**CHEMICAL KINETICS**

**REACTION RATES AND REVERSIBLE REACTION**

**REACTION RATES**

* The rate of a chemical reaction is the time taken for a given amount of reactant to be consumed or of products to be formed.
* 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.

As the reaction proceeds the amount of reactants decrease as the amount of products increase.

**products**

**Concentration**

**In mol-1**

**reactants**

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

**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.

Thecollision theory proposes that

1. For a reaction to occur, reacting particles must collide.
2. Not all collisions between reacting particles are successful in a reaction. Collisions that initiate a chemical reaction are called successful / fruitful/ effective collisions
3. The speed at which particles collide is called **collision frequency**. The higher the collision frequency, the higher the **chances** of successful collisions to form products.
4. The higher the chances of successful collisions, the faster the reaction.
5. The average distance between solid particles from one another is too big for them to meet and collide successfully.
6. 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.

1. 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.

**The Activation Energy (Ea) theory**

* The **Enthalpy of activation (**∆**Ha) /Activation Energy (Ea)** is the minimum amount of energy required by the reacting particles to cause a successful collision to form products.
* Activation Energy (Ea) is usually required /needed in bond breaking of the reacting particles.
* 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.

Activated complex

A B

A-B A-B

B

A

A-A B-B

Ea

Energy

kJ

Reaction path

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

**Activated complex**

A B

∆**Hr**

A-B A-B

A-A B-B

Ea

B

A

Reaction path

Energy

kJ

**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.

**Factors affecting 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

1. **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.

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

Sample results: the time taken for the cross(X) to disappear at different concentration of the acid is recorded below.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **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**  **1**  **t** |
| 20.0 | 0.0 | 20.0 | 20.0 | 5.0 x 10-2 |
| 18.0 | 2.0 | 20.0 | 23.0 | 4.35 x 10-2 |
| 16.0 | 4.0 | 20.0 | 27.0 | 3.7 x 10-2 |
| 14.0 | 6.0 | 20.0 | 32.0 | 3.13 x 10-2 |
| 12.0 | 8.0 | 20.0 | 42.0 | 2.38 x 10-2 |
| 10.0 | 10.0 | 20.0 | 56.0 | 1.78 x 10-2 |

**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.

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 x 10-2**

t = 1 / 2.75 x 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 x 10-2  = **29.8507 seconds**

(iii) 15cm3

From a correctly plotted graph

1/t at 17cm3 on the graph = **4.0 x 10-2**

t = 1 / 4.0 x 10-2  = **25.0 seconds**

(iv) 19cm3

From a correctly plotted graph

1/t at 19cm3 on the graph = **4.65 x 10-2**

t = 1 / 4.65 x 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 x 10-2**

**Reading**from a correctly plotted graph;

4.0 x 10-2 correspond to **17.0 cm3**

(ii) 30 seconds

1/t = 1/30 = **3.33 x 10-2**

**Reading**from a correctly plotted graph;

3.33 x 10-2 correspond to **14.7 cm3**

(iii) 40 seconds

1/t = 1/40 = **2.5 x 10-2**

**Reading**from a correctly plotted graph;

2.5 x 10-2 correspond to **12.3 cm3**

5. Write the equation for the reaction taking place

**Na2S2O3 (aq) + 2HCl(aq) 2NaCl (aq)+ SO2 (g) + S(s) + H2O(l)**

Ionically:

**S2O32- (aq) + 2H+ (aq) SO2 (g) + S(s) + H2O(l)**

6. Name the yellow precipitate

* **Colloidal sulphur**

**Reaction of Magnesium with dilute hydrochloric acid**

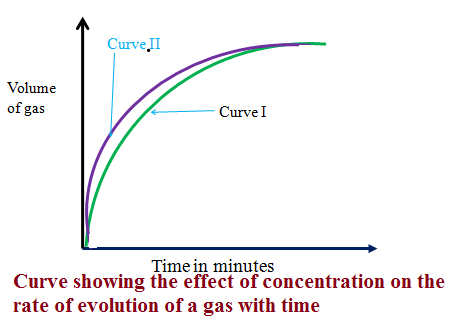
* The volume of the gas produced during the reaction is recorded after every 30 seconds sa shown in the table below.

Sample results: Table II

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

Sample practice questions

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



1. **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.

