CHEMICAL EQUILIBRIA

THE CONCEPT OF CHEMICAL EQUILIBRIUM

Chemical reactions, just like physical changes can reach a state of equilibrium. Although some reactions take place in one direction, like the when magnesium burns in air to form magnesium oxide, other reactions take place in both forward and backward directions at comparable rates for example the thermal dissociation of calcium carbonate.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The products of thermal dissociation of calcium carbonate are calcium oxide, a base and carbon dioxide, an acidic gas which can react to form calcium carbonate again.

Apart from thermal dissociation of calcium carbonate, many other reactions do not go to completion and then stop, since the products of the reaction themselves react to form original reactants. Such reactions are called **reversible reactions**. Therefore, for equilibrium to be established there is both a **forward** and **backward reaction**.

The characteristics of a chemical equilibrium

(i) The reaction in which it occurs should be reversible

(ii) The reaction should occur in a closed system

(iii) Temperature should be constant

(iv) Rate of forward reaction should be equal to the rate of backward reaction

Reversible and irreversible reactions

A reversible reaction is a reaction takes place in both forward and backward directions such that both the reactants and products are present in the equilibrium hence does not go to completion.

For example;

(i) the reaction between hydrogen gas and gaseous iodine to form hydrogen iodide

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(ii) the esterification reaction for formation of ethylethanoate from ethanoic acid and ethanol

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

(iii) reaction between heated iron and steam to form iron(II) diiron(III) oxide and hydrogen

$$3Fe(s) + 4H_2O\ (l) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

An irreversible reaction is a reaction takes place only in the forward direction, such that only the products are formed during the reaction hence the reaction can never be at equilibrium.

(i) For example, the combustion of ethene to form carbon dioxide and water

$$H_2C = CH_2(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O\ (l)$$

(ii) Burning magnesium in air to form magnesium oxide

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

(iii) Alkaline hydrolysis of an ethylethanoate to form ethanoate ions and ethanol

$$CH_3COOC_2H_5\ (aq) + \bar{O}H(aq) \longrightarrow CH_3CO\bar{O}(aq) + CH_3CH_2OH\ (aq)$$

Dynamic equilibrium

A dynamic equilibrium is the equilibrium established when the rate of forward reaction is equal to the rate of backward reaction, such that the concentration of reactants and products remains constant.

For the reaction between known amounts of hydrogen and iodine in a sealed glass tube heated to a higher constant temperature and then allowed to cool, the equilibrium mixture formed contains hydrogen, iodine and hydrogen iodide.

$$H_2(g) + I_2\ (g) \rightleftharpoons 2HI(g)$$

This implies that both forward and backward reactions are still taking place and the rate of formation of hydrogen iodide is equal to rate of dissociation of hydrogen iodide and the concentrations of each species remains constant and the system is said to be in dynamic equilibrium.

This can be proven by injecting iodine containing a small quantity of radioactive iodine-131 into the equilibrium mixture. Radioactive iodine appears in the hydrogen iodide. This confirms that both forward reaction and backward reaction are still occuring.

Types of chemical equilibria

There are two types equilibrium systems namely;

(i) Homogeneous equilibrium systems
(i) Heterogeneous equilibrium systems

A homogeneous equilibrium system is one in which all the reactants and products of a reaction are in the same phase.

They can all gases, all liquids or all in solution.

For example;

(i) the reaction between ethanol and ethanoic acid to form ethyl ethanoate /diethyl ether (esterification)

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

(ii) the reaction between hydrogen gas and gaseous iodine to form hydrogen iodide

$$H_2(g) + I_2\ (g) \rightleftharpoons 2HI(g)$$

(iii) Dissociation of dinitrogen tetroxide to form nitrogen dioxide.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

A heterogeneous equilibrium system is one in which two or more phases are involved.

For example;

(i) Dissociation of calcium carbonate to form calcium oxide and carbon dioxide.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

(ii) Reaction between iron and steam to form triiron tetraoxide and hydrogen

$$3Fe(s) + 4\ H_2O\ (g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

(iii) Reaction between bismuth chloride and water to form bismuth oxychloride and hydrochloric acid

$$BiCl_3(aq) + H_2O\ (l) \rightleftharpoons BiOCl(s) + 2HCl(aq)$$

Note; if only ions are involved in an equilibrium, an ionic equilibrium (check next chapter) is established.

THE LAW OF MASS ACTION OR EQUILIBRIUM LAW

For a homogeneous equilibrium, represented as;

$$wA + xB \rightleftharpoons y\,C + zD$$

$$\frac{[C]^y[D]^z}{[A]^w[B]^x} = \boldsymbol{a\ constant\ at\ a\ given\ temperature = K_c}$$

Where **[ ]** *represents molar concentration at equilibrium and*

K_c is the <u>concentration equilibrium constant</u>

The equilibrium law/ law of mass action therefore states that if a <u>reversible reaction</u> is allowed to <u>reach equilibrium</u> at a <u>particular temperature</u>, the product of the molar concentrations of the products raised to appropriate powers divided by the product of the molar concentrations of the reactants raised to appropriate powers is <u>a constant</u>

or

The law of mass action states that the in a <u>reversible reaction</u>, there is <u>a fixed relationship</u> at a <u>given temperature</u> between the molar concentrations of the products and those of the reactants in the equilibrium mixture.

The concentration equilibrium constant, K_c

Equilibrium constant is the ratio of the product of molar concentration of products raised to their appropriate powers to the product of molar concentration or reactants raised to their appropriate powers in a stoichiometric equation of a reversible reaction at constant temperature.

The pressure equilibrium constant, K_p

For reactions involving gases, it is often more convenient to measure and express the gas concentrations in partial pressures in atmospheres. If this is done, the equilibrium constant is known as $\boldsymbol{K_p}$

For example;

$$aX(g) + bY(g) \rightleftharpoons cZ(g)$$

$$\boldsymbol{K_p} = \frac{(\boldsymbol{p_Z})^{\boldsymbol{C}}}{(\boldsymbol{p_X})^{\boldsymbol{a}}(\boldsymbol{p_Y})^{\boldsymbol{b}}}$$

USING THE LAW OF MASS ACTION TO WRITE EQUILIBRIUM CONSTANT EXPRESSIONS (K_c or K_p) AND UNITS

When writing expressions for equilibrium constants, the following should be noted;

1. Check whether **only the concentrations /moles in a given volume** are given or total pressure at equilibrium
2. If **only concentration/ moles** are given, then an expression for $\boldsymbol{K_c}$ should be written.
3. If **total pressure** at equilibrium is given, then expression for $\boldsymbol{K_p}$should be written.
4. Solids **do not** appear in the equilibrium constant expression since their concentration is assumed to be constant.
5. For a $\boldsymbol{K_p}$ expression, only gaseous reactants and products appear.
6. If water is **one of the reactants**, and its **concentration is not given**, or remains unchanged, it is assumed to be present in a large excess hence does not appear in the equilibrium constant expression. If water is in gaseous state, then include it in the expression.
7. When only the expression is required, do not write the equation also as part of the answer

8. In the case of $\boldsymbol{K_c}$, strictly square brackets must be used.
9. Sometimes the question may specify for you whether to write a $\boldsymbol{K_c}$ or $\boldsymbol{K_p}$ expression.

In each of the cases below, write the equation for the equilibrium, the equilibrium constant expression in terms of either $\boldsymbol{K_c}$ and $\boldsymbol{K_p}$ or both , depending on what is indicated in brackets and state the units.

1. Reaction between ethanol and ethanoic acid in presence of an acid catalyst ($\boldsymbol{K_c}$
2. The reaction between hydrogen gas and gaseous iodine.(*both* $\boldsymbol{K_c}$*and* $\boldsymbol{K_p}$)
3. Dissociation of dinitrogen tetroxide to form nitrogen dioxide.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
4. Reaction between iodine solution and potassium iodide.($\boldsymbol{K_c}$
5. Thermal dissociation of calcium carbonate.(*both* $\boldsymbol{K_c}$*and* $\boldsymbol{K_p}$)
6. Reaction between iron and steam to form triiron tetraoxide and hydrogen . (*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$
7. Hydrolysis of bismuth(III) chloride.($\boldsymbol{K_c}$**)**
8. Reaction between hydrogen and nitrogen.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
9. Hydrolysis of ethylethanoate using dilute hydrochloric acid.($\boldsymbol{K_c}$**)**
10. Reaction of phosphorus trichloride and chlorine.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
11. Reaction between nitrogen and oxygen.(*both* $\boldsymbol{K_c}$*and* $\boldsymbol{K_p}$)
12. Conversion of Sulphur dioxide to Sulphur trioxide.(*both* $\boldsymbol{K_c}$*and* $\boldsymbol{K_p}$)
13. Reaction between carbon monoxide and hydrogen to form gaseous methanol.(*both* $\boldsymbol{k_c}$ *and* $\boldsymbol{K_p}$
14. Dissociation of hydrogen iodide.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
15. Dissociation of phosphorus(V) chloride to phosphorus(III) chloride and chlorine.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
16. Dissociation of Sulphur trioxide.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
17. Reaction between carbon disulphide and hydrogen to form methane and hydrogen sulphide. .(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
18. Reaction between ammonia and oxygen to form nitrogen monoxide and water. (*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
19. Redox reaction between iron metal and chromium(III) ions. ($\boldsymbol{K_c}$)
20. Hydrogenation of nitrogen dioxide to form ammonia and water.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)

The relationship between K_p and K_c

k_p is related to k_c by the expression;

$$\boldsymbol{k_p = K_c(RT)^{\Delta n}}$$

where $\boldsymbol{K_p}$ *is the pressure equilibrium constant*
$\boldsymbol{K_c}$ *is the concentration equilibrium constant*
$\boldsymbol{R}$ *is the molar gas constant* $(8.314 Jmol^{-1}K^{-1})$
$\boldsymbol{T}$ *is the absolute temperature(K)*
$\boldsymbol{\Delta n}$ *is the difference between total moles of gaseous products and total moles of gaseous reactants*

Derivation;

Consider a reversible reaction;

$$wA + xB \rightleftharpoons yC + zD$$

$$\boldsymbol{K_c} = \frac{[C]^y[D]^z}{[A]^w[B]^x} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$$

If the reactants and products are gaseous,

$$\boldsymbol{K_p} = \frac{(p_c)^y(p_D)^z}{(p_A)^w(p_B)^x} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (ii)$$

If the gases are ideal, then according to the ideal gas equation

$$pV = nRT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (iii)$$

$$p = \frac{nRT}{V} \; but \; \frac{n}{V} = C \; (concentration)$$

$$pV = CRT$$

p is therefore proportional to C

From equation (iii), $p_A = [A]RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots *_1$

$$p_B = [B]RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots *_2$$

$$p_C = [C]RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots *_3$$

$$p_D = [D]RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots *_4$$

Substituting for p_A , p_B, $p_C$and p_D in equation (ii) gives;

$$\boldsymbol{K_p} = \frac{([C]RT)^y([D]RT)^z}{([A]RT)^w([B]RT)^x}$$

$$\boldsymbol{K_p} = \left(\frac{[C]^y[D]^z}{[A]^w[B]^x}\right)\frac{(RT)^y(RT)^z}{(RT)^w(RT)^x}$$

Since $\boldsymbol{K_c} = \frac{[C]^y[D]^z}{[A]^w[B]^x}$, *then* $\boldsymbol{K_p}$ *becomes*;

$$\boldsymbol{K_p} = \boldsymbol{K_c}\frac{(RT)^{(y+z)}}{(RT)^{(w+x)}}$$

$$\boldsymbol{K_p} = \boldsymbol{K_c}(\boldsymbol{RT})^{((y+z)-(w+x))}$$

$$(y+z)-(w+x) = \Delta n$$

$$\boldsymbol{K_p} = \boldsymbol{K_c}(\boldsymbol{RT})^{\Delta \boldsymbol{n}}$$

Where Δn *is the total number of moles of gaseous products− total number of moles of gaseous reactants in a balanced equation.*

EXPERIMENTS ON CHEMICAL EQUILIBRIUM

(a) Experiment to determine the equilibrium constant for the hydrolysis of ethylethanoate using hydrochloric acid.

A ***known amount of ethylethanoate (a moles)*** *is mixed with a* ***known amount of water (b moles)***

A known volume of concentrated hydrochloric acid is added to catalyze the reaction*.*

The mixture is kept in a ***sealed glass tube*** *at a* ***constant temperature for a week.***

The tube is broken in cold water and the solution ***titrated*** *with* ***a standard solution of sodium hydroxide using phenolphthalein indicator***

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O\ (l)$$

The ***amount of ethanoic acid present at equilibrium is obtained*** *(x moles)*

Treatment of results

Let V be the volume of the solution in dm^3

If there are x moles of ethanoic acid at equilibrium, there are also x moles of ethanol at equilibrium since mole ratio of $CH_3COOH : CH_3CH_2OH = 1:1$

Moles of ester hydrolysed and moles of ***water used are both equal to x, since mole ratio is also 1:1***

	$\boldsymbol{CH_3COOCH_2CH_3\ (l) + H_2O\ (l) \rightleftharpoons CH_3COOH(l) + CH_3CH_2OH(l)}$			
Initial moles	a	b	0	0
Moles reacted/formed	x	x	x	x
Moles at equilibrium	$\boldsymbol{a-x}$	$\boldsymbol{b-x}$	$\boldsymbol{x}$	$\boldsymbol{x}$
concentration	$\frac{a-x}{v}$	$\frac{b-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

$$\boldsymbol{K_c} = \frac{[CH_3COOH][CH_3CH_2OH]}{[CH_3COOCH_2CH_3][H_2O]}$$

$$\boldsymbol{K_c} = \frac{(^{x}/_{v})(^{x}/_{v})}{\left(\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)\right)}$$

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

(b) Experiment to determine the equilibrium constant for the esterification reaction between ethanoic acid and ethanol

*A **known amount of ethanoic acid (a moles)** is mixed with a **known amount of ethanol (b moles)** and put in **a sealed glass tube.***
*The sealed tube and its contents is **left in a water bath at $60°C$ to $70°C$ for 7 hours***
*The tube is broken in cold water and the solution **titrated** with **a standard solution of sodium hydroxide using phenolphthalein indicator***

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O\ (l)$$

*The **amount of ethanoic acid present at equilibrium is obtained** (x moles)*

Treatment of results

Let V be the volume of the solution in dm^3
moles of ethanoic acid at equilibrium=x
moles of ethanoic acid converted to ester and water =(a-x)
since mole ratio of $CH_3COOH : CH_3COOCH_2CH_3 : H_2O = 1:1:1$
(a-x) moles of CH_3COOH form (a-x) moles of H_2O and (a-x) moles of $CH_3COOCH_2CH_3$ at equilibrium.
Since mole ratio of $CH_3COOH : CH_3CH_2OH = 1:1$
Moles of ethanol that react=(a-x)
Moles of ethanol at equilibrium=b-(a-x) =(b-a+x)

	$\boldsymbol{CH_3COOH(l)}$	$\boldsymbol{+ CH_3CH_2OH(l) \rightleftharpoons}$	$\boldsymbol{CH_3COOCH_2CH_3\ (l) + H_2O\ (l)}$	
Initial moles	a	b	0	0
Moles reacted/ formed	$a-x$	$a-x$	$a-x$	$a-x$
Moles at equilibrium	$\boldsymbol{x}$	$\boldsymbol{b-a+x}$	$\boldsymbol{a-x}$	$\boldsymbol{a-x}$
Concentration	$\frac{x}{v}$	$\frac{b-a+x}{v}$	$\frac{a-x}{v}$	$\frac{a-x}{v}$

$$\boldsymbol{K_c} = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$\boldsymbol{K_c} = \frac{\left(\frac{a-x}{v}\right)\left(\frac{a-x}{v}\right)}{\left(\left(\frac{x}{v}\right)\left(\frac{b-a+x}{v}\right)\right)}$$

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

(c) Experiment to determine the equilibrium constant for the dissociation of hydrogen iodide to hydrogen and iodine.

