



Dr. Bbosa Science

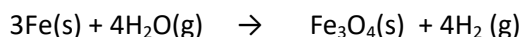
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## Chemical equilibrium

It is a branch of physical chemistry that deals with reversible reactions or reactions that proceed in either direction.

For example, when steam passed over heated iron, hydrogen and iron (II) diiron (III) oxide is formed. If, however, hydrogen is passed over heated iron (II) diiron (III) oxide, steam and iron are produced. Such reactions are said to be reversible and the equation for this reversible reaction is expressed as follows:



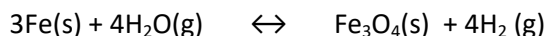
The direction of the reaction depends on the conditions: if hydrogen gas is removed as fast as it has formed, the reaction proceeds from left to right. Alternatively, if steam is removed as fast as it is formed the reaction will proceed from right to left.

By having steam and iron in a closed vessel, a state is reached at which all the four substance exist in equilibrium but the equilibrium in a balanced reaction is a dynamic one, that is, the substances are still reacting together except that the velocities of the forward and backward reaction are equal.

### Equilibrium constant, $K_c$

The state of equilibrium of a reversible reaction at a given temperature is defined by equilibrium constant  $K_c$  as follows

For a reaction

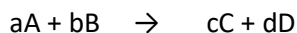


$$K_c = \frac{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}{[\text{Fe}]^3[\text{H}_2\text{O}]^4}$$

Where [ ] means concentration of the item in moles per litre or moles per  $\text{dm}^3$

For a general equation

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

Units of  $K_c$

The units of  $K_c$  are derived by principles of dimension  
for instance

$$K_c = \frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4} = \frac{[mol\,dm^{-3}][mol\,dm^{-3}]^4}{[mol\,dm^{-3}]^3[mol\,dm^{-3}]^4}$$

$\therefore$  units =  $mol^{-2}dm^6$

### Trail 1

Write expressions for  $K_c$  for the following reaction and state their units

- (i)  $N_2 + 3H_2 \leftrightarrow 2NH_3$
- (ii)  $2NH_3 \leftrightarrow N_2 + 3H_2$
- (iii)  $N_2 + O_2 \leftrightarrow 2NO$
- (iv)  $C_2H_5OH + HCl \leftrightarrow C_2H_5Cl + H_2O$

### Implication of $K_c$

When  $K_c$  is high it implies that there are more products at equilibrium than the reactants

### Application of equilibrium constant $K_c$

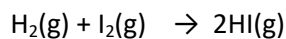
To calculate the amounts of the reactants and product at equilibrium

### Summary of characteristics of equilibrium

- Occurs at constant temperature
- Occurs in closed system
- It is dynamic equilibrium

### Example 1

Hydrogen reacts with iodine according to the following equation



A mixture of 0.8 moles of hydrogen and 0.6 moles of iodine was allowed to react in a sealed tube at  $450^\circ C$  at equilibrium 0.2 moles of iodine had reacted.

- (i) Write the expression for the equilibrium constant,  $K_c$  for the reaction

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

- (ii) Calculate the value of  $K_c$  (2marks)

First we calculate the moles at equilibrium  
mole of  $I_2$  at equilibrium =  $0.6 - 0.2 = 0.4$  moles

Moles of  $H_2$  at equilibrium

Mole of  $H_2$  that reacted = moles  $I_2$  that reacted  
= 0.2 moles

Thus, mole of  $H_2$  at equilibrium =  $0.8 - 0.2$   
= 0.6 moles

Moles of HI at equilibrium

1 mole of  $I_2$  that reacted produces 2 moles of HI

$\therefore$  0.2 moles of  $I_2$  produced 0.4 mole of HI

Secondly, we substitute in  $K_c$  expression

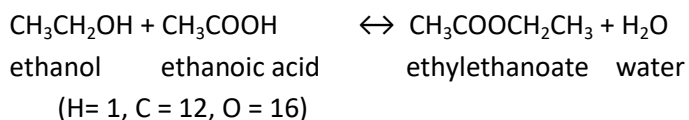
$$K_c = \frac{[0.4]^2}{[0.6][0.4]} = 0.67$$

### Example 2

(i) When 8.28g of ethanol were heated with 60g of ethanoic acid, 49.74g of the acid remained at equilibrium. Calculate  $K_c$

(ii) What mass of ethylethanoate should be present in equilibrium mixture formed from 13.8g of ethanol and 12g of ethanoic acid

Ethanol and ethanoic acid react as follow:



### Solution

(i) Relative molecular mass of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$  = 46

Initial moles of ethanol =  $\frac{8.28}{46}$  = 0.18 moles

Relative molecular mass of ethanoic acid,  $\text{CH}_3\text{COOH}$  = 60

Initial moles of ethanoic acid =  $\frac{60}{60}$  = 1 moles

Final moles of ethanoic acid =  $\frac{49.74}{60}$  = 0.829 moles

From the reaction equation

Moles of ethanoic acid that reacted	=	Moles of ethanol that reacted	=	Moles of ethylethanoate that formed
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Mole of ethanoic reacted =  $1 - 0.829 = 0.171$  moles

Moles of water formed = moles of ethanoic acid reacted = 0.171 moles

moles of ethanol that remained =  $0.18 - 0.171$   
= 0.009 moles

$$K_c = \frac{[\text{ethylethanoate}][\text{water}]}{[\text{ethanoic acid}][\text{ethanol}]}$$
$$= \frac{0.171 \times 0.171}{0.829 \times 0.009} = 3.92$$

