

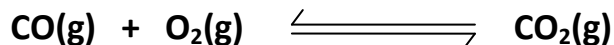
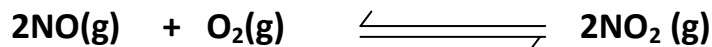
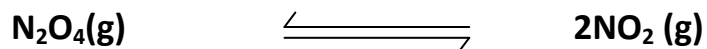
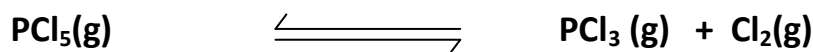
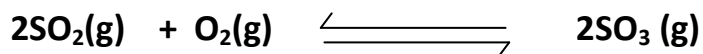
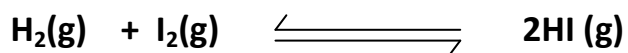
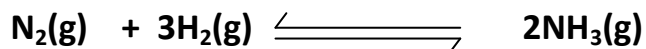
CHEMICAL EQUILIBRIA

It deals with reversible reactions that involve molecules. In a reversible reaction, reactants form products which also react to form reactants. The reaction takes place in both directions, from left to right and from right to left (i.e in the forward and backward directions).The reaction does not go to completion. At equilibrium the forward and backward reactions are taking place at the same rate (equilibrium is dynamic). The mixture contains both reactants and products. The equations are represented with reversible arrows.

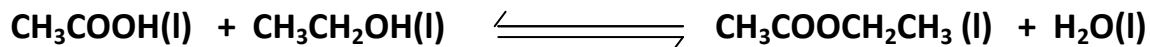
Examples of reversible reactions

- Homogeneous reactions (where both reactants and products are in the same phase)

i) Involving gases which are in a closed container

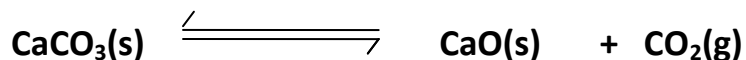


ii) involving liquids

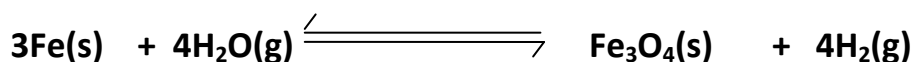


- Heterogeneous reactions (reactants and products are in different phases)

when calcium carbonate is heated in a sealed container



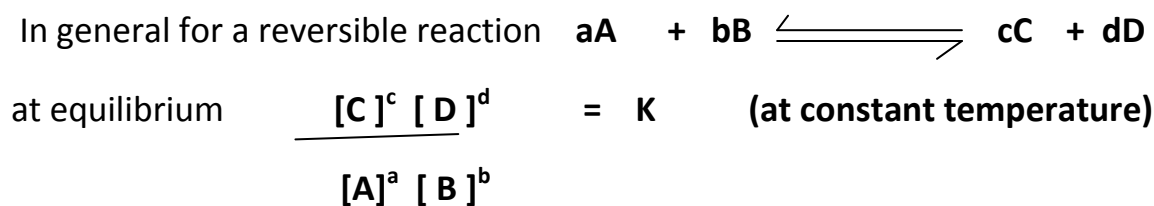
When iron and steam are heated in a closed container



LAW OF MASS ACTION (THE EQUILIBRIUM LAW)

Reversible reactions at equilibrium obey the law of mass action which states that **at equilibrium the ratio of the product of concentrations of products (raised to their coefficients in the equation) to the product of concentrations of reactants (raised to their coefficients) is a constant at constant temperature**

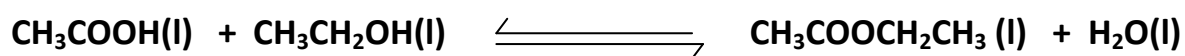
"appropriate power" means raised to the power of number of moles taking part in the balanced equation



[] = concentration in moles/dm³

K is the equilibrium constant. It is a constant for a particular reaction and it only changes with change in temperature. It is not affected by the amounts of reactants, catalysts, pressure and other factors.

For reactions which involve gases and liquids, the amounts are expressed as concentrations in moles dm⁻³. The equilibrium constant is in terms of concentrations and has symbol K_c. e.g for the reaction



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

At 25°C, K_c is 4.0 .

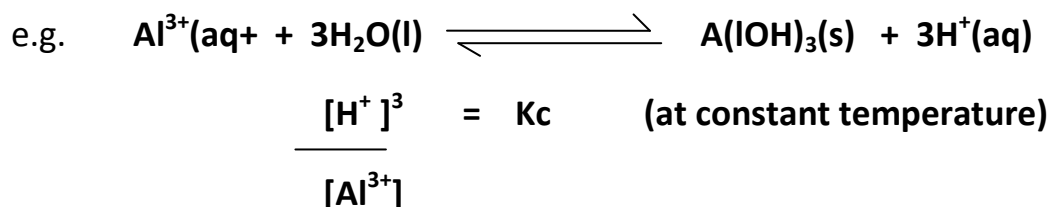
The units of K_c depend on a particular reaction. If the number of moles on the left are equal to the moles on the right, K_c has no units (the units cancel out).

e.g. For this reaction above, Kc has no units because the units of concentration cancel out. The number of moles of reactants are equal to number of moles of products

NOTE

i) For reactions involving water as a solvent i.e in aqueous solution water is in excess and its concentration is constant It is not involved in the expression of the equilibrium constant

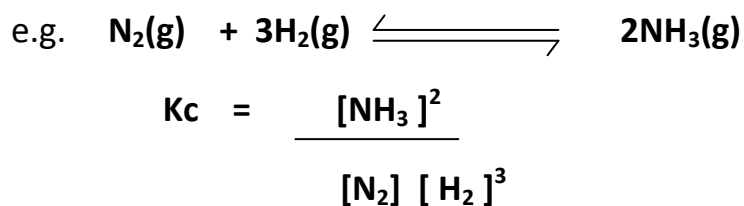
ii) If a solid is present in a reaction it is not involved in the expression of the equilibrium constant because its concentration is constant.



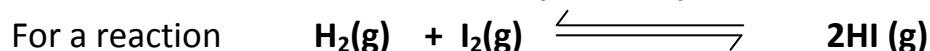
The units of Kc for this reaction is $(\text{mol dm}^{-3})^2 = \text{mol}^2 \text{dm}^{-6}$ or $\text{mol}^2 \text{l}^{-2}$

When the reaction is in gaseous phase concentrations can be expressed

i) in mol dm^{-3} (or mol l^{-1}). The equilibrium constant is Kc



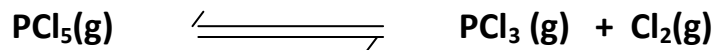
The units of Kc for this reaction is $(\text{mol dm}^{-3})^{-2} = \text{mol}^{-2} \text{dm}^6$ or $\text{mol}^{-2} \text{l}^2$ e.g.



