**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.) $\text{Zn(s) + 2HCl(aq) \rightarrow H}_2(g) + \text{ZnCl}_2(aq)$

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

$r = \frac{\Delta \text{volume } H_2}{\Delta \text{time}}$  

Suggested practice
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.  $\text{Mg(s) + 2HCl(aq) \rightarrow H}_2(g) + \text{MgCl}_2(aq)$

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)

[Cl$^-$] does not change as rx. proceeds (spectator ion)
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.) \( \frac{0.020 \text{ mol}}{\text{min.}} = ? \text{ mol} \frac{\text{min}}{\text{s}} \)

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

You also must use molar mass to go grams \( \Leftrightarrow \) moles.

Eg.) \( \frac{0.26 \text{ mol Zn}}{\text{min}} = ? \text{ g of Zn} \frac{\text{min}}{\text{s}} \)

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

You would use \( \frac{22.4 \text{ L}}{1 \text{ mol}} \) for conversions \( \text{moles} \Leftrightarrow \text{L (STP)} \) for gases.

Eg.) \( \frac{0.030 \text{ mol O}_2}{\text{s}} = \text{_____ L/s (STP)} \)

Solution: \( \frac{0.030 \text{ mol O}_2}{1 \text{ s}} \times \frac{22.4 \text{ L}}{1 \text{ mol}} = 0.67 \text{ L O}_2 \frac{\text{s}}{\text{s}} \)

(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!
Comparing rates using balanced equations

- use **coefficient ratios** - only proportional to \( \text{mol}/s \) (not to g/s)

  eg.) ethane

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

  consumed

  produced

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

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

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

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

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

  \( \text{you may go from L} \rightarrow \text{L of one gas to another at STP} \)

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

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

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

  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!

Measuring Reaction Rates

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

eg. \( \text{CaCO}_3(s) + 2\text{HCl(aq)} \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) + \text{CaCl}_2(aq) \)

\[
\text{CO}_2 \text{ gas is escaping}
\]

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: \[ \text{CaCO}_3(s) + 2\text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) + \text{Ca}^{2+}(\text{aq}) \]

- as \( \text{CO}_2 \) escapes, **mass** of the rest of the system will ______________________________

- so rate could be expressed as...

\[
\text{rate} = \frac{\Delta \text{mass of container and contents}}{\Delta \text{time}} \quad \text{(open system)}
\]

**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 \( \Delta \text{amount}/\Delta \text{time} \) )

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

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

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

eg.) \( \text{Cu(s) + 4HNO}_3(aq) \rightarrow \text{Cu(NO}_3)_2(aq) + 2\text{H}_2\text{O}(l) + 2\text{NO}_2(g) + \text{heat} \)

- in this case could measure - intensity of blue
  - intensity of brown gas

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

- 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**

eg. of rate equation

\[ \text{rate} = \frac{\Delta \text{ colour intensity}}{\Delta \text{ time}} \]
2.) **Temp changes**

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

3.) **Pressure changes** (constant volume or sealed container)

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

\[
\text{Zn(s) + } 2\text{HCl(aq) } \rightarrow \text{H}_2(\text{g}) + \text{ZnCl}_2(\text{aq}) \\
\text{O m.o.g. } \quad 1 \text{ m.o.g.}
\]

- If more MOG in reactants - pressure will decrease

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

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

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

4.) **Volume change** (constant pressure eg. balloon or manometer)

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

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

5.) **Mass changes**

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

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

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

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

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

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

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

not acceptable

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

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

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

- could monitor [H⁺] - it will decrease

eg.) rate = Δ[Mg²⁺]  

[ Mg²⁺] - will increase

Note: Does the [Br⁻] change? Why?

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

7.) **Changes in Acidity**  

[H⁺]

- special case of #6

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

pH is a measure of acidity

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

$$[H^+] \text{ will decrease so pH will INCREASE!}$$

(less acidic)

rate = $\frac{\Delta \text{pH}}{\Delta \text{time}}$

- **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)

  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(s)$
      (both \text{(aq)})

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

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

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

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

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

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

   Note: a **decrease in the volume** of reaction container increases the pressure (therefore rate)

4.) **Nature of reactant**
   - rate depends on **how strong & how many bonds** in reactants need to be broken.
Chemistry 12—Unit 1-Reaction Kinetics—Notes

in general **covalent bonds** are **strong** and **slow** to break.

