

# CHAPTER # 7

## CHEMICAL EQUILIBRUM

**Q1. Differentiate between reversible and irreversible reaction.**

**Ans:**

Reversible Reaction	Irreversible Reaction
i. The reactions which can proceed in both the directions i.e. forward and backward and are called reversible reactions.	i. The reactions that virtually go to completion i.e., reactants are completely consumed and converted into the products. Such reactions are called irreversible reactions.
ii. The reactants are not completely consumed.	ii. The limiting reactant is consumed completely.
iii. In reversible reactions the reaction never goes to completion.	iii. The reaction virtually goes to completion in irreversible reactions.
iv. These reactions reach at a stage called chemical equilibrium. At this stage the concentration of reactants and products become constant. But the reaction continues to proceed in both the directions without any change in concentrations of reactants and products under existing conditions.	iv. The concept of chemical equilibrium is not applicable on irreversible reactions.
v. It is represented by $\rightleftharpoons$ double arrow.	v. It is represented by $\longrightarrow$ single arrow.
vi. Examples: i. $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ ii. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ iii. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	vi. Examples: i. $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{g})$ ii. $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$ iii. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g})$

**Q2. What do you know about reversible reaction?**

**Ans: Reversible reaction:**

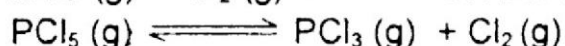
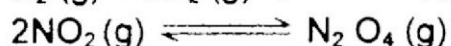
The reactions which can proceed in both the directions i.e. forward and backward directions are called reversible reactions.

**Explanation:**

A reversible reaction is one in which the products once formed can react to form reactants. Such reactions do not go to completion even if stoichiometric amounts of the reactants are taken. These reactions take place both in the forward and backward directions under the existing conditions.

**Examples:**

Some examples of reversible reactions are given below:



The **double arrow** tells that the reaction is reversible.

Consider the reaction between steam and carbon monoxide under appropriate conditions.

On mixing, macroscopic changes are observed (e.g, changes in concentration).

**Q3. Define and explain dynamic equilibrium give its examples also draw the graph to explain your answer.**

**Ans: Dynamic Equilibrium/Chemical Equilibrium:**

"The state of a reversible reaction at which compositions of the reaction mixture does not change is called the state of chemical equilibrium."

**Explanation:**

Suppose that the reaction is started with same number of moles of both the reactants. When steam and carbon monoxide are mixed, a maximum number of collisions per second between them will occur. Therefore the forward reaction has its maximum speed at the beginning. This leads to a decrease in the concentration of the reactants.

**Example 1:**



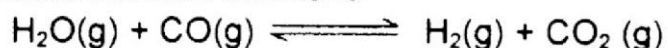
As  $\text{H}_2\text{O}$  and  $\text{CO}$  are gradually used up, the forward reaction gradually slows down. As the molecules of  $\text{H}_2$  and  $\text{CO}_2$  accumulate reverse reaction also starts. With the increase in concentrations of  $\text{H}_2$  and  $\text{CO}_2$  more and more collisions per second between these molecules occur.

Therefore reverse reaction proceeds with increasing speed. This means that forward reaction starts with maximum speed and gradually slows down, whereas the reverse reaction starts at zero speed and gradually increases its speed.