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

Kc has no units because the number of moles of reactants are equal to number of moles of products. The units cancel out

For the reaction

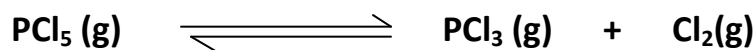


$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

The units of K_c for this reaction is mol dm^{-3} or mol l^{-1}

Example

3. Phosphorus (v) chloride dissociates when heated according to the equation



At equilibrium the mixture contained 4.20 of chlorine, 8.13g of phosphorus(III) chloride and 196.1 of phosphorus(V) chloride in a 4.5dm^3 container. Calculate the equilibrium constant K_c (P = 31, Cl = 35.5

$$\text{PCl}_5 = 31 + (5 \times 35.5) = 208.5$$

$$\text{PCl}_3 = 31 + (3 \times 35.5) = 137.5$$

$$\text{Cl}_2 = 2 \times 35.5 = 71$$

$$\text{Moles of PCl}_5 = \frac{196.1}{208.5} = 0.9405 \quad [\text{PCl}_5] = \frac{0.9405}{4.5} = 0.209 \text{ mol dm}^{-3}$$

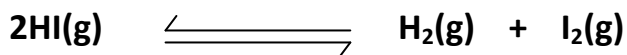
$$\text{Moles of PCl}_3 = \frac{8.13}{137.5} = 0.0591 \quad [\text{PCl}_3] = \frac{0.0591}{4.5} = 0.01313 \text{ mol dm}^{-3}$$

$$\text{Moles of Cl}_2 = \frac{4.20}{71} = 0.0591 \quad [\text{Cl}_2] = \frac{0.0591}{4.5} = 0.01313 \text{ mol dm}^{-3}$$

$$\begin{aligned} K_c &= \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \\ &= \frac{0.01313 \times 0.01313}{0.209} \\ &= 8.25 \times 10^{-4} \text{ mol l}^{-1} \end{aligned}$$

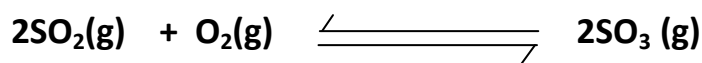
Questions

1) Hydrogen iodide decomposes according to the equation



At equilibrium at 450°C the mixture contained 2.48×10^{-3} moles of hydrogen, 2.51×10^{-3} moles of iodine and 1.70×10^{-2} moles of hydrogen iodide in a 1 litre container. Calculate the equilibrium constant K_c .

2) sulphur dioxide and oxygen react according to the equation



At equilibrium at a certain temperature the mixture contained 1.33 moles of sulphur dioxide, 0.667 moles of oxygen and 0.667 moles sulphur trioxide in a 500cm^3 vessel. Calculate the equilibrium constant K_c

Equilibrium constant in terms of partial pressures of gases (K_p)

The amounts of gases in a mixture can also be expressed as partial pressures (p). The partial pressure (p_x) of a gas in a mixture of gases is the pressure that gas will exert if it occupied the available space alone. It is a product of the total pressure and mole fraction of the component gas (it is the pressure contributed by a component in a mixture of gases to the total pressure of the gas)

$$P_x = \frac{n}{N} \times P_{\text{Total}}$$

n = no. of moles of the gas. N = Total no of moles of all gases. P_{Total} is the total pressure.

The mole fraction of a component in a mixture is the ratio of the number of moles of that component to the total number of moles of all the components.

$$X_a = \frac{n_a}{n_a + n_b + n_c \dots}$$

The total pressure of a gas is the sum of the partial pressures of the gases in the mixture

$$P = P_a + P_b + P_c \dots$$

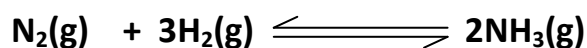
e.g. Atmospheric pressure is 101325 Nm^{-2} or 760mmHg or 1atmosphere.

The partial pressure of nitrogen is $P_{\text{N}_2} = \frac{78}{100} \times 101325 = 79033.5 \text{ Nm}^{-2}$

The partial pressure of oxygen is $P_{\text{O}_2} = \frac{21}{100} \times 101325 = 21278.25 \text{ Nm}^{-2}$

The sum of partial pressures (including other components of air) is 101325 Nm^{-2}

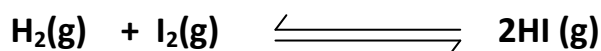
The equilibrium constant is in terms of partial pressures with symbol K_p for the reaction



is
$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3}$$
 p is the partial pressure of the gas

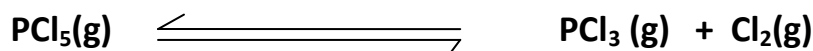
The units of K_p for this reaction are the units of (pressure)⁻² e.g atm^{-2} , Pa^{-2} or $(\text{Nm}^{-2})^{-2} = \text{N}^{-2}\text{m}^4$

For a reaction



$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} \times P_{\text{I}_2}}$$
 $p = \text{partial pressure}$
 K_p has no units .

For the reaction

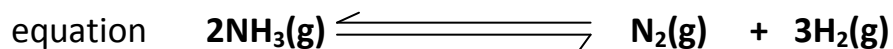


$$K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

The units of Kp for this reaction are the units of pressure i.e. atm, Pa or Nm⁻²

Example

2 moles of ammonia was heated in a closed container at 700K at a pressure of 79atm. At equilibrium the mixture contained 21% of nitrogen and 63% of hydrogen. Calculate the equilibrium constant Kp



$$\% \text{NH}_3 = 100 - (21 + 63) = 16\%$$

$$P_{\text{NH}_3} = 79 \times \frac{16}{100} = 12.64 \text{ atm.}$$

$$P_{\text{N}_2} = 79 \times \frac{21}{100} = 16.59 \text{ atm.}$$

$$P_{\text{H}_2} = 79 \times \frac{63}{100} = 49.77 \text{ atm.}$$

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

$$\begin{aligned} K_p &= \frac{16.59 \times (49.77)^3}{(12.64)^2} \\ &= 1.28 \times 10^4 \text{ atm}^2 \end{aligned}$$

Questions.



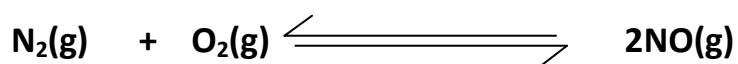
Write the expression for the equilibrium constant Kc or Kp and give its units if

- A, B, C and D are all liquids
- A, B, C and D are all gases
- A and C are liquids but B and D are solids
- Only C is a gas but A, B and D are solids

2) 4 moles of dinitrogen tetroxide was heated at 420K at a pressure of 9atmospheres. At equilibrium the mixture was found to contain 1.5 moles of nitrogen dioxide and 2.50 moles of dinitrogen tetroxide. Find the equilibrium constant Kp

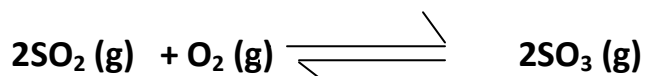
3) 1 mole of phosphorus(V) chloride was heated in a closed container at 400°C. At equilibrium, the partial pressures of phosphorus(V) chloride, phosphorus(III) chloride and chlorine were 5.1Kpa, 95Kpa and 95Kpa respectively. Calculate the equilibrium constant Kp

4)Nitrogen reacts with oxygen according to the equation



At equilibrium at a pressure of 5 atmospheres, the mixture contains 5% of nitrogen(II) oxide, 47.5% of nitrogen and 47.5% of oxygen. Calculate the equilibrium constant Kp

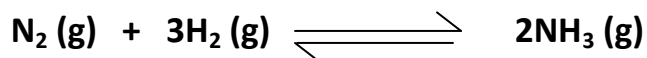
5)Sulphur dioxide is oxidized to sulphur trioxide according to the equation



At 700°C and a total pressure of one atmosphere the equilibrium partial pressures of sulphur dioxide and oxygen are 0.27 and 0.41 atmospheres respectively.

Calculate the equilibrium constant Kp for the reaction.

6)Nitrogen and hydrogen react to form ammonia according to the equation

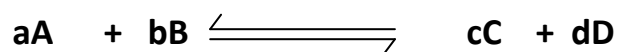


At 650°C the equilibrium constant Kp is $4.82 \times 10^{-5} \text{ atm}^{-2}$ and the partial pressures of nitrogen and hydrogen were 30 and 120 atmospheres respectively.