1. **Calculate the rate of reaction at 120 seconds**

**Form a tangent** at 120 seconds rate of reaction = Change in volume of gas

Change in time

=**From the tangent** at 120seconds V2 - V1 = 96-84 = 12 = **0.2cm3sec-1**

T2 - T1 150-90 60

1. **Write an ionic equation for the reaction taking place.**

Mg2+(s) + 2H+(aq) Mg2+(aq) + H2 (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**

**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.

1. **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.
* A decrease in volume of the container, bring the reacting particles closer to each other which increases their chances of effective/successful 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:

1. Haber process for manufacture of ammonia

N2(g) + 3H2(g) 2NH3(g)

1. Contact process for manufacture of sulphuric(VI)acid

2SO2(g) + O2(g) 2SO3(g)

1. Ostwalds process for the manufacture of nitric(V)acid

4NH3(g) + 5O2(g) 4NO (g) + 6H2O (l)

**NB**/ 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 be easily compressed.

1. **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 **10oC rise** in temperature doubles the rate of reaction by reducing the time taken for the reaction to complete by **a half.**
* In the reaction of sodium thiosulphate with dilute hydrochloric acid, the time taken for the cross(X) to disappear decreases thus faster rate of reaction.

Sample results:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temperature of Na2S2O3 | Room temperature | 30 | 40 | 50 | 60 |
| Time taken for mark X to be invisible (seconds) | 50.0 | 40.0 | 20.0 | 15.0 | 10.0 |
| 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 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 oC**

**II. 0.07**

Reading directly from a correctly plotted graph = **48.0 oC**

**(ii) t is;**

**I. 30 seconds**

30 seconds => 1/t =1/30 =**0.033**

Reading directly from a correctly plotted graph 0.033 => **33.5 oC**

**II. 45 seconds**

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

Reading directly from a correctly plotted graph 0.022 => **29.0 oC**

**III. 25 seconds**

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

Reading directly from a correctly plotted graph 0.04 => **36.0 oC**

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

**(i) 57.5 oC**

Reading directly from a correctly plotted graph at 57.5 oC= **0.094**

=>1/t = **0.094**

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

**(ii) 45 oC**

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

=>1/t = **0.062**

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

**(iii) 35 oC**

Reading directly from a correctly plotted graph at 35 oC = **0.047**

=>1/t = **0.047**

t= 1/0.047 => 2**1.2766 seconds**

**Method 2**

**Reaction of Magnesium with dilute hydrochloric acid**

Sample results:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temperature of acid(oC) | Room temperature | 30 | 40 | 50 | 60 |
| Time taken effervescence to stop (seconds) | 80.0 | 50.0 | 21.0 | 13.5 | 10.0 |
| 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 1/t**

1/t

Temperature(oC)

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

Moles = Mass of magnesium => 1.0 = **4.167 x 10 -2 moles**

Molar mass of Mg 24

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

Moles of acid = molarity x volume of acid

1000

=> 1.0 x 20 = **2.0 x 10 -2 moles**

1000

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

Mole ratio Mg: HCl = 1:2

Moles Mg = ½ moles HCl

=> ½ x 2.0 x 10 -2 moles = **1.0 x 10 -2 moles**

Mass of reacted Mg = moles x molar mass

=> 1.0 x 10 -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 : H2 = 1:1

Moles of Mg that reacted per experiment = moles H2 =**1.0 x 10 -2 moles**

Volume of Hydrogen at s.t.p produced per experiment = moles x 24 dm3

=> 1.0 x 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 oC**

**(ii) 40seconds**

40 seconds => 1/t =1/40 =**0.025**

Reading directly from a correctly plotted graph **0.025** => **32.0 oC**

**(b)What is the time taken for magnesium to react if the reaction was done at:**

**(i) 55.0 oC**

Reading directly from a correctly plotted graph at 55.0 oC=> 1/t = **8.0 x 10-2**

=> t = 1/8.0 x 10-2 = **12.5 seconds**

**(ii) 47.0 oC**

Reading directly from a correctly plotted graph at 47.0 oC=> 1/t = **6.0 x 10-2**

=> t = 1/6.0 x 10-2 = **16.6667 seconds**

**(iii) 33.0 oC**

Reading directly from a correctly plotted graph at 33.0 oC=> 1/t = **2.7 x 10-2**

=> t = 1/2.7 x 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.

