

6. CHEMICAL EQUILIBRIA.

Many reactions do not go to completion, and at a certain point, the products of the reaction themselves react to form the reactants.

The reaction may provide a mixture of reactants and products, and a dynamic equilibrium will be established when the reactants and products are both reacting at the same rates.

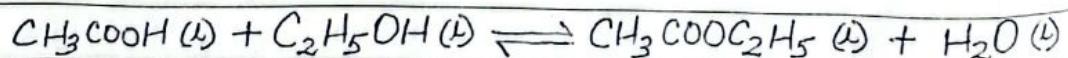
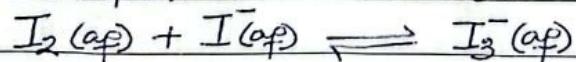
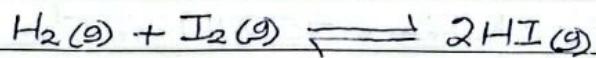
Characteristics of a system in a dynamic equilibrium

- (i) the rates of the forward and reverse reactions are equal.
- (ii) the system does not undergo any observable change.
- (iii) the system is closed.
- (iv) the amount of reactants and products at equilibrium remains fixed.
- (v) the equilibrium is established at a fixed temperature.

Types of Chemical equilibria.

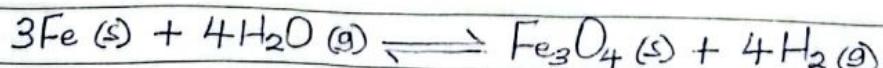
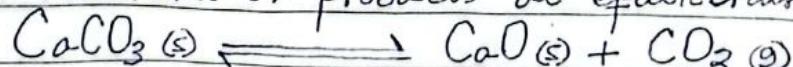
(a) Homogeneous equilibrium.

This occurs when all the reactants and products of a given reaction are in the same phase. e.g;



(b) Heterogeneous equilibrium.

This occurs if two or more phases are involved in the reactants or products at equilibrium. e.g;



The equilibrium Law.

Consider the following homogeneous equilibrium;



$$\frac{[C]^w [D]^z}{[A]^x [B]^y} = \text{Constant at a given temperature.}$$

This is the mathematical expression of the equilibrium law, and the constant is K_C , which is known as the equilibrium constant.

$$K_C = \frac{[C]^w [D]^z}{[A]^x [B]^y}$$

Where $[]$ is concentration of, in mol dm^{-3} .

Note: The concentrations are those existing at the point of equilibrium. They are not the initial concentrations before the reaction has taken place.

A higher value of K_C shows that the products are present in higher concentrations than the reactants.

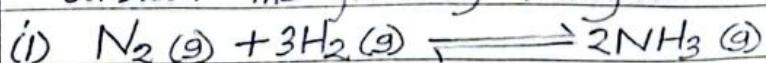
The equilibrium law states that; If a reversible reaction is allowed to reach equilibrium, the product of the concentrations of the products each raised to the appropriate power, divided by the product of the concentrations of the reactants, each raised to the appropriate power is a constant value at a fixed temperature.

Units for the equilibrium Constant, K_C .

The equilibrium constant may or may not have units depending on the form of the equilibrium expression.

When the numerator units cancel out those of the denominator, the equilibrium constant has no units.

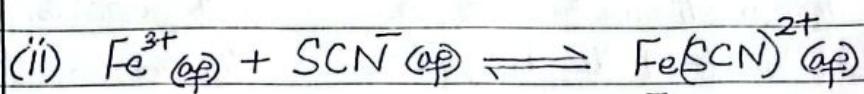
Consider the following homogeneous equilibria;



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$= \frac{\text{mol}^2 \text{dm}^{-6}}{\text{mol dm}^{-3} (\text{mol}^3 \text{dm}^{-9})}$$

Units : $\text{mol}^{-2} \text{dm}^6$



$$K_c = \frac{[\text{Fe}(\text{SCN})^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]}$$

$$= \frac{\text{mol dm}^{-3}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}$$

Units : $\text{Mol}^{-1} \text{dm}^3$.



$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$= \frac{\text{mol}^2 \text{dm}^{-6}}{\text{mol}^2 \text{dm}^{-6}}$$

$$= \text{No units.}$$

INVESTIGATION OF EQUILIBRIUM MIXTURES.

To investigate an equilibrium mixture and measure K_c values, it is necessary to establish the equilibrium at a particular temperature and then find the composition of the mixture by some method which does not change the composition.

(Q) Determining the equilibrium Constant, K_c , for the reaction between ethanol and ethanoic acid.

- A known amount of ethanoic acid, a moles, is mixed with a known amount, b moles, of ethanol.

- The mixture is kept in a sealed glass tube for sometime at a fixed temperature of about 50°C .

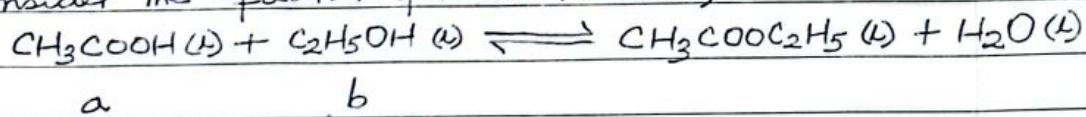
- After sometime when the acid and alcohol have reacted to form an equilibrium mixture, the tube is broken after cooling to room temperature. The cooling is to ensure that the equilibrium does not shift appreciably during the measurement of the concentrations.

- The mixture at equilibrium is titrated with standard sodium hydroxide solution to determine the amount of ethanoic acid, x moles, remaining at equilibrium.

- The titration is carried out using phenolphthalein indicator.

The results of the experiment are then treated as shown below;

Consider the equation for the reaction;

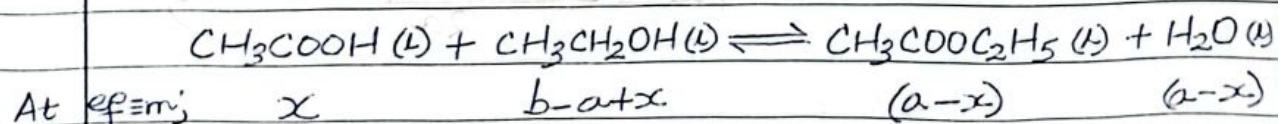


Since the moles of acid remaining at equilibrium is x moles;

moles of acid that reacted = $(a-x)$ moles.

moles of ethanol that reacted = $(a-x)$ moles.

moles of ethanol remaining = $b - (a-x) = b - a + x$ moles.



At equilibrium; x $b - a + x$ $(a-x)$ $(a-x)$

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$
$$= \frac{(a-x)^2}{x(b-a+x)}$$

Example:

A mixture of 0.69g of ethanol and 0.9g of ethanoic acid were allowed to react at 90°C until equilibrium was reached. Calculate the mass of ethylethanoate formed at equilibrium. ($K_c = 3.6$)

Solution.

$$RFM \text{ of } C_2H_5OH = (12 \times 2) + (1 \times 6) + 16 = 46$$

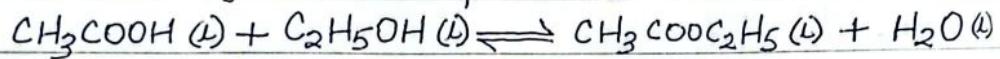
$$RFM \text{ of } CH_3COOH = (12 \times 2) + (1 \times 4) + (16 \times 2) = 60$$

Moles of;

$$C_2H_5OH = \frac{0.69}{46} = 0.015 \text{ moles.}$$

$$CH_3COOH = \frac{0.9}{60} = 0.015 \text{ moles.}$$

Let the moles of the ester formed be x moles.