Calculate the partial pressure of ammonia.

POSITION OF EQUILIBRIUM

It is a measure of the extent to which a reversible reaction has taken place. e.g.in a reaction



If small amounts of A and B have reacted compared to C and D, the equilibrium mixture contains small amounts of C and D and large amounts of A and B. The position of equilibrium lies to the left hand side. The equilibrium constant is small. The reaction yields small amounts of products

If large amounts of A and B have reacted compared to C and D, the equilibrium mixture contains large amounts of C and D and small amounts of A and B. The position of equilibrium lies to the right hand side. The equilibrium constant is big. The reaction yields large amounts of products

EFFECT OF CHANGING VARIOUS CONDITIONS ON A REVERSIBLE REACTION AT EQUILIBRIUM (Le Chaterier's principle)

Le Chaterier's principle states that **When an external factor is applied to a reversible reaction that is at equilibrium, the position of equilibrium will shift in a direction that cancels out the effect of the applied factor.** The position of equilibrium shifts in the opposite direction. The factors are

- 1.Change in temperature
- 2.Change in pressure (for gases)
- 3.Change in concentration
- 4.Addition of a catalyst
5. Addition of an inert gas (for gases)

1)Effect of changing temperature

This depends on whether the forward reaction is exothermic or endothermic. An exothermic reaction takes place with liberation of heat in the forward direction. The backward reaction is endothermic. e.g.



increase in temperature

effect on position of equilibrium Since the forward reaction is exothermic (liberates heat), **increase in temperature shifts the position of equilibrium from right to left.** More of ammonia reacts to form nitrogen and hydrogen.

effect on the equilibrium constant since the position of equilibrium shifts from right to left, the concentration of ammonia will reduce whereas that of nitrogen and hydrogen will increase. The value of the equilibrium constant reduces.

For all exothermic reactions increase in temperature reduces the equilibrium constant.

effect on the rate of attainment of equilibrium

For a reversible reaction increase in temperature increases the rate of both the forward and backward reaction equally. It therefore increases the rate of attainment of equilibrium (equilibrium is reached in a shorter time)

For an endothermic reaction The forward reaction takes place with absorption of heat hence with decrease in temperature. If temperature is increased

The position of equilibrium shifts from left to right. More nitrogen and hydrogen combine to form ammonia.

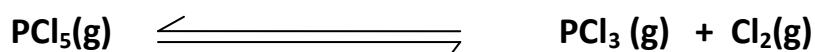
The concentration of nitrogen and hydrogen reduces whereas that of ammonia increases. **The value of the equilibrium constant increases.** For all endothermic reactions, increase in temperature increases the equilibrium constant.

The rate of attainment of equilibrium increases since increase in temperature increases the rate of both the forward and backward reactions equally.

2) Effect of changing pressure

Change in pressure only affects reactions involving gases. It has no effect on reactions involving liquids or solids. The effect of pressure depends on the change in number of moles (or volume) of gases as follows

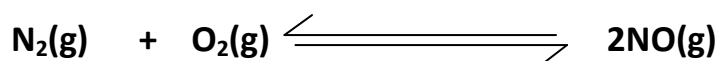
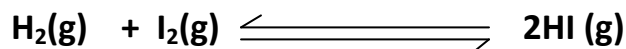
Reactions in which the forward reaction takes place with increase in number of moles(or volume) e.g.



The number of moles on the right hand side is greater than that on the left.

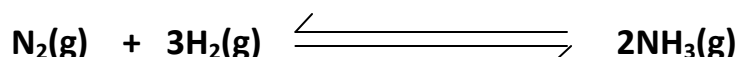
Increase in pressure shifts the position of equilibrium from right to left. The amount of phosphorus(III) chloride and chlorine reduce whereas that of phosphorus(V) chloride increases. **But there is no change in the equilibrium constant** (it only changes with change in temperature). This means the individual concentrations or partial pressures of gases will adjust themselves in order to maintain a constant value of the equilibrium constant (K_c or K_p) . **Increase in pressure increases the rate of attainment of equilibrium.**

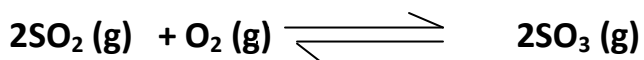
For reactions which take place with no change in number of moles (or volume) e.g



Change in pressure has no effect on the position of equilibrium and on the **equilibrium constant**. **Increase in pressure increases the rate of attainment of equilibrium**

For reactions which take place with decrease in number of moles (or volume) of gas e.g





Increase in pressure shifts the position of equilibrium from left to right . It has no effect on the value of the equilibrium constant. This means the individual concentrations or partial pressures of gases will adjust themselves in order to maintain a constant value of the equilibrium constant (K_c or K_p) . **Increase in pressure increases the rate of attainment of equilibrium.**

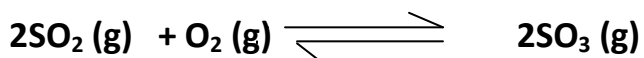
3)Effect of adding a catalyst

When a reversible reaction is at equilibrium, addition of a catalyst has no effect on position of equilibrium and on the value of the equilibrium constant (It does not change the amounts of reactants or products). A catalyst increases the rate of both the forward and backward reactions. It increases the rate of attainment of equilibrium.

4)Effect of changing concentration of one of the substances

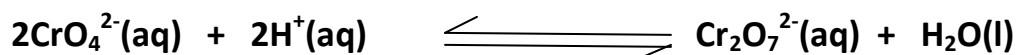
examples.

For the following reversible reaction at equilibrium



If the concentration of oxygen or sulphur dioxide is increased, the position of equilibrium will shift from left to right in order to reduce that concentration. If sulphur trioxide is added to the equilibrium mixture, the position of equilibrium will shift from right to left. The concentrations must adjust themselves in order to maintain a constant value of the equilibrium constant. If the concentration of sulphur trioxide is reduced, the position of equilibrium will shift from left to right to increase its amount.

For a reversible reaction



yellow

orange

If an acid is added to the equilibrium mixture (concentration of hydrogen ions is increased) the position of equilibrium will shift from left to right. Hydrogen ions will react with chromate(VI) ions to form dichromate(VI) ions. The colour of the solution changes from yellow to orange.

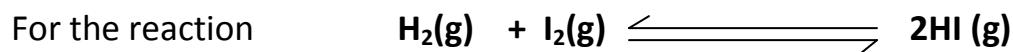
If an alkali is added, the hydroxide ions react with hydrogen ions. The concentration of hydrogen ions is reduced. The position of equilibrium will shift from right to left. The colour of the solution changes from orange to yellow. So if the concentration of something is increased, the position of equilibrium will shift to the opposite direction. If it is reduced, the position of equilibrium will shift in its direction

5) Effect of adding an inert gas

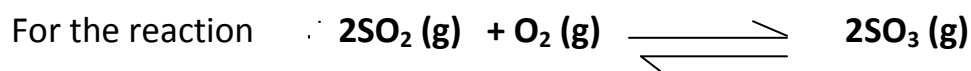
An inert gas is a gas which will not react with any of the substances in the equilibrium mixture. When it is added to a reaction involving gases at equilibrium

a) At constant pressure the partial pressures of individual gases must reduce so that the total pressure remains constant. So addition of an inert gas at constant pressure reduces the partial pressures. The position of equilibrium will shift in a direction where the partial pressures are higher i.e. where the number of moles are more. Addition of an inert gas has no effect on the equilibrium constant.

