>** (therefore rate)

4.) Nature of reactants

-rate depends on **how strong** & **how many bonds** in **reactants** need to be broken.
in general **covalent bonds** are **strong** and **slow** to break.

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)} \quad (\textbf{slow at \underline{room} temp})$$
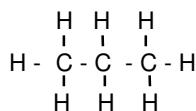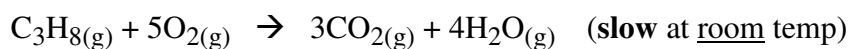
strong **covalent** bonds between C-C and C-H atoms

eg.) $\quad 5C_2O_4{}^{2-} \quad + 2MnO_4{}^- + 16H^+ \rightarrow 10CO_2 \quad + \quad 8H_2O$
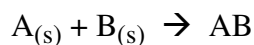

$O=C=O$ $\quad$ $H\diagdown O\diagup H$ $\quad$ (**slow**)
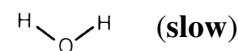
Many bonds have to be broken and many new bonds have to form. So this reaction is **slow** at room temperature.

Eg.) $\quad H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ (H_2 and Cl_2 are diatomic)

H - H + $\quad\quad$ Cl - Cl

covalent bonds $\quad\quad\quad$ **slow** at room temp.

<u>Consider Phase</u>

$A_{(s)} + B_{(s)} \rightarrow AB$
both solids $\quad\quad\quad\quad$ **slow** at room temp.

<u>Fast reactions at room temperature:</u>
-simple **electron transfer** (no bonds broken)

eg.) $Sn^{2+} + Te^{4+} \rightarrow Sn^{4+} + Te^{2+}$ (2 electrons have been transferred from _____ to _____)
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ **fast** at room temp
.

-**precipitation** reactions:
$\quad\quad$ eg.) $\quad Fe^{2+}{}_{(aq)} + S^{2-}{}_{(aq)} \rightarrow FeS_{(s)} \quad$ **fast** at room temp.
$\quad\quad\quad\quad$ both reactants $_{(aq)}$ - no bonds to break.
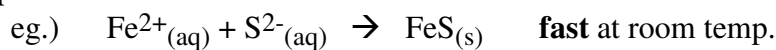
-**acid base** (proton transfers)
-intermediate in rate

eg.) $NH_4^+ + SO_3^{2-} \rightarrow NH_3 + HSO_3^-$
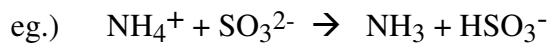
- Do ex. 10 p.7 SW. Also, do this question:

Which of the following reactions will be slowest at 25°C?

A. $Cu_{(s)} + S_{(s)} \rightarrow CuS_{(s)}$

B. $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)}$

C. $Pb^{2+}_{(aq)} + 2Cl^-_{(aq)} \rightarrow PbCl_{2(s)}$
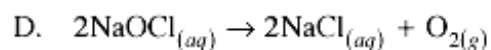
D. $2NaOCl_{(aq)} \rightarrow 2NaCl_{(aq)} + O_{2(g)}$
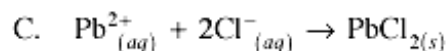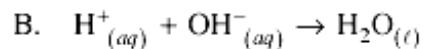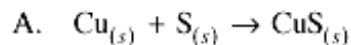
5.)   <u>Catalysts</u>
- a substance which can be added to increase the rate of a rx. without being
   consumed itself.   (reactants are consumed)

Demo with $H_2O_2 + MnO_2$

$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$ *uncatalyzed* - **slow**
$2H_2O_{2(l)} \xrightarrow{MnO_2} 2H_2O_{(l)} + O_{2(g)}$ *catalyzed* - **fast**
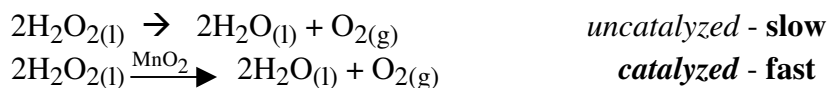
<u>Inhibitors</u>
- a substance which can be added to <u>reduce</u> the rate of a reaction.
(can combine with a catalyst or a reactant & prevent it from reacting)
-eg. poisons (cyanide) - organophosphates (diazinon)
         -antibiotics
         -antidepressants (serotonin uptake inhibitors)
         -sunscreens

Factor which affects only _heterogeneous_ reactions (more than one phase)

6.)   **Surface area**

-when 2 different phases react, reaction can only take place on **surface**.
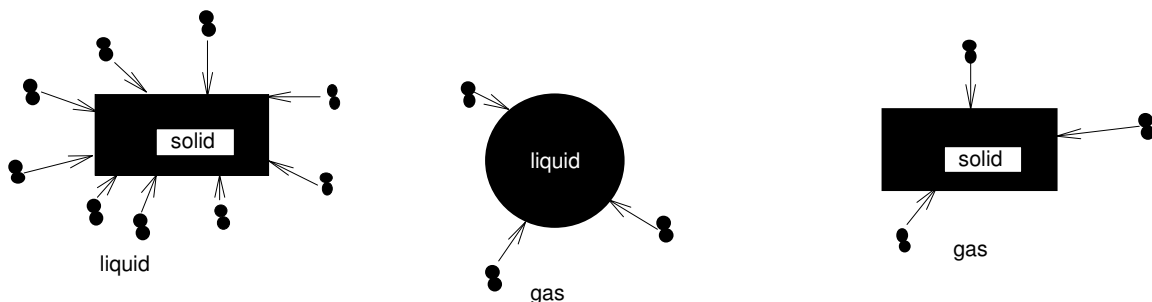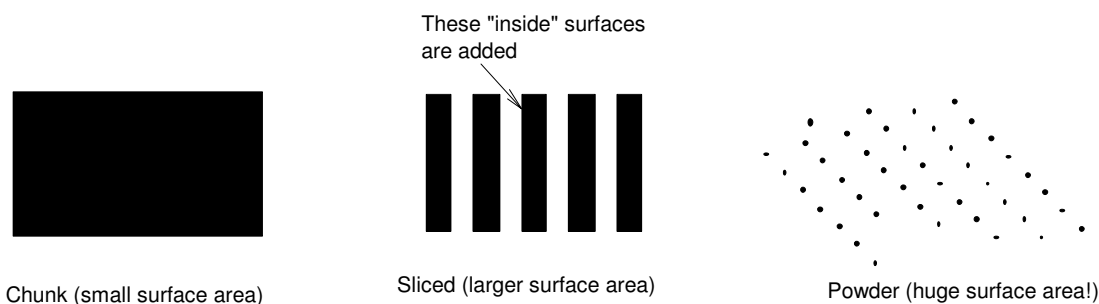

- increase **surface area** by cutting solid into smaller pieces (liquids in smaller droplets)

Chunk (small surface area)   Sliced (larger surface area)   Powder (huge surface area!)

- do lycopodium powder demo

- <u>In general</u>   - reactants with **solids** are **slow** (except powdered)
                            - **gaseous** reactants are **faster** (but watch for **diatomic bonds**!)
                            - reactants in **ionic solution**. are **fastest** if **no bonds to break**

eg. ppt$\underline{^n}$ Ag$^+_{(aq)}$ + Cl$^-_{(aq)}$ →   AgCl $_{(s)}$

(aqueous ions are mobile (unlike in a solid) and more concentrated than molecules in a gas)

 - Read pages 5-9 SW.
- do ex. 12-14 SW. (page 8)

<u>Some points</u>
          1.) **Temperature** affects rate of **all** reactions
          2.) **Pressure** (or **volume**) affect reactions with **gaseous reactants**
          3.) **Concentration** only affects **(aq)** or **(g) reactants**
          4.) **Surface area** - affects only **heterogeneous** reactions.

- do ex. 15-17 p. 9-10 SW. ***Pay close attention to the <u>graphs</u> in question 17!***

Everyday situations which require control of reaction rate

- **Body chemistry**
      eg.) - metabolism
            - fever can destroy bacteria
            - neurotransmitters - awareness, sleep etc.
              hormones - messengers (adrenaline, sex hormones)
              catalysts - enzymes (digestive etc)
            - aging
- **Fuels**   - concentration of O_2 important
            - to **increase** combustion rate - increase [O_2]
                                          - increase surface area
                                          - increase temperature
                                          - catalyst (wood stoves etc)
            - to **decrease** combustion rate
                        - water on fire   -smothers it (decreases O_2)
                                          - cools it
                        - fire retardant   - forest fires
                                          - children's clothing
                        - airplane fuels- when spilled

-<u>Industrial Processes</u>
      - **produce product quickly**
      eg.)   - fiberglass   - uses catalyst (hardener)
                              hardens fast but not too fast

            - glue   - epoxy uses catalyst
                              - contact cement fast
            - concrete   - ceramics - paint
            - oxy- acetylene welding (must be very hot)
            - oil refining
            - sewage treatment   - use microbes to speed up breakdown
      - **slow down reactions**.
      eg.) nitroglycerine - keep cool - if too warm explodes

-<u>Rusting</u>   -(oxidation) of cars etc.
                  - paint, sealers, etc. prevents O_2 from contact with surface
                  - keep cool & dry

- <u>Cooking</u>   - improves taste
                  - kills some bacteria
                  - if too hot causes burning and productions of carcinogens
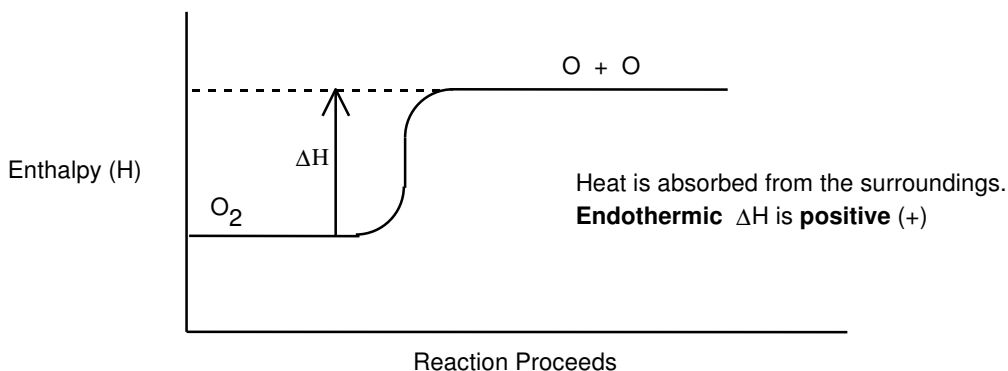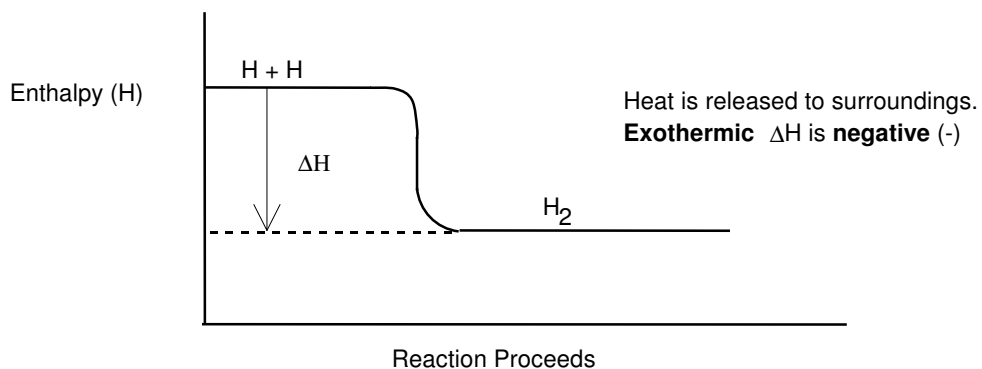   (benzopyrenes)

- <u>Food preservation</u>
                  - lower temperature
                  - anti-oxidants (eg. ascorbic acid)
                  - keep from O_2 (sealing)
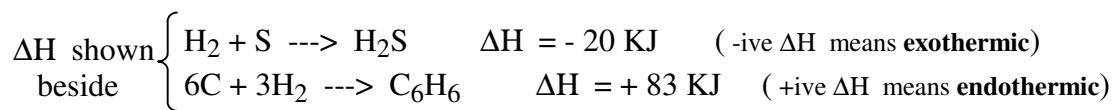   - preservatives (nitrates, nitrites) Think of more!

