

NLSC (New Lower Secondary Curriculum) by kisjo.

# RATE OF CHEMICAL REACTIONS, REVERSIBLE AND IRREVERSIBLE REACTIONS

# Rate of reaction

Some reactions proceed very fast. For example, when aqueous ammonia is added to a solution of lead (II) salts, a white precipitate form immediately.

Some reactions proceed at moderate speed. For example, it takes some time for the reaction between calcium carbonate and dilute hydrochloric acid to come to completion.

Other reactions are slow. For example, it takes iron a few days to rust in moist air. The above-mentioned reactions proceed at different rates.

The rate of a chemical reaction is the speed at which products are formed or the speed at which reactants are used up in the reaction.

Rate of reaction = <u>concentration in moles per litre</u>

Time in seconds

Units for the rate of reaction are moles/litre/second (i.e mol/l/s). **Determination of rate of reaction** 

Let us consider the reaction between magnesium and dilute hydrochloric acid.

 $Mg_{(s)} + 2HCI_{(aq)} \rightarrow MgCI_{2(aq)} + H_{2(g)}$ 

The determination of the rate of this reaction can be done by either measuring the volume of hydrogen evolved with time or by measuring the time a given length of magnesium ribbon takes to dissolve in varying concentrations of the acid.

Determination of rates of reaction by measuring the volume of the gas evolved with time

A known mass of magnesium and a known volume of dilute hydrochloric acid in a testtube tied with a thread, are placed in a conical flask and the experiment is set up as shown in the figure below.

The stopper is opened for a moment so that thread is free. The test-tube drops pouring hydrochloric acid into the conical flask.

At the same time, the clock is started. The volume of hydrogen in the syringe is Always revise as if tomorrow is not there! Page 1 | 18

recorded at regular intervals until the reaction is complete

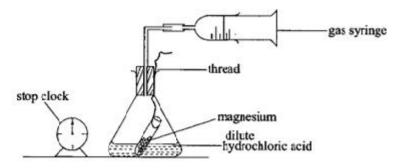
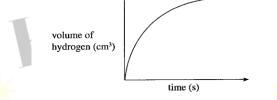
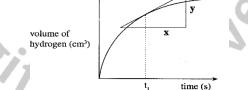


Fig 11.1 Determination of rate of reaction

A graph of volume of hydrogen evolved against time is plotted. A typical graph has the form below.



To determine the rate of reaction at a given time, say  $t_1$ , the tangent to the curve is drawn at that time as shown in the figure below. The gradient of the tangent is the rate of reaction at that time that is y/x. the units are cm<sup>3</sup>/s.



# Factors affecting the rate of chemical reactions

Factors which affect the rate of a chemical reaction are;

- Concentration
- Temperature
- Catalyst
- Surface area (particle size),
- Light
- Pressure

# Effect of concentration of reactants on the rate of reaction

The higher the concentration, the higher the rate of reaction and the lower the concentration, the lower the rate of reaction.

This is because increase in concentration brings the reactant particles close to one another hence increasing the chances of the reactant particle to collide and react

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#### with one another.

volume (cm<sup>3</sup>)

### Experiment to investigate the effect of concentration on the rate of the reaction

Make a mark with blue or black ink on a piece of paper. Place 50 cm<sup>3</sup> of 0.05 M sodium thiosulphate solution into a beaker. Add 10 cm<sup>3</sup> of 1 M hydrochloric acid to the sodium thiosulphate and at the same time start the stop clock.

Gently shake the mixture to mix the solution well and place the beaker on the paper over the mark. Watch the mark through the solution from above the beaker.

Stop the clock when the mark just disappears. Vary the concentration of the thiosulphate solution by taking 40, 30, 20 and 10cm<sup>3</sup> each time by adding distilled water.

Tabulate your results including 1/time. Plot graphs of volume of sodium thiosulphate solution against1/time (time<sup>-1</sup>) and against time.

The rate of reaction is proportional to the reciprocal of time (time<sup>-1</sup>). Your graphs should appear as shown in figure 11.4a and 11.4b.

