# Rates of reaction Equilibria

## A.THE RATE OF CHEMICAL REACTION (CHEMICAL KINETICS)

#### 1.Introduction

The rate of a chemical reaction is the time taken for a given mass/amount of products to be formed. The rate of a chemical reaction is also the time taken for a given mass/amount of reactant to be consumed /used up.

Some reactions are too slow to be determined. e.g rusting ,decomposition of hydrogen peroxide and weathering.

Some reactions are too fast and instantaneous e.g. neutralization of acid and bases/alkalis in aqueous solution and double decomposition/precipitation.

Other reactions are explosive and very risky to carry out safely e.g. reaction of potassium with water and sodium with dilute acids.

The study of the rate of chemical reaction is useful in knowing the factors that influence the reaction so that efficiency and profitability is maximized in industries.

#### Theories of rates of reaction.

The rate of a chemical reaction is defined as the rate of change of concentration/amount of reactants in unit time. It is also the rate of formation of given concentration of products in unit time. i.e.

Rate of reaction = Change in concentration/amount of reactants

Time taken for the change to occur

Rate of reaction = Change in concentration/amount of products formed

Time taken for the products to form

For the above, therefore the rate of a chemical reaction is rate of decreasing reactants to form an increasing product.

The SI unit of **time** is **second**(s) but minutes and hours are also used.

#### (a) The collision theory

The collision theory is an application of the Kinetic Theory of matter which assumes matter is made up of small/tiny/minute particles like ions atoms and molecules.

The collision theory proposes that

(i) for a reaction to occur, reacting particles must collide.

(ii)not all collisions between reacting particles are successful in a reaction. Collisions that initiate a chemical reaction are called successful / fruitful/ effective collisions

(iii)the speed at which particles collide is called **collision frequency**.

The higher the collision frequency the higher the **chances** of successful / fruitful/ effective collisions to form products.

- (iv)the higher the chances of successful collisions, the faster t on.

(vi)dissolving substances in a solvent ,make the solvent a medium for the reaction to take place.

The solute particle distance is reduced as the particle ions are free to move in the solvent medium.

(vii)successful collisions take place if the particles colliding have the required **energy** and right **orientation** which increases their **vibration** and **intensity** of successful / fruitful/ effective collisions to form products.

#### (b) The Activation Energy (Ea) theory

The Enthalpy of activation ( $\Delta H_a$ ) /Activation Energy(Ea) is the minimum amount of energy which the reactants must overcome before they react. Activation Energy(Ea) is usually required /needed in bond breaking of the reacting particles.

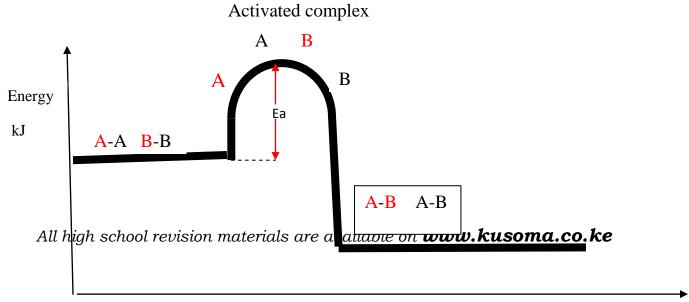
Bond breaking is an endothermic process that require an energy input.

The higher the bond energy the slower the reaction to **start of**.

Activation energy does not influence whether a reaction is exothermic or endothermic.

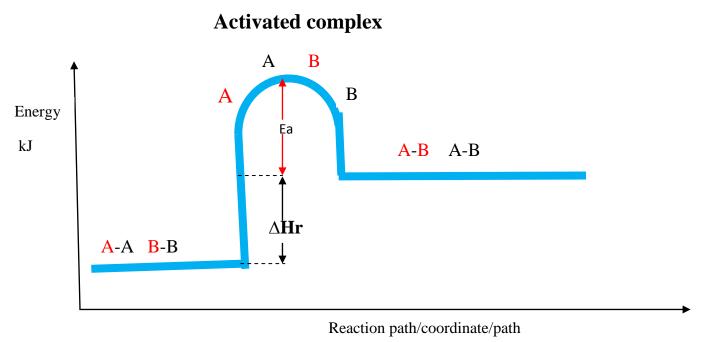
The energy level diagrams below shows the activation energy for exothermic and endothermic processes/reactions.

Energy level diagram showing the activation energy for exothermic processes /reactions.



Deagtion math/acardinata/math

Energy level diagram showing the activation energy for endothermic processes /reactions.



xture of many intermediate possible

The activated complex is a mixture of many intermediate possible products which may not exist under normal physical conditions, but can theoretically exist.

Exothermic reaction proceeds without further heating /external energy because it generates its own energy/heat to overcome activation energy.

Endothermic reaction cannot proceed without further heating /external energy because it does not generates its own energy/heat to overcome activation energy. It generally therefore requires continuous supply of more energy/heat to sustain it to completion.

#### 3. Measuring the rate of a chemical reaction.

The rate of a chemical reaction can be measure as:

- (i) Volume of a gas in unit time;
  - if reaction is producing a gas as one of the products.
  - if reaction is using a gas as one reactants

- (ii)Change in mass of reactants/products for solid products/reactants in unit time.
  - (iii)formation of a given mass of precipitate in unit time
  - (iv)a certain mass of reactants to completely form products/diminish.

Reactants may be homogenous or heterogenous.

- **-Homogenous** reactions involve reactants in the **same phase/state** e.g. solid-solid,gas-gas,liquid-liquid.
- **-Heterogenous** reactions involve reactants in the **different phase/state** e.g. solid-liquid,gas-liquid,solid-gas.

#### 4. Factors influencing/altering/affecting/determining rate of reaction

The following factors alter/influence/affect/determine the rate of a chemical reaction:

- (a)Concentration
- (b)Pressure
- (c) Temperature
- (d)Surface area
- (e)Catalyst

#### a) Influence of concentration on rate of reaction

The higher the concentration, the higher the rate of a chemical reaction. An increase in concentration of the reactants reduces the distance between the reacting particles increasing their collision frequency to form products. Practically an increase in concentration **reduces** the time taken for the reaction to take place.

#### Practical determination of effect of concentration on reaction rate

#### Method 1(a)

Reaction of sodium thisulphate with dilute hydrochloric acid

#### **Procedure:**

Measure 20cm3 of 0.05M sodium thisulphate into a 50cm3 glass beaker. Place the beaker on a white piece of filter paper with ink **mark** 'X' on it. Measure 20cm3 of 0.1M hydrochloric acid solution using a 50cm3 measuring cylinder. Put the acid into the beaker containing sodium thisulphate. Immediately start off the stop watch/clock. Determine the time taken for the ink **mark** 'X' to become

invisible /obscured when viewed from above. Repeat the procedure by measuring different volumes of the acid and adding the volumes of the distilled water to complete table 1.

Sample results: Table 1.

| Volume of acid(cm3) | Volume of water(cm3) | Volume of sodium thiosulphate(cm3) | Time taken for mark 'X' to be invisible/obscured(seconds) | Reciprocal of time $\frac{1}{t}$ |
|---------------------|----------------------|------------------------------------|---|----------------------------------|
| 20.0                | 0.0                  | 20.0                               | 20.0  | $5.0 \times 10^{-2}$             |
| 18.0                | 2.0                  | 20.0                               | 23.0  | $4.35 \times 10^{-2}$            |
| 16.0                | 4.0                  | 20.0                               | 27.0  | $3.7 \times 10^{-2}$             |
| 14.0                | 6.0                  | 20.0                               | 32.0  | $3.13 \times 10^{-2}$            |
| 12.0                | 8.0                  | 20.0                               | 42.0  | $2.38 \times 10^{-2}$            |
| 10.0                | 10.0                 | 20.0                               | 56.0  | $1.78 \times 10^{-2}$            |

For most examining bodies/councils/boards the above results score for:

- (a) **complete table** as evidence for all the practical work done and completed.
- (b) (i) Consistent use of **a decimal point** on time as evidence of understanding/knowledge of the degree of accuracy of stop watches/clock.
- (ii)Consistent use of a minimum of <u>four</u> decimal points on inverse/reciprocal of time as evidence of understanding/knowledge of the degree of accuracy of scientific calculator.
- (c) accuracy against a school value based on candidate's teachers-results submitted.
- (d) correct **trend** (time increase as more water is added/acid is diluted) in conformity with expected **theoretical** results.

#### Sample questions

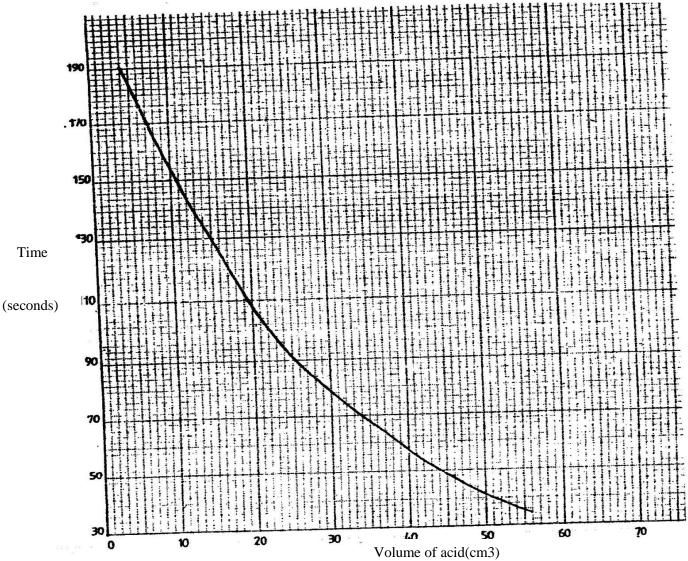
- 1. On separate graph papers plot a graph of:
  - (i)volume of acid used(x-axis) against time. Label this graph I
  - (ii) volume of acid used(x-axis) against 1/t. Label this graph II

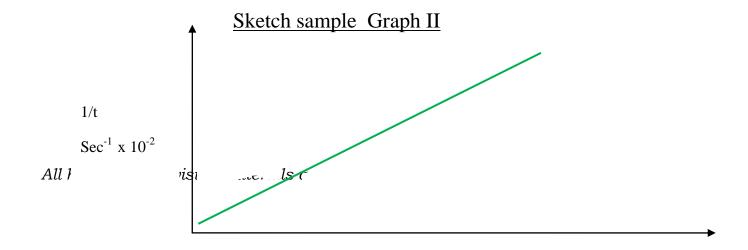
#### 2. Explain the shape of graph I

Diluting/adding water is causes a decrease in concentration.