<u>Collision theory</u>

- explains rates on the molecular level http://chem.salve.edu/chemistry/temp2a.asp
<u>Basic idea (basic premise)</u>
http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/NO+O3singlerxn.html
- before molecules can react, they must **<u>collide</u>**.

H_2 + I_2 ⟶ 2HI

first   later   later still

successful collision (reaction)

How collision theory explains :
Effect of concentration

low conc. both	high conc. blue low conc. red	high conc. both
low chance of collision (slow reaction)	higher chance of collision (faster reaction)	very high chance of collision (much faster reaction)

<u>**Effect of temperature**</u>
- when molecules move **faster → more collisions** per unit time → **faster** rate
- also - when they move faster they **collide with more kinetic energy**. (hit harder)
[Read page 12 SW.   Do Ex. 20-22 on page 12 of SW.]

- *we'll come back to collision theory*

Enthalpy (H) & enthalpy change (ΔH)

Enthalpy - the "heat content" of a substance

or - the total KE & PE of a substance at const. pressure.

Chemists interested in **enthalpy changes** (ΔH)

Enthalpy (H)

H + H

ΔH

H$_2$

Heat is released to surroundings.
Exothermic ΔH is **negative** (-)

Reaction Proceeds

O + O

Enthalpy (H)

ΔH

O$_2$

Heat is absorbed from the surroundings.
Endothermic ΔH is **positive** (+)

Reaction Proceeds

Equations and heat

ΔH shown beside

$H_2 + S ---> H_2S$ ΔH = - 20 KJ   (-ive ΔH means **exothermic**)

$6C + 3H_2 ---> C_6H_6$ ΔH = + 83 KJ   (+ive ΔH means **endothermic**)

Thermochemical equations:

("**Heat Term**" is right in the equation. NO "ΔH" shown beside the equation!)

- "heat term" shown on **left** side of arrow - **endo**thermic ("it uses up heat like a reactant")

eg. CH_3OH + **201KJ** → $C_{(s)} + 2H_{2(g)} + ½ O_{2(g)}$
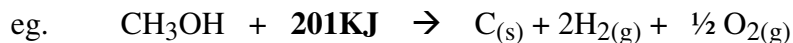
- "heat term" shown on **right** side of arrow - **exo**thermic ("it gives off heat like a product")

eg. $S_{(g)} + O_{2(g)} ---> SO_{2(g)}$ + **296 kJ**
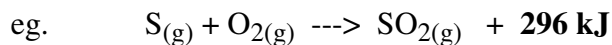
Read page 13-16 in SW. Do ex. 24-28 on page 16 of SW.

Kinetic energy distributions http://www.wwnorton.com/chemistry/tutorials/ch14.htm

(- demo "glass beads" molecular model.)
- look at a graph of kinetic energy & the number of molecules with each KE
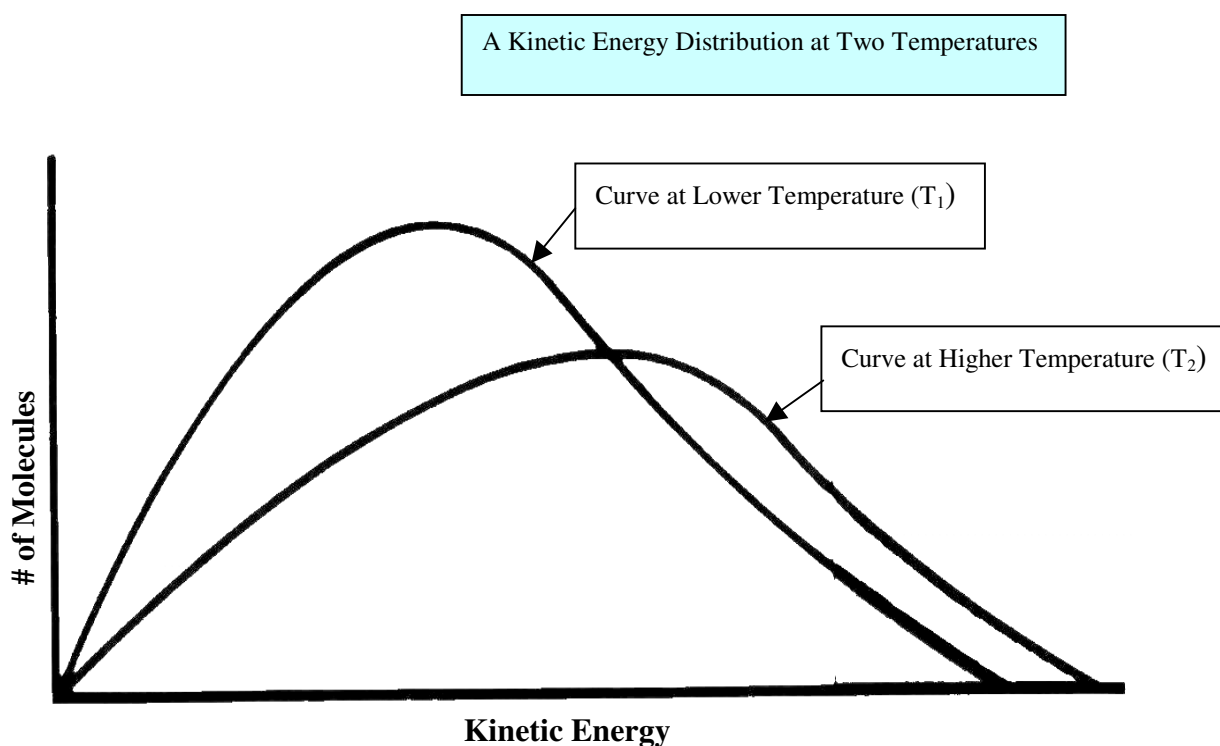reminder: $KE = \frac{1}{2} mv^2$ <--- if mass is equal KE is proportional to velocity

A KINETIC ENERGY DISTRIBUTION

A few molecules are SLOW (low KE)

A large number of molecules have "medium" KE.

A few molecules are moving FAST (high KE)
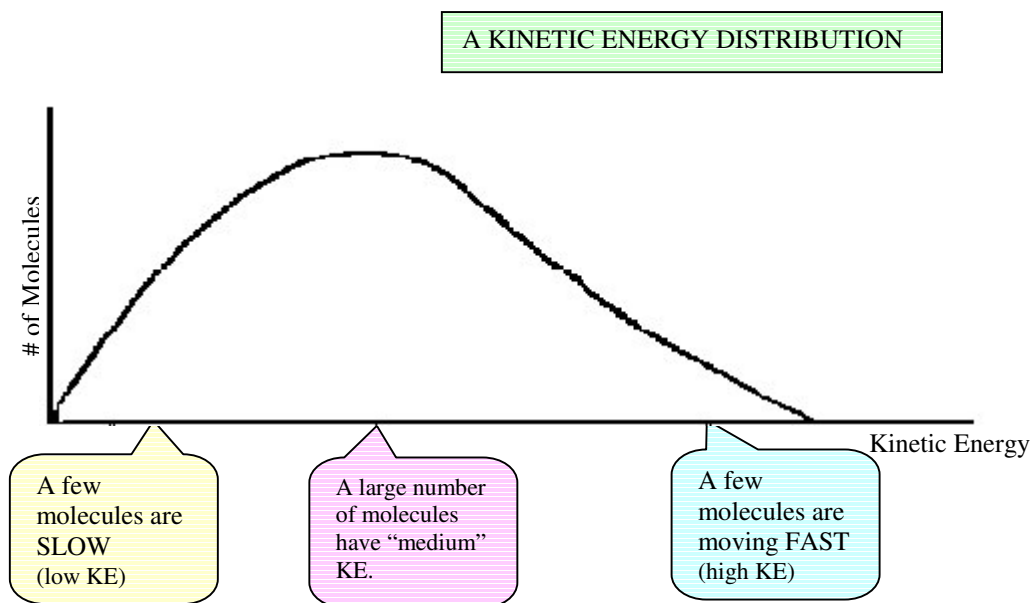
-when the **temperature** is **increased**

- average KE increases   - fewer slow ones
                                 - more fast ones

See the next page for the Kinetic Energy Distribution at a low and a high temperature…

A Kinetic Energy Distribution at Two Temperatures

Curve at Lower Temperature (T_1)

Curve at Higher Temperature (T_2)

# of Molecules

Kinetic Energy

NOTICE: -That at the higher temperature, there are less slow (low KE) molecules and
more fast (high KE) molecules

-That the curve is more spread out at the higher temperature.

-The **TOTAL** AREA UNDER THE CURVE is the same for the high temperature
as for the low temperature.

Activation Energy

-<u>minimum</u> energy needed in a collision before a reaction take place.
- it can also be defined as the minimum energy colliding particles must have in order to
have a "successful" collision (ie. one that results in a reaction.) (SW p.19 called M.E.)

A Collision in which the molecules have sufficient energy for a reaction to
take place is called a SUCCESSFUL COLLISION.

SEE THE GRAPH ON THE NEXT PAGE....

Page 14
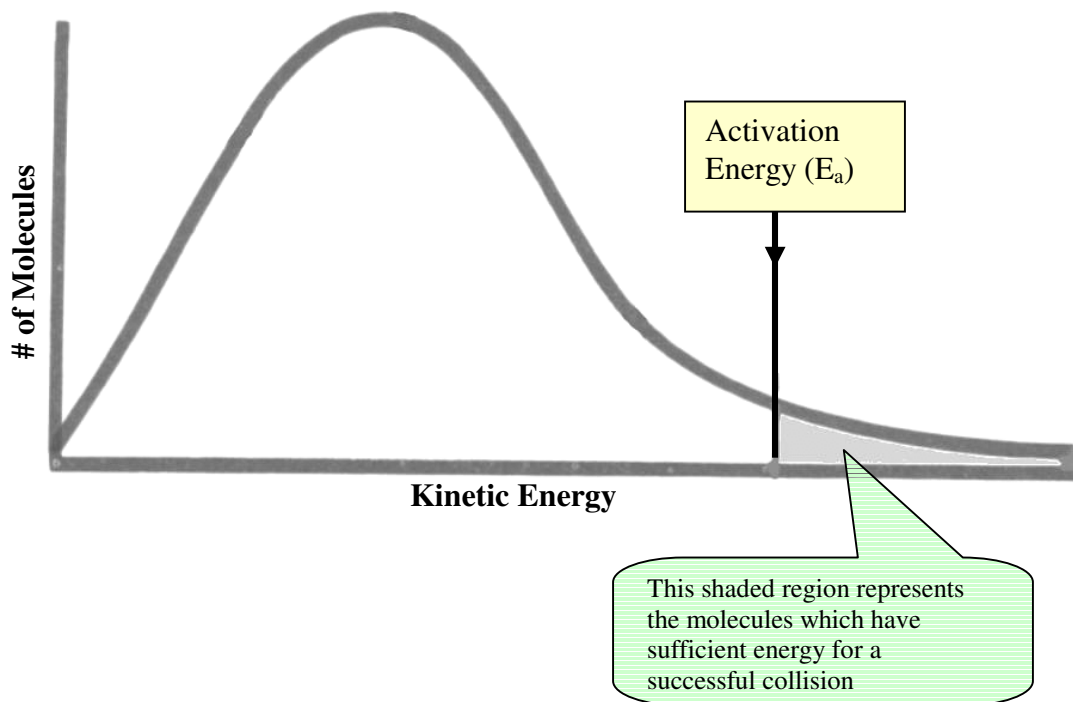
NOTE: - area under curve is proportional to # of molecules with that range of K.E.
  - on the graph above - a small fraction of the molecules (~ 1/10 - 1/15)
    (fraction of shaded area compared to total area under curve) have
    enough energy to react →   therefore it is a **slow** reaction

if temp is <u>increased</u> ...