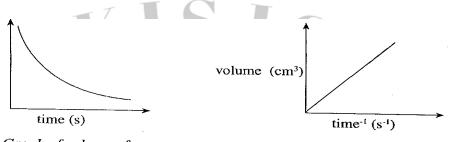


Fig 11.4a Graph of volume of sodium thiosulphate against time

Fig 11.4b Graph of volume of sodium thiosulphate agaist time -1

The mark disappears because the reaction between hydrochloric acid and sodium thiosulphate forms a precipitate of sulphur which renders the mixture opaque.

 $Na_2S_2O_{3(aq)} + 2HCI_{(aq)} \rightarrow 2NaCI_{(aq)} + S_{(s)} + H_2O_{(l)} + SO_{2(g)}$ 

Figure 11.4a shows that the higher the volume of the sodium thiosulphate, the less the time taken to form a precipitate.

Figure 11.4b shows that the rate of the reaction increases with increase in volume of sodium thiosulphate solution.

### Effects of temperature on the rate of reaction

The higher the temperature, the higher the rate of reaction and the lower the temperature the lower the rate of reaction.

This is because increase in temperature increases the kinetic energy of the reactant particles which increases their speed of movement.

The frequency at which the reacting particles collide increases and thus the rate of the reaction increases.

#### Experiment to investigate the effect of temperature on the rate of reaction

The previous experiment can be repeated by reacting sodium thiosulphate solution and hydrochloric acid at varying temperatures, using the same concentration of the thiosulphate.

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Put a test- tube containing 1 M hydrochloric acid into a beaker of water maintained at 30  $^{\circ}C$ . After sometime, add at the same time start of 0.05 M sodium thiosulphate solution in a beaker and at the same time start mark.

Note the time taken for the mark to disappear. The experiment is repeated using different temperatures. Tabulate your results including 1/time. Plot graphs of temperature against 1/time. The shapes of typical graphs are shown in figure 11.5a and 11.5b.

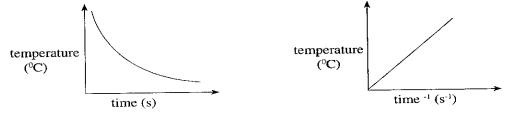


Fig 11.5a Graph of temperature against time

Fig 11.5b Graph of temperature against time -<sup>1</sup>

Figure 11.5a shows that the higher the temperature the less the time taken to form a precipitate.

Figure 11.5b shows that the rate of the reaction increases with increase in temperature.

Effect of a catalyst on the rate of reaction

A catalyst is a substance which changes the rate of chemical reactions without undergoing any overall chemical change itself.

Most catalysts speed up the rate of reaction.

The greater the amount of the catalyst but within the limits, the higher the rate of reaction.

Powdered catalysts offer a larger surface area over which the reaction takes place and therefore are more effective than one in lump form.

Catalysts remain unchanged chemically after a reaction has taken place. Catalysts are very specific to a particular chemical reaction.

A catalyst which slows down a reaction is called a negative catalyst.

Experiment to investigate the effect of catalyst on the rate of reaction The effect of catalysts during the local preparation of alcohol.

In the carbon in life/organic chemistry chapter, you learnt that ethanol is manufactured using traditional method.

One of the raw materials used during the manufacture is roasted germinated sorghum.

Which substance is added to roasted germinated sorghum and why?

#### Collision theory and activation energy

### Collision theory

Collision theory states that for a chemical reaction to occur, the reacting particles must collide

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with one another.

The rate the reaction depends on the frequency of successful collisions

#### Activation energy

This is the minimum amount of energy that the colliding particles must have in order to react and form products.

•

# Principles of collision theory

- Particles must collide.
- Particles must collide with energy above the activation energy.
- Particles must collide with proper orientation

# Sample question

Use collision theory to explain why decrease in;

- (i) concentration of reactants decrease the rate of reaction.
- (ii) temperature decreases the rate of reaction.
- (iii) surface area decreases the rate of reaction.

