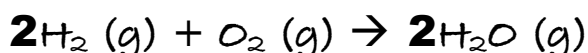## 6.4 and 6.5 FACTORS AFFECTING REACTION RATES

Homogeneous reactions are chemical **reactions** in which all chemical species are in the same phase.
(all reactants and products are gases,
all reactants and products are aqueous solutions,
all reactants and products are solids, etc.)
example:

$2H_2$ (g) + O_2 (g) → $2H_2O$ (g)

Heterogeneous reactions have reactants in two or more phases.
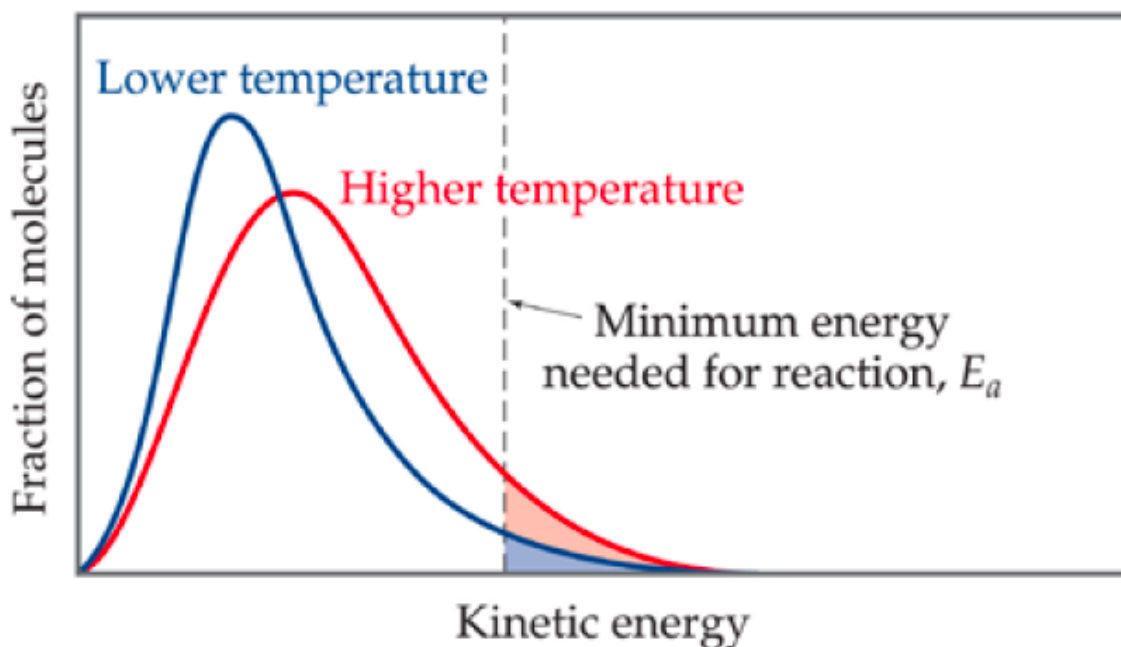example:

Mg (s) + $2HCl$ (aq) → $MgCl_2$ (aq) + H_2 (g)

Factors Affecting the Rate of a Homogenous or Heterogeneous Reaction:

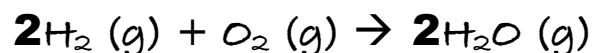1. Temperature

Maxwell-Boltzmann Distribution Curve:

The two areas are the same because the number of particles doesn't change.

6.4 and 6.5 FACTORS AFFECTING REACTION RATES

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==Factors Affecting the Rate of a Homogenous or Heterogeneous Reaction:==

1. Temperature

Maxwell-Boltzmann Distribution Curve:

6.4 and 6.5 FACTORS AFFECTING REACTION RATES

1. Temperature   *Maxwell - Boltzmann Distribution Curve:*

E_a = activation energy barrier

- The minimum amount of KE which a molecule must possess in order to react.

- i.e. the minimum increase in PE (conversion of KE) during the collision of reactant particles necessary to initiate a reaction

- or create an "activated complex";

- hence it acts as a barrier to the reaction

eg. *shaded area of curve:* **at T_1** only the moles in the **blue shaded area   have enough energy to successfully react**

-**However at T_2** both the **blue shaded area** and the **red shaded area** *have particles with sufficient KE to successfully react*

- Therefore at the higher temperature, there are more particles with the energy necessary to overcome the activation energy barrier and react

- These are called "effective collisions" i.e. when two particles collide and go on to form a product or products

- higher temp == faster particles = more KE = harder collisions = faster rate!