(see what happens on the next page…)
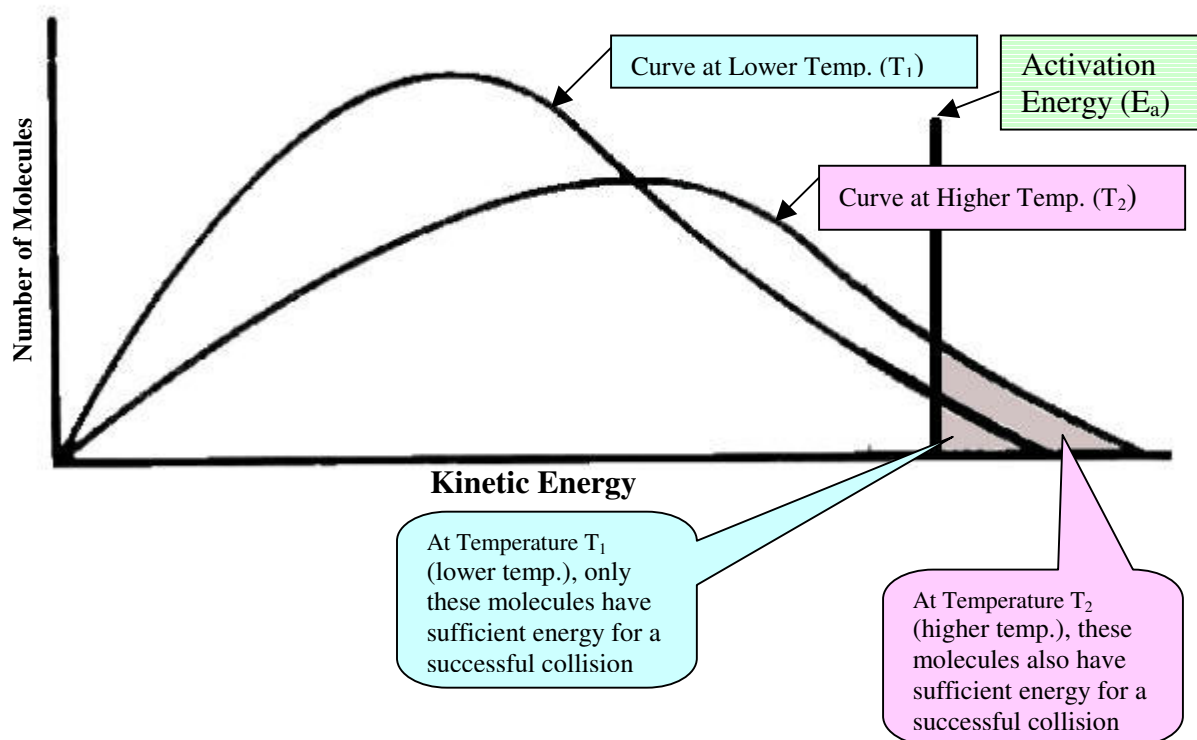
With the higher temperature, a greater fraction of the molecules have KE which is **>** or = the Ea. In this case about $1/5^{th}$ to $1/6^{th}$ of the molecules have sufficient KE.
(*the shaded region is about $1/5^{th}$ to $1/6^{th}$ the total area under the "Temperature T_2 curve*)

Rule of thumb

-if the **activation energy** (threshold) is near the **tail** of the curve:

- *if the temperature is increased by $10^{o}C$ reaction rate will about <u>double</u>.*
 (*ie. about **twice** the number of molecules have sufficient KE for a successful collision.*)
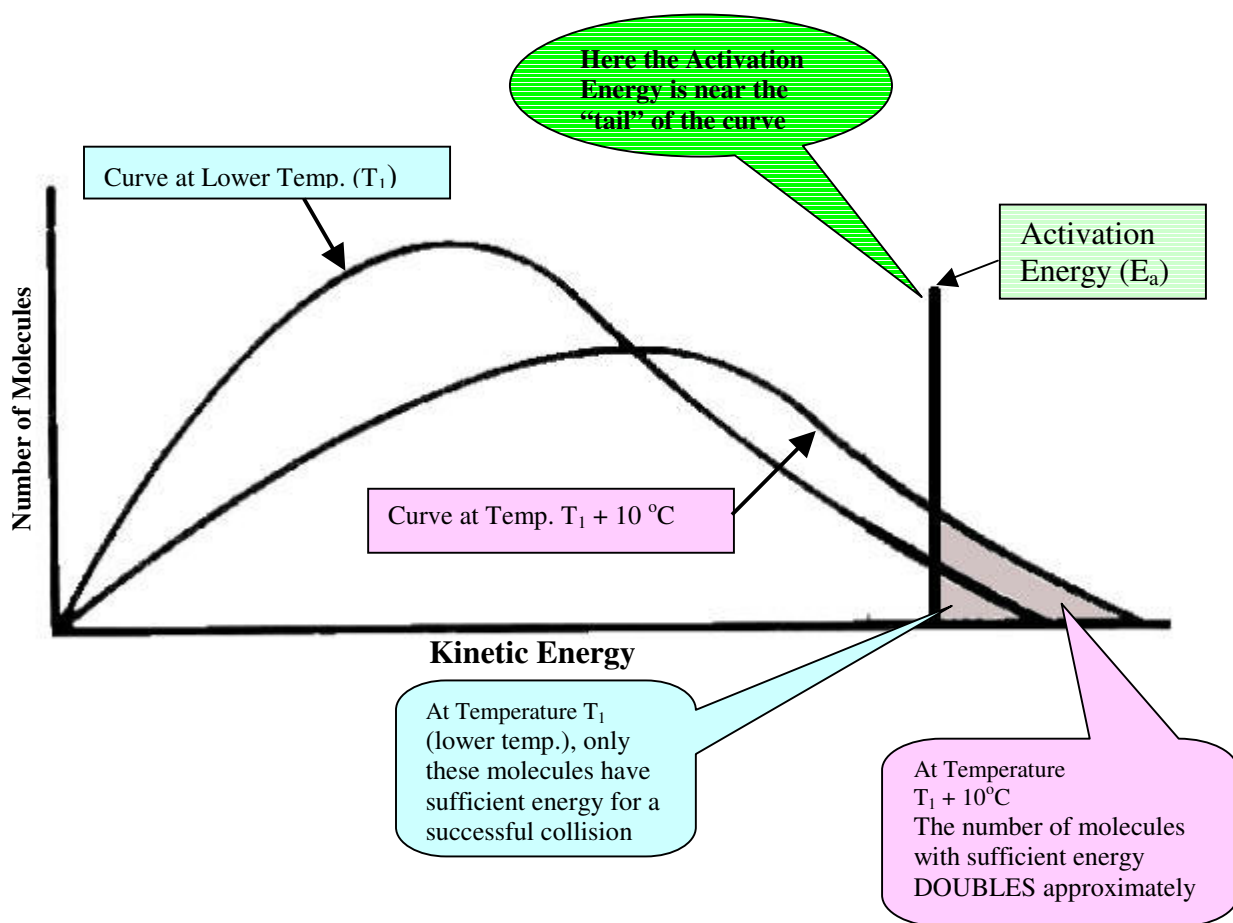
On the graph above, temperature T_2 is about 10°C higher that T_1. Notice that the area under the T_2 curve to the right of the Activation Energy is about **twice** the area under the T_1 curve. This means that the number of molecules with sufficient KE at T_2 is about double the number of molecules with sufficient KE at T_1.

> Note - if Activation Energy or ME is near the middle of the curve (or left side)
> - reaction is already fast, so an increase in temperature has a **less drastic** effect on the reaction rate.

See the graph on the next page, where Ea is a lot lower (NOT near the "tail" of the curve)

E_a

Curve at T_1

Curve at T_1 + 10 ^{o}C

Number of Molecules

Kinetic Energy

When the E_a is low, there is not a great difference between the areas under each curve with energies greater than E_a. So when E_a is low, an increase in temperature has **less effect**.
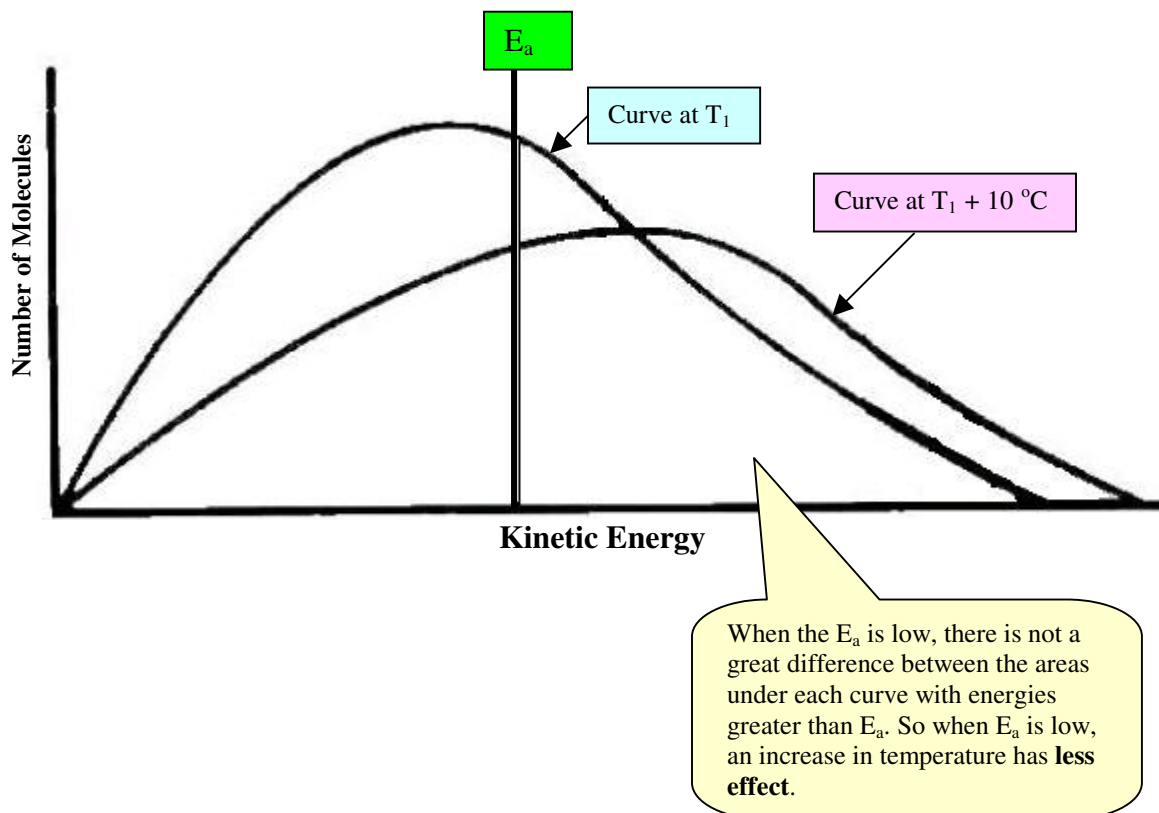
Read p. 17-19 SW.   Do Ex. 29-32 on pages 19-20 SW.

Activation energies   http://www.wwnorton.com/chemistry/tutorials/ch14.htm

(back to collision theory.....)

Potential and Kinetic energy during a collision

e^- e^- e^- e^- (+) e^- e^- e^-

e^- e^- e^- e^- (+) e^- e^- e^-

negatively charged electron cloud

Repulsive Force

negatively charged electron cloud
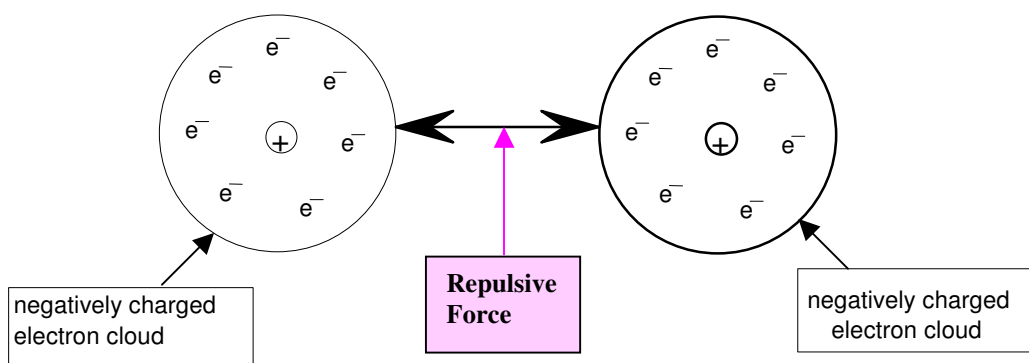
- as colliding molecules approach the repulsion **slows** them down so **kinetic energy decreases**.

- as they push against the **repulsive** force **potential energy** <u>increases</u>

(like compressing a spring)

- so: **Kinetic Energy** $\xrightarrow{\text{is converted to}}$ **Potential Energy**

KE + PE = Total E (*stays constant*)

⬆ ⬆

| if one goes down, the other goes up. |

<u>Potential energy diagrams</u>

Potential Energy (kJ)

Progress of Reaction

As molecules approach each other, KE is converted to PE

Molecules form a temporary, unstable species called the ACTIVATED COMPLEX

Activated Complex rearranges to form the PRODUCT molecules

Product Molecules move apart and speed up. PE is converted to KE.