**Example 2:**



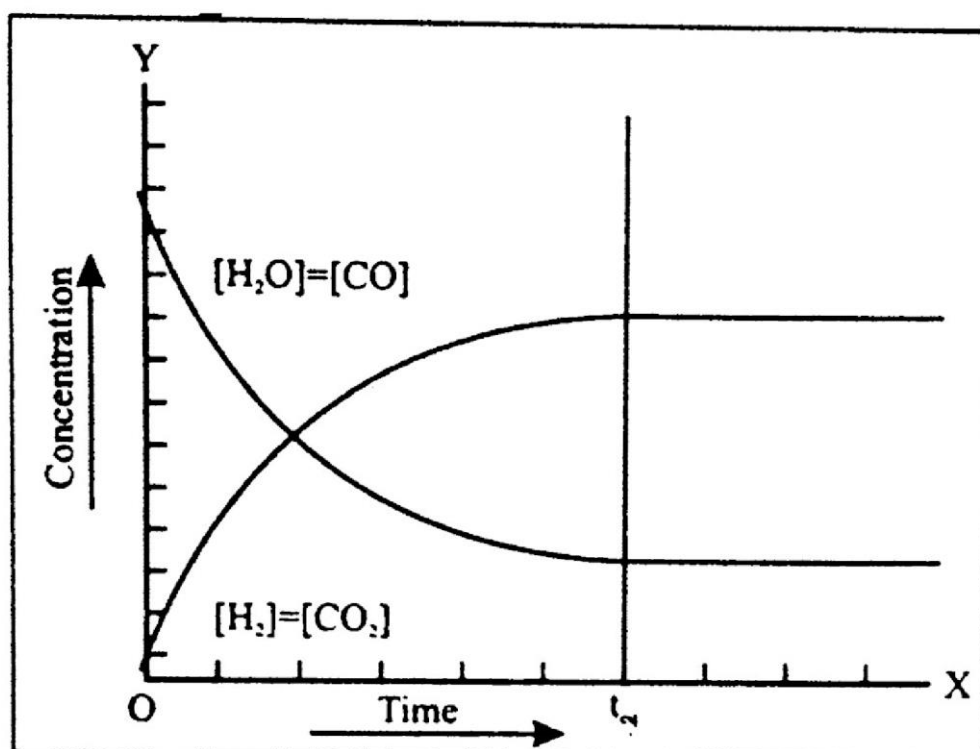
Eventually a time comes when both reactions proceed at the same speed. The reaction at this stage is said to be in chemical equilibrium. The concentrations of reactants and products become constant.



Unless the system is somehow disturbed no further changes in concentration will occur.

**Graphical representation:**

The plots of the concentrations of reactants and products versus time are shown in Fig.



The plots of concentrations of reactants and products versus time.

### Microscopic analysis:

Since the concentration of reactants and products become constant it may appear that the reaction has stopped. But this is not true.

On the microscopic level there is excited activity. Individual molecules of reactants continue to combine. Individual molecules of products also continue to combine. But the rate of one process is exactly balanced by the rate of the other. Therefore this is a **dynamic equilibrium**.

### Dynamic System:

The system is dynamic because individual molecules react continuously, but the rate of the forward and reverse reactions are equal. It is at equilibrium because no net change occurs.

**Q4. State law of mass action also derive equilibrium constant equation with the help of this law.**

**Ans: The Equilibrium Constant:**

Two chemists C.M Guldberg and P. Wage in 1864 proposed the law of mass action.

It states that "the rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances".

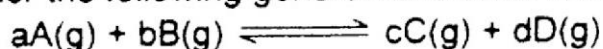
It can also be defined as "the rate of chemical reaction is proportional to the product of molar concentration of each reacting substance raised to a power equal to its stoichiometric coefficient in the balanced chemical equation."

### Active mass:

The term active mass means, the concentration of the reactants and products in moles  $\text{dm}^{-3}$  for a dilute solution.

**Derivation:**

Consider the following general reversible reaction.



Where A, B, C and D represent chemical species and a, b, c and d are their coefficients in the balanced equation.

According to the law of mass action.

$$\text{Rate of forward reaction, } R_f \propto [A]^a [B]^b = k_f [A]^a [B]^b \quad \dots\dots\dots (i)$$

Where  $k_f$  is the rate constant for the forward reaction.

$$\begin{aligned} \text{Rate of reverse reaction, } R_r &\propto [C]^c [D]^d \\ &= k_r [C]^c [D]^d \quad \dots\dots\dots (ii) \end{aligned}$$

Where  $k_r$  is the rate constant for the reverse reaction.

