NTARE SCHOOL
S.6 CHEMISTRY
CHEMICAL EQUILIBRA

Equilibrium is a dynamic state in which two opposing processes occur at the same time and rate.
This kind of equilibrium occurs in reversible reactions.
A reversible reaction is a reaction that does not proceed to completion but instead stops at a point where the rate of the forward reaction equals to the rate of the backward reaction.
If such equilibrium occurs in a closed system where nothing added except heat and from which nothing escapes except heat.
Then, at the point of dynamic equilibrium in a closed system, no further change in composition can be detected with time provided the temperature and pressure remain constant. i.e the forward reaction and backward reaction take place simultaneously at the same rate.

Characteristics of a dynamic equilibrium

1. It occurs in reversible reactions
2. It occurs at a constant temperature.
3. It is attained in a closed system.
4. The amount of reactants and products at the point of dynamic equilibrium remains constant.
5. All reactants are not used up.

TYPES OF CHEMICAL EQUILIBRIUM

1. Homogeneous equilibrium

This is the kind of equilibrium in which all the substances involved in a reversible reaction are in the same phase
E.g
(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
(c) $CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

2. Heterogeneous equilibrium

This is the kind of equilibrium in which the substances involved in a reversible reaction are in more than one phase
E.g
(a) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
(b) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
(c) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

THE EQUILIBRIUM CONSTANT, K_C

This constant is derived from the concentrations of the substances present at the point of equilibrium which may be gases or liquids.
Consider a dynamic homogenous equilibrium below
$aA + bB \rightleftharpoons cC + dD$
The equilibrium constant K_C for the above reaction is got from the expression

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The powers a, b, c and d are the values used to balance the equation.

Equilibrium law (Law of mass action)

When a reversible reaction is at a point of dynamic 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 at a constant temperature.
Note.
The value of the equilibrium constant K_C is always constant as long as the temperature is kept constant.

Units of the equilibrium constant K_C
These units vary from case to case and they are worked out according to the expression for K_C for a given reversible reaction.
e.g
(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_C = \frac{[NH_3]^2}{[N_2]^1[H_2]^3}$$

Its units are $\frac{(mol\ dm^{-3})^2}{(mol\ dm^{-3})(mol\ dm^{-3})^3} = \frac{mol^2\ dm^{-6}}{mol\ dm^{-3} \times mol^3\ dm^{-9}} = \frac{mol^2\ dm^{-6}}{mol^4\ dm^{-12}} = mol^{-2}\ dm^6$

(b) $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$

$$K_C = \frac{[C_2H_5OH]}{[C_2H_4][H_2O]}$$

Its units are $= \frac{mol\ dm^{-3}}{mol\ dm^{-3} \times mol\ dm^{-3}} = \frac{mol\ dm^{-3}}{mol^2\ dm^{-6}} = mol^{-1}\ dm^3$

Factors affecting the position of equilibrium.
Position of equilibrium is the direction in which a reversible reaction proceeds which either can be forward or backward.
The factors affecting equilibrium position are;
- 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 for equilibrium position is in accordance with Lechatelier's principle.
The principle states that when a system is in equilibrium and one of the factors holding it in equilibrium is altered or changed, the system will adjust itself in order to nullify the effect of the change.

1. Effect of change in concentration
   For a system at equilibrium, when the concentration of the reactants is increased, the reaction will proceed in the direction that will reduce the concentration of those reactants such that equilibrium is restored again.
   Consider the following reaction at the point of equilibrium in a closed system
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   Addition of more nitrogen to the system increases the nitrogen concentration in the reaction mixture.
   This results into shifting of the equilibrium position from left to right whereby hydrogen combines with the excess nitrogen to produce more ammonia. i.e the concentration of nitrogen is reduced while that of ammonia is increased and the system is brought back to equilibrium.
   Conversely, when some nitrogen is removed from the equilibrium mixture, ammonia decomposes to produce nitrogen and hydrogen and thus the equilibrium position shifts from right to left.

