

Chemistry 12

Unit I – Reaction Kinetics

Notes

I.1 - Introduction:

- Reaction kinetics is the study of rates (speeds) of chemical reactions and factors which affect the rates.
- Rates of reaction are usually expressed in terms of a concentration change per unit of time.
- The speed at which a reaction occurs is called the rate of reaction. We can express the rate of a reaction in terms of the amount of a reactant consumed or amount of a product formed per unit of time

$$\text{Reaction Rate} = \frac{\text{amount of product formed}}{\text{time interval}}$$

or

$$= \frac{\text{amount of reactant used}}{\text{time interval}}$$

or, basically

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

(where Δ means “change in”)

Example: (August 2005)

Which of the following could **not** be units for reaction rate?

- A. sec^{-1}
- B. g/mL
- C. M/min
- D. $^{\circ}\text{C/hour}$

*****You will also need to be able to calculate the rate given the data.*****

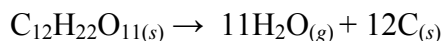
Examples:

1. If 16.0g of HCl are used up after 10 min in a certain reaction, calculate the average rate of the reaction.

2. (January 2002)

Consider the following reaction:

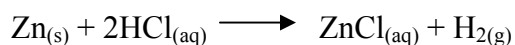
(3 marks)



The rate of decomposition of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is 0.75mol/min. What mass of C is produced in 10.0 seconds? (Ans: 18 g)

3. 3.01 g/s of Iron is reacted with excess Cl_2 to produce Iron (III) chloride. Find the rate of Cl_2 used in g/min. (Ans: 3.44×10^2 g Cl_2 /min)

4. What is the rate of reaction (g/s) for the Zn in the following problem? (Ans: 1×10^1 g/s)



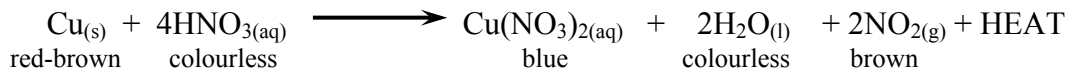
<u>Mass (g)</u>	<u>Time (s)</u>
230	0
228	5
226	10
224	15
222	20

- The rate of a reaction can be calculated from a graph. Graph must be of the form “amount” vs. time (e.g. temp vs. time, mass vs. time, mol/time etc.). *The rate of the reaction is equal to the slope of the graph.*

*****Do Hebden Questions #1 - 6, pgs 2 - 3*****

I.2 - Methods of Measuring Reaction Rates:

- In order to illustrate the methods used to determine the rate of a reaction, we will consider a specific reaction, the reaction of copper metal with nitric acid.



To determine the rate of the above reaction, we could measure at least five different physical properties:

a) **Color changes**

The $\text{Cu}(\text{NO}_3)_2$ has a characteristic blue color. The intensity of the blue color could be measured in a spectrophotometer.

$$\text{Rate} = \frac{\Delta(\text{color intensity})}{\Delta \text{time}}$$

b) **Temperature changes**

Since the reaction is producing heat, we could perform the reaction in a CALORIMETER and measure and graph the temperature changes.

$$\text{Rate} = \frac{\Delta(\text{temperature changes})}{\Delta \text{time}}$$

c) **Mass changes**

Since copper metal is the only solid present in the reaction, we could measure the rate at which the copper is used up by measuring its change in mass.

$$\text{Rate} = \frac{\Delta(\text{mass})}{\Delta \text{time}}$$

d) **Acidity changes**

Since the reaction uses up nitric acid, HNO_3 , we can measure the change in the $[\text{H}^+]$ with a pH meter. (Recall that $[\text{H}^+]$ means “concentration of H^+ in moles/litre”.)

$$\text{Rate} = \frac{\Delta[\text{H}^+_{(aq)}]}{\Delta \text{time}}$$

e) **Pressure changes**

Since the gas NO_2 is being produced, we could measure the rate at which NO_2 is produced by measuring the change in pressure.

$$\text{Rate} = \frac{\Delta(\text{pressure})}{\Delta \text{time}}$$

Example: (April 2003)

Consider the following reaction occurring in an open container:



The reaction rate could be calculated by using which of the following?

- A. a change in $[\text{Cl}^-]$
- B. a decrease in pH value
- C. a change in gas pressure
- D. a decrease in the mass of the system

*****Do Hebden Questions #7 - 9, pg 5*****

I.3 - Factors That Affect Reaction Rates:

- The rate of a reaction depends on both the nature of the reactants and on the conditions under which the reaction occurs:

a) Temperature

Increasing the temperature increases the average kinetic energy of the particles. An increase in temperature will always increase the rate. In general, each increase in temperature of 10°C will double the reaction rate.

b) Concentration of the Reactants

The rates of both homogeneous and heterogeneous reactions are increased by an increase in concentration of reactants (gas and aqueous...NOT SOLIDS!). Increasing concentration increases the probability of successful collisions. Increasing the pressure of a gaseous reaction increases the concentration of gaseous reactant molecules and therefore reaction rate.

c) Pressure (Gas)

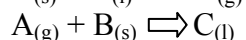
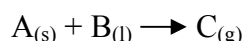
Pressure is just another way to define concentration. If you increase the pressure, you increase the rate. When the pressure on a system is increased, the volume of the system decreases, and vice versa.

$$\text{Examples: } \frac{10 \text{ mol}}{5\text{L}} = 2 \text{ M}$$

$$\frac{10 \text{ mol}}{2\text{L}} = 5 \text{ M}$$

$$\frac{10 \text{ mol}}{2\text{L}} = 5 \text{ M}$$

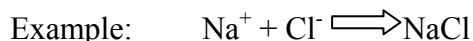
$$\frac{10 \text{ mol}}{5\text{L}} = 2 \text{ M}$$



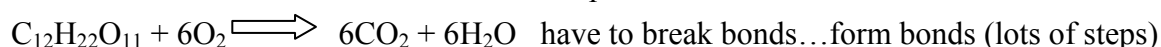
pressure does not affect products in reaction rates
only reactants

d) The Nature of Reactants

Some reactions are naturally slow because the bonds involved are very strong and unreactive, or the electrons involved are tightly held. Other reactions are naturally fast because the reaction involves the breakage of weak bonds or the removal of loosely held electrons. We have no control over these big differences in the rate of a reaction.



simple faster reaction

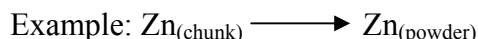


have to break bonds...form bonds (lots of steps)

e) The Ability for Reactants to Meet (Surface Area and Phase Considerations)

i) Surface Area (only affects heterogeneous reactions, not homogeneous reactions)

The greater the surface area available for the reaction, the greater the rate of the reaction. This is because the greater the surface area, the greater the ability of the reactants to meet.



ii) Phase considerations

The phases (solid, liquid, gas) of reactants also has an effect on reaction rates.

Homogeneous Reactions

Reactions in which all the reactants are in the same phase is are homogenous reactions. These tend to be faster reactions because the reactant molecules are fully mixed and able to collide.

Examples:

- a reaction between two gases
- a reaction between two substances dissolved in water
- a reaction between two liquids which can easily dissolve in each other (are “miscible”)

Heterogeneous Reactions

Reactions in which the reactants are present in different phases are heterogeneous reactions. These reactions tend to be slower reactions because the reaction can only take place on the interface between the two phases. The greater the surface area, the greater the rate of reaction.

Examples:

- a reaction between a solid and a liquid
- a reaction between a liquid and a gas
- a reaction between a solid and a gas
- a reaction between two liquids that DO NOT dissolve in each other (are “immiscible”)

Heterogeneous = different phases, not totally mixed

l – g, s – l, g – s, s – s (powder, chunk)

Homogenous = same phase (all mixed up...can't affect surface area)

l – l, g – g, l – l (are immiscible)

Another important consideration regarding phases is the actual phase in which a reactant occurs:

Solid phase reactions – tend to be slow because the reacting species cannot move freely.

Liquid phase reactions – tend to be fast because of the close proximity of the particles.

Gas phase reactions – tend to be fast because of the speed of gas particles.