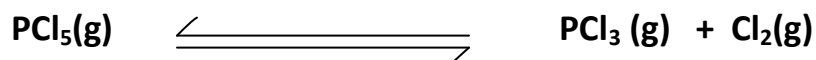
Examples



It takes place with no change in number of moles of a gas. Addition of an inert gas at constant pressure has no effect on the position of equilibrium



The forward reaction takes place with a decrease in number of moles (and partial pressure). Addition of an inert gas at constant pressure reduces the partial pressures of the gases. The position of equilibrium shifts from right to left but there is no change in the value of the equilibrium constant.



The forward reaction takes place with increase in number of moles (and partial pressure). Addition of an inert gas at constant pressure reduces the partial pressures of gases. The position of equilibrium shifts from left to right.

b) At constant volume. If an inert gas is added to the reaction mixture at equilibrium at constant volume, the pressure increases whereas the partial pressures do not change. It therefore has no effect on the position of equilibrium and the value of the equilibrium constant.

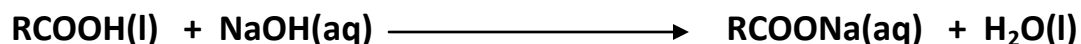
EXPERIMENTS TO FIND EQUILIBRIUM CONSTANTS

Summary

Known amounts of reactants (in moles) are put in a sealed container. The mixture is shaken and left to settle at constant temperature until equilibrium is established. At equilibrium, a known volume of the solution is pipetted and titrated against a standard solution of a suitable reagent. The concentration of one of the substances is calculated. It is used to find the concentrations of each of the substances present at equilibrium. The equilibrium constant is calculated from the expression .

1) To find the equilibrium constant for the reaction between a carboxylic acid and an alcohol

A known mass of a carboxylic acid and a known mass of an alcohol are mixed in sealed container. The mixture is shaken and left to settle at constant temperature until equilibrium is established. At equilibrium a known volume of the mixture is pipetted and titrated against standard sodium hydroxide solution using phenolphthalein indicator. It reacts with the acid



The number of moles of the acid is calculated. Using the equation for the reaction the number of moles of the alcohol, water and the ester is calculated. The molar concentration of each is calculated.

If the original moles of acid and the alcohol are **a** and **b** respectively and the number of moles of the acid at equilibrium is **x** (from the calculation). Then

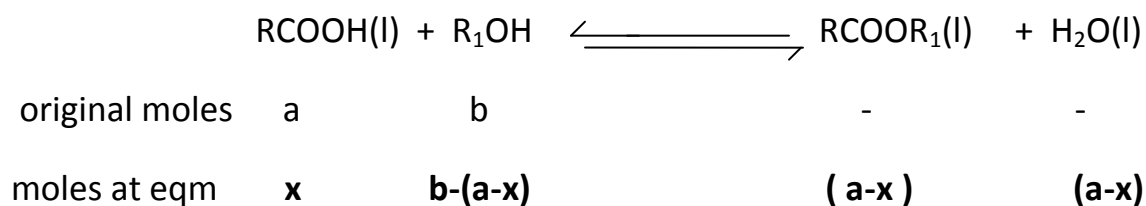
no. of moles of acid that reacted = (a -x)

no. of moles of the alcohol that reacted = (a-x) since mole ratio is 1 : 1

no. of moles of alcohol present = b - (a-x)

no. of moles of the ester = (a-x) they are equal to moles of acid that reacted

no. of moles of the water = (a-x) . It is summarised as follows



$$K_c = \frac{[\text{RCOOR}_1] [\text{H}_2\text{O}]}{[\text{RCOOH}] [\text{R}_1\text{OH}]}$$

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

Examples

1) 24g of ethanoic acid and 23g of ethanol were mixed and left to reach equilibrium at 298K. At equilibrium the mixture was poured in water and made to 250cm³. 25cm³ of the solution required 26.5 cm³ of 0.4M sodium hydroxide. Calculate the equilibrium constant Kc

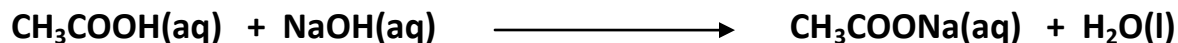
$$\text{CH}_3\text{COOH} = (2 \times 12) + (2 \times 16) + (4 \times 1) = 60$$

$$\text{Moles of CH}_3\text{COOH} = \frac{24}{60} = 0.4$$

$$\text{CH}_3\text{CH}_2\text{OH} = (2 \times 12) + 16 + 6 \times 1 = 46$$

$$\text{Moles of CH}_3\text{CH}_2\text{OH} = \frac{23}{46} = 0.5$$

$$\text{NO of moles of NaOH that reacted with CH}_3\text{COOH} = \frac{26.5 \times 0.4}{1000} = 0.0106$$

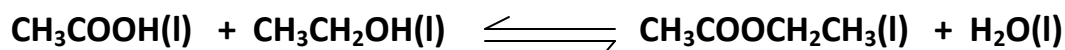


$$\text{Moles of CH}_3\text{COOH} = 0.0106 \text{ (mole ratio between CH}_3\text{COOH : NaOH is 1:1)}$$

25 cm³ of solution contain 0.0106 moles of CH₃COOH

$$250\text{cm}^3 \text{ contain } \frac{0.0106 \times 250}{25} = 0.106$$

number of moles of each present at equilibrium can be summarized as



$$\text{at eqm.} \quad (0.4 - x) \quad (0.5 - x) \quad \times \quad \times$$

where x is the number of moles of the acid that reacted

$$\text{Hence } (0.4 - x) = 0.106$$

$$x = 0.294$$

Therefore moles of each present at equilibrium are as follows:

$$\text{Moles of CH}_3\text{COOH} = 0.106$$

$$\text{Moles of CH}_3\text{CH}_2\text{OH} = 0.5 - 0.294 = 0.206$$

$$\text{Moles of CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 = 0.294$$

$$\text{Moles of H}_2\text{O} = 0.294$$

Molar concentrations at equilibrium are as follows :

$$[\text{CH}_3\text{COOH}] = \frac{0.106 \times 1000}{250} = 0.424 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{CH}_2\text{OH}] = \frac{0.206 \times 1000}{250} = 0.824 \text{ mol dm}^{-3}$$

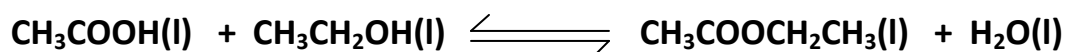
$$[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3] = \frac{0.294 \times 1000}{250} = 1.176 \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{O}] = \frac{0.294 \times 1000}{250} = 1.176 \text{ mol dm}^{-3}$$

$$\begin{aligned} K_c &= \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]} \\ &= \frac{1.176 \times 1.176}{0.424 \times 0.824} \\ &= 3.96 \end{aligned}$$

2) 1 mole of ethanoic acid was reacted with 4 moles of ethanol at 25°C. At equilibrium the mixture contained 0.93 moles of ethylethanoate. Calculate the equilibrium constant K_c

The number of moles of each present at equilibrium can be summarized as



at eqm. (1 - x) (4 - x) x x

where x is the number of moles of ethylethanoate

$$x = 0.93$$

Therefore moles of each present at equilibrium are as follows:

$$\text{Moles of CH}_3\text{COOH} = 1 - 0.93 = 0.07$$

$$\text{Moles of CH}_3\text{CH}_2\text{OH} = 4 - 0.93 = 3.07$$

$$\text{Moles of CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 = 0.93$$

$$\text{Moles of H}_2\text{O} = 0.93$$

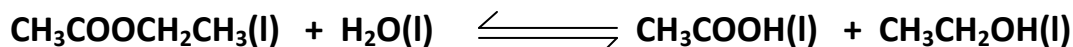
Since volume is not given assume it is 1 dm³

$$\begin{aligned}
 K_c &= \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3] [\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}] [\text{CH}_3\text{CH}_2\text{OH}]} \\
 &= \frac{0.93^2}{0.07 \times 0.307} \\
 &= 4.02
 \end{aligned}$$

Questions

1) 44g of ethylethanoate was mixed with 36g of water. At equilibrium the mixture was diluted to 250cm³. 25cm³ of the solution required 29.5 cm³ of 1M sodium hydroxide. Calculate the equilibrium constant K_c.