   Note.
   The rate of attainment of equilibrium is increased by increase in concentration.
   However, the change in concentration does not affect the value of the equilibrium constant as long as temperature is kept constant.

Example 1

Manganese(II) sulphide reacts with acids according to the equation

$$MnS(s) + 2H_3O^+(aq) \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l) + H_2S(g)$$

State giving the reason, what would happen to the equilibrium position when;

(i) water is added to the equilibrium mixture

(ii) hydrogen chloride is bubbled into the equilibrium mixture

(iii)the pH of the equilibrium mixture is increased.

Solution

(i) Addition of water results into an increase of water in the mixture and therefore manganese(II) ions and hydrogen sulphide combine with the excess water shifting the equilibrium position from right to left.

(ii) Bubbling hydrogen chloride results into an increase in the hydroxonium ion (H_3O^+) concentration. The excess hydroxonium ions react with Manganese(II) sulphide shifting the equilibrium position from left to right.

(iii) Increase in the pH means addition of hydroxyl ions [alkali]. The added hydroxyl ions would react with hydroxonium ions reducing their concentration in the mixture. Therefore, equilibrium position shifts from right to left to compensate for the hydroxonium ions lost.

Example 2

Sodium chromate (VI) reacts with dilute acids to produce sodium dichromate (VI) according to the equation

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

(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 the resultant mixture in (a) is added

(i) to sodium hydroxide solution

(ii) water

Solution

(a) The yellow solution turns to orange

(b) (i) The orange solution turns back to yellow. The added alkali reduces the hydrogen ion concentration by neutralization and thus the equilibrium position shifts from right to left to compensate for the reduced hydrogen ion concentration.

(ii) Addition of water increases the amount of water in the mixture resulting into the solution turning from orange to yellow.

Thus the equilibrium position shifts from right to left.

2. Effect of change in temperature

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

If the forward reaction is endothermic such as

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)\ , \Delta H = +ve$$

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

If the forward reaction is exothermic such as

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)\ , \Delta H = -ve$$

An increase in temperature favours the backward reaction i.e 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 equilibrium constant because the amount of products is higher than that of reactants.
If the forward reaction is exothermic, an increase in temperature results into a decrease in the value of equilibrium constant because the amount of products is lower than that of reactants.

3. Effect of change in pressure
The effect of pressure on the reversible reaction depends on whether the reaction proceeds with change in volume/number of moles/molecules.
For a reaction that proceeds with an increase in volume (number of molecules) of gases such as
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
An increase in pressure shifts the equilibrium position from right to left i.e the backward reaction is favoured.
For a reaction that proceeds with a decrease in volume (molecules) of gases such as
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
An increase in pressure shifts the equilibrium position from left to right i.e it favours the forward reaction.
For a reaction that involves no change in volume or number of molecules of gases such as
$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
A change in pressure does not affect the equilibrium position.
An increase in pressure increases the rate of attainment of equilibrium because of the increases in the frequency of collision between the reacting particles.
Change in pressure has no effect on the value of the equilibrium constant as long as temperature is kept constant.

Note
Pressure of a gas depends on the number pf gaseous molecules in a given volume of the container.
The greater the number of gaseous molecules, the more the collisions and the higher the exerted 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 increases.

Question
(a) State the Lechatelier's principle
(b) Nitrogen reacts with hydrogen to produce ammonia according to the equation

$$N_2(g) + H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -ve$$

(i) Write an expression for the equilibrium constant K_C for the reaction and state its units.
(ii) State and discuss the effect of change in temperature on the position of equilibrium, rate of attainment of equilibrium and value of equilibrium constant K_C for the above reaction.

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

5. Effect of adding a noble/inert gas
Addition of an inert gas to a system at equilibrium is similar to increasing pressure.
An inert gas leads to an increase in the number of molecules in a container but the gas itself does not take part in the chemical reaction.
The inert gas therefore only increases the pressure of the gaseous mixture.

