

# CHEMISTRY

## LEVEL 4C

(CHM 415115)

# REACTION KINETICS

## THEORY SUMMARY

&

## REVISION QUESTIONS

Tasmanian TCE Chemistry Revision Guides by [Jak Denny](#) are licensed under a [Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License](#).

©JAK DENNY

# INDEX

	PAGES
• INTRODUCTION	3
• MEASURING RATES	3
• COLLISION THEORY	4
• ACTIVATION ENERGY BARRIERS	5
• POTENTIAL ENERGY DIAGRAMS	5
• FACTORS AFFECTING RATES	6-9
• REACTION MECHANISM	10-11
• CATALYSIS	12-13
• CATALYSTS & $E_p$ DIAGRAMS	14
• CATALYSTS & $E_k$ DISTRIBUTION	15
• INTERMEDIATE COMPOUND THEORY	16-17
• THRESHOLD & ACTIVATION ENERGY	18-19
• THEORY SUMMARY	20
• REVISION QUESTIONS	21-23
• REVISION TEST	24-25
• REVISION TEST ANSWERS	26-27

# REACTION KINETICS (RATES OF REACTIONS)

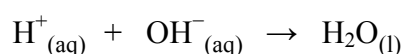
## INTRODUCTION

This topic deals with the *rates* of chemical reactions.

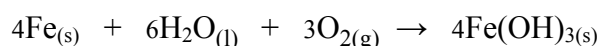
Chemical equations give no information at all about how quickly a reaction will occur.

The rate of chemical reactions at room temperature varies enormously from reactions that are very fast to those that are extremely slow.

e.g. **VERY FAST:** acid ~ base neutralisation.



e.g. **VERY SLOW:** corrosion of iron.



Reactions that involve the breaking of chemical bonds tend to be much slower at room temperature than reactions not requiring bond breaking.

Q1. Give two further examples of chemical reactions that at 25°C are:

- (i) very fast chemical reactions.
- (ii) very slow chemical reactions.

Q2. Suggest a reason why petrol does not undergo a chemical reaction with oxygen at 25°C and yet it is explosively reactive at high temperatures.

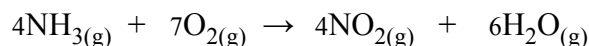
## MEASURING RATES

The units used depend on a number of factors such as whether the reaction involves solids, solutions, gases or combinations of these.

Thus possible rate units include:  $\text{g s}^{-1}$ ,  $\text{L s}^{-1}$ ,  $\text{mol s}^{-1}$  or  $\text{mol L}^{-1} \text{s}^{-1}$ .

The most frequently used unit for measuring reaction rates is  $\text{mol L}^{-1} \text{s}^{-1}$ .

Q3. Given that for the chemical reaction:



the rate of consumption (using up) of ammonia gas ( $\text{NH}_3$ ) is  $7.20 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

- (i) what is the rate of consumption of oxygen gas ( $\text{O}_2$ )? **( $1.26 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ )**
- (ii) what is the rate of formation of steam ( $\text{H}_2\text{O}_{(\text{g})}$ )? **( $1.08 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ )**

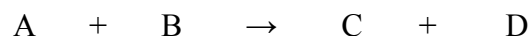
Q4. In a particular reaction involving the decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), 0.150 mol of oxygen is released from 0.350 L of peroxide solution in 29.0 seconds. What is the rate of formation of oxygen for this reaction in units of  $\text{mol L}^{-1} \text{ s}^{-1}$ ?

**( $1.48 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ )**

# COLLISION THEORY

## 1. INTRODUCTION

Consider the general chemical reaction between A and B to form products C and D;  
i.e.

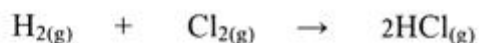


For a chemical reaction to occur between particles A and B, the particles must firstly come in contact in such a way as to allow for the rearrangement of the sharing or the transfer of electrons. This means the electron orbitals of A and B must 'overlap' sufficiently which will only occur if the particles A and B collide with sufficient energy to overcome the repulsive forces that occur between the negatively charged electron clouds.

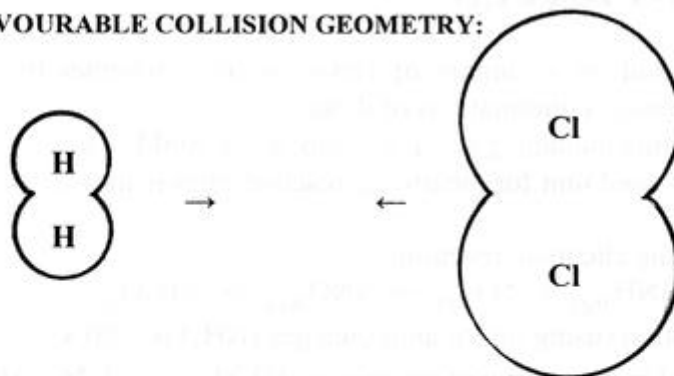
In summary, for A and B to undergo reaction, the following conditions must occur:

- (i) particles of A and B must firstly undergo collision.
- (ii) the collisions between A and B must have sufficient kinetic energy ( $E_K$ ) to overcome the barrier to reaction caused by electron ~ electron orbital repulsion.
- (iii) the collisions between A and B must occur with the appropriate orientation or geometry to ensure the electrons can undergo the changes required.

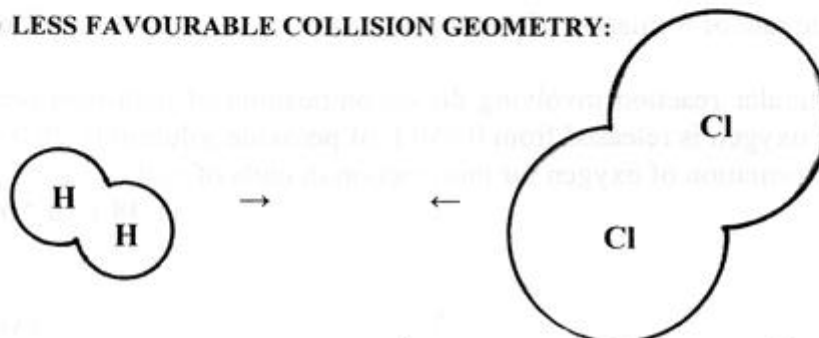
For example, consider the reaction:



(a) FAVOURABLE COLLISION GEOMETRY:



(b) LESS FAVOURABLE COLLISION GEOMETRY:



## 2. ACTIVATION ENERGY BARRIERS

Consider the chemical reaction between A and B to form products C and D:

i.e.



Approaching particles A and B will naturally tend to move apart from each other as their negative electron clouds meet and cause repulsion forces to bring about re-separation.

If A and B collide with sufficient kinetic energy ( $E_K \geq E_a$ ) to overcome these repulsion forces, then the reaction will take place.

In order to be assured of undergoing a reaction, the collision between A and B must pass through an “activated complex” state  $(AB)^*$  which is the result of kinetic energy ( $E_K$ ) being transformed into potential energy ( $E_P$ )

(This somewhat like a high jumper or pole-vaulter using running speed to gain  $E_K$  prior to crossing a vertical barrier!)

## 3. POTENTIAL ENERGY DIAGRAMS

The energy changes occurring during the change from reactants to products in this exothermic reaction can be represented in a “potential energy diagram” such as shown below.

### NOTES ON $E_P$ DIAGRAM:

A and B = reactants

C and D = products

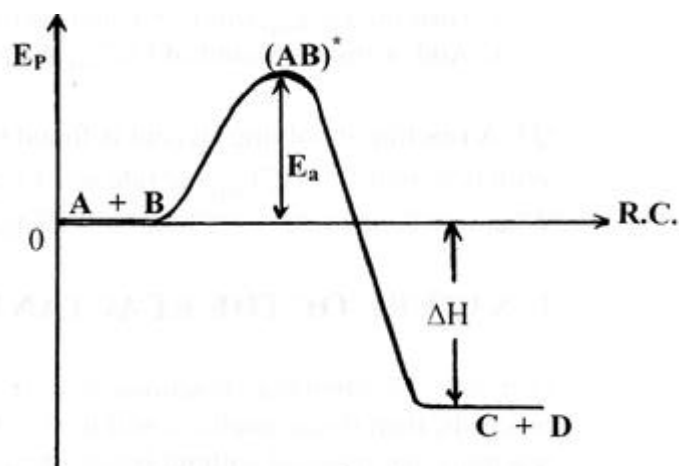
$E_a$  is called the Activation Energy Barrier

$\Delta H$  is the heat of reaction

$(AB)^*$  is called the activated complex

R.C. = reaction co-ordinate (“time”)

$E_P$  is potential energy



(i) Collisions that occur between A and B that have sufficient energy to cross the  $E_a$  barrier and thus lead to the formation of products, are called “EFFECTIVE COLLISIONS”.

(ii) Collisions that occur between A and B that do not have sufficient energy to cross the  $E_a$  barrier and thus don't lead to the formation of products, are called “INEFFECTIVE COLLISIONS”.

(iii) In accordance with our discussion above, the Collision Theory states that the rate of any chemical reaction is directly related to the number of *effective collisions* occurring per unit time.

Q5. Sketch appropriate potential energy diagrams for the reactions with:

(i)  $\Delta H = -255 \text{ kJ mol}^{-1}$  and  $E_a = +165 \text{ kJ mol}^{-1}$ .

(ii)  $\Delta H = +85 \text{ kJ mol}^{-1}$  and  $E_a = +145 \text{ kJ mol}^{-1}$ .

# FACTORS AFFECTING RATES

There are a number of factors that will affect the rate of a given chemical reaction. These include:

- (i) concentration of the reactants.
- (ii) partial pressures of gaseous reactants.
- (iii) temperature.
- (iv) surface area of reactants.
- (v) presence of catalysts.
- (vi) whether bonds need to be broken initially; i.e. the nature of the reactants.