**If two particles collide but just bounce off one another, this is an ineffective collision and does not lead to a reaction, (therefore they did not have sufficient KE).
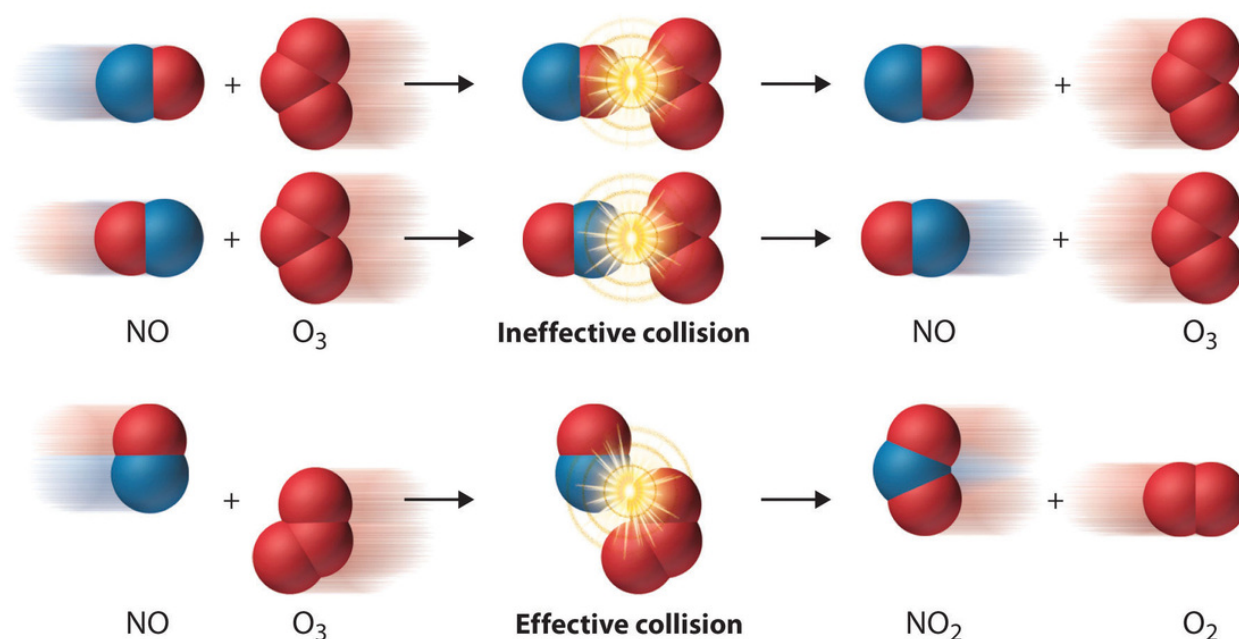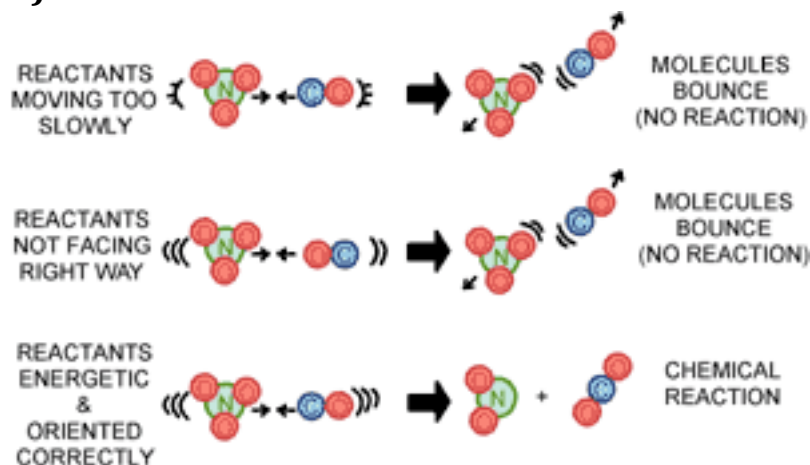
Collision Theory:
Chemical reactions occur due to collisions of the reacting particles
The rate of a reaction is proportional to the number of collisions.

Very few collisions result in reactions because of these two necessary conditions:

1) the orientation of particles

NO O_3 **Ineffective collision**   NO O_3

NO O_3 **Ineffective collision**   NO O_3

NO O_3 **Effective collision** NO_2 O_2

2) must have a certain minimum threshold KE called E_a

REACTANTS MOVING TOO SLOWLY   MOLECULES BOUNCE (NO REACTION)

REACTANTS NOT FACING RIGHT WAY   MOLECULES BOUNCE (NO REACTION)

REACTANTS ENERGETIC & ORIENTED CORRECTLY   CHEMICAL REACTION

Q10 rule

The Q_{10} **temperature coefficient** is a measure of the rate of change of a biological or chemical system as a consequence of increasing the temperature by 10 °C.

$$Q_{10} = \left(\frac{R_2}{R_1} \right)^{\left(\frac{10}{T_2 - T_1} \right)}$$

As a very general rule:

The rate of a reaction doubles for each 10°C rise in temperature.

Transition State Theory

When molecules collide they slow down, stop, & fly apart again.
Therefore, because of Cons. of Energy, KE is converted to PE at the time of collision.

Transition state theory describes a hypothetical transition state that exists between reactants and products during a chemical reaction. The species formed in this hypothetical transition state is called the activated complex. This theory is used to explain how chemical reactions take place. If the rate constant has been experimentally determined, the theory can also be used to determine the standard Gibbs free energy, enthalpy and entropy of the reaction. It is closely related to Collision Theory.

According to TST, between the state where molecules are reactants and the state where molecules are products, there is a state known as the transition state. In the transition state, the reactants are combined in a species called the activated complex. The theory suggests that there are three major factors that determine whether a reaction will occur:

1. The concentration of the activated complex
2. The rate at which the activated complex breaks apart
3. The way in which the activated complex breaks apart: whether it breaks apart to reform the reactants or whether it breaks apart to form a new complex, the products.