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

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

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

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

Eg.) \[ \text{Sn}^{2+} + \text{Te}^{4+} \rightarrow \text{Sn}^{4+} + \text{Te}^{2+} \]  
*2 electrons have been transferred from Sn\^{2+} to Te\^{4+}*

- **precipitation** reactions:
  \[ \text{Fe}^{2+}\text{(aq)} + \text{S}^{2-}\text{(aq)} \rightarrow \text{FeS}(\text{s}) \]  
*both reactants (aq)* - no bonds to break.

**-acid base** (proton transfers)
- intermediate in rate

Eg.) \[ \text{NH}_4^+ + \text{SO}_3^{2-} \rightarrow \text{NH}_3 + \text{HSO}_3^- \]
Example question from Provincial

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

Answer is A

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

\[
\begin{align*}
2\text{H}_2\text{O}_2(l) & \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) & \text{uncatalyzed - slow} \\
2\text{H}_2\text{O}_2(l) & \xrightarrow{\text{MnO}_2} 2\text{H}_2\text{O}(l) + \text{O}_2(g) & \text{catalyzed - fast}
\end{align*}
\]

**Inhibitors**
- a substance which can be added to reduce the rate of a reaction.
- 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)

- 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. pptn $\text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \rightarrow \text{AgCl}(s)$

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

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.

**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 $\text{O}_2$ important
    - to **increase** combustion rate - increase [ $\text{O}_2$ ]
    - increase surface area
- increase temperature
- catalyst (wood stoves etc)

- to decrease combustion rate
- water on fire  -smothers it (decreases O₂)
  - 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 O₂ 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 O₂ (sealing)
- preservatives (nitrates, nitrites) Think of more!
Collision theory

- explains rates on the molecular level

**Basic idea (basic premise)**
- before molecules can react, they must **collide**.

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

How collision theory explains:

**Effect of concentration**

<table>
<thead>
<tr>
<th>Low concentration both</th>
<th>High concentration blue</th>
<th>High concentration both</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low chance of collision</td>
<td>Higher chance of collision</td>
<td>Very high chance of collision</td>
</tr>
<tr>
<td>(slow reaction)</td>
<td>(faster reaction)</td>
<td>(much faster reaction)</td>
</tr>
</tbody>
</table>
**Effect of temperature**
- when molecules move faster → more collisions per unit time → faster rate
- also - when they move faster they collide with more kinetic energy. (hit harder)

**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)

- Heat is released to surroundings. Exothermic ΔH is negative (-)
- Heat is absorbed from the surroundings. Endothermic ΔH is positive (+)

**Equations and heat**

ΔH shown beside:
- \( H_2 + S \rightarrow H_2S \) \( \Delta H = -20 \text{ KJ} \) ( -ive ΔH means exothermic)
- \( 6C + 3H_2 \rightarrow C_6H_6 \) \( \Delta H = +83 \text{ KJ} \) ( +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 - endothermic (“it uses up heat like a reactant”)

  eg. \( \text{CH}_3\text{OH} + 201\text{KJ} \rightarrow \text{C}_8\text{(s)} + 2\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \)

- “heat term” shown on right side of arrow - exothermic (“it gives off heat like a product”)
eg. \( S(g) + O_2(g) \rightarrow SO_2(g) + 296 \text{ kJ} \)

- now back to collision theory...

**Kinetic energy distributions**

- 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

- 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 → 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 1/5th to 1/6th of the molecules have sufficient KE. 
*(the shaded region is about 1/5th to 1/6th the total area under the “Temperature T₂ curve)*

**Rule of thumb**

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

- **if the temperature is increased by 10ºC 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 $10\degree C$ 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 $E_a$ is a lot lower (NOT near the “tail” of the curve)
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: Kinetic Energy is converted to Potential Energy

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

if one goes down, the other goes up.

**Potential energy diagrams**

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.
ACTIVATION ENERGY ($E_a$)

- 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 Δtemperature or Δconcentration!

Temperature’s role
- the temperature determines how many (or what fraction of the) molecules will have energy ≥ 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):

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!!
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. $A_2 + B_2 \rightarrow 2AB$:

- **Unfavourable alignment** (need higher energy for collision to be effective)
- **Favourable alignment** (less energy needed for an effective collision)

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** \( > \text{E}_\text{a} \)
3.) - they need to have **correct alignment** (collision geometry)
   (to keep \( \text{E}_\text{a} \) as low as possible)

**\( \text{E}_\text{a} \), \( \Delta \text{H} \) and bond strengths for forward and reverse reactions**
Try this question: Answers at end of notes

Using the graph above, find:

$E_a$ (forward rx.) = _______ kJ \hspace{1cm} \Delta H$ (forward rx.) = _______ kJ

This forward reaction is _____ thermic

- Considering reverse rx.