Potential Energy (kJ)

REACTANTS

(High KE, Low PE)

PRODUCTS

(High KE, Low PE)

Progress of Reaction

ACTIVATION ENERGY (E_a) http://chem.salve.edu/chemistry/temp2a.asp

   - The minimum energy required for a successfull collision. (or) The minimum energy
     reacting molecules must have in order to form the **Activated Complex**.
The **Activated Complex** can be defined as a very **short-lived**, **unstable** combination of reactant
atoms that exists before products are formed.

NOTE: The Activation Energy (E_a) is fixed by the **nature of the reactants**
(#'s and strengths of bonds in reactants.)
E_a is **NOT** affected by Δtemperature or Δ concentration.!

Ea = 85 - 50
= 35 kJ

REACTANTS

PRODUCTS

Progress of Reaction
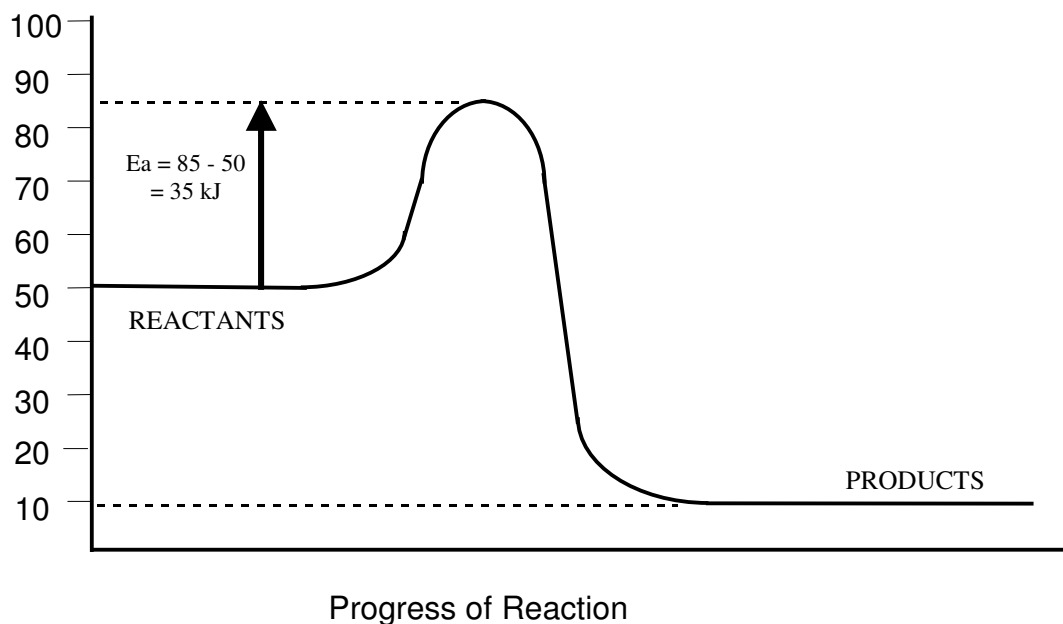
Temperature's role
- the temperature determines how many (or what fraction of the) molecules will have
energy $\geq$ Ea (to make it over the barrier & have a successful collision)

Recall KE distributions: eg.) At a **LOW** temperature:

Curve at Lower Temp. (T_1)

Activation
Energy (E_a)

Number of Molecules

Kinetic Energy

At Temperature T_1 (lower
temp), the molecules
represented by this area do
NOT have sufficient KE for
a successful collision

At Temperature T_1
(lower temp.), only
these molecules have
sufficient energy for a
successful collision
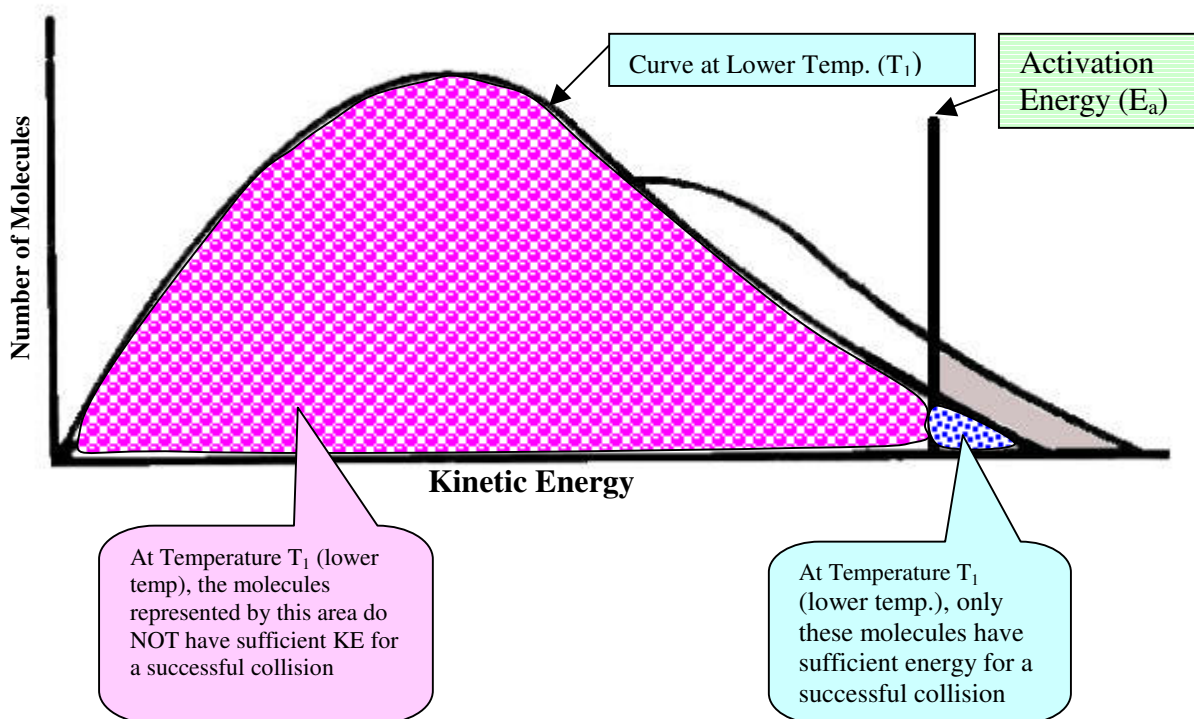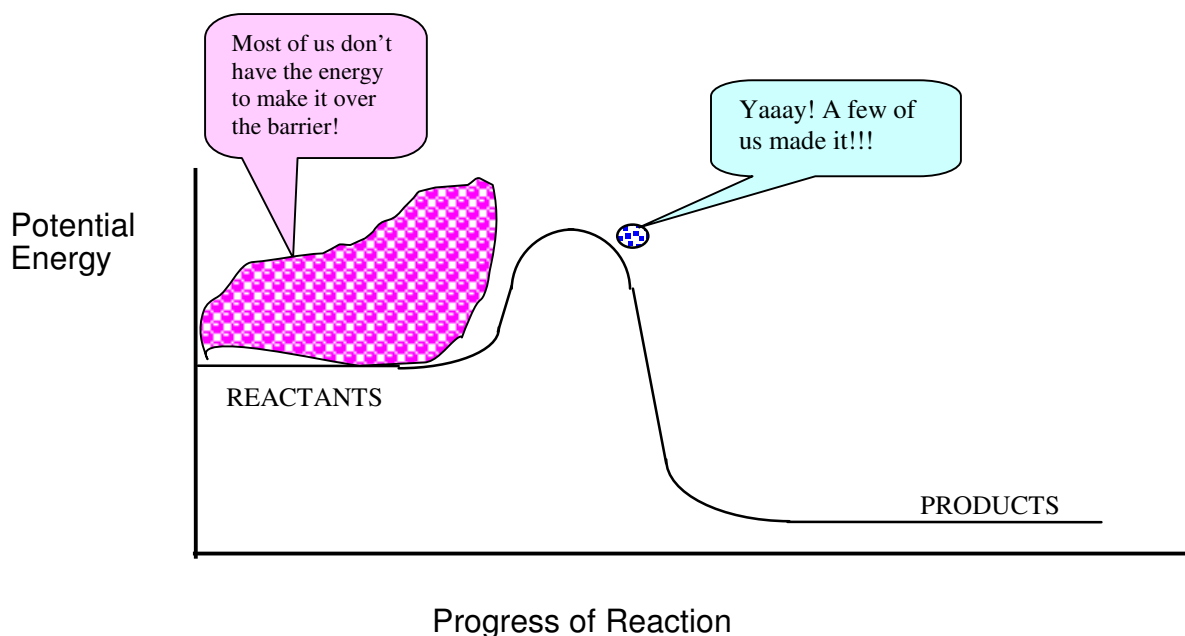
Notice in the diagrams on the previous page and above, that only a **small fraction** of the molecules had enough energy to overcome the **Activation Energy barrier**.

<u>Now, at a Higher Temperature:</u>
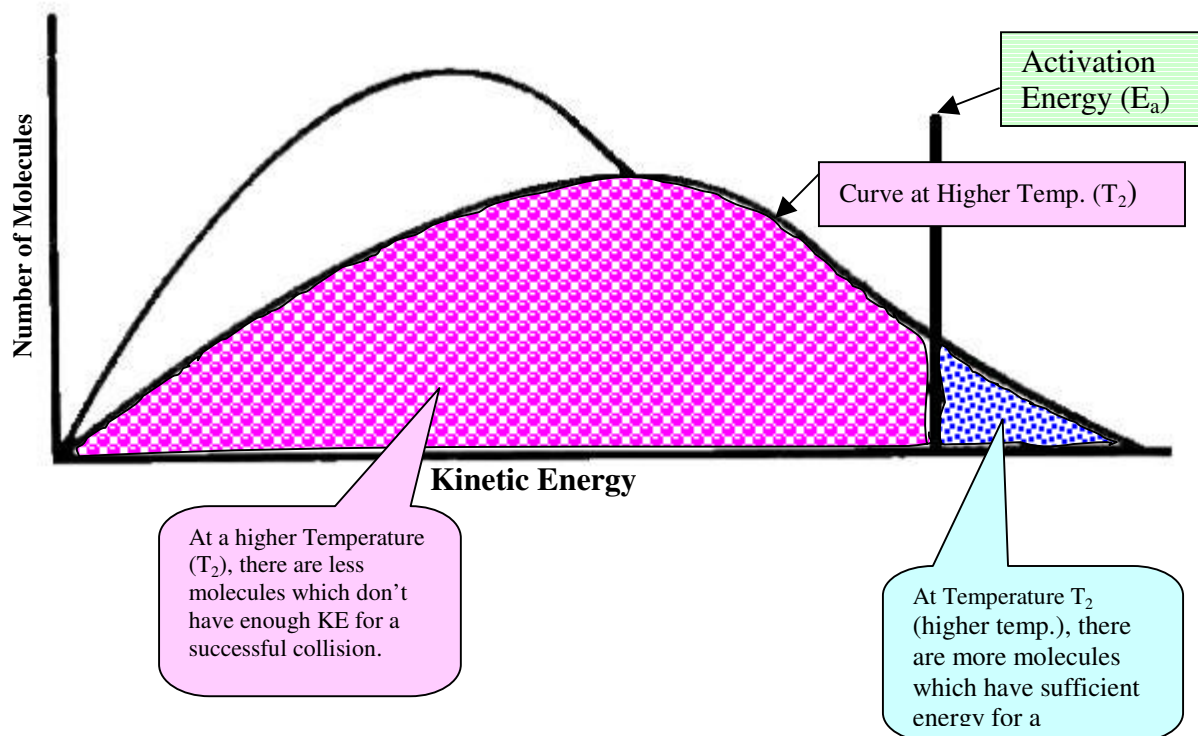
At the higher temperature, a **greater fraction** of the molecules have sufficient energy to "make it over" the **Activation Energy barrier**. (ie. a greater fraction of the molecules posses enough energy to form the **Activated Complex**):

A few of us don't have the energy to make it over the barrier!

Yaaay! A **greater fraction** of us made it this time!