*A **known amount of hydrogen iodide (n moles)** is put **in a sealed glass bulb** of **a fixed volume (v dm^3)** and kept in a **thermostat at a temperature of** $\mathbf{450}$℃ until **equilibrium is established.***

*At equilibrium, the **bulb is removed and rapidly cooled to stop the reaction** and **fix the equilibrium** such that the **equilibrium does not adjust itself to the equilibrium value at a lower temperature**.*

*The tube is then **broken under an aqueous solution of potassium iodide** to **dissolve the iodine present at equilibrium**.*

*The **resultant mixture is titrated with a standard solution of sodium thiosulphate** using **starch indicator***

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

*The **amount of iodine present at equilibrium is obtained**.*

Treatment of results

Total volume of the bulb= v dm^3

Number of moles of hydrogen iodide heated= c moles

Degree of dissociation of hydrogen iodide= α

	$\boldsymbol{2HI(g)}$ $\rightleftharpoons$	$\boldsymbol{H_2(g)}$ +	$\boldsymbol{I_2\,(g)}$
Initial moles	n	*0*	*0*
Moles dissociated/formed	$n\alpha$	$\frac{n\alpha}{2}$	$\frac{n\alpha}{2}$
Moles at equilibrium	$\boldsymbol{n - n\alpha}$	$\boldsymbol{\frac{n\alpha}{2}}$	$\boldsymbol{\frac{n\alpha}{2}}$
Concentration at equilibrium	$\frac{n(1-\alpha)}{v}$	$\frac{n\alpha}{2v}$	$\frac{n\alpha}{2v}$

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

$$\boldsymbol{K_c} = \frac{\left(\frac{n\alpha}{2v}\right)^2}{\left(\frac{n(1-\alpha)}{v}\right)^2}$$

$$\boldsymbol{K_c} = \frac{\boldsymbol{\alpha^2}}{\boldsymbol{4(1-\alpha)^2}}$$

(d) Experiment to determine the equilibrium constant for the reaction between hydrogen and iodine to form hydrogen iodide.

*A **known amount of hydrogen (a moles)** and **a known amount of iodine (b moles)** are put in a **sealed glass bulb** of a **fixed volume (v dm^3)**, kept in a **thermostat at a temperature of** $\mathbf{450}$℃ until **equilibrium is established.***

*At equilibrium, the **bulb is removed and rapidly cooled to stop the reaction** and **fix the equilibrium** such that the **equilibrium does not adjust itself to the equilibrium value at a lower temperature**.*

*The tube is then **broken under an aqueous solution of potassium iodide** to **dissolve the iodine present at equilibrium**.*

*The **resultant mixture is titrated with a standard solution of sodium thiosulphate** using **starch indicator***

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

*The **amount of iodine present at equilibrium is obtained**.*

Treatment of results

Total volume of the bulb= v dm^3

Let number of moles of iodine converted to hydrogen iodide= x moles

Moles of hydrogen iodide formed = 2x moles

	$\boldsymbol{H_2(g)}$ +	$\boldsymbol{I_2\,(g)} \rightleftharpoons$	$\boldsymbol{2HI(g)}$
Initial moles	a	b	0
Moles reacted/formed	x	x	$2x$
Moles at equilibrium	$\boldsymbol{a-x}$	$\boldsymbol{b-x}$	$\boldsymbol{2x}$
Concentration at equilibrium	$\frac{(a-x)}{v}$	$\frac{b-x}{v}$	$\frac{2x}{v}$

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

$$\boldsymbol{K_c} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

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

CALCULATIONS INVOLVING USE OF CONCENTRATION EQUILIBRIUM CONSTANT, K_c AND PRESSURE EQUILIBRIUM CONSTANT, K_p

(a) Equilibria for esterification.

Examples

1. **When 60g of ethanoic acid were heated with 46g of ethanol until equilibrium was established, 12g of water and 58.7g of ethylethanoate were formed. Calculate;**
   (a) the equilibrium constant for the reaction
   (b) the mass of ethylethanoate that would be formed under the same conditions if 90g of ethanoic acid and 92g of ethanol were heated.

(a)

$$Molar\ mass\ of \boldsymbol{CH_3COOH} = (2\times 12) + (2\times 16) + (4\times 1) = 60g$$

$$Molar\ mass\ of \boldsymbol{CH_3CH_2OH} = (2\times 12) + (6\times 1) + (1\times 16) = 46g$$

$$Moles\ of \boldsymbol{CH_3COOH} = \frac{60}{60} = 1.0\ moles$$

$$Moles\ of \boldsymbol{CH_3CH_2OH} = \frac{46}{46} = 1.0\ moles$$

$$Molar\ mass\ of\ \boldsymbol{H_2O} = 2 + 16 = 18g$$

$$Molar\ mass\ of \boldsymbol{CH_3COOCH_2CH_3} = (4\times 12) + (8\times 1) + (2\times 16) = 88g$$

$$Moles\ of \boldsymbol{H_2O}\ at\ equilibrium = \frac{12}{18} = 0.667\ moles$$

$$Moles\ of \boldsymbol{CH_3COOCH_2CH_3}\ at\ equilibrium = \frac{58.7}{88} = 0.6670\ moles$$

	$\boldsymbol{CH_3COOH(l)}$	$+\ \boldsymbol{CH_3CH_2OH(l)} \rightleftharpoons$	$\boldsymbol{CH_3COOCH_2CH_3\ (l)}$	$+\ \boldsymbol{H_2O\ (l)}$
Initial moles	1.0	1.0	*0*	*0*
Moles reacted/ formed	0.667	0.667	0.667	0.667
Moles at equilibrium	$\mathbf{1-0.667}$ $\mathbf{=0.333}$	$\mathbf{1-0.667}$ $\mathbf{=0.333}$	$\mathbf{0.667}$	$\mathbf{0.667}$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$K_c = \frac{(0.667)^2}{(0.333)^3}$$

$$\boldsymbol{K_c = 4.01}$$

(b) $$Moles\ of \boldsymbol{CH_3COOH} = \frac{90}{60} = 1.5\ moles$$

$$Moles\ of \boldsymbol{CH_3CH_2OH} = \frac{92}{46} = 2.0\ moles$$

$$\boldsymbol{CH_3COOH(l)} + \boldsymbol{CH_3CH_2OH(l)} \rightleftharpoons \boldsymbol{CH_3COOCH_2CH_3\ (l)} + \boldsymbol{H_2O\ (l)}$$

Initial moles	1.5	2.0	*0*	*0*
Moles reacted/ formed	x	x	x	x
Moles at equilibrium	$\boldsymbol{1.5 - x}$	$\boldsymbol{2.0 - x}$	$\boldsymbol{x}$	$\boldsymbol{x}$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$4.01 = \frac{x^2}{(1.5 - x)(2.0 - x)}$$

$$3.01x^2 - 14.035x + 12.03 = 0$$

$$x = \frac{-(-14.035) \pm \sqrt{(-14.035)^2 - (4 \times 3.01 \times 12.03)}}{2 \times 3.01}$$

$$x = 3.48\ or\ 1.14$$

But x cannot be 3.48 *since number of reacted moles cannot be greater than original moles*

$$\boldsymbol{x = 1.14}$$

$$Moles\ of \boldsymbol{CH_3COOCH_2CH_3}\ at\ equilibrium = x = 1.14\ moles$$

$$\boldsymbol{Mass\ of CH_3COOCH_2CH_3\ at\ equilibrium} = (\boldsymbol{1.14 \times 88}) = \boldsymbol{100.32g}$$

2. A 10.0cm^3 mixture initially contained 0.0515 moles of ethanol, 0.0525 moles of ethanoic acid, 0.0314 moles of ester, 0.0167 moles of water and 0.001 moles of hydrochloric acid. If at equilibrium 0.0255 moles of ethanoic acid were found. Calculate the equilibrium constant for the reaction.

Hydrochloric acid is simply added to catalyse the reaction

$$\boldsymbol{CH_3COOH(l)} + \boldsymbol{CH_3CH_2OH(l)} \rightleftharpoons \boldsymbol{CH_3COOCH_2CH_3\ (l)} + \boldsymbol{H_2O\ (l)}$$

Initial moles	0.0525	0.0515	0.0314	0.0167
Moles reacted/ formed	$0.0525 - 0.0255 = \mathbf{0.027}$	0.027	0.027	0.027
Moles at equilibrium	$\mathbf{0.0255}$	$\mathbf{0.0515 - 0.027 = 0.0245}$	$\mathbf{0.0314 + 0.027 = 0.0584}$	$\mathbf{0.0167 + 0.02 = 0.0437}$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$K_c = \frac{0.0437 \times 0.0584}{0.0255 \times 0.0245}$$

$$\boldsymbol{K_c = 4.08}$$

3. **1 mole of ethanoic acid was mixed with 5 moles of ethanol in a sealed glass tube left in a water bath at 60°C for some hours. The tube was then broken in cold water and the resultant solution required 289cm^3 of 0.2 M sodium hydroxide for complete neutralisation. Calculate the equilibrium constant, K_c for the reaction.**

$$Moles\ of NaOH\ that\ reacted\ with\ CH_3COOH\ present\ at\ equilibrium$$
$$= \left(\frac{289 \times 0.2}{1000}\right) = 0.0578\ moles$$
$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$
$$Mole\ ratio\ of CH_3COOH : NaOH = 1:1$$
$$Moles\ of\ CH_3COOH\ present\ at\ equilibrium = (0.0578 \times 1) = 0.0578\ moles$$

	$\boldsymbol{CH_3COOH(l)}$	$+\ \boldsymbol{CH_3CH_2OH(l)} \rightleftharpoons$	$\boldsymbol{CH_3COOCH_2CH_3\ (l)}$	$+\ \boldsymbol{H_2O\ (l)}$
Initial moles	1.0	5.0	*0*	*0*
Moles reacted/ formed	$1 - 0.0578 = 0.9422$	0.9422	0.9422	0.9422
Moles at equilibrium	$\mathbf{0.0578}$	$5 - 0.9422 = \mathbf{4.0578}$	$\mathbf{0.9422}$	$\mathbf{0.9422}$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$
$$K_c = \frac{(0.9422)^2}{(0.0578 \times 4.0578)}$$
$$\boldsymbol{K_c = 3.79}$$

(b) Equilibria involving hydrogen, iodine and hydrogen iodide.

NOTE: All dissociations will be treated in terms involving degree of dissociation for calculations.

The degree of dissociation (α) ***is the fraction or percentage of the original undissociated molecules which have dissociated.***

Examples

1. **(a) 3 moles of hydrogen and 1 mole of iodine were heated together in a sealed tube at 500°C until equilibrium was established. Calculate the number of moles of hydrogen iodide present in the equilibrium mixture at 500°C.** ***(The equilibrium constant , K_c for the reaction between hydrogen and iodine is 50)***
   (b) Describe briefly how the concentration of iodine at equilibrium can be obtained.

(a)	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial moles	3		1		*0*
Moles reacted/formed	x		x		$2x$
Moles at equilibrium	$\mathbf{3-x}$		$\mathbf{1-x}$		$\mathbf{2x}$

Taking volume of vessel to be one litre;

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

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

$$46x^2 - 200x + 150 = 0$$

$$x = \frac{-(-200) \pm \sqrt{(-200)^2 - (4 \times 46 \times 150)}}{2 \times 46}$$

$x_1 = 3.384 \quad and \; x_2 = 0.964$

but x cannot be 3.384, *because it gives a negative value for moles of hydrogen and iodine at equilibrium*

therefore $\boldsymbol{x = 0.964}$

Moles of hydrogen iodide at equilibrium $= \mathbf{2x = 2 \times 0.964 = 1.938\ moles}$

(b) *The tube is* ***broken under an aqueous solution of potassium iodide*** *to* ***dissolve the iodine present at equilibrium****.*

The ***resultant mixture is titrated with a standard solution of sodium thiosulphate*** *using* ***starch indicator****. The* ***amount of iodine present at equilibrium is calculated using the equation below****.*

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

2. (a) State three characteristics of a chemical equilibrium.

(b) 25 moles of hydrogen and 18 moles of iodine vapour were heated in a 1 litre sealed tube at 465 ^{o}C. When equilibrium was attained, the tube was rapidly cooled and found to contain 30.8 moles of hydrogen iodide.

(i) Give a reason why the tube was rapidly cooled.

(ii) Calculate the value of the equilibrium constant for the reaction taking place in the flask and the degree of dissociation of hydrogen iodide.

(b) (i) Tube is rapidly cooled <u>to stop the reaction</u> *and* ***<u>fix the equilibrium</u>*** *such that the* ***equilibrium <u>does not adjust itself</u> to the <u>equilibrium value at a lower temperature</u>****.*

(ii)	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial moles	25		18		*0*
Moles reacted/formed	x		x		$2x$
Moles at equilibrium	$\mathbf{25-x}$		$\mathbf{18-x}$		$\mathbf{30.8}$

$2x = 30.8, \quad x = 15.4$ $[HI] = 30.8$ $[H_2] = 25 - 15.4 = 9.6$ $[I_2] = 18 - 15.4 = 2.6$	$K_c = \frac{[HI]^2}{[H_2][I_2]}$ $K_c = \frac{(30.8)^2}{9.6 \times 2.6}$ $\boldsymbol{K_c = 38}$

Note that K_c for the dissociation of HI is the reciprocal of K_c for reaction between hydrogen and iodine to form HI

For dissociation of hydrogen iodide,

	$\boldsymbol{2HI(g)}$	$\rightleftharpoons$	$\boldsymbol{H_2(g)}$ +	$\boldsymbol{I_2\,(g)}$
Initial moles	c		0	0
Moles dissociated/formed	$c\alpha$		$\frac{c\alpha}{2}$	$\frac{c\alpha}{2}$
Moles at equilibrium	$\boldsymbol{c - c\alpha}$		$\boldsymbol{\frac{c\alpha}{2}}$	$\boldsymbol{\frac{c\alpha}{2}}$
Concentration at equilibrium	$\frac{c(1-\alpha)}{v}$		$\frac{c\alpha}{2v}$	$\frac{c\alpha}{2v}$

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

$$K_c = \frac{\left(\frac{c\alpha}{2v}\right)^2}{\left(\frac{c(1-\alpha)}{v}\right)^2}$$

$$\boldsymbol{K_c = \frac{\alpha^2}{4(1-\alpha)^2}}$$

$$\boldsymbol{But\ K_c\ for\ dissociation\ of\ HI = \frac{1}{38}}$$

$$\frac{1}{38} = \frac{\alpha^2}{4(1-\alpha)^2}$$

$$4 - 8\alpha + 4\alpha^2 = 38\alpha^2$$

$$34\alpha^2 + 8\alpha - 4 = 0$$

$$\alpha = \frac{-(8) \pm \sqrt{(8)^2 - (4 \times 34 \times 4)}}{2 \times 34}$$

$$\alpha = -0.48 \ or\ 0.24$$

But α cannot be negative

Therefore $\boldsymbol{\alpha = 0.24}$

3. When stoichiometric amounts of hydrogen and iodine were allowed to reach equilibrium in a 1 litre vessel at 450 ^{o}C and $1.01 \times 10^5 Nm^{-2}$, 1.56 moles of hydrogen iodide were formed at equilibrium. Calculate the equilibrium constant , K_p.