Aqueous ion reactions – have the fastest reaction rates because of their close proximity, their ability to move throughout the solution, and their strong positive-negative attraction.

Aqueous >> Gases and Liquids >> Solids
(fastest) (slowest)

f) Catalysts and Inhibitors

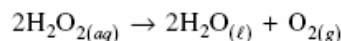
A **catalyst** is a chemical that can be added to a reaction to INCREASE the rate of the reaction. Catalysts are NOT used up in a reaction. After the reaction is complete, there will be as much of the catalyst as was originally put into the reaction. Catalysts provide an easier pathway to the products. Example: enzymes, platinum.

An **inhibitor** is a chemical that REDUCES the reaction rate by combining with a catalyst or one of the reactants in such a way as to prevent the reaction from occurring. Examples of inhibitors are poisons and antibiotics.

Examples:

1. April 2002

Consider the following reaction:



Which factor explains why the above reaction speeds up in the presence of $\text{MnO}_{2(s)}$?

- A. temperature
- B. concentration
- C. nature of reactants
- D. presence of catalyst

2. August 1998

Which of the following would react most rapidly?

- A. Powdered Zn in 1.0 M HCl at 25° C
- B. Powdered Zn in 2.0 M HCl at 40° C
- C. A lump of Zn in 2.0 M HCl at 25° C
- D. A lump of Zn in 1.0 M HCl at 40° C

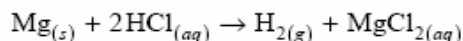
3. January 2002

Which of the following has the greatest reaction rate?

- A. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
- B. $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$
- C. $2Al_{(s)} + 3CuCl_{2(aq)} \rightarrow 2AlCl_{3(aq)} + 3Cu_{(s)}$
- D. $NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$

4. June 1999

Consider the following reaction:



The rate of this reaction increases when more magnesium is added.
This change is caused by the

- A. addition of a catalyst.
- B. increase in surface area.
- C. change in nature of the reactants.
- D. increase in concentration of reactants.

5. August 2004

Which of the following would change the value of the activation energy for a heterogeneous reaction?

- A. adding a catalyst
- B. changing the surface area
- C. changing the temperature
- D. changing the average kinetic energy

*****Do Hebden Questions #10 - 19, pgs 7 - 11*****

I.5 - Reaction Rates and Collision Theory:

- Collision theory (or K.M.T) states that molecules act like small hard spheres that bounce off each other and transfer energy among themselves during their collisions.
- For a reaction to happen:
 1. Collision between reactants
 2. Sufficient kinetic energy (speed) to collide
 3. Correct geometry – hit at the right (proper) angle.

Effect of Temperature: If you **increase** the temperature, you **increase** the rate.

1. Increase the kinetic energy
2. Increase the frequency of collisions

Effect of Concentration: If you *increase* the concentration (reactants), you *increase* the rate.

1. Increase the number of collisions between molecules

Examples:

1. April 2004

Which of the following are necessary for successful collisions between reactant molecules?

I.	high concentration
II.	sufficient energy
III.	correct geometry
IV.	presence of a catalyst

- A. I and II only
- B. II and III only
- C. III and IV only
- D. I, II and III only

2. January 2003

Which of the following would result in a successful collision between reactant particles?

- A. particles have sufficient KE
- B. particles convert all their PE into KE
- C. particles are in an excited state and are catalyzed
- D. particles have sufficient KE and proper molecular orientation

3. August 2002

As an activated complex changes into products, what changes occur in the chemical bonds of the activated complex and the PE of the system?

	Bonds	PE
A.	form	increases
B.	form	decreases
C.	break	increases
D.	break	decreases

*****Do Hebden Questions #20 - 22, pg 12*****

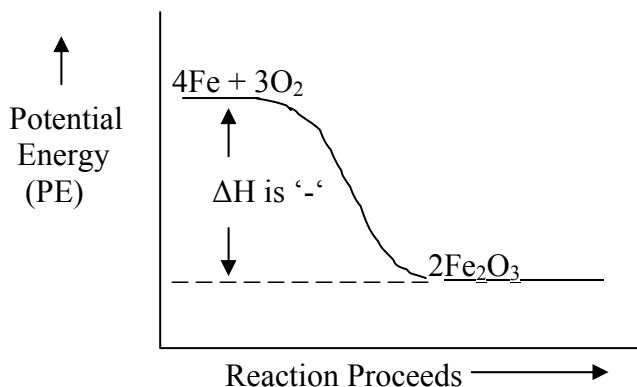
I.6 - Enthalpy Changes in Chemical Reactions:

- The amount of energy required to break a bond between two atoms is **bond energy**.
- If we break a bond, an amount of energy equal to the bond energy must be added to the bond:
$$\text{Cl}_{2(g)} + 243\text{kJ} \rightarrow 2\text{Cl}_{(g)}$$
- Conversely, if two atoms form a bond, an amount of energy equal to the bond energy is released by the atoms:
$$2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)} + 243\text{kJ}$$
- When a chemical reaction occurs, new molecules are formed as chemical bonds are broken and formed.
- Since molecules are different after the reaction, we would expect the **POTENTIAL ENERGY (PE)** of the products would differ from that of the reactants.

Therefore, two things are possible:

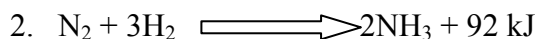
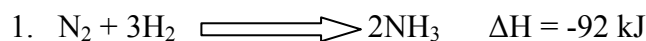
1. Energy has been added to the reactants in order to form products
 2. The reactants will give off their excess energy in order to allow the products to form
- **Enthalpy (H)** = total kinetic and potential energy which exists in the system at constant pressure. (Def)
 - **Enthalpy** is the Heat of the reaction. ΔH = 'Delta H' this is the change in enthalpy (heat).

Exothermic: products have *less* energy than reactants (Heat is released).

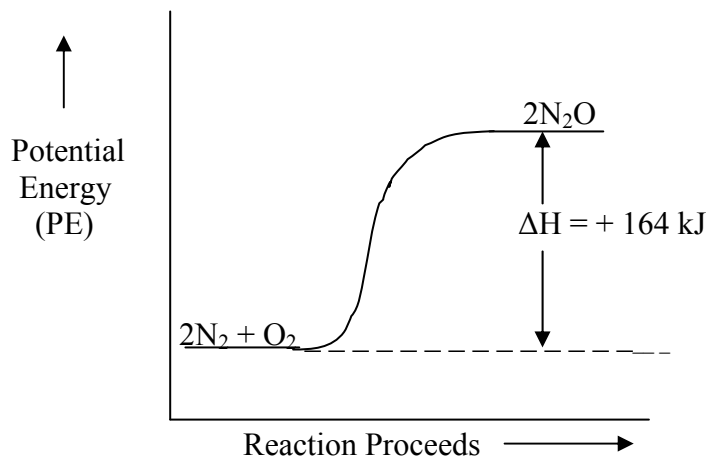
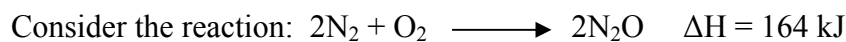


*** ΔH is negative for exothermic reactions***

Let's look at another reaction, the Haber process. It is an exothermic reaction that gives off 92 kJ of heat. It can be written the following ways...



Endothermic: products have *more* energy than reactants (Heat is added).



*** ΔH is positive for endothermic reactions***

The following are all ways to write an endothermic reaction...

1. $\text{A} + \text{B} + \text{heat} \rightleftharpoons \text{C}$
2. $\text{A} + \text{B} \longrightarrow \text{C} \quad \Delta H = \text{positive}$
3. $\text{A} + \text{B} \rightleftharpoons \text{C} - \text{heat}$

Examples:

1. August 2004

Which of the following reactions is endothermic?