Q6. For the chemical reaction between magnesium metal ribbon and  $0.50 \text{ mol L}^{-1}$  hydrochloric acid at S.L.C., suggest **four** changes that would **increase** the reaction rate.

## ANSWER

1. Use a higher molarity acid e.g.  $5.00 \text{ mol L}^{-1} \text{HCl}_{(\text{aq})}$ . **(concentration effect)**
2. Use magnesium metal powder rather than Mg ribbon. **(surface area effect)**
3. Heat the  $\text{HCl}_{(\text{aq})}$  from  $25^\circ\text{C}$  to (say)  $70^\circ\text{C}$ . **(temperature effect)**
4. Add a small amount of  $\text{Cu}^{2+}_{(\text{aq})}$  to the  $\text{HCl}_{(\text{aq})}$ . **(catalytic effect)**

Q7. A reaction involving an acid is found to have a rate proportional to the  $[\text{H}^+_{(\text{aq})}]^2$ .  
With  $0.50 \text{ mol L}^{-1} \text{HCl}_{(\text{aq})}$  the rate is  $0.13 \text{ mol L}^{-1} \text{s}^{-1}$ .  
What will be the rate if  $1.50 \text{ mol L}^{-1} \text{HCl}_{(\text{aq})}$  is used instead?

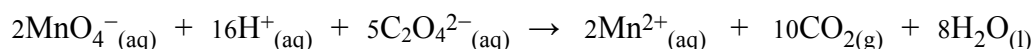
**( $1.17 \text{ mol L}^{-1} \text{s}^{-1}$ )**

## 1. NATURE OF THE REACTANTS

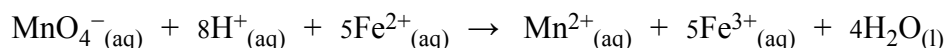
Generally, if chemical reactions require bond **breaking** to occur before the reaction proceeds, then these reactions will tend to be much slower at room temperature than those reactions that proceed without bonds having to be broken.

For example, oxalate ions are oxidised extremely slowly by acidified permanganate at  $25^\circ\text{C}$  whereas iron(II) ions are oxidised very rapidly under the same conditions. The difference is that the C–C bond in the oxalate ion must be broken in the oxidation process but to oxidise iron(II) to iron(III) requires only the loss of an electron.

This reaction is **very slow** at  $25^\circ\text{C}$

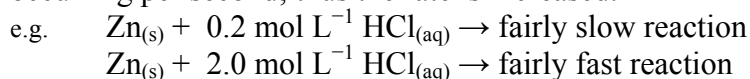


This reaction is **very fast** at  $25^\circ\text{C}$



## 2. REACTANT CONCENTRATION

Increasing the concentration of a reactant increases the number of collisions occurring between the reactants and thus, (usually) increases the number of *effective collisions* occurring per second; thus the rate is increased.



In general, increasing the concentration of a reactant increases the rate of that chemical reaction.

## 3. GAS PRESSURE

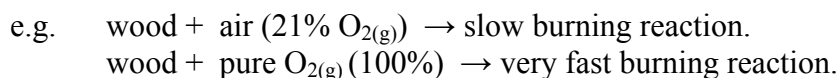
Increasing the partial pressure of a gaseous reactant increases the concentration of that gas and thus the reaction rate is likely to increase in accordance with the discussion above in 2.

NOTE: From the General Gas Equation we get;

$$p_A \cdot V = n_A \cdot R \cdot T \quad \rightarrow \quad p_A = (n_A/V) \cdot R \cdot T$$
$$p_A = [A] \cdot R \cdot T \quad (n_A/V) = \text{molarity of A}$$
$$p_A \propto [A] \quad \infty = \text{'proportional to'}$$

This shows that the partial pressure of a reactant gas is directly proportional to its molar concentration.

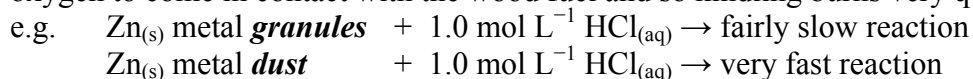
The higher the partial pressure of the gas, generally the faster it reacts.



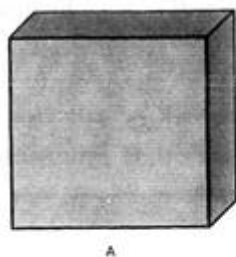
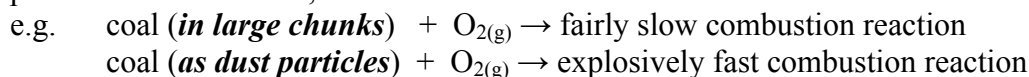
## 4. SURFACE AREA

Increasing the surface area of a reactant increases the number of collisions occurring between reactants and thus increases the number of effective collisions occurring per unit time.

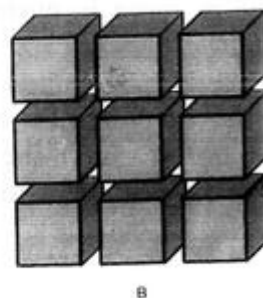
e.g. Splitting a log of wood up into smaller and smaller pieces of kindling opens up sites for oxygen to come in contact with the wood fuel and so kindling burns very quickly.



This factor is a key to the situation where there is combustible dust in the atmosphere and a small spark is all that's needed to start a catastrophic explosion. This is particularly a problem for coal mines, wheat silos and flour mills.



An illustration of the effect of subdivision. "Samples" A and B both have a volume of 9 cm<sup>3</sup>. What is the total surface area of each sample?

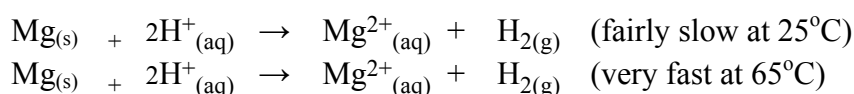


## 5. TEMPERATURE

Increasing the temperature of reactants increases the rate of most chemical reactions because an increase in temperature results in the reactant molecules or ions having increased kinetic energy ( $E_K$ ) and thus moving *faster* which results in two significant changes. A temperature rise causes:

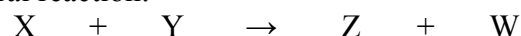
- (i) more frequent collisions → more effective collisions per second → faster reaction rate.
- (ii) higher energy collisions → more effective collisions per second → faster reaction rate.

e.g. Consider the reaction between magnesium ribbon and  $0.2 \text{ mol L}^{-1} \text{ HCl}_{(\text{aq})}$



### EXPLANATION:

Consider the general reaction:



In a batch of X and Y molecules at  $25^\circ\text{C}$  the particles (atoms, molecules or ions) have a range of kinetic energy ( $E_K$ ) values from **low** through to **high** with the majority having values close to the **average** value. This is best expressed as a  $E_K$  distribution curves; (see next page).

If the reaction has an activation energy barrier of  $E_a$ , then only those molecules X and Y colliding with combined kinetic energy greater than or equal to  $E_a$  will undergo effective collisions and so react to form Z plus W.

The proportion of molecules thus reacting at  $25^\circ\text{C}$  is shown by the shaded area to the right of the  $E_a$  cut-off. This cut-off kinetic energy value which is directly determined by the  $E_a$  barrier height is called the **THRESHOLD ENERGY**.

Raising the temperature to say  $60^\circ\text{C}$  increases the average  $E_K$  of molecules so the  $E_K$  distribution curve shifts to the right and flattens out as shown in the second (middle) diagram opposite.

Despite the increases in kinetic energies, the height of the  $E_a$  barrier is unaltered and thus the cut-off point is the same as it was for  $25^\circ\text{C}$ .

This means that a much greater proportion of molecules now have kinetic energies that exceed the threshold energy value and the larger shaded area indicates that the number of molecules now reacting is much greater than previously at  $25^\circ\text{C}$ .

i.e. raising the temperature has caused an increase in reaction rate.

Lowering the temperature lowers the average kinetic energy of the molecules and the  $E_K$  distribution curve is pushed back into lower values (to the left). See bottom diagram opposite.