Note that stoichiometric amounts mean amounts of moles as shown by the balanced equation

	$\boldsymbol{H_2(g)}$	+	$\boldsymbol{I_2\,(g)}$	$\rightleftharpoons$	$\boldsymbol{2HI(g)}$
Initial moles	1		1		*0*
Moles reacted/formed	x		x		$2x$
Moles at equilibrium	$\boldsymbol{1-x}$		$\boldsymbol{1-x}$		$\boldsymbol{1.56}$

$$2x = 1.56, \quad x = 0.78$$

$$Total\ moles\ at\ equilibrium = 1 - x + 1 - x + 2x = 2$$

$$p_{H_2} = \left(\frac{1 - 0.78}{2}\right) \times 1.01 \times 10^5 = \mathbf{1.111 \times 10^4 Nm^{-2}}$$

$$p_{I_2} = \left(\frac{1 - 0.78}{2}\right) \times 1.01 \times 10^5 = \mathbf{1.111 \times 10^4 Nm^{-2}}$$

$$p_{HI} = \left(\frac{1.56}{2}\right) \times 1.01 \times 10^5 = \mathbf{7.878 \times 10^4 Nm^{-2}}$$

$$K_p = \frac{(p_{HI})^2}{p_{H_2} \times p_{I_2}} = \frac{(7.878 \times 10^4)^2}{(1.111 \times 10^4)^2}$$

$$\boldsymbol{K_p = 50.28}$$

4. The equilibrium constant for the dissociation of hydrogen iodide is 0.02. 1 mole of hydrogen and $\frac{1}{3}$ moles of iodine are heated together at 450 °C. Calculate the mass of hydrogen iodide present in the equilibrium mixture at that temperature.

$$\boldsymbol{H_2(g)} \quad + \quad \boldsymbol{I_2\,(g)} \quad \rightleftharpoons \quad \boldsymbol{2HI(g)}$$

Initial moles	1	$\frac{1}{3}$	*0*
Moles reacted/formed	x	x	$2x$
Moles at equilibrium	$\mathbf{1 - x}$	$\mathbf{\frac{1}{3} - x}$	$\mathbf{2x}$

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

$$\boldsymbol{K_c\ for\ the\ reaction} = \frac{\mathbf{1}}{\boldsymbol{K_c\ for\ dissociation\ of\ HI}}$$

$$\frac{1}{0.02} = \frac{(2x)^2}{(1 - x)\left(\frac{1}{3} - x\right)}$$

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

$$x = \frac{-(-100) \pm \sqrt{(-100)^2 - (4 \times 69 \times 25)}}{2 \times 69}$$

$$x = 0.321\ or\ 1.128$$

But x cannot be 1.128 *since it gives negative values of* $(1 - x)$ *and* $\left(\frac{1}{3} - x\right)$

$$Therefore\ \boldsymbol{x = 0.321}$$

$$Moles\ of\ HI\ at\ equilibrium = 2x = 2 \times 0.321 = 0.642$$

$$Molar\ mass\ of\ HI = (1 + 127) = 128g$$

$$\boldsymbol{Mass\ of\ HI\ present\ at\ equilibriun = (128 \times 0.642) = 82.176g}$$

5. 1g of hydrogen and 127g of iodine are allowed to attain equilibrium in an evacuated container of volume $10dm^3$ at a temperature of 450 °C. If the equilibrium constant at the same temperature, K_c is 50. Calculate the;

(i) the value of K_p

(ii) the total pressure in the container

(iii) the partial pressure of hydrogen in the container

(i) $Molar\ mass\ of\ \boldsymbol{H_2} = (2 \times 1) = 2g$

$Molar\ mass\ of\ \boldsymbol{I_2} = (2 \times 127) = 254g$

$Mole\ ratio\ of\ H_2 : HI = 1:2$

$Moles\ of\ HI = (2 \times 0.5) = 1\ mole$

$K_c = 50$

$R = 8.314 Jmol^{-1}K^{-1}$

$V = 10 \times 10^{-3} m^3$

$Moles\ of\ \boldsymbol{H_2} = \frac{1}{2} = 0.5\ moles$

$Moles\ of\ \boldsymbol{I_2} = \frac{127}{254} = 0.5\ moles$

$T = (450 + 273) = 723K$

$\Delta n = 1 - (0.5 + 0.5) = 0$

$K_p = K_c(RT)^{\Delta n}$

$\boldsymbol{K_p = 50(8.314 \times 723)^0 = 50}$

	$\boldsymbol{H_2(g)}$	+	$\boldsymbol{I_2\ (g)}$	$\rightleftharpoons$	$\boldsymbol{2HI(g)}$
Initial moles	0.5		0.5		*0*
Moles reacted/formed	x		x		$2x$
Moles at equilibrium	$\boldsymbol{0.5 - x}$		$\boldsymbol{0.5 - x}$		$\boldsymbol{2x}$

(ii) $Total\ moles\ \ equilibrium\ mixture,$

$n = 0.5 - x + 0.5 - x + 2x = 1$

$\boldsymbol{pV = nRT}$

$p = \frac{1 \times 8.314 \times 723}{10 \times 10^{-3}}$

$\boldsymbol{p = 6011022.2\ Nm^{-2}}$

But x cannot be 0.697 *since it gives negative values of* $(0.5 - x)$

$Therefore\ \boldsymbol{x = 0.390}$

(iii) $K_c = \frac{[HI]^2}{[H_2][I_2]}$

$50 = \frac{(2x)^2}{(0.5-x)^2}$

$92x^2 - 100x + 25 = 0$

$x = \frac{-(-100) \pm \sqrt{(-100)^2 - (4 \times 92 \times 25)}}{2 \times 92}$

$x = 0.390\ or\ 0.697$

Partial pressure of hydrogen

$= \left(\frac{0.5 - x}{1}\right) \times 6011022.2$

$= \left(\frac{0.5 - 0.390}{1}\right) \times 6011022.2$

$\boldsymbol{p_{H_2} = 661212.442\ Nm^{-2}}$

6. 3.20g of hydrogen iodide were heated at 450 °C in a glass bulb of volume 800cm^3. When equilibrium was attained, the bulb was rapidly cooled to room temperature and then broken under a solution of potassium iodide. The iodine formed required 36.0 cm^3 of a 0.2M sodium thiosulphate solution in the presence of starch indicator for complete reaction.

(i) Explain why the bulb broken under potassium iodide solution

(ii) Calculate the equilibrium constant for the reaction at 450 °C

(i) *The bulb is broken under an aqueous solution of potassium iodide to* ***dissolve the iodine present at equilibrium***.

$$\boldsymbol{I_2\,(aq) + I^-(aq) \longrightarrow I_3^-(aq)}$$

(ii)

$$Molar\ mass\ of\ HI = (1 + 127) = 128g$$

$$Moles\ of\ HI = \frac{3.20}{128} = 0.025\ moles$$

$$Moles\ of\ Na_2S_2O_3 that\ reacted\ with\ I_2 = \left(\frac{0.2 \times 36.0}{1000}\right) = 0.0072\ moles$$

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

$$Mole\ ratio\ of\ S_2O_3^{2-}: I_2 = 2:1$$

$$Moles\ of\ I_2 = \left(\frac{1}{2} \times 0.0072\right) = 0.0036\ moles$$

	$\boldsymbol{2HI(g)}$	$\rightleftharpoons$	$\boldsymbol{H_2(g)}$ +	$\boldsymbol{I_2\,(g)}$
Initial moles	0.025		*0*	*0*
Moles dissociated/formed	0.025α		$\frac{0.025\alpha}{2}$	$\frac{0.025\alpha}{2}$
Moles at equilibrium	$\boldsymbol{0.025 - 0.025\alpha}$		$\boldsymbol{\frac{0.025\alpha}{2}}$	$\boldsymbol{\frac{0.025\alpha}{2}}$

$$\frac{\mathbf{0.025\alpha}}{\mathbf{2}} = \mathbf{0.0036}$$

$$\boldsymbol{\alpha = 0.288}$$

$$moles\ of\ HI\ at\ equilibrium = 0.025(1 - 0.288) = 0.0178$$

$$[HI] = \left(\frac{0.0178 \times 1000}{800}\right) = 0.02225M$$

Note: The volume was given in $\boldsymbol{cm^3}$. Multiplying moles in $\boldsymbol{800cm^3}$ by 1000 converts the concentration to moles per litre

$$[H_2] = \left(\frac{0.0036 \times 1000}{800}\right) = 0.0045M$$

$$[HI] = \left(\frac{0.0036 \times 1000}{800}\right) = 0.0045M$$

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

$$K_c = \frac{(0.0045)^2}{(0.02225)^2}$$

$$\boldsymbol{K_c = 0.04}$$

7. The degree of dissociation of 0.5 moles of hydrogen iodide was found to be 25% at a certain temperature in a $\boldsymbol{1.5dm^3}$ vessel. Calculate the equilibrium constant, $\boldsymbol{K_p}$

	$\boldsymbol{2HI(g)}$	$\rightleftharpoons$	$\boldsymbol{H_2(g)}$ +	$\boldsymbol{I_2\,(g)}$
Initial moles	0.5		*0*	*0*
Moles dissociated/formed	0.5α		$\frac{0.5\alpha}{2}$	$\frac{0.5\alpha}{2}$
Moles at equilibrium	$\boldsymbol{0.5 - 0.5\alpha}$		$\boldsymbol{\frac{0.5\alpha}{2}}$	$\boldsymbol{\frac{0.5\alpha}{2}}$

$$\boldsymbol{\alpha = \frac{25}{100} = 0.25}$$

$$Total\ moles\ at\ equilibrium = 0.5 - 0.5\alpha + \frac{0.5\alpha}{2} + \frac{0.5\alpha}{2} = 0.5$$

$$p_{HI} = \left(\frac{0.375}{0.5}\right)P$$

$$p_{H_2} = \left(\frac{0.0625}{0.5}\right)P$$

$moles\ of\ HI\ at\ equilibrium = 0.5(1-0.25) = 0.375$ $moles\ of\ H_2\ at\ equilibrium = \frac{0.5}{2} \times 0.25 = 0.0625$ $moles\ of\ I_2\ at\ equilibrium = 0.0625$ $Let\ the\ total\ pressure\ at\ equilibrium\ be\ P$	$p_{I_2} = \left(\frac{0.0625}{0.5}\right)P$ $K_p = \frac{p_{H_2} \times p_{I_2}}{(p_{HI})^2}$ $K_p = \frac{\left(\left(\frac{0.0625}{0.5}\right)P\right)^2}{\left(\left(\frac{0.375}{0.5}\right)P\right)^2} = \frac{0.015625P^2}{0.5625P^2}$ $\boldsymbol{K_p = 0.0278}$

(c) Equilibria involving hydrogen, nitrogen and ammonia.

Examples

1. Nitrogen reacts with hydrogen according to the following equation

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

(a) Write expression for equilibrium constant, K_c

(b) Stoichiometric amounts of nitrogen and hydrogen were reacted in a 2 litre vessel. At equilibrium, 0.8moles of ammonia was formed. Calculate:

(i) the amount of hydrogen at equilibrium.

(ii) the value of equilibrium constant, K_c.

(a) $\boldsymbol{K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}}$

(b)(i)

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial moles	1		3		0
Moles dissociated/formed	x		$3x$		$2x$
Moles at equilibrium	$\boldsymbol{1-x}$		$\boldsymbol{3-3x}$		$\boldsymbol{2x}$

$\boldsymbol{2x = 0.8.\ Therefore\ x = 0.4}$ $moles\ of\ H_2\ at\ equilibrium = 3(1-0.4) = 1.8$ $moles\ of\ N_2\ at\ equilibrium = (1-0.4) = 0.6$ $moles\ of\ NH_3\ at\ equilibrium = (2 \times 0.4) = 0.8$ $[N_2] = \left(\frac{0.6}{2}\right) = 0.3M$	$[H_2] = \left(\frac{1.8}{2}\right) = 0.9M$ $[NH_3] = \left(\frac{0.8}{2}\right) = 0.4M$ $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ $K_c = \frac{(0.4)^2}{0.3 \times (0.9)^3}\ \frac{mol^2dm^{-6}}{moldm^{-3} \times mol^3dm^{-9}}$ $\boldsymbol{K_c = 0.732\ mol^{-2}dm^6}$

2. 0.8 moles of nitrogen and 0.9 moles of hydrogen were heated in a 1500$\boldsymbol{cm^3}$ closed vessel. At equilibrium, the mixture contained 20% hydrogen. Find the value of equilibrium constant, K_c.

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial moles	0.8		0.9		0
Moles dissociated/formed	x		$3x$		$2x$
Moles at equilibrium	$\mathbf{0.8 - x}$		$\mathbf{0.9 - 3x}$		$\mathbf{2x}$

$$Total\ moles\ at\ equilibrium = 0.8 - x + 0.9 - 3x + 2x = \mathbf{1.7 - 2x}$$

$$\boldsymbol{But}\ \left(\frac{\mathbf{0.9 - 3x}}{\mathbf{1.7 - 2x}}\right) \times \mathbf{100} = \mathbf{20}$$

$$0.9 - 3x = 0.2(1.7 - 2x)$$

$$x = 0.215$$

$$moles\ of\ H_2\ at\ equilibrium = 0.9 - (3 \times 0.215) = 0.255$$

$$moles\ of\ N_2\ at\ equilibrium = (0.8 - 0.215) = 0.585$$

$$moles\ of\ NH_3\ at\ equilibrium = (2 \times 0.215) = 0.430$$

$$[N_2] = \left(\frac{0.585 \times 1000}{1500}\right) = 0.39M$$

$$[H_2] = \left(\frac{0.255 \times 1000}{1500}\right) = 0.17M$$

$$[NH_3] = \left(\frac{0.430 \times 1000}{1500}\right) = 0.287M$$

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

$$K_c = \frac{(0.287)^2}{0.39 \times (0.17)^3} \quad \frac{mol^2dm^{-6}}{moldm^{-3} \times mol^3dm^{-9}}$$

$$\boldsymbol{K_c = 42.99\ mol^{-2}dm^6}$$

3. When 3 moles of hydrogen and 1 mole of nitrogen were mixed and allowed to attain equilibrium at 100 atm and 400°C, the equilibrium mixture contained 25% of ammonia by volume. Calculate;

(i) Number of moles of nitrogen and hydrogen at equilibrium.

(ii) Value of K_p at 400°C

(i)	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial moles	1		3		0
Moles dissociated/formed	x		$3x$		$2x$
Moles at equilibrium	$\mathbf{1 - x}$		$\mathbf{3 - 3x}$		$\mathbf{2x}$

$$Total\ moles\ at\ equilibrium = 1 - x + 3 - 3x + 2x = \mathbf{4 - 2x}$$

$$\boldsymbol{But}\ \left(\frac{\mathbf{2x}}{\mathbf{4 - 2x}}\right) \times \mathbf{100} = \mathbf{25}$$

$$2x = 1 - 0.5x$$

$$x = 0.4$$

$$moles\ of\ H_2\ at\ equilibrium = 3(1 - 0.4) = 1.8\ moles$$

(ii) $$moles\ of\ N_2\ at\ equilibrium = (1 - 0.4) = 0.6\ moles$$

$$moles\ of\ NH_3\ at\ equilibrium = (2 \times 0.4) = 0.8\ moles$$

$$Total\ moles\ at\ equilibrium = 4 - 2(0.4) = 3.2$$

$$p_{N_2} = \left(\frac{0.6}{3.2} \times 100\right) = 18.75\ atm$$

$$p_{H_2} = \left(\frac{1.8}{3.2} \times 100\right) = 56.25\ atm$$

$$p_{NH_3} = \left(\frac{0.8}{3.2} \times 100\right) = 25\ atm$$

$$K_p = \frac{\left(p_{NH_3}\right)^2}{p_{N_2} \times \left(p_{H_2}\right)^3}$$

$$K_p = \frac{25^2}{18.75 \times 56.25^3} \quad \frac{atm^2}{atm \times atm^3}$$

$$\boldsymbol{K_p = 1.87 \times 10^{-4} atm^{-2}}$$

4. Ammonia dissociates according to the following equation

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

Calculate the equilibrium constant, K_C for the reaction given 3.0 moles of ammonia were found to be 15% dissociated.

	$2NH_3(g)$	$\rightleftharpoons$	$N_2(g)$	$+$	$3H_2(g)$
Initial moles	3.0		0		0
Moles dissociated/formed	3α		$\frac{3\alpha}{2}$		$3\left(\frac{3\alpha}{2}\right)$
Moles at equilibrium	$\mathbf{3-3\alpha}$		$\mathbf{\frac{3\alpha}{2}}$		$\mathbf{\frac{9\alpha}{2}}$

$$\textbf{But } \alpha = \frac{15}{100} = \mathbf{0.15}$$

$$moles\ of\ H_2\ at\ equilibrium = \frac{9 \times 0.15}{2}$$

$$= 0.675\ moles$$

$$moles\ of\ N_2\ at\ equilibrium = \frac{3 \times 0.15}{2}$$

$$= 0.225\ moles$$

$$moles\ of\ NH_3\ at\ equilibrium$$

$$= 3(1 - 0.15) = 2.55\ moles$$

Assuming volume is one litre

$$[N_2] = 0.255M$$

$$[H_2] = 0.675M$$

$$[NH_3] = 2.55M$$

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

$$K_c = \frac{0.255 \times (0.675)^3}{(2.55)^2}\ \frac{moldm^{-3} \times mol^3dm^{-9}}{mol^2dm^{-6}}$$

$$\boldsymbol{K_c = 0.012\ mol^2dm^{-6}}$$

5. 1.75 moles of ammonia were heated in a 1 litre vessel and the equilibrium mixture was found to contain 42.9% hydrogen. Calculate the equilibrium constant, K_C.