- A. $\text{H}_{2(g)} + \text{S}_{(s)} \rightarrow \text{H}_2\text{S}_{(g)} + 20 \text{ kJ}$
- B. $4\text{Fe}_{(s)} + 3\text{O}_{2(g)} - 821 \text{ kJ} \rightarrow 2\text{Fe}_2\text{O}_{3(s)}$
- C. $\text{CO}_{2(g)} \rightarrow \text{C}_{(s)} + \text{O}_{2(g)} \quad \Delta H = +393 \text{ kJ}$
- D. $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)} \quad \Delta H = -92 \text{ kJ}$

Do Hebden Questions #23 - 28, pgs 13 - 16

I.7 - Kinetic Energy Distributions:

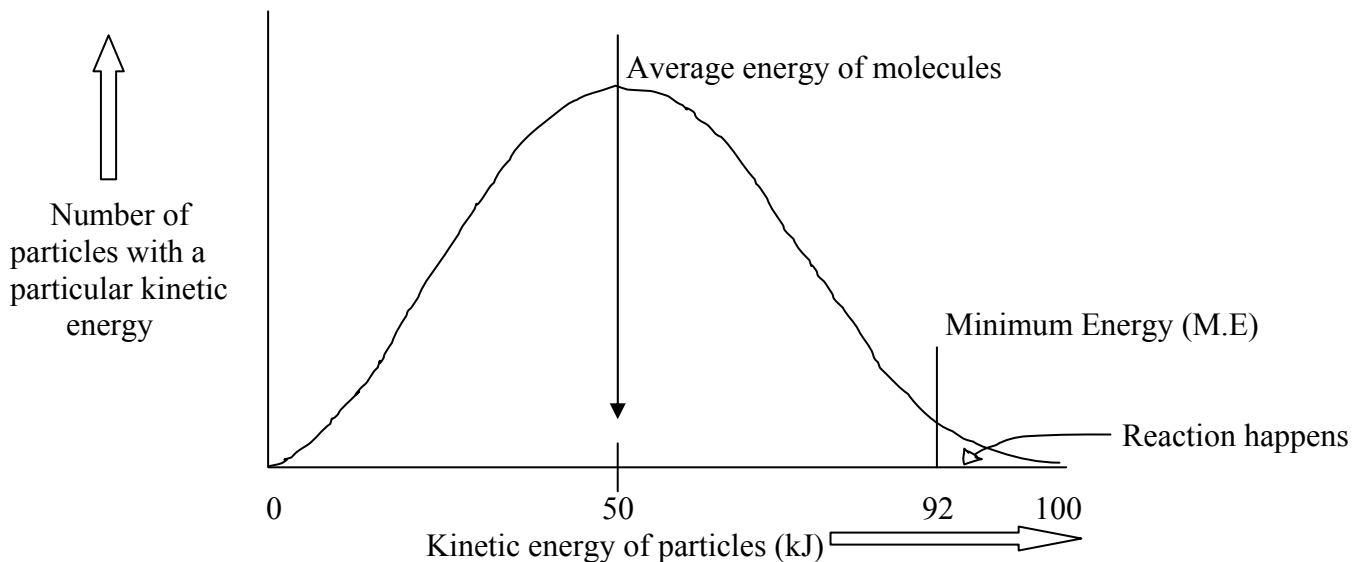
- Consider the reaction: $C_2H_2 + H_2 \rightarrow C_2H_4$

At room temperature (25°C) the reaction rate is very slow.

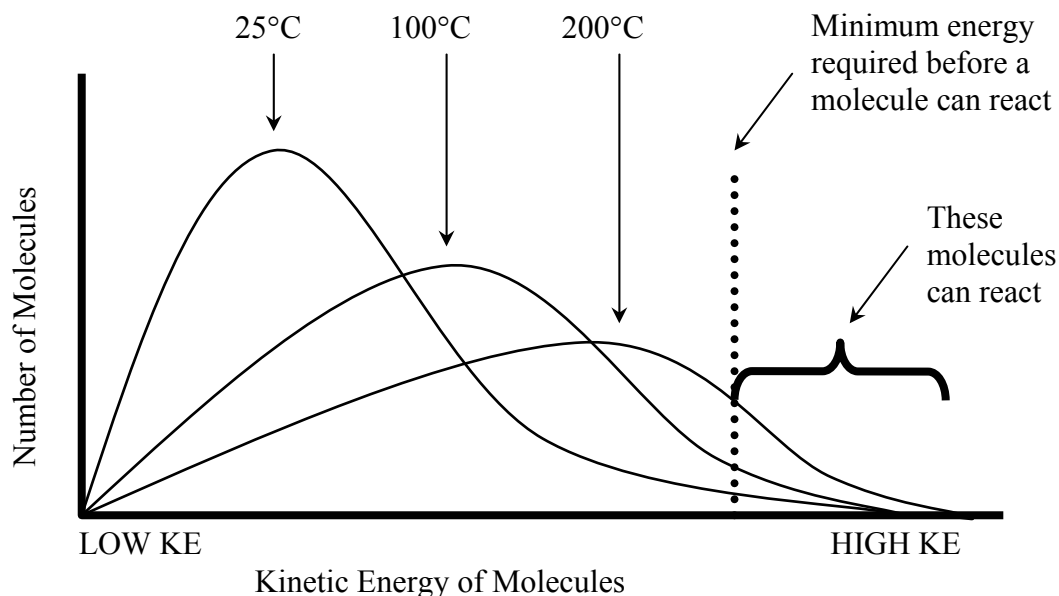
At 100°C the reaction rate is faster, but still quite slow.

At 200°C the reaction rate is relatively rapid.

- Molecules at room temperature and pressure undergo about 10^{10} collisions/second, so we can conclude that the **lack of reactivity at room temperature is not due to a lack of collisions**. Molecules need to have a sufficient amount of energy to react. The higher the temperature, the greater the average energy of the molecules and the more molecules with a sufficient amount of energy to react.
- At a given temperature some molecules DO react and some DO NOT, so there MUST be CONTINUOUS DISTRIBUTION of energies among the molecules. (See graph below).



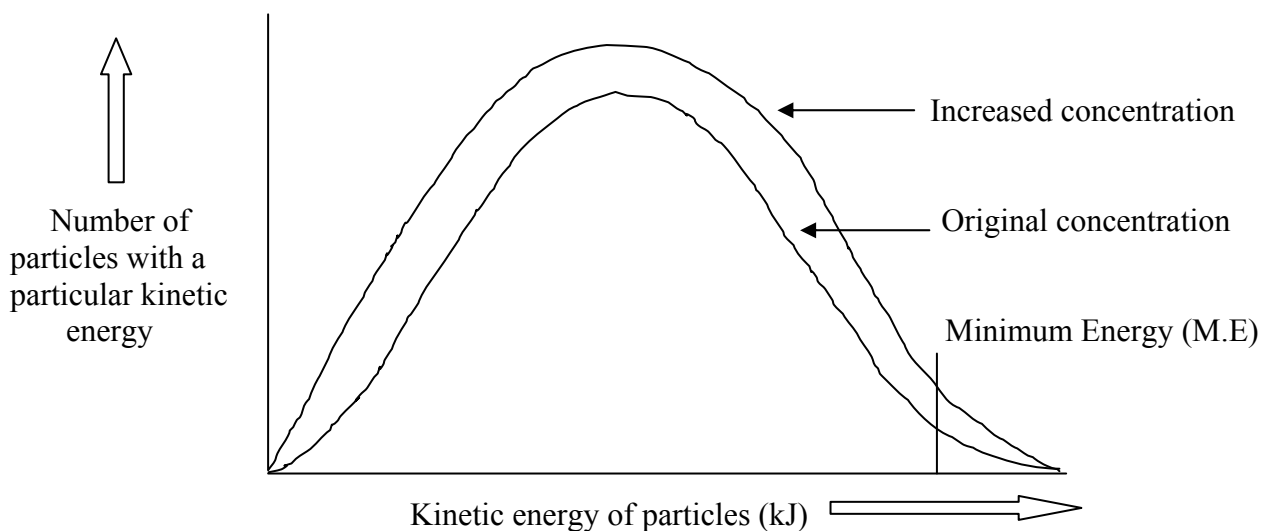
- Note that some molecules have low KE and some have very high KE
- M.E is the minimum energy necessary to react. $A + B + 92 \text{ kJ} \longrightarrow C$
- What happens when the temperature is increased...what happens to the rate? It goes up!!! That means there should be a bigger fraction of particles that have M.E (See the graph below).