Initially: 0.015 0.015

At equilibrium; 0.015 - x 0.015 - x x x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$3.6 = \frac{x^2}{(0.015-x)^2}$$

$$3.6(0.015-x)^2 = x^2$$

$$3.6(2.25 \times 10^{-4} - 0.03x + x^2) = x^2$$

$$2.6x^2 - 0.108x + 8.1 \times 10^{-4} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = 0.00982$$

$$\text{Formula mass of } CH_3COOC_2H_5 = (12 \times 4) + (1 \times 8) + (16 \times 2) = 88 \text{ g}$$

$$\begin{aligned}\text{Mass of ester} &= 88 \times 0.00982 \\ &= 0.864 \text{ g.}\end{aligned}$$

(b) Determining the equilibrium constant, K_c , for the reaction between hydrogen and iodine.

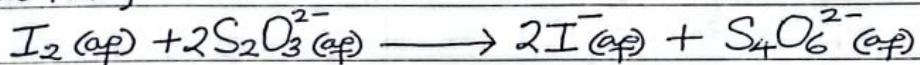
A known amount of hydrogen, a moles, is mixed with a known amount, b moles, of iodine in a bulb of a known volume.

The mixture is kept in a sealed tube at 450°C until equilibrium is established.

The bulb is rapidly cooled to room temperature and then broken under potassium iodide solution to dissolve the iodine remaining at equilibrium.

The aqueous potassium iodide solution containing dissolved iodine is titrated against standard sodium thiosulphate solution using starch indicator.

The concentration of iodine is calculated using the equation;



The results of the experiment are then treated as shown below;

If x moles of iodine are found to have reacted; then
moles of HI formed at equilibrium = $2x$



At eqm :

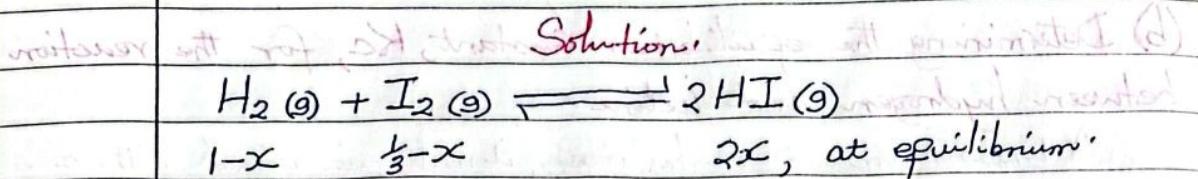


$$K_c = \frac{(2x)^2}{(a-x)(b-x)}$$

$$= \frac{4x^2}{(a-x)(b-x)}$$

Example:

- 1 mole of hydrogen and $\frac{1}{3}$ mole of iodine were heated together at 450°C until equilibrium was established. Calculate the number of moles of hydrogen iodide present in the equilibrium mixture at 450°C . ($K_c = 50$)



$$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

$$50 = \frac{(2x)^2}{(1-x)(\frac{1}{3}-x)}$$

$$50 = \frac{4x^2}{1(\frac{1}{3}-x)-x(\frac{1}{3}-x)}$$

$$50 = \frac{4x^2}{\frac{1}{3}-x-\frac{x}{3}+x^2}$$

$$= \frac{4x^2}{\frac{1}{3}-\frac{3x-x}{3}+x^2}$$

$$50 = \frac{4x^2}{\frac{1}{3}-\frac{4x}{3}+\frac{x^2}{1}}$$

$$50 = \frac{4x^2}{\frac{1}{3}-4x+3x^2}$$

$$50 = \frac{12x^2}{1-4x+3x^2}$$

$$50 - 200x + 138x^2 = 0$$

Hence;

$$138x^2 - 200x + 50 = 0$$

or

$$69x^2 - 100x + 25 = 0$$

$$x = 0.32$$

moles of HI at equilibrium

$$= 2 \times 0.32$$

= 0.64 moles.

FACTORS AFFECTING THE POSITION OF EQUILIBRIUM

- Concentration
- temperature
- Pressure (for reactions involving gaseous reactants and products)
- Addition of a catalyst.
- Addition of an inert gas.

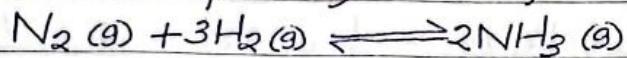
The effect of each of the above factors on equilibrium position is in accordance with Le Chatelier's principle.

The principle states that; "When a system is in equilibrium and one of the factors holding it in equilibrium is altered, the system will adjust itself in order to ~~to~~ ^{minimize} the effect of the change."

a) Effect of Change in Concentration.

For a system at equilibrium, when the concentration of the reactants is increased, the reaction will proceed in a direction that will reduce the concentration of the reactants such that the equilibrium is restored.

Consider the following reaction;



If the concentration of hydrogen is increased by addition of excess hydrogen into the vessel containing the reacting mixture, the concentration of nitrogen falls because the nitrogen would react with excess hydrogen added to produce more ammonia. The equilibrium position thus shifts from left to right.

If instead the concentration of ammonia was reduced by removing it as soon as it is formed, more nitrogen and hydrogen would react to compensate for the removed ammonia and the equilibrium position would shift from left to right.

If the concentration of hydrogen was reduced by removing some, then ammonia would decompose to compensate for the hydrogen removed. Thus concentration of ammonia reduces while that of hydrogen and nitrogen increases. The equilibrium position shifts from right to left.

Note:- The altering in equilibrium position is to maintain the value of K_c constant. The value remains constant as long as temperature is not changed.

- The rate of attainment of equilibrium is increased by increase in concentration, and it is decreased by a decrease in concentration.

Questions:

1. In the reaction;



State what would happen to the position of equilibrium when;

- a) a few drops of hydrochloric acid are added.
b) more water is added.

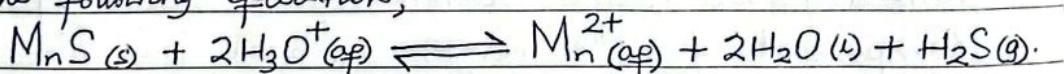
Solution:

a) Addition of drops of hydrochloric acid results into an increase in the concentration of the acid. To restore the equilibrium, the excess HCl added reacts with solid BiOCl to produce BiCl₃ and H₂O. Thus, the precipitate of bismuth(II)chloride oxide redissolves shifting the equilibrium position from right to left.

- b) Addition of more water would cause more precipitate to form.

This is because the excess water added is removed by the reaction with BiCl₃ to form more of HCl and BiOCl. The equilibrium position shifts from left to right.

2. Manganese Sulphide reacts with dilute acids according to the following equation;



State, giving a reason, what would happen to the position of equilibrium if;

- Water is added to the equilibrium mixture.
- Hydrogen Chloride is added/bubbled into the equilibrium mixture.
- pH of the equilibrium mixture is increased.