Decrease in concentration reduces the rate of reaction by increasing the time taken for reacting particle to collide to form products.

Sketch sample Graph I





- 3.From graph II, determine the time taken for the cross to be obscured/invisible when the volume of the acid is:
  - (i) 13cm3

From a correctly plotted graph 1/t at 13cm3 on the graph  $=> 2.75 \times 10^{-2}$   $t = 1 / 2.75 \times 10^{-2} = 36.3636$  seconds

(ii) 15cm3

From a correctly plotted graph 1/t at 15cm3 on the graph => 3.35 x  $10^{-2}$  t =  $1/3.35 \times 10^{-2} = 29.8507$  seconds

(iii) 15cm3

From a correctly plotted graph 1/t at 17cm3 on the graph => **4.0** x **10**<sup>-2</sup>  $t = 1 / 4.0 \times 10^{-2} = 25.0$  seconds

(iv) 19cm3

From a correctly plotted graph 1/t at 19cm3 on the graph => **4.65** x **10**<sup>-2</sup>  $t = 1 / 4.65 \times 10^{-2} = 21.5054$  seconds

- 4. From graph II, determine the volume of the acid used if the time taken for the cross to be obscured/invisible is:
  - (i)25 seconds

$$1/t = 1/25 = 4.0 \times 10^{-2}$$

**Reading** from a correctly plotted graph;

4.0 x 10<sup>-2</sup> correspond to **17.0 cm3** 

(ii)30 seconds

$$1/t = 1/30 = 3.33 \times 10^{-2}$$

Reading from a correctly plotted graph;

 $3.33 \times 10^{-2}$  correspond to **14.7 cm3** 

(iii)40 seconds

$$1/t = 1/40 = 2.5 \times 10^{-2}$$

Reading from a correctly plotted graph;

2.5 x 10<sup>-2</sup> correspond to **12.3 cm3** 

4. Write the equation for the reaction taking place

$$Na_2S_2O_3(aq) + 2HCl(aq) -> 2NaCl(aq) + SO_2(g) + S(s) + H_2O(l)$$

Ionically:

$$S_2O_3^{2-}(aq) + 2H^+(aq) -> SO_2(g) + S(s) + H_2O(l)$$

5. Name the yellow precipitate

Colloidal sulphur

#### Method 1(b)

Reaction of sodium thisulphate with dilute hydrochloric acid

You are provided with

- 2.0M Hydrochloric acid
- 0.4M sodium thiosulphate solution

#### **Procedure:**

Measure 10cm3 of sodium thisulphate into a 50cm3 glass beaker. Place the beaker on a white piece of filter paper with ink **mark** 'X' on it.

Add 5.0cm3 of hydrochloric acid solution using a 10cm3 measuring cylinder into the beaker containing sodium thisulphate.

Immediately start off the stop watch/clock. Determine the time taken for the ink mark 'X' to become invisible /obscured when viewed from above.

Repeat the procedure by measuring different volumes of the thiosulphate and adding the volumes of the distilled water to complete table 1.

Sample results: Table 1.

| Volume<br>of<br>acid(cm3) | Volume<br>of water<br>(cm3) | Volume of sodium thiosulphate (cm3) | Concentation<br>of sodium<br>thisulphate in<br>molesdm <sup>-3</sup> | Time(T) taken<br>for mark 'X' to<br>be invisible/<br>obscured(second<br>s) | T <sup>-1</sup>         |
|---------------------------|-----------------------------|-------------------------------------|--|--|-------------------------|
| 5.0                       | 0.0                         | 25.0                                | 0.4  | 20.0   | $5.0 \times 10^{-2}$    |
| 5.0                       | 5.0                         | 20.0                                | 0.32   | 23.0   | 4.35 x 10 <sup>-2</sup> |
| 5.0                       | 10.0                        | 15.0                                | 0.24   | 27.0   | $3.7 \times 10^{-2}$    |
| 5.0                       | 15.0                        | 10.0                                | 0.16   | 32.0   | $3.13 \times 10^{-2}$   |

Note concentration of diluted solution is got:

 $C_1V_1=C_2V_2$  => 0.4 x 25 =  $C_2$ x 25 =0.4M  $C_1V_1=C_2V_2$  => 0.4 x 20 =  $C_2$ x 25 =0.32M  $C_1V_1=C_2V_2$  => 0.4 x 15 =  $C_2$ x 25 =0.24M  $C_1V_1=C_2V_2$  => 0.4 x 10 =  $C_2$ x 25 =0.16M

#### Sample questions

- 1. On separate graph papers plot a graph of:
  - (i)Concentration of sodium thiosulphate against time. Label this graph I
- (ii)Concentration of sodium thiosulphate against against T<sup>-1</sup>.Label this graph II

#### 2. Explain the shape of graph I

Diluting/adding water causes a decrease in concentration.

Decrease in concentration reduces the rate of reaction by increasing the time taken for reacting particle to collide to form products.

From graph II

Determine the time taken if

(i)12cm3 of sodium thisulphate is diluted with 13cm3 of water.

At 12cm3 concentration of sodium thisulphate

$$= C_1V_1 = C_2V_2$$
 => 0.4 x 1 2 =  $C_2$ x 25 =0.192M

From correct graph at concentration  $0.192M \Rightarrow 2.4 \times 10^{-2}$ 

$$I/t = 2.4 \times 10^{-2} t = 41.6667 seconds$$

(ii)22cm3 of sodium thisulphate is diluted with 3cm3 of water.

At 22cm3 concentration of sodium thisulphate

$$= C_1V_1 = C_2V_2$$
 => 0.4 x 22 =  $C_2$ x 25 =0.352M

From correct graph at concentration  $0.352M \Rightarrow 3.6 \times 10^{-2}$ 

$$I/t = 3.6 \times 10^{-2} t = 27.7778$$
seconds

Determine the volume of water and sodium thiosulphate if T<sup>-1</sup> is 3.0 x10<sup>-1</sup>

From correct graph at  $T^{-1} = 3.0 \times 10^{-1} = 0.65 \text{ M}$ 

$$= C_1V_1 = C_2V_2$$
 => 0.4 x 25 = 0.65 M x  $V_2$  = **15.3846cm3**

Volume of water = 25 - 15.3846cm3 = 9.6154cm3

Determine the concentration of hydrochloric acid if 12cm3 of sodium thiosulphate and 13cm3 of water was used.

At 12cm3 concentration of sodium thisulphate

$$= C_1 V_1 = C_2 V_2$$
 => 0.4 x 1 2 =  $C_2 x$  25 =0.192M

Mole ratio  $Na_2S_2 O_3$ : HCl =1:2

Moles of Na<sub>2</sub>S<sub>2</sub> O<sub>3</sub> = 
$$0.192M \times 12 = 2.304 \times 10^{-3}$$
 moles  $1000$   
Mole ratio HCl =  $2.304 \times 10^{-1}$  moles  $= 1.152 \times 10^{-3}$  moles  $= 1.152$ 

Mole ratio HCl = 
$$\frac{2.304 \times 10^{-1} \text{ moles}}{2}$$
 =  $\frac{1.152 \times 10^{-3}}{2}$  moles

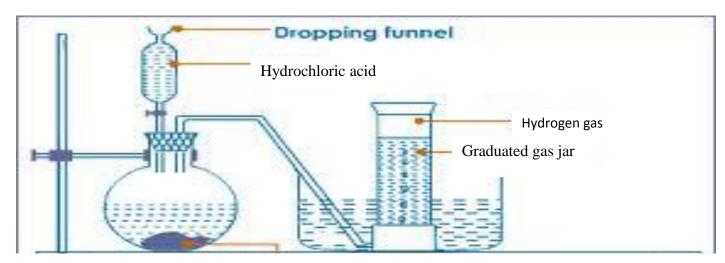
Molarity of HCl = 
$$1.152 \times 10^{-3}$$
 moles x 1000 =  $0.2304$ M  $0.000 \times 10^{-3}$ 

#### Method 2

Reaction of Magnesium with dilute hydrochloric acid

#### **Procedure**

Scub 10centimeter length of magnesium ribbon with sand paper/steel wool. Measure 40cm3 of 0.5M dilute hydrochloric acid into a flask .Fill a graduated gas jar with water and invert it into a trough. Stopper the flask and set up the apparatus to collect the gas produced as in the set up below:



Magnesium ribbon

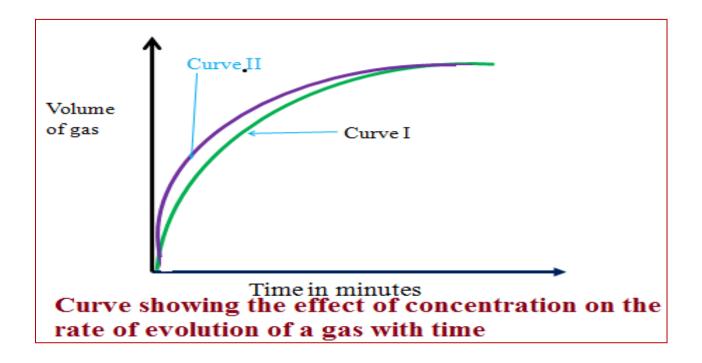
Carefully remove the stopper, carefully put the magnesium ribbon into the flask . cork tightly. Add the acid into the flask. Connect the delivery tube into the gas jar. Immediately start off the stop watch and determine the volume of the gas produced after every 30 seconds to complete table II below.

#### Sample results: Table II

| Time(seconds) | 0   | 30   | 60   | 90   | 120  | 150  | 180  | 210  | 240  |
|---------------|-----|------|------|------|------|------|------|------|------|
| Volume of gas | 0.0 | 20.0 | 40.0 | 60.0 | 80.0 | 90.0 | 95.0 | 96.0 | 96.0 |
| produced(cm3) |     |      |      |      |      |      |      |      |      |

#### Sample practice questions

1.Plot a graph of volume of gas produced (y-axis) against time



#### 2. Explain the shape of the graph.

The rate of reaction is faster when the concentration of the acid is high.

As time goes on, the concentration of the acid decreases and therefore less gas is produced.

When all the acid has reacted, no more gas is produced after 210 seconds and the graph flattens.