# Suggested answers

(i) When the concentration of the acid is high, the reaction goes faster. In concentrated hydrochloric acid, there are more particles, which means there is a high chance of an acid particle colliding with magnesium atom. In less concentrated acid, there are less acid particles, hence there are less chances of successful collision occurring.

- (ii) Increase in temperature increases the rate of reaction, at low temperature, few reacting particles have energy above the activation energy. However when the temperature is increased, more particles gain energy above the activation energy, thereby increasing the effective collision.
- (iii) Rate of reaction increases with increase in surface area, when the reactant are granular.

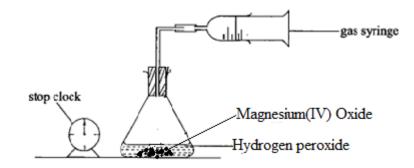
# Investigating the effect of a manganese (IV) oxide on the decomposition of hydrogen peroxide.

Place 100 cm<sup>3</sup> of 0.1M hydrogen peroxide in a conical flask.

Add 0.5g of manganese (IV) oxide to the hydrogen peroxide.

Then set up the experiment as shown in figure below.

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Equation for the reaction

 $H_2O_2(I) \longrightarrow 2H_2O(I) + O_2(g)$ 

Record the volume of oxygen in the syringe at regular intervals until the reaction is complete.

Repeat the experiment using 1g of manganese (IV) oxide.

Record the results of oxygen obtained in the table below.

Number of experiments	1 <sup>st</sup> experiment	2 <sup>nd</sup> experiment
Amount of gas produced.		$\mathbf{T}$

Sample questions.

1. Write an equation for the decomposition of hydrogen peroxide.

 $H_2O_2(I) \longrightarrow 2H_2O(I) + O_2(g)$ 

2. Describe the role of manganese (IV) oxide in the first experiment.

To speed up or increase the rate of decomposition of hydrogen peroxide.

3. Describe the role of germinated barley seed during the preparation of alcohol locally.

Germinated barley seeds act as a catalyst increasing the rate of the chemical reactions.

- 4. In the Haber process a catalyst called Ruthenium is used or iron fillings. In the contact process Vanadium(V) oxide or platinum is used. In the Ostwald's process platinum foil or copper is used.
  - a) What do these catalysts do?

They increase the speed or rate at which reactions take place.

b) How do they do it?

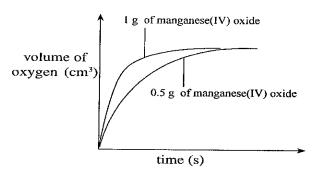
They lower the activation energy.

Plotting of the graphs.

When the graphs of volume of oxygen against time are plotted using the same axes, they

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appear as shown in figure below.



# Effect of surface area on the rate of reaction

Increase in surface area increases the rate of reaction and reduction in surface area reduces the rate of reaction.

This is because increase in surface area exposes the reactant molecules to be able to react with one another.

Solids react much more rapidly when powdered than when in large lumps. This is because reactions with solids take place at the surface.

Powdered solids present a large surface area over which the reaction occurs than solids in lump form.

#### Effect of surface area on the rate of reaction

Powdered limestone is usually added by farmers to neutralize acidic soil instead of lumps of limestone.

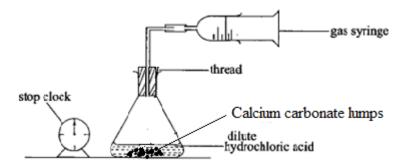
#### Why is this so?

This because powdered solids present a large surface area over which the reaction occurs than solids in lump form.

# Investigating the effect of surface area on the rate of reaction.

Pour 20 cm³ of 1 M hydrochloric acid in a conical flask.

To the conical flask add 10 g of calcium carbonate lumps and then set up the experiment as shown in figure below.

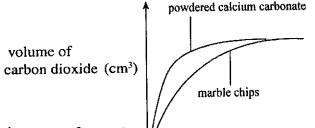


Record the volume of carbon dioxide in the syringe at regular intervals until the reaction is complete like for 8 minutes.