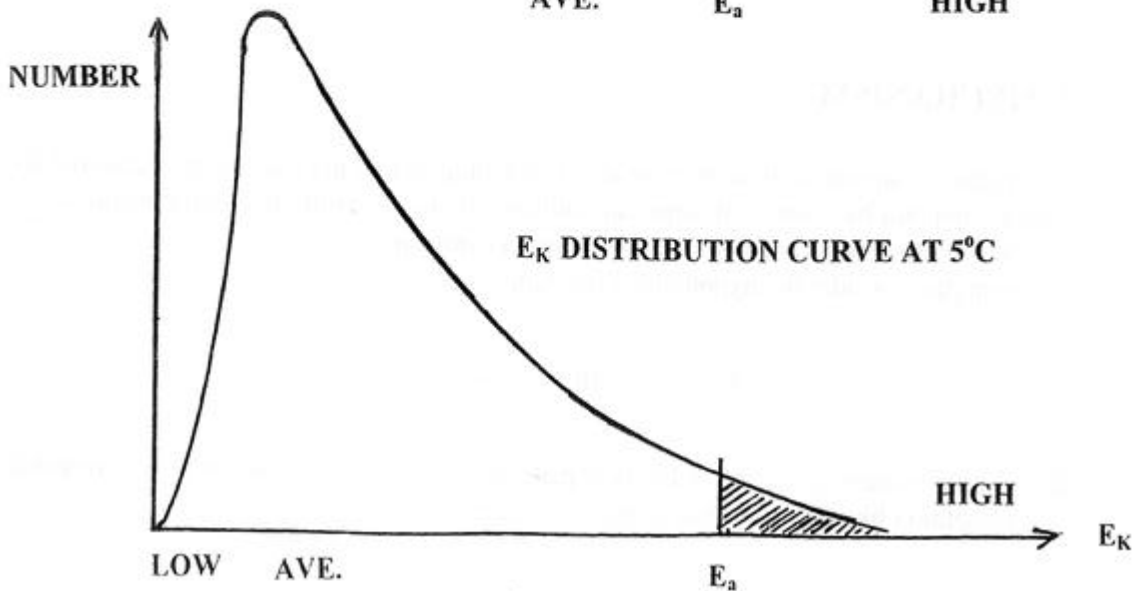
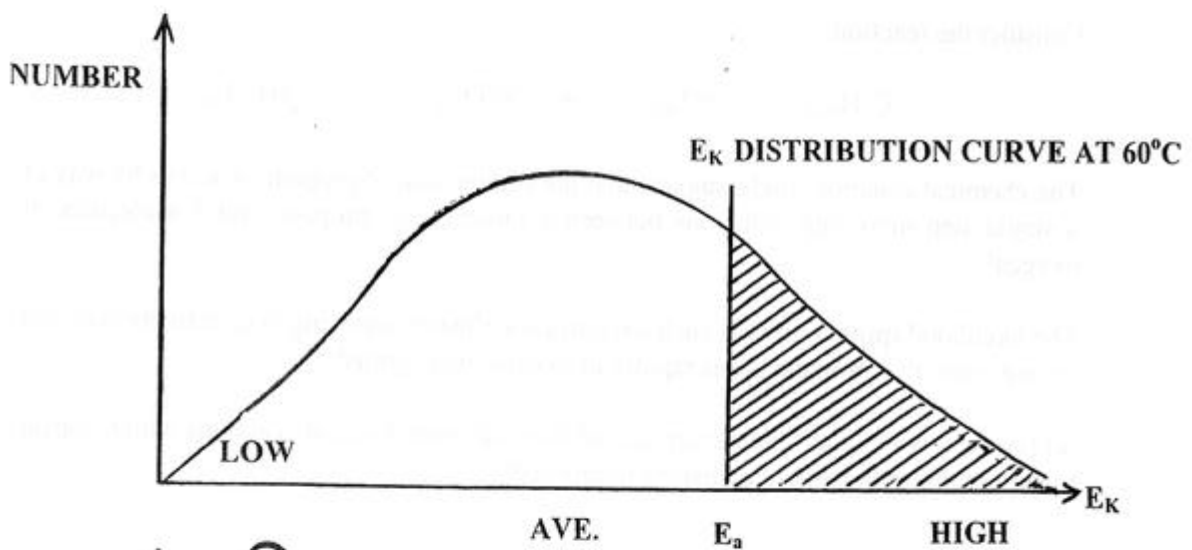
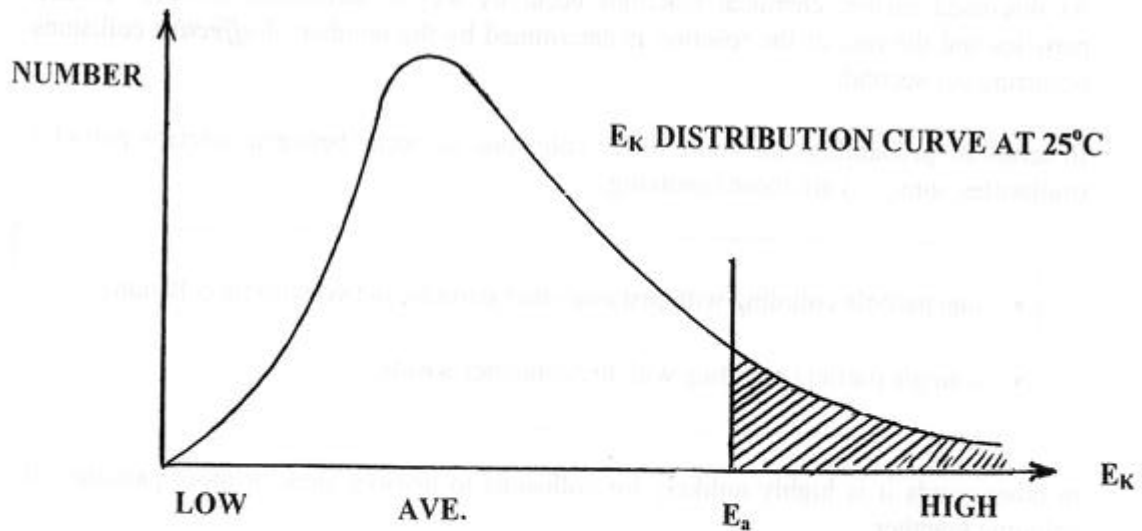
Consequently, a lowered temperature means that fewer molecules now possess the threshold energy and the reaction rate will have decreased considerably. The very much smaller shaded area in the lower diagram (to the right) indicates that few molecules will be sufficiently energetic to undergo effective collisions and react.



NOTE:

(i) It doesn't necessarily need a large temperature increase to produce a dramatic effect on the rates of reactions.

(ii) By lowering the temperature one can slow down chemical reactions too. This has applications in terms of food storage in refrigerators and freezers.



# REACTION MECHANISM

## 1. INTRODUCTION

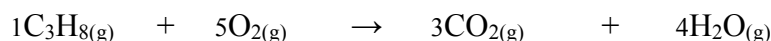
As discussed earlier, chemical reactions occur by way of collisions between reactant particles and the rate of the reaction is determined by the number of *effective* collisions occurring per second.

In terms of probability, the most likely collisions to occur between reactant particles (molecules, ions,....) are those involving:

- one particle colliding with just *one* other particle; (a two particle collision).
- a single particle colliding with the container's wall.

In other words it is highly unlikely for collisions to involve three or more particles all colliding together.

Consider the reaction:



The chemical equation might suggest that the combustion of propane proceeds by way of a single step involving collisions between 1 molecule of propane and 5 molecules of oxygen!

The likelihood (probability) of such a 6 particle collision occurring is effectively zero and yet we know that propane burns rapidly in oxygen once ignited.

So how can we explain the occurrence of this and other familiar reactions which appear to require multiple particle collisions to proceed?

## 2. MECHANISM

To explain situations such as the case above, we suggest that the reaction proceeds not by a single step but by a series of steps that individually involve only two particle collisions. This sequence of steps is called the "*reaction mechanism*".

For example, consider the hypothetical reaction:



Rather than occurring by the unlikely 5 particle collision of a single step, it is possible that something like the following sequence occurs:

STEP 1.	A	+	B	→	X	X = an intermediate species
STEP 2.	X	+	B	→	Y	Y = another intermediate
STEP 3.	Y	+	A	→	Z	Z = another intermediate
STEP 4.	Z	+	B	→	products	
Summing gives:	2A	+	3B	→	products	(note: X, Y & Z don't appear)

In other words we can explain complex reactions occurring by way of a sequence of 2 particle collision steps which often involve the formation and subsequent decomposition of intermediate species. (See page 16 for more details on ‘intermediates’)

When the net reaction is considered, the intermediates drop out.

Some reaction mechanisms involve steps where the collision between a single intermediate particle and the container wall is a key to the process.

This is probably the case in step 3 below:

i.e.

Consider	Q	+	2R	→	products	
STEP 1.	Q	+	R	→	X	X = intermediate
STEP 2.	X	+	R	→	Y	Y = another intermediate
STEP 3.			Y	→	products	
Summing gives:	Q	+	2R	→	products	(note: X & Y don't appear)

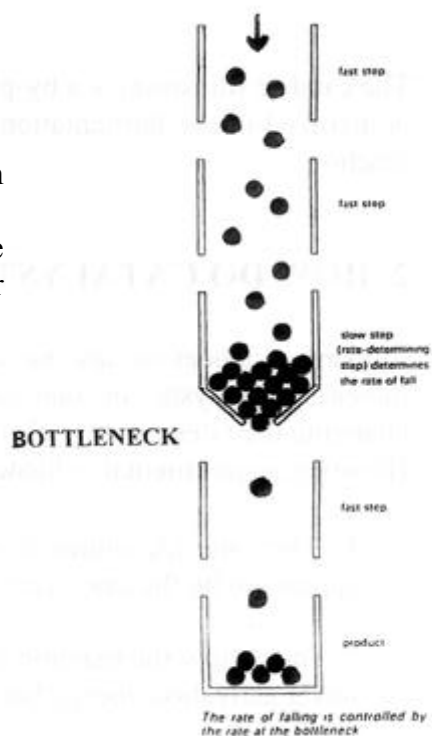
### 3. RATE DETERMINING STEP (R.D.S.)

Each of the individual steps in a reaction mechanism will have its own individual  $\Delta H$  and  $E_a$  barrier.

Whichever step has the highest  $E_a$  barrier will be the slowest step and is called the “rate determining step” or R.D.S.

This situation is easily understood if we consider a line of cars travelling along the road. The progress of the group of cars will be no faster than the slowest car.

The so-called “bottleneck” analogy to the right illustrates this rate determining step process very well!



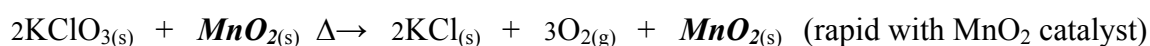
# CATALYSIS

## 1. INTRODUCTION

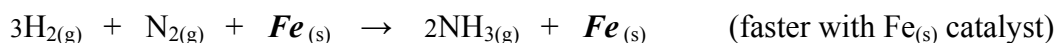
Catalysts are chemical reagents that have the capacity to make some chemical reactions occur faster and yet at the end of the reaction the catalyst is regenerated (i.e. it is not used up!)

There are thousands of examples of catalysts but the one key property is that they are regenerated at the completion of the reaction. (NOTE:  $\Delta \rightarrow$  means heating)

e.g. 1

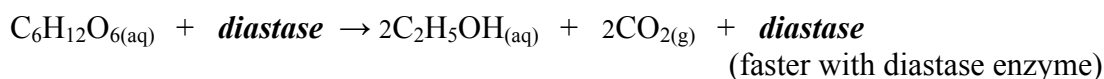
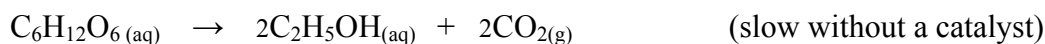


e.g. 2



Many biochemical reactions require catalysts in order to occur at all and the catalysts themselves are usually biochemical compounds which we call enzymes. Most enzymes have names with “*ase*” as the suffix.

e.g. 3 The process of fermentation of sugars such as glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) to produce the alcohol ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is familiar to home brewers and wine-makers. The reaction doesn't occur unless the enzyme **diastase** is present; i.e.