Collision theory proposes that not all reactants that combine undergo a reaction. However, assuming the stipulations of the collision theory are met and a successful collision occurs between the molecules, transition state theory allows one of two outcomes: a return to the reactants, or a rearranging of bonds to form the products.

ACTIVATION ENERGY: (PE DIAGRAM)

- an artistic representation of the change in stored energy (converted from KE) as the reaction proceeds.

ACTIVATED COMPLEX:

is a transitory, unstable, high PE intermediate in the rxn process.
-it is the turning point at which A + B is forming C + D

Therefore E_a is the minimum amount of energy that the colliding species must have to form the activated complex.
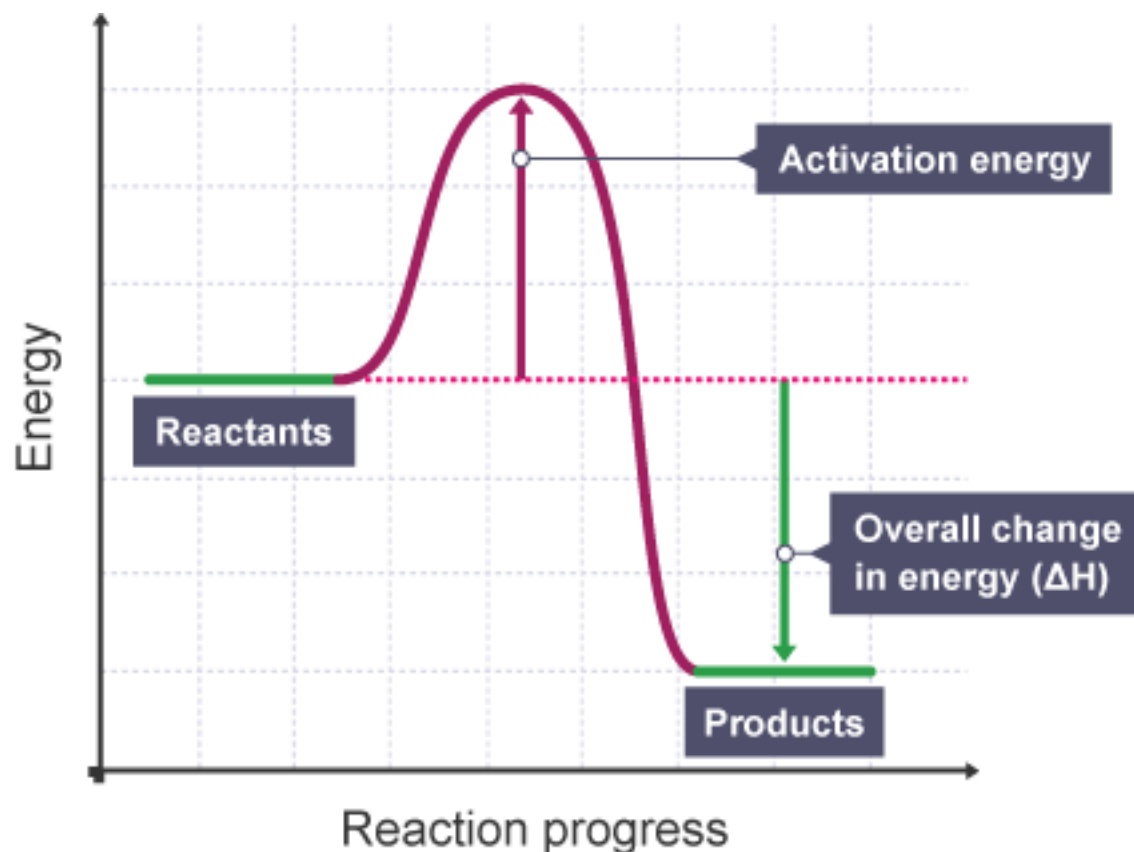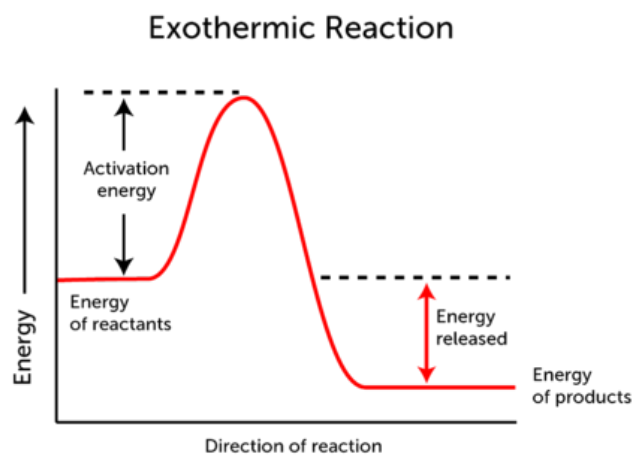
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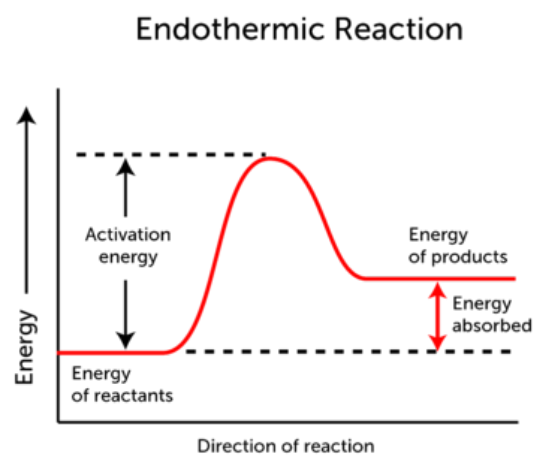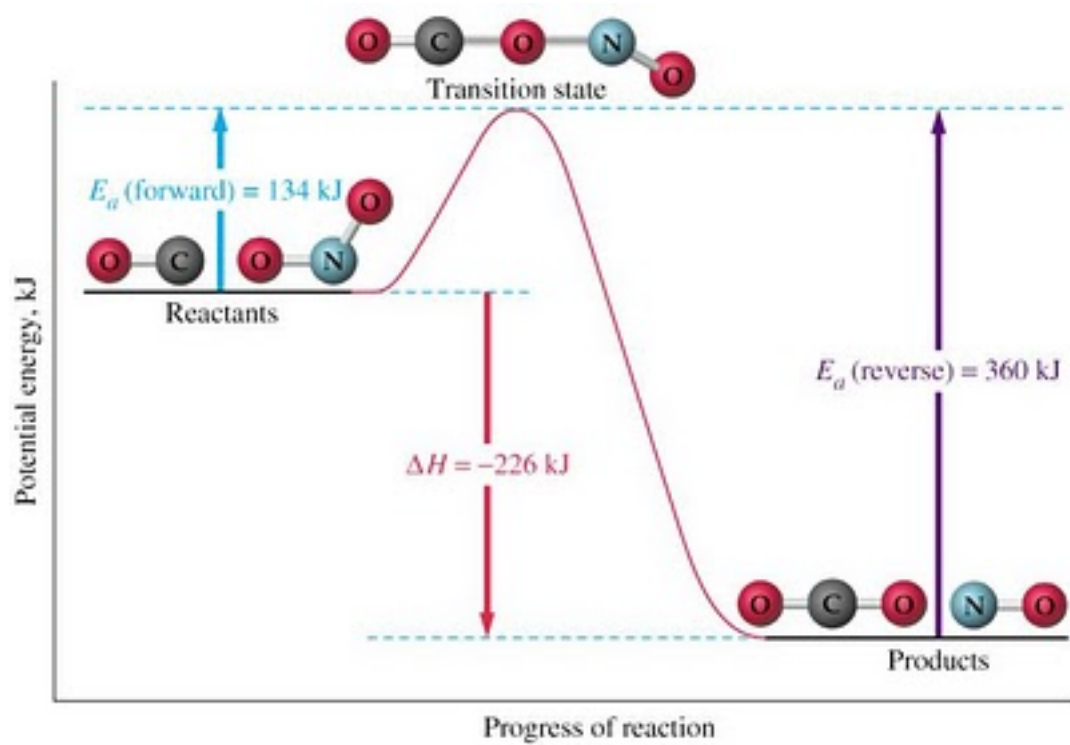
ACTIVATED COMPLEX:

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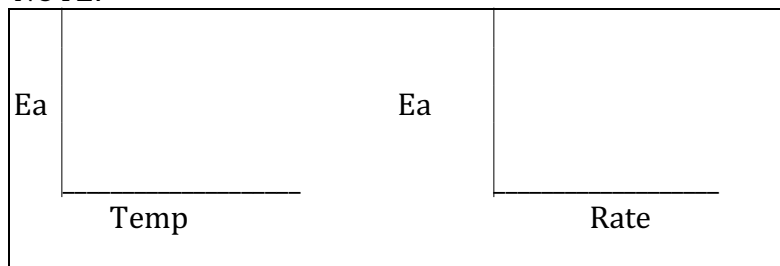-it is the turning point at which A + B is forming C + D

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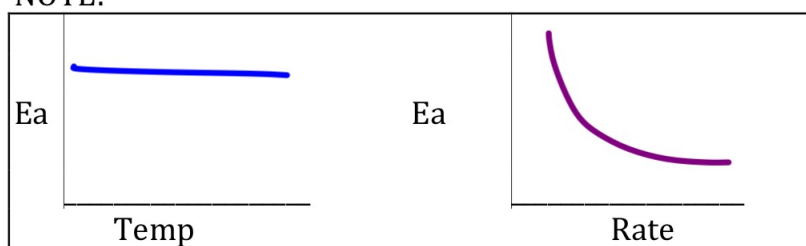
Transition state

E_a (forward) = 134 kJ

Reactants

E_a (reverse) = 360 kJ

$\Delta H = -226$ kJ

Potential energy, kJ

Products

Progress of reaction

Endothermic Reaction

Energy

Activation
energy

Energy
of products

Energy
absorbed

Energy
of reactants

Direction of reaction

Exothermic Reaction

Energy

Activation
energy

Energy
of reactants

Energy
released

Energy
of products

Direction of reaction

Can you draw a graph representing each of the following?

NOTE:

| Ea		Ea	
Temp		Rate	

CONSIDER THE FOLLOWING:

NOTE:

Ea is a contant value;
As temp increases, all that changes is that the number of molecules that are moving at sufficient KE to effectively collide, is now a greater number of molecules at the higher temps.