1. **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 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 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**

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 CaCO3 | **2.5** | **2.0** | **1.8** | **1.4** | **1.2** | **1.0** | **0.8** | **0.5** | **0.5** |
| 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 CaCO3 | **2.5** | **1.9** | **1.5** | **1.3** | **1.0** | **0.8** | **0.5** | **0.5** | **0.5** |
| 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 CaCO3 | **2.5** | **1.8** | **1.4** | **1.0** | **0.8** | **0.5** | **0.5** | **0.5** | **0.5** |
| 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 reacts with the acid to form carbon (IV) oxide gas that escape to the atmosphere.

1. **Write an ionic equation for the reaction that take place**

CaCO3(s) + 2H+(aq) Ca2+(aq) + H2O(l) + CO2(g)

1. **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.

1. **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 CaCO3(s) : CO2(g) = 1:1

Moles CaCO3(s) used = Mass CaCO3(s) = **0.025 moles**

Molar mass CaCO3(s)

Moles CO2(g) = 0.025 moles

Volume of CO2(g) = moles x molar gas volume

=>0.025 moles x 24 dm3 = **0.600 dm3/600cm3**

**Method II**

Molar mass of CaCO3(s) = 100g produce 24 dm3 of CO2(g)

Mass of CaCO3(s) =2.5 g produce 2.5 x 24 = **0.600dm3**

100

1. **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 = M2-M1  => 2.08 – 1.375 = 0.625 = **0.006944g sec-1**

T2- T1  222-132 90

1. **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 =M2-M1  => 1.80 – 0.0 = 1.8 = **9.00g min-1**

T2- T1  2.0 – 0.0 2

**(i) 6 to 8 minutes**

Average rate =M2-M1  => 3.20 – 2.95 = 0.25 = **0.125g min-1**

T2- T1  8.0 – 6.0 2

**(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.**

CaCO3(s) + 2HCl (aq) CaCO3 (aq) + H2O(l) + CO2(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 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**

Ca2+(aq) + SO42-(aq)->CaSO4(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 =M2-M1 => 2.25 – 1.30 = 0.95 = **0.3958g min-1**

T2- T1  3.20 – 0.8 2.4

(**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 alters the rate /speed of a chemical reaction but remains 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
* Catalyst works by lowering the Enthalpy of activation(∆Ha)/activation energy (Ea) of the reactants .
* The catalyst lowers the activation energy (Ea) by:

1. forming short lived intermediate compounds called activated complex that break up to form the final product/s
2. Being absorbed by the reactants thus providing the surface area on which reaction occurs.

* A catalyst has no effect on the enthalpy of reaction ∆Hr but only lowers the activation energy (Ea)
* It thus do not 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.

Activated complex

A B

Ea Catalysed

Ea uncatalysed

A-B A-B

B

A

A-A B-B

Reaction path/coordinate/path

Energy

kJ

Examples of industrial catalysed reactions

**(a)The contact process**

Vanadium(V) Oxide(V2O5) or platinum(Pt) catalyses the oxidation of sulphur(IV)oxide during the manufacture of sulphuric(VI) acid from contact process.

SO2(g) + O2(g) **V2O5** SO3(g)

To **reduce** industrial cost of manufacture of sulphuric (VI) acid from contact process Vanadium (V) Oxide(V2O5) 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

4NH3(g) +5O2(g) **Pt/Rh** 4NO (g) + 6H2O(l)

**(c)Haber process**

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

N2(g) + 3H2(g) -**Pt or Fe** 2NH3(g)

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

**Nickel (Ni)** catalyses the hydrogenation of unsaturated compound containing 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.

2H2O2 (g) **MnO2** O2(g) + 2H2O(l)

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

**Copper (II)sulphate** 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.

H2 SO4 (aq) + Zn(s) CuSO4 ZnSO4 (aq) + H2(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. CH4(g) + Cl2(g) **u.v. light** CH3Cl(g) + HCl(g)

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

Catalysed reaction

Uncatalysed reaction

The mass of MnO2 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.

**CHEMICAL EQUILIBRIA**

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* Chemical equilibrium is a chemical reaction in which the rate of forward reaction is equal to the rate of backward reaction.
* 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 irreversible i.e.