#### 3. Calculate the rate of reaction at 120 seconds

From a tangent at 120 seconds rate of reaction =  $\frac{\text{Change in volume of gas}}{\text{Change in volume of gas}}$ 

Change in time

=> From the tangent at 120seconds 
$$\frac{V_2 - V_1}{T_2 - T_1} = \frac{96-84}{150-90} = \frac{12}{60} = \frac{\textbf{0.2cm3sec}^{-1}}{60}$$

4. Write an ionic equation for the reaction taking place.

$$Mg^{2+}(s) + 2H^{+}(aq) -> Mg^{2+}(aq) + H_2(g)$$

- 5. On the same axis sketch then explain the curve that would be obtained if:
  - (i) 0.1 M hydrochloric acid is used –Label this curve I
  - (ii)1.0 M hydrochloric acid is used -Label this curve II

#### **Observation:**

Curve I is to the right Curve II is to the left

#### **Explanation**

A decrease in concentration shift the rate of reaction graph to the right as more time is taken for completion of the reaction.

An increase in concentration shift the rate of reaction graph to the left as less time is taken for completion of the reaction.

Both graphs **flatten** after some time indicating the **completion** of the reaction.

#### b)Influence of pressure on rate of reaction

Pressure affects only gaseous reactants.

An increase in pressure reduces the volume(Boyles law) in which the particles are contained.

Decrease in volume of the container bring the reacting particles closer to each other which increases their chances of effective/successful/fruitful collision to form products.

An increase in pressure therefore increases the rate of reaction by reducing the time for reacting particles of gases to react.

At industrial level, the following are some reactions that are affected by pressure:

(a) Haber process for manufacture of ammonia

$$N_2(g) + 3H_2(g) -> 2NH_3(g)$$

(b)Contact process for manufacture of sulphuric(VI)acid

$$2SO_2(g) + O_2(g) -> 2SO_3(g)$$

(c)Ostwalds process for the manufacture of nitric(V)acid

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$

The influence of pressure on reaction rate is not felt in solids and liquids. This is because the solid and liquid particles have fixed positions in their strong bonds and therefore no degree of freedom (Kinetic Theory of matter)

c) Influence of temperature on rate of reaction

An increase in temperature increases the kinetic energy of the reacting particles by increasing their collision frequency.

Increase in temperature increases the particles which can overcome the activation energy (Ea).

A 10°C rise in temperature doubles the rate of reaction by reducing the time taken for the reaction to complete by a half.

### Practical determination of effect of Temperature on reaction rate $\underline{\text{Method }1}$

#### Reaction of sodium thisulphate with dilute hydrochloric acid

#### **Procedure:**

Measure 20cm3 of 0.05M sodium thisulphate into a 50cm3 glass beaker.

Place the beaker on a white piece of filter paper with ink mark 'X' on it.

Determine and record its temperature as room temperature in table 2 below.

Measure 20cm3 of 0.1M hydrochloric acid solution using a 50cm3 measuring cylinder.

Put the acid into the beaker containing sodium thisulphate.

Immediately start off the stop watch/clock.

Determine the time taken for the ink **mark** 'X' to become invisible /obscured when viewed from above.

Measure another 20cm3 separate portion of the thisulphate into a beaker, heat the solution to 30°C.

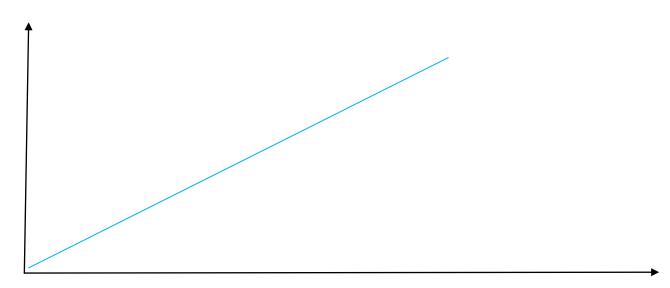
Add the acid into the beaker and repeat the procedure above. Complete table 2 below using different temperatures of the thiosulphate.

#### Sample results: Table 2.

| Temperature of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> | Room temperature | 30    | 40   | 50     | 60   |
|--|------------------|-------|------|--------|------|
| Time taken for mark X to                                     | 50.0             | 40.0  | 20.0 | 15.0   | 10.0 |
| be obscured /invisible                                       |                  |       |      |        |      |
| (seconds)  |                  |       |      |        |      |
| Reciprocal of time( $^{1}/_{t}$ )                            | 0.02             | 0.025 | 0.05 | 0.0667 | 0.1  |

#### Sample practice questions

#### 1. Plot a graph of temperature(x-axis) against $\frac{1}{t}$



#### 2(a) From your graph determine the temperature at which:

#### (i)1/t is;

I. 0.03

Reading directly from a correctly plotted graph = 32.25 °C

II. 0.07

Reading directly from a correctly plotted graph = 48.0 °C

#### (ii) t is;

#### I. 30 seconds

 $30 \text{ seconds} \Rightarrow 1/t = 1/30 = 0.033$ 

Reading directly from a correctly plotted graph  $0.033 \Rightarrow 33.5$  °C

#### II. 45 seconds

45 seconds => 1/t = 1/45 = 0.022

Reading directly from a correctly plotted graph  $0.022 \Rightarrow 29.0$  °C

#### III. 25 seconds

25 seconds => 1/t = 1/25 = 0.04

Reading directly from a correctly plotted graph  $0.04 \Rightarrow 36.0$  °C

### (b) From your graph determine the time taken for the cross to become invisible at:

(i) 57.5 °C

Reading directly from a correctly plotted graph at 57.5  $^{\circ}$ C= **0.094** =>1/t = **0.094** 

t= 1/0.094 => **10.6383 seconds** 

#### (ii) 45 °C

Reading directly from a correctly plotted graph at 45 °C = **0.062** 

$$=>1/t = 0.062$$

t= 1/0.094 => **16.1290 seconds** 

#### (iii) 35 °C

Reading directly from a correctly plotted graph at 35  $^{\circ}$ C = **0.047** 

$$=>1/t = 0.047$$

t= 1/0.047 => 21.2766 seconds

#### Method 2

#### Reaction of Magnesium with dilute hydrochloric acid

#### **Procedure**

Scub 5centimeter length of magnesium ribbon with sand paper/steel wool.

Cut the piece into five equal one centimeter smaller pieces.

Measure 20cm3 of 1.0M dilute hydrochloric acid into a glass beaker.

Put one piece of the magnesium ribbon into the acid, swirl.

Immediately start off the stop watch/clock.

Determine the time taken for the effervescence/fizzing/bubbling to stop when viewed from above.

Record the time in table 2 at room temperature.

Measure another 20cm3 portions of 1.0M dilute hydrochloric acid into a clean beaker.

Heat separately one portion to  $30^{\circ}\text{C}$ ,  $40^{\circ}\text{C}$ ,  $50^{\circ}\text{C}$  and  $60^{\circ}\text{C}$  and adding 1cm length of the ribbon and determine the time taken for effervescence /fizzing /bubbling to stop when viewed from above .

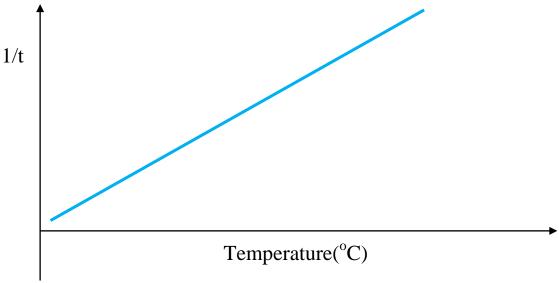
Record each time to complete table 2 below using different temperatures of the acid.

#### Sample results: Table 1.

| Temperature of acid(°C)           | Room temperature | 30   | 40     | 50     | 60   |
|-----------------------------------|------------------|------|--------|--------|------|
| Time taken effervescence          | 80.0             | 50.0 | 21.0   | 13.5   | 10.0 |
| to stop (seconds)                 |                  |      |        |        |      |
| Reciprocal of time( $^{1}/_{t}$ ) | 0.0125           | 0.02 | 0.0476 | 0.0741 | 0.1  |

#### Sample practice questions

#### 1. Plot a graph of temperature(x-axis) against $\frac{1}{t}$



### 2.(a)Calculate the number of moles of magnesium used given that 1cm of magnesium has a mass of 1g.(Mg=24.0)

Moles = 
$$\frac{\text{Mass of magnesium}}{\text{Molar mass of Mg}} \Rightarrow \frac{1.0}{24} = 4.167 \times 10^{-2} \text{ moles}$$

#### (b) Calculate the number of moles of hydrochloric acid used

Moles of acid = 
$$\frac{\text{molarity x volume of acid}}{1000}$$
  
=>  $\frac{1.0 \times 20}{1000}$  = 2.0 x 10<sup>-2</sup> moles

#### (c)Calculate the mass of magnesium that remain unreacted

Mole ratio Mg: HCl = 1:2 Moles Mg =  $\frac{1}{2}$  moles HCl =>  $\frac{1}{2}$  x 2.0 x 10  $\frac{-2}{2}$  moles = **1.0** x **10**  $\frac{-2}{2}$  moles Mass of reacted Mg = moles x molar mass => 1.0 x 10  $\frac{-2}{2}$  moles x 24 = **0.24** g Mass of unreacted Mg = Original total mass - Mass of reacted Mg => 1.0 g - 0.24 = **0.76** g

### (b) Calculate the total volume of hydrogen gas produced during the above reactions.

Mole ratio  $Mg : H_2 = 1:1$ 

Moles of Mg that reacted per experiment = moles  $H_2 = 1.0 \times 10^{-2}$  moles

Volume of Hydrogen at s.t.p produced per experiment = moles x 24 dm3 =>  $1.0 \times 10^{-2}$  moles x 24 dm3 = **0.24dm3** 

Volume of Hydrogen at s.t.p produced in 5 experiments =0.24 dm3 x 5 = **1.2 dm3** 

### 3.(a)At what temperature was the time taken for magnesium to react equal to:

(i)70seconds

70 seconds => 1/t = 1/70 = 0.01429

Reading directly from a correctly plotted graph **0.01429** => **28.0** °C

(ii)40seconds

 $40 \text{ seconds} \Rightarrow 1/t = 1/40 = 0.025$ 

Reading directly from a correctly plotted graph 0.025 => 32.0 °C

- (b) What is the time taken for magnesium to react if the reaction was done at:
  - (i) 55.0 °C

Reading directly from a correctly plotted graph at 55.0 °C=>  $1/t = 8.0 \times 10^{-2}$  =>  $t = 1/8.0 \times 10^{-2} = 12.5$  seconds

(ii) 47.0 °C

Reading directly from a correctly plotted graph at  $47.0 \,^{\circ}\text{C} => 1/\text{t} = 6.0 \,\text{x} \, 10^{-2}$ => t =  $1/6.0 \,\text{x} \, 10^{-2} = 16.6667 \,\text{seconds}$ 

(iii) 33.0 °C

Reading directly from a correctly plotted graph at 33.0 °C=>  $1/t = 2.7 \times 10^{-2}$  =>  $t = 1/2.7 \times 10^{-2} = 37.037$  seconds

#### 4. Explain the shape of the graph.

Increase in temperature increases the rate of reaction as particles gain kinetic energy increasing their frequency and intensity of collision to form products.