(ii) 13.8g of ethanol =  $\frac{13.8}{46} = 0.3$  moles

12g of ethanoic acid =  $\frac{12}{60} = 0.2$  moles

Let the mass of ethylethanoate that formed be  $x$  moles; employing  $K_c$  for part (i)

$$3.92 = \frac{x^2}{(0.2-x)(0.3-x)}$$

$$\text{or } 2.92x^2 - 1.96x + 0.235 = 0$$

Using the general quadratic equation

$$x = 0.514 \text{ or } 0.158$$

The first value is inadmissible, since the number of moles of alcohol or acid which reacted cannot exceed the initial amount

Hence  $x = 0.158$  moles

Amount of ethylethanoate formed

$$= 0.158 \text{ moles}$$

$$\text{or } = 0.158 \times 88 = 13.9 \text{ g}$$

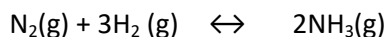
## Trial 2

When 6.22 moles of hydrogen were heated with 5.71 moles of iodine in a sealed tube at  $356^\circ\text{C}$  it was found that 9.60 moles of hydrogen iodide were present at equilibrium. Calculate

- (i) the equilibrium constant
- (ii) the moles of hydrogen iodide in equilibrium mixture formed by heating 6.41 moles of hydrogen and 10.40 moles of iodine at  $356^\circ\text{C}$

### Trial 3

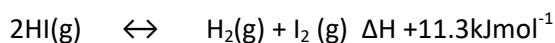
Nitrogen reacts with hydrogen according to the following equation



- (a) Write expression for equilibrium constant,  $K_C$
- (b) Stoichiometric amounts of nitrogen and hydrogen were reacted in a 2litre vessel. At equilibrium, 0.8moles of ammonia was formed
- Calculate
- the amount of hydrogen at equilibrium
  - the value of equilibrium constant,  $K_C$ .

### Trial 4

Hydrogen iodide decomposes when heated according to equation



- (a) Write an expression for equilibrium constant,  $K_C$  for the reaction (1mark)
- (b) 1.54g of HI was heated in a 600cm<sup>3</sup> bulb at 530<sup>0</sup>C. When equilibrium was attained, the bulb was rapidly cooled to room temperature and broken down under potassium iodide solution. The iodine formed from decomposition required 67.0cm<sup>3</sup> of 0.1M sodium thiosulphate solution.
- Calculate
- the number of moles of HI in 1.54g (1mark)
  - number of moles of iodine formed when hydrogen iodide decomposed (3marks)
  - The value of  $K_C$
- (c) State what would be the effect on  $K_C$  if
- the temperature was raised from 530<sup>0</sup>C to 800<sup>0</sup>C
  - the volume of the bulb was increased to 1200cm<sup>3</sup>.

### Trial 5

1mole of H<sub>2</sub> and 1mole of I<sub>2</sub> were introduced into 2litre vessel at temperature at which the equilibrium constant is 55.3. How many moles of H<sub>2</sub>, I<sub>2</sub> and HI are there after equilibrium has been established.

### Trial 6

A reaction occurs according to the following Stoichiometric equation  $\text{A} + 2\text{B} \leftrightarrow 2\text{C}$ ; 3moles of A and 5moles of B were brought together in a volume of 3litres and after equilibrium has been established, 1mole of A remained. Calculate the equilibrium constant  $K_C$  for the reaction

### Trial 7

A reaction occurs according to the following Stoichiometric equation  $2\text{A} + \text{B} \leftrightarrow 3\text{C}$  and has equilibrium constant of  $\frac{1}{10}$ . How many moles of B must be brought into contact with 5moles of A to produce at equilibrium 5moles of C.?

### Trial 8

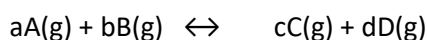
5 moles of ethanol, 6 moles of ethanoic acid, 6 moles of ethylethanoate and 4 moles of water were mixed together in a stoppered bottle at 15°C. After equilibrium had been attained the bottle was found to contain only 4 moles of ethanoic acid.

- (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) How many moles of ethanol, ethanoic acid, ethylethanoate and water are present in the equilibrium mixture?
- (d) What is the value for  $K_c$  for this reaction
- (e) Suppose 1 mole of ethanol, 1 mole of ethanoic acid, 3 moles of ethylethanoate and 3 moles of water are mixed together in a stoppered flask at 15°C. How many moles of
- ethanol,
  - ethanoic acid
  - ethylethanoate
  - water are present

### Equilibrium Constant in terms of, $K_p$

When at least one of the substances in equilibrium is gases, the state of equilibrium may be defined by equilibrium constant  $K_p$  as follows

For a reaction;



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

where  $P_A, P_B, P_C, P_D$  are the respective partial pressures of components A, B, C and D

and  $P_{total} = P_A + P_B + P_C + P_D$

$$P_A = X_A P_{total}$$

where  $X_A$  is mole fraction of A or the number of moles of component A over the total moles of components in the mixture and  $P_{total}$  is the total pressure of the system.