	$2NH_3(g)$	$\rightleftharpoons$	$N_2(g)$	$+$	$3H_2(g)$
Initial moles	1.75		0		0
Moles dissociated/formed	1.75α		$\frac{1.75\alpha}{2}$		$3\left(\frac{1.75\alpha}{2}\right)$
Moles at equilibrium	$\mathbf{1.75-1.75\alpha}$		$\mathbf{\frac{1.75\alpha}{2}}$		$\mathbf{\frac{5.25\alpha}{2}}$

$$Total\ moles\ at\ equilibrium$$

$$= 1.75 - 1.75\alpha + 0.875\alpha + 2.625\alpha$$

$$= \mathbf{1.75 + 1.75\alpha}$$

$$\textbf{But } \frac{\mathbf{2.625\alpha}}{\mathbf{1.75 + 1.75\alpha}} \times \mathbf{100} = \mathbf{42.9}$$

$$1.87425\alpha = 0.75075$$

$$\boldsymbol{\alpha = 0.4}$$

$$moles\ of\ H_2\ at\ equilibrium$$

$$= (2.625 \times 0.4)$$

$$= 1.05\ moles$$

$$moles\ of\ N_2\ at\ equilibrium$$

$$= (0.875 \times 0.4) = 0.35\ moles$$

$$moles\ of\ NH_3\ at\ equilibrium$$

$$= 1.75(1 - 0.4)$$

$$= 1.05\ moles$$

Since volume is one litre

$$[N_2] = 0.35M \quad [H_2] = 1.05M$$

$$[NH_3] = 1.05M$$

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

$$K_c = \frac{0.35 \times (1.05)^3}{(1.05)^2}\ \frac{moldm^{-3} \times mol^3dm^{-9}}{mol^2dm^{-6}}$$

$$\boldsymbol{K_c = 0.3675\ mol^2dm^{-6}}$$

(d) Equilibria involving phosphorus, chlorine and phosphorus(V) chloride

Examples

1. **Phosphorus(V) chloride dissociates at high temperatures according to the equation**

$$\boldsymbol{PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)}$$

83.4 g of phosphorus(V) chloride were placed in a vessel of $9.23dm^3$.At equilibrium at a certain temperature, 11.1g of chlorine were formed at a total pressure of $250kPa$.

(a) Calculate the number of moles of phosphorus(V) chloride and chlorine in the vessel at equilibrium.

(b) Determine the equilibrium constant, K_c , for the reaction and state its units.

(c) Calculate the value of the equilibrium constant, K_p , for the reaction and state its units.

(a)

$$Molar\ mass\ of\ PCl_5 = 31 + (5 \times 35.4) = 208$$

$$moles\ of\ PCl_5\ before\ equilibrium = \frac{83.4}{208} = 0.401$$

$$Molar\ mass\ of\ Cl_2 = (35.4 \times 2) = 70.8$$

$$\boldsymbol{moles\ of\ chlorine\ at\ equilibrium = \frac{11.1}{70.8} = 0.15678\ moles}$$

$$Molar\ concetration\ of\ Cl_2 = \frac{0.1186}{9.0} = 0.0132M$$

	$\boldsymbol{PCl_5(g)}$	$\rightleftharpoons$	$\boldsymbol{PCl_3(g)}$	+	$\boldsymbol{Cl_2(g)}$
Initial moles	0.401		0		0
Moles dissociated/formed	0.401α		0.401α		0.401α
Moles at equilibrium	$\boldsymbol{0.401(1-\alpha)}$		$\boldsymbol{0.401\alpha}$		$\boldsymbol{0.401\alpha}$

$$\boldsymbol{But\quad 0.401\alpha = 0.15678}$$

$$\boldsymbol{\alpha = 0.391}$$

$$moles\ of\ PCl_5\ at\ equilibrium = 0.401(1 - 0.391) = 0.24421\ moles$$

$$moles\ of\ Cl_2\ at\ equilibrium = 0.15679\ moles$$

(b) $moles\ of\ PCl_3\ at\ equilibrium = (0.401 \times 0.391) = 0.15679\ moles$

$$Since\ volume\ is\ 9.23\ litres$$

$$[PCl_5] = \left(\frac{0.24421}{9.23}\right) = 0.0265M$$

$$[Cl_2] = \left(\frac{0.15679}{9.23}\right) = 0.0170M$$

$$[PCl_3] = 0.0170M$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{0.0170 \times 0.0170}{0.0265}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$$

$$\boldsymbol{K_c = 0.011moldm^{-3}}$$

(c) $Total\ moles\ at\ equilibrium$ $= 0.24421 + 0.15679 + 0.15679$ $= 0.55779$ $p_{PCl_5} = \left(\frac{0.24421}{0.55779} \times 250\right) = 109.45kPa$ $p_{PCl_3} = \left(\frac{0.15679}{0.55779} \times 250\right) = 70.27kPa$	$p_{Cl_2} = \left(\frac{0.15679}{0.55779} \times 250\right) = 70.27kPa$ $K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$ $K_p = \frac{70.27 \times 70.27}{109.45} \frac{kPa^2}{kPa}$ $\boldsymbol{K_p = 45.13\ kPa}$

2. 1.0 mole of phosphorus(V) chloride was strongly heated in a one litre closed bulb until equilibrium was obtained. The glass bulb was then rapidly broken under potassium iodide solution. The bulb was found to contain 40.70% of chlorine.

(a) Write equations for the reactions that took place when:

(i) the glass bulb was strongly heated

(ii) the glass bulb was broken under potassium iodide solution.

(b) State the reasons why the bulb;

(i) was rapidly broken

(ii) was broken under potassium iodide solution

(c) Determine the;

(i) degree of dissociation of phosphorus(V) chloride

(ii) equilibrium constant for the reaction.

(a) (i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(ii) $Cl_2(g) + 2I^-(aq) \longrightarrow I_2(aq) + 2Cl^-(aq)$

(b) ***(i) Bulb was rapidly broken <u>to stop the reaction</u> and <u>fix the equilibrium</u> such that the equilibrium <u>does not adjust itself</u> to the <u>equilibrium value at a lower temperature</u>.***

(ii) Bulb is broken under potassium iodide to <u>dissolve and oxidise chlorine present at equilibrium to chloride ions</u> as the <u>potassium iodide is reduced to iodine</u>.

(c) (i)

	$\boldsymbol{PCl_5(g)}$	$\rightleftharpoons$	$\boldsymbol{PCl_3(g)}$	+	$\boldsymbol{Cl_2(g)}$
Initial moles	1		0		0
Moles dissociated/formed	α		α		α
Moles at equilibrium	$\boldsymbol{(1-\alpha)}$		$\boldsymbol{\alpha}$		$\boldsymbol{\alpha}$

$\boldsymbol{Total\ moles\ at\ equilibrium}$

$= 1 - \alpha + \alpha + \alpha = \boldsymbol{(1+\alpha)}$

$\boldsymbol{But}\quad \boldsymbol{\frac{\alpha}{1+\alpha} \times 100 = 40.70}$

$\boldsymbol{0.593\alpha = 0.407}$

$\boldsymbol{\alpha = 0.686}$

$moles\ of\ PCl_5\ at\ equilibrium$ $= (1 - 0.686) = 0.314\ moles$ $moles\ of\ Cl_2\ at\ equilibrium = 0.686\ moles$ $moles\ of\ PCl_3\ at\ equilibrium$ $= 0.686\ moles$ $Since\ volume\ is\ 1\ litre$ $[PCl_5] = 0.314M$	$[Cl_2] = 0.686M$ $[PCl_3] = 0.686M$ $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$ $K_c = \frac{0.686 \times 0.686}{0.314}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$ $\boldsymbol{K_c = 1.499\ moldm^{-3}}$

3. 2.085g of phosphorus(V) chloride was heated in a 1 litre vessel until equilibrium was attained. The vessel was then broken under excess potassium iodide solution. The iodine liberated required 40 $\boldsymbol{cm^3}$ of 0.1M sodium thiosulphate solution. Calculate the equilibrium constant, $\boldsymbol{K_c}$, for the reaction.

$$Molar\ mass\ of\ PCl_5 = 31 + (5 \times 35.4) = 208$$

$$moles\ of\ PCl_5\ before\ equilibrium = \frac{2.085}{208} = 0.01$$

$$Moles\ of\ Na_2S_2O_3 that\ reacted\ with\ I_2 = \left(\frac{40 \times 0.1}{1000}\right) = 0.004\ moles$$

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

$$Mole\ ratio\ of\ S_2O_3^{2-}: I_2 = 2:1$$

$$Moles\ of\ I_2\ that\ were\ formed\ from\ KI = \left(\frac{1}{2} \times 0.004\right) = 0.002\ moles$$

$$From\ Cl_2(g) + 2I^-(aq) \longrightarrow I_2(aq) + 2Cl^-(aq)$$

$$1\ mole\ of\ I_2\ is\ formed\ from\ 1\ mole\ of\ Cl_2$$

$$Therefore\ moles\ of\ Cl_2\ at\ equilibrium = 0.002\ moles$$

	$\boldsymbol{PCl_5(g)}$	$\rightleftharpoons$	$\boldsymbol{PCl_3(g)}$	+	$\boldsymbol{Cl_2(g)}$
Initial moles	1		0		0
Moles dissociated/formed	0.002		0.002		0.002
Moles at equilibrium	$\boldsymbol{(1 - 0.002)}$		0.002		$\boldsymbol{0.002}$

$moles\ of\ PCl_5\ at\ equilibrium = (1 - 0.002)$ $= 0.998\ moles$ $moles\ of\ Cl_2\ at\ equilibrium = 0.002\ moles$ $moles\ of\ PCl_3\ at\ equilibrium$ $= 0.002\ moles$ $Since\ volume\ is\ 1\ litre$ $[PCl_5] = 0.998\ M$	$[Cl_2] = 0.002M$ $[PCl_3] = 0.002M$ $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$ $K_c = \frac{0.002 \times 0.002}{0.998}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$ $\boldsymbol{K_c = 4.01 \times 10^{-6}\ moldm^{-3}}$

4. 2.00 g of phosphorus(V) chloride were allowed to reach equilibrium at 200°C in a 1 $\boldsymbol{dm^3}$ capacity vessel. If the equilibrium constant of the above reaction is $\boldsymbol{0.008\ moldm^{-3}}$ at this temperature and in the conditions stated. Calculate the percentage dissociation of phosphorus pentachloride at equilibrium.

$$Molar\ mass\ of\ PCl_5 = 31 + (5 \times 35.4) = 208g$$

$$moles\ of\ PCl_5\ before\ equilibrium = \frac{2.00}{208} = 0.009615$$

	$\boldsymbol{PCl_5(g)}$	$\rightleftharpoons$	$\boldsymbol{PCl_3(g)}$	$+$	$\boldsymbol{Cl_2(g)}$
Initial moles	0.009615		0		0
Moles dissociated/formed	0.009615α		0.009615α		0.009615α
Moles at equilibrium	$\mathbf{0.009615(1-\alpha)}$		$\mathbf{0.009615\alpha}$		$\mathbf{0.009615\alpha}$

$$Since\ volume\ is\ 1\ litre$$
$$[PCl_5] = (0.009615(1-\alpha))\ M$$
$$[Cl_2] = (0.009615\alpha)M$$
$$[PCl_3] = (0.009615\alpha)M$$
$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$
$$0.008 = \frac{(0.009615\alpha)^2}{0.009615(1-\alpha)}$$
$$9.244\alpha^2 + 7.962\alpha - 7.962 = 0$$

$$\alpha = \frac{-(7.962) \pm \sqrt{(7.962)^2 - (4 \times 9.244 \times -7.962)}}{2 \times 9.244}$$
$$\alpha = -1.454\ or\ 0.592$$
$$But\ \alpha\ cannot\ be\ negative.$$
$$Therefore\ \boldsymbol{\alpha = 0.592}$$
$$\boldsymbol{Percentage\ dissociation\ of\ PCl_5}$$
$$\boldsymbol{= 0.592 \times 100 = 59.2\%}$$

5. 3.6 moles of phosphorus(V) chloride in a vessel of volume 2 litres was found to be 38% dissociated. Calculate the equilibrium constant, K_c, for the reaction.

	$\boldsymbol{PCl_5(g)}$	$\rightleftharpoons$	$\boldsymbol{PCl_3(g)}$	$+$	$\boldsymbol{Cl_2(g)}$
Initial moles	3.6		0		0
Moles dissociated/formed	3.6α		3.6α		3.6α
Moles at equilibrium	$\mathbf{3.6(1-\alpha)}$		$\mathbf{3.6\alpha}$		$\mathbf{3.6\alpha}$

$$But\ \alpha = \frac{38}{100} = 0.38$$

$$Moles\ of\ PCl_5\ at\ equilibrium$$
$$= 3.6(1 - 0.38)$$
$$= 2.232\ moles$$

$$moles\ of\ Cl_2\ at\ equilibrium = (3.6 \times 0.38)$$
$$= 1.368\ moles$$
$$moles\ of\ PCl_3\ at\ equilibrium = 1.368\ moles$$

$$Since\ volume\ is\ 2\ litres$$
$$[PCl_5] = \left(\frac{2.232}{2}\right) = 1.116\ M$$
$$[Cl_2] = \left(\frac{1.368}{2}\right) = 0.684M$$
$$[PCl_3] = 0.684M$$
$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$
$$K_c = \frac{(0.684)^2}{1.116}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$$
$$\boldsymbol{K_c = 0.419\ moldm^{-3}}$$

6. Calculate the percentage of chlorine is the equilibrium mixture formed when 0.4 moles of phosphorus(V) chloride were heated in a one litre vessel. ($\boldsymbol{The\ equilibrium\ constant\ is\ 0.02moldm^{-3}}$).

	$\boldsymbol{PCl_5(g)}$	$\rightleftharpoons$	$\boldsymbol{PCl_3(g)}$	+	$\boldsymbol{Cl_2(g)}$
Initial moles	0.4		0		0
Moles dissociated/formed	0.4α		0.4α		0.4α
Moles at equilibrium	$\boldsymbol{0.4(1-\alpha)}$		$\boldsymbol{0.4\alpha}$		$\boldsymbol{0.4\alpha}$

$$Since\ volume\ is\ 1\ litre$$
$$[PCl_5] = (0.4(1-\alpha))\ M$$
$$[Cl_2] = (0.4\alpha)M$$
$$[PCl_3] = (0.4\alpha)M$$
$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$
$$0.02 = \frac{(0.4\alpha)^2}{0.4(1-\alpha)}$$
$$\alpha^2 + 0.05\alpha - 0.05 = 0$$

$$\alpha = \frac{-(0.05) \pm \sqrt{(0.05)^2 - (4 \times 1 \times -0.05)}}{2 \times 1}$$
$$\alpha = -0.25\ or\ 0.2$$
$$But\ \alpha\ cannot\ be\ negative.$$
$$Therefore\ \boldsymbol{\alpha = 0.2}$$
$$Total\ moles\ at\ equilibrium$$
$$= 0.4(1-0.2) + 0.4(0.2) + 0.4(0.2) = 0.48$$
$$Percentage\ of\ chlorine$$
$$= \left(\frac{\boldsymbol{0.4 \times 0.2}}{\boldsymbol{0.48}}\right) \times \boldsymbol{100} = \boldsymbol{16.67\%}$$

(e) Equilibria involving sulphur trioxide, sulphur dioxide and oxygen

Examples

1. At 700°C, and total pressure of 1.0 atm, the partial pressure at equilibrium for sulphur dioxide and oxygen are 0.27 and 0.41 atm respectively. Calculate the equilibrium constant, K_p for the reaction.

$$\boldsymbol{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}$$

$$p_{Total} = 1.0\ atm$$
$$p_{SO_2} = 0.27\ atm$$
$$p_{O_2} = 0.41\ atm$$
$$p_{SO_3} = 1.0 - (0.27 + 0.41) = 0.32$$

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 \times p_{O_2}}$$
$$K_p = \frac{0.32^2}{0.27^2 \times 0.41} \frac{atm^2}{atm^2 \times atm}$$
$$\boldsymbol{K_p = 3.426\ atm^{-1}}$$

2. 0.425 moles of sulphur dioxide and 0.294 moles of oxygen were heated in a 1.6 litre vessel and at equilibrium, it was found that 52% of oxygen had reacted. Calculate the value of equilibrium constant, K_c.

