Chemistry 12 - Notes on Unit 1 - Reaction Kinetics

**Reaction Kinetics** [http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA0/MOVIES/NJ3IOD.html](http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA0/MOVIES/NJ3IOD.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** = \( \frac{\Delta \text{ amount (a reactant or product)}}{\Delta \text{ time}} \)

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

eg.) \[ \text{Zn(s) + 2HCl(aq) } \rightarrow \text{ H}_2(g) + \text{ZnCl}_2(aq) \]

\[ r = \frac{\Delta \text{ mass of Zn}}{\Delta \text{ time}} \]

\[ r = \frac{\Delta [ \text{HCl} ]}{\Delta \text{ time}} \]  (note: [ ] = molar concentration)

\[ r = \frac{\Delta \text{ volume H}_2}{\Delta \text{ time}} \]

Do ex. 1-5 p.2 S.W. (SW is Hebden’s Student Workbook)

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

eg. \[ \text{Mg(s) + 2HCl(aq) } \rightarrow \text{ H}_2(g) + \text{MgCl}_2(aq) \]

NOTE: To write an equation in IONIC FORM, dissociate all the aqueous (aq) compounds:

ionic form : \[ \text{Mg(s) + 2H}^+(aq) + 2\text{Cl}^-(aq) \rightarrow \text{ H}_2(g) + \text{Mg}^{2+}(aq) + 2\text{Cl}^-(aq) \]

(use ion chart)

[\text{Cl}^- \text{ does not change as rx. proceeds (spectator ion)}]

**Write** 4 possible equations which express rate.
Calculations Involving Reaction Rates

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

\[
\text{Rate} = \frac{\Delta \text{ amount \ (g, mol, L)}}{\Delta \text{ time \ (s, min)}} \quad \text{or} \quad \Delta \text{ amount} = \text{Rate} \times \Delta \text{ time}
\]

or \[
\Delta \text{ time} = \frac{\Delta \text{ amount}}{\text{Rate}}
\]

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.) \[
0.020 \text{ mol/min} = ? \text{ mol/s}
\]

Solution: \[
0.020 \text{ mol/min} \times \frac{1 \text{ min}}{60 \text{ s}} = 3.3 \times 10^{-4} \text{ mol/s}
\]

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 \(\Leftrightarrow\) moles.

Eg.) \[
0.26 \text{ mol Zn/min} = ? \text{ g of Zn/s}
\]

Solution: \[
0.26 \text{ mol Zn/min} \times \frac{65.4 \text{ g Zn}}{1 \text{ mol Zn}} \times \frac{1 \text{ min}}{60 \text{ s}} = 0.28 \text{ g of Zn/s}
\]

You would use 22.4 L for conversions moles \(\Leftrightarrow\) L (STP) for gases.

Eg.) \[
0.030 \text{ mol O}_2/\text{s} = ? \text{ L/s (STP)}
\]

Solution: \[
0.030 \text{ mol O}_2/\text{s} \times \frac{22.4 \text{ L}}{1 \text{ mol O}_2} = 0.67 \text{ L O}_2/\text{s}
\]

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

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 \( \text{mol/s} \) (not to g/s)

eg.) ethane

\[
2 \text{C}_2\text{H}_6 + 7 \text{O}_2 \rightarrow 4 \text{CO}_2 + 6 \text{H}_2\text{O}
\]

consumed  produced

eg.) if ethane is consumed at a rate of 0.066 mol /s, calculate the rate of consumption of \( \text{O}_2 \) in mol /s

Solution: \[
\frac{0.066 \text{ mol C}_2\text{H}_6}{s} \times \frac{7 \text{ mol} \text{O}_2}{2 \text{ mol C}_2\text{H}_6} = \frac{0.23 \text{ mol O}_2}{s}
\]

if ethane is consumed at a rate of 0.066 mol /s calculate rate of production of \( \text{CO}_2 \)

Solution: \[
\frac{0.066 \text{ mol C}_2\text{H}_6}{s} \times \frac{4 \text{ mol CO}_2}{2 \text{ mol C}_2\text{H}_6} = \frac{0.13 \text{ mol CO}_2}{s}
\]

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

eg.) given: \( 2 \text{Al} + 3 \text{Br}_2 \rightarrow 2 \text{AlBr}_3 \)

if 67.5 g of Al are consumed per second - calculate the rate of consumption of \( \text{Br}_2 \) in g/s.