Solution:

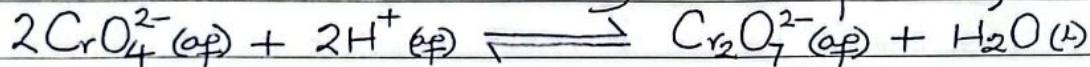
(i) The equilibrium position would shift from right to left. Adding water to the equilibrium mixture would increase its concentration in the mixture, and therefore to restore equilibrium, the water added is removed by the reaction with Mn²⁺ and H₂S to produce MnS and 2H₃O⁺.

This decreases the concentration of Mn²⁺ and H₂S while the concentrations of MnS and H₃O⁺ increase.

(ii) The equilibrium position shifts from left to right. Bubbling hydrogen chloride gas increases the concentration of hydroxonium ions in the mixture such that in order for the value of K_c to be kept constant, the excess hydroxonium ions are removed by reacting with MnS .

(iii) The equilibrium position shifts from right to left. Increasing pH means addition of hydroxyl ions. The OH^- ions added would react with hydroxonium ions causing a decrease in hydroxonium ion concentration in the equilibrium mixture. To restore the equilibrium, Mn^{2+} , H_2O and H_2S react to compensate for the hydroxonium ions.

3. Sodium chromate (VI) reacts with dilute acids to produce Sodium dichromate (VI) according to the equation;



(a) State what is observed when dilute Sulphuric acid is added to the solution of a Chromate.

(b) State and explain what is observed when to the resultant mixture in (a) is added;

(i) Sodium hydroxide solution.

(ii) Water.

Solution.

a) The yellow solution turns orange.

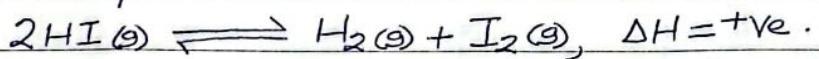
b) i) The orange solution turns back to yellow. This is because the added alkali neutralises hydrogen ions in the equilibrium mixture hence reducing their concentration. For equilibrium to be restored, the equilibrium position shifts from right to left.

(ii) The orange solution turns back to yellow. Addition of water results into an increase in its concentration in the mixture, and therefore to restore equilibrium, the water added is removed by the reaction with dichromate (VI) ions to produce chromate (VI) ions. The equilibrium position shifts right to left.

b) Effect of Change in Temperature.

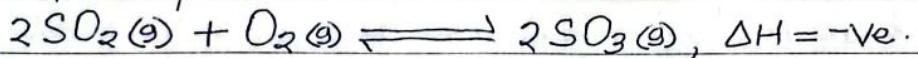
The effect of temperature on the position of equilibrium depends on whether the forward reaction is exothermic or endothermic.

If the forward reaction is endothermic such as;



An increase in temperature favours the forward reaction, i.e. it shifts the equilibrium position to the right.

If the forward reaction is exothermic such as;



An increase in temperature favours the backward reaction.

It shifts the equilibrium position from right to left.

An increase in temperature increases the rate at which equilibrium is attained for both endothermic and exothermic reactions.

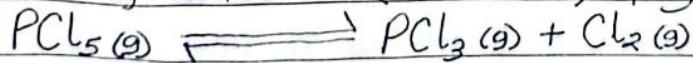
If the forward reaction is endothermic, an increase in temperature increases the value of the equilibrium constant.

If the forward reaction is exothermic, an increase in temperature results into a decrease in the value of the equilibrium constant.

c) Effect of change in pressure.

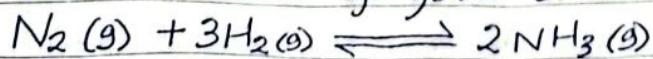
The effect of pressure on a reversible reaction depends on whether the reaction proceeds with a change in volume.

For a reaction that proceeds with an increase in the number of molecules (or volume) of gases such as;



An increase in pressure shifts the equilibrium position from right to left. i.e., it favours the backward reaction.

For a reaction that proceeds with a decrease in volumes or molecules of gases such as;



An increase in pressure shifts the equilibrium position from left to right. i.e. it favours the forward reaction.

For a reaction involving no change in volume or number of molecules of gases such as;



a change in pressure does not affect the equilibrium position.

Note:

- (i) - An increase in pressure increases the rate of attainment of equilibrium because of the increase in the frequency of collisions between the particles/molecules in the container.
- (ii) - Change in pressure has no effect on the value of the equilibrium constant as long as the temperature is kept constant.
- (iii) - Pressure of a gas depends on the number of molecules in a given volume of the container. The greater the number of molecules, the more the collisions and the higher the pressure.

An increase in pressure brings the gas molecules closer to each other increasing the frequency of collision hence the rate of attainment of equilibrium.

d) Effect of a Catalyst.

For a reversible reaction, a catalyst favours both the forward and backward reactions to the same extent. The catalyst only speeds up the rate of attainment of equilibrium. It has no effect on the position of equilibrium and the value of equilibrium constant.

e) Effect of adding a noble or Inert gas.

Addition of an inert gas to a system at eqm is the same as increasing pressure.

An inert gas leads to an increase in the number of molecules colliding in a container but the inert gas does not take part in the chemical reaction.

The inert gas only increases the pressure of the gaseous mixture.

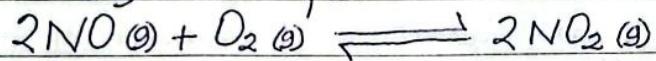
For a reaction proceeding with an increase in volume

or number of moles of gases, addition of an inert gas favours the backward reaction. i.e It shifts the equilibrium position from right to left.

For a reaction proceeding with a decrease in number of molecules, addition of an inert gas favours the forward reaction i.e Shifts equilibrium position from left to right.

Questions:

- Nitrogen monoxide reacts with oxygen to form nitrogen dioxide according to the equation:



(a) Write expression for the equilibrium Constant, K_c .

(b) 3 moles of nitrogen monoxide and 1.5 moles of oxygen were mixed into a vessel and heated to 400°C .

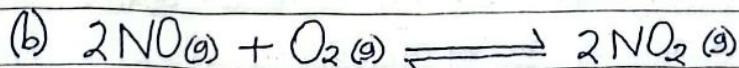
At equilibrium, 0.5 moles of oxygen were found. Calculate the value of K_c at this temperature.

(c) When the temperature was raised to 500°C , the mixture in (b) was found to contain 25% of the initial nitrogen monoxide. Calculate the equilibrium Constant, K_c at this temperature.

(d) From your answers in (b) and (c), deduce whether the process is endothermic or exothermic. Explain.

Solution.

$$(a) K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]}$$



$3-2x \quad 1.5-x \quad 2x$, At equilibrium.

$$1.5-x = 0.5$$

$$x = 1.$$

$$\text{Thus; } [\text{NO}] = 3-2 = 1$$

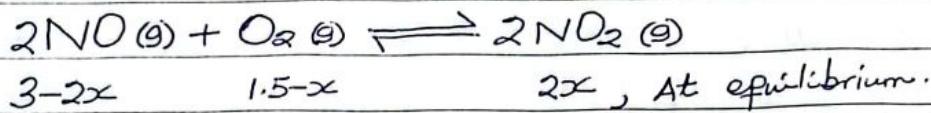
$$[\text{NO}_2] = 2$$

$$[\text{O}_2] = 0.5$$

$$K_c = \frac{x^2}{1^2 \times 0.5}$$

$$= 8 \text{ mol}^{-1} \text{ dm}^3$$

(c) moles of NO at 500°C = $\frac{25}{100} \times 3 = 0.75$ moles.