The catalyst (diastase) is a by-product of the growth of a yeast plant! Note that although it is involved in the fermentation reaction, diastase is regenerated at the completion of the reaction!

## 2. HOW DO CATALYSTS WORK?

In many instances we are not totally sure how the catalyst brings about this reaction rate increase. Catalysts for one particular reaction don't necessarily have any effect on changing the rates of other chemical reactions.

However, experimental evidence suggests that catalysts work in one of two main ways:

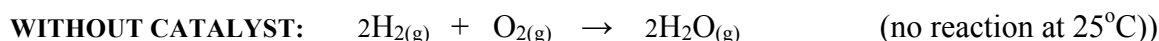
1. They provide a more favourable **surface** on which the reaction can take place. This appears to be the case when metals such as Pt and Fe act as catalysts.
2. They allow the reaction to proceed via a **different reaction mechanism** which has a lower activation energy barrier.

### 3. CATALYTIC SURFACES

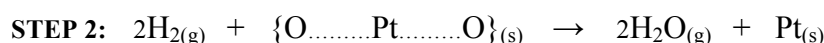
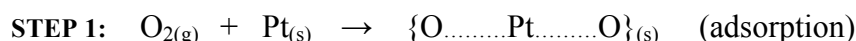
Mixtures of hydrogen and oxygen gases do not undergo reaction at 25°C. However, if the mixture is passed over a platinum metal surface, reaction does occur and yet the Pt surface is not altered.

It is thought that the oxygen molecules (O<sub>2</sub>) are adsorbed onto the surface of the Pt and separate into individual atoms of oxygen (O). This allows more effective collisions between H<sub>2</sub> molecules and O atoms and so the rate of reaction increases:

i.e.



**WITH Pt CATALYST:**



At the end of the reaction, the platinum surface is regenerated; a key factor in determining that Pt is acting as a catalyst!

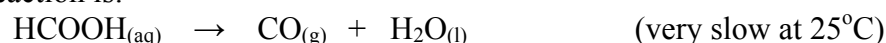
### 4. CATALYSTS & REACTION MECHANISM

For many processes it is clear that with a catalyst present, the reaction follows a completely *different pathway* (reaction mechanism) with the new pathway having a lower overall activation energy barrier (E<sub>a</sub>) than before.

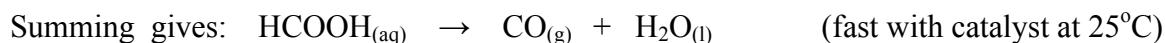
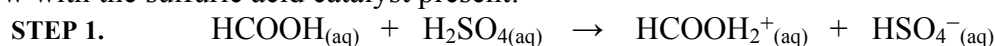
This lowered E<sub>a</sub> barrier means that some collisions between reactants that were previously ineffective, will now be effective, thus the rate is increased.

One well understood catalytic process is where concentrated sulfuric acid catalyses the decomposition of methanoic acid (HCOOH) into carbon monoxide and water.

The uncatalysed reaction is:



Now with the sulfuric acid catalyst present:



Note that the sulfuric acid *does* get chemically changed during the catalytic process, but in the final step (3) it is regenerated!

The catalysed reaction pathway has a lower E<sub>a</sub> barrier than the uncatalysed pathway and thus the **THRESHOLD ENERGY** is lowered. (See diagrams on pages 14 & 15)

With a catalyst present:

**THINGS THAT CHANGE**

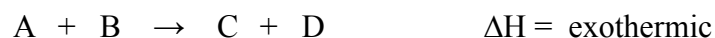
1. the reaction rate
2. the reaction mechanism (pathway)
3. the activation energy barrier (E<sub>a</sub>)
4. the threshold energy (E<sub>a</sub>)

**THINGS THAT DON'T CHANGE**

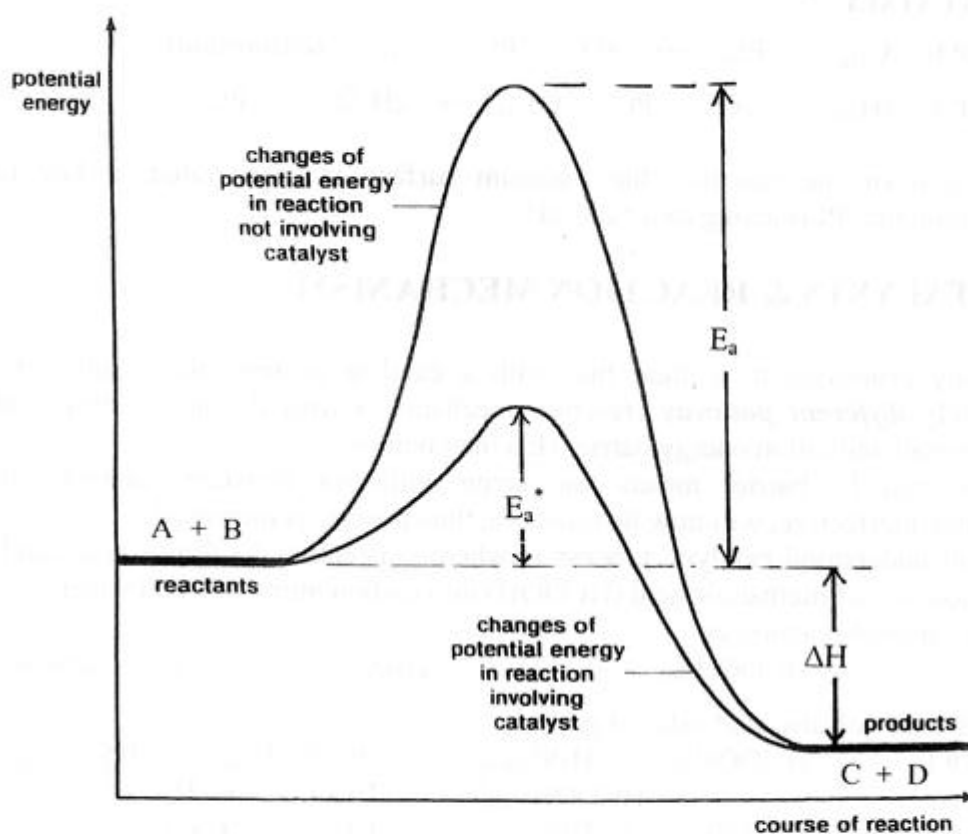
1. the reactants and products
2. the heat of reaction (ΔH)
3. the catalyst is (finally) unaltered
4. the E<sub>K</sub> distribution curve

## CATALYSTS & E<sub>p</sub> DIAGRAMS

Consider the chemical reaction between A and B to form products C and D:  
i.e.



The E<sub>p</sub> diagram below shows the effect of adding a catalyst and the subsequent lowering of the activation energy barrier. It can be seen from the diagram that the reaction proceeds via a one step mechanism!



In the presence of a catalyst, a different mechanism becomes available. The mechanism involving the catalyst has a lower activation energy than the mechanism which does not involve the catalyst.

### NOTES ON E<sub>p</sub> DIAGRAM ABOVE

A and B = reactants

C and D = products

E<sub>a</sub> = activation energy barrier (no catalyst)

E<sub>a</sub>\* = activation energy barrier (with catalyst)

R.C. = reaction co-ordinate ("time")

ΔH is the heat of reaction

E<sub>p</sub> is potential energy

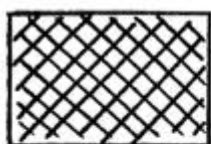
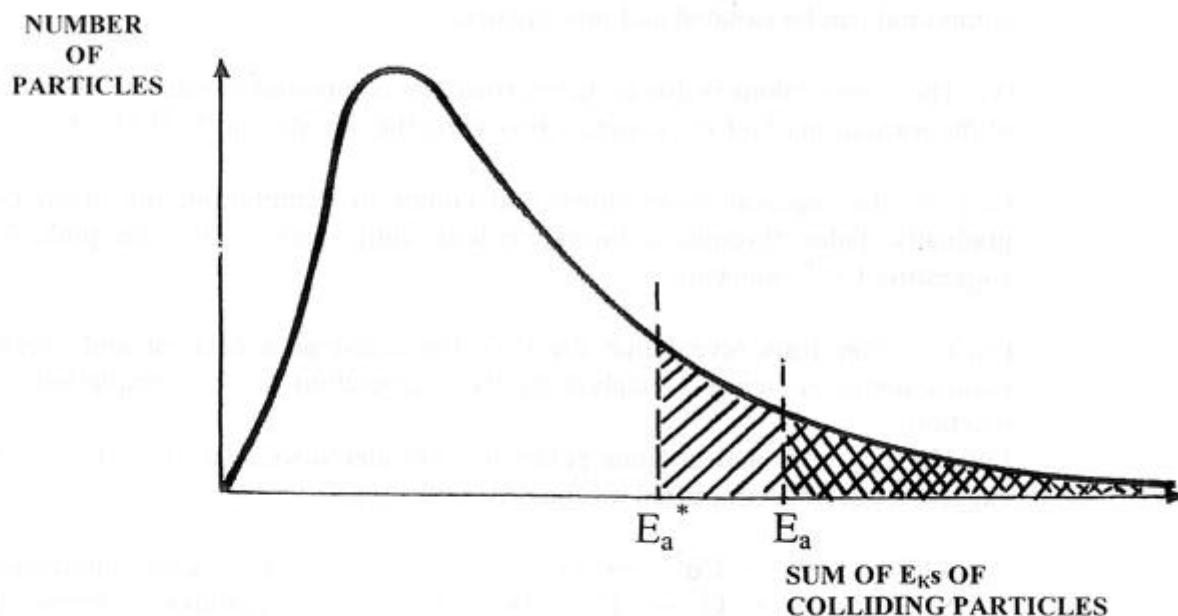
## CATALYSTS & THE $E_K$ DISTRIBUTION CURVE

As shown in the  $E_K$  distribution curve below, the addition of a catalyst lowers the threshold energy ( $E_a$ ), meaning that a greater proportion of reactants can undergo effective collisions and thus the reaction rate will have increased. The kinetic energy of the reactants hasn't altered but the  $E_a$  cut-off point has been lowered! Note:

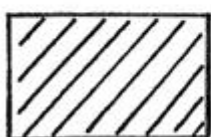
(i) Threshold energy **without** a catalyst =  $E_a$

(ii) Threshold energy **with** a catalyst =  $E_a^*$

This means that particles that previously didn't possess sufficient kinetic energy to undergo effective collisions and react, may now, in the presence of the catalyst, be able to react. The greater shaded area shows the increased proportion of molecules that may now undergo effective collisions.