Implications of  $K_p$

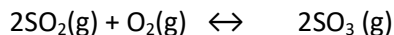
The bigger the value of  $K_p$  the higher the amount of product in the reaction mixtures

Application of  $K_p$

Like  $K_c$ ,  $K_p$  is used to predict the proportion of the products and reactants at the equilibrium point in the mixture

### Example 3

At 700°C and total pressure of one atmosphere the partial pressure 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



Calculate the equilibrium constant,  $K_p$ , for the reaction (4marks)

Solution

$$\begin{aligned} \text{Partial pressure of SO}_3 &= (1 - (0.27 + 0.41)) \\ &= 0.32 \text{ atm.} \end{aligned}$$

$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = \frac{[0.32]^2}{[0.27]^2 \times [0.41]} = 3.46 \text{ atm}^{-1}$$

### Trial 9

1 mole of hydrogen iodide at 25°C was introduced into a container of 20 liters

- Calculate the pressure of the gas, assuming ideal behavior (1 mole of a gas occupies 22.4 dm<sup>3</sup> under standard conditions).
- The sample of hydrogen iodide considered above was raised to a temperature of 300°C and partially decomposed into hydrogen and iodine gases; at equilibrium 0.1 mole of iodine was found to be present
  - Write an equation for decomposition
  - Calculate the pressure of the equilibrium mixture at 300°C, assuming no volume change.
  - Calculate the equilibrium constant at 300°C
- $\Delta H_f^\circ \text{ HI} = 26.5 \text{ kJ mol}^{-1}$ . Explain giving reasons how you would expect the equilibrium constant to change with temperature.

### Trial 10

Nitrogen reacts with hydrogen according to the following equation



- Write the equation for the equilibrium constant for the reaction in terms of partial pressure and indicate units (2marks)
- Stoichiometric amounts of nitrogen and hydrogen were reacted at 50 atmospheres and at equilibrium, 0.8 moles of ammonia were formed.  
calculate
  - the amount of hydrogen at equilibrium (2½ marks)
  - The value of equilibrium constant for the reaction (4½ marks)

### Trial 11

Consider the following reaction



At a certain temperature, analysis of an equilibrium mixture of the gases yielded the following results

$$P_{\text{H}_2} = 2.5 \times 10^{-1} \text{ atm.}$$

$$P_{\text{I}_2} = 1.6 \times 10^{-1} \text{ atm.}$$

$$P_{\text{HI}} = 4.0 \times 10^{-1} \text{ atm.}$$

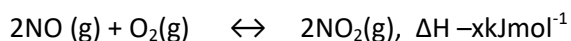
- Calculate the equilibrium constant for the reaction and state its units.
- In second experiment at the same temperature, iodine and hydrogen were mixed together with each gas at a partial pressure of  $3 \times 10^{-1}$  atm. what are the partial pressures of hydrogen, iodine and HI at equilibrium?
- In the third experiment at the same temperature, pure hydrogen iodide was injected into the flask at a pressure of  $6 \times 10^{-1}$  atm. What are the partial pressures of hydrogen, iodine and hydrogen iodide at equilibrium?
- What effect, if any, will decreasing the temperature have on the value of  $K_p$ ? Explain your answer.

### Trial 12

0.196g nitrogen and 0.146g hydrogen were heated together until equilibrium is established at a given temperature. The pressure found at equilibrium was found to be 90% its value at the beginning. Calculate the percentage composition by volume of the resulting mixture (H = 1, N = 14)

### Trial 13

(a)(i) Nitrogen (II) oxide combines with  $\text{O}_2$  at  $80^\circ\text{C}$  and 200atmosphere to form Nitrogen (IV) oxide according to equation



- Write an expression for the equilibrium constant  $K_p$  for the reaction
  - Calculate  $K_p$ , if the mixture contained 67% nitrogen (IV) oxide (3 ½ marks)
- (b) State how the value of  $K_p$  will be affected if
- Temperature is increased
  - Catalyst is added

(c) The kinetic data for the reaction in (a) is shown in the table below

Initial rate/ $\text{Nm}^{-2}\text{s}^{-1}$	6.8	27.2	61.2	108
$P_{\text{NO}}^2/\text{N}^2\text{M}^4$	0.04	0.16	0.36	0.64

$P_{\text{NO}}$  =the partial pressure of NO

- Plot a graph of initial rate against  $P_{\text{NO}}^2$  (03mark)
- Using a graph, determine the order of reaction with respect to nitrogen II oxide



- (iii) Give a reason for your answer
- (d) When the partial of O<sub>2</sub> was doubled to a new constant value, the gradient of the graph in C(i) doubles
- (i) Determine the order of reaction with respect to O<sub>2</sub>. Explain your answer.
- (ii) Write the rate equation for the reaction in (d)
- (iii) Calculate the rate constant when the initial rate is 170Nm<sup>-2</sup>s<sup>-1</sup>, P<sub>NO</sub> = 0.1NM<sup>-2</sup>,  
 $P_{O_2} = 1.36Nm^{-2}$  PO<sub>2</sub>
- (e) State the effect of the following on the rate of the reaction
- (i) Having partial of nitrogen II oxide while that of oxygen is kept constant
- (ii) Doubling partial pressure of both nitrogen II oxide and O<sub>2</sub>.