Solution: \[
\frac{67.5 \text{ g Al}}{s} \times \frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \times \frac{3 \text{ mol Br}_2}{2 \text{ mol Al}} \times \frac{159.8 \text{ g Br}_2}{1 \text{ mol Br}_2} = \frac{599 \text{ g Br}_2}{s}
\]

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:

\[
2\text{Al}(s) + 6 \text{HCl}(aq) \rightarrow 3 \text{H}_2(g) + 2 \text{AlCl}_3(aq)
\]

It is found that the rate of production of \(\text{H}_2(g)\) 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. \(\text{CaCO}_3(s) + 2\text{HCl}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) + \text{CaCl}_2(aq)\)

**Ionic form:** \(\text{CaCO}_3(s) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) + \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq)\)

**Net ionic form:** \(\text{CaCO}_3(s) + 2\text{H}^+(aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) + \text{Ca}^{2+}(aq)\)

- As \(\text{CO}_2\) escapes, mass of the rest of the system will ________________
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- 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 \(\Delta \text{amount}/\Delta \text{time} \))

![Graph showing mass of container and contents versus time](image1)

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

![Graph showing average slope](image2)

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

![Graph showing rate at a point](image3)
[ do ex.6 on page 3 of SW. ] [ Read page 11 and do ex. 18-19 on p. 11 SW. ]
[ do experiment 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 & HNO₃
  discuss colour, mass, conc., pressure (volume) change

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

  eg.) \( \text{Cu}(s) + 4\text{HNO}_3(aq) \rightarrow \text{Cu(NO}_3\text{)}_2(aq) + 2\text{H}_2\text{O}(l) + 2\text{NO}_2(g) + \text{heat} \)
  
  - in this case could measure - intensity of blue
  - intensity of brown gas

  \( \text{Cu(NO}_3\text{)}_2(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn(NO}_3\text{)}_2(aq) \)

  blue grey reddish colourless

  - as this reaction proceeds the blue colour fades

  in ionic form: \( \text{Cu}^{2+}(aq) + 2\text{NO}_3^-(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq) + 2\text{NO}_3^-(aq) \)
  
  net ionic: \( \text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq) \)

  [\text{Cu}^{2+} \text{is blue!}]

  - colour intensity can be measured quantitatively using a spectrophotometer
  (see p. 4 S.W.)

  eg. of rate equation
  
  \( \text{rate} = \frac{\Delta \text{colour intensity}}{\Delta \text{time}} \)
2.) **Temp changes**

- in exothermic reaction temperature of surroundings will ____________________
- in endothermic reaction temperature of surroundings will ____________________
  - measured in insulated container (calorimeter)
  
  \[ \text{rate} = \frac{\Delta \text{temp}}{\Delta \text{time}} \]

3.) **Pressure changes**  \((\text{constant volume or sealed container})\)

- if more **moles of gas** (coefficient) in **products** pressure will go **up**
  
  \[ \text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{H}_2(g) + \text{ZnCl}_2(aq) \]
  
  O m.o.g. \hspace{1cm} 1 m.o.g.
  
  - If more MOG in reactants - pressure will ______________________________

  \[ \text{rate} = \frac{\Delta \text{pressure}}{\Delta \text{time}} \] \((\text{constant volume})\)

- If equal MOG, pressure will **not** change:

  \[ \text{NO}_2(g) + \text{CO(g)} \rightarrow \text{CO}_2(g) + \text{NO(g)} \]
  
  2 m.o.g. \hspace{1cm} 2 m.o.g.

4.) **Volume change**  \((\text{constant pressure eg. balloon or manometer})\)

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

  \[ \text{rate} = \frac{\Delta \text{volume}}{\Delta \text{time}} \] \((\text{constant pressure})\)

5.) **Mass changes**

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

  \[ \text{Mg(s)} + 2\text{HCl(aq)} \rightarrow \text{H}_2(g) + \text{MgCl}_2(aq) \]

  (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)

\[
\text{eg) } \text{heat} + \text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})
\]

\[
\text{rate} = \frac{\Delta \text{mass of container & contents}}{\Delta \text{time}}
\]

Note: it’s **not practical** to measure masses of (aq) substances separately since they are mostly water.

\[
\text{eg) } \text{Ca}(\text{s}) + 2\text{HNO}_3(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{Ca(NO}_3)_2(\text{aq})
\]

\[
\frac{\Delta \text{mass of HNO}_3(\text{aq})}{\Delta \text{time}}
\]

6.) **Changes in molar concentration of specific ions**

\[
\text{eg) } \text{Mg}(\text{s}) + 2\text{HBr}(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{MgBr}_2(\text{aq})
\]

ionic form: \[
\text{Mg}(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{Br}^-(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{Mg}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq})
\]

- could monitor \([\text{H}^+]\) - it will __________crease

\[
\text{eg.) rate} = \frac{\Delta [\text{Mg}^{2+}]}{\Delta \text{time}} [\text{Mg}^{2+}] - \text{will __________crease}
\]

Note: Does the \([\text{Br}^-]\) change? ______________ Explain.