This shaded area represents the proportion of colliding particles that possess sufficient  $E_K$  to undergo a reaction when NO catalyst is present.



This shaded area represents the **additional** proportion of colliding particles that possess sufficient  $E_K$  to undergo a reaction when a catalyst is present.

# INTERMEDIATE COMPOUND THEORY

We now see that catalysts allow chemical reactions to follow alternative pathways which have lowered activation energy barriers.

The alternative pathway often involves the formation of intermediate compounds which may even be isolated and chemically investigated.

A very good illustration of the formation of an **intermediate** is seen with the following experiment.

(i) Dissolve 3 g of sodium potassium tartrate (Rochelle's salt) in 50 mL of distilled water and heat to approximately 80°C.

(ii) Add 20 mL of 20 'vol'  $\text{H}_2\text{O}_{2(\text{aq})}$  and observe that no apparent reaction occurs.

(iii) Add 0.5 g of pink  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  crystals.  $\text{Co}^{2+}$  is a catalyst for this reaction.

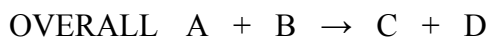
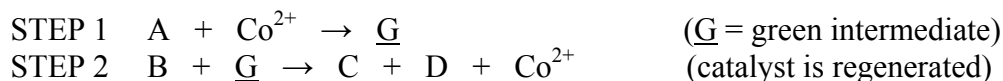
(iv) A vigorous reaction takes place in which a distinctive green intermediate compound is formed. Carbon dioxide gas is one of the products.

(v) By rapidly cooling the system whilst in the 'green' form, the intermediate compound can be isolated and investigated.

(vi) The green colour is due to an intermediate compound thought to be the result of the formation of a  $\text{Co}^{3+}$  complex involving the tartrate ion ( $\text{C}_4\text{H}_4\text{O}_6^{2-}$ ).

(vii) As the reaction slows down and comes to completion, the green colour gradually fades through a muddy colour until, once again the pink colour suggesting  $\text{Co}^{2+}$  reappears.

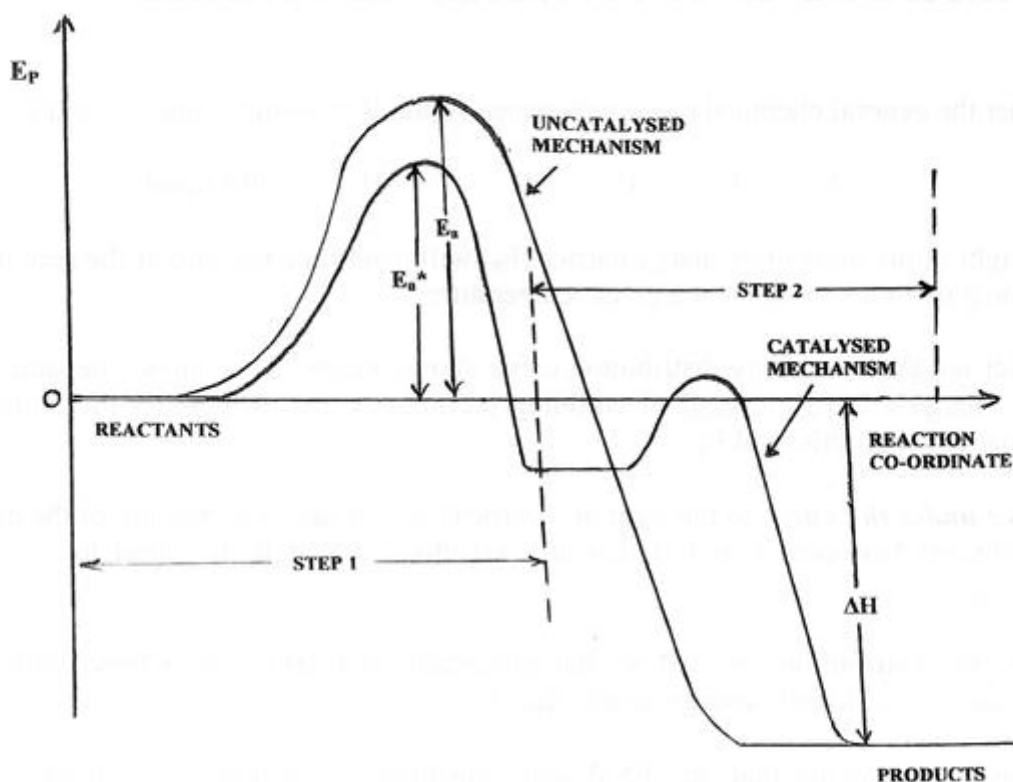
(viii) Further tests reveal that the  $\text{Co}^{2+}$  has acted as a catalyst and meets the requirements of being a catalyst by its regeneration at the completion of the reaction. Let  $\text{H}_2\text{O}_{2(\text{aq})} = \text{A}$  and sodium potassium tartrate ( $\text{NaKC}_4\text{H}_4\text{O}_6$ ) = B. We might suggest a possible simplified mechanism of the type:



In this 2 step proposed mechanism, the overall  $E_a$  barrier has been lowered and thus more effective collisions occur per second than previously, giving a faster reaction rate. The lowering of the barrier doesn't have to be very significant to often have dramatic effects on the rate.



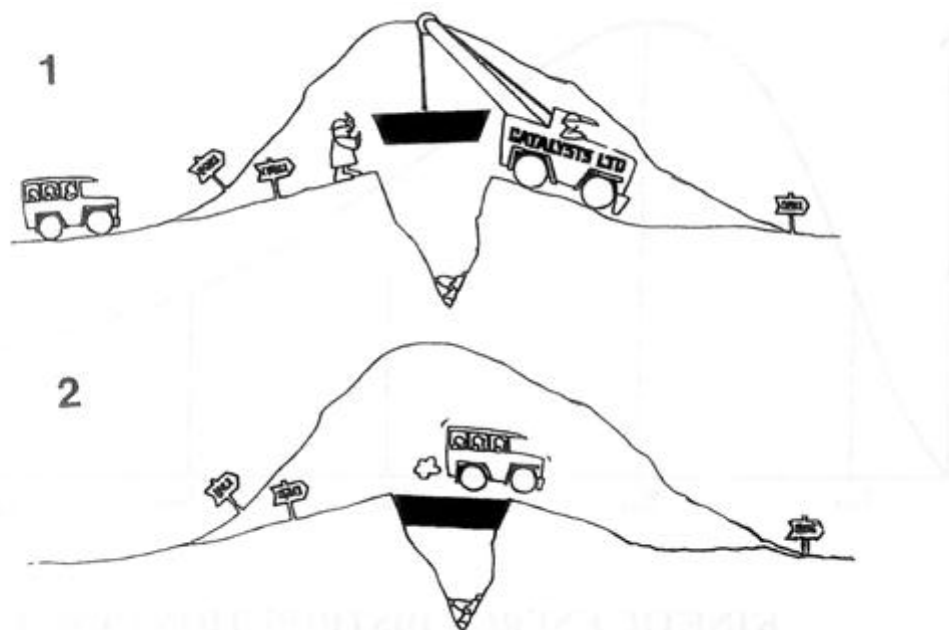
## A POSSIBLE $E_p$ DIAGRAM FOR THIS TWO STEP MECHANISM



NOTE:

The **higher** of the two activation energy barriers for the catalysed two step mechanism determines the rate of the catalysed reaction.

The lowering of the activation energy barrier from  $E_a$  down to  $E_a^*$  has not been a huge change and yet the reaction rate increases dramatically



A catalyst allows the reaction to proceed via a different 'pathway' (mechanism) with a lowered  $E_a$  barrier. This concept is neatly illustrated by the car analogy above!

Q8. If there was to be a third picture shown above, what should it indicate?

## THRESHOLD & ACTIVATION ENERGIES

Consider the general chemical reaction between A and B to form products C and D;  
i.e.



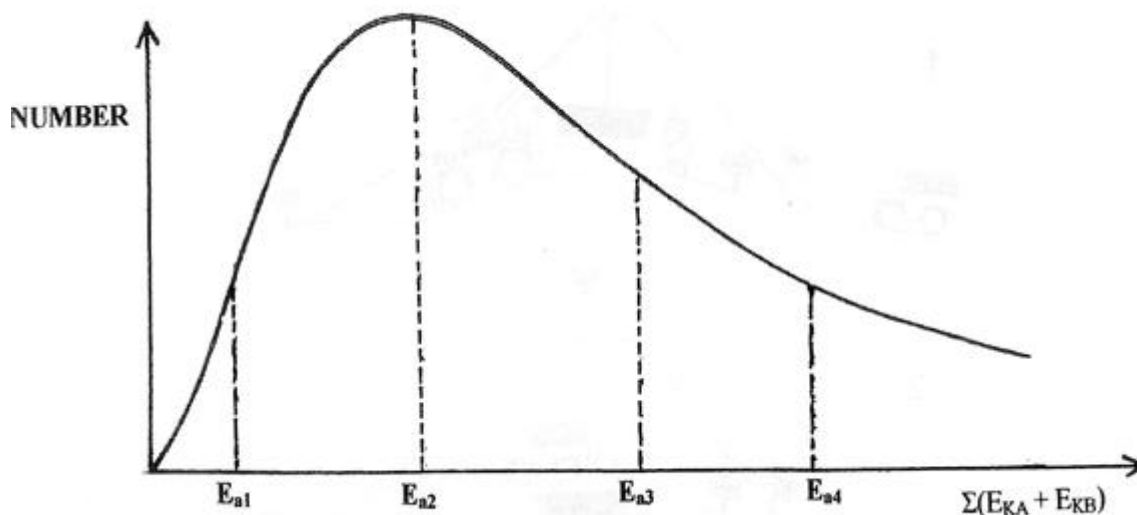
The height of the activation energy barrier ( $E_a$ ) will determine the rate of the reaction for combining particles A and B at a given temperature.