	$\boldsymbol{2SO_2(g)}$	+	$\boldsymbol{O_2(g)}$	$\rightleftharpoons$	$\boldsymbol{2SO_3(g)}$
Initial moles	0.425		0.294		0
Moles reacted/formed	$2x$		x		$2x$
Moles at equilibrium	$\boldsymbol{(0.425-2x)}$		$\boldsymbol{(0.294-x)}$		$\boldsymbol{2x}$

$Total\ moles\ at\ equilibrium$ $= 0.425 - 2x + 0.294 - x + 2x = (0.719 - x)$ $Moles\ of\ O_2\ that\ reacted = x$ $x = \frac{52}{100} \times 0.294 = 0.15288$ $Moles\ of\ O_2\ at\ equilibrium = 0.294 - 0.15288$ $= 0.14112$ $Moles\ of\ SO_2\ at\ equilibrium$ $= 0.425 - 2(0.15288) = 0.11924$ $Moles\ of\ SO_3\ at\ equilibrium$ $= 2(0.15288) = 0.30576$	$Since\ volume\ is\ 1.6\ litres,$ $[O_2] = \left(\frac{0.14112}{1.6}\right) = 0.0882M$ $[SO_2] = \left(\frac{0.11924}{1.6}\right) = 0.0745M$ $[SO_3] = \left(\frac{0.30576}{1.6}\right) = 0.1911M$ $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ $K_c = \frac{(0.1911)^2}{(0.0745)^2 \times 0.0882}\ \frac{mol^2dm^{-6}}{mol^3dm^{-9}}$ $\boldsymbol{K_c = 74.6\ mol^{-1}dm^3}$

3. 1 mole of sulphur trioxide was introduced into a $1dm^3$ vessel. The vessel was heated to 1000K until equilibrium was attained. At equilibrium, 0.35 moles of sulphur trioxide was present.

(i) Write equation for the dissociation of sulphur trioxide.

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

(iii) **Calculate the value of K_c.**

(i) $\boldsymbol{2SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)}$

(ii) $K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$

Initial moles	1	0	0
Moles dissociated/formed	α	α	$\frac{\alpha}{2}$
Moles at equilibrium	$\boldsymbol{1-\alpha}$	$\boldsymbol{\alpha}$	$\boldsymbol{\frac{\alpha}{2}}$

$Total\ moles\ at\ equilibrium$ $= 1 - \alpha + 2\alpha + \alpha = \boldsymbol{1 + 0.5\alpha}$ $\boldsymbol{But\ 1 - \alpha = 0.35}$ $\boldsymbol{\alpha = 0.65}$ $Moles\ of\ O_2\ at\ equilibrium$ $= \frac{0.65}{2} = 0.325$ $Moles\ of\ SO_2\ at\ equilibrium = 0.65$ $Moles\ of\ SO_3\ at\ equilibri\ = 0.35$	$Since\ volume\ is\ one\ litre$ $[O_2] = 0.325M \quad [SO_2] = 0.65M$ $[SO_3] = 0.35M$ $K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$ $K_c = \frac{0.65^2 \times 0.325}{(0.35)^2}\ \frac{mol^3dm^{-9}}{mol^2dm^{-6}}$ $\boldsymbol{K_c = 1.12\ moldm^{-3}}$

(f) Examples involving other equilibria systems

1. Dinitrogen tetroxide and nitrogen dioxide exist in the following equilibrium.

$$\boldsymbol{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)}$$

When 11.04g of dinitrogen tetroxide were placed in a vessel of volume $\boldsymbol{4.80dm^3}$ at a fixed temperature, 5.52g of nitrogen dioxide were produced at equilibrium under a pressure of 100kPa. Calculate the:

(a) equilibrium number of moles of each gas

(b) equilibrium constant, $\boldsymbol{K_c}$.

(c) equilibrium constant, $\boldsymbol{K_p}$.

(a)

$$Molar\ mass\ of\ N_2O_4 = (2 \times 14) + (4 \times 16) = 92g$$

$$Initial\ moles\ of\ N_2O_4 = \frac{11.04}{92} = 0.12\ moles$$

$$Molar\ mass\ of\ NO_2 = (1 \times 14) + (2 \times 16) = 46g$$

$$\boldsymbol{Moles\ of\ NO_2\ at\ equilibrium = \frac{5.52}{46} = 0.12\ moles}$$

	$\boldsymbol{N_2O_4(g)}$	$\boldsymbol{\rightleftharpoons}$	$\boldsymbol{2NO_2(g)}$
Initial moles	0.12		0
Moles dissociated/formed	0.12α		$2(0.12\alpha)$
Moles at equilibrium	$\boldsymbol{0.12(1-\alpha)}$		$\boldsymbol{0.24\alpha}$

$$\boldsymbol{But\ 0.24\alpha = 0.12}$$

$$\boldsymbol{\alpha = 0.5}$$

$$\boldsymbol{Moles\ of\ NO_2\ at\ equilibrium = 0.12\ moles}$$

$$\boldsymbol{Moles\ of\ N_2O_4\ at\ equilibrium = 0.12(1-0.5) = 0.06\ moles}$$

(b)

$$[N_2O_4] = \frac{0.06}{4.8} = 0.0125M$$

$$[NO_2] = \frac{0.12}{4.8} = 0.025\ M$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{(0.025)^2}{0.0125}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$$

$$\boldsymbol{K_c = 0.05\ moldm^{-3}}$$

(c)

$$Total\ moles\ at\ equilibrium = 0.12 + 0.06 = 0.18\ moles$$

$$p_{N_2O_4} = \frac{0.06}{0.18} \times 100 = 33.333\ kPa$$

$$p_{NO_2} = \frac{0.12}{0.18} \times 100 = 66.667\ kPa$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}}$$

$$K_p = \frac{(66.667)^2}{33.333}\ \frac{(kPa)^2}{kPa}$$

$$\boldsymbol{K_p = 133.336\ kPa}$$

2. For the following gas equilibrium, $\boldsymbol{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)}$ at 333K, the equilibrium constant, $\boldsymbol{K_p}$ is 1.33 atmospheres. Calculate the degree of dissociation of one mole of dinitrogen tetraoxide at 333K if the total pressure of the system is 2 atmospheres.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial moles	1		0
Moles dissociated/formed	α		2α
Moles at equilibrium	$(\mathbf{1-\alpha})$		$\mathbf{2\alpha}$

$$\textbf{Total moles at equilibrium} = 1-\alpha+2\alpha = (\mathbf{1+\alpha})$$

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}\times 2 = \frac{2(1-\alpha)}{1+\alpha}\ atm$$

$$p_{NO_2} = \frac{2\alpha}{1+\alpha}\times 2 = \frac{4\alpha}{1+\alpha}\ atm$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = 1.33$$

$$\frac{\left(\frac{4\alpha}{1+\alpha}\right)^2}{\frac{2(1-\alpha)}{1+\alpha}} = 1.33$$

$$\left(\frac{16\alpha^2}{(1+\alpha)^2}\right)\times\left(\frac{1+\alpha}{2(1-\alpha)}\right) = 1.33$$

$$\frac{16\alpha^2}{2(1+\alpha)(1-\alpha)} = 1.33$$

$$16\alpha^2 = 2.66(1-\alpha^2)$$

$$16\alpha^2 + 2.66\alpha^2 = 2.66$$

$$18.66\alpha^2 = 2.66$$

$$\alpha^2 = 0.142551$$

$$\boldsymbol{\alpha = 0.378}$$

***The degree of dissociation of N_2O_4 is* $\mathbf{0.378}$**

3. When heated, carbon dioxide dissociates according to the equation:

$$\mathbf{2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)}$$

If at a certain temperature and a pressure of one atmosphere, 60% of the original carbon dioxide remained undissociated. Calculate the equilibrium constant K_p for the reaction.

	$2CO_2(g)$	$\rightleftharpoons$	$2CO(g)$	+	$O_2(g)$
Initial moles	n		0		0
Moles dissociated/formed	$n\alpha$		$n\alpha$		$\frac{n\alpha}{2}$
Moles at equilibrium	$\mathbf{n(1-\alpha)}$		$\mathbf{n\alpha}$		$\mathbf{\frac{n\alpha}{2}}$

$$\textbf{But}\quad \frac{\mathbf{n(1-\alpha)}}{\mathbf{n}}\times\mathbf{100} = \mathbf{60}$$

$$\mathbf{1-\alpha = 0.6}$$

$$\boldsymbol{\alpha = 0.4}$$

$$\textbf{Total moles at equilibrium} = \mathbf{n(1-\alpha)} + \mathbf{n\alpha} + \frac{\mathbf{n\alpha}}{\mathbf{2}}$$

$$= \mathbf{n\left(1-\alpha+\alpha+\frac{\alpha}{2}\right)}$$

$$= \mathbf{n\left(1+\frac{\alpha}{2}\right) = 1.2n}$$

$$p_{CO_2} = \frac{0.6n}{1.2n}\times 1 = 0.5\ atm$$

$$p_{CO} = \frac{0.4n}{1.2n}\times 1 = 0.333\ atm$$

$$p_{O_2} = \frac{0.2n}{1.2n}\times 1 = 0.167\ atm$$

$$K_p = \frac{(p_{CO})^2\times p_{O_2}}{(p_{CO_2})^2}$$

$$K_p = \frac{(0.333)^2\times 0.167}{(0.5)^2}\ \frac{atm^3}{atm^2}$$

$$\boldsymbol{K_p = 0.0741\ atm}$$

4. Nitrogen monoxide reacts with oxygen according to the reaction:

$$\boldsymbol{2NO(g) \quad + \quad O_2(g) \rightleftharpoons 2NO_2(g)}$$

At equilibrium, the equilibrium constant is $375\ mol^{-1}l$ at a given temperature in a container of volume, $755cm^3$. The equilibrium mixture was found to contain 0.0148 moles of oxygen. Calculate the ratio of $[NO]$ to $[NO_2]$ in the equilibrium mixture.

	$2NO(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2NO_2(g)$
Moles at equilibrium	?		$\mathbf{0.0148}$		***?***

Since volume is $755\ cm^3$,

$$[O_2] = \left(\frac{0.0148 \times 1000}{755}\right) = 0.0196M$$

$[NO] = ?$ $[NO_2] = ?$

$$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} = 375$$

$$\frac{[NO_2]^2}{[NO]^2} = 375[O_2]$$

$$\frac{[NO_2]^2}{[NO]^2} = 375 \times 0.0196$$

$$\frac{[NO_2]}{[NO]} = \sqrt{375 \times 0.0196}$$

$$\frac{[NO_2]}{[NO]} = 2.711$$

$$\frac{[\boldsymbol{NO}]}{[\boldsymbol{NO_2}]} = \frac{\mathbf{1}}{\mathbf{2.711}} = \mathbf{0.3689}$$

5. For the equilibrium system below:

$$\boldsymbol{CO\ (g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)}$$

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

(b) When 1 mole of steam and 1 mole of carbon monoxide are allowed to reach equilibrium, 33.3% of the equilibrium mixture is hydrogen. Calculate the value of K_p and state its units.

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial moles	1		1		0		0
Moles reacted/formed	x		x		x		x
Moles at equilibrium	$\mathbf{1-x}$		$\mathbf{1-x}$		$\boldsymbol{x}$		$\boldsymbol{x}$

Total moles at equilibrium

$$= \mathbf{1 - x + 1 - x + x + x = 2}$$

$$\boldsymbol{But\ \frac{x}{2} \times 100 = 33.3}$$

$$\boldsymbol{x = 0.666}$$

Let the total pressure be P

$$p_{CO} = \frac{1 - 0.666}{2} P = 0.167\ units$$

$$p_{H_2O} = \frac{1 - 0.666}{2} P = 0.167\ units$$

$$p_{CO_2} = \frac{0.666}{2} P = 0.333\ units$$

$$p_{H_2} = \frac{0.666}{2} P = 0.333\ units$$

$$K_p = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}}$$

$$K_p = \frac{(0.333)^2}{(0.167)^2}$$

$$\boldsymbol{K_p = 3.976}$$

6. Methane reacts with steam according to the equation

$$\boldsymbol{CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)}$$

When 0.18 moles of methane and 0.22 moles of steam were heated in a 5 litre vessel, 0.1 mole of carbon dioxide was found to be present at equilibrium. Calculate the value of K_c.

	$\boldsymbol{CH_4(g)}$	$\boldsymbol{+\ 2H_2O(g)}$	$\boldsymbol{\rightleftharpoons\ CO_2(g)}$	$\boldsymbol{+\ 4H_2(g)}$
Initial moles	0.18	0.22	0	0
Moles reacted/formed	x	$2x$	x	$4x$
Moles at equilibrium	$\boldsymbol{0.18 - x}$	$\boldsymbol{0.22 - 2x}$	$\boldsymbol{x}$	$\boldsymbol{4x}$

$\boldsymbol{But\ number\ of\ moles\ of\ CO_2\ at\ equilibrium = 0.1}$

$\boldsymbol{Therefore\ x = 0.1}$

$Moles\ of\ CH_4\ at\ equilibrium = 0.18 - 0.1 = 0.08$

$Moles\ of\ H_2O\ at\ equilibrium = 0.22 - 2(0.1) = 0.02$

$Moles\ of\ CO_2\ at\ equilibrium = 0.1$

$Moles\ of\ H_2\ at\ equilibrium = 4(0.1) = 0.4$

$Since\ volume\ is\ 5\ litres,$

$$[CH_4] = \left(\frac{0.08}{5}\right) = 0.016M$$

$$[H_2O] = \left(\frac{0.02}{5}\right) = 0.004M$$

$$[CO_2] = \left(\frac{0.1}{5}\right) = 0.02M$$

$$[H_2] = \left(\frac{0.4}{5}\right) = 0.08M$$

$$K_c = \frac{[CO_2][H_2]}{[CH_4]\,[H_2O]}$$

$$K_c = \frac{0.02 \times 0.08}{0.016 \times 0.004}$$

$$\boldsymbol{K_c = 25}$$

7. Sulphoryl dichloride dissociates when heated according to the following equation: $\boldsymbol{SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)}$

When 67.5g of Sulphoryl dichloride was heated in a 1 litre vessel at 120°C and 3.6 atmospheres, it was found that at equilibrium, 45% of it had dissociated.

(i) Write the expression for the equilibrium constant, K_p.

(ii) Calculate the number of moles of each substance present at equilibrium.

(iii) Calculate the equilibrium constant, K_c.

(i) $\boldsymbol{K_p = \frac{p_{SO_2} \times p_{Cl_2}}{p_{SO_2Cl_2}}}$

(ii) $Molar\ mass\ of\ SO_2Cl_2 = 32 + (2 \times 16) + (2 \times 35.4) = 134.8g$

$$Initial\ moles\ of\ SO_2Cl_2 = \frac{67.5}{134.8} = 0.5$$

	$\boldsymbol{SO_2Cl_2(g)}$	$\boldsymbol{\rightleftharpoons\ SO_2(g)}$	$\boldsymbol{+\ Cl_2(g)}$
Initial moles	0.5	0	0
Moles dissociated/formed	0.5α	0.5α	0.5α
Moles at equilibrium	$\boldsymbol{0.5(1-\alpha)}$	$\boldsymbol{0.5\alpha}$	$\boldsymbol{0.5\alpha}$

$\boldsymbol{But\ \alpha = \frac{45}{100} = 0.45}$ $\boldsymbol{Moles\ of\ SO_2Cl_2\ at\ equilibrium}$ $\boldsymbol{= 0.5(1 - 0.45) = 0.275}$ $\boldsymbol{Moles\ of\ SO_2\ at\ equilibrium}$ $\boldsymbol{= (0.5 \times 0.45) = 0.225}$ $\boldsymbol{Moles\ of\ Cl_2\ at\ equilibrium = 0.225}$	**(iii)** *Since volume is 1 litre* $[SO_2Cl_2] = 0.275\ M$ $[SO_2] = 0.225\ M$ $[Cl_2] = 0.225\ M$ $K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{(0.225)^2}{0.275} = \boldsymbol{0.184\ moldm^{-3}}$

8. The equilibrium constant, K_p for the reaction below at 250℃ is $1.08 \times 10^{-1} atm^2$:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Calculate the

(i) total pressure of the system at equilibrium.