### Relationship between $K_c$ and $K_p$

We have already seen that equilibrium constants are normally expressed in term of concentration using the symbol  $K_c$  and that, for reaction involving gases; it is usually convenient to express the amount of gases in terms of partial pressure rather than its molar concentration using the Ideal equation

$$PV = nRT$$

$$P = \frac{n}{V}RT$$

where p is the pressure in atmosphere, n is the number of moles, V, is the volume in cubic decimeter and T is the temperature in Kelvin. In this case R, the gas constant, has units are atmdm<sup>-3</sup>K<sup>-1</sup>mol<sup>-1</sup>

$$P = [\text{gas}]RT$$

Where [gas] is the concentration of the gas in moldm<sup>-3</sup>

Thus, at constant temperature, the pressure of a particular gas is proportional to concentration

i.e.  $P \propto [\text{gas}]$

This means that for equilibrium



we can either write

$$K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} \text{ or } K_p = \frac{P_{HI}^2}{P_{I_2} \times P_{H_2}}$$

Now since  $P_{HI} = [HI(g)]RT$

$$P_{H_2} = [H_2(g)]RT$$

and  $P_{I_2} = [I_2(g)]RT$

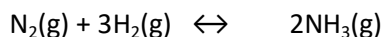
It follows that;

$$K_p = \frac{P_{HI}^2}{P_{I_2} \times P_{H_2}} = \frac{[HI(g)]^2 (RT)^2}{[H_2(g)]RT \cdot [I_2(g)]RT}$$

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

In this particular example  $K_p = K_c$  and neither  $K_p$  nor  $K_c$  has units, but this is not always the case;

Consider another reaction



$$\begin{aligned} K_p &= \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3} = \frac{[\text{NH}_3(\text{g})]^2 (\text{RT})^2}{[\text{N}_2(\text{g})] \text{RT} \times [\text{H}_2(\text{g})]^3 [\text{RT}]^3} \\ &= \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} \times [\text{RT}]^{-2} \\ &= K_c (\text{RT})^{-2} \end{aligned}$$

It implies that the numerical value of  $K_p$  is the same as that of  $K_c$  only where there are the same number of moles on each side of the Stoichiometric equation.

Although the SI unit of pressure is  $\text{Nm}^{-2}$ , it is standard practice to use atmospheres as pressure unit in expressing  $K_p$  values.

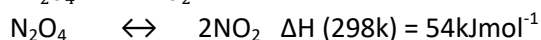
In general,  $K_p = K_c (\text{RT})^{\Delta n}$

where  $\Delta n$  = number moles on the right of the equation minus number of moles on the left.

#### Example 4

(a) Write an equation to show the relationship between the equilibrium constant,  $K_p$  and partial pressure

$P_{\text{N}_2\text{O}_4}$  and  $P_{\text{NO}_2}$  of the reactants in the following gaseous equilibrium



solution

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

(b) State the effect, if any, on above equilibrium of

(i) increasing the pressure

*Equilibrium shift from right to left leading to reduction in number of moles to fit in small volume.*

(ii) raising the temperature . Give reason for your answer.

*Equilibrium shifts from left to right to reduce on the increase in temperature since the forward reaction is endothermic.*

(c) It was found that one  $\text{dm}^3$  of the gaseous mixture weighed 2.777g at  $50^\circ\text{C}$  and pressure of  $1.01 \times 10^5 \text{Nm}^{-2}$  (1 atmosphere)

Calculate

(i) The fraction of  $\text{N}_2\text{O}_4$  that dissociated

solution

$$\begin{aligned} \text{Moles of } \text{N}_2\text{O}_4 \text{ initially} &= \frac{2.777}{(14 \times 2 + 16 \times 4)} \\ &= 0.0302 \text{ moles} \end{aligned}$$

Moles at equilibrium

From ideal gas equation,  $PV = nRT$

$$n = \frac{1.01 \times 10^5 \times 10^{-3}}{8.31 \times (273+50)}$$

$$n = 0.03763 \text{ moles}$$

If  $\alpha$  is the fraction ionizes

Then

[1 mole of a gas occupies 22.4dm<sup>3</sup> at s.t.p]



Initial moles,                    0.0302            0

mole at equilibrium 0.0302(1- $\alpha$ ) 0.0302(2 $\alpha$ )

total moles at equilibrium

$$= 0.0302(1-\alpha) + 0.0302(2\alpha) = 0.03763 \text{ mole}$$

$$\Rightarrow \alpha = 0.25$$

Mole

(ii) The percentage of NO<sub>2</sub> molecules in the mixture

solution:

$$= \frac{2 \times 0.25 \times 0.0302}{0.03763} \times 100 = 40\%$$

(iii) The value of  $K_p$

$$P_{\text{NO}_2} = \frac{40 \times 1.01 \times 10^5}{100} = 40400 \text{ Nm}^{-2}$$

$$P_{\text{N}_2\text{O}_4} = 1.01 \times 10^5 - 40400 = 60600 \text{ Nm}^{-2}$$

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{40400^2}{60600} = 2.69 \times 10^4 \text{ Nm}^{-2}$$

### Factors affecting equilibriums

these are

1. Temperature
2. Pressure
3. Catalyst
4. Concentration

The effect of the above factors on equilibrium position for the equilibrium mixture can be explained qualitatively by Le Chatelier's Principles that states that; 'if a system in equilibrium is subjected to a change, processes occur which tend to counteract the change imposed'.