Ethylethanoate reacts with water (undergoes hydrolysis) according to the equation



2) 1 mole of ethanoic acid and 0.5 moles of ethanol were reacted at 30°C. At equilibrium 0.42 moles of ethanoic acid had reacted. Calculate K_c.

3) 1mole of ethanoic acid was mixed with 2 moles of ethanol and 1 mole of water. At equilibrium 0.257 moles of ethanoic acid was present. Calculate K_c.

Calculation of molar concentrations given K_c

example

0.9g of ethanoic acid and 0.69g of ethanol were allowed to reach equilibrium at 30°C. Calculate the

a) number of moles of each at equilibrium. (K_c = 3.6).

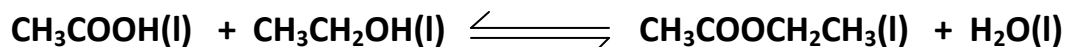
b) mass of ethyl ethanoate at equilibrium

$$\text{CH}_3\text{COOH} = (2 \times 12) + (2 \times 16) + (4 \times 1) = 60$$

$$\text{Moles of CH}_3\text{COOH} = \frac{0.9}{60} = 0.015$$

$$\text{CH}_3\text{CH}_2\text{OH} = (2 \times 12) + 16 + 6 \times 1 = 46$$

$$\text{Moles of CH}_3\text{CH}_2\text{OH} = \frac{0.69}{46} = 0.015$$



$$\text{at eqm. } (0.015 - x) \quad (0.015 - x) \quad \quad \quad x \quad \quad \quad x$$

x is the number of moles of ethyl ethanoate at equilibrium

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

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

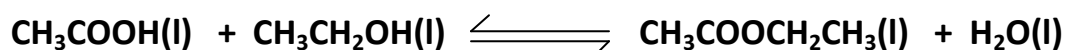
$$x = 9.83 \times 10^{-3} \text{ moles}$$

$$\text{b) CH}_3\text{COOCH}_2\text{CH}_3 = (4 \times 12) + (2 \times 16) + 8 = 88$$

$$\text{Mass of CH}_3\text{COOCH}_2\text{CH}_3 = (9.83 \times 10^{-3}) \times 88$$

$$= 0.86\text{g}$$

2) 2 moles of ethanoic acid and 1 mole of ethanol were allowed to reach equilibrium at 20°C. Calculate the mass of ethylethanoate at equilibrium ($K_c = 4$)



$$\text{initially} \quad 2 \quad \quad 1 \quad \quad \quad - \quad \quad \quad -$$

$$\text{at eqm. } (2 - x) \quad (1 - x) \quad \quad \quad x \quad \quad \quad x$$

x is the number of moles of ethyl ethanoate at equilibrium

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

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

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

$$3x^2 - 12x + 8 = 0$$

$x = 0.85$ or 3.16 but there can't be 2 amounts of the ester. only one of them is correct. 3.16 is not possible since it is greater than the initial amounts of the acid and alcohol. $x = 0.85$

No. of moles of ethylethanoate at eqm = 0.85

$$\text{CH}_3\text{COOCH}_2\text{CH}_3 = (4 \times 12) + (2 \times 16) + 8 = 88$$

Mass of ethylethanoate at eqm = $0.85 \times 88 = 74.8\text{g}$

Question

1 mole of ethanoic acid, 3 moles of ethanol and 3 moles of water were left to come to equilibrium at room temperature. Calculate the mass of

a) ethanol

b) ethyl ethanoate at equilibrium (Kc = 4.0)

2) 0.5 moles of ethylethanoate and 2 moles of water were left to reach equilibrium at 25°C . Calculate the mass of

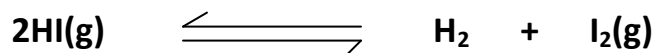
a) ethylethanoate

b) ethanoic acid present at equilibrium (Kc = 0.25)

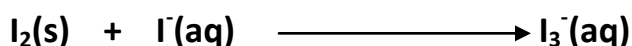
3) 1mole of ethyl ethanoate was left with 1 mole of water to come to equilibrium. Calculate the mass of ethylethanoate present at equilibrium (Kc = 0.25)

To find the equilibrium constant(Kc) for the decomposition of hydrogen iodide

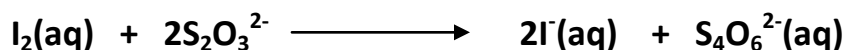
A known amount (a moles) of hydrogen iodide is put in a glass bulb. The bulb is heated and maintained at constant temperature until equilibrium is established. They react according to the equation



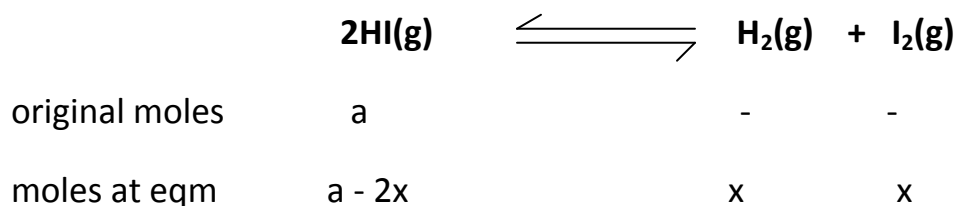
At equilibrium, the bulb is rapidly cooled and broken under potassium iodide solution. It dissolves iodine to form triiodide ions.



The iodine liberated is titrated against a standard solution of sodium thiosulphate using starch indicator.



The number of moles of iodine is calculated. Using the mole ratio for the reaction between hydrogen and iodine, the number of moles of each at equilibrium is calculated



where x are moles of iodine present

x = moles of iodine that reacted.

If the volume of the glass bulb is known, the molar concentration of each is calculated (in moles dm^{-3})

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

$$\text{Moles of HI at eqm} = 0.012 - 2x = 0.012 - 2(0.00335) = 0.0053$$

$$\text{moles of H}_2 = x = 0.00335$$

$$\text{moles of I}_2 = x = 0.00335$$

$$\text{c) } K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \quad [] \text{ is conc. in moles/litre}$$

$$[\text{H}_2] = \frac{0.00335 \times 1000}{600} = 5.583 \times 10^{-3}$$

$$[\text{I}_2] = \frac{0.00335 \times 1000}{600} = 5.583 \times 10^{-3}$$

$$[\text{HI}] = \frac{0.0053 \times 1000}{600} = 8.833 \times 10^{-3}$$

$$K_c = \frac{(5.583 \times 10^{-3})^2}{(8.833 \times 10^{-3})^2} = 0.399$$

$$= 0.40$$

d) The reaction is exothermic in the forward direction. Increase in temperature shifts the position of equilibrium from right to left. The concentration of hydrogen and iodine reduces whereas the concentration of hydrogen iodide increases. The value of the equilibrium constant reduces.