A + B C + D

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

A + B C + 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:

1. Change of state from solid, liquid, gas or aqueous solutions. States of matter are inter-convertible and a reaction involving a change from one state can be reversed back to the original.
2. 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**) 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**) 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.

I2(**s**) I2(**g**)

(grey crystalline solid (purple vapour

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.

Melting boiling

H2O(**s**)

H2O(**s**)

H2O(**l**)

Freezing condensing

(**iv**)**Dissolving/ crystallization/distillation**

**S**olid 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**) + H2O(l) NaCl(**aq**)

**(b) Reversible chemical changes**

**A reversible chemical** reaction is a reaction that proceeds in forward and reverse direction.

* They involve a chemical change of the reactants which can be reversed back by recombining the products.
* In this reaction none of the reagents is completely used up and thus the reaction does not go to completion.

**Examples of Reversible chemical changes**

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

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

**Sample observations**

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

* 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.**

CuSO4(**s**) + 5H2 O(**l**) CuSO4.5H2 O(**s**/**aq**)

(white anhydrous) (blue hydrated)

CoCl2(**s**) + 6H2 O(**l**) CoCl2.6H2 O(**s**/**aq**)

(blue anhydrous) (pink hydrated)

**(ii)Chemical sublimation**

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

Heating ammonium chloride

* 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**.

NH4Cl(s) NH3(g) + HCl(g)

(Turns moist (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.

Reactants concentration

Equilibrium established /rate of formation of products equal to rate of formation of reactants.

Decreases from time= 0.0

Reaction progress/path/coordinate

Concentration

Mole dm-3

Products concentration increases from time=0.0

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 equilibriumis therefore a balance of the rate of formation of products and reactants. This balance continues until the reactants or products are disturbed.
* 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:

* **Le Chatelliers Principle** states that if a stress/change is applied to a system in equilibrium, the system readjust/shift counteract/ oppose the stress/change”
* Le Chatelliers Principle is applied in determining the effect of several factors on systems in equilibrium. The following are the main factors that influence /alter/ affect systems in dynamic equilibrium:

(a)Concentration

(b)Pressure

(c)Temperature

(d)Catalyst

1. **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 readjusts so as to reduce concentration or add the reduced concentration.

Examples of influence of concentration on equilibrium

1. Chromate (VI)/CrO42- ions in solution are **yellow**. Dichromate (VI)/Cr2O72- ions in solution are **orange**. The two solutions exist in equilibrium as in the equation:

2H+ (aq) + 2CrO42- (aq) Cr2O72- (aq) + H2O(l)

(Yellow) (Orange)

**I**. If an acid is/H+ (aq) is added to the equilibrium mixture a stress is created on the reactant side where there is already H+ ions.

The equilibrium shift forward to the right to reduce the **excess** H+ ions added. Solution mixture becomes MoreCr2O72- ions formed in the solution mixture make 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 on the H+ ions. H+ ions react with OH- (aq) to form water.

H+ (aq) +OH- (aq) H2O(l)

The equilibrium shift backward to the left to add/replace the H+ ions that have reacted with the OH- (aq) ions. More of the CrO42- ions formed in the solution mixture make it to be more **yellow** in colour.

(ii)

2OH- (aq) + 2Cr2O72- (aq) CrO42- (aq) + H2O(l)

(Orange) (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) H2O(l)

The equilibrium shift backward to the left to add/replace the 2OH- (aq) that have reacted with the H+ (aq) ions . More Cr2O72- (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. Moreof the Cr2O72- ions are formed in the solution mixture making it to be more **orange** in colour.

1. **Influence of Pressure on dynamic equilibrium**

* Pressure affects gaseous reactants/products.
* Increase in pressure favours the equilibrium towards the side with **less volume/molecules**.
* Decrease in pressure shift the equilibrium towards the side with more volume/molecules.
* 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:

1. **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.

2NO2(g) **=====**  N2 O4 (g)

**2**Volume **1**Volume

**2**molecule **1**molecule

* Increase in pressure shift the equilibrium forward to the left where there is less volume/molecules. The equilibrium mixture becomes more **yellow**.
* Decrease in pressure shift the equilibrium backward to the right where there is more volume/molecules. The equilibrium mixture becomes browner**.**

1. **Haber process.**

N2(g)+ 3H2 (g) 2NH3 (g)

**1**Volume **3**Volume **2**Volume

**1**molecule **3**molecule **2**molecule

* 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.