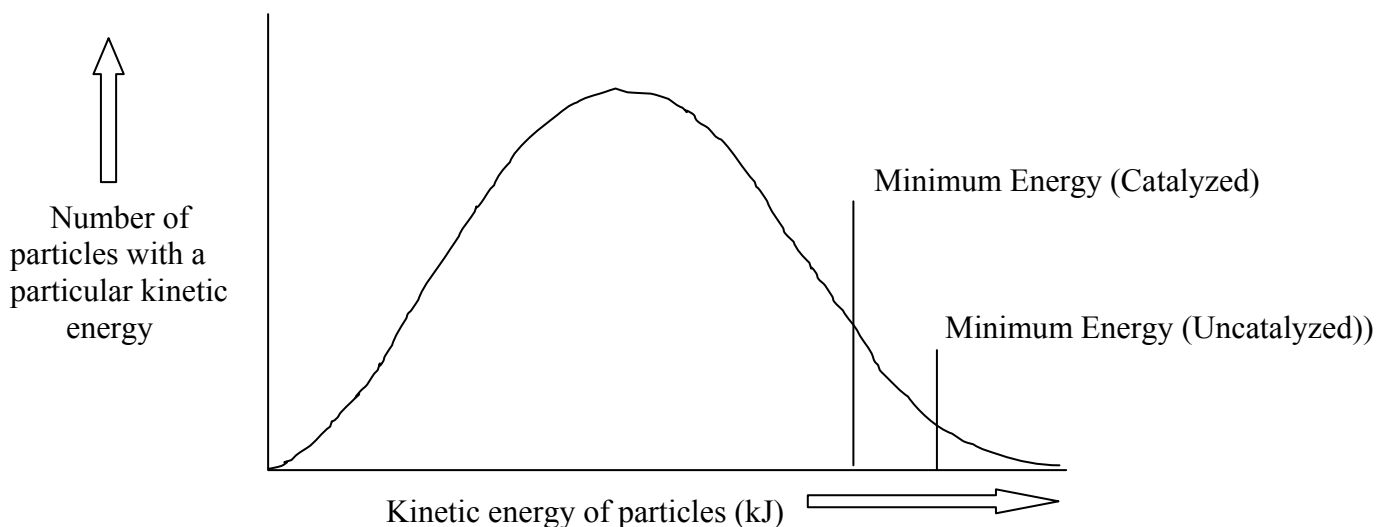
- As the temperature increases the particles undergo more collisions, but the increase in collisions is relatively small, only about a 1% increase.
- **The increased reaction rate due to an increase in temperature is primarily due to the increased number of molecules with sufficient energy to react, and not due to the increased number of collisions.**
- *Rule of thumb:*

For a **SLOW** reaction, a 10°C increase in temperature **DOUBLES** the rate.

Change concentration...



- Has **NO EFFECT** on M.E...just changes the number of particles (curve gets bigger!!!)
- If you want to change the M.E, you have to add a **catalyst** (See below).

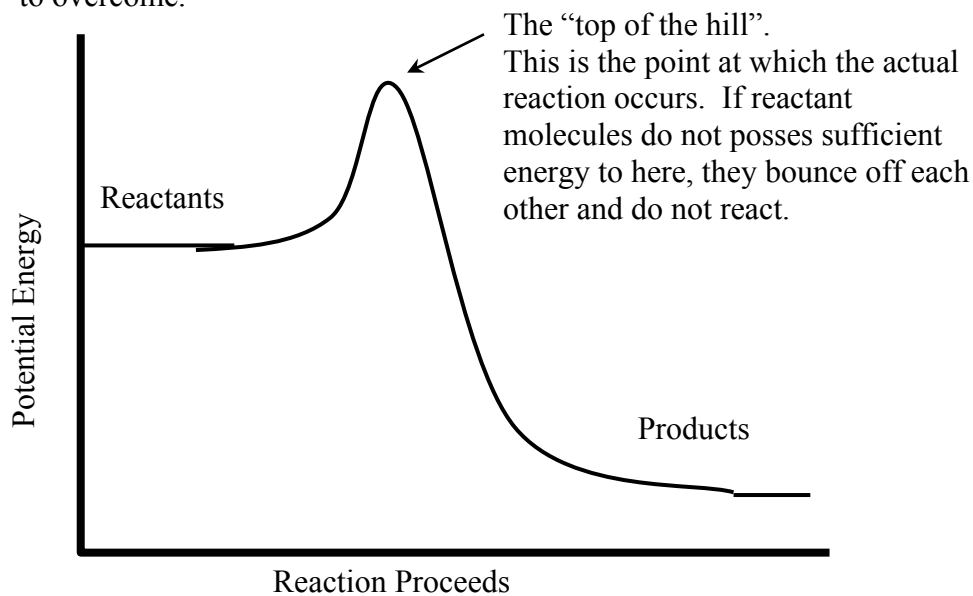


- Catalysts lower the M.E, so more particles react.

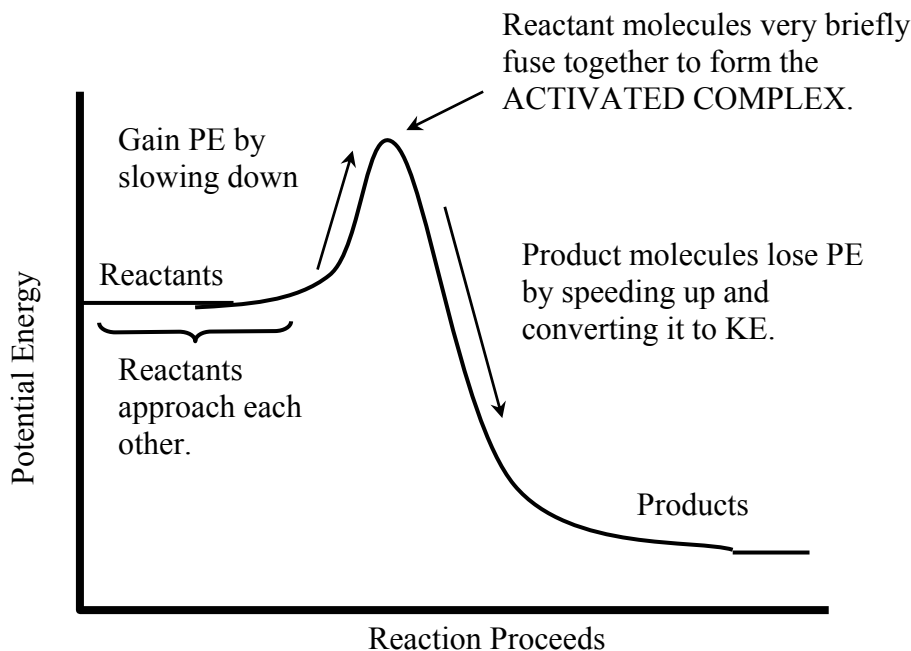
*****Do Hebden Questions #29 - 32, pgs 19 - 20*****

I.8 - Activation Energies:

- The existence of a minimum energy requirement before a molecule can react means the molecule has an energy “barrier” to overcome.