$E_a$ (reverse rx.) = _______ kJ \hspace{1cm} \Delta H$ (reverse rx.) = _______ 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 \( A_2 \) & \( B_2 \)
  - A-A   B-B  ___________ KJ
- **c)** \( \text{Ea (reverse)} = \) ___________ 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.
Reaction Mechanisms

“every long journey begins with a single step”
-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) Diagrams

step 1: \[ \text{HBr} + \text{O}_2 \rightarrow \text{HOOBr} \] (found to be slow)
step 2: \[ \text{HBr} + \text{HOOBr} \rightarrow 2\text{HOBr} \] (fast)
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 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.) \[ \text{HBr} + \text{O}_2 \rightarrow \text{HOOBr} \]
2.) \[ \text{HBr} + \text{HOOBr} \rightarrow 2\text{HOBr} \]
3.) \[ 2\text{HBr} + 2\text{HOBr} \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2 \]

overall rx: \[ 4\text{HBr} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2 \]

eg.) 1.) \[ \text{A} + 2\text{X} \rightarrow \text{AX}_2 \]
2.) \[ \text{AX}_2 + \text{X} \rightarrow \text{AX} + \text{X}_2 \]
3.) \[ \text{AX} + \text{A} \rightarrow \text{A}_2 + \text{X} \]
overall rx: ______2A + 2X \rightarrow A_2 + X_2

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: \( \text{Cl}_2 \rightarrow \text{Cl} + \text{Cl} \)

Step 2:

Step 3: Cl + CCl3 \( \rightarrow \) CCl4

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

Step 2: ______Cl + CHCl3 \( \rightarrow \) HCl + CCl3

**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) \( \text{HBr} + \text{HOOBr} \rightarrow 2\text{HOBr} \)
3) \( 2\text{HBr} + 2\text{HOBr} \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2 \)

**Intermediates** are \( \text{HOOBr} \) & \( 2\text{HOBr} \)

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”.
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. Ea 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. Ea (reverse rx.) = ______ kJ  
9. RDS for reverse rx. is step ____________________________  

**How catalysts work**  
- “to avoid a hill, build a tunnel“  

**Catalyst**- an introduced substance which produce an alternate mechanism with a lower activation energy.  

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 (e.g., lower standards for a pass, e.g., 30% will let more students pass!)

- Catalyzed reactions usually involve more steps but its 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\(^-\))

Catalyzed Mechanism:

\[
\begin{align*}
\text{step 1) } & \text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{O}^- \text{I}^- \quad \text{(The catalyst I}^-\text{ is put in.)} \\
\text{step 2) } & \text{H}_2\text{O}_2 + \text{O}^- \text{I}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{I}^- \quad \text{(The catalyst I}^-\text{ is regenerated.)}
\end{align*}
\]

overall rx. \( 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \)
Answers:

a) \( \text{Ea (forward)} = 20 \text{ KJ} \)

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

\[
\begin{array}{cc}
\text{A-A} & \text{B-B} \\
\end{array}
\]

\( \equiv 20 \text{ KJ} \)

c) \( \text{Ea (reverse)} = 40 \text{ KJ} \)

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

\( \equiv 40 \text{ KJ} \)

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

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

(low/high) Lower on the graph

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

\( A_2B_2 \). This species is the most unstable. It is called the activated complex

h) Which set of species has the highest PE? \( A_2B_2 \)

i) Which set of species has the highest KE? \( AB \)

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

It will be the inverse graph

1. This mechanism has \( 3 \) steps

2. Ea for overall rx. = \( 30 \text{ KJ} \)

3. Step \( 2 \) is the RDS

4. Step \( 3 \) is the fastest step.

5. The overall rx. is \( \text{exo thermic} \)

6. \( \Delta H = +19 \text{ KJ} \)

7. \( \Delta H \) for reverse rx. = \( -19 \text{ KJ} \)

8. Ea (reverse rx.) = \( +11 \text{ KJ} \)

9. RDS for reverse rx. is step \( 2 \)