At equilibrium state

Rate of forward reaction = Rate of reverse reaction

$$\text{Thus } k_f [A]^a [B]^b = k_r [C]^c [D]^d$$

$$\begin{aligned} \text{On rearranging } \frac{k_f}{k_r} &= \frac{[C]^c [D]^d}{[A]^a [B]^b} \\ K_c &= \frac{[C]^c [D]^d}{[A]^a [B]^b} \end{aligned}$$

Where  $K_c = \frac{k_f}{k_r}$  and is known as **equilibrium constant**, and the above

equation is known as **equilibrium constant expression**. The square brackets indicate the **concentration** of the chemical species at equilibrium.

**Method to write equilibrium constant expression:**

Thus the equilibrium constant expression for any reaction can be written from its balanced equation. Concentration of products are taken in the numerator and concentration of reactants in the denominator.

**Q5. Differentiate between rate law and equilibrium constant equation.**

**Ans:**

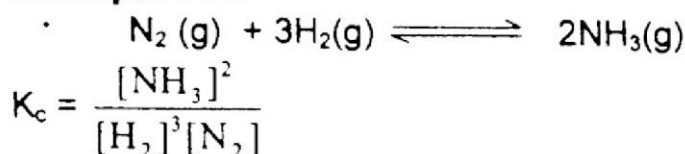
Rate law	Equilibrium constant equation
i. The rate law describes how the rate of a reaction changes with concentration.	i. The equilibrium expression describes the concentration of reactants and products when the net rate of reaction is zero.
ii. It cannot be written from the balanced chemical equation.	ii. It can be written from a balanced chemical equation.
iii. It can be determined only with the help of experiment.	iii. It can be determined theoretically with the help of balanced chemical equation.
iv. Rate law is given by the equation $\text{Rate} = k[A]^x$	iv. Equilibrium constant equation for the given reaction is given below $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$ $\frac{k_f}{k_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$



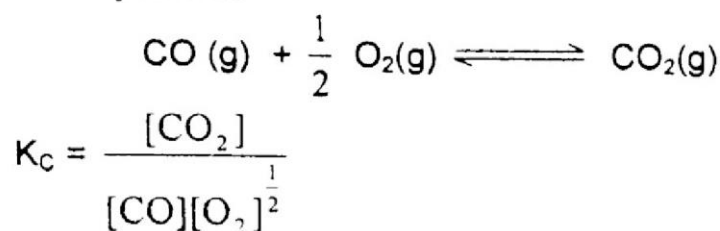
**Note:** In both these expressions, concentration terms are raised to powers.

### Examples of Equilibrium Constant Expression:

#### Example 7.1:

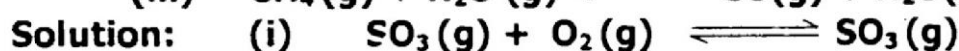
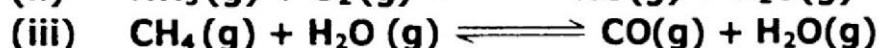
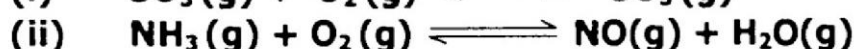
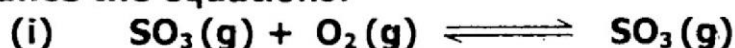


#### Example 7.2:

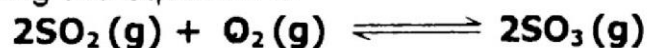


### SELF-CHECK EXERCISE 7.1

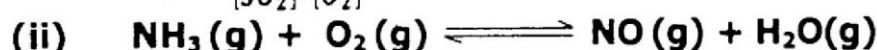
i. The following equations represent various industrial reactions at equilibrium. Write  $K_c$  expression for each of these reactions. Do not forget to balance the equations:



Balancing the equation is



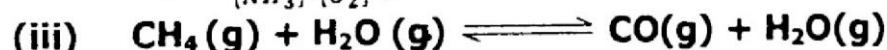
$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$