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

Calculating the K_C values

The bigger the value of K_C, the more are the reactants converted to products.

The smaller the value of K_C, the less are the reactants converted to products.

Example 1

Hydrogen reacts with iodine according to the equation; $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

A mixture of 0.8 moles of H_2 and 0.6 moles of iodine was allowed to react in a sealed tube at 550°C. At equilibrium 0.2 moles of iodine had reacted.

(i) Write the expression for the equilibrium constant K_C

(ii) Calculate the value of K_C at 550°C.

Solution. Let x moles of iodine react.

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

$H_2(g)$	$+$	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
0.8		0.6		$-$ (initial amounts)
$0.8 - x$		$0.6 - x$		$2x$ (at equilibrium)

At equilibrium, for I_2, $x = 0.2$ moles

Thus moles of H_2 remaining $= 0.8 - 0.2 = 0.6$ moles

moles of I_2 remaining $= 0.6 - 0.2 = 0.4$ moles

moles of HI formed $= 2x = 2 \times 0.2 = 0.4$ moles

$K_C = \frac{(0.4)^2}{(0.6)(0.4)} = 0.67$

Example 2

Nitrogen dioxide reacts with oxygen to form nitrogen dioxide according to the equation

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

(a) Write the expression for the equilibrium constant K_C

(b) 3 moles of NO and 1.5 moles of O_2 were mixed in a vessel and heated to 400°C. At equilibrium 0.5 moles of O_2 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 NO. 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 your answer.

Solution.Let x moles of oxygen react.

(a) $K_C = \frac{[NO_2]^2}{[NO]^2[O_2]}$

(b)

$2NO(g)$	$+$	$O_2(g)$	$\rightleftharpoons$	$2NO_2(g)$
3		1.5		$-$(Initial amounts)
$3 - 2x$		$1.5 - x$		$2x$ (at equilibrium)

At equilibrium, for O_2, $1.5 - x = 0.5$

$x = 1$ mole

Thus moles of NO remaining $= 3 - 2 \times 1 = 1$ mole

moles of O_2 remaining $= 1.5 - 1 = 0.5$ moles

moles of NO_2 formed $= 2x = 2 \times 1 = 2$ moles

$K_C = \frac{(2)^2}{(1)^2(0.5)} = 8 \text{ mol}^{-1} \text{ dm}^3$

(c) $\frac{25}{100} \times 3 = 0.75$ moles of NO at equilibrium

$2NO(g)$	$+$	$O_2(g)$	$\rightleftharpoons$	$2NO_2(g)$
$3 - 2x$		$1.5 - x$		$2x$ (at equilibrium)

At equilibrium, for NO, $3 - 2x = 0.75$

$x = 1.125$ moles

Thus moles of NO remaining $= 3 - 2 \times 1.125 = 0.75$ mole

moles of O_2 remaining $= 1.5 - 1.125 = 0.375$ moles

moles of NO_2 formed $= 2x = 2 \times 1.125 = 2.25$ moles

$K_C = \frac{(1.25)^2}{(0.75)^2(0.375)} = 24 \text{ mol}^{-1} \text{ dm}^3$

(d) The reaction is endothermic. This is because the value of equilibrium constant K_C increases with increase in temperature.

Questions

1. Carbon monoxide reacts with hydrogen to form gaseous methanol according to the equation
   $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g);\ \Delta H = -92kJmol^{-1}$
   (a) Write an expression for the equilibrium constant for the reaction
   (b) When 1 mole of carbon monoxide was mixed with 2 moles of hydrogen and the reaction carried out at 200℃, 1.6 moles of hydrogen remained in the equilibrium mixture. Calculate the value of equilibrium constant K_C

2. Substance X decomposes reversibly on heating according to the equation
   $X(g) \rightleftharpoons Y(g) + Z(g)$
   (a) When 1 mole of X was heated at 200℃ in a container of volume 25 dm^3.
   The equilibrium mixture was found to contain 0.2 moles of Y. Calculate the value of K_C at this temperature.
   (b) When the equilibrium constant was measured at 500℃, it was found to be
   4.0×10^{-3} mol dm^{-3}.
   (i) State whether the decomposition of X is exothermic or endothermic.
   (ii) Explain your answer in (b)(i) above.