Alternatively, 'if the concentration of one of the reacting substance is altered, the equilibrium will shift in such a way as to oppose the change in concentration'

### Effect of temperature

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

- (i) For exothermic reactions ( $\Delta H^0$  negative) equilibrium position shifts to the left as temperature rise leading to a reduction in equilibrium constants
- (ii) for endothermic reactions ( $\Delta H^0$  positive) equilibrium position shift the right as temperature increases leading to increase in the value of equilibrium constants.

Alternatively, the direction of change is given by Vant Hoff's Law of mobile equilibrium: "if a system is in equilibrium raising the temperature will favor that reaction which is accompanied by absorption of heat, and lowering temperature will favor that reaction which is accompanied by evolution of heat.

NB. It must be emphasized that it is only temperature that can alter the equilibrium positions and values of equilibrium constants among the factors states above whereas other factors alter only the equilibrium positions.

### Effect of a catalyst

Catalysts have no effect on the equilibrium constants  $K_c$  or  $K_p$  because they increase the rate of both forward and backward reaction in an equilibrium equally. However, they increase the rate at which equilibrium is attained.

### Effect of concentration on equilibrium mixture

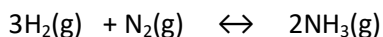
Variations in concentration of the reactant at constant temperature has no effect on the value of equilibrium constants  $K_c$  and  $K_p$ . However, if the concentration of one of the reacting substance in a reversible equilibrium is altered, the equilibrium will shift in such away as to oppose the change in concentration.

Effect of pressure changes on equilibrium

1. Pressure has appreciable effects when at least one of the reactant or product in a reversible reaction is a gas because unlike liquids and solids, gases are compressible.
2. The effect of pressure on equilibrium where reactants and/or products are in gaseous form depends on whether there is change in the number of molecules of the gases as the reaction proceeds from left to right.
  - (i) In general, for gaseous reaction in which there is a change in the number of molecules, increase in pressure favors a reaction which produces fewer molecules or number of moles of the products.
  - (ii) Pressure has no effect on those gaseous reactions in which there is no change in number of molecules as the reaction shifts from left to the right. e.g.  
$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2\text{HI}(\text{g})$$
3. Generally high pressure increases the rate at which equilibrium is attained in gaseous mixture because it increases the rate of collision of the reacting molecules.
4. Pressure has no effect on numerical values of  $K_c$  and  $K_p$  at constant temperature although the equilibrium concentration of reactants and product can vary over a wide range.

### Example 5

Hydrogen reacts with nitrogen to produce ammonia according the following equation



- (a) Write an expression for the equilibrium constant,  $K_c$  (1mark)

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

- (b) State, giving reasons, what would happen to the value of the equilibrium constant when

- (i) Pressure is increased at constant temperature (3marks)

*There will be no effect on the equilibrium constant because only temperature varies the value of the constant.*

(ii) argon is added to the reaction mixture at constant pressure (2marks)

*There will be no effect on the equilibrium constant as long as temperature is constant.*

(ii) Argon is added to the reaction mixture at constant volume (3marks)

*This will increase pressure but there will be no change on the value of equilibrium constant of mixture because this value is not altered by pressure.*

#### Trial 14

(a) Manganese sulphate reacts with acids according to the following equation



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

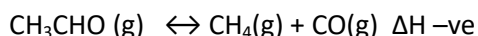
(i) Water is added to the equilibrium mixture (2marks)

(ii) Hydrogen chloride is bubbled into the equilibrium mixture (2marks)

(iii) pH of equilibrium mixture is increased.

#### Trial 15

Ethanol decomposes according to the equation



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

(b) Explain how  $K_p$  would be affected if

(i) the temperature is increased

(ii) Pressure is increased

#### Trial 16

Phosphorous (V) chloride when heated decompose according to the following equation



A sample of pure phosphorus (V) chloride was heated in a closed vessel to 250°C. When equilibrium was attained the vessel was found to contain 40.7% chlorine

(a) Calculate

(i) the molar concentration of phosphorus (V) chloride at equilibrium (4 ½ marks)

(ii) the equilibrium constant  $K_c$  for the reaction at 250°C (2 ½ marks)

#### Trial 17

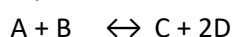
(a) Discuss the effect of each of the following on the position of a reversible reaction, the rate of at which the equilibrium is attained and the value of the equilibrium constant.

(i) temperature (5marks)

(ii) pressure (7marks)

(iii) catalyst (2marks)

(b) Write an expression for the equilibrium constant  $K_c$  or  $K_p$  as appropriate to the following reactions at equilibrium and indicate units in each case



where under the conditions of experiment

(i) A, B, C, and D are all gases.

(ii) A, B, C and D are all liquids

(iii) A, B, C are solids and D is a gas

### Trial 18

(a) In the manufacture of methanol, carbon monoxide and hydrogen react according to the following equation  
 $\text{CO(g)} + 2\text{H}_2\text{(g)} \leftrightarrow \text{CH}_3\text{OH(g)} \quad \Delta\text{H} = -65\text{kJmol}^{-1}$

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

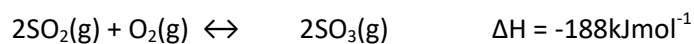
(ii) Calculate the standard enthalpy of formation of methanol (standard enthalpy of formation of Carbon monoxide =  $-108\text{kJ}$ ) (2marks)

(b)(i) Write an expression for the equilibrium constant,  $K_p$  (1mark)

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

### Trial 19

During the manufacture of sulphuric acid by contact process, sulphur dioxide is oxidized to sulphur (VI) oxide according to the following equation.