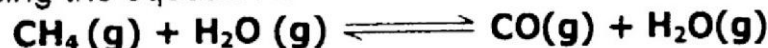
Balancing the equation is



$$K_c = \frac{[\text{NO}]^2[\text{H}_2\text{O}]^3}{[\text{NH}_3]^2[\text{O}_2]^{5/2}}$$

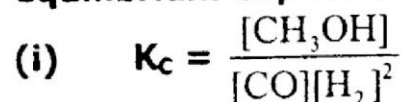


Balancing the equation is



$$K_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]}$$

ii. Give the balanced equations that correspond to following equilibrium expressions.



$$(ii) \quad K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$$

**Solution:**

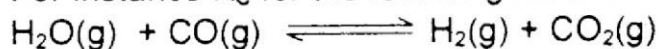


**Q6. How can we determine units for equilibrium constant give at least two examples?**

**Ans: Units of Equilibrium Constant:**

Equilibrium constant may or may not have units. Equilibrium constant has no units if the number of moles of the reactants are equal to the number of moles of the products.

For instance  $K_c$  for the following reaction has no units.

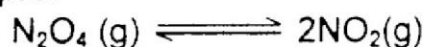


$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

$$K_c = \frac{(\text{mol dm}^{-3})(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = \text{No units}$$

On the other hand if the number of moles of products and reactants are not equal,  $K_c$  has units.

**Example:**



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

$$K_c = \text{mole dm}^{-3}$$

In this way we can determine the units for  $K_c$ . However units of equilibrium constant are not usually written.

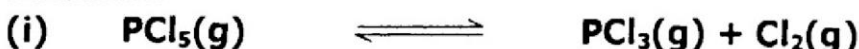
## SELF-CHECK EXERCISE 7.2

**Determine the units for  $K_c$  for the following reactions:**



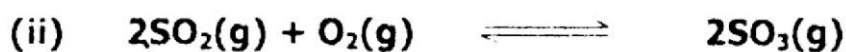
The value of  $K_c$  at a given temperature can be calculated if we know the equilibrium concentration of the reaction components.

**Solution:**



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

$$K_c = \frac{(\text{mole dm}^{-3})(\text{mole dm}^{-3})}{(\text{mole dm}^{-3})} = \text{mole dm}^{-3}$$



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

$$K_c = \frac{(\text{mole dm}^{-3})^2}{(\text{mole dm}^{-3})^2(\text{mole dm}^{-3})} = \frac{1}{(\text{mole dm}^{-3})} = \text{mole}^{-1} \text{ dm}^3$$

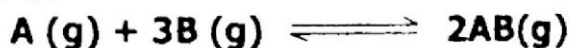


$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$K_c = \frac{(\text{mole dm}^{-3})^2}{(\text{mole dm}^{-3})(\text{mole dm}^{-3})} = \text{No units}$$

**Example 7.3:**

The following equilibrium concentrations were observed for the reaction at 500°C.



$$[\text{A}] = 0.399\text{M}, [\text{B}] = 1.197\text{M}, [\text{AB}] = 0.203\text{M}$$

Calculate  $K_c$

**Solution:**

$$K_c = \frac{[\text{AB}]^2}{[\text{A}][\text{B}]^3}$$

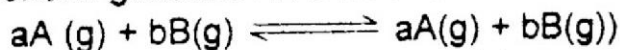
$$K_c = \frac{(0.203 \text{ mole dm}^{-3})^2}{(0.399 \text{ mole dm}^{-3})(1.197 \text{ mole dm}^{-3})^3}$$

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

**Q7. State Henry's law and how can we determine equilibrium constant expressions involving partial pressure, number of moles and mole fraction.**

**Ans: Equilibrium Expressions Involving Partial Pressure, Number of Moles and Mole Fraction:**

Consider the general gaseous reversible reaction



For gases the expression is often expressed in terms of partial pressure of each gas

According to **Henry's Law**

**"At constant temperature, the partial pressure of gas is directly proportional to its molar concentration."**

**Equilibrium constant  $K_p$  (For partial pressure):**

Equilibrium constant  $K_p$  in term of partial pressures is given by:

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

Where  $P_A$ ,  $P_B$ ,  $P_C$  and  $P_D$  are partial pressures of gas A, B, C and D respectively  $K_p$  is related with  $K_c$  by the following equation.