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Repeat the experiment using the same mass of powdered calcium carbonate.

When the graphs of volume of carbon dioxide against time for both powdered calcium carbonate and calcium carbonate lumps, are plotted using the same axes, they appear as shown in figure below.



# Effect of light on the rate of reaction

For reactions which are **photosensitive**, increase in light intensity increases the rate of reaction and reduction in light intensity reduces the rate of reaction.

This is because light is a source of energy and can therefore influence some chemical reactions considerably by providing energy to the reactant molecules.

For example, the reaction between chlorine and hydrogen is very slow in darkness but very fast in sunlight.

# Investigation of the effect of light on the rate of reaction

Add 1 cm<sup>3</sup> of sodium chloride solution to two test- tubes. To each test- tube add a few drops of silver nitrate solution.

Immediately, a white precipitate forms. Put one test- tube in a dark cup board and the other in sunlight for about 4 minutes. Record your observations.

Sodium chloride solution forms a white precipitate with silver nitrate solution according to the equation.

 $Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$ 

In presence of light, the precipitate darkens because of the decomposition of silver chloride to solver and chlorine.

In absence of light, the precipitate remains white.

# $2AgCl_{(s)} \rightarrow 2Ag_{(s)} + Cl_{2(g)}$

The effects of light on hydrogen peroxide and concentrated nitric acid explain why they are stored in dark- glass bottles.

# Effect of pressure on the rate of reaction

Pressure only affects reactions which occur in the gaseous phase. When pressure of a gaseous mixture is increased, the gases are compressed.

This brings the reacting particles together and thus increases the frequency at which the reacting particles collide hence increased rate of reaction.

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#### **Reversible reactions**

Reversible reactions are reactions that can be made to go forward and backward by changing the conditions.

For example, when copper (II) sulphate-5-water crystals are heated, they turn from blue to white as they lose water of crystallization.

 $CuSO_{4.}5H_2O_{(s)} \longrightarrow CuSO_{4} (s) + 5H_2O_{(l)}$ 

If water is added to the white solid, it turns blue again.

 $\begin{array}{rcl} CuSO_{4(s)} & + & 5H_2O_{(s)} & \longrightarrow & CuSO_4.5H_2O_{(s)} \\ The two equations can be combined into one equation by introducing a double arrow () \\ CuSO_4.5H_2O_{(s)} & \longrightarrow & CuSO_{4}_{(s)} & + & 5H_2O_{(l)} \end{array}$ 

This equation indicates a reversible reaction.

In reversible reactions, it is possible to have both reactants and products present. If the forward and backward rates are equal, there is a state of **balance**.

# Applications of reversible reaction

# 1) Haber process

This is the process in which ammonia is manufactured on large scale. The equation for the reaction is as shown below.

 $3H_{2(g)} + N_{2(g)} \implies 2NH_{3(g)} = \Delta H_{G} - veless You$ 

If we need to yield high amount of ammonia, the optimum conditions are;

- High pressure of 200 300 atmospheres
- Low temperature of 450°C
- Iron catalyst (finely divided)
- By recycling hydrogen and nitrogen that leaves un reacted back into the reactor to form ammonia.
- Use the heat released during this exothermic reaction to provide heat needed to reduce on costs.

# 2) Contact process

This is the process in which sulphuric acid is manufactured on large scale.

In the manufacture of sulphuric acid by contact process, sulphur dioxide and oxygen are the starting materials.

The sulphur dioxide is oxidized to sulphur trioxide which is then absorbed by concentrated sulphuric acid forming oleum (fuming sulphuric acid) to which water is added to form the sulphuric acid.