2. Carbon monoxide reacts with steam according to the equation



Equal volumes of carbon monoxide and steam were reacted in a 2dm³ vessel at 1023 K. At equilibrium the vessel was found to contain 27.2% of hydrogen.

a) Calculate the value of K_c

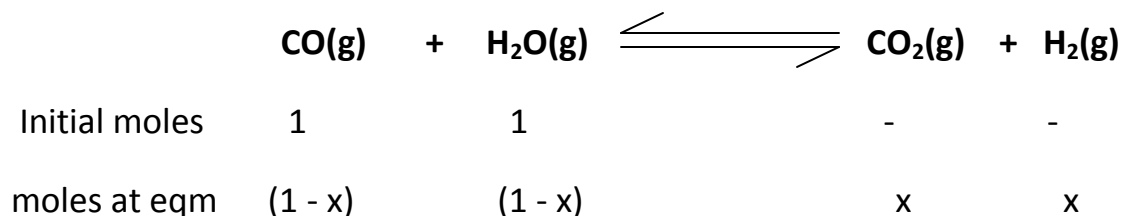
b) State the effect on the position of equilibrium and the value of K_c if

i) Temperature is increased

ii) an inert gas was added at constant temperature

iii) pressure was increased

Assuming the initial moles of CO and H₂ were 1 each



$$\text{Total no. of moles at eqm} = (1 - x) + (1 - x) + x + x = 2$$

$$\% \text{ of hydrogen} = \frac{x}{2} \times 100 = 27.2$$

$$x = 0.544$$

so the number of moles of each at equilibrium are as follows

$$\text{CO} = 1 - 0.544 = 0.456$$

$$\text{H}_2\text{O(g)} = 1 - 0.544 = 0.456$$

$$\text{CO}_2 = 0.544$$

$$\text{H}_2 = 0.544$$

molar concentrations are:

$$[\text{CO}] = \frac{0.456}{2} = 0.228 \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{O}] = \frac{0.456}{2} = 0.228 \text{ mol dm}^{-3}$$

$$[\text{CO}_2] = \frac{0.544}{2} = 0.272 \text{ mol dm}^{-3}$$

$$[\text{H}_2] = \frac{0.544}{2} = 0.272 \text{ mol dm}^{-3}$$

$$K_c = \frac{[\text{CO}_2] [\text{H}_2]}{[\text{CO}] [\text{H}_2\text{O}]}$$

$$= \frac{(0.272)^2}{(0.228)^2}$$

$$= 1.42$$

b) i) The forward reaction is exothermic. Increase in temperature shifts the position of equilibrium from right to left (in the backward direction). This reduces the concentration of carbon dioxide and hydrogen and increases the concentration of carbon monoxide and steam. The equilibrium constant reduces.

ii) The forward reaction takes place with no change in volume. Addition of an inert gas at constant temperature has no effect on the position of equilibrium and the value of the equilibrium constant.

iii) The forward reaction takes place with no change in volume. Increase in pressure has no effect on the position of equilibrium and on the value of the equilibrium constant.

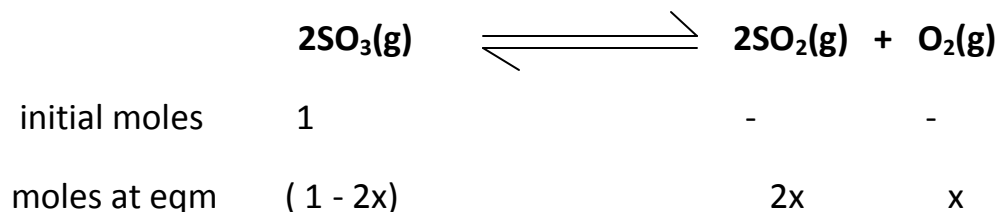
3) 1 mole of sulphur trioxide was put in a 1 dm³ vessel at 1000K. At equilibrium the vessel contained 0.35 moles of sulphur trioxide

a) Calculate the equilibrium constant K_c

b) At equilibrium at 1000K, 0.2 moles of sulphur dioxide, 0.1 mole of oxygen and 0.7 moles of sulphur trioxide were introduced in the vessel.

i) Calculate the equilibrium constant

ii) State how the position of equilibrium was affected.



where x is the number of moles of oxygen formed

$$1 - 2x = 0.35$$

$$x = 0.325$$

moles of each at equilibrium

$$\text{moles of SO}_3 = 0.35$$

$$\text{moles of SO}_2 = 0.325 \times 2 = 0.65$$

$$\text{moles of O}_2 = 0.325$$

$$K_c = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2}$$

$$= \frac{0.65^2 \times 0.325}{0.35^2}$$

$$= 1.12 \text{ mol dm}^{-3}$$

$$\text{b) i) New } [\text{SO}_3] = 0.35 + 0.7 = 1.05$$

$$\text{New } [\text{SO}_2] = 0.65 + 0.2 = 0.85$$

$$\text{New } [\text{O}_2] = 0.325 + 0.1 = 0.425$$

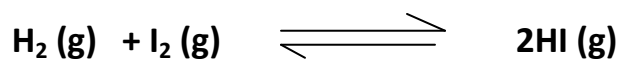
$$K_c = \frac{0.85^2 \times 0.425}{1.05^2}$$

$$= 0.279 \text{ mol dm}^{-3}$$

ii) The equilibrium constant seems to have reduced but since the temperature was not changed it remained constant but the position of equilibrium shifted from right to left

Questions

1) Hydrogen reacts with iodine according to the equation



A mixture of 0.8 moles of hydrogen and 0.6 moles of iodine was allowed to react in a sealed container at 450°C. At equilibrium 0.2 moles of iodine had reacted.

Calculate the value of the equilibrium constant at this temperature.

2. Equal amounts of hydrogen and iodine were reacted at a certain temperature. At equilibrium 20% of hydrogen had remained. Calculate the equilibrium constant at this temperature.

3) 1 mole of hydrogen iodide was put in a container of 20 litres at 25°C.

a) Calculate the pressure of the gas assuming it was ideal.

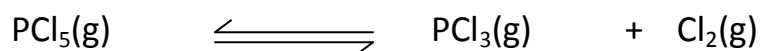
b) The sample was heated to 500°C. It partly decomposed to hydrogen and iodine. At equilibrium 0.1 mole of iodine was found present.

i) Calculate the pressure of the equilibrium mixture.

ii) Calculate the equilibrium constant K_c .

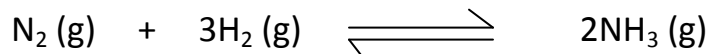
c) If the enthalpy of formation of hydrogen iodide is +11.3°C explain how the equilibrium constant would change with change in temperature.

4) Phosphorus(v) chloride decomposes according to the equation



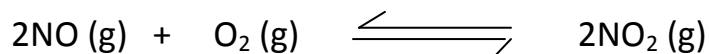
4.02 g of phosphorus(v) chloride was heated in a 450cm³ vessel at 450°C and at equilibrium 0.42g of chlorine was present. Calculate the equilibrium constant at this temperature.

5) Nitrogen and hydrogen react according to the equation



a) Stoichiometric amounts of nitrogen and hydrogen were heated in a container at 500K. At equilibrium 0.2 moles of ammonia were present. Calculate the value of K_c .

6) Nitrogen monoxide reacts with oxygen according to the equation



a) 3 moles of nitrogen monoxide and 1.5 moles of oxygen were heated in a closed vessel at 450°C . At equilibrium the vessel was found to contain 0.5 moles of oxygen.