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

7.) **Changes in Acidity** \([\text{H}^+]\)

- special case of #6

\[
\text{rate} = \frac{\Delta [\text{H}^+]}{\Delta \text{time}}
\]

**pH** is a measure of **acidity**

\[
\begin{array}{c|c|c}
\text{pH} & 0 & 7 & 14 \\
\hline
\text{less acidic} & \text{less basic} & \text{more basic} & \text{more acidic}
\end{array}
\]
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if H⁺ is a reactant (or any acid HCl, HNO₃ etc.)

[H⁺] will decrease so pH will INCREASE!
(less acidic)

rate = \( \frac{\Delta \text{pH}}{\Delta \text{time}} \)  

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

- Do Hand-In Assignment on Reaction Rates

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

- Factors affecting reaction rates
- 2 kinds of reactions:

  **Homogeneous** reactions
  - all reactants are in the same phase
  (don’t consider products)

  eg.) \( 3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) \) 
  (both gases)
  \( \text{Ag}^+{}(\text{aq}) + \text{Cl}^-{}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) \)  
  (both \( \text{(aq)} \))

  **Heterogeneous** Reactions
  - more than one phase in reactants.

  eg.) \( \text{Zn}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{ZnCl}_2(\text{aq}) \)  
  (2 diff. phases)

  eg.) \( \text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \)  
  (2 diff. phases)

**Factors that affect both homogeneous & heterogeneous reactions**

1.) Temperature - as temperature increases, rate ________________

2.) Concentration of reactants
- as cons. of one or more reactants increases, rate ________________
  - also **partial pressure** 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.) \( \text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \)
  - as pressure increases, rate ________________

Note: a decrease in the **volume** of reaction container increases the **pressure** (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.

\[
\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g}) \quad (\text{slow at room temp})
\]

eg.) \[
\text{5C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 10\text{CO}_2 + 8\text{H}_2\text{O}
\]

Many bonds have to be broken and many new bonds have to form. So this reaction is **slow** at room temperature.

Eg.) \[
\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g}) \quad (\text{H}_2 \text{ and } \text{Cl}_2 \text{ are diatomic})
\]

\[\text{H} - \text{H} + \text{Cl} - \text{Cl} \quad \text{covalent bonds} \quad \text{slow at room temp.}\]

Consider Phase

\[\text{A}_{(s)} + \text{B}_{(s)} \rightarrow \text{AB} \quad \text{both solids} \quad \text{slow at room temp.}\]

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

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

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

  eg.) \( \text{NH}_4^+ + \text{SO}_3^{2-} \rightarrow \text{NH}_3 + \text{HSO}_3^- \)

- Do ex. 10 p.7 SW. Also, do this question:

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

  A. \( \text{Cu}_{(s)} + \text{S}_{(s)} \rightarrow \text{CuS}_{(s)} \)

  B. \( \text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} \)

  C. \( \text{Pb}^{2+}_{(aq)} + 2\text{Cl}^-_{(aq)} \rightarrow \text{PbCl}_2_{(s)} \)

  D. \( 2\text{NaOCl}_{(aq)} \rightarrow 2\text{NaCl}_{(aq)} + \text{O}_2(g) \)

5.) **Catalysts**
- a substance which can be added to increase the rate of a rx. without being consumed itself. (reactants are consumed)

Demo with \( \text{H}_2\text{O}_2 + \text{MnO}_2 \)

\[
2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \quad \text{uncatalyzed - slow}
\]

\[
2\text{H}_2\text{O}_2(l) \xrightarrow{\text{MnO}_2} 2\text{H}_2\text{O}(l) + \text{O}_2(g) \quad \text{catalyzed - fast}
\]

**Inhibitors**
- a substance which can be added to reduce 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
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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)

- do lycopodium powder demo

- In general
  - 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. \( \text{ppt } \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \rightarrow \text{AgCl(s)} \)

(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)

**Some points**

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 graphs 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

- **Industrial Processes**
  - 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

- **Rusting**
  - (oxidation) of cars etc.
  - paint, sealers, etc. prevents $O_2$ from contact with surface
  - keep cool & dry