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

Where  $\Delta n$  is the difference between the total number of moles of the products and the reactants.

### Equilibrium constant $K_n$ (For number of moles):

When equilibrium concentrations of reactants and products are expressed in terms of their moles, the equilibrium constant is represented by  $K_n$  and is given by the following equation.

$$K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}$$

Where  $n_A$ ,  $n_B$ ,  $n_C$  and  $n_D$  are the moles of A, B, C and D respectively at the equilibrium state.  $K_p$  is also related with  $K_n$ .

$$K_p = K_n \left( \frac{P}{N} \right)^{\Delta n}$$

Where  $P$  is the pressure of reaction mixture at equilibrium and  $N$  is the total number of moles of reactants and products as shown by the balanced equation.

### Equilibrium constant $K_x$ (For mole fraction):

When the equilibrium concentration of the reactants and products are expressed by their mole fractions, the equilibrium constant is represented by  $K_x$  and is given by the following equations.

$$K_x = \frac{x_C^c \times x_D^d}{x_A^a \times x_B^b}$$

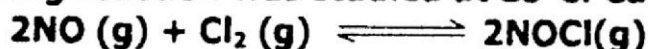
Where  $x_A$ ,  $x_B$ ,  $x_C$  and  $x_D$  are mole fractions of A, B, C and D respectively.  $K_p$  is related with  $K_x$  by the following expression.

$$K_p = K_x (P)^{\Delta n}$$

Where  $P$  is the pressure of the equilibrium mixture.

### Example 7.4:

Following reaction was studied at 25°C. Calculate its  $K_p$  and  $K_c$ .



The partial pressures at equilibrium were found to be

$$P_{\text{NOCl}} = 1.2 \text{ atm}$$

$$P_{\text{NO}} = 5.0 \times 10^{-2} \text{ atm}$$

$$P_{\text{Cl}_2} = 3.0 \times 10^{-1} \text{ atm}$$

$$K_p = \frac{(P_{\text{NOCl}})^2}{(P_{\text{NO}})(P_{\text{Cl}_2})}$$

$$K_p = \frac{(1.2)^2}{(5.0 \times 10^{-2})(3.0 \times 10^{-1})}$$

$$K_p = 1.9 \times 10^3$$

Now

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

$$\Delta n = 2 - (2 + 1) = -1$$

$$R = 0.0820 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1}$$

$$T = 25^{\circ}\text{C} + 273 = 298\text{K}$$

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

$$1.9 \times 10^3 = K_c (0.08205 \times 298)^{-1}$$

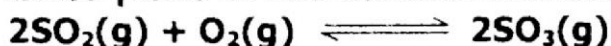
$$1.9 \times 10^3 = \frac{K_c}{(0.08205 \times 298)}$$

$$K_c = 1.9 \times 10^3 \times 0.08205 \times 298$$

$$K_c = 4.65 \times 10^4$$

### SELF-CHECK EXERCISE 7.3

The contact process prepares purest sulphuric acid commercially. Following reaction takes place in the contact chamber in the presence of  $\text{V}_2\text{O}_5$ .