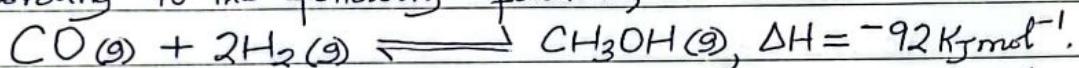
$$\begin{aligned} 3-2x &= 0.75 \\ 2x &= 3-0.75 \\ x &= 1.125 \end{aligned}$$
$$K_C = \frac{(2.25)^2}{(0.75)^2 \cdot 0.375} = 24 \text{ mol}^{-1} \text{ dm}^3.$$

Thus; $[\text{O}_2] = 1.5 - 1.125 = 0.375$ moles.

$$[\text{NO}_2] = 1.125 \times 2 = 2.25$$
 moles.

$$[\text{NO}] = 0.75$$
 moles.

2. Carbon monoxide reacts with hydrogen to form methanol according to the following equation;



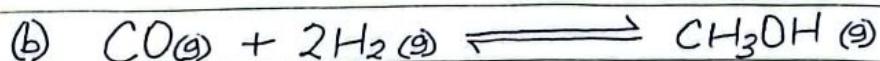
- (a) Write the expression for the equilibrium Constant, K_C , for the reaction.

- (b) When 1 mole of carbon monoxide was mixed with 2 moles of hydrogen and the reaction carried out at 200°C , 1.6 moles of hydrogen remained in the equilibrium mixture.

Calculate the value of the equilibrium Constant, K_C .

Solution.

$$(a) K_C = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$



1-x 2-2x x, At equilibrium.

Considering H_2 , $2-2x = 1.6$

$$\begin{aligned} 2x &= 2-1.6 \\ x &= 0.2 \end{aligned}$$
$$K_C = \frac{0.2}{0.8(1.6)^2}$$

Thus;

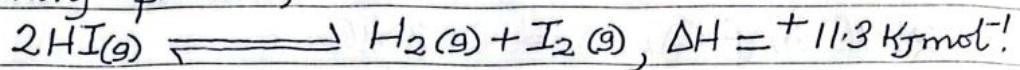
$$= 9.77 \times 10^{-2} \text{ mol}^{-2} \text{ dm}^6$$

$$[\text{CO}] = 0.8$$
 moles

$$[\text{CH}_3\text{OH}] = 0.2$$
 moles

$$[\text{H}_2] = 1.6$$
 moles

3. Hydrogen iodide decomposes when heated according to the following equation;



(a) Write an expression for the equilibrium constant, K_c , for the reaction.

(b) 1.54g of hydrogen iodide was heated in a 600cm^3 bulb at 530°C . When equilibrium was attained, the bulb was rapidly cooled to room temperature and broken under potassium iodide solution.

The iodine formed from the decomposition required 67.0cm^3 of 0.1M Sodium thiosulphate solution for complete reaction.

Calculate the;

(i) moles of "hydrogen iodide" in 1.54g ($\text{H}=1$, $\text{I}=12.7$)

(ii) moles of iodine formed when hydrogen iodide was decomposed.

(iii) Value of K_c at 530°C

(c) Explain why the bulb in (b) was rapidly cooled and broken under potassium iodide solution.

(d) State what would be the effect on the value of K_c when;

(i) the temperature is raised from 530°C to 800°C .

(ii) the volume of the bulb is increased to 1200cm^3 .

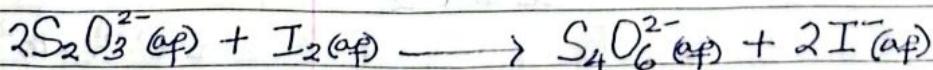
Solution:

$$(a) K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

(b) (i) Formula mass of HI = $1 + 127 = 128$

$$\text{moles of HI} = \frac{1.54}{128} = 1.203 \times 10^{-2} \text{ moles.}$$

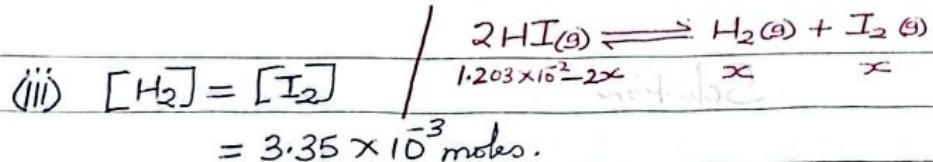
$$(ii) \text{moles of S}_2\text{O}_3^{2-} = \frac{67.0 \times 0.1}{1000} = 6.7 \times 10^{-3} \text{ moles.}$$



2 moles of $\text{S}_2\text{O}_3^{2-}(aq)$ react with 1 mole of I_2 .

6.7×10^{-3} moles of $\text{S}_2\text{O}_3^{2-}$ react with $6.7 \times 10^{-3} \times$

$$= 3.35 \times 10^{-3} \text{ moles of I}_2.$$



$$\text{moles of HI that reacted} = 3.35 \times 10^{-3} \times 2$$

$$= 6.7 \times 10^{-3} \text{ moles.}$$

$$\text{moles of HI that remained} = 1.203 \times 10^2 - 6.7 \times 10^{-3}$$

$$= 5.33 \times 10^{-3} \text{ moles.}$$

$$K_c = \frac{(3.35 \times 10^{-3})^2}{(5.33 \times 10^{-3})^2}$$

$$= 0.395$$

(c) To allow equilibrium to be established at a lower temperature, and to fix equilibrium concentrations.

Potassium iodide dissolves ^{the} iodine produced to give an aqueous solution of iodine for titration.

(d) (i) The value of K_c would increase because the forward reaction is endothermic.

(ii) The value of K_c would not change. It is constant at a fixed temperature.

4. X decomposes reversibly on heating according to the equation



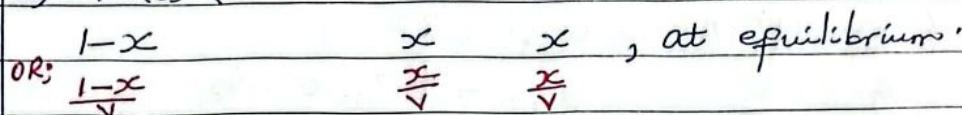
(a) When 1 mole of X was heated at 200°C in a container of volume 25dm^3 , the equilibrium mixture was found to contain 0.2 mole of Y. Calculate the value of K_c at this temperature.

(b) When the equilibrium constant, K_c , was measured at 500°C , it was found to be $4.0 \times 10^3 \text{ mol dm}^{-3}$.

(i) State whether the decomposition of X is exothermic or endothermic.

(ii) Explain your answer in b(i) above.

Solution



Thus, Since moles of Y = 0.2, $[Y] = \frac{0.2}{25}$

$$= 0.008 \text{ mol dm}^{-3}$$

From the reaction equation;

$$[Z] = [Y]$$

$$= 0.008 \text{ mol dm}^{-3}$$

$$[X] = \frac{1-0.2}{25} = 0.032 \text{ mol dm}^{-3}$$

$$K_c = \frac{[Y][Z]}{[X]} = \frac{(0.008)^2}{0.032}$$

$$K_c = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

b) (i) The decomposition of X is an endothermic process.

(ii) The Value of the equilibrium Constant, K_c , increases with increase in temperature showing that Concentrations of Y and Z increase as temperature is increased.