(ii) degree of dissociation of ammonium hydrogen sulphide

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
Initial moles	n		0		0
Moles dissociated/formed	$n\alpha$		$n\alpha$		$n\alpha$
Moles at equilibrium	$\boldsymbol{n(1-\alpha)}$		$\boldsymbol{n\alpha}$		$\boldsymbol{n\alpha}$

$\boldsymbol{Total\ moles\ at\ equilibrium}$ $\boldsymbol{= n(1 - \alpha) + n\alpha + n\alpha}$ $\boldsymbol{= n(1 - \alpha + \alpha + \alpha)}$ $\boldsymbol{= n(1 + \alpha)}$ ***Let the total pressure at equilibrium be P*** $p_{NH_3} = p_{H_2S} = \frac{n\alpha}{n(1+\alpha)}P = \frac{\alpha}{(1+\alpha)}P$ $K_p = p_{NH_3} \times p_{H_2S}$ *Since* $p_{NH_3} = p_{H_2S}$; $K_p = (p_{NH_3})^2$	$1.08 \times 10^{-1} = (p_{NH_3})^2$ $p_{NH_3} = \sqrt{1.08 \times 10^{-1}}$ $p_{NH_3} = 0.3286\ atm$ $P = p_{NH_3} + p_{H_2S}$ $= 2(0.3286) = \boldsymbol{0.6572\ atm}$ ***From*** $p_{NH_3} = \frac{\alpha}{(1+\alpha)}P$ $0.3286 = \frac{\alpha}{(1+\alpha)} \times 0.6572$ $\frac{\alpha}{(1+\alpha)} = \frac{0.3286}{0.6572} = 0.5$ $\alpha = 1$

General questions involving calculations on chemical equilibria

1. When 3.12g of ethanoic acid and 2.07g of ethanol were reacted in a 1 litre closed vessel at 50ºC. 0.36g of water was found at equilibrium. Calculate the value of equilibrium constant for the reaction, K_c.
2. When 8.28g of ethanol were heated with 60g of ethanoic acid, 49.74g of the acid remained at equilibrium. Calculate the;
   (i) value of the equilibrium constant, K_c.
   (ii) mass of ester present in the equilibrium mixture formed from 13.8g of ethanol and 12g of ethanoic acid.
3. When equimolar quantities of ethanoic acid and ethanol were heated, one third of each reactant remained at equilibrium. Calculate the equilibrium constant for the reaction
4. 1 mole of ethanol was reacted with 2 moles of ethanoic acid at 60℃. If the equilibrium constant for the reaction at the same temperature is 4. Calculate the mass of ethylethanoate in the equilibrium mixture.
5. 5moles of ethanol, 6 moles of ethanoic acid, 6 moles of ethylethanoate and 4moles of water were mixed together in a stoppered bottle at 15℃. At equilibrium, the bottle was found to contain 4 moles of ethanoic acid.
   (a) (i) Write an equation for the reaction between ethanol and ethanoic acid to form ethylethanoate and water.
   (ii) Suggest a mechanism for the reaction
   (b) Write an expression for the equilibrium constant, K_c for this reaction
   (c) Determine the number of moles of ethanol, ethylethanoate and water present in the equilibrium mixture hence the value of K_c for this reaction
   (d) If 1moleof ethanol, 1mole of ethanoic acid, 3 moles of ethylethanoate and 3 moles of water are mixed together in a stoppered flask at 15℃. Determine the number of moles of each compound present in the equilibrium mixture.
6. 3.0g of ethanoic acid and 2.3g of ethanol were equilibrated at 100℃ for an hour and then quickly cooled in an ice bath. 50 cm^3 of 1.0 M sodium hydroxide solution were added. When the mixture was titrated with 1.0M hydrochloric acid, 33.3cm^3 of the acid were required for complete reaction.
   (a) Explain why the mixture was cooled in an ice bath.
   (b) Calculate the equilibrium constant, K_c for the reaction.
7. 4.6g of ethanol and 12.0g of ethanoic acid were mixed in a stoppered flask with 20cm^3 of 1M hydrochloric acid as catalyst at 20℃. The mixture was left for a week to attain equilibrium, and then titrated with 137cm^3 of 1.0M sodium hydroxide. (Of the total volume of base used, only 20 cm^3 were used to react with hydrochloric acid)
   (a)Work out the concentrations of the equilibrium mixture
   (b) Calculate the value of equilibrium constant, K_c.

8. When 60g of ethanoic acid and 46g of ethanol were made to react to equilibrium at 100ºC, the percentage of esterification was 54%
   (i) Write equation for the esterification reaction.
   (ii) Calculate the value of the concentration equilibrium constant, K_c.
   (iii) Outline the mechanism for the reaction between ethanoic acid and ethanol.
9. When $6.22cm^3$ of hydrogen were heated with $5.71cm^3$ of iodine in a sealed tube at 356 ^{o}C, it was found out that 9.60 cm^3 of hydrogen iodide were present at equilibrium. Calculate the:
   (i) equilibrium constant
   (ii) volume of hydrogen iodide in the equilibrium mixture formed by reacting together $6.41cm^3$of hydrogen and $10.40cm^3$ of iodine at 356 ^{o}C.
   (Hint: Number of moles of a gas is directly proportional to volume)
10. A mixture of 0.8 mole of hydrogen and 0.6 mole of iodine was allowed to react in a sealed tube at 450ºC. At equilibrium, 0.2 mole of iodine had reacted.
   (i) Write an expression for the equilibrium constant, K_c, for the reaction
   (ii) Calculate the value of K_C, at 450ºC.
11. Hydrogen reacts with iodine according to the equation

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

   (a) Calculate the equilibrium concentration of each of the following when:
      (i) 0.2 mole of iodine and 0.3 moles of hydrogen are reacted in a one litre vessel.
      (ii) 0.5 mole of iodine and 0.8 mole of hydrogen are reacted in a 4 litre vessel $(The\ equilibrium\ constant, K_c, for\ the\ reaction\ is\ 50)$
   (b) Equimolar quantities of hydrogen and iodine were heated in a 1 litre vessel until equilibrium was attained. The equilibrium mixture was found to contain 20.5% hydrogen iodide Determine the equilibrium constant, K_c.
12. (a) State the **law of mass action**
   (b) Explain what is meant by the following terms:
      (i) equilibrium constant
      (ii) dynamic equilibrium
   (c) Describe an experiment to determine the equilibrium constant for the reaction between hydrogen and iodine
   (d) 1.54g of hydrogen iodide were heated in a 600cm^3 bulb at 530 ^{o}C. When equilibrium was attained, the bulb was rapidly cooled to room temperature and broken under potassium iodide solution. The iodine formed required 67 cm^3 of 0.1M sodium thiosulphate solution for complete reaction. Calculate ;
      (i) Number of moles of hydrogen iodide in 1.54g
      (ii) Number of moles of iodine formed

(iii) Value of $\boldsymbol{K_c}$ at 530 ^{o}C

13. 1.0g of hydrogen iodide was heated to a certain temperature in a sealed vessel and the products rapidly cooled. The iodine which had been liberated required 15.0 cm^3 of 0.1M sodium thiosulphate for complete reaction. Calculate the percentage by mass of hydrogen iodide which remained undissociated at that temperature.
14. (a) 3.4 moles of hydrogen iodide at 460ºC are found to be 20% dissociated. Calculate the:
    (i) number of moles of hydrogen iodide, hydrogen and iodine formed at equilibrium
    (ii) equilibrium constant for the dissociation reaction.
    (b) A mixture containing 28 moles of hydrogen and 22 moles of iodine was heated in a sealed tube at 460 ºC until equilibrium was attained and 36 moles of hydrogen iodide was obtained. Calculate the degree of dissociation of hydrogen iodide at 460ºC
15. (a)The equilibrium constant for the dissociation of hydrogen iodide into hydrogen and iodine is 0.02. Calculate the equilibrium composition of the following if they are heated.
    (i) 0.05 mole of hydrogen iodide.
    (ii) 0.2 mole of hydrogen iodide.
    (b) When 0.4 mole of hydrogen iodide was heated to equilibrium, it dissociated. Determine the degree of dissociation of hydrogen iodide, given that the equilibrium constant is 0.025
16. (a) 1 mole of hydrogen iodide gas at 25℃ was introduced into a container of volume 20 litres. Calculate the pressure of the gas assuming ideal behaviour.(*1 mole of an ideal gas occupies 22.4 litres under standard conditions*)
    (b) The sample of hydrogen iodide, considered above was raised to a temperature of 300℃ and it partially dissociated into hydrogen and iodine. At equilibrium, 1 mole of iodine was found to be present.
    (i) Write an equation for the dissociation
    (ii) Calculate the pressure of the equilibrium mixture at 300℃ assuming no change in volume.
    (iii) Calculate the equilibrium constant at 300℃
17. Derive an expression for the equilibrium constant for the reaction;

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

in terms of a, b, x and P, where a and b are the original number of moles of hydrogen and nitrogen respectively, and x is the number of moles of nitrogen which react at a total pressure of P Pa.

18. When 0.2 moles and 0.47 moles of nitrogen and hydrogen respectively were heated to equilibrium in a 1 litre vessel, 0.18 moles of ammonia were formed. Calculate the equilibrium constant, $\boldsymbol{K_c}$.
19. When 1.65 moles of hydrogen and 0.6 moles of nitrogen were heated to 150ºC in a 1.5 litre closed vessel, equilibrium was attained when 0.9 moles of ammonia were formed. Calculate the value of equilibrium constant, $\boldsymbol{K_c}$ for the reaction.
20. Nitrogen and hydrogen are mixed in a ratio 1:3. At equilibrium at 600^{O}C and 10 atmospheres, the percentage of ammonia in the mixture of gases is 15%
    (a) Write equation for the reaction
    (b) Write an expression for the equilibrium constant.
    (c) Calculate the equilibrium constant at that temperature and state its units.
21. Stoichiometric amounts of hydrogen and nitrogen were reacted at 50 atm. At equilibrium, 0.8 moles of ammonia were formed. Calculate:
    (i) Amount of hydrogen and nitrogen present at equilibrium
    (ii) Value of the equilibrium constant
22. (a) For the reaction,

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

Calculate the molar percentage of ammonia in the equilibrium mixture formed at 400^{o}C and at a pressure of 3×10^7 Pa, when gaseous hydrogen and nitrogen are mixed in a 3:1 ratio and there is 61% conversion of nitrogen to ammonia.

(b) (i) Determine the equilibrium constant, $\boldsymbol{K_p}$of the reaction.
    (ii) Given that the value of $\boldsymbol{K_p}$ at a given temperature is $2.0 \times 10^{-14}Pa^2$, calculate the pressure at which ammonia is 95% dissociated into its elements at that temperature.
23. (a) Write equation for the reaction leading to formation of ammonia
    (b) The value of the pressure equilibrium constant, $\boldsymbol{K_p}$ for the reaction in (a) above is $1.5 \times 10^{-5}atm^{-2}$ at 500℃ . Calculate the percentage of a 1:3 mixture of nitrogen and hydrogen that would be converted to ammonia at 500 atmospheres.
24. (a) Write an equation for the reaction between hydrogen and nitrogen.

(b) At 500 ^{o}C, the equilibrium concentration of hydrogen is *0.250 moll^{-1}* and that of nitrogen is *2.7 moll^{-1}* Calculate the equilibrium concentration of ammonia at the same temperature given that $K_c = 6 \times 10^{-2}mol^{-2}l^2$ at 500 ^{o}C.

25. When nitrogen was reacted with hydrogen at 690K, the total pressure of the system at equilibrium was 32 atmospheres and the partial pressures of hydrogen and nitrogen were 8 and 3 atmospheres respectively. Calculate the:
    (i) partial pressure of ammonia in equilibrium mixture.
    (ii) equilibrium constant for the reaction

26. At a certain temperature, the equilibrium constant for the reaction between nitrogen and hydrogen, $\boldsymbol{K_p}$, is $4.82 \times 10^{-2} atm^{-2}$ and the partial pressures of nitrogen and hydrogen are 30 and 120 atm respectively.
    (i) Write the expression for the equilibrium constant, $\boldsymbol{K_p}$.
    (ii) Calculate the partial pressure of ammonia at equilibrium.
27. When 80.4 g of phosphorus(V) chloride were placed in a 9.0 litre vessel and heated at a certain pressure, 8.4 g of chlorine were formed at equilibrium. Calculate the:
    (i) amount of phosphorus(V) chloride and phosphorus(III) chloride at equilibrium in moles per litre.
    (ii) equilibrium constant, $\boldsymbol{K_c}$, for the reaction and state its units.
28. (a) When 2.6 mole of phosphorus(V) chloride was heated in a $1.5 dm^3$vessel, equilibrium was established when 1.04 mole of phosphorus(III) chloride was formed. Calculate the value of equilibrium constant, $\boldsymbol{K_c}$.
    (b) 3.0 mole of phosphorus pentachloride was heated in a 1 litre vessel and when equilibrium was attained, it was found to contain 1.14 mole of chlorine gas. Determine the value of equilibrium constant, $\boldsymbol{K_c}$.
29. **75.06g** of phosphorus(V) chloride were heated to 200ºC in a vessel of volume $1000 cm^3$ at a pressure of 170kPa. Calculate the;
    (a) degree of dissociation of phosphorus(V) chloride
    (b) value of equilibrium constant, $\boldsymbol{K_p}$, at 200ºC
30. 0.2 moles of phosphorus pentachloride were heated at 500K in 5 litre flask. At equilibrium, 60% of phosphorus pentachloride was found to have dissociated and the total pressure was found to be 300mmHg.
    (a) Calculate the equilibrium constant, $\boldsymbol{K_p}$.
    (b) What will be the total pressure if phosphorus pentachloride dissociated only by 35%
31. When 2.4 moles of phosphorus pentachloride were heated in a $1.5 dm^3$ vessel and at equilibrium, it was found to contain 23.53% phosphorus trichloride.

(a) Write equation for the dissociation of phosphorus pentachloride

(b) Write the expression for the equilibrium constants, $\boldsymbol{K_c}$, and $\boldsymbol{K_p}$, for the reaction.

(c) Determine the value of equilibrium constant, $\boldsymbol{K_c}$.

32. (a) 2.6 mole of phosphorus pentachloride was heated in a 500 cm^3 closed vessel. At equilibrium, it was found to contain 1.04 mole of phosphorus trichloride. Determine the value of equilibrium constant, $\boldsymbol{K_c}$.
    (b) 3.0 mole of phosphorus pentachloride was heated in a 750 cm^3vessel until equilibrium was established. The vessel contained 1.14 moles of chlorine. Determine the value of equilibrium constant, $\boldsymbol{K_c}$.

33. Determine the mass of each of the components of the equilibrium mixture formed when 0.52 moles of phosphorus(V) chloride is heated at equilibrium. ($The\ equilibrium\ constant\ is\ 0.043\ moldm^{-3}$)
34. 0.04 moles of sulphur trioxide were allowed to dissociate at 900K in a flask of volume 3.04 litres. At equilibrium, 0.0289 moles of sulphur trioxide were found to be present.
    (i) Derive the relationship between K_c and K_p for this reaction. Show clearly how you arrive at your answer.
    (ii) Calculate equilibrium constants K_c and K_p.
35. At 700℃ and total pressure of one atmosphere, the partial pressures at equilibrium for sulphur dioxide and oxygen are 0.27 and 0.41 atmospheres respectively. Sulphur dioxide is oxidized to sulphur trioxide according to the following equation:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Calculate the equilibrium constant, K_p, for the reaction
36. When 0.6 and 0.425 moles of sulphur dioxide and oxygen respectively were reacted in a 1litre vessel to equilibrium, the equilibrium mixture contained 18.75% sulphur dioxide. Calculate the equilibrium constant value, K_p.
37. Dinitrogen tetraoxide dissociates at 40 ^oC and 1 atm according to the following equation.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad \Delta H = +57kJmol^{-1}$$

    (i) Write an equation for the equilibrium constant , $\boldsymbol{K_p}$**.**
    (ii) Draw a well labelled energy level diagram for the reaction in (i) above
    (iii) The reaction mixture of the reaction was found to contain 60% by volume of nitrogen dioxide at equilibrium. Calculate the equilibrium constant $\boldsymbol{K_p}$ at 40 ^oC for the reaction.
38. (a) At 40℃ and under a pressure of 1 atmosphere, dinitrogen tetraoxide contains 60% by volume of nitrogen dioxide molecules. Calculate the percentage dissociation of dinitrogen tetraoxide and equilibrium constant in terms of the partial pressures of the two gases.
    (b) Deduce the:
        (ii) percentage dissociation of dinitrogen tetraoxide at the same temperature when the gases are under a pressure of 6 atm.
        (iii) the pressure at which dinitrogen tetraoxide would be dissociated to an extent of 80% at the same temperature.
39. 1 mole of dinitrogen tetra oxide was allowed to dissociate to nitrogen dioxide in a 5 litre flask at 50℃. At equilibrium one mole of nitrogen dioxide was found to be present. Calculate equilibrium constant for the reaction.

40. Propene reacts with steam according to the following equation.

$$CH_3CH = CH_2\,(g) + H_2O(g) \rightleftharpoons CH_3\underset{OH}{C}HCH_3(g)$$

At a certain temperature and total pressure of 197.38 atmospheres, the equilibrium partial pressures of propene and steam are 74.02 and 93.76 atmospheres respectively. Calculate the value of $\boldsymbol{K_p}$ at this temperature and state its units.