#### d)Influence of surface area on rate of reaction

Surface area is the area of contact. An increase in surface area is a decrease in particle size. Practically an increase in surface area involves chopping /cutting

solid lumps into smaller pieces/chips then crushing the chips into powder. Chips thus have a higher surface area than solid lumps but powder has a highest surface area.

An increase in surface area of solids increases the area of contact with a liquid solution increasing the chances of successful/effective/fruitful collision to form products. The influence of surface area on rate of reaction is mainly in heterogeneous reactions.

#### Reaction of chalk/calcium carbonate on dilute hydrochloric acid Procedure

Measure 20cm3 of 1.0 M hydrochloric acid into three separate conical flasks labeled  $C_1$   $C_2$  and  $C_3$ .

Using a watch glass weigh three separate 2.5g a piece of white chalk. Place the conical flask  $C_1$  on an electronic balance.

Reset the balance scale to 0.0.

Put one weighed sample of the chalk into the acid in the conical flask.

Determine the scale reading and record it at time =0.0.

Simultaneously start of the stop watch.

Determine and record the scale reading after every 30 seconds to complete Table I.

Repeat all the above procedure separately with  $C_2$  and  $C_3$  to complete Table II and Table III by cutting the chalk into small pieces/chips for  $C_2$  and crushing the chalk to powder for  $C_3$ 

Sample results: Table 1.

| Time(seconds)     | 0.0 | 30.0 | 60.0 | 90.0 | 120.0 | 150.0 | 180.0 | 210.0 | 240.0 |
|-------------------|-----|------|------|------|-------|-------|-------|-------|-------|
| Mass of           | 2.5 | 2.0  | 1.8  | 1.4  | 1.2   | 1.0   | 0.8   | 0.5   | 0.5   |
| CaCO <sub>3</sub> |     |      |      |      |       |       |       |       |       |
| Loss in mass      | 0.0 | 0.5  | 0.7  | 1.1  | 1.3   | 1.5   | 1.7   | 2.0   | 2.0   |

Sample results: Table 1I.

| Time(seconds)     | 0.0 | 30.0 | 60.0 | 90.0 | 120.0 | 150.0 | 180.0 | 210.0 | 240.0 |
|-------------------|-----|------|------|------|-------|-------|-------|-------|-------|
| Mass of           | 2.5 | 1.9  | 1.5  | 1.3  | 1.0   | 0.8   | 0.5   | 0.5   | 0.5   |
| CaCO <sub>3</sub> |     |      |      |      |       |       |       |       |       |
| Loss in mass      | 0.0 | 0.6  | 1.0  | 1.2  | 1.5   | 1.7   | 2.0   | 2.0   | 2.0   |

Sample results: Table III.

| Time(seconds)     | 0.0 | 30.0 | 60.0 | 90.0 | 120.0 | 150.0 | 180.0 | 210.0 | 240.0 |
|-------------------|-----|------|------|------|-------|-------|-------|-------|-------|
| Mass of           | 2.5 | 1.8  | 1.4  | 1.0  | 0.8   | 0.5   | 0.5   | 0.5   | 0.5   |
| CaCO <sub>3</sub> |     |      |      |      |       |       |       |       |       |
| Loss in mass      | 0.0 | 0.7  | 1.1  | 1.5  | 1.7   | 2.0   | 2.0   | 2.0   | 2.0   |

#### Sample questions:

- 1. Calculate the loss in mass made at the end of each time from the original to complete table I,II and III
- 2.On the same axes plot a graph of total loss in mass against time (x-axes) and label them curve I, II, and III from Table I, II, and III.
- 3.Explain why there is a loss in mass in all experiments.

Calcium carbonate react with the acid to form carbon(IV)oxide gas that escape to the atmosphere.

4. Write an ionic equation for the reaction that take place

$$CaCO_3(s) + 2H^+(aq) -> Ca^{2+}(aq) + H_2O(1) + CO_2(g)$$

5.Sulphuric(VI)acid cannot be used in the above reaction. On the same axes sketch the curve which would be obtained if the reaction was attempted by reacting a piece of a lump of chalk with 0.5M sulphuric(VI)acid. Label it curve IV. Explain the shape of curve IV.

Calcium carbonate would react with dilute 0.5M sulphuric(VI)acid to form insoluble calcium sulphate(VI) that coat /cover unreacted Calcium carbonate stopping the reaction from reaching completion.

6.Calculate the volume of carbon(IV)oxide evolved(molar gas volume at room temperature = 24 dm3, C= 12.0, O= 16.O Ca=40.0)
Method I

Mole ratio 
$$CaCO_3(s) : CO_2(g) = 1:1$$
  
Moles  $CaCO_3(s)$  used  $= \underbrace{Mass \ CaCO_3(s)}_{Molar \ mass \ CaCO_3(s)} = 0.025 \ moles$ 

Moles 
$$CO_2(g) = 0.025$$
 moles

Volume of 
$$CO_2(g)$$
 = moles x molar gas volume  
=>0.025 moles x 24 dm3 = **0.600 dm3/600cm3**

#### Method II

Molar mass of 
$$CaCO_3(s) = 100g$$
 produce 24 dm3 of  $CO_2(g)$   
Mass of  $CaCO_3(s) = 2.5$  g produce  $2.5 \times 24$  =  $0.600dm3$ 

7.From curve I ,determine the rate of reaction (loss in mass per second)at time 180 seconds on the curve.

From tangent at 180 seconds on curve I

Rate = 
$$\frac{M_2-M_1}{T_2-T_1}$$
 =>  $\frac{2.08-1.375}{222-132}$  =  $\frac{0.625}{90}$  = **0.006944g sec<sup>-1</sup>**

#### 8. What is the effect of particle size on the rate of reaction?

A larger surface area is a reduction in particle size which increases the area of contact between reacting particles increasing their collision frequency.

#### **Theoretical examples**

1. Excess marble chips were put in a beaker containing 100cm3 of 0.2M hydrochloric acid. The beaker was then placed on a balance and total loss in mass recorded after every two minutes as in the table below.

| Time(minutes)   | 0.0 | 2.0  | 4.0  | 6.0  | 8.0  | 10.0 | 12.0 |
|-----------------|-----|------|------|------|------|------|------|
| Loss in mass(g) | 0.0 | 1.80 | 2.45 | 2.95 | 3.20 | 3.25 | 3.25 |

#### (a) Why was there a loss in mass?

Carbon (IV) oxide gas was produced that escape to the surrounding

#### (b) Calculate the average rate of loss in mass between:

(i) 0 to 2 minutes

Average rate = 
$$\frac{M_2-M_1}{T_2-T_1}$$
 =>  $\frac{1.80-0.0}{2.0-0.0}$  =  $\frac{1.8}{2}$  = **9.00g min<sup>-1</sup>**

(i) 6 to 8 minutes

Average rate = 
$$\frac{M_2-M_1}{T_2-T_1}$$
 =>  $\frac{3.20-2.95}{8.0-6.0}$  =  $\frac{0.25}{2}$  = **0.125g min<sup>-1</sup>**

(iii) Explain the difference between the average rates of reaction in (i) and(ii) above.

Between 0 and 2 minutes , the concentration of marble chips and hydrochloric acid is high therefore there is a higher collision frequency between the reacting particles leading to high successful rate of formation of products.

Between 6 and 8 minutes, the concentration of marble chips and hydrochloric acid is low therefore there is low collision frequency between the reacting particles leading to less successful rate of formation of products.

(c)Write the equation for the reaction that takes place.

$$CaCO_3(s) + 2HCl (aq) \rightarrow CaCO_3 (aq) + H_2O(l) + CO_2(g)$$

- (d)State and explain three ways in which the rate of reaction could be increased.
- (i) Heating the acid-increasing the temperature of the reacting particles increases their kinetic energy and thus collision frequency.
- (ii)Increasing the concentration of the acid-increasing in concentration reduces the distances between the reacting particles increasing their chances of effective/fruitful/successful collision to form products faster.
- (iii) Crushing the marble chips to powder-this reduces the particle size/increase surface area increasing the area of contact between reacting particles.
- (e)If the solution in the beaker was evaporated to dryness then left overnight in the open, explain what would happen.

It becomes wet because calcium (II) chloride absorbs water from the atmosphere and form solution/is deliquescent.

- (f)When sodium sulphate (VI) was added to a portion of the contents in the beaker after the reaction , a white precipitate was formed .
  - (i)Name the white precipitate.

Calcium(II)sulphate(VI)

- (ii) Write an ionic equation for the formation of the white precipitate  $Ca^{2+}(aq) + SO_4^{2-}(aq) -> CaSO_4(s)$
- (iii)State one use of the white precipitate
  - -Making plaster for building
  - -Manufacture of plaster of Paris

#### -Making sulphuric(VI)acid

#### (g)(i) Plot a graph of total loss in mass(y-axes) against time

(ii) From the graph, determine the rate of reaction at time 2 minutes. From a tangent/slope at 2 minutes;

Rate of reaction = Average rate = 
$$\frac{M_2 - M_1}{T_2 - T_1}$$
 =>  $\frac{2.25 - 1.30}{3.20 - 0.8}$  =  $\frac{0.95}{2.4}$  = **0.3958g min**<sup>-1</sup>

(iii)Sketch on the same axes the graph that would be obtained if 0.02M hydrochloric acid was used. Label it curve II

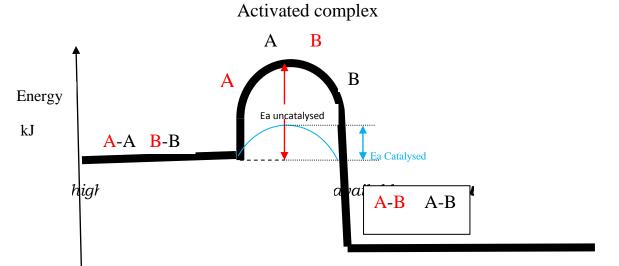
#### e) Influence of catalyst on rate of reaction

Catalyst is a substance that alter the rate /speed of a chemical reaction but remain chemically unchanged at the end of a reaction. Biological catalysts are called **enzymes**. A catalyst does not alter the amount of products formed but itself may be altered **physically** e.g. from solid to powder to fine powder. Like biological enzymes, a catalyst only catalyse specific type of reactions Most industrial catalysts are **transition metals** or their compounds. Catalyst works by lowering the Enthalpy of activation( $\Delta H_a$ )/activation energy (Ea) of the reactants .The catalyst lowers the Enthalpy of activation( $\Delta H_a$ )/activation energy (Ea) by:

- (i) forming short lived intermediate compounds called activated complex that break up to form the final product/s
- (ii) being absorbed by the reactants thus providing the surface area on which reaction occurs.