There may be many graphs that we could draw to relate Ea to Rate. This is one correct relationship. To explain, we see that this graph is saying that reactions with a high Ea value will have a very low rate, and reactions with a very low Ea value will have a very high rate.
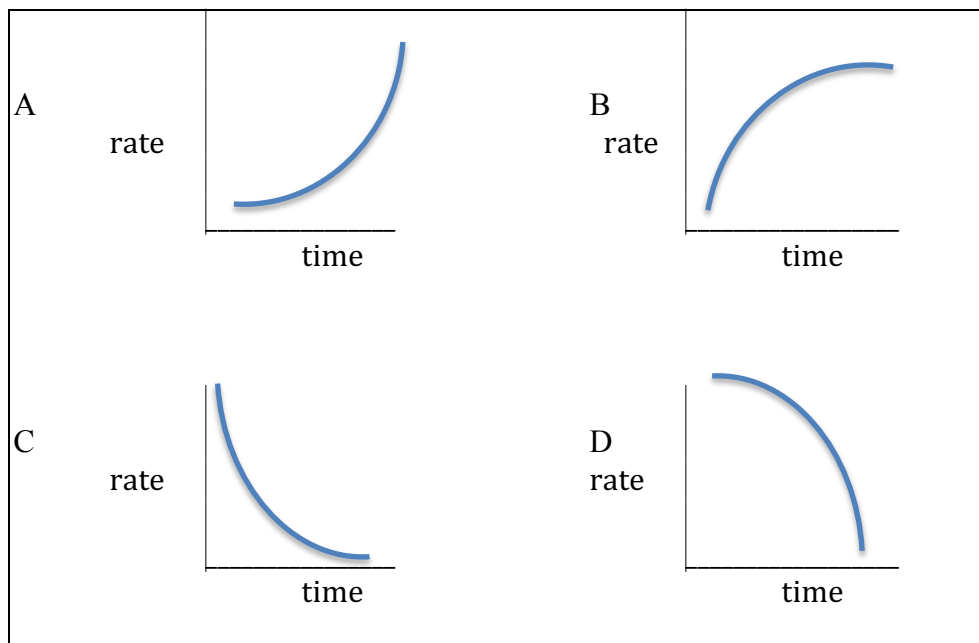
CONSIDER:

A [reactant]	B [reactant]
time	time
C [product]	D [product]
time	time
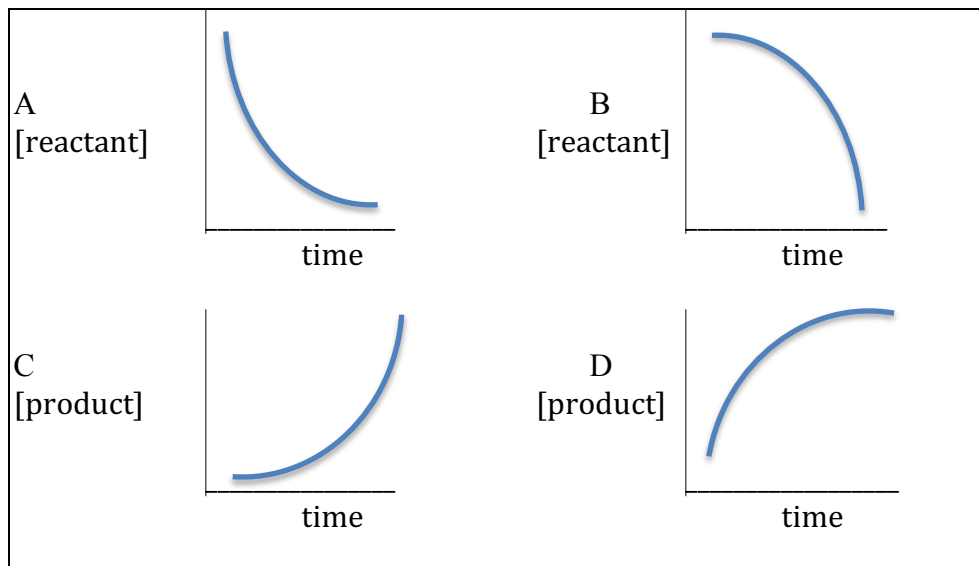
WHICH GRAPH (above) BEST REPRESENTS:

i) product concentration vs. time   ii) reactant concentration vs. time

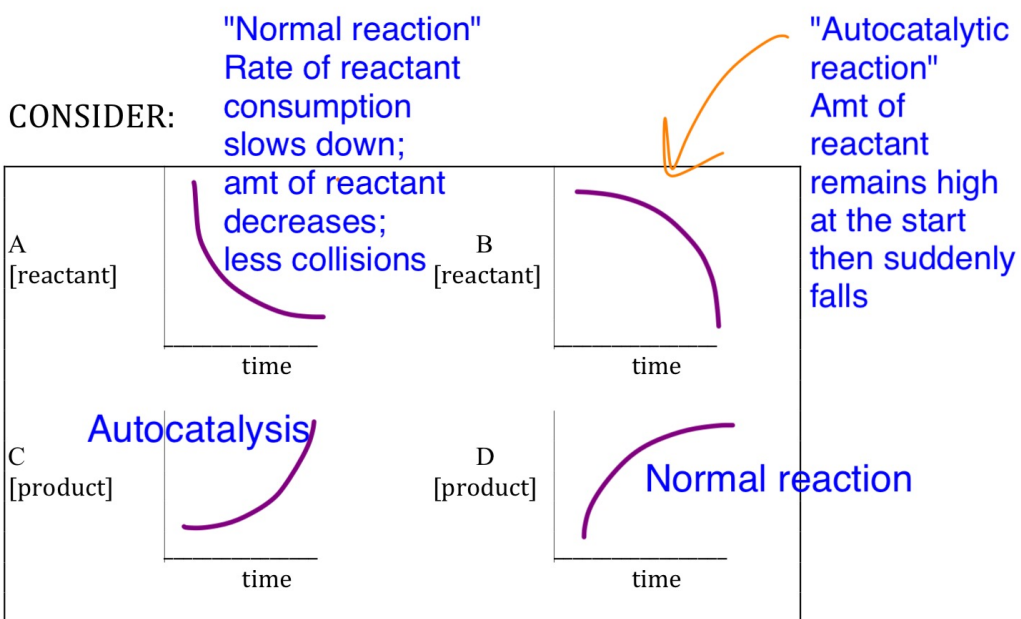|	
A rate	B rate
time	time
C rate	D rate
time	time

WHICH GRAPH (above) BEST REPRESENTS:

i) rate of reactants used vs. time   ii)   rate of products produced vs. time

CONSIDER:

"Normal reaction"
Rate of reactant consumption slows down; amt of reactant decreases; less collisions

"Autocatalytic reaction"
Amt of reactant remains high at the start then suddenly falls

A [reactant]
time

B [reactant]
time

Autocatalysis
C [product]
time

D [product]
Normal reaction
time

WHICH GRAPH (above) BEST REPRESENTS:
i) product concentration vs. time   **D**   ii) reactant concentration vs. time   **A**

A rate
time

B rate
time

C rate
time

D rate
time
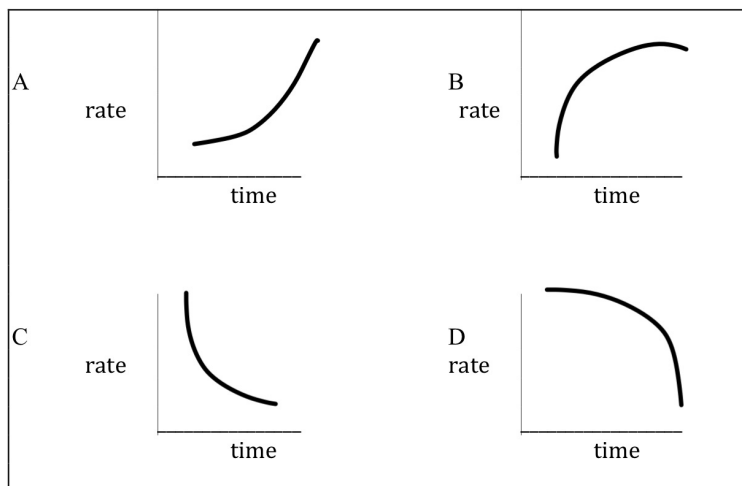
WHICH GRAPH (above) BEST REPRESENTS:
i) rate of reactants used vs. time   **C**   ii) rate of products produced vs. time   **C**

Because the rate of reactants used up is EQUAL to or PROPORTIONAL to the rate of products produced. Think of our Mg/HCl lab!!

FACTORS AFFECTING REACTION RATES continued

2. Concentration of Reactants

The rate of a reaction is directly proportional to the concentration of the reactants.
As the concentration of the reactants increases there will be more "effective collisions" between reactant molecules per unit of time.

Consider the Chemical reaction: **A + B → C**

$v \propto [A]^x$ [A] = concentration of A in moles per litre
where v = velocity or rate of a reaction measured in moles / L / s

i.e.   v   is $\dfrac{concentration}{time}$ = $\dfrac{moles / L}{s}$

also $v \propto [B]^y$

                                                            x and y are exponents which must be found experimentally

therefore $v \propto [A]^x[B]^y$

$v = k [A]^x[B]^y$ this is the rate equation for the reaction A + B → C

The concentration of the reactants can be increased by
either adding more of the reactants **per unit volume**
(i.e. you can't just put more reactants in; you must put proportionally more moles of the reactant in the total volume of the reaction).
or decreasing the size of the container
- which applies to reactions in the gaseous phase.

For gases, pressure is the same as concentration:
$PV = nRT$
$\dfrac{n}{V} = \dfrac{moles}{L} = concentration$

$\dfrac{n}{V} = \dfrac{P}{RT}$ *at constant temperature, R and T are constant*

therefore $\dfrac{n}{V} \propto P$ (at constant T)

                                    This is a GOOD TIME TO DO the IODINE CLOCK REACTION

3. Nature of Reactants

i.e. the chemical properties of the substance
(not the physical properties such as solid, liquid or gas)
for example, the bonding (double vs. single vs. triple - or in other words saturated vs. unsaturated), the molecule geometry, the available electrons, etc.