3. Phosphorous (V) chloride decomposes at high temperature according to the equation
   $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
   When 40.2g of PCl_5 was placed in 4.5 litre vessel and heated at a certain pressure, 4.2g of Cl_2 was formed at equilibrium.
   (a) Calculate the
   (i) amount of PCl_5 and PCl_3 at equilibrium
   (ii) equilibrium constant K_C for the reaction and state its units
   (b) State how the value of K_C would be affected and in each case give a reason for your answer if;
   (i) pressure was increased
   (ii) some $Cl_2$was removed at equilibrium.

4. Carbon monoxide reacts with steam according to the equation
   $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g);\ \Delta H = -40kJmol^{-1}$
   (a) Write an expression for the equilibrium constant K_C for the reaction
   (b) Equal moles of CO and H_2O was reacted in a 1 litre vessel. When equilibrium was attained at 750℃, the equilibrium mixture contained 26.7% carbon dioxide.
   Calculate value of at $K_C$for the reaction at 750℃.
   (c) State giving reasons how the concentration of CO_2 would be affected if at equilibrium;
   (i) temperature was increased
   (ii) pressure was increased
   (iii)an inert gas was added at a constant temperature.

EXPERIMENTAL DETERMINATION OF EQUILIBRIUM CONSTANT K_C

(a) determining equilibrium constant for the reaction between Ethanol and Ethanoic acid to form Ethyl ethanoate and water.

A known amount of ethanoic acid, a moles of acid is mixed with a known amount, b moles of ethanol.
The mixture is kept in a sealed glass tube for some time at a fixed temperature.
After some time, when the acid and alcohol have reacted to form an equilibrium mixture. The tube is broken under water at room temperature such that the equilibrium does not shift appreciably during measurement of concentration.
The solution is titrated with standard sodium hydroxide solution to determine the amount of ethanoic acid, x moles remaining at equilibrium.
This titration is done using phenolphthalein indicator.
The results of experiment are shown below.
If the moles of ethanoic acid remaining at equilibrium $= x$ moles
Then the moles of the acid that reacted $= (a - x)$ moles

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CO_2CH_2CH_3(l) + H_2O(l)$$

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

$$K_C = \frac{[CH_3CO_2CH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

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

Example

A mixture of 0.69g of ethanol and 0.9g of ethanoic acid were allowed to react at 90℃ until equilibrium was attained. Calculate the mass of ethyl ethanoate formed at equilibrium. ($K_C = 3.6$)

Solution

Formula mass of CH_3CH_2OH =46g
Formula mass of CH_3COOH =60g
Initial moles of $CH_3CH_2OH = \frac{0.69}{46} = 0.015$ moles
Initial moles of $CH_3COOH = \frac{0.9}{60} = 0.015$ moles
From the equation of reaction

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CO_2CH_2CH_3(l) + H_2O(l)$$

At equilibrium; $0.015 - x$ $\quad 0.015 - x$ $\quad x$ $\quad x$

$K_C = \frac{[CH_3CO_2CH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$

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

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

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

On solving using $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$; either $x = 0.0317$ or $x = 0.009823$

Formula mass of $CH_3CO_2CH_2CH_3$ =88g
=88× 0.009823
= 0.864g

(b) determining the equilibrium constant K_C for the reaction between iodine and hydrogen to form hydrogen iodide.