41. Nitrogen monoxide combines with oxygen according to the equation

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

A closed vessel of 500 cm^3 containing 0.33 moles of nitrogen monoxide and 0.355 moles of oxygen was heated. Equilibrium was established when 0.105 moles of oxygen had reacted. Calculate the value of $\boldsymbol{K_c}$.

42. Carbon monoxide reacts with steam according to the reaction;

$$CO\,(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

When 6.5 cm^3 of carbon monoxide were heated with 4.8 cm^3 of steam at 45℃ until equilibrium, 4.6 cm^3 of carbon dioxide was formed. Calculate the;

(a) volume of carbon monoxide and steam left at equilibrium.

(b) equilibrium constant, $\boldsymbol{K_c}$.

43. At 700℃, the equilibrium constant for the reaction $CO\,(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 1.4. Calculate the percentage by volume of the gases in the equilibrium mixture at the same temperature when one volume of carbon monoxide and two volumes of steam are mixed.

44. Sulphur dioxide dichloride dissociates when heated according to the equation:

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

When 1.33 moles of sulphur dioxide dichloride were heated in a 2 litre vessel, equilibrium mixture contained 5.98% sulphur dioxide dichloride. Calculate the value of equilibrium constant, $\boldsymbol{K_c}$.

45. Ammonium hydrogen sulphide was allowed to dissociated into ammonia and hydrogen sulphide gases at $500K$. At equilibrium the total pressure was measured and found to be 0.6 atm. Calculate the:

(i) partial pressure of each gas at equilibrium.

(ii) pressure equilibrium constant

Determining equilibrium constants using partition coefficients

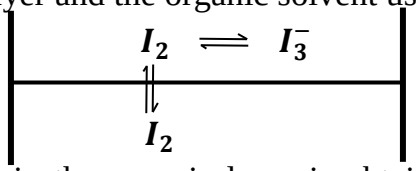
Iodine reacts with potassium iodide to form potassium triiodide according to the equation;

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

The equilibrium constant for the above reaction is given by the expression below and is measured by partition method.

$$K_c = \frac{[I_3^-]}{[I_2][I^-]}$$

A known mass of iodine is dissolved in a standard solution of potassium iodide and the resultant mixture shaken with trichloromethane or trichloromethane or benzene or carbon disulphide. Some iodine forms a complex with potassium iodide according to the above equation and some iodine remains free in the solution. The free iodine then distributes itself between the aqueous layer and the organic solvent used.



Aqueous layer

Trichloromethane layer

The concentration of iodine in the organic layer is obtained by titrating a portion of a known volume of it with standard sodium thiosulphate solution.

The concentration of free iodine in the aqueous layer is then got from the expression below, if the partition coefficient value is known;

$$K_D = \frac{[I_2]\ in\ free\ aqueous\ layer}{[I_2]\ free\ in\ organic\ layer}$$

$$[I_2]_{total}\ in\ aqueous\ layer = [I_2]_{free(aqueous\ layer)} + [I_3^-]$$

The total concentration of iodine in the aqueous layer, $[I_2]_{total}$ is obtained by titrating a portion of a known volume of it with standard sodium thiosulphate solution.

$$[I_2]_{total}\ in\ aqueous\ layer = [I_2]_{free(aqueous\ layer)} + [I_3^-]$$

Since $[I_2]_{free(aqueous\ layer)}$ is known, then $[I_3^-]$ can be obtained.

The total iodide ion concentration in the aqueous layer is obtained from the concentration of potassium iodide used.

$$[I^-]_{total} = [I^-]_{aqueous} + [I_3^-]$$

Since $[I_3^-]$ is known, then$[I^-]_{aqueous}$ can be obtained and the value of K_c then determined.

Example

4g of potassium iodide was dissolved in 500cm^3 of water and about 1g of iodine was dissolved in 100cm^3 of benzene. The two solutions were then mixed and allowed to stand. 10 cm^3 of the benzene layer required 5.1cm^3 of 0.1M sodium thiosulphate solution while 50 cm^3 of the aqueous layer required 2.9 cm^3 of 0.1M sodium thiosulphate solution for complete reaction. The distribution coefficient of iodine between benzene and water is 130. Calculate the value of the equilibrium constant for the reaction:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

$$Molar\ mass\ of\ KI = 39 + 127 = 166g$$

$$Moles\ of\ Na_2S_2O_3\ that\ reacted\ with\ I_2\ in\ benzene\ layer = \left(\frac{5.1 \times 0.1}{1000}\right) = 0.00051\ moles$$

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

$$Mole\ ratio\ of S_2O_3^{2-}: I_2 = 2:1$$

$$Moles\ of\ I_2\ in\ \ 10\ cm^3\ of\ benzene\ layer = \frac{1}{2} \times 0.00051 = 0.000255\ moles$$

$$10\ cm^3\ of\ benzene\ layer\ contain\ 0.000255\ moles\ of\ I_2$$

$$1000\ cm^3\ of\ benzene\ layer\ contain\ \left(\frac{1000 \times 0.000255}{10}\right) moles\ of\ I_2$$

$$[I_2]\ in\ benzene\ layer = 0.0255M$$

$$K_D = \frac{[I_2]\ free\ in\ benzene}{[I_2]\ free\ in\ aqueous\ layer} = 130$$

$$[I_2]\ free\ in\ aqueous\ layer = \frac{0.0255}{130} = 0.000196M$$

$$Moles\ of\ Na_2S_2O_3\ that\ reacted\ with\ free\ I_2\ in\ aqueous\ layer = \left(\frac{2.9 \times 0.1}{1000}\right) = 0.00029\ moles$$

$$Mole\ ratio\ of S_2O_3^{2-}: I_2 = 2:1$$

$$Moles\ of\ total\ \ I_2\ in\ \ 50\ cm^3\ of\ aqueous\ layer = \frac{1}{2} \times 0.00029 = 0.000145\ moles$$

$$50\ cm^3\ of\ aqueous\ layer\ contain\ 0.000145\ moles\ of\ total\ I_2$$

$$1000\ cm^3\ of aqueous\ layer\ contain\ \left(\frac{1000 \times 0.000145}{50}\right) moles\ of\ total\ I_2$$

$$[I_2]\ \ total\ in\ aqueous\ layer = 0.0029M$$

$$[I_2]\ \ total\ in\ aqueous\ layer = [I_2]\ free + [I_3^-]$$

$$[I_2]\ free + [I_3^-] = 0.0029$$

$$[I_3^-] = 0.0029 - 0.000196 = 0.0027$$

$$Moles\ of\ KI\ in\ 500cm^3 = \frac{4}{166} = 0.0241\ moles$$

$$Molar\ concentration\ of\ KI\ solution = \left(\frac{1000 \times 0.0241}{500}\right) = 0.0482\ M$$

$$[I^-]_{total} = [I^-]_{aqueous} + [I_3^-]$$

$$[I^-]_{aqueous} = 0.0482 - 0.0027 = 0.0455$$

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} = \frac{0.0027}{0.000196 \times 0.0455} = \mathbf{302.8 mol^{-1} dm^3}$$

Questions

1. A solution containing 12.7g of iodine and 166.1g of potassium iodide in 1 litre of water was shaken with 1 litre of benzene. If the partition coefficient of iodine between benzene and water is 400 and the equilibrium constant for the reaction: $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$ is 730. Calculate the concentration of:
   (i) iodine in benzene
   (ii) triiodide ions in water

Compare concentration equilibrium constant, K_c and pressure equilibrium constant, K_p

Concentration equilibrium constant, K_c	**Pressure equilibrium constant, K_p**
It can be measured for any reversible reaction	Measured for only reversible reactions involving gases
Expressed in terms of molar concentrations	Expressed in terms of partial pressures
N.B The two equilibrium constants are always the same value at a given temperature for equilibria where $\Delta n = 0$ (*where total number of moles of products − total number of moles of reactants is zero*)	

Interpretation of magnitude of K_c or K_p in relation to equilibrium position

Consider the reversible reaction, $wA + xB \rightleftharpoons yC + zD$

The proportion of products to reactants in the equilibrium mixture is described as the **position of the equilibrium**.

The magnitude of the equilibrium constant, ***K_c or K_p*** indicates the extent to which a reaction will proceed and the position of the equilibrium.

When K_c or K_p is small (k<1), it implies that the conversion of A and B into C and D is small and the position of the equilibrium lies to the left.

When K_c or K_p is large(k>1), it implies that the equilibrium mixture is largely composed of C and D is small and the position of the equilibrium lies to the right.

If K is about 1, the equilibrium is reached at some intermediate mixture.

Comparing the reaction quotient (Q) and k_c to determine direction of chemical reaction

The reaction quotient(Q) *is defined as the ratio of the molar concentrations of the product species over those of the reactant species involved in the chemical reaction, taking stoichiometric coefficients of the reaction into account as powers of the concentrations.*

The **reaction quotient**, *Q*, has the same mathematical form as the equilibrium-constant expression, but *Q* is a ratio of the actual concentrations (not a ratio of equilibrium concentrations).

For a given reaction, $wA + xB \rightleftharpoons yC + zD$

The reaction quotient is given as;

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

- At equilibrium, $\boldsymbol{K_c = Q}$ **,** and this is defined as the **equilibrium condition.**
- If $\boldsymbol{K_c < Q}$, the backward reaction is favoured, the reaction moves from right to left, until equilibrium is established.
- If $\boldsymbol{K_c > Q}$, the forward reaction is favoured, the reaction moves from left to right, until equilibrium is established.

Examples

1. **In the water–gas shift reaction, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:**

$$\boldsymbol{CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)}$$

If $K_c = 0.64$ at 900 K and 0.010 moles of carbon monoxide and 0.010 moles of water, 0.0080 moles of carbon dioxide, and 0.012 moles of hydrogen are injected into a 4.0 litre reactor and heated to 900 K, will the reaction proceed to the left or to the right ?

$$[CO] = \frac{0.01}{4} = 0.0025M$$
$$[H_2O] = \frac{0.01}{4} = 0.0025M$$
$$[CO_2] = \frac{0.008}{4} = 0.002M$$
$$[H_2] = \frac{0.012}{4} = 0.003M$$

$$Q = \frac{[CO_2] \times [H_2]}{[CO] \times [H_2O]}$$
$$Q = \frac{0.002 \times 0.003}{0.0025 \times 0.0025}$$
$$\boldsymbol{Q = 0.96}$$

Since $Q > K_c$, **the reaction proceeds from right to left, until equilibrium is established.**

2. **Consider the following reversible reaction; $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$. At a certain temperature, the partial pressure were measured and found to be $0.57atm$ for sulphur trioxide, $0.4\ atm$ for sulphur dioxide and $0.16\ atm$ for oxygen. Predict the direction in which the reaction should proceed in order to attain equilibrium.**
($K_p = 3.4\ atm^{-1}$)

$p_{SO_3} = 0.57\ atm$ $p_{SO_2} = 0.4\ atm$ $p_{O_2} = 0.16\ atm$ $Q = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 \times p_{O_2}}$	$Q = \frac{0.57^2}{0.4^2 \times 0.16}$ $Q = 12.69\ atm^{-1}$ **$Since\ Q > K_p$, the reaction proceeds from right to left, until equilibrium is established.**

Questions

1. For the reaction: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the equilibrium constant, K_c, is 1.0×10^{-5} at 1500 K. Predict the direction the reaction will move in if the reactants and products have the following concentrations: $[N_2] = 0.05\ mol\ l^{-1}$, $[O_2] = 0.02\ mol\ l^{-1}$, and $[NO] = 0.30\ mol\ l^{-1}$.
2. For the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the equilibrium constant, K_c, is 5.0×10^{-1} at 100°C. Predict the direction the reaction will move in if the concentration of N_2O_4 is $0.02\ mol\ l^{-1}$ and the concentration of NO_2 is $0.10\ mol\ l^{-1}$
3. 1 mole of Sulphur trioxide was introduced into a 1 dm^3 vessel. The vessel was heated to 1000K until equilibrium was attained. At equilibrium, 0.35 mole of Sulphur trioxide was present.
   (a) Write:
      (i) equation for the decomposition of Sulphur trioxide
      (ii) an expression for the equilibrium constant, K_c
   (b) Calculate the value of K_c.
   (c) 0.2 mole of Sulphur dioxide, 0.1 mole of oxygen and 0.7 mole of Sulphur trioxide, were introduced into the vessel in (a) at 1000K. Calculate the new K_c value for the reaction.
   (d) Using your answers in (b) and (c) above, state how the position of the equilibrium was affected.

L*é* CHATELIER'S PRINCIPLE AND THE EFFECTS OF VARIOUS FACTORS ON THE EQUILIBRIUM OF REVERSIBLE CHEMICAL REACTIONS

L*é* Chatelier's Principle

The principle states that if a system in equilibrium is subjected to any change, the equilibrium will shift if possible, to a direction which causes an opposite change.

or

If a system in equilibrium is subjected to a constraint, that change takes place which tends to remove the constraint

The system cannot completely cancel the change in the external factor, but it will move in a direction that will minimize the change.

The external factor may be **pressure**, **temperature**, **concentration**, **adding a noble gas** or **a catalyst**.

(a) Effect of pressure

Since pressure has a negligible effect on the volumes of solids and liquids, it only affects reactions in which gases are involved.

Any reaction that occurs with an increase in volume is favoured by a decrease in pressure.

A reaction that occurs with a decrease in volume is favoured by an increase in pressure.

Any change in pressure of the system **changes the position of the equilibrium** and the **rate of attainment of the equilibrium** but has **no effect on the equilibrium constant**.

Sample questions

1. Nitrogen and hydrogen react according to the equation

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

Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if ;

(i) **the pressure was decreased**

Note that $\mathbf{1\ volume\ of}\ N_2 + \mathbf{3\ volumes\ of}\ H_2\ (\mathbf{a\ total\ of\ 4\ volumes})\mathbf{produce\ 2\ volumes\ of\ ammonia}$

There forward reaction occurs by a reduction in volume, hence favoured by an increase in pressure.

A decrease in pressure ***shifts equilibrium from right to left*** *since* ***backward reaction occurs by an increase in volume***. ***Ammonia dissociates*** *to form nitrogen and hydrogen, keeping the* ***equilibrium constant value unchanged***. ***Rate of attainment of equilibrium decreases*** *because there are* ***fewer gas molecules in a given volume***, ***molecules are far apart*** *hence there are* ***fewer chances of successful collisions*** *between particles.*

(ii) the pressure was increased

Increase in pressure ***shifts equilibrium from left to right*** *since* ***forward reaction occurs by a decrease in volume****. Nitrogen will react with hydrogen* ***to form ammonia*** *so as to keep the* ***equilibrium constant value unchanged****.* ***Rate of attainment of equilibrium increases*** *because there are* ***more gas molecules in a given volume****,* ***molecules are closer together*** *hence there are* ***more chances of successful collisions*** *between particles.*

2. When hydrogen iodide is heated it decomposes according to the equation

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if the pressure of the reaction was increased

Note that $\mathbf{2\ volumes\ of\ HI\ produce\ 1\ volume\ of H_2 + 1\ volume\ of\ I_2 = 2\ volumes\ of\ products}$

Increase in pressure has ***no effect on position of equilibrium*** *since* ***both forward and backward reactions proceed with no change in volume****. Equilibrium constant* ***remains unchanged*** *but the* ***rate of attainment of equilibrium increases*** *because there are* ***more gas molecules in a given volume****,* ***molecules are closer together*** *hence there are* ***more chances of successful collisions*** *between particles.*

(b) Effect of concentration

Increasing concentration of any reagent in an equilibrium mixture shifts the equilibrium in the direction that converts some of the reagent into other products.

Addition of a reagent that reacts with one of the reactants/products, reduces the concentration of the reactant/product in an equilibrium mixture and shifts the equilibrium in the direction to which the reactant/ product is removed so that it is replaced.

Any change in concentration of one of the species in an equilibrium mixture **changes the position of the equilibrium** and the **rate of attainment of the equilibrium** but has **no effect on the equilibrium constant**.

Sample question

1. Sulphur dioxide reacts with oxygen according to the equation;

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if;

(i) more Sulphur dioxide was added

*The **concentration of sulphur dioxide increases** and the **excess sulphur dioxide reacts with oxygen** to produce sulphur trioxide, so as to keep the **equilibrium constant value the same**. Equilibrium therefore **shifts from left to right** and equilibrium constant value remains unchanged. The **rate of attainment of equilibrium increases** since **there is an increase in the number of particles** in the reaction vessel.*

(ii) Sulphur trioxide was added.