- As molecules approach each other, the outer electrons of each molecule repel the other, thus slowing down the molecules and converting their **KE into PE**. If the electrons can gain enough PE, the reactant bonds can be broken and the product bonds can be formed. At this critical moment a very short lived, high energy chemical species is formed – the **ACTIVATED COMPLEX**.
- After the reaction, the newly formed product molecules repel each other (outer electrons) and the molecules start to move away. (See graph below)



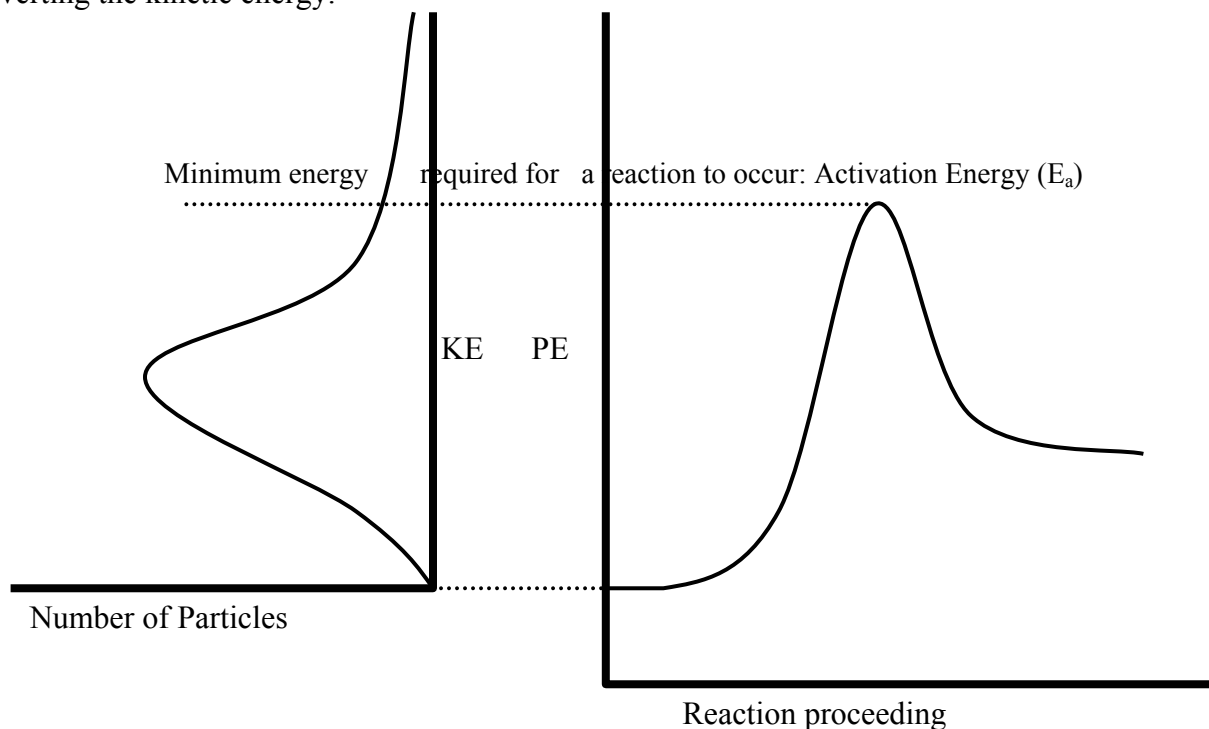
- The ‘barrier’ exists because of the mutual repulsion of the outer electrons as the reactants approach each other as well as the energy required to begin breaking bonds. The barrier gets bigger as a result of more electrons at the reaction site or when there are greater bond strengths

Activated Complex: The very short lived (unstable) molecule that forms at the moment of collision when the reactant molecules are in the process of rearranging to form products.

- The *formula* of an activated complex is found by simply adding up all the atoms involved in the two reacting molecules

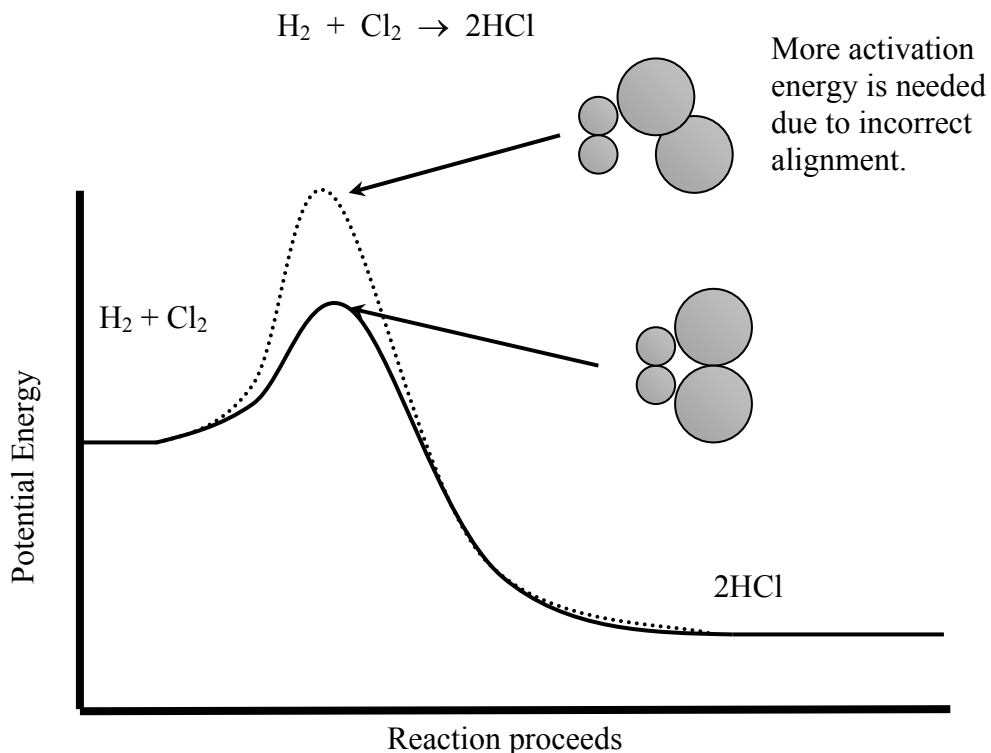
Activation Energy (E_a): The minimum potential energy required to change the reactants into the activated complex.

- A collision between a pair of particles is said to be **effective** if the collision results in a reaction occurring.
- We can now explain why a reaction proceeds at a fast rate, a slow rate, or even an effectively zero rate.
- The graph below shows that when two molecules collide, they need sufficient kinetic energy (KE) (that is, they have to be moving fast enough) for the reaction to occur. Potential Energy (PE) is gained by converting the kinetic energy.



- The KE diagram shows how many particles have a SPECIFIC AMOUNT OF KINETIC ENERGY AVAILABLE. We can see in the graph above that quite a few particles possess a KE greater than or equal to the “minimum energy required for a reaction to occur”. As a result this reaction would be relatively fast (Note: the graphs are not perfect...for a fast rate you expect that the PE hill would be lower. See pg 21)
- For a slow rate, the PE hill would be higher and the very few molecules would possess the necessary M.E
- At the start of the reaction, most of the energy is stored as KE. As the particles (molecules) approach each other, they lose KE and gain PE. After the reaction, the molecules separate and the KE increases as the PE decreases. **The total energy of the system never changes: $PE + KE = \text{constant}$**
- For a chemical reaction to occur, the reactant molecules must have two things
 - Sufficient KE** (as explained above in Figure 6)
 - Correct alignment (a.k.a. reaction geometry)**
- If the reactants are not correctly aligned, the reaction will need more energy to be completed (Higher activation energy).

- Consider the example of hydrogen gas reacting with chlorine gas to form hydrochloric acid:



Examples:

- January 2004

Consider the following reaction mechanism:

Step 1	$\text{O}_3 \rightarrow \text{O}_2 + \text{O}$
Step 2	$\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$

Which of the following could represent the activated complex for Step 2?

- O
- O_2
- O_3
- O_4

- January 2003

Which of the following best describes the E_a of a fast reaction and the stability of its activated complex?

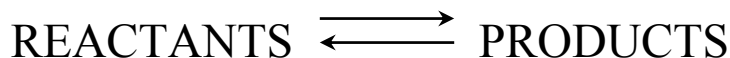
	E_a	Activated Complex
A.	small	unstable
B.	small	stable
C.	large	unstable
D.	large	stable

*****Do Hebden Questions #33 - 40, pgs 23 - 24*****

- We now introduce an extremely important concept...prepare yourselves ☺

Many reactions can go **FORWARD** or **BACKWARD**

That is:



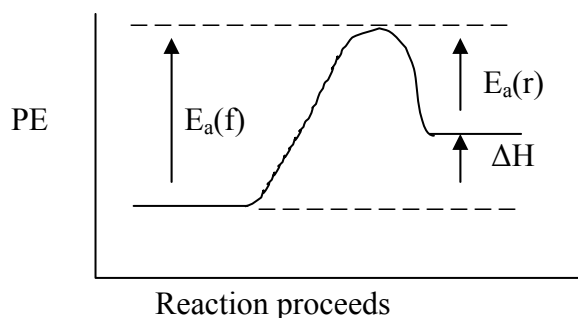
- The following Potential Energy diagram is the same as those we have seen before, however it shows that for all reversible reactions there is a **Forward Activation Energy ($E_a(\mathbf{f})$)** and a **Reverse Activation Energy ($E_a(\mathbf{r})$)** where:

$E_a(\mathbf{f})$ = the activation energy for the FORWARD reaction.