Consider the kinetic energy distribution curve shown below. This shows the sum of the kinetic energies,  $\Sigma(E_{KA} + E_{KB})$  of colliding particles A and B together the number of combinations with this total  $E_K$ .

The area ***under the curve*** to the right of a vertical cut-off line is a measure of the number of collisions between A and B that are 'effective' and will thus lead to a reaction occurring.

(i) From the distribution curve we see that practically **ALL** collisions between particles A and B have a total kinetic energy greater than  $E_{a1}$ .

(ii) Conversely, we see that very **FEW** collisions between particles A and B have a total kinetic energy greater than  $E_{a4}$ .



**KINETIC ENERGY DISTRIBUTION CURVE  
SHOWING 4 DIFFERENT THRESHOLD VALUES**

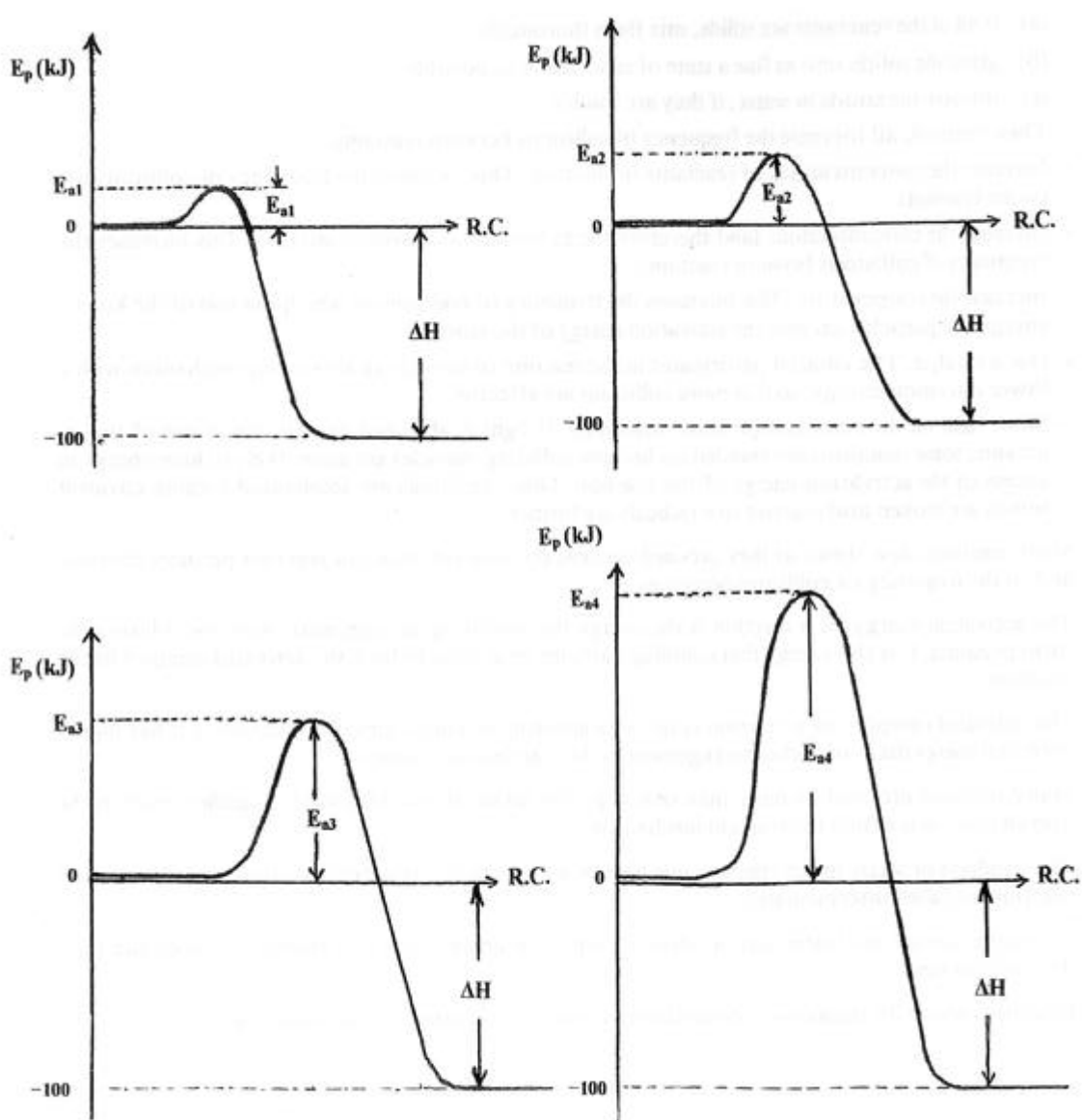
(CONTINUED)

The four potential energy curves shown below represent four different situations depending upon the height of the activation energy barrier.

If the barrier is very low as occurs with  $E_{a1}$ (diagram 1) it means that the majority of collisions between particles A and B will be effective and thus the reaction rate will be high.

If the barrier is very high as occurs with  $E_{a4}$ (diagram 4) it means that very few of the collisions between particles A and B will be effective and thus the reaction rate will be very low.

The other two diagrams show the intermediate situations.



**FOUR DIFFERENT ACTIVATION ENERGY BARRIERS**

# THEORY SUMMARY

## SUMMARY

Some reactions are fast and others are slow.

The simplest ways to express the rate of a chemical reaction are

- the amount of reactant used up in a given time
- the amount of product formed in a given time.

The rate of a reaction can be increased in the following ways:

- For reactions involving solids,
  - (a) if all of the reactants are solids, mix them thoroughly
  - (b) grind the solids into as fine a state of subdivision as possible
  - (c) dissolve the solids in water, if they are soluble.

These methods all increase the frequency of collisions between reactants.

- Increase the concentrations of reactants in solution. This increases the frequency of collisions between reactants.
- Increase the concentrations (and therefore the pressures) of gaseous reactants. This increases the frequency of collisions between reactants.
- Increase the temperature. This increases the frequency of collisions in which the sum of the kinetic energies of particles exceeds the activation energy of the reaction.
- Use a catalyst. The catalyst participates in the reaction to provide an alternative mechanism with a lower activation energy, so that more collisions are effective.
- Shine light on the reactants (of some reactions). If light is absorbed by particles of one of the reactants, some reactions are speeded up because colliding particles are more likely to have energy in excess of the activation energy of the reaction. Other reactions are accelerated because covalent bonds are broken and reactive free radicals are formed.

Most reactions slow down as they proceed because the concentrations of reactant particles decrease and so the frequency of collisions decreases.

The activation energy of a reaction is the energy that colliding particles must have for collisions to form products. It is the energy that colliding particles must have to form the activated complex of the reaction.

The activated complex of a reaction is the arrangement of atoms, ions or molecules that has higher potential energy than any other arrangement in the reaction mechanism.

Many reactions proceed by more than one step. The series of reactions which together result in the overall reaction is called the reaction mechanism.

The products of steps in the reaction mechanism which are not reactants or products of the overall reaction are called intermediates.

A reaction cannot go faster than its slowest step. The slowest step in a reaction is called the rate-determining step.

Inhibitors react with important intermediates in reactions, causing the reactions to go slower.

## REVISION QUESTIONS

Q9. In a given reaction, 0.126 mole of product A ( $M_r(A) = 80.0$ ) is formed within a solution of volume 750 mL during a period of 2 minutes 16 seconds.

- (i) What is the rate of formation of A in units of  $\text{mol s}^{-1}$ ? **( $9.26 \times 10^{-4} \text{mol s}^{-1}$ )**  
(ii) What is the rate of formation of A in units of  $\text{g s}^{-1}$ ? **( $0.0741 \text{g s}^{-1}$ )**  
(iii) What is the rate of formation of A in units of  $\text{mol L}^{-1} \text{s}^{-1}$ ? **( $1.24 \times 10^{-3} \text{mol L}^{-1} \text{s}^{-1}$ )**

Q10. Which is likely to be the faster reaction at  $25^\circ\text{C}$ :

- (i)  $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$  or  
(ii)  $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4$ ? Explain your answer. **(ii)**

Q11. A mixture of propane gas and oxygen is quite stable at  $25^\circ\text{C}$  (i.e. no reaction occurs). However, if the mixture is sparked, an explosion occurs. Why?

Q12. Once a match has been used to ignite the bunsen burner gas, it continues to burn when the match is taken away. Why?

Q13. In terms of the factors that affect reaction rates, explain the following observations:

- an iron anchor left in deep sea-water corrodes very slowly.
- bushfires are more likely to occur on hot, dry and windy days.
- food stored in a freezer may keep in good condition for many months.
- aluminium powder is highly explosive if ignited in air.
- an egg fries much faster in hot oil at  $250^\circ\text{C}$  than an egg cooks in water at  $100^\circ\text{C}$ .
- people with lung disorders are often required to breathe pure  $\text{O}_2$  rather than air.
- a few drops of  $\text{CuSO}_{4(\text{aq})}$  increases the reaction rate between zinc and  $\text{HCl}_{(\text{aq})}$  and yet the  $\text{CuSO}_{4(\text{aq})}$  is not consumed.