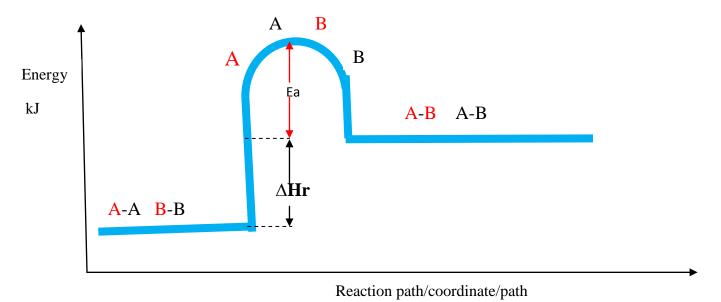
A catalyst has no effect on the enthalpy of reaction  $\Delta H_r$  but only lowers the Enthalpy of activation ( $\Delta H_a$ )/activation energy (Ea)It thus do not affect/influence whether the reaction is exothermic or endothermic as shown in the energy level diagrams below.

Energy level diagram showing the activation energy for exothermic processes /reactions.



Energy level diagram showing the activation energy for endothermic processes /reactions.

#### **Activated complex**



The following are some catalysed reaction processes.

#### (a) The contact process

Vanadium(V) Oxide( $V_2O_5$ ) or platinum(Pt) catalyses the oxidation of sulphur(IV)oxide during the manufacture of sulphuric(VI) acid from contact process.

$$SO_2(g) + O_2(g) ----V_2O_5--> SO_3(g)$$

To **reduce** industrial cost of manufacture of sulphuric (VI) acid from contact process  $Vanadium(V) Oxide(V_2O_5)$  is used because it is **cheaper** though it is **easily poisoned** by impurities.

#### (b)Ostwalds process

Platinum promoted with Rhodium catalyses the oxidation of ammonia to nitrogen(II)oxide and water during the manufacture of nitric(V)acid

$$4NH_3(g) + 5O_2(g) ----Pt/Rh--> 4NO(g) + 6H_2O(l)$$

#### (c)Haber process

Platinum or iron catalyses the combination of nitrogen and hydrogen to form ammonia gas

$$N_2(g) + 3H_2(g)$$
 ---**Pt or Fe**--->  $2NH_3(g)$ 

#### (d) Hydrogenation/Hardening of oil to fat

**Nickel** (**Ni**) catalyses the hydrogenation of unsaturated compound containing - C≡C- or −C=C- to saturated compounds without double or triple bond This process is used is used in hardening oil to fat.

#### (e)Decomposition of hydrogen peroxide

Manganese(IV)oxide speeds up the rate of decomposition of hydrogen peroxide to water and oxygen gas.

This process/reaction is used in the school laboratory preparation of Oxygen.

$$2H_2O_2(g)$$
 ----  $MnO_2$ -->  $O_2(g) + 2H_2O(1)$ 

#### (f)Reaction of metals with dilute sulphuric(VI)acid

**Copper(II)sulphate(VI)** speeds up the rate of production of hydrogen gas from the reaction of Zinc and dilute sulphuric(VI)acid.

This process/reaction is used in the school laboratory preparation of Hydrogen.

$$H_2 SO_4 (aq) + Zn(s)$$
 ----  $CuSO_4$ -->  $ZnSO_4 (aq) + H_2(g)$ 

#### (g) Substitution reactions

When placed in bright **sunlight** or **U.V** /**ultraviolet** light, a mixture of a halogen and an alkane undergo substitution reactions **explosively** to form halogenoalkanes. When paced in **diffused** sunlight the reaction is very **slow**.

e.g. 
$$CH_4(g) + Cl_2(g)$$
 ---**u.v. light**-->  $CH_3Cl(g) + HCl(g)$ 

#### (h)Photosynthesis

Plants convert carbon(IV)oxide gas from the atmosphere and water from the soil to form glucose and oxygen as a byproduct using sunlight / ultraviolet light.

$$6CO_2(g) \ + \ 6H_2O(l) \ --- \ \textbf{u.v. light} --> \ C_6H_{12}O_6(g) \ + \ O_2(g)$$

#### (i)Photography

Photographic film contains silver bromide emulsion which decomposes to silver and bromine on exposure to **sunlight**.

$$2AgBr(s)$$
 ---u.v/sun light-->  $2Ag(s) + Br_2(l)$ 

When developed, the silver deposits give the picture of the object whose photograph was taken depending on **intensity** of light. A picture photographed in **diffused** light is therefore **blurred**.

### Practical determination of effect of catalyst on decomposition of hydrogen peroxide

Measure 5cm3 of 20 volume hydrogen peroxide and then dilute to make 40cm3 in a measuring cylinder by adding distilled water.

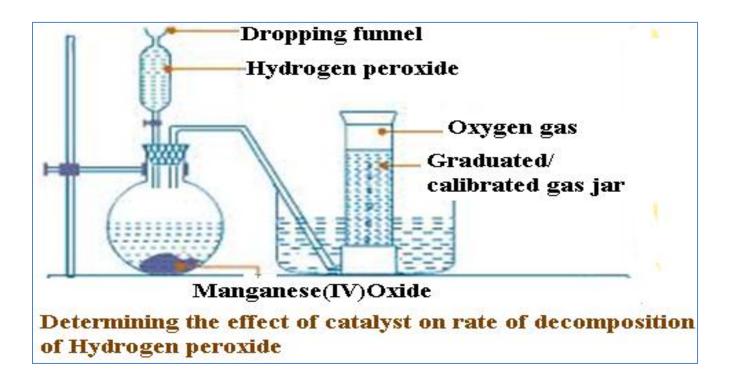
Divide it into two equal portions.

- (i)Transfer one 20cm3volume hydrogen peroxide into a conical/round bottomed/flat bottomed flask. Cork and swirl for 2 minutes. Remove the cork. Test the gas produced using a glowing splint. Clean the conical/round bottomed/flat bottomed flask.
- (ii)Put 2.0g of Manganese (IV) oxide into the clean conical/round bottomed/flat bottomed flask. Stopper the flask.

Transfer the second portion of the 20cm3volume hydrogen peroxide into a conical/round bottomed/flat bottomed flask through the dropping/thistle funnel. Connect the delivery tube to a calibrated/graduated gas jar as in the set up below.

Start off the stop watch and determine the volume of gas in the calibrated/graduated gas jar after every 30 seconds to complete Table 1.

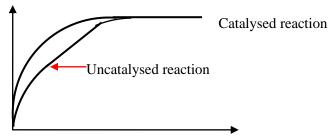
(iii) Weigh a filter paper .Use the filter paper to filter the contents of the conical conical/round bottomed/flat bottomed flask. Put the residue on a sand bath to dry. Weigh the dry filter paper again .Determine the new mass Manganese (IV) oxide.



| Time(seconds) | 0.0 | 30.0 | 60.0 | 90.0 | 120.0 | 150.0 | 180.0 | 210.0 | 240.0 | 270.0 |
|---------------|-----|------|------|------|-------|-------|-------|-------|-------|-------|
| Volume of gas | 0.0 | 20.0 | 40.0 | 60.0 | 80.0  | 90.0  | 95.0  | 96.0  | 96.0  | 96.0  |
| (cm3)         |     |      |      |      |       |       |       |       |       |       |

| Mass of MnO <sub>2</sub> <b>before</b> reaction(g) | Mass of MnO <sub>2</sub> after reaction(g) |
|--|--|
| 2.0  | 2.0  |

Plot a graph of volume of gas produced against time(x-axes)



- b) On the same axes, plot a graph of the uncatalysed reaction.
- (c) Explain the changes in mass of manganese(IV)oxide before and after the reaction.

The mass of MnO<sub>2</sub> before and after the reaction is the same but a more fine powder after the experiment. A catalyst therefore remains unchanged chemically but may physically change.

#### **B.EQUILIBRIA** (CHEMICAL CYBERNETICS)

Equilibrium is a state of balance.

Chemical equilibrium is state of balance between the reactants and products.

As reactants form products, some products form back the reactants.

Reactions in which the reactants form products to completion are said to be reversible i.e.

$$A + B \rightarrow C + D$$

Reactions in which the reactants form products and the products can reform the reactants are said to be reversible.

$$A + B + D$$

Reversible reactions may be:

- (a)Reversible physical changes
- (b)Reversible chemical changes
- (c)Dynamic equilibrium

#### (a)Reversible physical changes

Reversible physical change is one which involves:

- (i) change of state/phase from solid, liquid, gas or aqueous solutions. States of matter are interconvertible and a reaction involving a change from one state/phase can be reversed back to the original.
- (ii) colour changes. Some substances/compounds change their colours without change in chemical substance.