- **Cooking**
  - improves taste
  - kills some bacteria
  - if too hot causes burning and productions of carcinogens
    (benzopyrenes)

- **Food preservation**
  - lower temperature
  - anti-oxidants (eg. ascorbic acid)
  - keep from $O_2$ (sealing)
  - preservatives (nitrates, nitrites) Think of more!
Collision theory

- explains rates on the molecular level [http://chem.salve.edu/chemistry/temp2a.asp](http://chem.salve.edu/chemistry/temp2a.asp)

Basic idea (basic premise) [http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/NO+O3singlerxn.html](http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/NO+O3singlerxn.html)

- before molecules can react, they must **collide**.

\[ \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} \]

How collision theory explains :

**Effect of concentration**

![Collision Diagram](image)

- 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)

**Effect of temperature**

- when molecules move faster \( \rightarrow \) more collisions per unit time \( \rightarrow \) 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)

\[ \text{Enthalpy (H)} \]

[Diagram showing ΔH with H2 and enthalpy change (ΔH) with H and O2]

Reaction Proceeds

Equations and heat

\[ \Delta H \text{ shown beside } \begin{cases} \text{H}_2 + S \rightarrow \text{H}_2\text{S} & \Delta H = -20 \text{ KJ} \quad (\text{-ive } \Delta H \text{ means exothermic}) \\
\text{6C} + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_6 & \Delta H = +83 \text{ KJ} \quad (\text{+ive } \Delta H \text{ means endothermic}) 
\end{cases} \]

Thermochemical equations:

(“Heat Term” is right in the equation. NO “ΔH” shown beside the equation!)

- “heat term” shown on left side of arrow - endothermic (“it uses up heat like a reactant”)

eg. \[ \text{CH}_3\text{OH} + 201\text{KJ} \rightarrow \text{C(s)} + 2\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \]

- “heat term” shown on right side of arrow - exothermic (“it gives off heat like a product”)

eg. \[ \text{S(g)} + \text{O}_2(g) \rightarrow \text{SO}_2(g) + 296 \text{kJ} \]

Read page 13-16 in SW. Do ex. 24-28 on page 16 of SW.
- now back to collision theory...


(- demo “glass beads” molecular model.)

- look at a graph of kinetic energy & the number of molecules with each KE

**reminder:** \[ KE = \frac{1}{2} \text{mv}^2 \] <- if mass is equal KE is proportional to velocity

-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…
**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**
- **Minimum** 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....
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 \( \Rightarrow \) therefore it is a slow reaction

if temp is increased ...

(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 $10^\circ C$ reaction rate will about **double**.

  (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 than $T_1$. 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)
Read p. 17-19 SW.  Do Ex. 29-32 on pages 19-20 SW.

**Activation energies**  

(back to collision theory.....)

**Potential and Kinetic energy during a collision**

- as colliding molecules approach the repulsion slows them down so kinetic energy decreases.
- as they push against the repulsive force potential energy increases (like compressing a spring)

- so:  \[
    \text{Kinetic Energy} \quad \text{is converted to} \quad \text{ Potential Energy}
\]

\[
    \text{KE} + \text{PE} = \text{Total E (stays constant)}
\]

if one goes down, the other goes up.

**Potential energy diagrams**

![Diagram of Potential Energy Changes](Image)

Potential Energy diagrams show the energy changes during a reaction. The diagram illustrates the conversion of kinetic energy to potential energy and vice versa as reactants form an activated complex, which then rearranges to form products. The progress of the reaction is depicted by the change in potential energy, with reactants (High KE, Low PE) transitioning to products (High KE, Low PE) through the formation of an unstable species, the activated complex.

- Molecules form a temporary, unstable species called the activated complex.
- As molecules approach each other, KE is converted to PE.
- Activated Complex rearranges to form the product molecules.
- Product molecules move apart and speed up, PE is converted to KE.
ACTIVATION ENERGY ($E_a$)  [http://chem.salve.edu/chemistry/temp2a.asp](http://chem.salve.edu/chemistry/temp2a.asp)

- The minimum energy required for a successful 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 $\Delta$temperature or $\Delta$ concentration!

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

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

**Now, at a Higher Temperature:**

At a higher Temperature ($T_2$), there are less molecules which don’t have enough KE for a successful collision.

At Temperature $T_2$ (higher temp.), there are more molecules which have sufficient energy for a successful collision.
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**):

![Diagram showing the effect of temperature on Reaction Kinetics]

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 **AH**!!

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**: 

Which reaction is faster? ________________ Explain why.