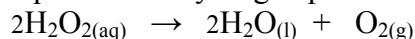
Q14. When 1.00 mole of methane ( $\text{CH}_4$ ) burns in oxygen gas ( $\text{O}_2$ ) the bond breaking process requires 3380 kJ of energy and then there is 4270 kJ of energy released as new bonds form. (The following questions relate to the equation showing 1 mole of methane)

- (i) Write a balanced chemical equation for this combustion process.  
(ii) Calculate the  $\Delta H$  value for the combustion (forward) reaction. **( $\Delta H = -890 \text{kJ}$ )**  
(iii) What is the activation energy for the combustion process? **( $E_a = +3380 \text{kJ}$ )**  
(iv) Draw and label a potential energy diagram for this combustion process.  
(v) What is the  $E_a$  barrier for the reverse reaction? **( $E_a = +4270 \text{kJ}$ )**  
(vi) What is the  $\Delta H$  value for the reverse reaction? **( $\Delta H = +890 \text{kJ}$ )**

Q15. Consider:  $\text{H}_{2(\text{g})} + \text{I}_{2(\text{g})} \rightarrow 2\text{HI}_{(\text{g})} \Delta\text{H} = +28 \text{ kJ} \ \& \ E_{\text{a}} = +167 \text{ kJ}$

- (i) What is the value of  $\Delta\text{H}$  for the reverse reaction? ( $\Delta\text{H} = -28 \text{ kJ}$ )  
(ii) What is the value of  $E_{\text{a}}$  for the reverse reaction? ( $E_{\text{a}} = +139 \text{ kJ}$ )

Q16. The decomposition of hydrogen peroxide is slow at room temperature:



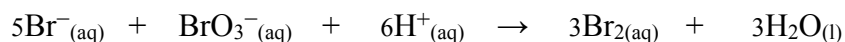
However if a few crystals of manganese dioxide or a piece of platinum metal foil is added to the hydrogen peroxide solution, it decomposes rapidly. What tests would you need to carry out to determine whether  $\text{MnO}_2$  (or Pt) was acting as a catalyst?

Q17. Consider the following methods for extinguishing different types of fires.

- (i) water is used to extinguish a burning wood fire.  
(ii) dry powder is used for extinguishing electrical fires.  
(iii) foam is used to extinguish volatile fuel fires such as burning petrol.

Explain why each is used and how the action causes the extinguishing of the fire.

Q18. Consider the chemical reaction between bromide ions and bromate ions in an acidic solution:



Is it likely that the reaction mechanism for this redox process occurs by a single step reaction? Explain your answer.

Q19. The reaction between marble chips ( $\text{CaCO}_{3(\text{s})}$ ) and dilute  $\text{HCl}_{(\text{aq})}$  is rapid initially but after a few minutes the rate slows and the reaction eventually stops.

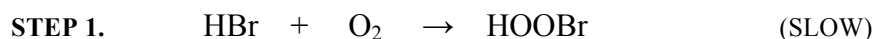
Why do the rates of chemical reactions such as this one, decrease as the reactions proceed? Explain carefully in terms of the factors that affect rates of reactions.

Q20. A chemist wishes to investigate the rate of the chemical reaction involving the oxidation of colourless nitric oxide gas ( $\text{NO}$ ) to form brown nitrogen dioxide gas ( $\text{NO}_2$ )



Suggest several simple methods for following the course of the reaction and hence determining the reaction's rate.

Q21. The mechanism for the reaction between  $\text{HBr}_{(\text{g})}$  and  $\text{O}_{2(\text{g})}$  gases is:



- (i) Use the three step mechanism given to deduce the *net* reaction occurring.  
(ii) Which of the chemical species shown are intermediates? Why?  
(iii) Which is the rate determining step? Why?

Q22. A student states that "the rate of a chemical reaction is directly proportional to the number of collisions occurring between reactants per unit time."

Comment on the validity of this statement and suggest a corrected alternative.

Q23. Just as catalysts enable reactions to go faster, we can also add chemicals that will slow down reaction rates. These substances are called **INHIBITORS**. We encountered some such chemicals in our discussion on corrosion protection.

- (i) How might an inhibitor react to slow down a chemical reaction?
- (ii) Why are inhibitors **not** referred to as “*negative catalysts*”?

Q24. Why is an ‘oxy-acetylene’ flame very much hotter than an ‘air-acetylene’ flame?

Q25. To produce hydrogen gas, a chemist added large chunks of zinc metal to dilute hydrochloric acid. She found that the rate of reaction was too slow.

Suggest 4 changes that she could use to increase the rate of this reaction.

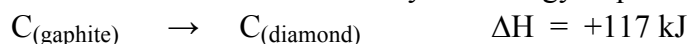
Q26. In industrial processes, the use of catalysts is much preferred to using high temperatures or pressures to increase rates. Why are catalysts a better option?

Q27. In the production of aluminium, the bauxite ore is crushed to a fine powder before the purification (leaching) process with  $\text{NaOH}_{(\text{aq})}$  commences. Why is this done?

Q28. (i) A mixture of hydrogen and chlorine is stable in the dark but will explode if exposed to daylight. Suggest a possible reason for the presence of daylight to cause the explosion?

(ii) Why is red wine usually stored in dark green or dark brown bottles but white wine isn’t?

Q29. The conversion of graphite into diamond has a relatively low energy requirement; i.e.



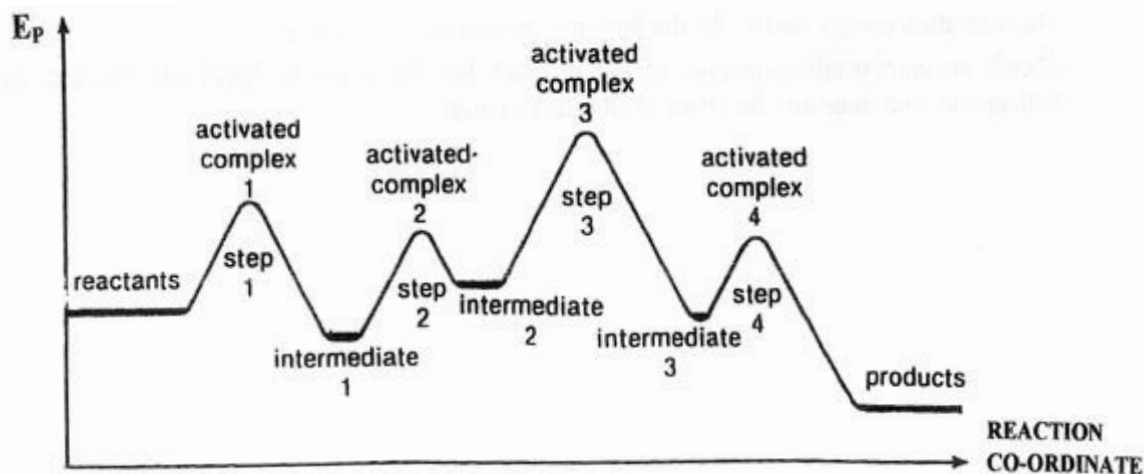
By considering the other features of the  $E_p$  diagram for this conversion, suggest why the process is extremely difficult to carry out even though  $\Delta H$  is quite small.

Q30. Some reactions are ones where the rate is not altered significantly by increases in temperature. What particular type of reaction might this apply to?

(HINT: would the  $E_a$  barrier be high or very low?)

Q31. Consider the following  $E_p$  diagram:

- (i) Indicate  $\Delta H$  for the overall process.
- (ii) Which step involved an endothermic change? **(step 2)**
- (iii) Which is likely to be the rate determining step? Why? **(step 3)**



# REVISION TEST

## CHEMISTRY (LEVEL 3C) CHEMICAL KINETICS TEST

(20 marks)

Q1. Consider the given chemical reaction:



A chemist wishes to investigate the **rate** of the decomposition reaction shown above.

(a) Suggest **two** possible variables in the system that would allow the chemist to measure the rate of the reaction.

(i) VARIABLE 1 = .....

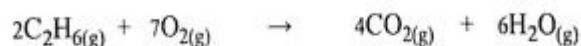
(ii) VARIABLE 2 = .....

(2 marks)

(b) Select one of these variables and explain how it will change as the forward reaction proceeds.

(2 marks)

Q2. Consider the reaction:



In a given experiment involving the combustion of ethane, the rate of consumption of ethane gas is  $6.40 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . What is the rate of:

(i) consumption of oxygen? .....

(ii) formation of water? .....

(iii) formation of carbon dioxide? .....

(3 marks)

Q3. Consider the hypothetical reaction:



The activation energy barrier for the forward reaction is  $E_a = +100 \text{ kJ}$ .

Sketch an appropriate potential energy diagram for the reaction. Label all relevant details. Indicate on your diagram the effect of adding a catalyst.