A known amount, a moles of hydrogen is mixed with a known amount, b moles of iodine in a bulb of a known volume.
The mixture is kept sealed at 450℃ 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 the dissolved iodine is titrated against standard sodium thiosulphate solution using starch indicator.
The concentration of iodine remaining at equilibrium is calculated using the equation

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons 2I^-(aq) + S_4O_6^{2-}(aq)$$

The results of the experiment are then treated as shown below.
Assume the moles of iodine found to have reacted $= x$ moles
Then according to equation for formation of hydrogen iodide

$$\begin{array}{lll} H_2(g) + & I_2(g) \rightleftharpoons & 2HI(g) \\ a & b & \\ a-x & b-x & 2x \end{array}$$

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(a-x)(b-x)} = \frac{4x^2}{(a-x)(b-x)}$$

Question

1. Hydrogen iodide decomposes when heated according to the equation
   $2HI(g) \rightleftharpoons H_2(g) + I_2(g); \quad \Delta H = +11.3\ kJmol^{-1}$
   (a) Write an expression for the equilibrium constant for the reaction
   (b) 1.54 g of hydrogen iodide was heated in a 600 cm^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 0.1 M sodium thiosulphate solution for complete reaction.
   Calculate
   (i) number of moles of hydrogen iodide in 1.54 g (H=1, I=127)
   (ii) number of moles of iodine formed when hydrogen iodide was decomposed
   (iii)value of at K_C 530°C.
   (c) State what would be the effect on the value of K_C when;
   (i) temperature is raised from 530°C to 800°C
   (ii) volume of the bulb is increased to 1200 cm^3.

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

EQUILIBRIUM CONSTANT IN TERMS OF PRESSURES, K_p

For a gas, concentration and pressure are proportional to each other. However, it is much easier to determine the pressure of a gas rather than its concentration.
The equilibrium constant for gaseous equilibria is better presented in terms of partial pressures.
Partial pressure in a gaseous mixture is the pressure which that particular gas would exert if it alone occupied the whole container.
Considering a gaseous mixture of components A, B and C at equilibrium, the total pressure
$P_{total} = P_A + P_B + P_C$
Partial pressure of component A is $P_A = X_A \cdot P_{total}$
Where X_A is the mole fraction of A.
Mole fraction is the ratio of the number of moles of a given component to the total number of moles in the system.
i.e $X_A = \frac{number\ of\ moles\ of\ A}{total\ moles\ of\ gaseous\ mixture}$

Writing the expression and determining units of K_p

Consider the following equilibria

1. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
   $K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \cdot P_{O_2}}$ or $K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})}$
   Units of K_p are $\frac{(atm)^2}{(atm)^2(atm)} = atm^{-1}$

2. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

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

Units of K_p are $\frac{(atm)^2}{(atm)^3(atm)} = atm^{-2}$

Example 1

Nitrogen reacts with hydrogen according to the following equation

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Stoichiometric(balancing ratios in the equation) amounts of nitrogen and hydrogen were reacted at a total pressure 50 atmospheres and at equilibrium, 0.8 moles of NH_3 were formed. Calculate the

(i) moles of hydrogen at equilibrium

(ii) value of equilibrium constant K_p for the reaction.

Solution. Let x moles of nitrogen react.

	$N_2(g)$	$+ 3H_2(g) \rightleftharpoons$	$2NH_3(g)$
Initial;	1	3	
At equilibrium;	$1 - x$	$3 - 3x$	$2x$

For NH_3; $2x = 0.8$

$x = 0.4$

(i) Moles of hydrogen remaining at equilibrium $= 3 - 3 \times 0.4 = 1.8$ moles

(ii) Total moles at equilibrium

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

Moles of H_2 remaining $= 1.8$ moles

Moles of NH_3 formed $= 2 \times 0.4 = 0.8$ moles

Total moles $= 0.6 + 1.8 + 0.8 = 3.2$ moles

$P_{N_2} = X_{N_2} \cdot P_{total} = \frac{0.6}{3.2} \times 50 = 9.375$ atm

$P_{H_2} = X_{H_2} \cdot P_{total} = \frac{1.8}{3.2} \times 50 = 28.125$ atm

$P_{NH_3} = X_{NH_3} \cdot P_{total} = \frac{0.8}{3.2} \times 50 = 12.5$

$K_p = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})} = \frac{(12.5)^2}{(28.125)^3(9.373)} = 7.492 \times 10^{-4}\ atm^{-2}$