Calculate the equilibrium constant at this temperature.

b) When the temperature was raised to 600°C the mixture in (a) was found to contain 25% of the initial nitrogen monoxide.

Calculate the equilibrium constant at 600°C .

c) Deduce whether the reaction is exothermic or endothermic. Explain your answer.

d) Explain the effect on K_c if

i) A catalyst was added to the reaction mixture.

ii) The pressure of the system was increased.

7. At a given temperature in a vessel of 10 dm^3 , 1 mole of hydrogen iodide was found to be 20% dissociated.

a) Calculate the number of moles of each constituent present at equilibrium

b) Calculate the value of the equilibrium constant K_c .

8) The solution of iodine in water and ether at 17°C and 25°C were in equilibrium as follows.

Temperature	Conc. of iodine in water	Conc. of iodine in ether.
17°C	0.28 g dm^{-3}	206 g dm^{-3}
25°C	0.30 g dm^{-3}	240 g dm^{-3}

b) What is the effect of changing temperature on the value of the partition coefficient?

c) State whether the dissolving of iodine in water is exothermic or endothermic. Explain your answer.

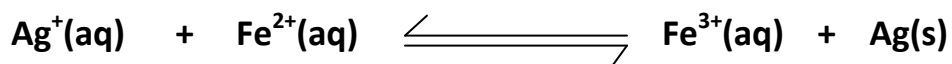
d) Name one other factor that affects the value of the partition coefficient.

a) Calculate the partition coefficient of iodine between ether and water.

i) At 17° C.

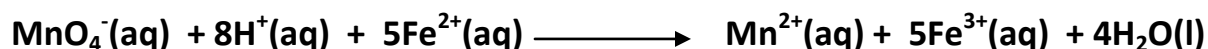
ii) At 25° C.

9) 500cm³ of 0.15M silver nitrate was added to 500cm³ of 1.09M iron(II) sulphate at 25° C. They react according to the equation



At equilibrium, 25cm³ of the solution required 30cm³ of 0.0832M potassium manganate (VII). Calculate the equilibrium constant K_c

Acidified potassium manganate(VII) solution reacts with iron(II) ions according to the equation



Calculations of K_p

K_p is the equilibrium constant expressed in terms of partial pressures of gases a mixture. The following steps are followed in calculating K_p

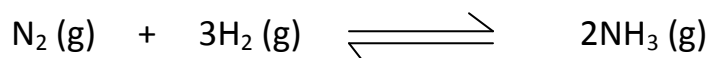
-calculate the number of moles of each at equilibrium

-calculate the mole fraction and the partial pressure of each

-substitute partial pressures in the expression of K_p and work out the answer.

Examples

1) Nitrogen and hydrogen react according to the equation

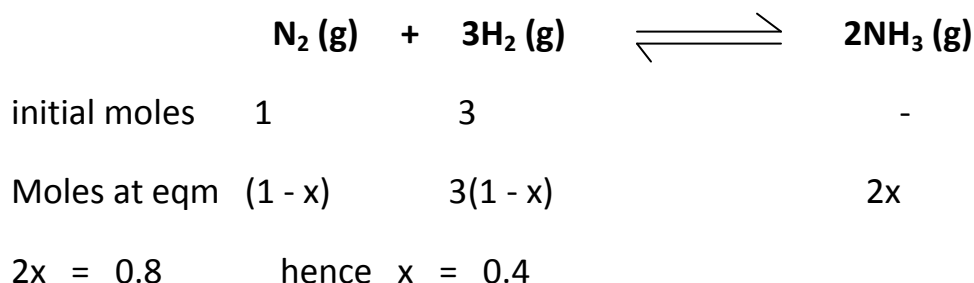


Stoichiometric amounts of nitrogen and hydrogen were reacted at 50 atmospheres and at equilibrium 0.8 moles of ammonia were formed. Calculate the

i) equilibrium amounts of hydrogen and nitrogen.

ii) equilibrium constant

'Stoichiometric amounts' means the amounts in moles that are in the equation i.e. in this case, 1mole of nitrogen and 3 moles of hydrogen



Moles of each at equilibrium

$$\text{moles of N}_2 = 1 - 0.4 = 0.6$$

$$\text{moles of H}_2 = 3(1 - 0.4) = 1.8$$

$$\text{moles of NH}_3 = 2 \times 0.4 = 0.8$$

$$\text{Total no. of moles at aqm} = 0.6 + 1.8 + 0.8 = 3.2$$

Partial pressures of each at eqm.(p_x)

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

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

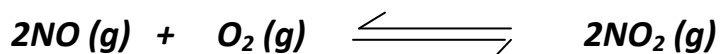
$$P_{\text{NH}_3} = \frac{0.8}{3.2} \times 50 = 12.50\text{atm.}$$

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{(12.50)^2}{9.375 \times (28.125)^3}$$

$$P_{N_2} \times P_{H_2}^3 = 9.375 \times (28.125)^3$$

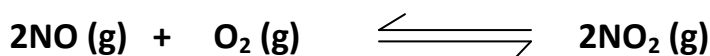
$$= 7.49 \times 10^{-4} \text{ atm}^{-2}$$

2. Nitrogen monoxide reacts with oxygen according to the equation



At 80°C and a pressure of 200 atm. Calculate the equilibrium constant Kp if the mixture contained 67% of nitrogen (IV) oxide at equilibrium.

Since you are not given the initial amounts you assume stoichiometric amounts



initial moles	2	1	-
moles at eqm	2(1 - x)	1 - x	2x

$$\text{Total no. of moles at eqm} = 2 - 2x + 1 - x + 2x = 3 - x$$

$$\% \text{ of } NO_2 = \frac{2x}{3 - x} = \frac{67}{100}$$

$$x = 0.753$$

Moles of each at eqm

$$\text{moles of NO} = 2(1 - 0.753) = 0.494$$

$$\text{moles of } O_2 = 1 - 0.753 = 0.247$$

$$\text{moles of } NO_2 = 2 \times 0.753 = 1.506$$

$$\text{Total no. of moles at eqm} = 0.494 + 0.247 + 1.506 = 2.247$$

Partial pressures

$$P_{NO} = \frac{0.494}{2.247} \times 200 = 43.97 \text{ atm}$$

$$P_{O_2} = \frac{0.247}{2.247} \times 200 = 21.98 \text{ atm}$$

$$P_{NO_2} = \frac{1.506}{2.247} \times 200 = 134.045 \text{ atm}$$

$$K_p = \frac{P_{NO_2}^2}{P_{NO}^2 \times P_{O_2}} = \frac{(134.045)^2}{(43.97)^2 \times 21.98}$$

$$= 0.42 \text{atm}^{-1}$$

alternative method

since the % of $\text{NO}_2 = 67\%$

the % of NO and $\text{O}_2 = 100 - 67 = 33$

since the initial ratio of $\text{O}_2 : \text{NO}$ is 1: 2 , it is still the same ratio at eqm.