(Ans: 0.1576)

Calculate  $K_p$  if the following concentrations are found at equilibrium.

$$[\text{SO}_2] = 0.59\text{M}, \quad [\text{O}_2] = 0.05\text{M} \quad \& \quad [\text{SO}_3] = 0.259\text{M}$$

**Solution:**

For  $K_c$

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

$$K_c = \frac{(0.259)^2}{(0.59)^2 (0.05)} = 3.85$$

For  $K_p$

As we know that

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

$$R = 0.0821 \text{ atm dm}^3 \text{ K}^{-1} \text{ mole}^{-1}$$

$$\Delta n = 2 - (2 + 1) = -1$$

$$T = 25^{\circ}\text{C} + 273 = 298 \text{ K}$$

$$K_c = 3.85$$

Putting values in equation (i)

$$K_p = 3.85 \times (0.0821 \times 298)^{-1}$$

$$K_p = \frac{3.85}{(0.0821 \times 298)^{-1}} = 0.1574$$

**Q8. Define and explain the following terms.**

i. **Homogeneous Equilibria:**

ii. **Heterogeneous Equilibria**

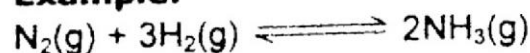
**Ans: Types of Equilibrium:**

With respect to the physical states of reactants and products, there are two types of Chemical Equilibrium.

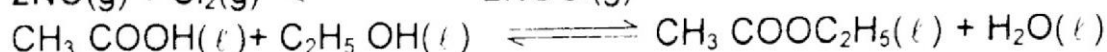
i. **Homogeneous Equilibria:**

An equilibrium system in which all of the reactants and products are in the same phase.

**Example:**



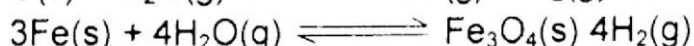
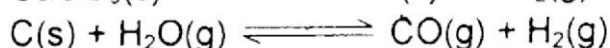
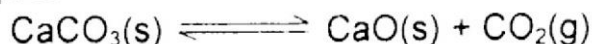




## ii. Heterogeneous Equilibria:

Equilibria which involve more than one phases are called Heterogeneous equilibria.

### Example:



### Note:

If pure solids or pure liquids are involved in an equilibrium system, **their concentrations are not included in the equilibrium constant expression.**

This is because the change in concentrations of any pure solid or liquid has no effect on the equilibrium system.



$$K_c = [\text{H}_2]^2 [\text{O}_2]$$

$$\text{and } K_p = p_{\text{H}_2}^2 \times p_{\text{O}_2}$$

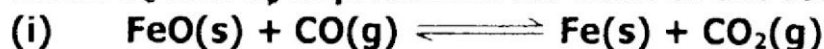


$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

$$\text{and } K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4}$$

## SELF-CHECK EXERCISE 7.4

Write  $K_c$  and  $K_p$  expressions for each of the following reactions.

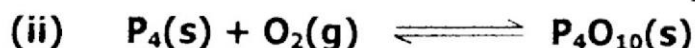


### Solution:



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

$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$$



$$K_c = [\text{O}_2]^{-5}$$

$$K_p = P_{\text{O}_2}^{-5}$$



$$K_c = \frac{[HCl]^4}{[CH_4][Cl_2]^2}$$

$$K_p = \frac{P_{HCl}^4}{P_{CH_4} \times P_{HCl}^4}$$

### Example 7.5:

At 100°C, 0.1 mole of  $N_2O_4$  is heated in a one  $dm^3$  flask. At equilibrium concentration of  $NO_2$  was found to be 0.12 moles. Calculate  $K_c$  for the reaction.

**Solution:**

$$[NO_2] = 0.12 \text{ mole}$$

Since one mole of  $N_2O_4$  gives 2 moles of  $NO_2$

$$2x = 0.12$$

$$x = \frac{0.12}{2}$$

$$x = 0.06$$

$$[N_2O_4] = 0.1 - 0.06$$

$$= 0.04 \text{ mole}$$

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial Conc	0.1		zero
(in moles)			
Eq. Conc	$0.1 - x$		$2x = 0.12$
(in moles)			
Eq. con C.	$\frac{0.04}{1}$		$\frac{0.12}{1}$
(mole/ $dm^3$ )	0.04		0.12

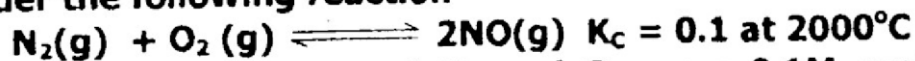
$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{(0.12)^2}{(0.04)}$$

$$K_c = 0.36$$

### Example 7.6:

Consider the following reaction



If original concentrations of  $N_2$  and  $O_2$  were 0.1M each. Calculate the concentrations of  $NO$  at equilibrium.