*The **concentration of sulphur trioxide increases** and the **excess sulphur trioxide dissociates** to produce sulphur dioxide and oxygen, so as to keep the **equilibrium constant value the same**. Equilibrium therefore **shifts from right to left** and equilibrium constant value remains unchanged. The **rate of attainment of equilibrium increases** since **there is an increase in the number of particles** in the reaction vessel.*

(iii) Removing the Sulphur trioxide formed

*Removing sulphur trioxide makes the **sulphur dioxide to react with oxygen** so as **to replace sulphur trioxide removed**, keeping the **equilibrium constant value unchanged**. Equilibrium therefore **shifts from left to right.** The **rate of attainment of equilibrium reduces** since **there is a reduction in the number of particles** in the reaction vessel.*

(c) Effect of temperature.

The effect of temperature on an equilibrium depends on whether the reaction is endothermic ($\Delta H\ is\ positive$) or exothermic ($\Delta H\ is\ negative$).
If the reaction is endothermic, increase in temperature favours it
If the reaction is exothermic, then it is favoured by lowering temperature.
Any change in temperature **changes the position of the equilibrium**, **rate of attainment of the equilibrium** and also the **value of the equilibrium constant**.
Among all the factors, it is **only temperature that affects the value of the equilibrium constant.**
For an **exothermic reaction**, **increase in temperature favours backward reaction, reducing the equilibrium constant value**.
For an **endothermic reaction, increase in temperature favours forward reaction, increasing the equilibrium constant value**.

Sample question

1. Ammonia is formed from nitrogen and hydrogen at 25°C and 10 atm.

$$N_2(g) \quad + \quad 3H_2(g) \rightleftharpoons \quad 2NH_3(g)\,,\ \Delta H^{\theta} = -92kJmol^{-1}$$

Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if the reaction is carried out at a temperature of 250°C, while the pressure remains at 10 atm.

Since forward reaction is ***exothermic****, increase in temperature from 25°C to 250°C will make* ***equilibrium shift from right to left****, favouring the* ***backward reaction which is endothermic****. The* ***ammonia dissociates*** *to form nitrogen and hydrogen according to Lé Chatelier's Principle. This* ***reduces the concentration of ammonia*** *but* ***increases the concentrations of nitrogen and hydrogen****,* ***reducing the equilibrium constant****.*

The ***rate of attainment of equilibrium increases*** *because* ***increase in temperature will increase both the forward reaction rate and the reverse reaction rate*** *and the* ***collision frequency between colliding particles****.*

2. Nitrogen reacts with oxygen according to the following equation

$$N_2(g) \quad + \quad O_2(g) \quad \rightleftharpoons 2NO(g)\,;\ \Delta H^{\theta} = +180\ kJmol^{-1}$$

Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if;

(i) the temperature was increased.

Increase in temperature will make ***equilibrium shift from left to right****, favouring the* ***forward reaction which is endothermic****. The* ***nitrogen reacts with oxygen*** *to form* ***nitrogen monoxide*** *according to Lé Chatelier's Principle. This* ***reduces the concentration of nitrogen and oxygen but increases the concentration of nitrogen monoxide****,* ***increasing the equilibrium constant****.*

The ***rate of attainment of equilibrium increases*** *because increase in temperature will* ***increase both the forward reaction rate and the reverse reaction rate*** *the* ***collision frequency between colliding particles****.*

(ii) the temperature was decreased.

Decrease in temperature will make ***equilibrium shift from right to left****, favouring the* ***backward reaction which is exothermic****. The nitrogen monoxide* ***dissociates to form oxygen and nitrogen*** *according to Lé Chatelier's Principle. This* ***increases the concentration of nitrogen and oxygen*** *but* ***decreases the concentration of nitrogen monoxide****,* ***reducing the equilibrium constant.***

The ***rate of attainment of equilibrium decreases*** *because* ***decrease in temperature will reduce the collision frequency between colliding particles****.*

(d) Effect of adding a noble gas

Addition of an inert gas for example argon to an equilibrium system does not affect the equilibrium constant.

The noble gas effect can be investigated under two conditions i.e constant volume (where total pressure of the system increases) and at constant pressure(where the total volume of the system increases).

When heated, carbon dioxide decomposes according to the equation:

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

Explain the effect on the equilibrium position and equilibrium constant and the rate of attainment of equilibrium when;

(i) argon is added to the equilibrium at constant volume

Argon being a noble gas, when added, the ***total pressure of the system increases,*** *but* ***there is no change in partial pressure/ concentrations of the reactants and products***. ***The position of the equilibrium is not affected***.

Since the ***concentration of argon does not apply in the*** K_c **or** K_p ***expression****, the* ***equilibrium constant also remains unchanged.***

The ***rate of attainment of equilibrium reduces*** *since* ***some of the particles on collision do not react.***

N.B Hence, when an inert gas is added to the system in equilibrium at constant volume there will be no effect on the equilibrium position or equilibrium constant but reduces the rate of attainment of equilibrium.

(ii) neon is added to the equilibrium at constant pressure

Neon being a noble gas, when added to the system at constant pressure, ***leads to an increase in the total volume****. As a result,* ***partial pressures/ concentrations of the reactants and products decrease****. According to Le Chatelier's Principle, the equilibrium will be* ***shifted from left to right*** *(in that direction where there is an increase in number of moles). The* ***equilibrium constant remains unchanged*** *since* ***the partial pressure/concentration of neon does not apply in the equilibrium constant expression****. The* ***rate of attainment of equilibrium reduces*** *as* ***some of the particles on collision do not react****.*

N.B Hence, when an inert gas is added to the system in equilibrium at constant pressure, there will be a shift of the equilibrium position to a direction where the number of moles increases, no effect on equilibrium constant but reduces the rate of attainment of equilibrium.

(e) Effect of adding a catalyst

***A catalyst is a substance which alters the rate of a chemical reaction but remains unchanged in quantity at the end of the reaction or at equilibrium*.**

A catalyst has **no effect on position of equilibrium** and **no effect on the value of equilibrium constant** but only **alters the rate of backward and forward reaction equally.** A catalyst therefore **increases the rate of attainment of equilibrium by decreasing the activation energy**.

The explanations given above are general. A question may require you just to state the effect of a constraint. This may not require you to go into details of explaining.

Questions

1. Sulphur dioxide reacts with oxygen according to the following equation.

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

   (a) State what would be happen to the **concentration of sulphur(VI) oxide** in the equilibrium mixture and give a reason for your answer if;
   - (i) the temperature was increased
   - (ii) nitrogen gas was added to the mixture at a constant pressure.
   - (iii) pressure was increased
   - (iv) more oxygen was added to system at equilibrium
   - (v) volume of the vessel in increased

2. The reaction between nitrogen and hydrogen at 25℃ and 10 atm takes place according to the following equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^{\theta} = -92\ kJmol^{-1}$$

   What would happen to the **concentration of ammonia** and the **value of the equilibrium constant** if;
   - (i) Helium was added to the equilibrium mixture at constant pressure?
   - (ii) the temperature was increased to 250℃ but the pressure remains at 10 atm?
   - (iii) Argon is added to the equilibrium mixture at constant volume?
   - (iv) some iron is added to the equilibrium mixture

3. Iodine is sparingly soluble in water but readily dissolves in potassium iodide according to the following equilibrium

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

   (a) Explain why iodine is sparingly soluble in water but very soluble in potassium iodide

   (b) (i) Write an expression for the concentration equilibrium constant, $\boldsymbol{K_c}$.

(ii) State any **three** characteristics of the above equilibrium.

(c) State and explain the effect of adding sodium thiosulphate solution to **the position of equilibrium**.

4. Phosphorus pentachloride decomposes at high temperatures according to the following equation.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

State how the **position of the equilibrium** and 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 added to the equilibrium
(iii) some phosphorus(III) chloride was removed from the equilibrium mixture
(iv) the temperature was increased
(v) volume of the container was decreased
(vi) adding a catalyst

5. When heated at 1atm, carbon dioxide decomposes according to the equation:

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

State and explain the effect of ;

(i) heating the carbon dioxide at 2 atmospheres on the equilibrium concentration of oxygen
(ii) carrying out the decomposition at a lower temperature on the value of the equilibrium constant, $\boldsymbol{K_p}$**.**

6. Hydrogen and iodine were heated in a 1 litre vessel. Explain what would happen to the equilibrium position of the reaction, equilibrium constant, and rate of attainment of equilibrium if;

(i) sodium thiosulphate solution was added to the vessel.
(ii) the pressure was increased
(iii) concentration of iodine was increased
(iv) helium gas was added at constant volume.

7. The esterification reaction for formation of ethylethanoate from ethanoic acid and ethanol is shown by the equation below.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l) \quad \Delta H = -ve$$

State how the amount of ethylethanoate and position of the equilibrium would be affected if:

(i) some ethanol is added to the system
(ii) some water is removed from the system
(iii) concentrated sulphuric acid is added
(iv) some sodium hydroxide solution is added
(v) the temperature was increased

8. Nitrogen and oxygen react endothermically at high temperatures according to the equation;

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

The equilibrium constant for the reaction at 2680K and 1 atm total pressure is 3.6×10^{-3}. Equal volumes of nitrogen and oxygen were mixed at 2680K and 1 atm total pressure and allowed to react until equilibrium is reached.

(a) Calculate the:
   (i) fraction of the original nitrogen used in the reaction
   (ii) fraction of nitrogen(II) oxide in the reaction mixture

(b) State what will happen to the value in (a)(ii) above and give a reason(s) if:
   (i) the pressure is increased to 10 atm
   (ii) the temperature is raised to 2780K
   (iii) a catalyst is added

9. Sulphur dioxide dichloride dissociates when heated according to the equation:

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

(a) At a temperature of 375℃ and an overall pressure of $101325 Nm^{-2}$, a sample of sulphur dioxide dichloride in the gas phase was found to be 84% dissociated. Calculate the value of equilibrium constant, $\boldsymbol{K_p}$.

(b) State, at constant temperature, the effect on the position of equilibrium and the value in (a) above of:
   (i) adding a catalyst
   (ii) compressing the system

10. Discuss the effect of each of the following factors on the position of equilibrium of a reversible reaction, the rate of attainment of equilibrium and the value of equilibrium constant.
   (i) Temperature
   (ii) Pressure
   (iii) Catalyst
   (iv) Concentration

INDUSTRIAL APPLICATION CHEMICAL EQUILIBRIUM

The knowledge of chemical equilibrium is applied industrially in the following processes;

- **Haber process**
- **Contact process**
- **Ostwald process**

1. Manufacture of ammonia (the Haber process)

The reaction between dry hydrogen (*obtained from natural gas*) and dry nitrogen (*from fractional distillation of liquid air*) to form ammonia is **exothermic** and occurs with a **decrease in volume**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\,;\ \Delta H^{\theta}(298K) = -92.4\ kJmol^{-1}$$

According to L*é* Chatelier's Principle , the yield of ammonia will be greatest at **low temperature** and **high pressure**.

At a low temperature however, rate of attainment of equilibrium is low and at high temperature, the position of the equilibrium is over to the left.

At high pressure, the cost of the equipment and running costs are high.

Therefore, in practice, a compromise has to be struck. The conditions used in this process are therefore;

- ***Pressures between 200-1000 atmospheres***
- ***Temperature of about 450-550^{o}C***
- ***Finely divided iron catalyst***

2. Manufacture of sulphuric acid (the Contact process)

The conversion of **Sulphur dioxide** (**obtained by burning Sulphur in air, roasting iron pyrites, copper pyrites or oxidation of zinc blende or burning hydrogen sulphide from crude oil in air**) and **oxygen** (obtained from **fractional distillation of liquid air**) to Sulphur trioxide is an **exothermic reaction** and occurs with a **decrease in volume**.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^{\theta}(298K) = -197.6\ kJmol^{-1}$$

According to L*é* Chatelier's Principle , the yield of ammonia will be greatest at **low temperature** and **high pressure**.

At a low temperature however, the rate of attainment of equilibrium is very slow.

Increase in pressure gives an increased yield of Sulphur trioxide but the effect is small and the yield is good even at pressures just above atmospheric pressure but not as high as those used in the Haber Process.

Still, at high pressures, sulphur dioxide liquefies.

Therefore, in practice, a compromise has to be struck. The conditions used in this process are therefore;

- ***Pressures between 1-3 atmospheres***
- ***Temperature of about 450-500 ^{o}C***
- ***Vanadium(V) oxide catalyst***

Question

Sulphur dioxide is a raw material used in manufacture of sulphuric acid by the contact process.

(a) With relevant equations, describe the various ways how sulphur dioxide used in this process may be obtained on a large scale.

(b) Describe how sulphuric acid can be manufactured using one of the sources above.

(c) Briefly describe how the sulphuric acid can be converted to superphosphate fertiliser.

(a) Sulphur dioxide can be obtained by burning sulphur in air

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

or by roasting iron pyrites in air

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

or roasting zinc blende in air

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

or roasting copper pyrites

$$2CuFeS_2(s) + 4O_2(g) \longrightarrow Cu_2S(s) + 3SO_2(g) + 2FeO(s)$$

(b) Iron pyrites are roasted in air to form iron(III) oxide and sulphur dioxide.

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

*The **sulphur dioxide** obtained above and **oxygen** obtained by fractional distillation of liquid air **are purified** to **clear them off any dust that may poison the catalyst** and **dried.** The purified gases are passed over **Vanadium(V) oxide catalyst** at **temperatures about 450-500 ^{o}C** and **pressures between 1-3 atmospheres** to form **sulphur trioxide.***

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

*The sulphur trioxide is **dissolved in concentrated sulphuric acid** to form a fuming liquid called **oleum**.*

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

*The oleum is carefully **diluted with a correct amount of water** to form 98% concentrated sulphuric acid.*

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

N.B. 1. Vanadium pentoxide is preferred over Platinum as catalyst because it is cheaper and not commonly poisoned by impurities

*2. The sulphur trioxide is not dissolved in water because its reaction with water is **highly exothermic** and it leads to **formation of sulphuric acid sprays** that damage plants and animals*

(c) Calcium phosphate is dissolved and stirred in about 65% sulphuric acid to form a mixture calcium sulphate and calcium dihydrogen phosphate. The product is dried and forms the superphosphate fertiliser.

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(aq) \longrightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4(s)$$

N.B; The Single Superphosphate(SSP) fertiliser made above is less efficient because it is contaminated with Calcium sulphate. A more efficient fertiliser called Triple Superphosphate fertiliser is formed by using concentrated sulphuric acid instead.

$$Ca_3(PO_4)_2(s) + 4H_3PO_4(aq) \longrightarrow 3Ca(H_2PO_4)_2(s)$$

Details of these process for conversion of ammonia formed by Haber process to nitric acid are discussed in DEMISTYFYING INORGANIC CHEMISTRY under chemistry of period 3 elements by the same author)

Questions

1. Ammonia is manufactured from hydrogen and nitrogen by the Haber process.
   (a) Write the equation for the reaction.
   (b) State one source of hydrogen and one source of nitrogen used in the above process
   (c) Write an expression for the equilibrium constant, K_p for the reaction.
   (d) State **Le Chatelier's principle**.
   (e) The reaction in (a) above is exothermic. State and explain the effect on the above equilibrium of:
      (i) increasing pressure
      (ii) removing ammonia from the mixture of gases
   (f) Explain why the synthesis of ammonia is operated at a temperature of 400℃.
   (g) (i) Name the catalyst used in the Haber process
      (ii) Describe how the catalyst works
      (iii) Explain the effect of the catalyst on the position of the equilibrium.
   (h) Write equations to show how ammonia is converted to nitric acid.
2. Sulphur dioxide is a raw material used in manufacture of sulphuric acid by the contact process. It is initially converted exothermically to sulphur trioxide during the process. On industrial scale, this conversion carried out at 450℃ and 2 atmospheres in presence of a catalyst.
   (a) Write equation for formation of sulphur trioxide in the contact process
   (b) Name the catalyst used

(c) State the reasons for the choice of the temperature and pressure used to convert sulphur dioxide to sulphur trioxide.

(d) Sulphur trioxide reacts with water to form sulphuric acid.

(i) Write equation for the reaction.

(ii) State the hazard of the reaction in d(i) above and describe how it is avoided in the contact process.

(e) Concentrated sulphuric acid contains 98% of the acid. Calculate the mass of concentrated sulphuric acid required to make $500cm^3$ of 1.5M solution of sulphuric acid.

(f) Name one reagent that can be used to identify the anion in sulphuric acid. State what would be observed and write the equation for the reaction that takes place when the reagent you have named is used.

(g) State two large scale uses of sulphuric acid.