Example 2

Sulphur dichloride dioxide decomposes at high temperature according to the following equation

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

When 13.5g of SO_2Cl_2 was passed in a 2 litre vessel and heated at a pressure of 2 atm, 1.5g of Cl_2 was formed at equilibrium.

a) Find the expression for the equilibrium constant K_p

b) Calculate the value of equilibrium constant K_p for the reaction and state its units.

c) State what would happen to the position of equilibrium when

(i) pressure is reduced

(ii) SO_2 is removed from the equilibrium mixture

(iii)Cl_2 is added to the equilibrium mixture

d) Explain your answer in (c) (iii) above.

Solution. Let x moles of chlorine be formed.

(a) $K_p = \frac{(P_{SO_2})(P_{Cl_2})}{(P_{SO_2Cl_2})}$

(b) Formula mass of $SO_2Cl_2 = 32 + 16 \times 2 + 35.5 \times 2 = 135$g

Formula mass of $Cl_2 = 71$g

Moles of SO_2Cl_2 in a litre $= \frac{13.5}{13.5} \times \frac{1}{2} = 0.05\ mol^{-1}$

Moles of Cl_2 in a litre $= \frac{1.5}{71} \times \frac{1}{2} = 0.0106\, mol^{-1}$
$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$
$0.05 - x \qquad x \qquad x$
For Cl_2; $x = 0.01$moles.
Thus

moles of SO_2Cl_2 remaining at equilibrium $= 0.05 - 0.01 = 0.04$ moles
moles of SO_2 = moles of $Cl_2 = 0.01$ moles
total moles $= 0.04 + 0.01 + 0.01 = 0.06$ moles

$P_{SO_2Cl_2} = X_{SO_2Cl_2} \cdot P_{total} = \frac{0.04}{0.06} \times 2 = 1.333$ atm

$P_{SO_2} = X_{SO_2} \cdot P_{total} = \frac{0.01}{0.06} \times 2 = 0.333$ atm

$P_{Cl_2} = X_{Cl_2} \cdot P_{total} = \frac{0.01}{0.06} \times 2 = 0.333$ atm

$K_p = \frac{(P_{SO_2})(P_{Cl_2})}{(P_{SO_2Cl_2})} = \frac{0.333 \times 0.333}{1.333} = 0.0830$ atm

(c)(i) Equilibrium position shifts from left to right when pressure is reduced.
Reason: the reaction proceeds with increase in number of moles
(ii) Equilibrium position shifts from left to right
(iii) Equilibrium position shifts from left right to left
(iv) Addition of chlorine increases the chlorine concentration in the mixture at equilibrium and therefore, the backward reaction will be favoured to restore the equilibrium.

Questions

1. Nitrogen(II)oxide combines with oxygen at 80 ℃ and 200 atmospheres to form nitrogen(IV)oxide according to the equation
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = -x\ kJmol^{-1}$$
   (a) Write the 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.
2. Stoichiometric amounts of nitrogen and hydrogen were mixed and exploded. When equilibrium was established at 600℃ and 10 atmospheres. The percentage of NH_3 in the mixture was found to be 15%. Calculate the K_p value at 600℃.

APPLICATION OF LECHATELIER'S PRINCIPLE

It is widely applied in manufacturing industry to determine conditions necessary to give a high yield of desired products at a reasonable rate.
It makes manufacturing industry viable i.e

- Manufacture of ammonia by Haber process
- Manufacturing of Sulphuric acid by contact process

Manufacturing of ammonia (Haber process)

Ammonia is synthesized from nitrogen and hydrogen according to the equation
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -ve$$
Nitrogen is obtained from the atmosphere by fractional distillation of liquid air while hydrogen is obtained from water gas, liquid ammonia etc.
From the above reaction equation, the conditions necessary for a high yield of ammonia are

- high pressure (150 – 350 atmospheres)
- optimum temperature of about 500 ℃

The reaction is carried out at a high pressure because the forward process proceeds with decrease in volume i.e number of moles and a low temperature is required because the forward reaction is exothermic.
However, at low temperature, the rate of reaction is very low and it would thus take time for equilibrium to be established. Thus there is need for a catalyst and finely divided iron catalyst is added to speed up the rate of attainment of equilibrium.