State the effect on the yield of sulphur (VI) oxide if

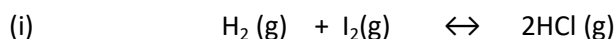
- (i) Temperature was increased
- (ii) Pressure was decreased
- (iii) Concentration of sulphur dioxide was increased

## Suggested answers

### Trial 1

- (i)  $\frac{[NH_3]^2}{[H_2]^3[N_2]}$  units =  $\frac{[mol\,dm^{-3}]^2}{[mol\,dm^{-3}]^3[mol\,dm^{-3}]} = mol^{-2}dm^6$
- (ii)  $\frac{[H_2]^3[N_2]}{[NH_3]^2}$  units =  $\frac{[mol\,dm^{-3}]^3[mol\,dm^{-3}]}{[mol\,dm^{-3}]^2} = mol^2dm^{-6}$
- (iii)  $\frac{[NO]^2}{[N_2][O_2]}$  units =  $\frac{[mol\,dm^{-3}]^2}{[mol\,dm^{-3}][mol\,dm^{-3}]} = \text{unitless}$
- (iv)  $\frac{[C_2H_5Cl][H_2O]}{[C_2H_5OH][HCl]}$  units =  $\frac{[mol\,dm^{-3}][mol\,dm^{-3}]}{[mol\,dm^{-3}][mol\,dm^{-3}]} = \text{unitless}$

### Trial 2



Initially      6.22      5.71      -

At equilibrium    1.42      0.91      9.60

Working

$$\text{Mole of } H_2 \text{ reacted} = \frac{\text{moles of HI}}{2} = \frac{9.6}{2} = 4.8$$

$$\text{Moles of } H_2 \text{ remained} = 6.22 - 4.8 = 1.42 \text{ moles}$$

$$\text{moles of } I_2 \text{ reacted} = \text{moles of } H_2 \text{ reacted} = 4.8 \text{ moles}$$

$$\text{moles of } I_2 \text{ remained} = 5.71 - 4.8 = 0.91 \text{ moles}$$

$$K_c = \frac{9.6^2}{1.42 \times 0.91} = 71.32$$

(ii) Let the moles of HI formed be 2x



Initially      6.41      10.40      -

At equilibrium    (6.41-x)    (10.40-x)    2x

$$K_c = 71.32 = \frac{[2x]^2}{[6.41-x][10.40-x]}$$

$$x = 5.96$$

$$\text{Moles of HI} = 5.96 \times 2 = 11.92 \text{ moles}$$

### Trial 3

$$(i) \quad \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

(ii)	Equation	N <sub>2</sub> (g)	+	3H <sub>2</sub> (g)	↔	2NH <sub>3</sub>
	Initially	1		3		-
	Moles at equilibrium	0.6		1.8		0.8
	Concentration at equilibrium	$\frac{0.6}{2} = 0.3$		$\frac{1.8}{2} = 0.9$		$\frac{0.8}{2} = 0.4$

Working

Mole H<sub>2</sub> that reacted

2moles of NH<sub>3</sub> are formed by 3 mole of H<sub>2</sub>.

0.8 moles of NH<sub>3</sub> are formed by  $\frac{3 \times 0.8}{2} = 1.2$

Moles of H<sub>2</sub> at equilibrium = 3 – 1.2 = 1.8moles

Mole N<sub>2</sub> that reacted

1moles of NH<sub>3</sub> are formed by 3 mole of N<sub>2</sub>.

0.8 moles of NH<sub>3</sub> are formed by  $\frac{1 \times 0.8}{2} = 0.4$

Moles of N<sub>2</sub> at equilibrium = 1 – 0.4 = 0.6moles

$$K_c = \frac{[0.4]^2}{[0.9]^3[0.3]} = 0.73$$

### Trial 4

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

$$(b) \quad (i) \quad HI = 1 + 127 = 128$$

$$\text{Moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{1.54}{128} = 0.012 \text{ moles}$$

$$(ii) \quad \text{Mole of sodium thiosulphate} = \frac{67 \times 0.1}{1000} = 0.0067 \text{ moles}$$

$$\text{Moles of iodine} = \frac{\text{moles of thiosulphate}}{2} = \frac{0.0067}{2} = 0.00335 \text{ moles}$$

Mole of hydrogen formed = moles of iodine = 0.00335 moles

Moles of HI decomposed = moles of iodine formed x 2 = 0.00335 x 2 = 0.0067

Moles of HI at equilibrium = 0.012 – 0.0067 = 0.0053

$$(iii) \quad K_c = \frac{0.00335 \times 0.00335}{[0.0053]^2} = 0.4$$

Since there is no change in number of moles of gas from left to the right, the volume of the container does not affect the value of K<sub>c</sub>

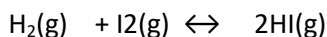
(c) (i) K<sub>c</sub> increases

(ii) K<sub>c</sub> remains unchanged



### Trial 5

Let the moles of HI = 2x



Initially            1            1            -

At equilibrium   1-x           1-x           2x

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[2x]^2}{[1-x][1-x]} = 55.3$$

$$x = 0.79$$

Moles of  $\text{H}_2$  = mole  $\text{I}_2$  = 1 - 0.79 = 0.21 moles

Moles of HI = 2x = 2 x 0.79 = 1.58 moles

### Trial 6

$$K_c = 48$$

### Trial 7

$$[\text{B}] = 457$$

### Trial 8

(a) (i)  $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \leftrightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3$