1. **Contact process.**

Chemical equation: 2SO2(g)+ O2 (g) 2SO3 (g)

**2**Volume **1**Volume **2**Volume

**2**molecule **1**molecule **2**molecule

* 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.

1. **Ostwalds process.**

Chemical equation: 4NH3(g)+ 5O2 (g) 4NO(g) + 6H2O(l)

**4**Volume **5**Volume **4**Volume **6**Volume

**4**molecule **5**molecule **4**molecule **6**Molecule

* 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**.

1. **Influence of Temperature on dynamic equilibrium**

* A **decrease** in temperature favours exothermic reaction (**-ΔH**).
* An **increase** in temperature favours thus **endothermic** reaction (**+ΔH**).

Endothermic reaction are thus favoured by high temperature/heating

Exothermic reaction is favoured by low temperature/cooling.

1. **Influence of Catalyst on dynamic equilibrium**

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

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

* The conditions required to obtain the highest yield of products within the shortest time at minimum cost are called **optimum conditions**

Optimum condition thus requires understanding the effect of various factors on:

1. rate of reaction
2. dynamic equilibrium(**Chemical equilibrium**)
3. **Optimum condition in Haber process**

**Chemical equation**

N2 (g) + 3H2 (g) ===Fe/Pt=== 2NH3 (g) ΔH = -92kJ

Equilibrium/Reaction rate considerations

1. **Removing ammonia** gas once formed shift the equilibrium forward to the right to replace the ammonia. More/higher yield of ammonia is attained.
2. **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 raise the **cost** of production because they are **expensive** to produce and maintain. An optimum pressure of about 500atmospheres is normally used.
3. **Increase in temperature** shift the equilibrium backward to the left because the reaction is exothermic (ΔH = -92kJ) . Ammonia formed **decomposes** back to Nitrogen and Hydrogen to remove excess heat therefore a **less** yield of ammonia is attained. Very **low** temperature decreases the collision frequency of Nitrogen and Hydrogen and thus the rate of reaction **too slow** and **uneconomical**.

An optimum temperature of about 450oC is normally used.

1. 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 Aluminium Oxide (Al2O3) 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**

**2**SO2 (g) + O2 (g) ===V2O5/Pt=== 2SO3 (g) ΔH = -197kJ

Equilibrium/Reaction rate considerations

1. **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.
2. **Increase in pressure** shift the equilibrium forward to the right where there is less volume/molecules. More**/**higheryield of sulphur(VI)oxide is attained. Very high pressures raise the **cost** of production because they are expensive to produce and maintain. An optimum pressure of about 1-2 atmospheres is normally used to attain about 96% yield of SO3.
3. **Increase in temperature** shift the equilibrium backward to the left because the reaction is exothermic (ΔH = -197kJ) . 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 low temperature decrease the collision frequency of Sulphur(IV)oxide and Oxygen and thus the rate of reaction tooslow and uneconomical.

An optimum temperature of about 450oC is normally used.

1. 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 very cheap even if it is easily poisoned by impurities. The catalyst does not increase the yield of Sulphur (VI) Oxide but it speed up its rate of formation.
2. **Optimum condition in Ostwalds process**

**Chemical equation**

4NH3 (g) + 5O2 (g) ===**Pt/Rh**=== 4NO (g) + 6H2O (**g**) ΔH = -950kJ

Equilibrium/Reaction rate considerations

1. **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.
2. **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 **low** pressures increases the distance between reacting NH3and O2 molecules.

An optimum pressure of about **9** atmospheres is normally used.

1. **Increase in temperature** shift the equilibrium backward to the left because the reaction is exothermic (ΔH = -950kJ) . 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 **low** temperature decreases the collision frequency of Ammonia and Oxygen and thus the rate of reaction **too slow** and **uneconomical**.

An optimum temperature of about 900oC 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.

**SAMPLE REVISION QUESTIONS**

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

**(i) N2(g) + O2(g) ===== 2NO(g)**

**(ii) 2H2(g) + CO(g) ===== CH3OH (g)**

1. **Explain the effect of increasing temperature on the following:**

2SO2(g) + O2 (g) ===== 2SO3 (g) ΔH = -189kJ

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