Examples of reversible physical changes

#### (i) colour change on heating and cooling:

**I.** Zinc(II)Oxide changes from white when cool/cold to yellow when hot/heated and back.

$$ZnO(s) \longrightarrow ZnO(s)$$
 (white when cold) (yellow when hot)

**II.** Lead(II)Oxide changes from yellow when cold/cool to brown when hot/heated and back.

$$PbO(s)$$
  $\longleftarrow$   $PbO(s)$ 

(brown when hot) (yellow when cold)

#### (ii)Sublimation

**I.** Iodine **sublimes** from a grey crystalline solid on heating to purple vapour. Purple vapour undergoes **deposition** back to the grey crystalline solid.

$$I_2(\mathbf{s}) \xleftarrow{} I_2(\mathbf{g})$$
(grey crystalline solid undergo sublimation) undergo deposition)

**II.** Carbon (IV)oxide gas undergoes **deposition** from a colourless gas to a white solid at very high pressures in a cylinder. It **sublimes** back to the colourless gas if pressure is reduced

$$CO_2(\mathbf{s}) \longrightarrow CO_2(\mathbf{g})$$
 (white powdery solid (colourless/odourless gas undergo sublimation) undergo deposition)

#### (iii) Melting/freezing and boiling/condensation

Ice on heating undergo **melting** to form a liquid/water. Liquid/water on further heating **boil**/vaporizes to form gas/water vapour. Gas/water vapour on cooling, **condenses**/liquidifies to water/liquid. On further cooling, liquid water **freezes** to ice/solid.

$$H_2O(s)$$

Melting
Freezing

 $H_2O(l)$ 

boiling

condensing

 $H_2O(s)$ 

#### (iv)Dissolving/crystallization/distillation

Solid crystals of soluble substances (solutes) dissolve in water /solvents to form a uniform mixture of the solute and solvent/solution. On crystallization /distillation /evaporation the solvent evaporate leaving a solute back. e.g.

$$NaCl(s) + aq \longrightarrow NaCl(aq)$$

#### (b)Reversible chemical changes

These are reactions that involve a chemical change of the reactants which can be reversed back by recombining the new substance formed/products.

Examples of Reversible chemical changes

(i) Heating Hydrated salts/adding water to anhydrous salts.

When **hydrated** salts are heated they **lose** <u>some/all</u> their **water** of crystallization and become **anhydrous**. Heating an unknown substance /compound that forms a **colourless liquid droplets** on the **cooler** parts of a dry test/boiling tube is in fact a **confirmation** inference that the substance/compound being heated is **hydrated**.

When anhydrous salts are added (back) some water they form hydrated compound/salts.

Heating Copper(II)sulphate(VI)pentahydrate and cobalt(II)chloride hexahydrate

- (i)Heat about 5.0g of Copper(II)sulphate(VI) pentahydrate in a clean dry test tube until there is no further colour change on a <u>small</u> Bunsen flame. Observe any changes on the side of the test/boiling tube. Allow the boiling tube to cool.Add about 10 drops of distilled water. Observe any changes.
- (ii)Dip a filter paper in a solution of cobalt(II)chloride hexahydrate. Pass one end the filter paper to a <u>small</u> Bunsen flame repeatedly. Observe any changes on the filter paper. Dip the paper in a beaker containing distilled water. Observe any changes.

Sample observations

| Hydrated           | Observation      | Observation after heating          | Observation on                  |
|--------------------|------------------|------------------------------------|---------------------------------|
| compound           | before heating   |                                    | adding water                    |
| Copper(II)sulphate | Blue crystalline | (i)colour changes from <b>blue</b> | (i)colour changes               |
| (VI) pentahydrate  | solid            | to <b>white</b> .                  | from white to blue              |
|                    |                  | (ii)colourless liquid forms on     | (ii)boiling tube                |
|                    |                  | the cooler parts of boiling /      | becomes warm /hot.              |
|                    |                  | test tube                          |                                 |
| Cobalt(II)chloride | Pink crystalline | (i)colour changes from <b>pink</b> | (i)colour changes               |
| hexahydrate        | solid/solution   | to <b>blue</b> .                   | from <b>blue</b> to <b>pink</b> |
|                    |                  | (ii) colourless liquid forms on    | (ii)boiling tube                |
|                    |                  | the cooler parts of boiling /      | becomes warm/hot.               |
|                    |                  | test tube (if crystal are used)    |                                 |
|                    |                  |                                    |                                 |

When blue Copper(II)sulphate (VI) pentahydrate is heated, it loses the five molecules of water of crystallization to form white anhydrous Copper(II)sulphate (VI). Water of crystallization form and condenses as colourless droplets on the cooler parts of a dry boiling/test tube. This is a chemical change that produces a new substance. On adding drops of water to an anhydrous white copper(II)sulphate(VI) the hydrated compound is

formed back. The change from **hydrated** to **anhydrous** and **back** is therefore **reversible chemical change.**Both anhydrous white copper(II)sulphate(VI) and blue cobalt(II)chloride hexahydrate are therefore used to test for the presence of water when they turn to blue and pink respectively.

#### (ii)Chemical sublimation

Some compounds sublime from solid to gas by dissociating into new different compounds. e.g.

#### Heating ammonium chloride

(i)Dip a glass rod containing concentrated hydrochloric acid. Bring it near the mouth of a bottle containing concentrated ammonia solution. Explain the observations made.

When a glass rod containing hydrogen chloride gas is placed near ammonia gas, they react to form ammonium chloride solid that appear as **white fumes**. This experiment is used interchangeably to test for the presence of hydrogen chloride gas (and hence Cl<sup>-</sup> ions) and ammonia gas (and hence NH<sub>4</sub><sup>+</sup> ions)

(ii)Put 2.0 g of ammonium chloride in a long dry boiling tube. Place wet / moist /damp blue and red litmus papers separately on the sides of the mouth of the boiling tube. Heat the boiling tube gently then strongly. Explain the observations made.

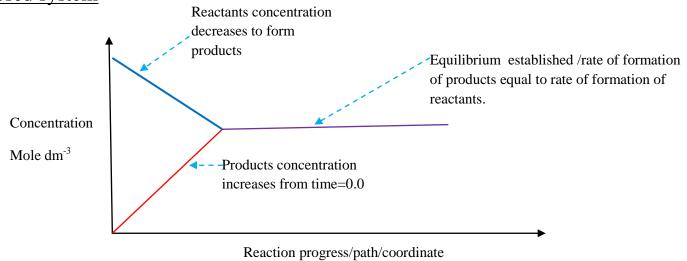
When ammonium chloride is heated it dissociates into ammonia and hydrogen chloride gases. Since ammonia is less dense, it diffuses faster to turn both litmus papers blue before hydrogen chloride turn red because it is denser. The heating and cooling of ammonium chloride is therefore a **reversible chemical change**.

$$NH_3(g)$$
 +  $HCl(g)$   $\longleftrightarrow$   $NH_4Cl(s)$  (Turns moist (forms white fumes) litmus paper blue) litmus paper red)

#### (c)Dynamic equilibria

For reversible reactions in a closed system:

- (i) at the beginning;
  - -the reactants are decreasing in concentration with time
  - -the products are increasing in concentration with time
- (ii) after some time a point is reached when as the reactants are forming products the products are forming reactants. This is called equilibrium. Sketch showing the changes in concentration of reactants and products in a closed system



For a system in equilibrium:

- (i) a reaction from left to right (reactants to products) is called forward reaction.
- (ii) a reaction from right to left (products to reactants) is called backward reaction.
- (iii) a reaction in which the rate of forward reaction is equal to the rate of backward reaction is called a **dynamic equilibrium.**

A dynamic equilibrium is therefore a balance of the rate of formation of products and reactants. This balance continues until the reactants or products are disturbed/changed/ altered.

The influence of different factors on a dynamic equilibrium was first investigated from 1850-1936 by the French Chemist Louis Henry Le Chatellier. His findings were called Le Chatelliers Principle which states that:

"if a stress/change is applied to a system in dynamic equilibrium, the system readjust/shift/move/behave so as to remove/ reduce/ counteract/ oppose the stress/change"

Le Chatelliers Principle is applied in determining the effect/influence of several factors on systems in dynamic equilibrium. The following are the main factors that influence /alter/ affect systems in dynamic equilibrium:

- (a)Concentration
- (b)Pressure
- (c)Temperature
- (d)Catalyst

#### (a)Influence of concentration on dynamic equilibrium

An increase/decrease in concentration of reactants/products at equilibrium is a stress. From Le Chatelliers principle the system redjust so as to remove/add the excessreduced concentration.

Examples of influence of concentration on dynamic equilibrium (i)Chromate(VI)/ $CrO_4^{2-}$  ions in solution are **yellow**. Dichromate(VI)/ $Cr_2O_7^{2-}$  ions in solution are **orange**. The two solutions exist in equilibrium as in the equation:

$$2H^{+}(aq) + 2CrO_{4}^{2-}(aq) = Cr_{2}O_{7}^{2-}(aq) + H_{2}O(l)$$
(Yellow) (Orange)

- I. If an acid is/H<sup>+</sup> (aq) is added to the equilibrium mixture a stress is created on the reactant side where there is already H<sup>+</sup> ions. The equilibrium shift forward to the right to remove/reduce the **excess** H<sup>+</sup> ions added. Solution mixture becomes More  $Cr_2O_7^{2-}$  ions formed in the solution mixture make it to be more **orange** in colour.
- **II**. If a base/OH<sup>-</sup> (aq) is added to the equilibrium mixture a stress is created on the reactant side on the H<sup>+</sup> ions. H<sup>+</sup> ions react with OH<sup>-</sup> (aq) to form water.

$$H^{+}(aq) + OH^{-}(aq) -> H_{2}O(1)$$

The equilibrium shift backward to the left to add/replace the  $H^+$  ions that have reacted with the  $OH^-$  (aq) ions . More of the  $CrO_4^{\ 2^-}$  ions formed in the solution mixture makes it to be more **yellow** in colour.

$$2OH^{-}(aq) + 2Cr_2O_7^{2-}(aq)$$
  $CrO_4^{2-}(aq) + H_2O(l)$  (Yellow)

**I.** If an acid/  $H^+$  (aq) is added to the equilibrium mixture a stress is created on the reactant side on the  $OH^-$  (aq).  $H^+$  ions react with  $OH^-$  (aq) to form water.

$$H^{+}(aq) + OH^{-}(aq) -> H_{2}O(1)$$

The equilibrium shift backward to the left to add/replace the  $2OH^-$  (aq) that have reacted with the  $H^+$  (aq) ions . More  $Cr_2O_7^{-2-}$  (aq)ions formed in the solution mixture makes it to be more **Orange** in colour.

- II. If a base  $/OH^-$  (aq) is added to the equilibrium mixture a stress is created on the reactant side where there is already  $OH^-$  (aq) ions. The equilibrium shift forward to the right to remove/reduce the **excess**  $OH^-$  (aq) ions added. More of the  $Cr_2O_7^{-2-}$  ions are formed in the solution mixture making it to be more **orange** in colour.
- (i) Practical determination of the influence of alkali/acid on  $Cr_2O_7^{2-}/CrO_4^{2-}$  equilibrium mixture

Measure about 2 cm3 of Potassium dichromate (VI) solution into a test tube.