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

(c) Ethanol = 3, ethanoic acid = 4, ethylethanoate = 8, water = 6

(d)  $K_c = 4$

(e) Ethanol = 1.33, ethanoic acid = 1.33, ethylethanoate = 2.67, water = 2.67

### Trial 9

(a) From  $\frac{PV}{T} = \text{constant}$

$$\frac{P \times 20}{(273+25)} = \frac{1 \times 22.4}{273} \Rightarrow P = 1.2 \text{ atmospheres}$$

(b) (i)  $2\text{HI}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

(ii) From  $\frac{PV}{T} = \text{constant}$

$$\frac{P \times 20}{(273+300)} = \frac{1 \times 22.4}{273} \Rightarrow P = 2.35 \text{ atmospheres}$$

(iii)             $2\text{HI}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

Initially            1            -            -

At equilibrium   0.8            0.1            0.1

Total mole at equilibrium = 0.8 + 0.1 + 0.1 = 1

$$P_{HI} = X_A P = 0.8 \times 2.35 = 1.88 \text{ atmospheres}$$

$$P_{H_2} = 0.1 \times 2.35 = 0.235 \text{ atmospheres}$$

$$P_{I_2} = 0.1 \times 2.35 = 0.235 \text{ atmospheres}$$

$$K_p = \frac{P_{H_2} \cdot P_{H_2}}{P_{HI}^2} = \frac{0.235 \times 0.235}{1.88^2} = 0.016$$

(c)  $K_p$  increases with increase in temperature because the reaction is endothermic.

### Trial 10

$$(a) K_p = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}^3} \text{ units: } \frac{atm^2}{atm \cdot atm^3} = atm^{-2}$$

	Equation	$N_2(g)$	+	$3H_2(g)$	$\leftrightarrow$	$2NH_3$
Initially	1	3	-			
Moles at equilibrium	0.6	1.8				0.8

Working

Mole  $H_2$  that reacted

2moles of  $NH_3$  are formed by 3 mole of  $H_2$ .

0.8 moles of  $NH_3$  are formed by  $\frac{3 \times 0.8}{2} = 1.2$

Moles of  $H_2$  at equilibrium =  $3 - 1.2 = 1.8$  moles

Mole  $N_2$  that reacted

1moles of  $NH_3$  are formed by 3 mole of  $N_2$ .

0.8 moles of  $NH_3$  are formed by  $\frac{1 \times 0.8}{2} = 0.4$

Moles of  $N_2$  at equilibrium =  $1 - 0.4 = 0.6$  moles

(ii) Total moles of a gas at equilibrium =  $0.6 + 1.8 + 0.8 = 3.2$

From  $P_A = X_A P$

$$P_{NH_3} = \frac{0.8 \times 50}{3.2} = 12.5 \text{ atm}$$

$$P_{H_2} = \frac{1.8 \times 50}{3.2} = 28.125 \text{ atm}$$

$$P_{N_2} = \frac{0.6 \times 50}{3.2} = 9.375 \text{ atm}$$

$$K_p = \frac{12.5^2}{28.125^3 \cdot 9.375} = 7 \times 10^{-5} \text{ atm}$$

### Trial 11

$$(a) K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}} = \frac{0.4^2}{0.25 \times 0.16} = 4$$

$$(b) P_t = 0.6$$

Partial pressure ( $P_{H_2}$ ) of  $H_2$  = partial pressure ( $P_{I_2}$ ) of  $I_2$  at equilibrium

$$\Rightarrow P_{HI} = 0.6 - 2P_{H_2}$$

$$\Rightarrow K_p = \frac{(0.6 - P_{H_2})^2}{P_{H_2}^2} = 4$$

$$P_{H_2} = P_{I_2} = 0.15 \text{ atm}$$

$$P_{HI} = 0.30 \text{ atm}$$

$$(c) P_t = 0.3 + 0.3 = 0.6$$

Partial pressure ( $P_{H_2}$ ) of  $H_2$  = partial pressure ( $P_{I_2}$ ) of  $I_2$  at equilibrium

$$\Rightarrow P_{HI} = 0.6 - 2P_{H_2}$$

$$\Rightarrow K_p = \frac{(0.6 - P_{H_2})^2}{P_{H_2}^2} = 4$$

$$P_{H_2} = P_{I_2} = 0.15 \text{ atm}$$

$$P_{HI} = 0.30 \text{ atm}$$

(d) Decreasing temperature increases  $K_p$  because the reaction is exothermic

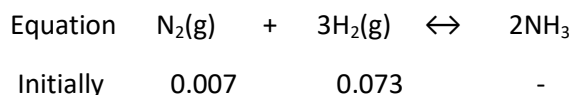
### Trial 12

$$\text{Moles of } N_2 = \frac{0.196}{28} = 0.007$$

$$\text{Mole of } H_2 = \frac{0.146}{2} = 0.073$$

$$\text{Total initial moles of a gas} = 0.007 + 0.073 = 0.08 \text{ moles}$$

Let the mole so  $NH_3$  formed at equilibrium =  $2x$



Moles at equilibrium	$0.007 - x$		$0.073 - 3x$		$2x$
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$$\text{Total moles at equilibrium} = 0.007 - x + 0.073 - 3x + 2x = 0.08 - 2x$$