In general the greater the number of bonds which must be broken in a collision between two molecules, the higher is the activation energy barrier.

Recall the breaking of bonds requires energy. The larger and more complex the reactant molecules are, the slower the reaction because few molecules will possess sufficient KE to overcome E_a.
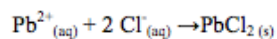Monatomic species usually react much more rapidly than polyatomic species. (polyatomic reacts slower because many more bonds to break)
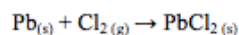
Eg.

Factors Influencing Reaction Rate - Nature of Reactants

1. Which one of the following reactions would you expect to be fastest at room temperature and why?
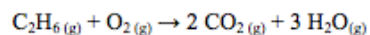
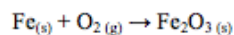|	SOLUTION
$Pb^{2+}_{(aq)} + 2\ Cl^{-}_{(aq)} \rightarrow PbCl_{2\ (s)}$	fastest - ions in aqueous solution react very quickly; all are in the same phase
$Pb_{(s)} + Cl_{2\ (g)} \rightarrow PbCl_{2\ (s)}$	slower - one of the reactants is a solid

2. Consider the following reactions. Which do you predict will occur most rapidly at room conditions? Slowest?
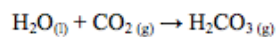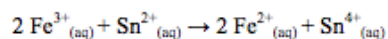
	SOLUTION
$C_2H_{6\ (g)} + O_{2\ (g)} \rightarrow 2\ CO_{2\ (g)} + 3\ H_2O_{(g)}$	slow due to covalent bonding (unless the reaction is highly exothermic)
$Fe_{(s)} + O_{2\ (g)} \rightarrow Fe_2O_{3\ (s)}$	slowest - solid reactant (Fe); this reaction describes the rusting of iron
$H_2O_{(l)} + CO_{2\ (g)} \rightarrow H_2CO_{3\ (g)}$	slow due to covalent bonding
$2\ Fe^{3+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2\ Fe^{2+}_{(aq)} + Sn^{4+}_{(aq)}$	fastest - ions in solution react very quickly

4. Catalyst

A substance which: speeds up a chemical reaction but remains unchanged at the end of the reaction.

A catalyst is thought to: lower the activation energy barrier by providing an alternative reaction pathway or a more favourable collision geometry. (more favourable collisions = faster rate)

In Biology, it is called an enzyme. In Chemistry, it is called a catalyst.
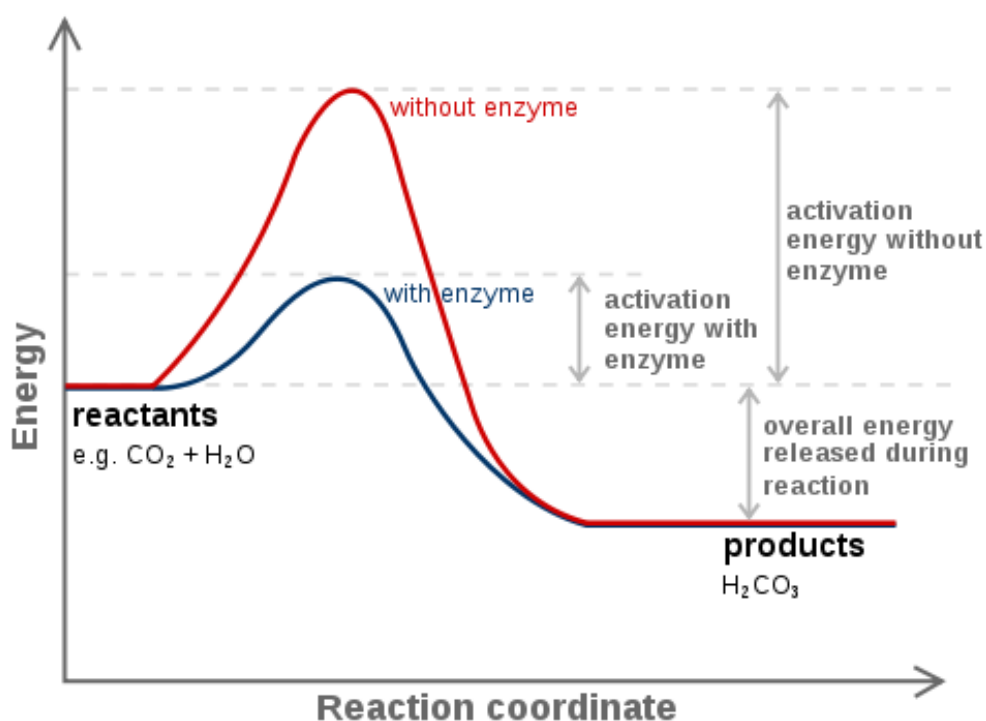
If E_a is lowered then: the number of molecules present of A and B with sufficient KE to collide effectively and overcome the activation energy barrier is increased. Therefore the rate of the reaction increases.