**Solution:**

	$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2NO(g)$
Initial Conc.	0.1M		0.1M		0
Eq. conc	$(0.1 - x)$		$(0.1 - x)$		$2x$
(mole/ $dm^3$ )					

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$0.1 = \frac{(2x)^2}{(0.1-x)(0.1-x)}$$

Taking square root of both the sides

$$0.32 = \frac{2x}{0.1-x}$$

$$x = 0.014\text{M}$$

$$[\text{N}_2] = [\text{O}_2] = 0.1 - x$$

$$= 0.1 - 0.014$$

$$= 0.086\text{M each}$$

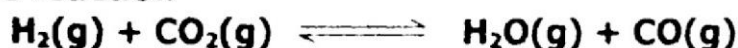
$$[\text{NO}] = 2x$$

$$= 2 \times 0.014$$

$$= 0.028\text{ M}$$

### SELF-CHECK EXERCISE 7.5

For the reaction



$K_c = 0.60$  at  $500^\circ\text{C}$ . If a mixture of  $0.30\text{M}$  of each  $\text{H}_2$  and  $\text{CO}_2$  is heated at  $500^\circ\text{C}$ , calculate the concentration of  $\text{CO}$  at equilibrium.

**Solution:**

	$\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$			
Initial Concentration (in moles)	0.3	0.3	zero	zero
Equation Concentration. (in moles)	$0.3 - x$	$0.3 - x$	$x$	$x$

$K_c$  is given as

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

$$0.60 = \frac{x^2}{(0.3-x)(0.3-x)} = \frac{x^2}{(0.3-x)^2}$$

Taking square root of both the sides

$$\sqrt{0.60} = \sqrt{\frac{x^2}{(0.3-x)^2}}$$

$$0.775 = \frac{x}{(0.3-x)}$$

$$x = 0.775(0.3-x)$$

$$x = 0.233 - 0.775x$$

$$x + 0.775x = 0.233$$

$$1.775x = 0.233$$

$$x = \frac{0.233}{1.775}$$

$$x = 0.131$$

Thus

$$[CO] = x = 0.131 \text{ moles}$$

**Example 7.7:**

When 60g of acetic acid and 46g of ethyl alcohol are heated to give and equilibrium mixture, 12g water and 58.7g of ethyl acetate are formed. Find  $K_c$  for the reaction.

**Solution:**

$$\text{Initial moles of } CH_3COOH = \frac{60g}{60g/\text{mole}} = 1 \text{ mole}$$

$$\text{Initial moles of } C_2H_5OH = \frac{46g}{46g/\text{mole}} = 1 \text{ mole}$$

At equilibrium

$$\text{Moles of } CH_3COOC_2H_5 = \frac{58.7g}{88g/\text{moles}} = 0.666 \text{ moles.}$$

$$\text{Moles of } H_2O = \frac{12g}{18g/\text{moles}} = 0.666 \text{ mole}$$

	$CH_3COOH(1) + C_2H_5OH(1) \rightleftharpoons CH_3COOC_2H_5(1) + H_2O(1)$			
Init. conc (in moles)	1	1	0	0
Eq. conc. (moles)	1 - 0.666 0.333	1 - 0.666 0.333	0.666	0.666

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

$$K_c = \frac{(0.666)(0.666)}{(0.333)(0.333)}$$

$$K_c = 4$$

## SELF-CHECK EXERCISE 7.6

- When dissolved in water, glucose and fructose exists in equilibrium as follows:



An analyst prepared a 0.25M fructose solution at room temperature. At equilibrium he found that its concentration decreased by 0.038M. Calculate  $K_c$  for the reaction. (Ans: 0.179)

**Solution:**

	<i>Fructose</i>	$\rightleftharpoons$	<i>Glucose</i>
Initial Concentration. (in moles)	0.25		zero
Equation Concentration. (in moles)	0.25 - x		x

Given that the concentration of fructose is decreases by 0.038M.