Uses of ammonia

1. used in the manufacture of fertilizers eg $(NH_4)_2SO_4$
2. used in the manufacture of explosives
3. used in the manufacture of nitric acid
4. ammonia solution is used for laundry work to soften water
5. liquid ammonia is used as a source of hydrogen

Manufacture of nitric acid (HNO_3)

Ammonia is first oxidized to nitrogen monoxide in presence of platinum catalyst at about 700 ℃ and a pressure of 9 atmospheres.

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

The nitrogen monoxide formed is then oxidized by more oxygen of the atmosphere to form nitrogen dioxide

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

The nitrogen dioxide obtained is reacted with water in the presence of oxygen to form nitric acid

$4NO_2(g) + 2H_2O(l) + O_2(g) \longrightarrow 4HNO_3(aq)$

Note;

If nitrogen dioxide is dissolved in water in the absence of oxygen, two acids i.e nitric acid and nitrous acid are formed.

$2NO_2(g) + H_2O(l) \longrightarrow HNO_3(aq) + HNO_2(aq)$

Uses of nitric acid

1. it is used in the manufacture of fertilizers e.g ammonia nitrate
2. it is used in the manufacture of explosives such as trinitrotoluene (TNT)
3. it is used in the manufacture of dyes

Manufacture of Sulphuric acid (contact process)

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

$S(s) + O_2(g) \longrightarrow SO_2(g)$

Or

$4FeS_2(s) + 11O_2(g) \longrightarrow 2Fe_2O_3(s) + 8SO_2(g)$

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

Sulphur dioxide and excess oxygen are passed over finely divided vanadium (V) oxide at ordinary pressure and temperature of about 250 – 500 ℃

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\ \Delta H = -ve$

Sulphur trioxide is dissolve in a fixed amount of concentrated Sulphuric acid to form Oleum.

$SO_3(g) + H_2SO_4(l) \longrightarrow H_2S_2O_7(l)$

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

$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$

Note;

When Sulphur trioxide is directly dissolved in water, a lot of heat is evolved(the reaction is highly exothermic) which vapourises the Sulphuric acid formed.

The Sulphuric acid vapour condenses to form tiny droplets which are slow to settle out.

The amount of Sulphuric acid produced by contact process depends on the amount of Sulphur trioxide which is formed from the reaction.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\ \Delta H = -ve$

The above equation shows that a high yield of Sulphur trioxide is favoured by

- high pressure
- low temperature

However, at low temperatures, the reaction rate would be slow and hence need for addition of a catalyst, hence finely divided vanadium (V) oxide is added to speed up the rate of the reaction.

Uses of Sulphuric acid

- This acid is mainly used in the manufacture of fertilizes, one such fertilizer is a superphosphate(calcium dihydrogen phosphate) , $Ca(H_2PO_4)_2$. This fertilizer is produced by heating calcium phosphate with concentrated Sulphuric acid.
  $Ca_3(PO_4)_2(s) + 2\,H_2SO_4(l) \longrightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4(s)$

  Other uses of Sulphuric acid;
- Manufacture of paints and pigments.
- Manufacture of detergents.
- Manufacture of plastics.
- Manufacture of dyes.

QNS:

1) Nitrogen and Hydrogen react to form Ammonia according to following equation
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92kJmol^{-1}$
State the conditions for the reaction which would give a maximum yield of Ammonia.
a. Write equations for the reactions that take place during the manufacture of nitric acid from ammonia.
b. Write equations for the reaction between copper and
   i Dilute nitric acid.
   ii Concentrated nitric acid.