$E_a(\mathbf{r})$ = the activation energy for the REVERSE reaction

NOTE: Activation energy is always endothermic, that is energy must be added to get to the top of the hill.

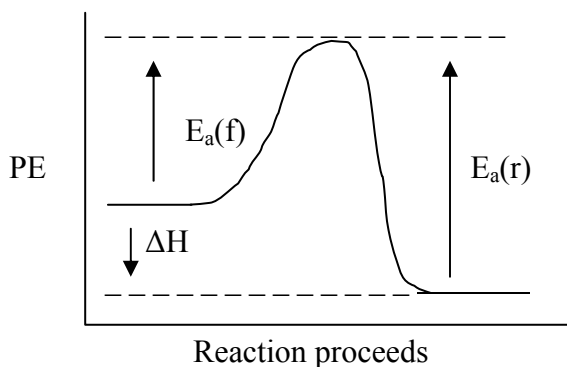
Endothermic Reactions



You can see from the diagram that:

$$E_a(\mathbf{f}) = E_a(\mathbf{r}) + \Delta H$$

Exothermic Reactions



Although it may not be obvious...

$$E_a(\mathbf{f}) = E_a(\mathbf{r}) + \Delta H$$

Examples:

1. January 2004

Which of the following best describes *activation energy*?

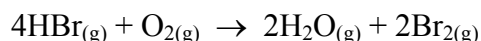
- PE of activated complex
- $(\text{PE of products}) - (\text{PE of reactants})$
- $(\text{PE of reactants}) - (\text{PE of activated complex})$
- $(\text{PE of activated complex}) - (\text{PE of reactants})$

*****Do Hebden Questions #41 - 45, pg 25*****

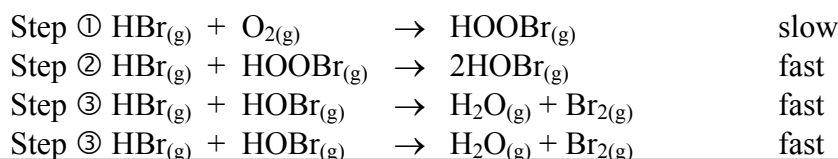
I.9 - Reaction Mechanisms:

- Most reactions occur in more than one step or *elementary process*.
- **Reaction Mechanism:** The actual sequence of steps that make up an overall reaction is a reaction mechanism.

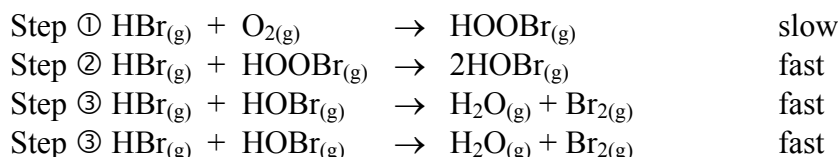
Consider the following reaction:



- It is unlikely that 4 HBr molecules and 1 O₂ molecule will collide simultaneously to undergo a chemical change. Instead, experiments show that the reaction occurs in more than one step. Complex reactions **CANNOT** go in a single step, but must consist of more than one step in getting from reactants to products.



- Steps ①, ② and ③ are called *ELEMENTARY PROCESSES*. **Elementary Process:** An individual step in a reaction mechanism.
- The slowest step in the mechanism determines the overall rate of the reaction and is called the **rate determining step** or **rate limiting step**.
- Step ① is the rate determining step in the above example. In other reactions, the rate determining step can be a first, last, or middle step and still control the overall rate.
- To determine the overall reaction from the reaction mechanism, we simply add up all the steps in the reaction equations and cancel any species that occur on both sides of the final equation.

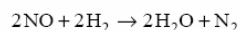


- In the above example HOBr and HOBr are “reaction intermediates” or simply “intermediates”. They are formed in one elementary process but subsequently, consumed in another and are therefore, not found written in the overall reaction. Unlike an activated complex, intermediates can exist on their own.
- The formula of an activated complex is found by simply adding up all the atoms involved in the two reacting molecules. For example, in Step 2 (above) the activated complex is H₂O₂Br₂ (the order of the atoms is not important).
- **NOTE:**☺ YOU WILL NEVER HAVE TO PREDICT A REACTION MECHANISM. Years of precise work and complex analysis through experimentation are normally required to determine a mechanism.

Examples:

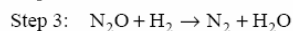
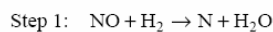
1. January 1996

1. Consider the following overall reaction:



a) Explain why the reaction is likely to involve more than one step.

b) A proposed mechanism for the reaction is:



i) Write the equation for Step 2.

ii) Identify all reaction intermediates.

2. January 2003

1. Consider the following reaction mechanism:

Step 1	$\text{Cl}_2 \rightarrow 2\text{Cl}$	(fast)
Step 2	$\text{Cl} + \text{CO} \rightarrow \text{COCl}$	(slow)
Step 3	$\text{COCl} + \text{Cl}_2 \rightarrow \text{COCl}_2 + \text{Cl}$	(fast)

Identify a reaction intermediate in the reaction mechanism and write the equation for the overall reaction. Explain why increasing the $[\text{CO}]$ will increase the reaction rate, but increasing the $[\text{Cl}_2]$ will not. (5 marks)

Reaction Intermediate: _____

Overall Reaction Equation: _____

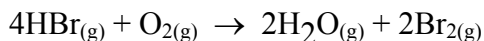
Explanation: _____

*****Do Hebden Questions #46 - 53, pg 28*****

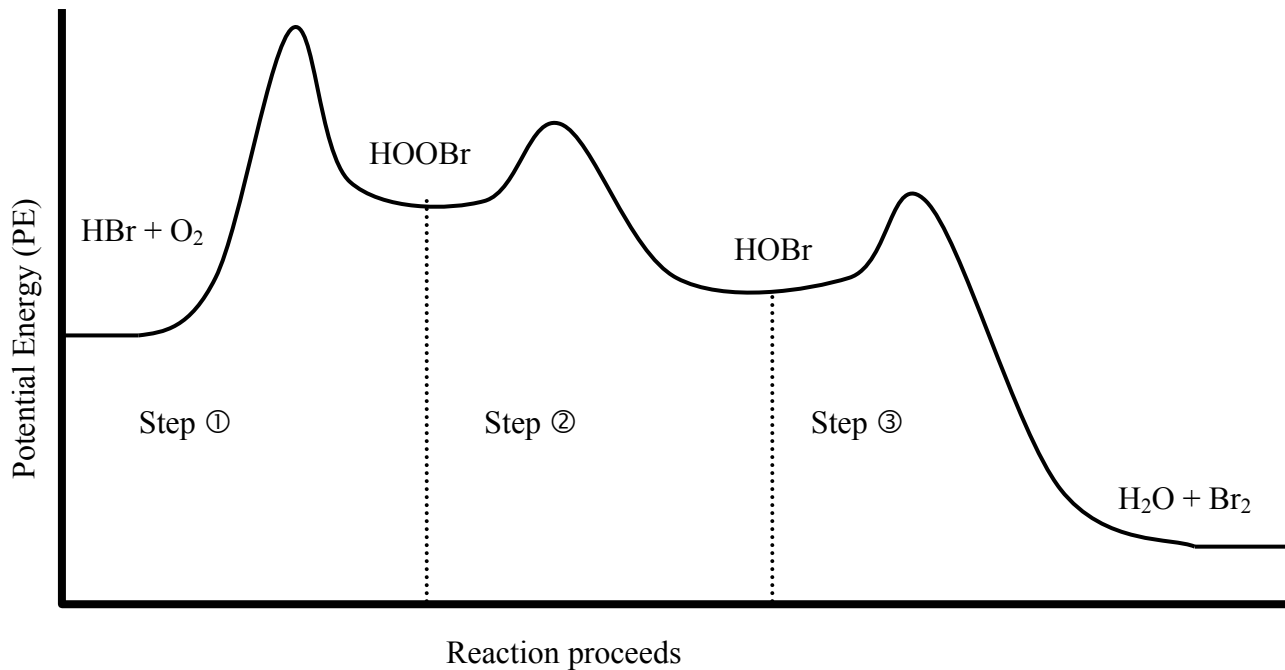
I.10 - Potential Energy Diagram of a Reaction Mechanism:

- Each step (“elementary process”) of a reaction mechanism involves an individual activated complex and activation energy.