If the % of O_2 is x

% of NO is $2x$

$$x + 2x = 33$$

$$x = 11 \quad \% \text{ O}_2 = 11\% \quad \text{and} \quad \% \text{ of NO} = 22\%$$

$$P_{\text{NO}_2} = \frac{67}{100} \times 200 = 134 \text{ atm}$$

$$P_{\text{NO}} = \frac{22}{100} \times 200 = 44 \text{ atm}$$

$$P_{\text{O}_2} = \frac{11}{100} \times 200 = 22 \text{ atm}$$

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}} = \frac{(134)^2}{(44)^2 \times 22}$$

$$= 0.42 \text{atm}^{-1}$$

Questions

1. In the manufacture of methanol, carbon monoxide and hydrogen react according to the following equation



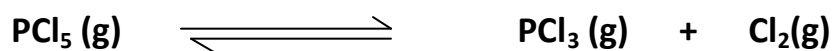
i) State the optimum temperature and pressure for the reaction. Explain your answer (3marks)

ii) Calculate the standard enthalpy of formation of methanol. (standard enthalpy of formation of carbon monoxide is -108 KJ /mole)

ii) At a certain equilibrium point 15% of carbon monoxide had reacted. Calculate the pressure ($K_p = 4 \times 10^{-10} \text{ Kpa}^{-2}$)

2) 2 moles of sulphur dioxide and 1 mole of oxygen were reacted at a pressure of 5 atmospheres. At equilibrium $\frac{1}{3}$ mole of sulphur dioxide was converted to sulphur trioxide. Calculate K_p

3). Phosphorus (v) chloride dissociates when heated according to the equation



1 mole of phosphorus (v) chloride was heated in a closed 1 litre vessel to 250°C . At equilibrium the vessel was found to contain 40.7% of chlorine.

a) Calculate the pressure assuming no dissociation took place.

b) At equilibrium at 400°C the pressure was found to be 6.07 atm. calculate the dissociation constant K_p .

b) If 2 moles of PCl_5 were placed in the same container at 400°C , would the dissociation constant be the same or different from that in (a) above?

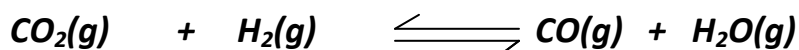
d) The enthalpies of formation of $\text{PCl}_5(\text{g})$ and $\text{PCl}_3(\text{g})$ are -375 and -287 kJ/mole respectively,

i) Calculate the enthalpy of dissociation of PCl_5 .

ii) How would you expect K_p to change with temperature? Explain your answer.

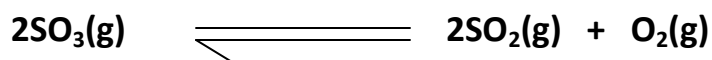
4). 1 mole of nitrogen and 3 moles of hydrogen were allowed to reach equilibrium at 500°C at a pressure of $1.0 \times 10^7 \text{ pa}$. The equilibrium mixture contained 20% of ammonia by volume. Calculate K_p .

5). Carbon dioxide reacts with hydrogen according to the equation



Calculate the composition of the equilibrium mixture if 5 moles of carbon dioxide and 1 mole of hydrogen are mixed at a pressure of 10 atm. ($K_p = 0.72$)

6) Sulphur trioxide was put in a closed container. It decomposed according to the equation



At equilibrium at 0.25 atmospheres 46% of sulphur trioxide had decomposed.

a) Calculate the equilibrium constant K_p

b) If the enthalpies of formation of sulphur trioxide and sulphur dioxide are -396 and -298 KJ/ mole respectively. Calculate the heat of decomposition of sulphur trioxide

c) Explain the effect of the following on the value of the equilibrium constant if

i) temperature is reduced

ii) pressure is increased

iii) a catalyst is added

7) Carbon reacts with steam according to the equation



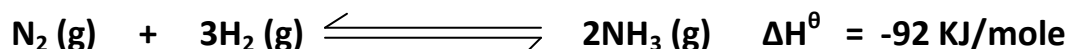
At equilibrium, 80% of steam had reacted. Calculate the pressure at equilibrium.

APPLICATIONS OF EQUILIBRIA

The principles of equilibria are applied in the following industrial reactions in order to increase the yield of the product in a short time.

1. Manufacture of ammonia (The Haber process)

Nitrogen (from air) and hydrogen (from natural gas) are mixed and reacted in a volume ratio of 1: 3



The reaction is reversible and exothermic in the forward reaction. The forward reaction proceeds with a decrease in volume. The following factors are applied to give a high yield of ammonia in a short time.

High pressure since the forward reaction takes place with a decrease in volume, increase in pressure shifts the position of equilibrium from left to right. The yield of ammonia is good if pressure is high. In practice a pressure of 200 - 1000 atmospheres is used.

Low temperature Since the forward reaction is exothermic, decrease in temperature shifts the position of equilibrium from left to right. Low temperature favours the high yield of ammonia. However, low temperature reduces the rate of formation of ammonia is low. In practice a temperature of about 450°C is used. The yield of ammonia is high and the reaction is reasonably fast.

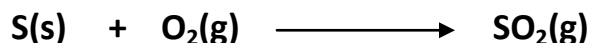
A catalyst The catalyst used is finely divided iron. It has no effect on the position of equilibrium hence does not affect the yield of ammonia. It increases the rate of formation of ammonia (equilibrium is attained in a shorter time)

Manufacture of sulphuric acid (The contact process)

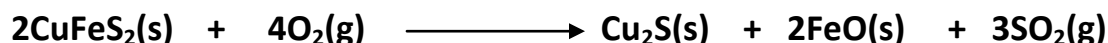
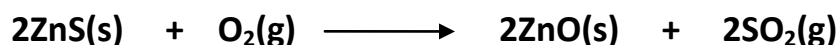
The contact process for the manufacture of sulphuric acid involves the following steps

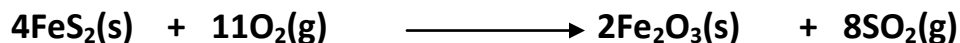
1) Formation of sulphur dioxide

sulphur is burnt in air to form sulphur dioxide



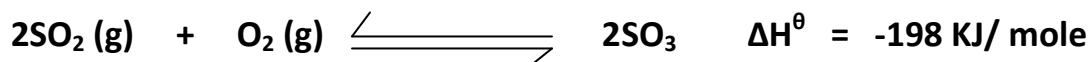
or a metal sulphide ore like iron pyrites(FeS₂) zinc blende (ZnS) or copper pyrites (CuFeS₂) is roasted in air during the extraction of the metal. Sulphur dioxide is formed





2) Conversion of sulphur dioxide to sulphur trioxide

Sulphur dioxide and oxygen are purified and combined to form sulphur trioxide



The forward reaction which produces sulphur dioxide is exothermic and takes place with a decrease in volume. The yield of sulphur trioxide is favoured using the following conditions

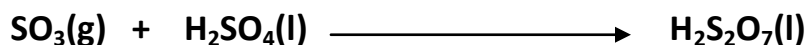
High pressure since the forward reaction takes place with a decrease in volume, increase in pressure shifts the position of equilibrium from left to right. The yield of sulphur trioxide is good if pressure is high. In practice a pressure of 1 - 10 atmospheres is used.

Low temperature Since the forward reaction is exothermic, decrease in temperature shifts the position of equilibrium from left to right. Low temperature favours the high yield of sulphur trioxide. However, low temperature reduces the rate of formation of sulphur trioxide. In practice a temperature of about 400 - 500°C is used. The yield of sulphur trioxide is high and the reaction is reasonably fast.

A catalyst The catalyst used is finely vanadium(V) oxide. It has no effect on the position of equilibrium hence does not affect the yield of sulphur trioxide. It increases the rate of formation of sulphur trioxide (equilibrium is attained in a shorter time)

3. Conversion of sulphur trioxide to sulphuric acid

Sulphur trioxide is not directly dissolved in water. This is because the reaction is very exothermic. The acid vapourises forming droplets of the acid. It is dissolved in concentrated sulphuric acid to form fuming sulphuric acid(oleum)



oleum is diluted with water to form concentrated sulphuric acid