Potential Energy

REACTANTS

PRODUCTS

Progress of Reaction
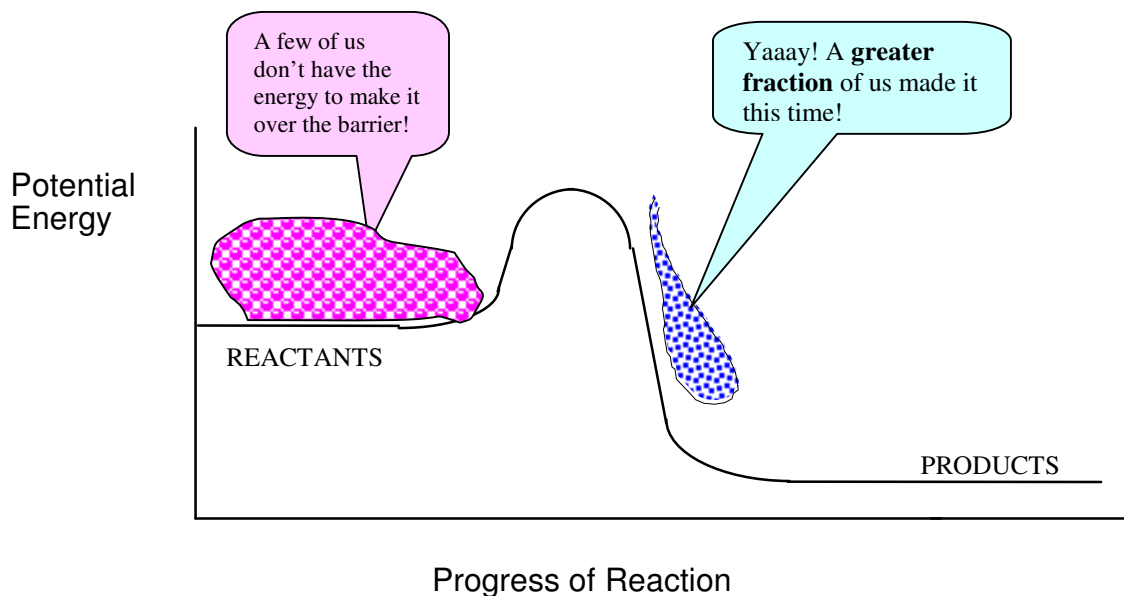
Looking at the diagram above, you can see that at a higher temperature, a **greater fraction** of the molecules have **sufficient energy** to make it over the barrier. Therefore the reaction is **faster**.

So if you study the graphs on the previous pages, you will see that:

> Increasing the **temperature** increases the **fraction of molecules which have sufficient energy to form the Activated Complex** (ie. sufficient energy to "make it over" the **activation energy barrier**.)

This is __one__ reason that increasing the temperature will INCREASE the rate of reaction.

Also, NOTICE that a change in temperature does NOT change the Potential Energy diagram at all. Temperature does __NOT__ affect the __Activation energy__ or the ΔH !!

Review the difference between "**Activated Complex**" and "**Activation Energy**" on the top of page 21 of SW.

See: The 3 "Cases" on Page 21 of SW. Also study the diagram at the bottom of page 21, where it compares the KE distribution and the PE diagram
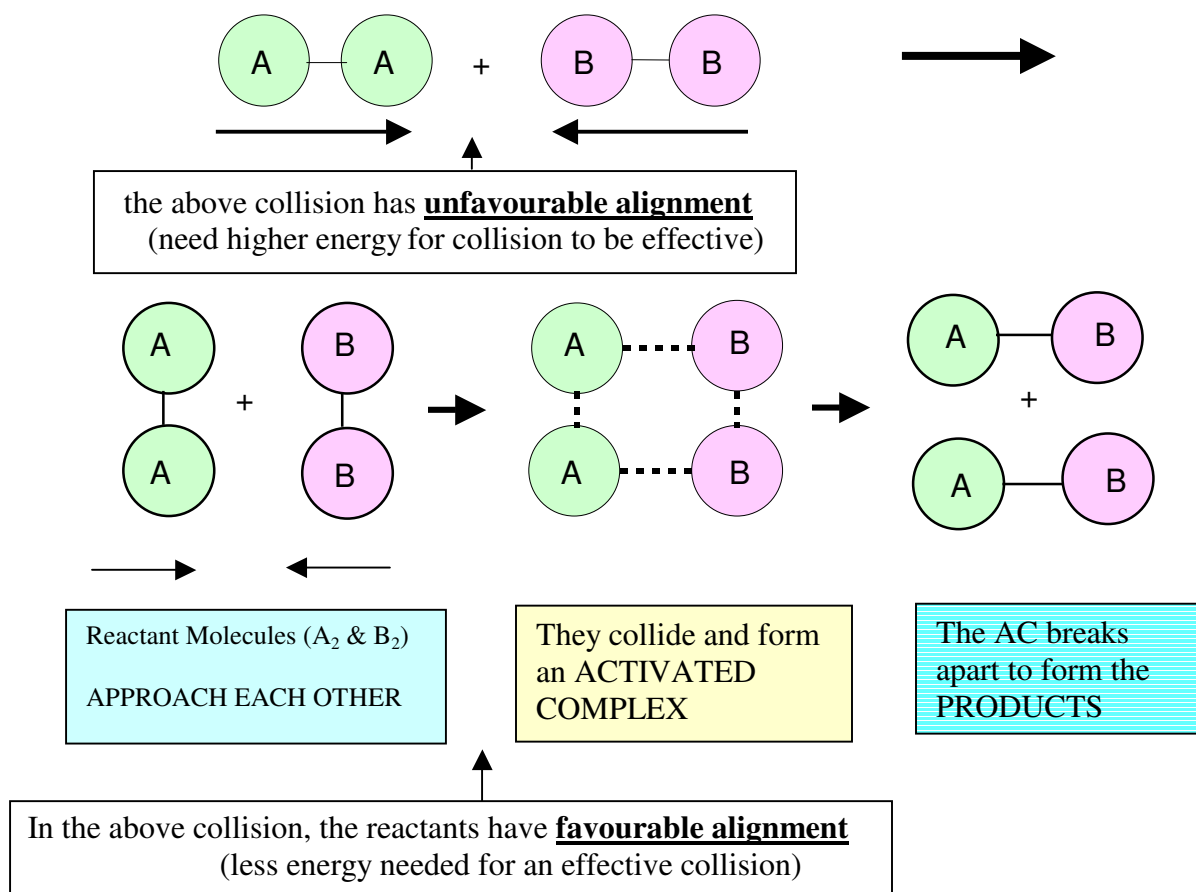
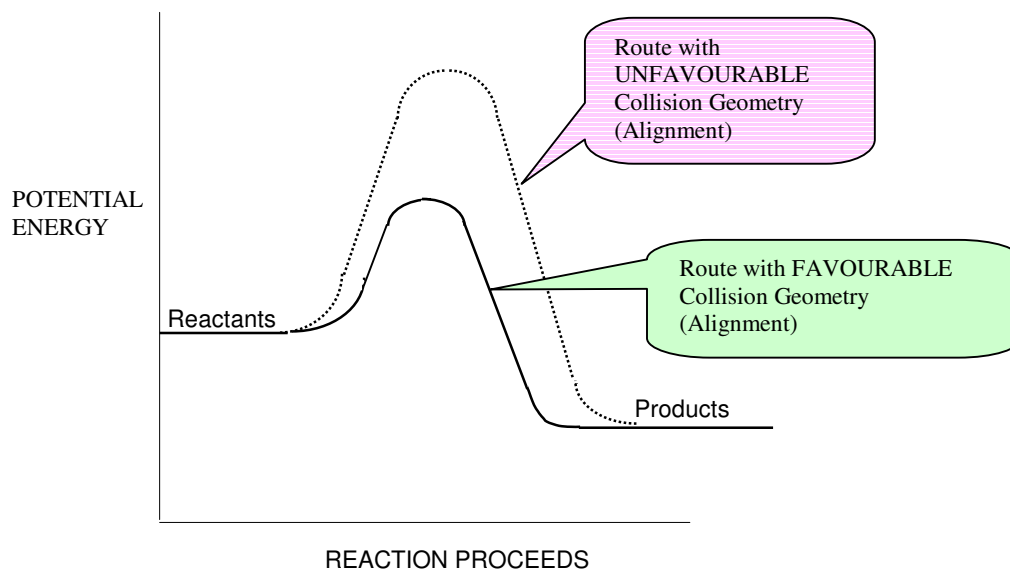Consider two reactions **AT THE SAME TEMPERATURE**:

Reaction A
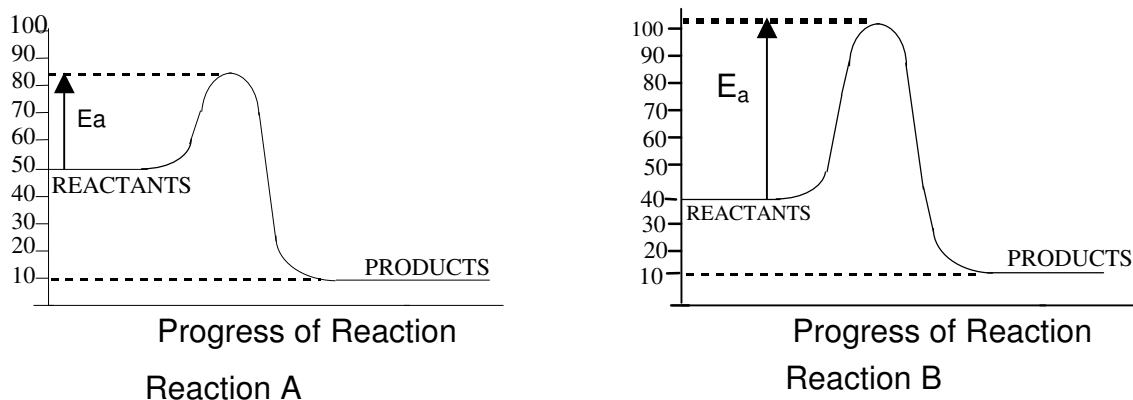
Reaction B

Which reaction is faster? _____ Explain why.

Collision Geometry (correct alignment) http://chem.salve.edu/chemistry/temp2a.asp

eg. for the rx. A_2 + B_2 → $2AB$:

the above collision has **unfavourable alignment**
(need higher energy for collision to be effective)

| Reactant Molecules (A_2 & B_2) APPROACH EACH OTHER | They collide and form an ACTIVATED COMPLEX | The AC breaks apart to form the PRODUCTS |

In the above collision, the reactants have **favourable alignment**
(less energy needed for an effective collision)

Potential energy diagram

To Summarize Collision Theory so far:

For any **successful collision** (one resulting in a reaction):

3 Requirements: **1.)** - particles must **collide**

2.) - they must collide with **sufficient energy > Ea**

3.) - they need to have **correct alignment** (collision geometry)
(to keep Ea as low as possible)