For the reaction:



There are three steps and therefore three “humps” in our PE Diagram.



- Each step of the mechanism has its own activation energy but the overall activation energy of a reaction does not equal the sum of the activation energies. Instead it is the same as the greatest peak (slowest step).
- The activation energy for a particular step in a reaction can be defined as:

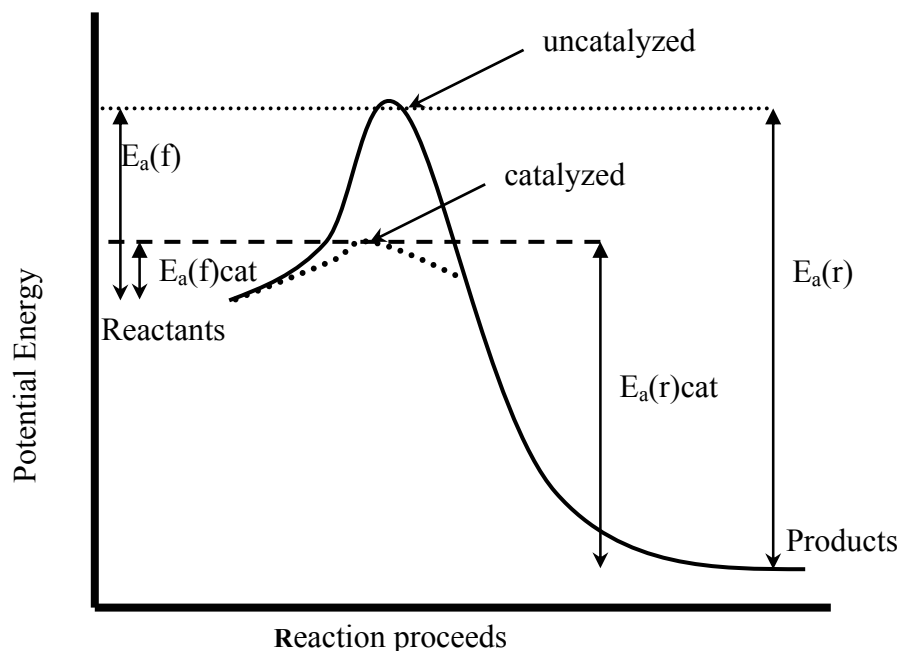
$$E_a = \text{PE}(\text{activated complex}) - \text{PE}(\text{reactants for the step})$$

*****Do Hebden Questions #54 - 55, pg 30*****

I.11 - The Effect of Catalysts on Activation Energy:

- A *catalyst* is a substance that provides an *alternative reaction mechanism* having lower activation energy.
- Catalysts are not used up in chemical reactions.
- Catalyst work by orienting colliding particles or stabilizing the activated complex.
- If we lower the activation energy by adding a catalyst, more reactant molecules will possess the minimum kinetic energy required to form the activated complex. Therefore, more molecules can react and the rate increases.

****Important Point:** It is not only the forward reaction rate that is increased; by lowering the “energy hump” we also lower the reverse activation energy and increase the rate of the reverse reaction.

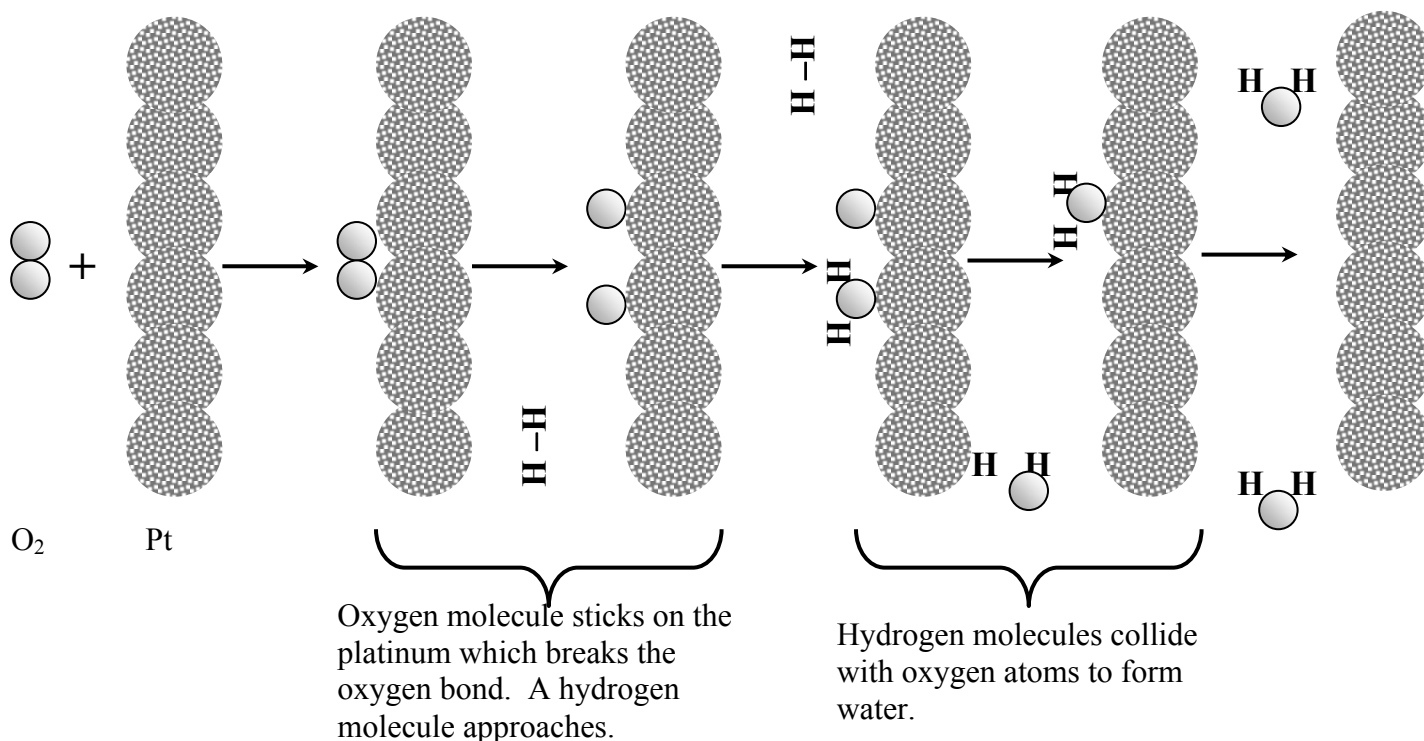
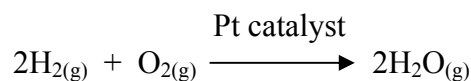


- Note:

- Those particles which go the uncatalyzed route require more PE (labeled U above) than those particles that go by the catalyzed route (labeled C above).
- The lower PE required in the catalyzed reaction translates as a lower KE requirement. Since more particles have this lower KE requirement, the reaction is faster for the catalyzed reaction.
- Uncatalyzed reaction is still available, but very few reactants will go over the ‘higher hump’.