ANS;

(c)(i) $3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$
(ii) with concentrated nitric acid
$Cu(s) + 4HNO_3(l) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$

PREPARATION OF DILUTE ACIDS

1. Concentrated Sulphuric acid is 98% weight by weight acid and has a density of $1.84\ \text{gcm}^{-3}$. Determine the volume of the concentrated acid that can be used to prepare 1 litre of 1M H_2SO_4.
   Solution
   $1cm^3$ of H_2SO_4 weighs 1.84g.
   $1000cm^3$ of H_2SO_4 weigh (1.84×1000)
   =1840g
   Mass of pure acid = $\frac{98}{100} \times 1840$
   =1803.2g
   Formula mass of H_2SO_4= $(1 \times 2) + 32 + (16 \times 4)$
   =98g
   98g of H_2SO_4 contain 1 mole
   1g of H_2SO_4 contain $\frac{1}{98} \times 1$ mole
   1803.2g of H_2SO_4 contains $\frac{1}{98}$ ×1803.3 moles =18.4M.
   18.4 moles are contained in $1000cm^3$ of conc. acid
   1 mole is contained in $\frac{1}{18.4}$ ×$1000cm^3$ =$54.35cm^3$ of conc. acid

2. Concentrated hydrochloric acid is 35.4% w/w acid and its density is $1.18gcm^{-3}$.
   i Determine the molar concentration of the concentrated acid.
   ii Calculate the volume of the concentrated acid required to produce 1 litre of 1M HCl.
   Solution
   i $1\ cm^3$ of HCl weighs 1.18g.
   $1000cm^3$ of HCl weigh (1.18×1000) =1180g
   Mass of pure acid; $\frac{35.4}{100}$ ×1180g =417.72g

Formula mass of HCl=1+35.5 =36.5g
36.5g of HCl contain 1 mole
1g of HCl contains $\frac{1}{36.5}$ mole
417.72g of HCl contain $\frac{1}{36.5} \times 417.72$ moles
=11.4444M of HCl

ii 11.44 moles are contained in 1000cm^{3}of conc. acid
1 mole is contained in $\frac{1}{11.44}$ ×1000cm^3
=87.41 cm^3 of conc. acid.

3. A constant boiling point mixture of 68% HNO_3 and H_2O has a density of 1.42gcm^{-3}
Calculate:
i Molarity of constant boiling point mixture.
ii 100cm^3 of the constant boiling point mixture was dissolved in water and the solution made up to 250 cm^3. Determine the molarity of the resultant solution.

<u>Solution</u>

i 1 cm^3 of constant boiling point mixture weigh 1.42g
1000 cm^3 of constant boiling mixture weigh (1.42 ×1000) =1420g
Mass of pure HNO_3 in mixture= $\frac{68}{100}$ ×1420 =965.6gl^{-1}
Formula mass of HNO_3 =1+14+ (16×3) =63g
63g contain 1 mole
965.6g contain $\left(\frac{965.6}{63}\right)$ moles =15.33M

ii 1000 cm^3 of pure HNO_3 contain 15.33 moles
100 cm^3 of pure HNO_3 contain $\left[\frac{(100\times15.33)}{1000}\right]$ moles =1.533 moles
250cm^3 of HNO_3 contain 1.533 moles
1 cm^3 of HNO_3 contains $\left[\frac{1}{250} \times 1.533\right]$ moles
1000 cm^3 of HNO_3 contain $\left[\frac{1}{250} \times 1.533 \times 1000\right]$ moles = 6.132M

QUESTIONS

1.(a) Concentrated nitric acid is 70% w/w and has a density of 1.42gcm^{-3}. Calculate the molarity of the concentrated acid.
(b) 12.68 cm^3 of the acid in (a) above was dissolved in water and the solution made up to 250cm^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.

2. Concentrated Sulphuric acid contains 98% of acid and its density is 1.98gcm^{-3}. Calculate the volume of acid required to prepare 250 cm^3 of a 0.2M dilute solution.

END