Ea, ΔH and bond strengths for forward and reverse reactions
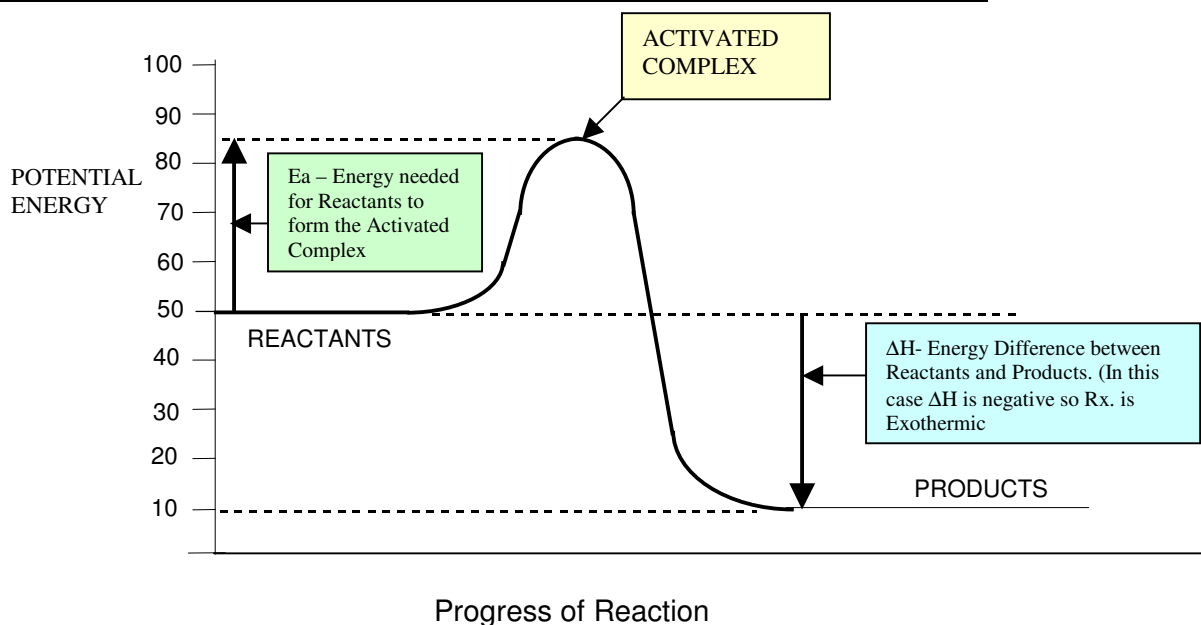
Try this question:
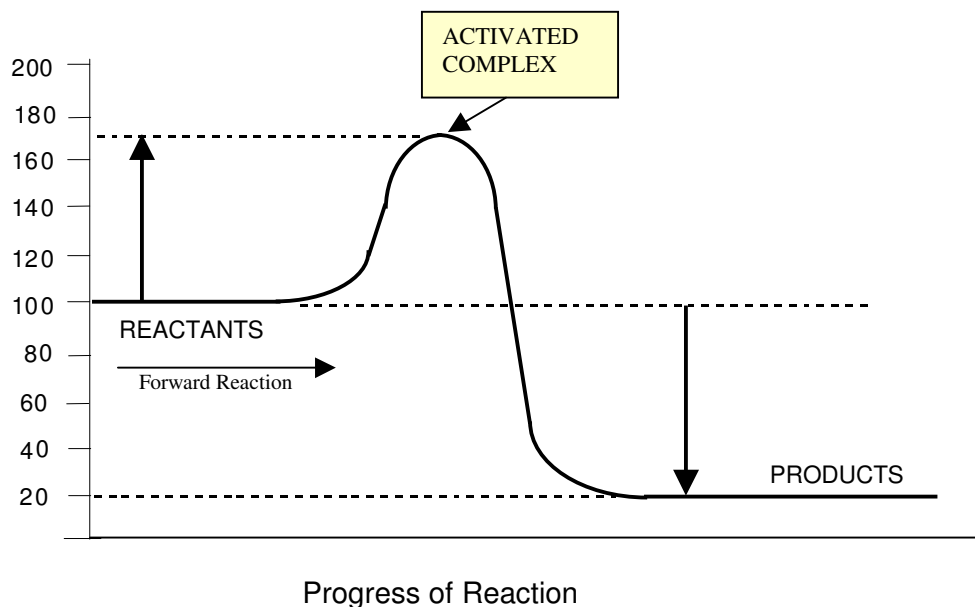
Using the graph above, find:

E_a (forward rx.) = _____kJ ΔH (forward rx.) = _____kJ

This forward reaction is _____thermic

-<u>Considering reverse rx.</u>
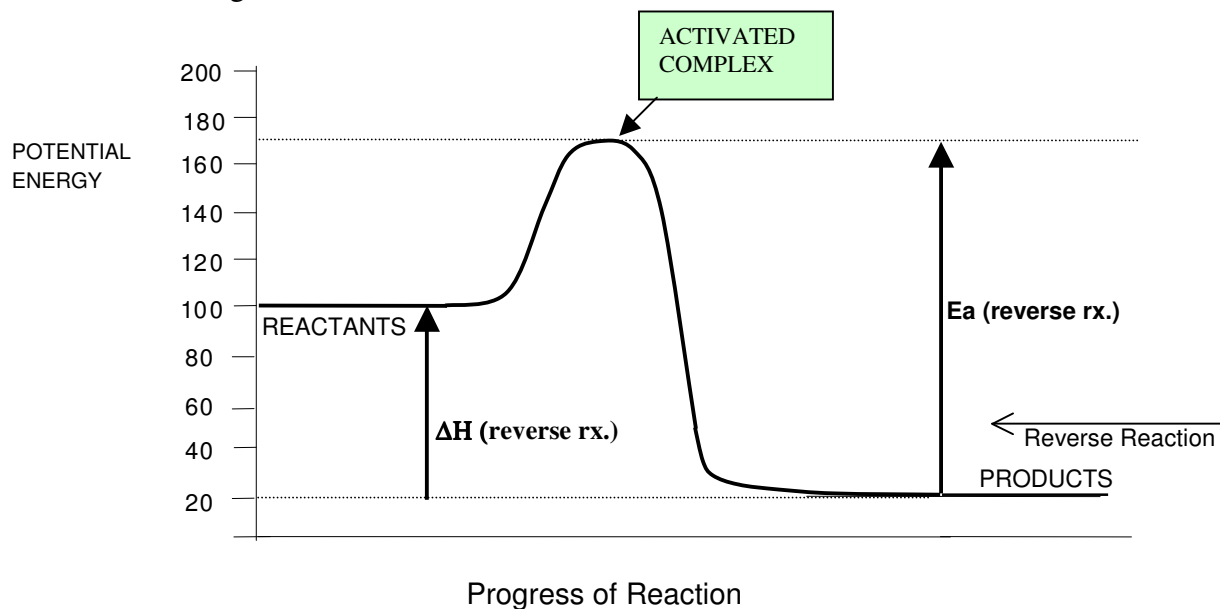
E_a (reverse rx.) = _____kJ ΔH (reverse rx.) = _____kJ

This reverse reaction is _____thermic

Given the following Potential Energy Diagram for the Reaction:

$$A_2 + B_2 \rightarrow 2AB$$

POTENTIAL ENERGY

Progress of Reaction
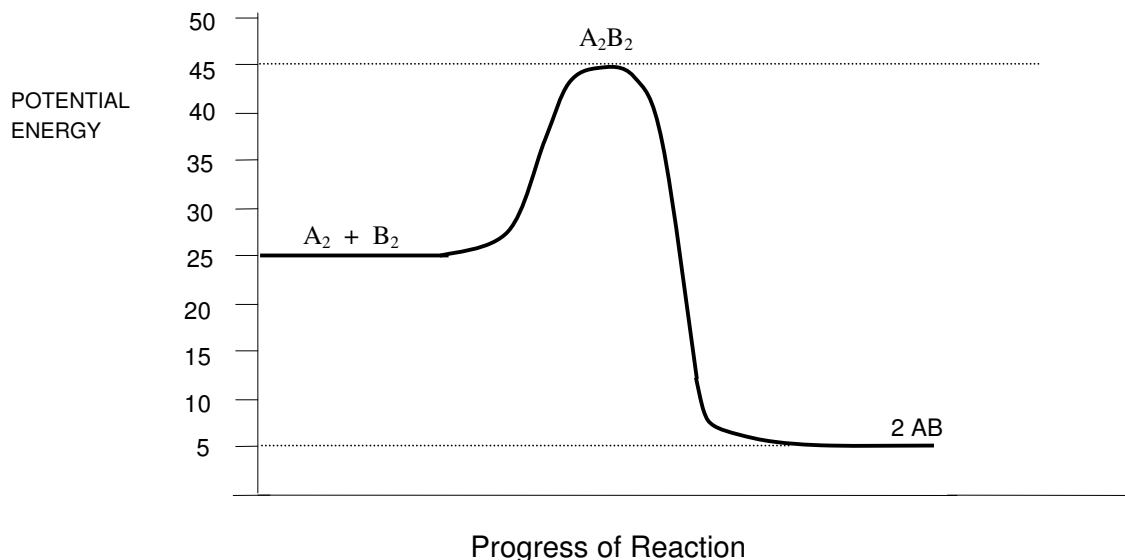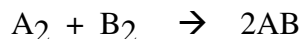
a) Ea (forward) = _____ KJ

b) Energy needed to break bonds in A_2 & B_2

                                       A-A   B-B   _____ KJ

c) Ea (reverse) = _____ KJ

d) Energy needed to break bonds in AB (A-B) _____ KJ

e) Which has the stronger bonds A_2 & B_2 or 2AB?

f) On a PE diagram, species with stronger bonds (more stable) are

    (low/high)_____er on the graph

g) Which set of species (A_2 & B_2, A_2B_2, or 2AB) have the weakest bonds?

    _____. This species is the most _____ stable. It is called the

    _____ _____

h) Which set of species has the highest PE?_____

i) Which set of species has the highest KE?_____

> j) Draw a graph of **KE** vs. reaction proceeds for the same forward rx.

**KINETIC
ENERGY**

Progress of Reaction
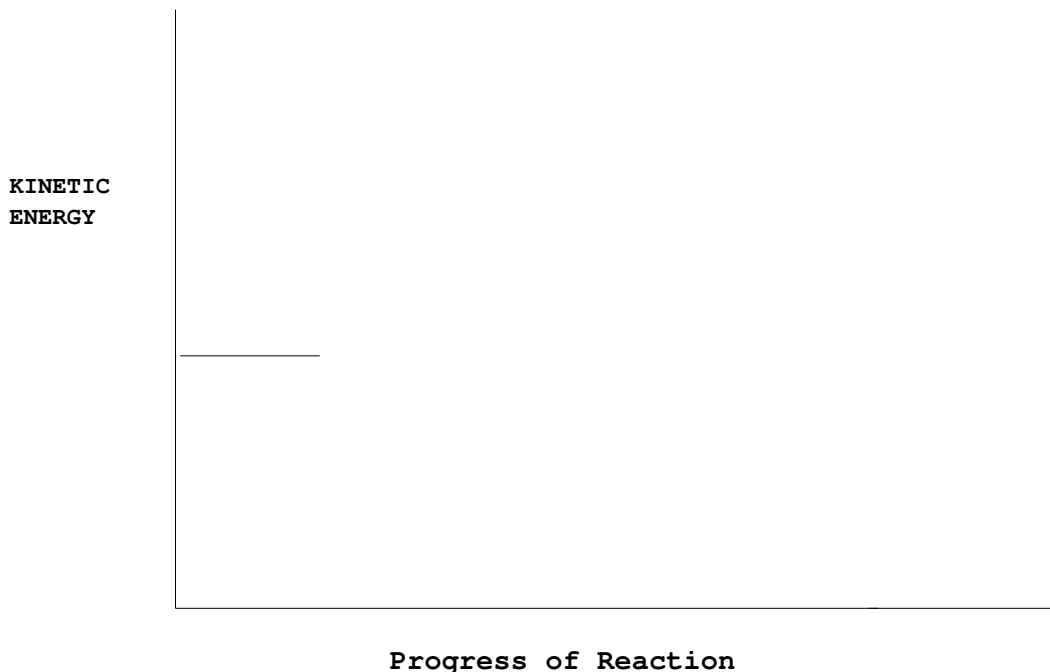
Read pages 20-22 and 24-25 in SW
Do Ex. 33-45 on pages 23 - 25 of SW
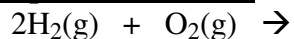Do **Worksheet 1-2** (Potential Energy Diagrams)

<u>Reaction Mechanisms</u>

"every long journey begins with a _____ "
-Car building analogy

<u>In a chemical rx.</u>
eg.) $5C_2O_4{}^{2-} + 2MnO_4{}^- + 16H^+ \rightarrow$

involves **23** reacting particles
-chances of this taking place in one step are almost "0"

<u>even a **3 particle collision**</u>
    $2H_2(g) + O_2(g) \rightarrow$
probably **doesn't** take place in a single step.
    (1,000 times less probable than a 2 particle collision)

Most reactions (other than simple 2 particle collisions eg. $Ag^+ + Cl^- \rightarrow AgCl_{(s)}$)
take place in a **<u>series</u>** of simple steps.

each step depends on the others before it

Reaction Mechanism

- the series (sequence) of steps by which a reaction takes place.

➢ **cannot** be determined by just looking at **overall reaction**.
➢ deduced through much study and research (up to years)
➢ you will **not** be asked to come up with mechanism from scratch.
➢ some mechanisms are known, many are yet to be discovered.

Example (known mechanism)

for the overall reaction: $\quad$ **4HBr + O$_2$ → 2H$_2$O + 2Br$_2$**

5 reactant particles. **Doesn't** take place in a single step!