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

eg. for the rx.  \[ A_2 + B_2 \rightarrow 2AB: \]

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

In the above collision, the reactants have **favourable alignment**  
(less energy needed for an effective collision)
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** > $E_a$
3. they need to have **correct alignment** (collision geometry)
   (to keep $E_a$ as low as possible)

**Ea, $\Delta H$ and bond strengths for forward and reverse reactions**
Try this question:

Using the graph above, find:

\[ E_a \text{ (forward rx.)} = \underline{\text{\phantom{0}}\text{kJ}} \quad \Delta H \text{ (forward rx.)} = \underline{\text{\phantom{0}}\text{kJ}} \]

This forward reaction is ______thermic

-Considering reverse rx.,

\[ E_a \text{ (reverse rx.)} = \underline{\text{\phantom{0}}\text{kJ}} \quad \Delta H \text{ (reverse rx.)} = \underline{\text{\phantom{0}}\text{kJ}} \]

This reverse reaction is ______thermic
Given the following Potential Energy Diagram for the Reaction:

\[ A_2 + B_2 \rightarrow 2AB \]

a) \( \text{Ea (forward)} = \) ___________ KJ

b) Energy needed to break bonds in \( A_2 \) & \( B_2 \):

\( \text{Ea (reverse)} = \) ___________ 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.

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)

**Reaction Mechanisms**

“every long journey begins with a ______________________________”
-Car building analogy

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

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

even a 3 particle collision
$2H_2(g) + O_2(g) \rightarrow$
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 series 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: \(4\text{HBr} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2\)

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

**Mechanism** *(determined from lots of research)*

**Step 1**:

\[\text{HBr} + \text{O}_2 \rightarrow \text{HOBr}\]  (found to be slow) see p. 26 for AC & products

**Step 2**:

\[\text{HBr} + \text{HOBr} \rightarrow 2\text{HOBr}\]  (fast) see page 27 SW

**Step 3**:

\[\text{HOBr} + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}_2\]  (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 \([\text{HBr}]\) or \([\text{O}_2]\) 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 \(\text{HOOB}_{\text{r}}\) or \(\text{HOBr}\) 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 + O2 \rightarrow HOBr
2.) HBr + HOBr \rightarrow 2HOBr
3.) 2HBr + 2HOBr \rightarrow 2H_2O + 2Br_2

overall rx: 4HBr + O_2 \rightarrow 2H_2O + 2Br_2

eg.)

1.) A + 2X \rightarrow AX_2
2.) AX_2 + X \rightarrow AX + X_2
3.) AX + A \rightarrow A_2 + X

overall rx: ________________________________

Question
the following reaction occurs in a 3 step mechanism:

\[ 2A^{4+} + B^+ \rightarrow 2A^{3+} + B^{3+} \]

this is the overall reaction

step 1: A^{4+} + C^{2+} \rightarrow C^{3+} + A^{3+}
step 2: A^{4+} + C^{3+} \rightarrow C^{4+} + A^{3+}


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

\[ \text{Cl}_2 + \text{CHCl}_3 \rightarrow \text{HCl} + \text{CCl}_4 \]

The following is the proposed reaction mechanism:

Step 1: Cl_2 \rightarrow Cl + Cl

Step 2:

Step 3: Cl + CCl_3 \rightarrow 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) \( \text{HBr} + \text{O}_2 \rightarrow \text{HOOBr} \)
2) \( \text{HBr} + \text{HOBr} \rightarrow 2\text{HOBr} \)
3) \( 2\text{HBr} + 2\text{HOBr} \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2 \)

**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  Do ex. 46-53 p.28 of SW.

**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.

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. $E_a$ for overall rx = _______ kJ
3. Step ______ is the RDS  
4. Step ______ is the fastest step.
5. The overall rx. is _______ thermic  
6. $\Delta H =$ _______ kJ
7. $\Delta H$ for reverse rx. = _______ kJ  
8. $E_a$ (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 $\Delta H$ for the forward reaction.

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 introduced 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....
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…
Catalysts sometimes work by...

- 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.)** \[ 2 \text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \]  
(very slow uncatalyzed) 
- add some KI (I\(^-\))  
**Demonstration**

**Catalyzed Mechanism:**

1. step 1) \( \text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{O}_2\text{I}^- \) (The catalyst I\(^-\) is put in.)
2. step 2) \( \text{H}_2\text{O}_2 + \text{O}_2\text{I}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{I}^- \) (The catalyst I\(^-\) is regenerated.)

overall rx. \[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]
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