This process can be divided into the following essential stages;

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#### a) Preparation of sulphur dioxide

Sulphur dioxide can be obtained from the following source;

i) Burning sulphur in air. This is cheap and produces sulphur dioxide in large quantities

 $S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$ 

ii) Roasting sulphide ores in air

$$4FeS_{2(s)} + 11O_{2(g)} \longrightarrow 8SO_{2(g)} + 2Fe_2O_{3(s)}$$

(Iron pyrite)

 $2ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2SO_{2(g)} + 2ZnO_{(s)}$ (Zinc blende)

Other sources of sulphur dioxide include; burning of hydrogen sulphide from crude oil in air; flue gas desulphurization in power stations e.t.c.

Oxygen is obtained from fractional distillation of liquid air.

# b) Purification of the gases

The sulphur dioxide and the oxygen are purified and dried (i.e. cleared off any dust particles and other impurities which can poison the catalyst especially if it is platinum.

# c) Preparation of sulphur trioxide BIESS YOU

The purified gases are passed over a finely divided vanadium (V)  $oxide_{1}(V_{2}O_{5})$  catalyst at a temperature of 450-500°C and a pressure of 2-3 atmospheres, sulphur trioxide is formed. Vanadium (V) oxide is commonly used because it is cheaper and not easily poisoned by impurities.

The catalyst Vanadium (V) oxide is so effective that 95% conversion of sulphur dioxide to sulphur trioxide is achieved at 450-500°C and 2 atmospheres. The reaction is exothermic and therefore produces heat enough to maintain the temperature of the catalyst.

#### d) Conversion of sulphur trioxide to sulphuric acid

Sulphur trioxide,  $SO_3$  must not be allowed to come in contact with water as the reaction is intensely exothermic that it vaporizes the sulphuric acid formed (i.e. produces a lot of mist consisting of dry droplets of  $H_2SO_4$ ).

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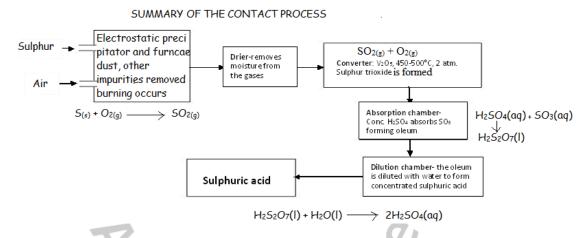
To prevent this happening, the sulphur trioxide,  $SO_3$  is absorbed in concentrated sulphuric acid,  $H_2SO_4$  to form an oily liquid called an Oleum

H₂SO₄(aq) + SO₃(aq) → H₂S₂O7(I)

The oleum produced is carefully diluted to give 95-98% pure concentrated sulphuric acid.

 $H_2S_2O_7(I) + H_2O(I) \longrightarrow 2H_2SO_4(aq)$ 

Banange, put more efforts on this summary of the contact process coz it can even be asked in any exam as a flow chart, so remember that friends. Mukilowoozeku.



In the above process, the following conditions favor high yield of sulphur trioxide:

- Presence of a catalyst. The catalyst must be finely divided to increase the surface area for the reaction.
- Low temperature(450-500C) as the reaction is exothermic (releases heat),
- Slightly high pressure above the atmospheric pressure as the reaction is accompanied by a decrease in volume.
- High concentration of oxygen or sulphur dioxide.

# Uses of sulphuric acid

- 1. Used in the manufacture of fertilizers like ammonium sulphate.
- 2. Making of paints and pigments
- 3. Manufacture of detergents and soap
- 4. Production of other chemicals such as metallic sulphates, hydrochloric acid, hydrofluoric acid and plastics.
- 5. Extraction of metals and metal manufacturing including pickling to clean metallic surfaces.
- 6. Extraction of alkenes in petroleum refinery.
- 7. With nitric acid, it is used to make dyes and explosives

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#### Sample questions on sulphuric acid.

#### Number one.

#### What are;

- (a) The raw materials required.
- (b) How does the following stages take place:
  - (i) Production of sulphur dioxide. Why should the reactants be purified and dried at this stage.
  - (ii) Conversion of sulphur dioxide to sulphur trioxide.
  - (iii) Production of oleum.
  - (iv) Dilution of oleum to form sulphuric acid.
- (c) Why is the process called the contact process.
- 2. Design a flow chart describing stages in the industrial manufacture of
- sulphuric acid.