Mechanism (*determined from lots of research*)

step 1: $\qquad$ **HBr + O$_2$ → HOOBr** (found to be slow)

step 2: $\qquad$ **HBr + HOOBr → 2HOBr** (fast)

step 3: $\qquad$ **HOBr + HBr → H$_2$O + Br$_2$** (very fast)

- Each step is called an **Elementary Process**

Rate determining step - the **slowest** step in the mechanism.

➢ the overall reaction can never be faster than the RDS
➢ the only way to speed up an overall reaction is to speed up the RDS (eg. by increasing. the concentration of a reactant in the RDS)
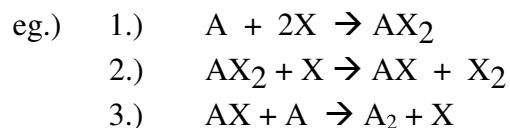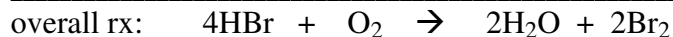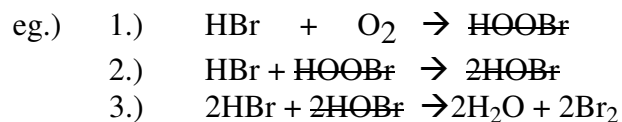
eg.) in this case, increasing [HBr] or [O$_2$] would speed up Step 1 (the RDS) and hence the overall rate.

- speeding up a **fast** step (not RDS) will have **no effect on the overall rate**. (eg. adding HOOBr or HOBr has **no effect**)
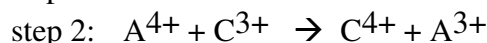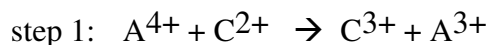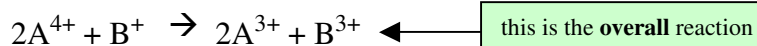
Determining overall reaction given steps (mechanism)

- cancel stuff which is identical on both sides   - add up what's left.

eg.)   1.) HBr + O_2 → $\cancel{HOOBr}$

2.) HBr + $\cancel{HOOBr}$ → $\cancel{2HOBr}$

3.) $2HBr$ + $\cancel{2HOBr}$ → $2H_2O + 2Br_2$

_____

overall rx: $4HBr$ + O_2 → $2H_2O$ + $2Br_2$

_____

eg.)   1.) A + $2X$ → AX_2

2.) $AX_2 + X$ → AX + X_2

3.) $AX + A$ → $A_2 + X$

_____

overall rx:_____

Question

the following reaction occurs in a **3 step mechanism**:

$$2A^{4+} + B^+ → 2A^{3+} + B^{3+}$$ ← this is the **overall** reaction

step 1: $A^{4+} + C^{2+}$ → $C^{3+} + A^{3+}$

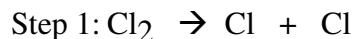step 2: $A^{4+} + C^{3+}$ → $C^{4+} + A^{3+}$

step 3: ?   find step 3.

Another Example:

Consider the following reaction for the formation of HCl in the presence of light.

$$Cl_2 + CHCl_3 → HCl + CCl_4$$
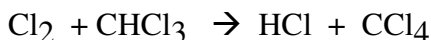
The following is the proposed reaction mechanism:

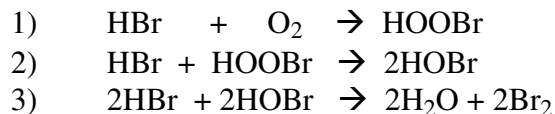Step 1: Cl_2 → Cl + Cl

Step 2:

Step 3: $Cl + CCl_3$ → CCl_4

Determine **Step 2** of the reaction mechanism.

Step 2: _____

Reaction intermediate

-a **species** (atom, molecule or ion) which is **produced in one step** and **used up** in a **later step**. (appears on **right** & also **lower on left**)

eg.)   For the mechanism:

1) $HBr + O_2 \rightarrow HOOBr$
2) $HBr + HOOBr \rightarrow 2HOBr$
3) $2HBr + 2HOBr \rightarrow 2H_2O + 2Br_2$

intermediates are _____ & _____

Notes:

➢ an **intermediate** doesn't accumulate (like a product) because as soon as it is formed, it gets used up again (like money)
➢ **intermediates** are not necessarily unstable. (in other circumstances, they may last a while)
➢ an **activated complex** is *very* unstable and ***short-lived***. It doesn't usually obey bonding "rules".
(see diagrams p. 26 & 27) (very high PE, temporary arrangement)

Read pages 26-27 in SW   <u>Do ex. 46-53   p.28 of SW.</u>
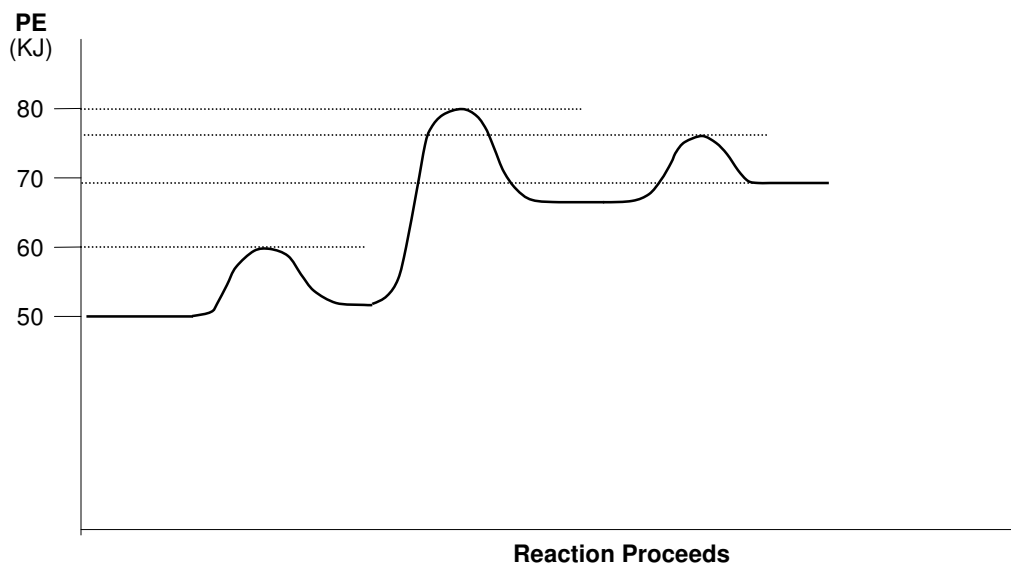
PE diagram for a reaction mechanism
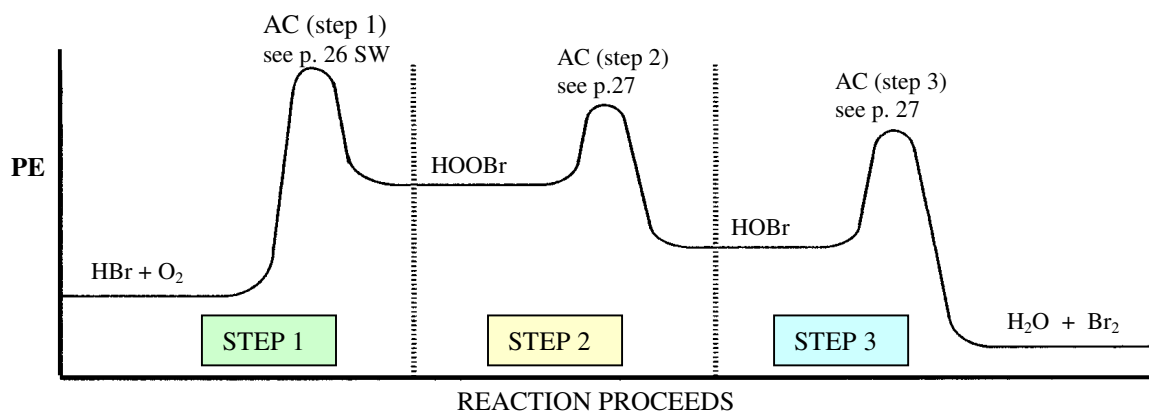
Notes:

➢ each "bump" is a step
➢ the **higher** the bump, (greater Ea) the **slower** the step
➢ the **highest** bump (from the reactants level) is for the **RDS**
➢ **AC's** at **top** of bumps, **intermediates** in middle "valleys", **products** in the final "valley"
➢ the Ea for the forward **overall rx**. is vertical distance from **reactants** to **top** of **highest bump**.

On the diagram for this mechanism on the previous page, label the **Rate Determining Step**. Draw an arrow to show the **Ea (overall reaction)** . Label it. Draw another labeled arrow to show the **Ea for Step 1**. Draw a labeled arrow to show **ΔH for the overall reaction**.

PE

E_a (Overall Rx.)

REACTION PROCEEDS

PE

E_a (Overall Rx.)

REACTION PROCEEDS
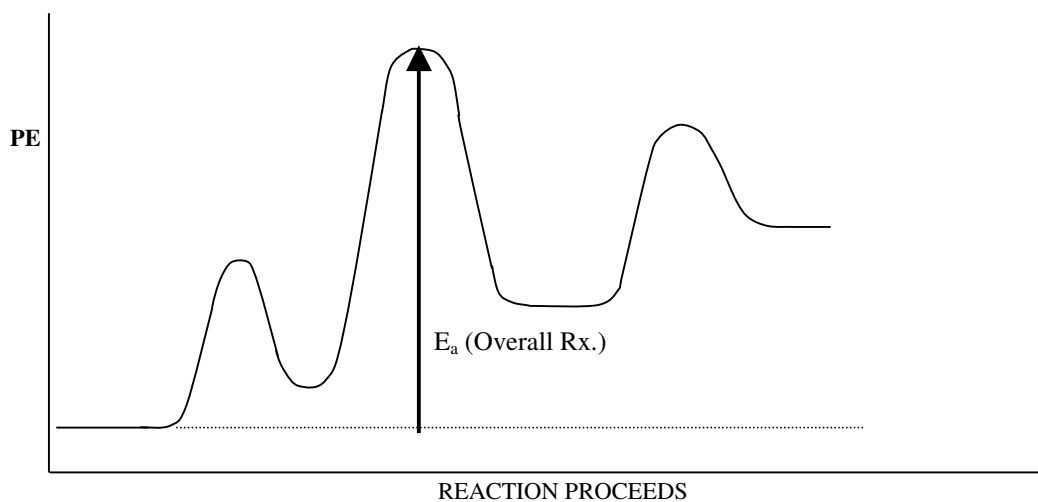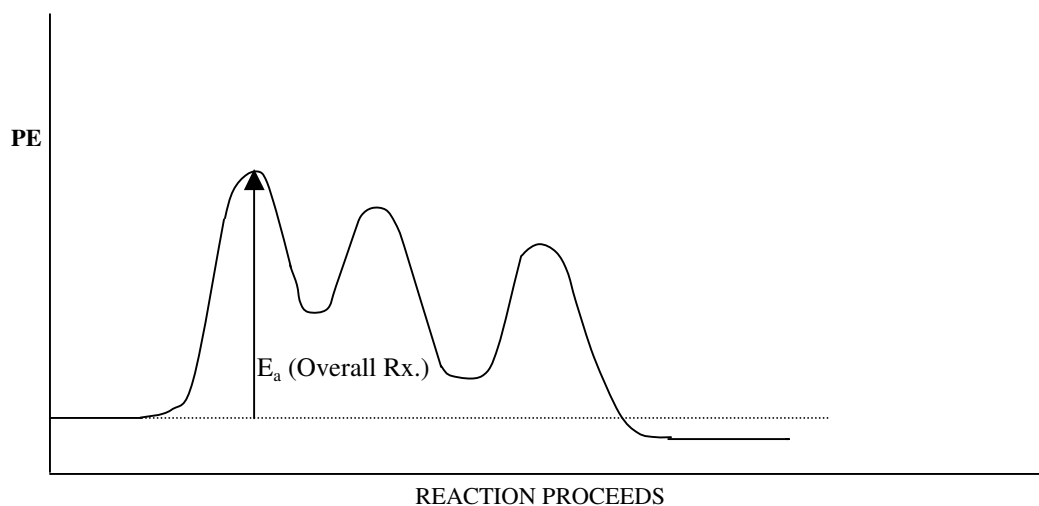
In each of the reactions in the diagram above, the **E_a for the overall forward reaction** is the **difference in energy** between the **reactants** and the **top of the highest peak**.