5. Phosphorus (V) Chloride decomposes at high temperatures according to the equation.



When 40.2g of phosphorus (V) chloride was placed in 4.5 litre vessel and heated at a certain fixed pressure, 4.2g of Chlorine was found at equilibrium.

(a) Calculate the;

(i) amount of phosphorus (V) chloride and phosphorus (III) chloride at equilibrium in mol dm^{-3} .

(ii) equilibrium Constant, K_c , for the reaction and state its units.

(b) State how the value of the equilibrium constant would

be affected and in each case give a reason for your answer if;

(i) the pressure was increased.

(ii) Some chlorine was removed at equilibrium.

Solution:

a) (i) Formula mass of;

$$PCl_5 = 31 + (35.5 \times 5) = 208.5 \text{ g}$$

$$Cl_2 = 35.5 \times 2 = 71 \text{ g}$$

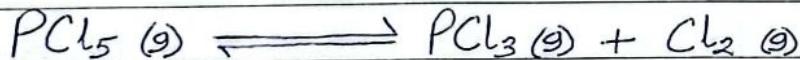
moles of;

$$PCl_5 = \frac{40.2}{208.5} = 0.1928$$

$$Cl_2 = \frac{4.2}{71} = 0.059$$

$$\text{Initial } [PCl_5] = \frac{0.1928}{4.5} = 0.0428 \text{ mol dm}^{-3}$$

$$[Cl_2] \text{ formed} = \frac{0.059}{4.5} = 0.0131 \text{ mol dm}^{-3}$$



$$\begin{array}{ccc} 0.0428-x & x & x, \text{ At equilibrium.} \\ \cancel{0.1928-x} & \cancel{x} & \cancel{x} \end{array}$$

$$\text{But; } x = 0.0131$$

$$\text{Thus; } [PCl_3] = 0.0131 \text{ mol dm}^{-3}$$

$$[PCl_5] = 0.0428 - 0.0131 = 0.0297 \text{ mol dm}^{-3}$$

(ii)

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.0131)^2}{0.0297}$$

$$K_c = 5.778 \times 10^{-3} \text{ mol dm}^{-3}$$

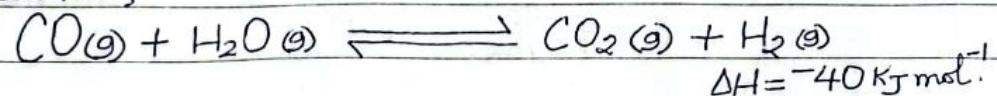
(b) (i) The value of the equilibrium Constant, K_c , remains unchanged.

The reaction proceeds with increase in volume. An increase in pressure thus favours the backward reaction to increase the concentration of PCl_5 . However, the concentrations of the products adjust to keep the K_c value fixed.

(ii) The value of the equilibrium Constant, K_C , remains the same.

The removal of Chlorine reduces its concentration in the equilibrium mixture. The equilibrium position thus shifts from left to right to compensate for the chlorine removed, and the K_C value is maintained fixed.

6. (a) Carbonmonoxide reacts with steam according to the equation;



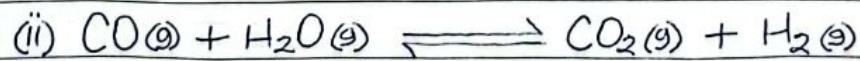
(i) Write expression for the equilibrium Constant, K_C .
(ii) Equal moles of carbonmonoxide and steam were reacted in a 1 litre vessel. When equilibrium was established at 750°C , the vessel contained 26.7% carbon dioxide. Calculate the value of the equilibrium Constant, K_C , for the reaction at 750°C .

(b) State, giving reasons, how the concentration of carbon dioxide would be affected if at equilibrium;

- (i) the temperature was increased.
(ii) the pressure was increased.
(iii) an inert gas was added at a constant temperature.

Solution.

$$(a) (i) K_C = \frac{[CO_2][H_2]}{[CO][H_2O]}$$



$1-x \quad 1-x \quad x \quad x$

$$\begin{aligned} \text{Total moles at equilibrium; } &= 1-x + 1-x + x + x \\ &= 2 \text{ moles.} \end{aligned}$$

$$\text{For } CO_2 \text{ at eqm; } \frac{x}{2} \times 100 = 26.7$$

$$100x = 53.4$$

$$x = 0.534$$

$$\text{moles of } \text{H}_2 = \text{moles of } \text{CO}_2 \\ = 0.534 \text{ moles.}$$

$$\text{moles of CO} = \text{moles of } \text{H}_2\text{O} \\ = 1 - 0.534 \\ = 0.466 \text{ moles.}$$

$$K_C = \frac{(0.534)^2}{(0.466)^2} \\ = 1.313.$$

(b) (i) The Concentration of CO_2 would decrease.

An increase in temperature results into the equilibrium position shifting from right to left due to the forward reaction being exothermic.

(ii) The Concentration of Carbon dioxide remains Unchanged.

An increase in pressure has no effect on equilibrium position since the reaction proceeds with no change in Volume.

(iii) The Concentration of Carbon dioxide remains Constant.

This is because addition of an inert gas increases the total pressure of the system which does not affect the equilibrium position.

EQUILIBRIUM CONSTANT IN TERMS OF PARTIAL PRESSURES.

The total pressure exerted by a gaseous mixture at equilibrium is obtained from the sum of the partial pressures of individual components.

Partial pressure of a gas in a gaseous mixture is the pressure which that particular gas would exert if it alone occupied the volume occupied by the gaseous mixture.

Considering a gaseous mixture of Components A, B and C at equilibrium;

$$\text{Total pressure, } P_{\text{Total}} = P_A + P_B + P_C$$

Partial pressure of A, $P_A = \text{mole fraction of A} \times \text{Total Pressure}$.
 $P_A = X_A P_{\text{Total}}$.

Mole fraction is the ratio of the number of moles of a given component to the total number of moles in the system.

$$X_A = \frac{\text{moles of gas A}}{\text{Total moles of gaseous mixture}}$$

The relationship between the partial pressure, P , of any gas in an equilibrium mixture and molar concentration is obtained using the ideal gas equation.

$$PV = nRT$$

Thus;

$$P = \left(\frac{n}{V}\right)RT$$

where $\frac{n}{V}$ is number of moles in a given volume, which is molar concentration.

Therefore, partial pressure of a gas in an equilibrium mixture is directly proportional to its concentration at a given temperature.

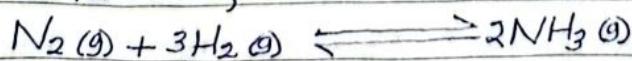
The equilibrium Constant expression can be given in terms of partial pressures as K_p .