# Suggested answers:

- 1. (a) Sulphur and oxygen.
  - (b) (i) Sulphur dioxide is produced by burning sulphur or ores of sulphur such as iron pyrites, (FeS<sub>2</sub>), zinc blende, (ZnS).

# Burning sulphur in air.

Sulphur + Oxygen	$\rightarrow$	Sulphur dioxide
$S(s) + O_2(g)$	$\rightarrow$	SO <sub>2</sub> (g)
Roasting zinc blend in	n air.	

soint to serve

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#### THE KISJO CONTENT NLSC CHEMISTRY Sulphur dioxide + Zinc oxide Zinc blend + Oxygen 2SO<sub>2</sub> (g) + 2ZnO (s) $2ZnS(s) + 3O_{2}(g)$ Roasting iron pyrite in air. Sulphur dioxide + iron(III) oxide Iron pyrite + Oxygen $4\text{FeS}_{2}(s) + 11O_{2}(g)$ $8SO_{2}$ (g) + 2Fe<sub>2</sub>O<sub>2</sub> (s) Purification is important to remove impurities that could otherwise poison the catalyst. (ii) The purified gases are then heated to a temperature of (450 - 500)°C and compressed over heated Vanadium(V) oxide as a catalyst. The reaction proceeds according to the equation: Sulphur + Oxygen Sulphur trioxide 2S (s) +3O<sub>2</sub> (g) 2SO<sub>3</sub> (g) (iii) The cooled sulphur trioxide is passed into the absorption tower. packed with ceramic rings through which concentrated sulphuric acid flows. The sulphur trioxide reacts with concentrated sulphuric acid forming an oily liquid called, oleum. Oleum $H_2SO_4(I) + SO_3(g)$ H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> (I) (iv) Oleum produced is mixed with a known volume of water to produce concentrated sulphuric acid.

(c) The reaction is called the contact process because the reaction takes place at the surface of the catalyst.

# ACTIVITY OF INTEGRATION ON RATES OF REACTIONS.

An industry is engaged in the production of fertilisers using ammonia as one of the raw materials. However, the amount of fertilisers being produced is too little to cater for the costs of production. The owners of the industry are concerned that the low yields of the fertilisers will collapse their industry since they are making losses. One of the stages identified as the cause of the problem is the reversible conversion of hydrogen and nitrogen to ammonia.

As the chief industrial chemist, write a report to the board of directors explaining how the yield can be increased.

### Try out this.

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#### Sample questions on rates of reactions

1. Calcium carbonate reacts with dilute hydrochloric acid according to the following equation.

 $CaCO_{3}(s) + 2HCI(aq) \longrightarrow CaCI_{2}(aq) + H_{2}O(l) + CO_{2}(g)$ 

- (a) Sketch a graph to show the rate of production of carbon dioxide when an excess of dilute hydrochloric acid is added. The reaction lasted for 40 s and produces 60 cm<sup>3</sup> of a gas.
- (b) Indicate on your graph the part which shows:
  - Where the reaction is at its fastest? (i)
  - (ii) When the reaction has stopped?
- (c) Calculate the mass of calcium carbonate used to produce 60cm3 of carbon dioxide. (Cu = 63.5, C = 12, O = 16. One mole of a gas occupies 24 dm<sup>3</sup> at room temperature).
- (d) Sketch a further graph using the same axes to show what happens to the rate at which the gas is produced if:
  - The concentration of the acid is decreased (i)
  - (ii) The temperature is increased.
- The parliament of Uganda has recently passed a law that all new cars must 2. be fitted with a catalytic converter as part of their exhaust fume system.
  - (a) What is the necessity of such a law?
  - (b) Which gases are removed by the catalytic converter?
  - (c) Which catalysts are often used in a catalytic converter?
  - (d) What does the term 'poisoned' mean with respect to a catalyst?
  - (e) The catalytic converter can remove unburnt petrol according to the following equation:

 $2 C_7 H_{14}(g) + 21 O_2(g) \longrightarrow 14 CO_2(g) +$ 14 H<sub>2</sub>O (g)

- Calculate the mass of carbon dioxide produced by 1.96 g of (i) unburnt fuel.
- (ii) Convert the mass of carbon dioxide into volume measured at r.t.p.
- (iii) If a Mercedes benz produces 7.84 of unburnt fuel each day.
- Calculate the volume of carbon dioxide produced by the catalytic converter measured at r.t.p. (C = 12; H = 1; O = 16; one mole of any gas occupies 24 dm3 at rtp).
- One of the stages in the manufacture of sulphuric acid is the production of sulphur trioxide which occurs according to the following equation: 3.

$$2 SO_{1}(g) + O_{2}(g) \longrightarrow 2 SO_{3}(g) + He$$

This reaction is carried out at specific conditions of temperature, pressure and a catalyst. What are the conditions for the optimal yield of sulphur trioxide?

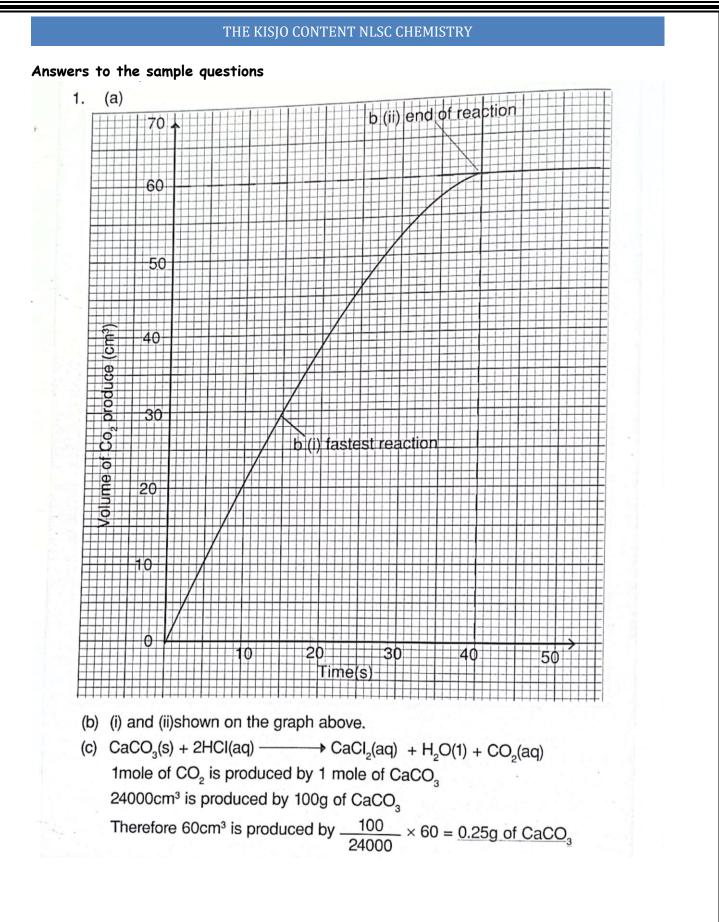
- (a) Explain why this reaction is not carried out: (b)
  - (i) at a temperature below or above the one mentioned in (a)
  - (ii) at a pressure below or above the one mentioned in (a)
- (c) Explain why the sulphur trioxide s not directly dissolved in water in the next stage.
- Sketch a graph to show how the percentage yield of sulphur trioxide (d) varies with:

pressure

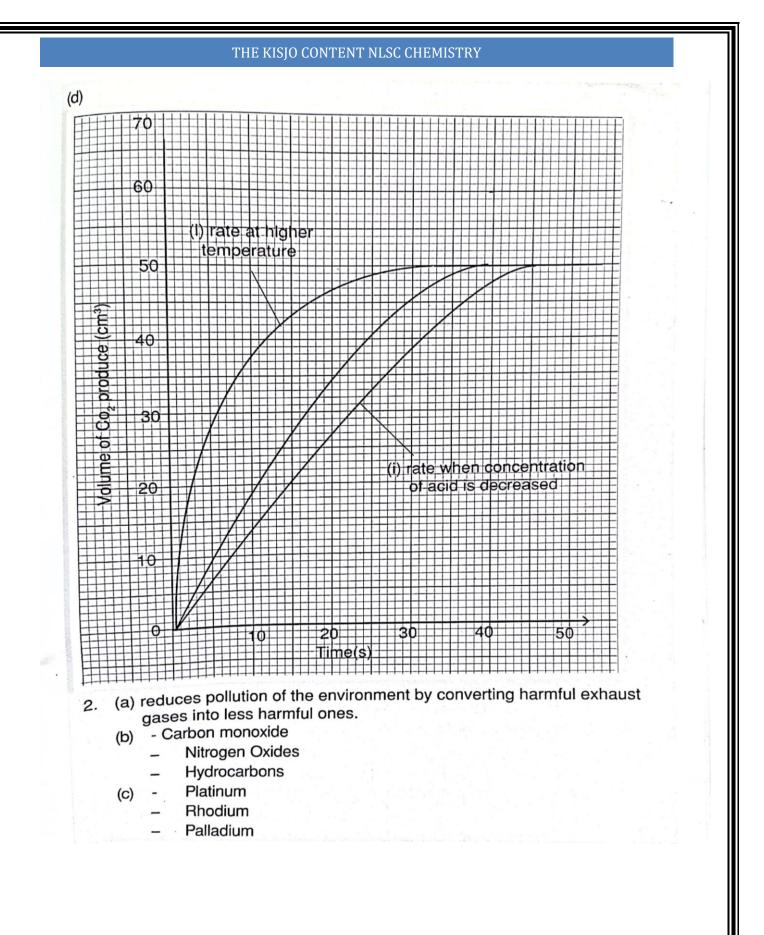
(i) temperature

(ii)

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(d) "Poisoned" means that the catalyst has been rendered useless.

(e) (i) 2 moles of unburnt fuel produces 14 moles of  $CO_2$ 

(2 × 7 × 12) + (2 × 1 × 14)g (168 + 28)g 196g Therefore 1.96g produce  $(14 \times 12) + (14 \times 2 \times 16)$ produce 168 + 448produce 616g of  $CO_2$ produce  $616 \times 1.96$ 196= 6.16g of  $CO_2$  produced.

(ii) 44g of CO<sub>2</sub> equal 1 mole of CO<sub>2</sub>

6.16g of CO<sub>2</sub> equal  $\underbrace{1}_{44} \times 6.16$ = 0.14 moles of CO<sub>2</sub> produced.

1 mole of CO<sub>2</sub> at R.T.P occupies 24dm<sup>3</sup>

0.14 moles of CO<sub>2</sub> at R.T.P occupies  $0.14 \times 24 \text{ dm}^3$ 

= 3.36dm<sup>3</sup> of CO<sub>2</sub> were produced.

(ii) 2 moles of unburnt fuel produces 14moles of  $CO_2$ 196g of unburnt fuel produces (14 × 24 )dm<sup>3</sup> of  $CO_2$ 

7.84g produced

3.

$$\left(\begin{array}{c} \underline{336}\\ \underline{196} \end{array} \times 7.84 \right) dm^3$$

= 13.44dm<sup>3</sup> of CO<sub>2</sub> is produced

Temperature of 400 - 450 °C

- High pressure of about 2 atmospheres.
- Vanadium (V) oxide catalyst.
- (b) (i) Temperature lower than the above would lead to slow production of sulphur dioxide which could increase production costs.
  - Temperature higher than the optimum would lead to very fast rate of reaction and production of  $SO_3$  which is uncontrollable.
  - (ii)- Pressure below optimum produce low yields / low amounts of SO<sub>3</sub>.
    - Pressure above optimum increases production costs.
- (c) Misty fumes of the acid would form.

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