#### Note that the solution mixture is orange.

Add three drops of 2M sulphuric(VI) acid. Shake the mixture carefully.

Note that the solution mixture is remains orange.

Add about six drops of 2M sodium hydroxide solution. Shake carefully.

Note that the solution mixture is turns yellow.

#### **Explanation**

The above observations can be explained from the fact that both the dichromate(VI) and chromate(VI) exist in equilibrium. Dichromate(VI) ions are stable in acidic solutions while chromate(VI)ions are stable in basic solutions. An equilibrium exist thus:

$$\operatorname{Cr}_2\operatorname{O_7}^{2-}$$
  $\stackrel{\operatorname{OH-}}{=}$   $\operatorname{CrO_4}^{2-}$ 

When an **acid** is added, the equilibrium shift **forward** to the right and the mixture become more **orange** as more  $Cr_2O_7^{2-}$  ions exist.

When a **base** is added, the equilibrium shift **backward** to the left and the mixture become more **yellow** as more  $CrO_4^{2-}$  ions exist.

### (ii) Practical determination of the influence of alkali/acid on bromine water in an equilibrium mixture

Measure 2cm3 of bromine water into a boiling tube. Note its colour.

#### **Bromine water is yellow**

Add three drops of 2M sulphuric(VI)acid. Note any colour change

#### Colour becomes more yellow

Add seven drops of 2M sodium hydroxide solution. Note any colour change.

#### Solution mixture becomes colourless/Bromine water is decolourized. <u>Explanation</u>

When added distilled water, an equilibrium exist between bromine liquid  $(Br_2(aq))$  and the bromide  $ion(Br^-)$ , hydrobromite  $ion(OBr^-)$  and hydrogen  $ion(H^+)$  as in the equation:

$$H_2O(1) + Br_2(aq) \longrightarrow OBr^-(aq) + H^+(aq) + Br^-(aq)$$

If an acid (H<sup>+</sup>)ions is added to the equilibrium mixture, it increases the concentration of the ions on the product side which shift backwards to the left to remove the excess H<sup>+</sup> ions on the product side making the colour of the solution mixture more yellow.

If a base/alkali OH<sup>-</sup> is added to the equilibrium mixture, it reacts with H<sup>+</sup> ions on the product side to form water.

$$H^{+}(aq) + OH^{-}(aq) -> H_{2}O(1)$$

This decreases the concentration of the H<sup>+</sup> ions on the product side which shift the equilibrium forward to the right to replace H<sup>+</sup> ions making the solution mixture colourless/less yellow (Bromine water is decolorized)

(iii)Practical determination of the influence of alkali/acid on common acid-base indicators.

Place 2cm3 of phenolphthalein, methyl orange and litmus solutions each in three separate test tubes.

To each test tube add two drops of water. Record your observations in Table 1 below.

To the same test tubes, add three drops of 2M sulphuric(VI)acid. Record your observations in Table 1 below.

To the same test tubes, add seven drops of 2M sodium hydroxide solution. Record your observations in Table 1 below.

To the same test tubes, repeat adding four drops of 2M sulphuric(VI)acid.

#### Table 1

| Indicator       | Colour of indicator in |                   |                |
|-----------------|------------------------|-------------------|----------------|
|                 | Water                  | Acid(2M sulphuric | Base(2M sodium |
|                 |                        | (VI) acid)        | hydroxide)     |
| Phenolphthalein | Colourless             | Colourless        | Pink           |
| Methyl orange   | Yellow                 | Red               | Orange         |
| Litmus solution | Colourless             | Red               | Blue           |

## Explanation

An indicator is a substance which shows whether **another** substance is an **acid**, **base** or **neutral**.

Most indicators can be regarded as very weak acids that are partially dissociated into ions. An equilibrium exist between the undissociated molecules and the dissociated anions. Both the molecules and anions are **coloured**. i.e.

When an acid H<sup>+</sup> is added to an indicator, the H<sup>+</sup> ions increase and equilibrium shift backward to remove excess H<sup>+</sup> ions and therefore the **colour** of the undissociated (**HIn**) molecule **shows/appears**.

When a base/alkali OH<sup>-</sup> is added to the indicator, the OH<sup>-</sup> reacts with H<sup>+</sup> ions from the dissociated indicator to form water.

$$H^{+}(aq) + OH^{-}(aq) \rightarrow H_2O(l)$$
 (from indicator) (from alkali/base)

The equilibrium shift forward to the right to replace the H<sup>+</sup> ion and therefore the colour of dissociated (In ) molecule shows/appears.

The following examples illustrate the above.

(i)Phenolphthalein indicator exist as:

On adding an acid ,equilibrium shift backward to the left to remove excess H<sup>+</sup> ions and the solution mixture is therefore **colourless.** 

When a base/alkali OH is added to the indicator, the OH reacts with H ions from the dissociated indicator to form water.

$$H^{+}(aq) + OH^{-}(aq) \rightarrow H_{2}O(l)$$
 (from indicator) (from alkali/base)

The equilibrium shift forward to the right to replace the removed/reduced H<sup>+</sup> ions. The **pink** colour of dissociated (**Ph**<sup>-</sup>) molecule **shows/appears.** 

(ii) Methyl Orange indicator exists as:

On adding an acid ,equilibrium shift backward to the left to remove excess H<sup>+</sup> ions and the solution mixture is therefore **red**.

When a base/alkali OH is added to the indicator, the OH reacts with H ions from the dissociated indicator to form water.

$$H^{+}(aq) + OH^{-}(aq) \rightarrow H_{2}O(l)$$
 (from indicator) (from alkali/base)

The equilibrium shift forward to the right to replace the removed/reduced H<sup>+</sup> ions. The **Orange** colour of dissociated (**Me**<sup>-</sup>) molecule **shows/appears.** 

## (b)Influence of Pressure on dynamic equilibrium

Pressure affects gaseous reactants/products. Increase in **pressure** shift/**favours** the equilibrium towards the side with **less volume/molecules**. Decrease in pressure shift the equilibrium towards the side with more volume/molecules. More yield of products is obtained if high pressures produce less molecules / volume of products are formed.

If the products and reactants have **equal** volume/molecules then pressure has **no effect** on the position of equilibrium

The following examples show the influence of pressure on dynamic equilibrium:

## (i)Nitrogen(IV)oxide /Dinitrogen tetroxide mixture

Nitrogen(IV)oxide and dinitrogen tetraoxide can exist in dynamic equilibrium in a closed test tube. Nitrogen(IV)oxide is a brown gas. Dinitrogen tetraoxide is a yellow gas.

Chemical equation:  $2NO_2(g) \leq ==== N_2 O_4(g)$  **Gay Lussacs law** 2Volume 1Volume**Avogadros law** 2molecule 1molecule

2 volumes/molecules of Nitrogen(IV)oxide form 1 volumes/molecules of dinitrogen tetraoxide

Increase in pressure shift the equilibrium forward to the left where there is less volume/molecules. The equilibrium mixture become more yellow.

Decrease in pressure shift the equilibrium backward to the right where there is more volume/molecules. The equilibrium mixture become more **brown**.

## (ii) Iodine vapour-Hydrogen gas/Hydrogen Iodide mixture.

Pure hydrogen gas reacts with Iodine vapour to form Hydrogen Iodide gas.

Chemical equation :  $I_2(g) + H_2(g) \leq ====$  2HI (g)

Gay Lussacs law
1Volume
1Volume
2Volume
2molecule

(1+1) **2** volumes/molecules of Iodine and Hydrogen gasform **2** volumes/molecules of Hydrogen Iodide gas.

Change in pressure thus has no effect on position of equilibrium.

## (iii) Haber process.

Increase in pressure of the Nitrogen/Hydrogen mixture favours the formation of **more** molecules of Ammonia gas in Haber process.

The yield of ammonia is thus favoured by high pressures

(1 + 3) 4 volumes/molecules of Nitrogen and Hydrogen react to form 2 volumes/molecules of ammonia.

Increase in pressure shift the equilibrium forward to the left where there is less volume/molecules.

The yield of ammonia increase.

Decrease in pressure shift the equilibrium backward to the right where there is more volume/molecules.

The yield of ammonia decrease.

## (iv)Contact process.

Increase in pressure of the Sulphur(IV)oxide/Oxygen mixture favours the formation of **more** molecules of Sulphur(VI)oxide gas in Contact process. The yield of Sulphur(VI)oxide gas is thus favoured by high pressures.

(2 + 1) **3** volumes/molecules of Sulphur(IV)oxide/Oxygen mixture react to form **2** volumes/molecules of Sulphur(VI)oxide gas.

Increase in pressure shift the equilibrium forward to the left where there is less volume/molecules. The yield of Sulphur(VI)oxide gas increase.

Decrease in pressure shift the equilibrium backward to the right where there is more volume/molecules. The yield of Sulphur(VI)oxide gas decrease.

## (v)Ostwalds process.

Increase in pressure of the Ammonia/Oxygen mixture favours the formation of **more** molecules of Nitrogen(II)oxide gas and water **vapour** in Ostwalds process. The yield of Nitrogen(II)oxide gas and water **vapour** is thus favoured by low pressures.

(4 + 5) 9 volumes/molecules of Ammonia/Oxygen mixture react to form 10 volumes/molecules of Nitrogen(II)oxide gas and water **vapour**.

Increase in pressure shift the equilibrium backward to the left where there is less volume/molecules. The yield of Nitrogen(II)oxide gas and water vapour **decrease**.

Decrease in pressure shift the equilibrium forward to the right where there is more volume/molecules. The yield of Nitrogen(II)oxide gas and water vapour **increase**.

#### Note

If the water vapour is **condensed** on cooling, then:

Chemical equation :  $4NH_3(g) + 5O_2(g) -> 4NO(g) + 6H_2O(l)$  **Gay Lussacs law** 4Volume 5Volume 4Volume 0Volume **Avogadros law** 4molecule 5molecule 4molecule 0Molecule

(4 + 5) 9 volumes/molecules of Ammonia/Oxygen mixture react to form 4 volumes/molecules of Nitrogen(II)oxide gas and no **vapour**.

Increase in pressure shift the equilibrium forward to the right where there is less volume/molecules. The yield of Nitrogen(II)oxide gas **increase**.

Decrease in pressure shift the equilibrium backward to the left where there is more volume/molecules. The yield of Nitrogen(II)oxide gas **decrease**.