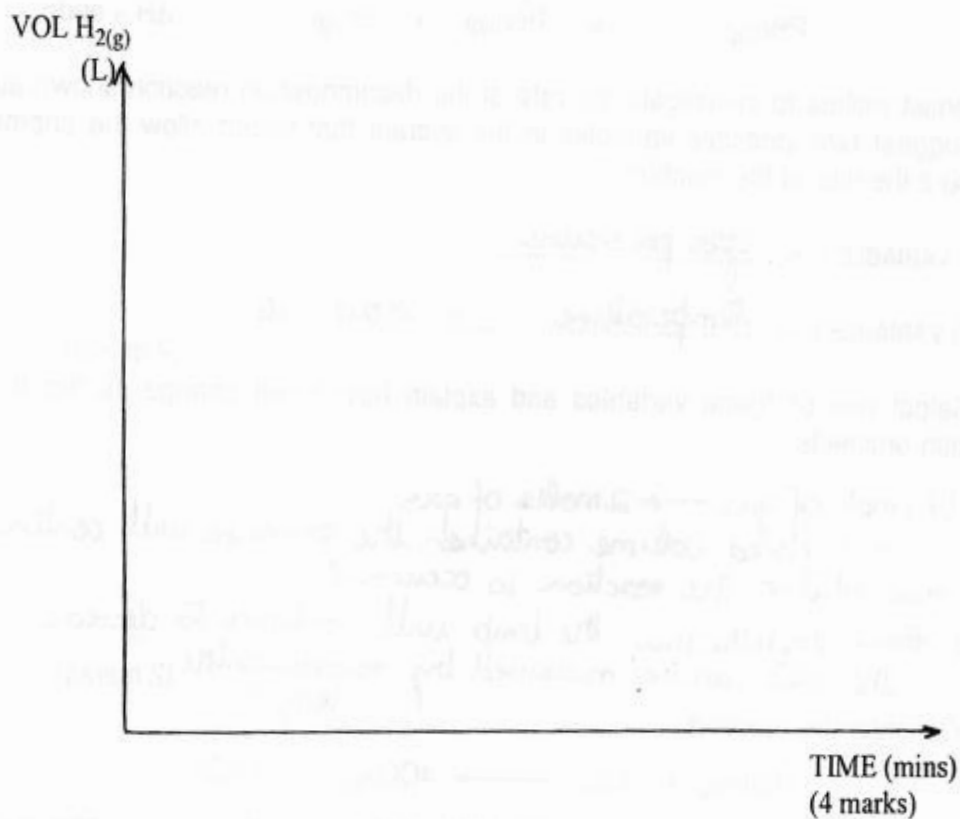


Q4. In two separate experiments, 0.100 mole of magnesium metal ( $\text{Mg}_{(s)}$ ) is reacted with excess hydrochloric acid ( $\text{HCl}_{(aq)}$ )

In experiment 1, the  $[\text{HCl}_{(aq)}] = 0.50 \text{ mol/L}$  ( $20^\circ\text{C}$ )

In experiment 2, the  $[\text{HCl}_{(aq)}] = 2.00 \text{ mol/L}$  ( $20^\circ\text{C}$ )

On the axes below sketch graphs of the volume of hydrogen gas at STP versus time for the two experiments.



Q5. Explain why the rate of many chemical reactions is increased by increasing the temperature of the reactants. Use diagram(s) to illustrate your answer.

# TEST ANSWERS

NAME: ANSWERS

## CHEMISTRY CHEMICAL KINETICS TEST

(20 marks)

Q1. Consider the given chemical reaction:



A chemist wishes to investigate the rate of the decomposition reaction shown above.

(a) Suggest two possible variables in the system that would allow the chemist to measure the rate of the reaction.

(i) VARIABLE 1 = gas pressure

(ii) VARIABLE 2 = temperature + colour ... etc

(2 marks)

(b) Select one of these variables and explain how it will change as the forward reaction proceeds.

(i) 1 mole of gas  $\rightarrow$  2 moles of gas  
 $\therefore$  in a fixed volume container, the pressure will continue to rise whilst the reaction is occurring.

(ii) Being 'endothermic', the temp. will continue to decrease  
 $\therefore$  the rate can be measured by recording the temp. (2 marks)

Q2. Consider the reaction:



In a given experiment involving the combustion of ethane, the rate of consumption of ethane gas is  $6.40 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . What is the rate of:

(i) consumption of oxygen?

$$6.40 \times 10^{-4} \times \frac{7}{2} = 2.24 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

(ii) formation of water?

$$6.40 \times 10^{-4} \times \frac{6}{2} = 1.92 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

(iii) formation of carbon dioxide?

$$6.40 \times 10^{-4} \times \frac{4}{2} = 1.28 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

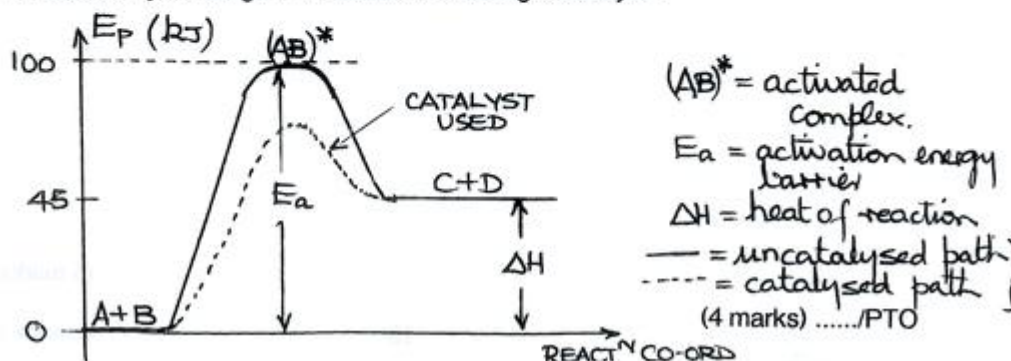
(3 marks)

Q3. Consider the hypothetical reaction:



The activation energy barrier for the forward reaction is  $E_a = +100 \text{ kJ}$ .

Sketch an appropriate potential energy diagram for the reaction. Label all relevant details. Indicate on your diagram the effect of adding a catalyst.

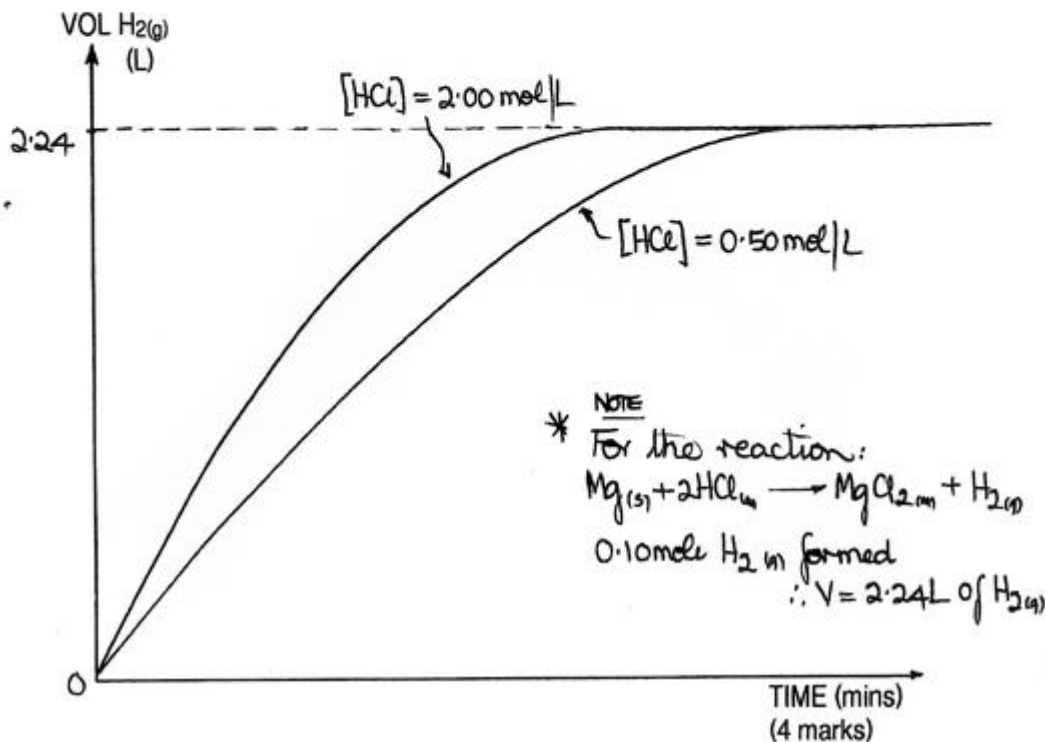


Q4. In two separate experiments, 0.10 mole of magnesium metal is reacted with excess hydrochloric acid.

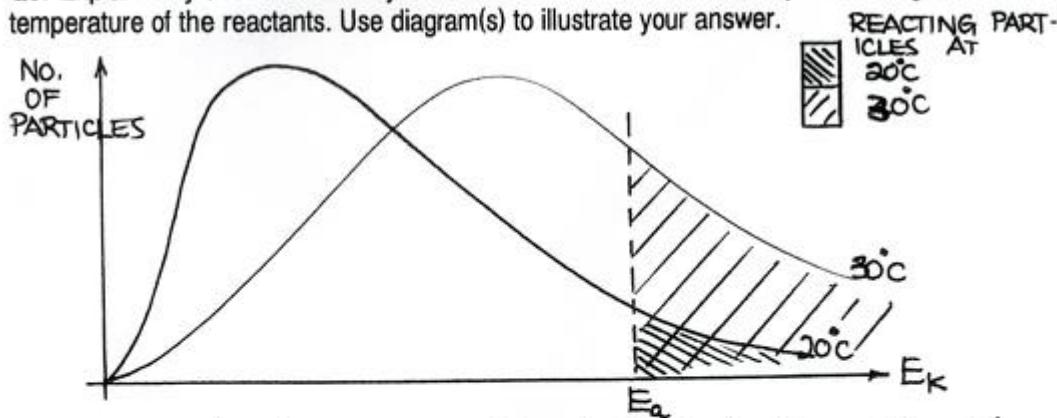
In experiment 1, the  $[HCl_{(aq)}] = 0.50 \text{ mol/L}$  ( $20^\circ\text{C}$ )

In experiment 2, the  $[HCl_{(aq)}] = 2.00 \text{ mol/L}$  ( $20^\circ\text{C}$ )

On the axes below sketch graphs of the volume of hydrogen gas at STP versus time for the two experiments.



Q5. Explain why the rate of many chemical reactions is increased by increasing the temperature of the reactants. Use diagram(s) to illustrate your answer.



Increasing the temperature of reactant species from  $20^\circ\text{C} \rightarrow 30^\circ\text{C}$  changes the distribution of molecular kinetic energies. Thus, at the higher temp. there are more collisions/sec and the collisions are more energetic  $\therefore$  more "EFFECTIVE" collisions/sec  $\therefore$  a greater number of collisions exceed the threshold energy ( $E_a$ ) i.e. <sup>more</sup> reactants cross the activation energy barrier/sec  $\Rightarrow$  faster reaction rate.