Consider an equilibrium gaseous mixture obtained from the following reaction;



$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

Thus for a reaction;



$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}^3}$$

$$\text{Units} = \frac{(\text{atm})^2}{\text{atm} (\text{atm})^3}$$

$$= \text{atm}^{-2}$$

Examples:

1. At 700°C and a total pressure of 1 atmosphere, the partial pressures at equilibrium for Sulphur dioxide and oxygen are 0.27 and 0.41 atm respectively. Calculate the equilibrium Constant, K_p , for the reaction $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$

Solution:

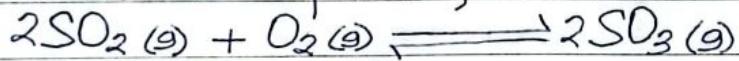
The total pressure at equilibrium = 1 atm.

$$P_{\text{SO}_2} + P_{\text{O}_2} + P_{\text{SO}_3} = 1$$

$$P_{\text{SO}_3} = 1 - (0.27 + 0.41)$$

$$= 0.32 \text{ atm.}$$

From the reaction equation;

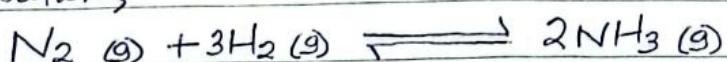


$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \cdot P_{\text{O}_2}}$$

$$= \frac{(0.32)^2}{(0.27)^2 \cdot 0.41}$$

$$= 3.42 \text{ atm}^{-1}$$

2. Nitrogen reacts with hydrogen according to the following equation;



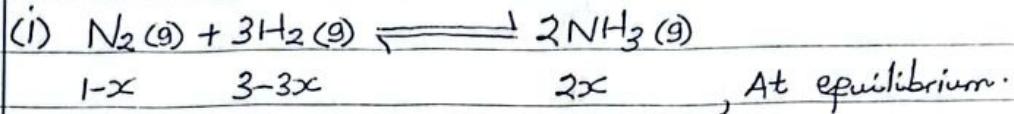
Stoichiometric amounts of nitrogen and hydrogen were reacted at 50 atmospheres, and at equilibrium 0.8 moles of ammonia was formed.

Calculate the;

(i) moles of hydrogen at equilibrium.

(ii) Value of the equilibrium Constant, K_p , for the reaction.

Solution.



For NH_3 at $ef \equiv m$; $2x = 0.8$
 $x = 0.4$

Thus;

moles of N_2 remaining = $1 - 0.4 = 0.6$ moles.

moles of H_2 remaining = $3 - 3(0.4) = 1.8$ moles.

(ii) Total moles at $ef \equiv m = 0.6 + 1.8 + 0.8$
= 3.2 moles.

$$P_{\text{N}_2} = \frac{0.6}{3.2} \times 50 = 9.375 \text{ atm}$$

$$P_{\text{H}_2} = \frac{1.8}{3.2} \times 50 = 28.125 \text{ atm}$$

$$P_{\text{NH}_3} = \frac{0.8}{3.2} \times 50 = 12.5 \text{ atm}$$

$$\begin{aligned} K_p &= \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3} \\ &= \frac{(12.5)^2}{(9.375)(28.125)^3} \\ &= 7.49 \times 10^{-4} \text{ atm}^{-2}. \end{aligned}$$

3. Sulphur dichloride dioxide decomposes at high temperatures according to the following equation;



When 13.5g of SO_2Cl_2 was placed in a 2 litre vessel and heated at a pressure of 2 atm, 1.5g of chlorine was formed at equilibrium.

- Write an expression for the equilibrium Constant, K_p .
- Calculate the value of K_p and state its units.
- State what would happen to the position of equilibrium when;
 - pressure is reduced.

- (ii) Sulphur dioxide is removed from the equilibrium mixture.
 (iii) Chlorine is added to the equilibrium mixture.
 (d) Explain your answer in C (ii) above.

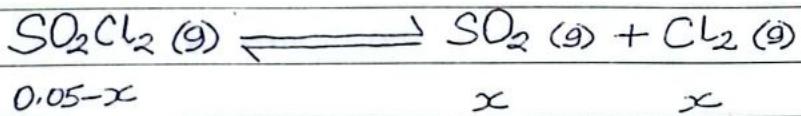
Solution.

$$(a) K_p = \frac{P_{SO_2} \times P_{Cl_2}}{P_{SO_2 Cl_2}}$$

$$(b) RFM of SO_2 Cl_2 = 32 + (16 \times 2) + (35.5 \times 2) = 135$$

$$\text{Initial moles of } SO_2 Cl_2 = \frac{13.5}{135} \times \frac{1}{2} = 0.05 \text{ mol dm}^{-3}$$

$$[Cl_2] \text{ at eqm} = \frac{1.5}{71} \times \frac{1}{2} = 0.01 \text{ mol dm}^{-3}$$



$$\text{moles of } Cl_2 \text{ at eqm} = x = 0.01 \text{ moles}$$

$$\text{moles of } SO_2 Cl_2 \text{ remaining} = 0.05 - 0.01 = 0.04 \text{ moles}$$

$$\begin{aligned} \text{Total moles of mixture at eqm} &= 0.04 + 0.01 + 0.01 \\ &= 0.06 \text{ moles.} \end{aligned}$$

$$P_{SO_2 Cl_2} = \frac{0.04}{0.06} \times 2 = 1.333 \text{ atm.}$$

$$P_{SO_2} = \frac{0.01}{0.06} \times 2 = 0.333 \text{ atm}$$

$$P_{Cl_2} = P_{SO_2} = 0.333 \text{ atm.}$$

$$\begin{aligned} K_p &= \frac{(0.333)^2}{1.333} \\ &= 0.083 \text{ atm.} \end{aligned}$$

- (c) (i) The equilibrium position shifts from left to right.
 (ii) The equilibrium position shifts from left to right.
 (iii) The equilibrium position shifts from right to left.
 (d) Addition of chlorine increases the chlorine concentration in the mixture and the backward reaction is favoured to restore equilibrium.

4. Nitrogen (ii) oxide combines with oxygen at 80°C and 200 atm, to form nitrogen (iv) oxide according to the following equation.

$$2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g), \Delta H = -X \text{ kJ mol}^{-1}$$

(a) Write an expression for the equilibrium constant, K_p , for the reaction.

(b) Calculate the value of K_p if the mixture contained 67% nitrogen (iv) oxide at equilibrium.

Solution:

$$(a) K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}} \times P_{\text{O}_2}}$$



$$\text{Total moles at equilibrium} = 2-2x + 1-x + 2x \\ = 3-x$$

$$\text{For } \text{NO}_2; \frac{2x}{3-x} \times 100 = 67$$

$$200x = 67(3-x)$$

$$200x = 201 - 67x$$

$$x = 0.753$$

$$\begin{aligned} P_{\text{NO}} &= \frac{2-2x}{3-x} \times 200 \\ &= \frac{2-2(0.753)}{3-0.753} \times 200 \\ &= 43.97 \text{ atm} \end{aligned}$$

$$\begin{aligned} P_{\text{NO}_2} &= \frac{2x}{3-x} \times 200 \\ &= \frac{2(0.753)}{3-0.753} \times 200 \\ &= 134 \text{ atm.} \end{aligned}$$

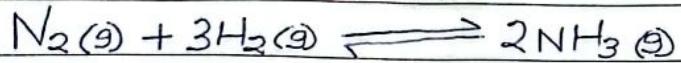
$$\begin{aligned} P_{\text{O}_2} &= \frac{1-x}{3-x} \times 200 \\ &= \frac{1-0.753}{3-0.753} \times 200 \\ &= 21.985 \text{ atm.} \end{aligned}$$

$$\begin{aligned} K_p &= \frac{(134)^2}{(43.97)^2 \times 21.985} \\ &= 0.422 \text{ atm}^{-1}. \end{aligned}$$

5. Stoichiometric amounts of nitrogen and hydrogen were mixed and exploded.

When equilibrium was established at 600°C and 10 atmospheres, the percentage of ammonia in the mixture of gases was found to be 15%. Calculate the K_p value at 600°C .