Example:

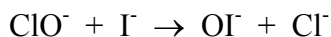
The reaction of hydrogen gas and oxygen gas to form water occurs slowly at room temperature since it has numerous steps. If a platinum catalyst is added, the reaction happens much faster with a two step mechanism.



I.12 - The Effect of Catalysts on the Reaction Mechanism:

- A Catalyst does take an active part in a chemical reaction. Catalysts are added as a “reactant” (but it is not a reactant) and **regenerated again in a later step of the reaction mechanism**. Therefore, at the end of a reaction, we have as much catalyst as we did at the beginning.
- Enthalpy (ΔH) for the overall reaction is the same for both the catalyzed and uncatalyzed reaction.
- Both intermediates and catalysts cancel out when we add up the individual steps in a mechanism to get the overall reaction.

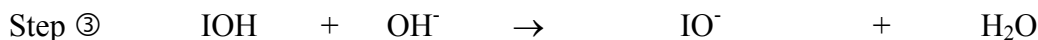
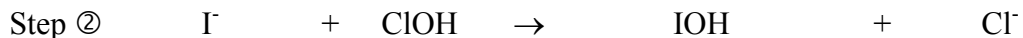
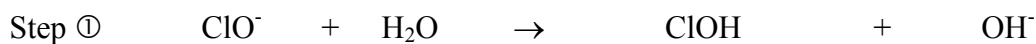
Example:



This reaction has very high activation energy since it demands that two negatively charged species approach each other and react. Therefore, this reaction if uncatalyzed is unlikely to occur.

Water acts as a catalyst for this reaction, providing an alternate mechanism having a lower overall activation energy.

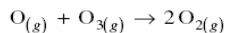
- What is the overall equation? Can you identify the catalyst? How can do you know?



Examples:

1. April 2004

Consider the following reaction:



Which of the following describes how the reaction's catalyzed PE diagram compares to the reaction's uncatalyzed PE diagram?

	E_a	ΔH
A.	E_a (catalyzed) < E_a	unchanged
B.	E_a (catalyzed) > E_a	unchanged
C.	E_a (catalyzed) < E_a	ΔH (catalyzed) < ΔH
D.	unchanged	ΔH (catalyzed) < ΔH

2. August 2001

1. Consider the following proposed reaction mechanism:

Step 1	$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{FeH}_2\text{O}_2^{3+}$
Step 2	$\text{FeH}_2\text{O}_2^{3+} \rightarrow \text{FeOH}^{3+} + \text{HO}$
Step 3	$\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$
Step 4	$\text{FeOH}^{3+} + \text{HO}_2 \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O} + \text{O}_2$

a) Write the overall reaction. (2 marks)

b) Define the term *catalyst* and identify a catalyst in the above mechanism. (2 marks)

Definition: _____

Catalyst: _____

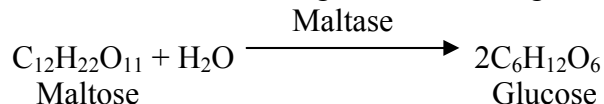
*****Do Hebden Questions #56 - 61, pg 34*****

I.13 - Some Uses of Catalysts:

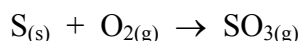
- Catalysts are presently used extensively in industry, and are actively being researched for further uses.
- Most biological reactions are initiated or aided by catalysts called enzymes. The particular molecule upon which an enzyme acts is called its substrate. A particular reaction may involve several enzymes working together.

Examples:

- a. The enzyme maltase breaks down the sugar maltose into glucose



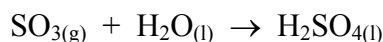
- b. The industrial process for making sulphuric acid, H_2SO_4 involves several steps. First, sulphur is burned to give SO_2 :



Next, the SO_2 is passed over a catalyst consisting of finely divided particles of platinum (Pt) or vanadium pentoxide (V_2O_5) to form SO_3 :



The resulting SO_3 can then be added to water to make sulphuric acid:



- c. Automobiles are equipped with a catalytic converter to reduce the amount of harmful pollutants that are released into the environment.

The production of nitric oxide (NO), NO_2 , carbon monoxide and unburned hydrocarbons are the chief concern. The following two equations show how NO and NO_2 (“ NO_x ”) are made.

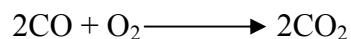


The catalytic converters have two reaction chambers.

- The first chamber uses platinum and rhodium (as a catalyst) to reduce the NO_x emissions. When a NO or NO_2 molecule contacts the catalyst, the catalyst rips the nitrogen atom out of the molecule and holds on to it, freeing the oxygen in the form of O_2 . The nitrogen atoms then bind with other nitrogen atoms that are stuck on the catalyst, forming N_2 .



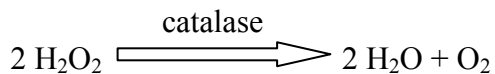
- The second chamber uses platinum and palladium as catalysts to reduce the unburned hydrocarbons and carbon monoxide.



Catalysts in action:

Decomposition of hydrogen peroxide, catalyzed by manganese (IV) oxide, Platinum, raw liver, blood

- Hydrogen peroxide is extremely toxic to cells because it attacks unsaturated fatty acids compounds of membrane lipids, thus damaging the membrane structure. Cells can protect themselves against peroxide by the action of catalase, which decomposes hydrogen peroxide.



Hydrogen peroxide undergoes disproportionation (both oxidation and reduction occur at the same time. The activation energy of the uncatalyzed reaction is 75 kJ/mol. Platinum metal can lower the activation energy to about 49 kJ / mol. The catalase enzyme (found in blood, liver) lowers the activation energy to below 8 kJ / mol which corresponds to an increase in the rate by a factor of 2×10^{11} or more!!

The reaction of the oxalate ion ($\text{C}_2\text{O}_4^{2-}$) with acidified potassium permanganate solution (KMnO_4), catalyzed by Mn^{2+}

- The equation for the oxidation of oxalate by permanganate in acidic solution is
$$2 \text{MnO}_4^-(\text{aq}) + 5 \text{H}_2\text{C}_2\text{O}_4(\text{aq}) + 6 \text{H}_3\text{O}^+(\text{aq}) \rightarrow 2 \text{Mn}^{2+}(\text{aq}) + 10 \text{CO}_2(\text{aq}) + 14 \text{H}_2\text{O}$$
- Do you notice anything special? The reaction actually produces Mn^{2+} , which is the catalyst!
- Addition of a few crystals of MnSO_4 greatly accelerates the reduction by oxalic acid of purple permanganate to the nearly colourless manganese(II). When no manganese(II) ion is added, the reaction initially proceeds slowly, but the rate gradually increases because the product autocatalyzes the reaction.
- Autocatalysis occurs when the product of a reaction serves as a catalyst for the reaction.

Example:

A dilute purple solution of potassium permanganate is added to each of two beakers of acidified oxalate solution. A few crystals of manganese(II) sulfate added to the solution on the right catalyze the reduction of permanganate to colorless manganese(II) ion. Note the initial red colour due to formation of a manganese (III) intermediate in the beaker on the right.

The other solution reacts more slowly, but its reaction rate eventually increases as it forms manganese(II) ion, which subsequently autocatalyzes its own formation.



Potassium permanganate is added.



Manganese(II) sulphate is added to the solution on the right.



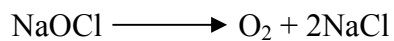
It catalyzes the reduction of permanganate to colourless manganese(II) ion.



The other solution's reaction rate eventually increases as it forms manganese(II) ion, which subsequently autocatalyzes its own formation.

The Decomposition of bleach, catalyst is cobalt (II) chloride (CoCl₂)

- The decomposition is as follows...



- Trace metals such as nickel, copper and cobalt will cause bleach to decompose to oxygen and sodium chloride.
- Light will also catalyze this reaction.

Examples:

1. April 2003

What is an important function of the catalyst found in an automobile exhaust system?

- A. increase fuel economy
- B. decrease the rate of CO₂ production
- C. increase the conversion rate of NO₂ to N₂
- D. increase the conversion rate of heat into work

*****Do Hebden Questions #61 - 63, pg 36*****