INHIBITORS: Chemicals which slow or retard the reaction rate without being consumed themselves
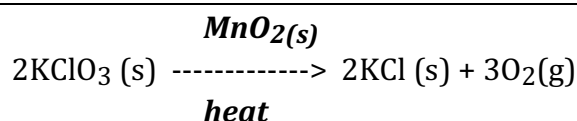eg.   food preservatives   medicine   fire retardants on clothing

Many different types of catalysts:

a) <u>IONS</u>   eg. Mn^{+2} in the reaction of MnO_4^- with Fe^{+2}

The Mn^{+2} ion makes this reaction go faster

b) <u>MOLECULES</u> eg. MnO_2 in making $O_2(g)$ out of $KClO_3(s)$

$MnO_{2(s)}$ $2KClO_3$ (s) ------------> $2KCl$ (s) + $3O_2(g)$ *heat*

c) <u>ACIDS</u>   (H^+ or H_3O^+)
Acid decomposition of formic acid
$HCOOH$ (l) ⇌ CO (g) + H_2O (l)   this is a slow reaction
Adding an acid (i.e. a hydrogen ion) speeds up the reaction

Proposal mechanism: (3 step mechanism)

$HCOOH + H^+ \rightleftharpoons$	$HCOOH_2^+$
$HCOOH_2^+$ ⇌	$HCO^+ + H_2O$ (l)
HCO^+ ⇌	$H^+ + CO$ (g)
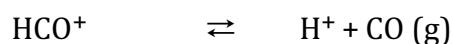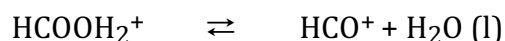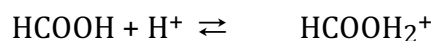
d) <u>ENZYMES (proteins)</u> large protein molecules found in all living organisms
            -proteins are long chains of amino acids
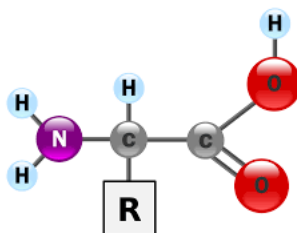
NH_2   amino group   **COOH**   carboxyl group
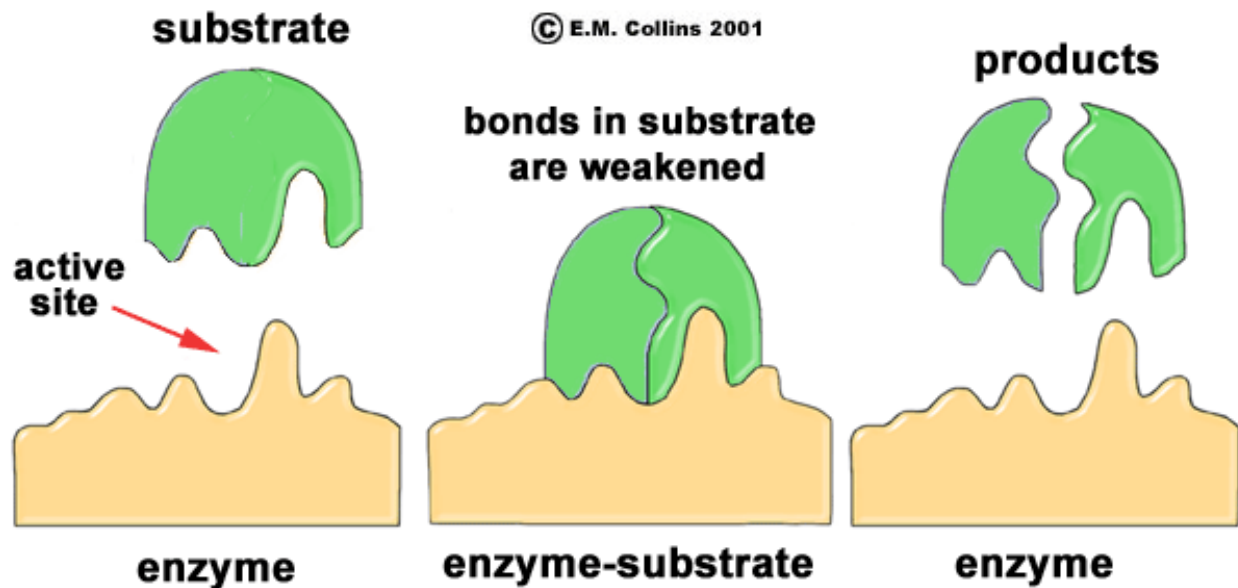   *R* changes from one amino acid to another

Your body needs 20 **different amino acids** to grow and function properly.
Though all 20 of these are important for your health, only nine **amino acids** are
classified as essential. These are histidine, isoleucine, leucine, lysine, methionine,
phenylalanine, threonine, tryptophan and valine.

Enzymes have an active site:

substrate

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bonds in substrate
are weakened

products

active
site

enzyme   enzyme-substrate   enzyme

An enzyme speeds up a reaction by lowering the E_a for both the forward and reverse reactions.

Each enzyme has a specific active site, therefore only one substrate molecule can fit into the active site, therefore each different reaction will have a different specific enzyme.

FACTORS AFFECTING REACTION RATES continued

for Heterogeneous reactions, add :

5. Surface Area

Therefore more collisions per unit of time between the reacting molecules.

FASTEST --->SLOWEST

Aqueous	>	gas	>	solids
Ions in		or		
solution		liquids		

6. Agitation (stirring)

increased KE	=	more particles	=	increased	=	increased rate
(eg. ultrasound		brought into		possibility		
stirring		contact			of reaction		
device)						