Since pressure is proportional to the number of moles of a gas

$$\frac{0.8 - 2x}{0.08} = \frac{90}{100}$$

$$x = 0.004$$

$$\%N_2 = \frac{(0.007 - 0.004) \times 100}{0.08 - 2 \times 0.004} = 4.2\%$$

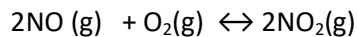
$$\%H_2 = 84.7\%$$

$$\%NH_3 = 11.1\%$$

### Trial 13

$$(a)(i) K_p = \frac{P_{NO_2}^2}{P_{NO}^2 \cdot P_{O_2}} \text{ atm}^{-1}$$

(ii) let the moles of  $NO_2$  at equilibrium be  $2x$



Initially            2            1            -

At equilibrium     $(2-2x)$          $(1-x)$          $2x$

$$\text{Then, } \frac{2x}{3-x} = 0.67 \quad \Rightarrow x = 0.75$$

Total moles at equilibrium =  $3 - 0.75 = 2.25$  moles

$$P_{NO_2} = \frac{1.5}{2.25} \times 200 = 133.3 \text{ atmospheres}$$

$$P_{O_2} = \frac{0.25}{2.25} \times 200 = 22.2 \text{ atmospheres}$$

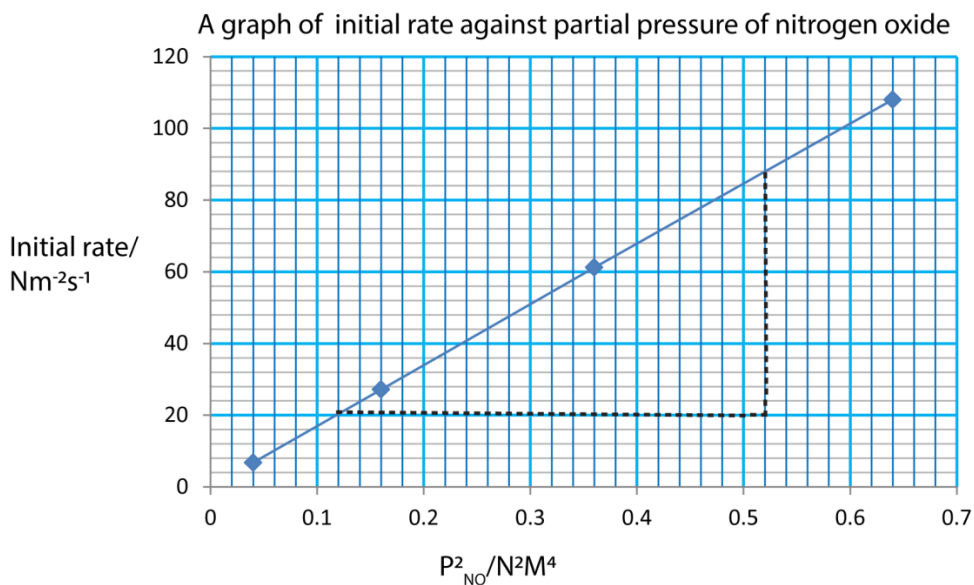
$$P_{NO} = \frac{0.5}{2.25} \times 200 = 44.4 \text{ atmospheres}$$

$$K_p = \frac{133.3^2}{44.4^2 \times 22.2} = 0.406 \text{ atm}^{-1}$$

(b) (i)  $K_p$  decreases

(ii)  $K_p$  remain unchanged

(c)(i)



- (ii) 1<sup>st</sup> order
- (iii) Rate is proportional to concentration
- (d)(i) 1<sup>st</sup> order the rate is proportional to concentration

(ii) Rate =  $K[\text{NO}][\text{O}_2]$

(iii)  $K = \frac{170}{0.1 \times 1.36} = 1250 \text{ N}^{-1} \text{ M}^2 \text{ s}^{-1}$

- (e) (i) the rate halves
- (iii) Rate is multiplied by 4

#### Trial 14

- (i) Equilibrium shifts to the left to reduce the concentration of water added.
- (ii) Equilibrium shifts to the right to reduce the concentration of hydrogen ions.
- (iii) Equilibrium shifts to the left to produce hydrogen ions and lower the pH.

#### Trial 15

(a)  $K_p = \frac{P_{\text{CH}_4} \times P_{\text{CO}}}{P_{\text{CH}_3\text{CHO}}}$

- (b) (i)  $K_p$  decrease because increasing temperature shifts equilibrium from right to the left since the reaction is endothermic.
- (ii)  $K_p$  remains unchanged since pressure has no effect on the value of  $K_p$ .

#### Trial 16

Let the mole of  $\text{PCl}_5$  decomposed be  $x$



Initially            1            -            -

At equilibrium     $1 - x$              $x$              $x$

Total moles =  $1 - x + x + x = 1 + x$

$$\% \text{Cl}_2 = \frac{x}{1+x} = \frac{40.7}{100} \Rightarrow x = 0.69$$

Mole of  $\text{PCl}_5$  at equilibrium =  $1 - 0.69 = 0.31$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.69 \times 0.69}{0.31} = 1.54 \text{ mol dm}^{-3}$$