## (c)Influence of Temperature on dynamic equilibrium

A **decrease** in temperature favours the reaction that liberate/generate more heat thus **exothermic** reaction( $-\Delta H$ ).

An **increase** in temperature favours the reaction that do not liberate /generate more heat thus **endothermic** reaction( $+\Delta H$ ).

Endothermic reaction are thus favoured by high temperature/heating Exothermic reaction are favoured by low temperature/cooling.

If a reaction/equilibrium mixture is neither exothermic or endothermic, then a change in temperature/cooling/heating has no effect on the equilibrium position.

## (i)Nitrogen(IV)oxide /Dinitrogen tetroxide mixture

Nitrogen(IV)oxide and dinitrogen tetraoxide can exist in dynamic equilibrium in a closed test tube. Nitrogen(IV)oxide is a brown gas. Dinitrogen tetraoxide is a yellow gas.

Chemical equation:  $2NO_2(g) \leq === = N_2 O_4(g)$ 

On heating /increasing temperature, the mixture becomes more brown. On cooling the mixture become more yellow.

This show that

(i) the forward reaction to the right is exothermic ( $-\Delta H$ ).

On heating an exothermic process the equilibrium shifts to the side that generate /liberate less heat.

(ii) the backward reaction to the right is endothermic  $(+\Delta H)$ .

On cooling an endothermic process the equilibrium shifts to the side that do not generate /liberate heat.

## (c)Influence of Catalyst on dynamic equilibrium

A catalyst has no effect on the position of equilibrium. It only speeds up the rate of attainment. e.g.

Esterification of alkanols and alkanoic acids naturally take place in fruits.In the laboratory concentrated sulphuric(VI)acid catalyse the reaction.The equilibrium mixture forms the ester faster but the yield does not increase.

# (d)Influence of rate of reaction and dynamic equilibrium (Optimum conditions) on industrial processes

Industrial processes are commercial profit oriented. All industrial processes take place in closed systems and thus in dynamic equilibrium.

For manufacturers, obtaining the highest yield at minimum cost and shortest time is paramount.

The conditions required to obtain the highest yield of products within the shortest time at minimum cost are called **optimum conditions**Optimum condition thus require understanding the effect of various factors on:

- (i)rate of reaction(Chemical kinetics)
- (ii)dynamic equilibrium(Chemical cybernetics)

## **1.Optimum condition in Haber process** Chemical equation

$$N_2(g) + 3H_2(g) = = Fe/Pt = 2NH_3(g) \Delta H = -92kJ$$

## Equilibrium/Reaction rate considerations

- (i)**Removing ammonia** gas once formed shift the equilibrium forward to the right to replace the ammonia. More/higher yield of ammonia is attained.
- (ii)**Increase in pressure** shift the equilibrium forward to the right where there is less volume/molecules . **More/higher yield** of ammonia is attained. Very **high** pressures raises the **cost** of production because they are **expensive** to produce and maintain. An <u>optimum</u> pressure of about <u>500</u> atmospheres is normally used.
- (iii)**Increase in temperature** shift the equilibrium backward to the left because the reaction is exothermic( $\Delta H = -92 \mathrm{kJ}$ ). Ammonia formed **decomposes** back to Nitrogen and Hydrogen to remove excess heat therefore a **less** yield of ammonia is attained. Very **low** temperature decrease the collision frequency of Nitrogen and Hydrogen and thus the rate of reaction **too slow** and **uneconomical**. An <u>optimum</u> temperature of about  $450^{\circ}\mathrm{C}$  is normally used.
- (iv)Iron and platinum can be used as catalyst. **Platinum** is a **better** catalyst but more **expensive** and easily **poisoned** by impurities than Iron. Iron is promoted /impregnated with AluminiumOxide( $Al_2O_3$ ) to increase its surface area/area of contact with reactants and thus efficiency. The catalyst does not increase the yield of ammonia but it speed up its rate of formation.

## 2.Optimum condition in Contact process

## **Chemical equation**

$$2SO_2(g) + O_2(g) ===V_2O_5/Pt=== 2SO_3(g) \Delta H = -197kJ$$

**Equilibrium/Reaction rate considerations** 

- (i)**Removing sulphur(VI)oxide** gas once formed shift the equilibrium forward to the right to replace the sulphur(VI)oxide. More/higher yield of sulphur(VI) oxide is attained.
- (ii)**Increase in pressure** shift the equilibrium forward to the right where there is less volume/molecules . **More/higher yield** of sulphur(VI)oxide is attained. Very **high** pressures raises the **cost** of production because they are **expensive** to produce and maintain. An <u>optimum</u> pressure of about <u>1-2</u> atmospheres is normally used to attain about 96% yield of SO<sub>3</sub>.
- (iii) Increase in temperature shift the equilibrium backward to the left because the reaction is exothermic ( $\Delta H = -197 kJ$ ). Sulphur (VI) oxide formed decomposes back to Sulphur (IV) oxide and Oxygen to remove excess heat therefore a less yield of Sulphur (VI) oxide is attained. Very <u>low</u> temperature decrease the collision frequency of Sulphur (IV) oxide and Oxygen and thus the rate of reaction too slow and uneconomical.

An <u>optimum</u> temperature of about <u>450°C</u> is normally used.

(iv)Vanadium(V)Oxide and platinum can be used as catalyst. **Platinum** is a **better** catalyst and **less** easily **poisoned** by impurities but more **expensive**. Vanadium(V)Oxide is <u>very cheap</u> even if it is <u>easily</u> poisoned by impurities. The catalyst does not increase the yield of Sulphur (VI)Oxide but it speed up its rate of formation.

## 3.Optimum condition in Ostwalds process

## **Chemical equation**

$$4NH_3(g) + 5O_2(g) = = Pt/Rh = = 4NO(g) + 6H_2O(g) \Delta H = -950kJ$$

## **Equilibrium/Reaction rate considerations**

- (i)**Removing Nitrogen(II)oxide** gas once formed shift the equilibrium forward to the right to replace the Nitrogen(II)oxide. More/higher yield of Nitrogen(II) oxide is attained.
- (ii)**Increase in pressure** shift the equilibrium backward to the left where there is less volume/molecules . **Less/lower yield** of Nitrogen(II)oxide is attained.

Very <u>low</u> pressures increases the distance between reacting NH<sub>3</sub>and O<sub>2</sub> molecules.

An optimum pressure of about 9 atmospheres is normally used.

(iii) Increase in temperature shift the equilibrium backward to the left because the reaction is exothermic ( $\Delta H = -950 \mathrm{kJ}$ ). Nitrogen(II) oxide and water vapour formed decomposes back to Ammonia and Oxygen to remove excess heat therefore a less yield of Nitrogen(II) oxide is attained. Very <u>low</u> temperature decrease the collision frequency of Ammonia and Oxygen and thus the rate of reaction too slow and uneconomical.

An <u>optimum</u> temperature of about <u>900°C</u> is normally used.

- (iv)Platinum can be used as catalyst. Platinum is very expensive.It is:
  - -promoted with Rhodium to increase the surface area/area of contact.
  - -added/coated on the surface of asbestos to form platinized –asbestos to reduce the amount/quantity used.

The catalyst does not increase the yield of Nitrogen (II)Oxide but it speed up its rate of formation.

## **C.SAMPLE REVISION QUESTIONS**

- 1.State two distinctive features of a dynamic equilibrium.
- (i)the rate of forward reaction is equal to the rate of forward reaction (ii)at equilibrium the concentrations of reactants and products do not change.
- 2. Explain the effect of increase in pressure on the following:

(i) 
$$N_2(g) + O_2(g) ==== 2NO(g)$$

Gay Lussacs law 1Volume 1Volume 2 Volume Avogadros law 1 molecule 1 molecule 2 molecule 2 volume on reactant side produce 2 volume on product side. Increase in pressure thus have no effect on position of equilibrium.

(ii) 
$$2H_2(g) + CO(g) = CH_3OH(g)$$

Gay Lussacs law 2Volume 1Volume 1 Volume Avogadros law 2 molecule 1 molecule 1 molecule 3 volume on reactant side produce 1 volume on product side.

Increase in pressure shift the equilibrium forward to the left. More yield of CH<sub>3</sub>OH is formed.

4. Explain the effect of increasing temperature on the following:

$$2SO_2(g) + O_2(g) ===== 2SO_3(g) \Delta H = -189kJ$$

Forward reaction is exothermic. Increase in temperature shift the equilibrium backward to reduce the excess heat.

5.120g of brass an alloy of copper and Zinc was put it a flask containing dilute hydrochloric acid. The flask was placed on an electric balance. The readings on the balance were recorded as in the table below

| Time(Seconds) | Mass of flask(grams) | Loss in mass(grams) |
|---------------|----------------------|---------------------|
| 0             | 600                  |                     |
| 20            | 599.50               |                     |
| 40            | 599.12               |                     |
| 60            | 598.84               |                     |
| 80            | 598.66               |                     |
| 100           | 598.54               |                     |
| 120           | 598.50               |                     |
| 140           | 598.50               |                     |
| 160           | 598.50               |                     |

- (a)Complete the table by calculating the loss in mass
- (b) What does the "600" gram reading on the balance represent **The initial mass of brass and the acid before any reaction take place.**
- (c)Plot a graph of Time (x-axes) against loss in mass.
- (d)Explain the shape of your graph

The reaction produce hydrogen gas as one of the products that escape to the atmosphere. This decreases the mass of flask. After 120 seconds, the

## react is complete. No more hydrogen is evolved. The mass of flask remain constant.

(d)At what time was the loss in mass equal to:

(i)1.20g

Reading from a correctly plotted graph =

(ii)1.30g

Reading from a correctly plotted graph =

(iii)1.40g

Reading from a correctly plotted graph =

(e)What was the loss in mass at:

 $(i)50^{\circ}C$ 

Reading from a correctly plotted graph =

(ii) 70°C

Reading from a correctly plotted graph =

(iii) 90°C g

Reading from a correctly plotted graph =

\*

<sup>❖</sup> All secondary school schemes of work.

<sup>❖</sup> Form 1-form 4 revision papers in all subjects.

- $\ \, \bigstar \,$  Marking schemes to most of the revision papers.
- ❖ K.C.S.E past papers.
- University past papers.
- ❖ K.A.S.N.E.B past papers e.g. C.P.A
- Primary school schemes of work.
- ❖ Primary school revision papers to all classes.
- ❖ Marking schemes to primary school past papers.
- \* K.C.P.E past papers.