Solution.



$$1-x \quad 3-3x \quad 2x, \text{ At equilibrium.}$$

$$\begin{aligned} \text{Total moles at equilibrium} &= 1-x+3-3x+2x \\ &= 4-2x \end{aligned}$$

$$\text{For } \text{NH}_3; \frac{2x}{4-2x} \times 100 = 15$$

$$200x = 15(4-2x)$$

$$200x = 60 - 30x$$

$$x = 0.261$$

$$P_{\text{N}_2} = \frac{1-x}{4-2x} \times 10$$

$$= \frac{1-0.261}{4-(0.261 \times 2)} \times 10$$

$$= 2.125 \text{ atm.}$$

$$P_{\text{H}_2} = \frac{3-3x}{4-2x} \times 10$$

$$= \frac{2.217}{3.478} \times 10$$

$$= 6.374 \text{ atm.}$$

$$P_{\text{NH}_3} = \frac{2x}{4-2x} \times 10$$

$$= \frac{2(0.261)}{3.478} \times 10$$

$$= 1.50 \text{ atm.}$$

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3}$$

$$= \frac{(1.50)^2}{2.125 \times (6.374)^3}$$

$$= 4.088 \times 10^{-3} \text{ atm}^{-2}.$$

APPLICATION OF LECHATELIER'S PRINCIPLE IN THE MANUFACTURING INDUSTRY.

The principle is widely applied in the manufacturing industry to choose conditions necessary to give a high yield of the desired product at a reasonable rate.

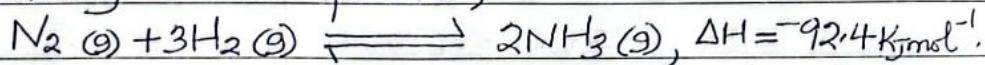
It makes the manufacturing process more efficient and economically viable.

Le Chatelier's principle is applied in;

- (i) manufacturing of ammonia by the Haber process.
- (ii) manufacturing of Sulphuric acid by the Contact process.

Manufacture of Ammonia (Haber Process)

Ammonia is synthesized from nitrogen and hydrogen according to the equation;



Nitrogen is obtained from the atmosphere by fractional distillation of liquid air while hydrogen is obtained from natural gas.

The above reaction equation shows that;

- the reaction is exothermic

- the reaction proceeds with a decrease in number of moles.

Therefore; the conditions for a maximum yield of ammonia are;

(i) low temperature of about 450°C . This is because the forward reaction is exothermic, and the equilibrium position shifts from left to right at a low temperature.

(ii) high pressure of about 200 atmospheres. This is b/c the number of moles decreases in the forward reaction and thus an increase in pressure shifts the equilibrium position from left to right.

(iii) Addition of finely divided Iron. At a low temperature, the reaction rate is slow and it would thus take time for equilibrium to be established. For the process to become economically viable, Iron catalyst is added to

Speed up the rate of attainment of equilibrium.

Note: Constant removal of ammonia as soon as it is produced shifts the equilibrium position from left to right hence increasing the yield of ammonia.

Uses of Ammonia.

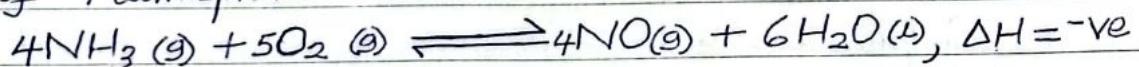
- (i) Used in the manufacture of fertilisers e.g Ammonium Sulphate
- (ii) Used in the manufacture of explosives.
- (iii) It is used in the manufacture of nitric acid.
- (iv) Ammonia solution is used in laundry work to soften water.

Manufacture of Nitric acid.

The process involves the following stages;

- (i) Catalytic oxidation of ammonia to nitrogen monoxide.

The catalyst used is platinum at about 700°C and a pressure of 9 atmospheres.



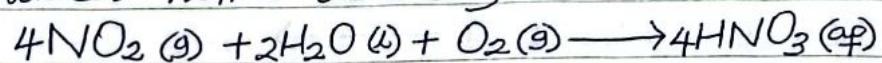
- (ii) Oxidation of nitrogen monoxide to nitrogen dioxide.



- (iii) The nitrogen dioxide obtained is reacted with water to form nitric acid and nitrous acid



When reacted with water in presence of oxygen, nitrogen dioxide produces nitric acid only.



Uses of Nitric acid.

- Used in the manufacture of fertilisers such as ammonium nitrate.
- manufacture of explosives e.g trinitrotoluene.
- manufacture of dyes.

Manufacture of Sulphuric acid: (Contact process)

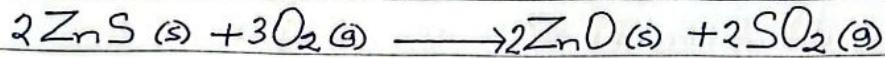
This is a three-stage process;

(i) Formation of Sulphur dioxide.

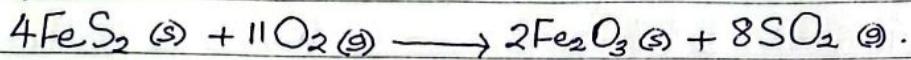
Sulphur dioxide is obtained by burning Sulphur or roasting metallic Sulphides in air.



or;



or;

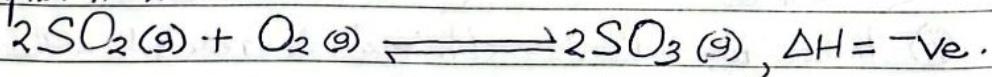


Iron(II) disulphide

The Sulphur dioxide formed is purified and dried to remove any impurities that would otherwise poison the catalyst as Sulphur dioxide is being reacted with air to form Sulphur trioxide.

(ii) Conversion of Sulphur dioxide to Sulphur trioxide.

Sulphur dioxide and excess oxygen are passed over finely divided Vanadium (V) oxide at ordinary pressure and a temperature of 450–500°C. They react to form Sulphur trioxide.

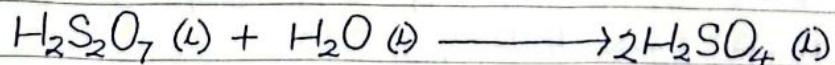


(iii) Conversion of Sulphur trioxide to Sulphuric acid.

Sulphur trioxide is dissolved in concentrated Sulphuric acid to form Oleum.



Oleum is then diluted with a calculated amount of water to form Sulphuric acid which is about 98% Concentrated.



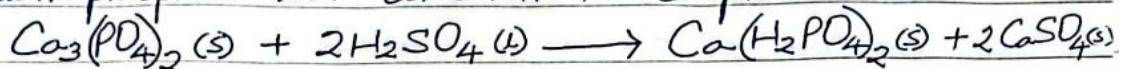
Note:

- (i) Sulphur trioxide cannot be directly dissolved in water because its reaction with water is very exothermic and would form a mist of the acid that is slow to settle out.

Uses of Sulphuric acid;

(i) manufacture of fertilisers.

One such fertiliser is a Superphosphate called Calcium dihydrogen phosphate which is produced by reacting Calcium phosphate with Concentrated Sulphuric acid.