Question: Given the following Potential Energy Diagram for a reaction mechanism:

1. This mechanism has _____ steps   2. Ea for overall rx = _____ kJ

3. Step _____ is the RDS   4. Step _____ is the fastest step.

5. The overall rx. is _____ thermic   6. ΔH = _____ kJ

7. ΔH for **reverse** rx. = _____ kJ   8. Ea (reverse rx.) = _____ kJ

9. RDS for **reverse** rx. is step _____

Draw a **Potential Energy Diagram** for a **reaction mechanism** with **2 steps**. The first step is **fast** and the second step is **slow**. The overall reaction is **exothermic**. With **labeled arrows** show the **overall Activation Energy (E_a)** and the ΔH for the **forward** reaction.
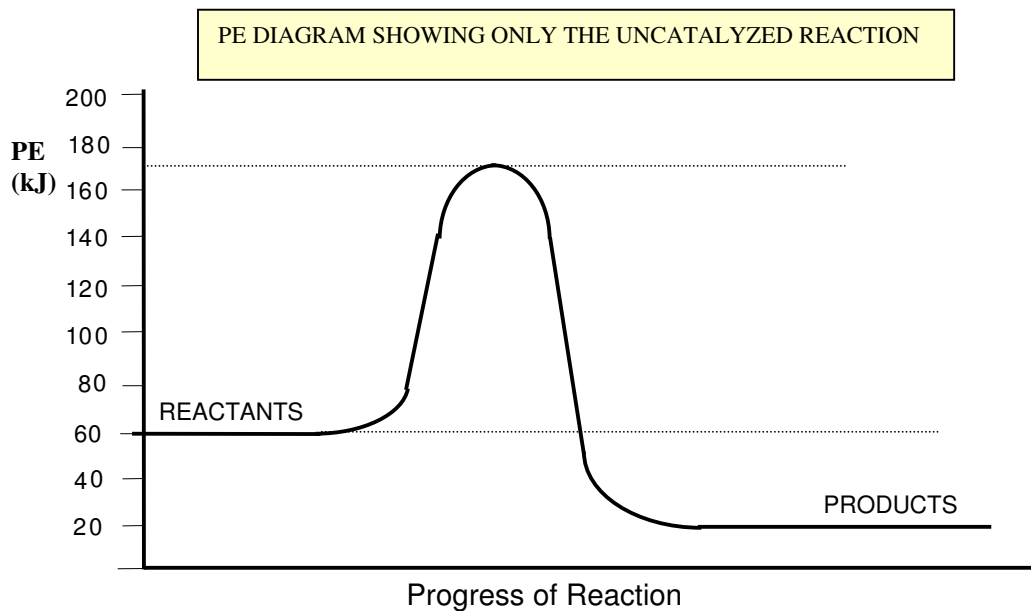

PE

Reaction Proceeds

Read p. 29-30 in SW. Do Ex. 54 and 55 on page 30 of SW.

How catalysts work

- "to avoid a hill, build a _____ "

catalyst- an <u>introduced </u>substance which produce an **alternate mechanism** with a
lower activation energy.

PE DIAGRAM SHOWING ONLY THE UNCATALYZED REACTION

Look on the next page to see the PE diagram showing the **uncatalyzed** and the
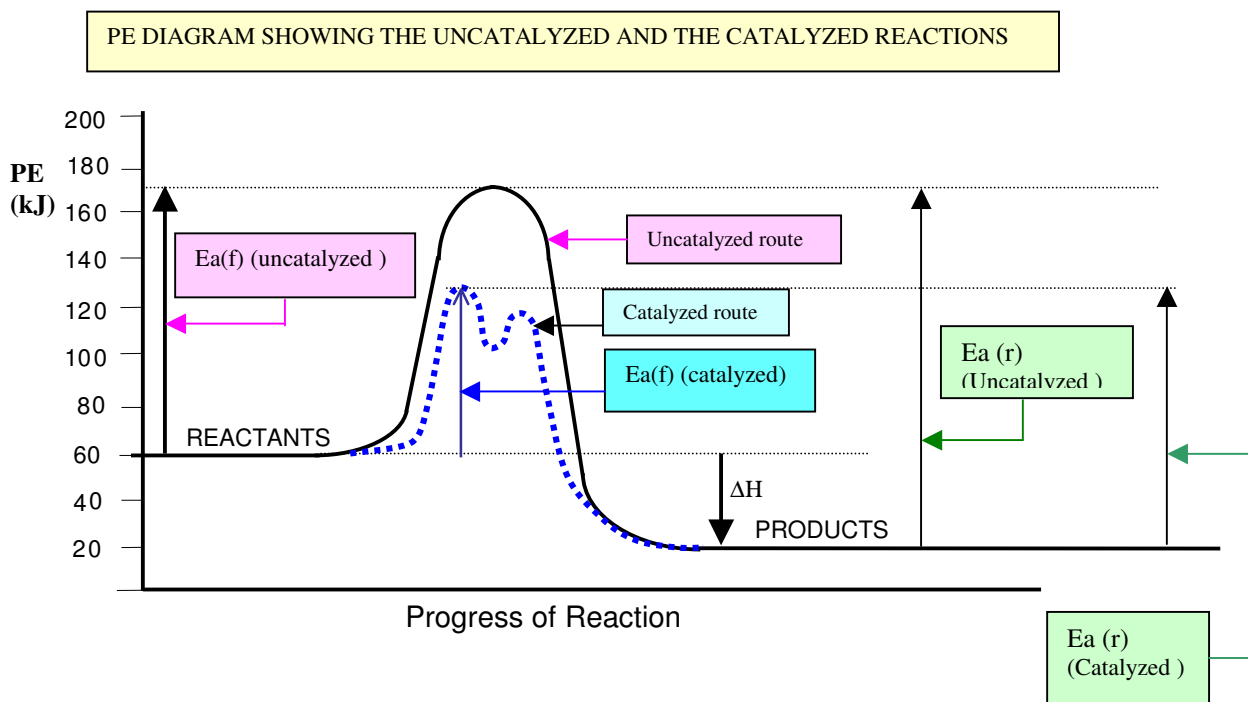**catalyzed** "routes" for the same reaction….

PE DIAGRAM SHOWING THE UNCATALYZED AND THE CATALYZED REACTION
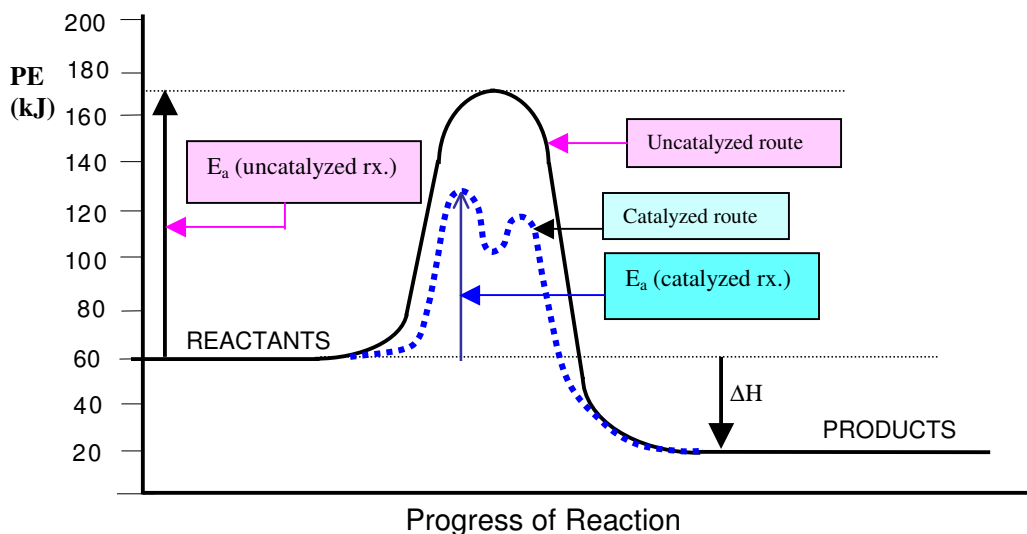
Notes

➢ energy required (Ea) is **less with the catalyst**, so at the same temperature, **more** molecules can make it over the "barrier" so **reaction rate speeds up** (eg. lower standards for a pass, eg. 30% will let more students pass!)

➢ catalyzed reactions usually involve **more steps** but it's highest Ea (highest bump) is never as high as the uncatalyzed reaction

➢ a catalyst **NEVER changes** the **PE of reactants of products** - only the **route** between them. (**no change in ΔH!**)

➢ **uncatalyzed** reaction **still continues** at its own slow rate when a catalyst is added. (usually insignificant compared to catalyzed rate)

➢ if catalyst speeds up **forward** reaction, it also speeds up (reduces Ea for) the **reverse** reaction.

Study the PE diagram on the next page which compares the Ea's for the forward and reverse uncatalyzed and catalyzed reactions…

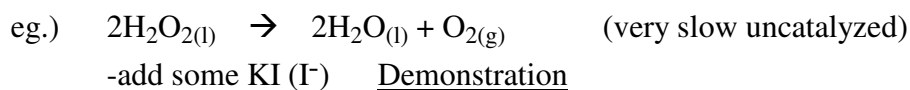PE DIAGRAM SHOWING THE UNCATALYZED AND THE CATALYZED REACTIONS

Catalysts sometimes work by...

http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/ethylene8.html
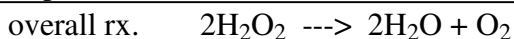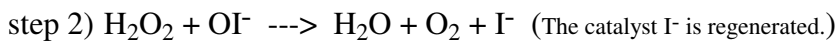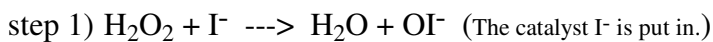http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/Catalyst2NOO2N28.html

➢ providing a **surface** whose spacing of atoms is just right to break a reactant molecule and hold it for an attack from another reactant.
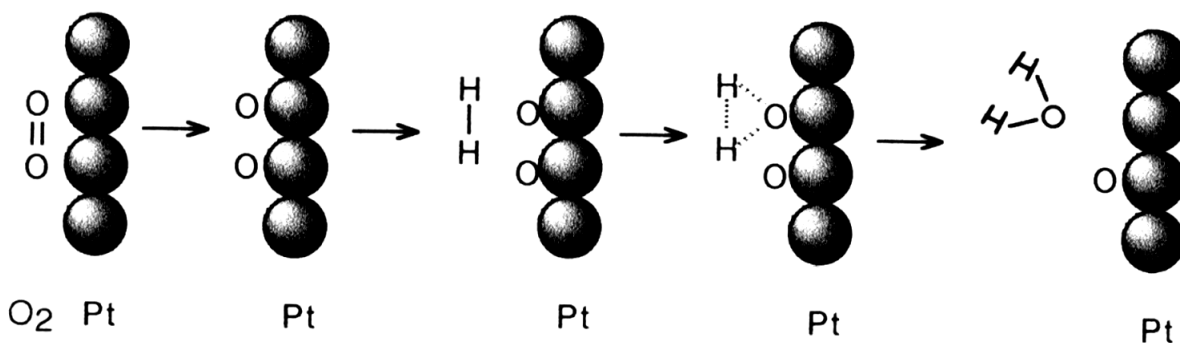
➢ helping to form an intermediate which can react more easily to form products.

eg.) $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$ (very slow uncatalyzed)

-add some KI (I^-) Demonstration

Catalyzed Mechanism:

step 1) $H_2O_2 + I^- ---> H_2O + OI^-$ (The catalyst I^- is put in.)

step 2) $H_2O_2 + OI^- ---> H_2O + O_2 + I^-$ (The catalyst I^- is regenerated.)

overall rx. $2H_2O_2 ---> 2H_2O + O_2$

See the example in the textbook on p. 32-33. In the diagrams on page 33, the Activated Complexes are also shown in the square brackets. Also compare the PE diagram for the uncatalyzed reaction (bottom of p. 32 SW.) and the PE diagram for the catalyzed reaction (middle of p. 33 SW.)

➢ **Read** pages 30-36 in SW.

➢ Do ex. 56-61 on page 34 SW

➢ See Examples of real Catalysts p.34-36 SW.

➢ Get **hand-out on catalysts** from teacher

➢ Do ex. 62 & 63 on page 36 of SW
.
➢ Do **Worksheet 1-3** (Reaction Mechanisms)

➢ Do **Provincial Questions on Unit 1**

THIS IS THE END OF UNIT 1