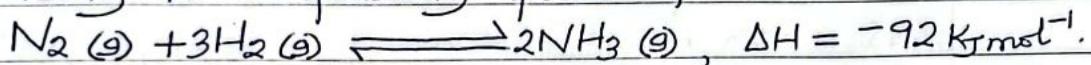
(ii) Manufacture of paints and pigments.

(iii) manufacture of detergents.

(iv) manufacture of organic chemicals such as drugs and dyes.

Questions:

1. Nitrogen reacts with hydrogen to form ammonia according to the following equation;



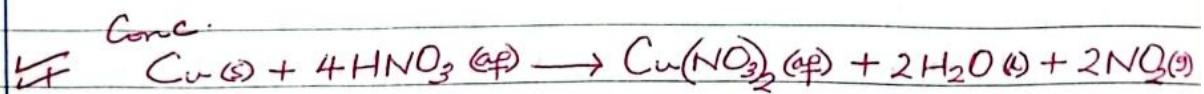
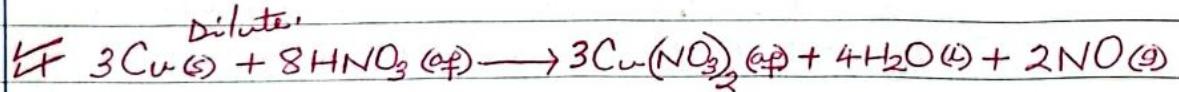
(a) State the Conditions for the reaction which would give a maximum yield of ammonia.

(b) Write equations for the reactions that take place during the manufacture of nitric acid from ammonia.

(c) Write equation for the reaction between Copper and;

(i) dilute nitric acid.

(ii) Concentrated nitric acid.



2. (a) Describe the industrial manufacture of Sulphuric acid.

(b) Describe the reaction of Sulphuric acid with;

(i) hydrogen bromide

(ii) Copper

(iii) Aluminium.

(c) Sulphur dioxide is oxidised to Sulphur trioxide according to the following equation;



Describe, giving reasons, the effect on the position of equilibrium of;

(i) increasing the temperature from 25°C to 150°C .

(ii) adding a reagent that reacts with Sulphur trioxide.

(d) 3 moles of Sulphur dioxide and 1.5 moles of oxygen were put in a sealed container at 700°C . At equilibrium and a total pressure of 20 atm, the equilibrium mixture contained 0.3 moles of oxygen. Calculate the;

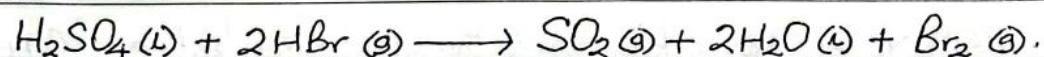
(i) partial pressures of each at equilibrium.

(ii) equilibrium constant, K_p , for the reaction.

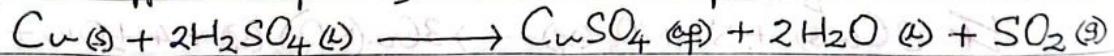
(e) Write equation to show how Sulphuric acid is used in the manufacture of a Super phosphate fertiliser.

Solution:

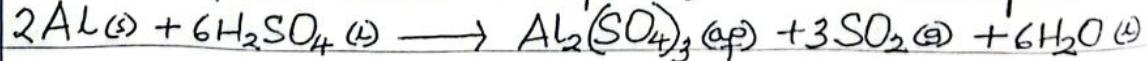
b) (i) Concentrated Sulphuric acid oxidises hydrogen bromide to bromine. The acid is itself reduced to Sulphur dioxide and water.



(ii) Hot concentrated Sulphuric acid reacts with copper to form Copper(II) sulphate, water and Sulphur dioxide.



(iii) Aluminium reacts with hot concentrated Sulphuric acid to form aluminium sulphate, water and Sulphur dioxide.



(c) (i) Increase in temperature shifts the equilibrium position from right to left. This is because the forward reaction is exothermic.

(ii) The reagent reduces the concentration of Sulphur trioxide. Equilibrium position thus shifts from left to right for the value of equilibrium Constant to remain fixed.

3. a) (i) Outline the chemical process involved in the manufacture of nitric acid. Illustrate your answer with Suitable equations
(ii) State two large scale uses of nitric acid.
(b) Concentrated nitric acid is 70% (w/w) and has a density of 1.42 g cm^{-3} . Calculate the molarity of Concentrated nitric acid.
(c) 12.68 cm^3 of the acid in (b) was dissolved in water and the solution made up to 250 cm^3 with distilled water. Calculate the volume of the solution that would react completely with 25.0 cm^3 of a 0.2M Sodium carbonate Solution.
(d) Briefly discuss the reaction between Copper and nitric acid. Illustrate your answers with equations.

Solution:

b) 1 cm^3 of Conc. HNO_3 weighs 1.42 g .

$$1000 \text{ cm}^3 \text{ of Conc. } \text{HNO}_3 \text{ weigh } \frac{(1000 \times 1.42)}{1} \\ = 1420 \text{ g}.$$

$$\text{mass of pure } \text{HNO}_3 = \frac{70}{100} \times 1420 \\ = 994 \text{ g}.$$

$$\text{Formula mass of } \text{HNO}_3 = 1 + 14 + (16 \times 3) = 63 \text{ g}.$$

63g of HNO_3 Contain 1 mole.

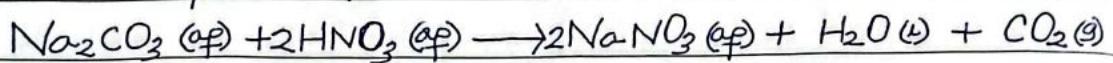
$$994 \text{ g of } \text{HNO}_3 \text{ Contain } \frac{(994 \times 1)}{63} = 15.778 \text{ moles.}$$

$$\text{Molarity of Conc. } \text{HNO}_3 = 15.778 \text{ M.}$$

$$(c) \text{ moles of } \text{Na}_2\text{CO}_3 = \left(\frac{25 \times 0.2}{1000} \right)$$

$$= 0.005 \text{ moles.}$$

Reaction equation;



1 mole of Na_2CO_3 reacts with 2 moles of HNO_3 .

$$0.005 \text{ moles of } \text{Na}_2\text{CO}_3 \text{ react with } \frac{(0.005 \times 2)}{1}$$

$$= 0.01 \text{ moles of } \text{HNO}_3.$$

1000 cm^3 of the pure Conc. HNO_3 contain 15.778 moles.

$$12.68 \text{ cm}^3 \text{ of the pure Conc. } \text{HNO}_3 \text{ contain } \left(\frac{12.68 \times 15.778}{1000} \right)$$

$$= 0.2 \text{ moles.}$$

moles in 250 cm^3 = moles in 12.68 cm^3 solution.

0.2 moles of acid are contained in 250 cm^3 .

$$0.01 \text{ moles of acid are contained in } \left(\frac{0.01 \times 250}{0.2} \right)$$

$$= 12.5 \text{ cm}^3 \text{ of acid.}$$

4. Concentrated hydrochloric acid is 20.2% w/w and has a density of 1.3 g cm^{-3} .

(a) Calculate the molarity of the concentrated acid.

(b) 120 cm^3 of the concentrated acid was diluted with water and the solution made up to 1000 cm^3 . Calculate the volume of the acid solution that would react completely with 25 cm^3 of 0.2M Sodium Carbonate Solution.