Thus,

$$x = 0.038$$

$$[\text{Fructose}] = 0.25 - x$$

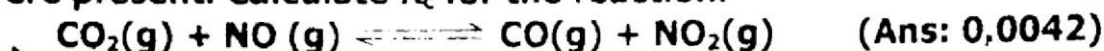
$$= 0.25 - 0.038 \text{ M}$$

$$= 0.212 \text{ M}$$

$$[\text{Glucose}] = x = 0.038 \text{ M}$$

$$K_c = \frac{[\text{Glucose}]}{[\text{Fructose}]} = \frac{0.038}{0.212} = 0.179$$

• When 3.88 moles of NO and 0.88 moles of CO<sub>2</sub> were heated in a flask at a certain temperature. At equilibrium 0.11 moles of each of the product were present. Calculate K<sub>c</sub> for the reaction.



Solution:

	$\text{CO}_2(\text{g}) + \text{NO}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{NO}_2(\text{g})$			
Initial Concentration.	0.88	3.88	zero	zero
(in moles)				
Equation Concentration.	0.88 - x	3.88 - x	x	x
(in moles)				

Given that 0.11 moles of each of the product are present at equilibrium,

Thus,  $x = 0.11$

$$[\text{CO}_2] = x = 0.11 \text{ moles}$$

$$[\text{NO}] = x = 0.11 \text{ moles}$$

$$[\text{CO}_2] = 0.88 - x = 0.88 - 0.11 = 0.77 \text{ moles}$$

$$[\text{NO}] = 3.88 - x = 3.88 - 0.11 = 3.77 \text{ moles}$$

$$K_c = \frac{[\text{CO}][\text{NO}_2]}{[\text{CO}_2][\text{NO}]}$$

$$0.60 = \frac{(0.11)(0.11)}{(0.77)(3.77)} = 0.0042$$

**Q9. Write the applications of the equilibrium constant K<sub>c</sub>.**

**Ans: Applications of the Equilibrium Constant:**

Equilibrium constant for a reaction can be used to predict many important features of the reactions.

For instance, it can be used to predict

- (i) Direction of the chemical reaction.
- (ii) Extent of the chemical reaction.
- (iii) Effect of changes in condition of the chemical reaction on the equilibrium position and equilibrium constant.

**Q10. How equilibrium constant K<sub>c</sub> help us to determine.**

- i. The Direction of a Reaction.
- ii. The Extent of Chemical Reaction.

**Ans: i. The Direction of a Reaction:**

The direction of reaction when reactants and products of a given chemical reaction are mixed, it is important to know whether the mixture is at equilibrium and



if not, in which direction it will move to achieve equilibrium state. For this purpose we use the **reaction quotient (Q)**.

**Reaction quotient (Q):**

The ratio of concentrations of products to reactant at any particular time is called reaction quotient. It is obtained by applying the law of mass action, using initial concentrations or concentrations at any particular time instead of equilibrium concentration.

$$Q = \frac{[\text{Products}]}{[\text{reactant}]}$$

The value Q leads to one of the following possibilities.

**a.  $Q < K_c$**

This indicates that more product is needed to acquire equilibrium. Therefore system must shift to the right until equilibrium is attained.

**b.  $Q > K_c$**

This indicates that less product or more reactant is needed to acquire equilibrium. Therefore system must shift to the left until equilibrium is reached.

**c.  $Q = K_c$**

This shows that reaction is at equilibrium. No shift will occur.

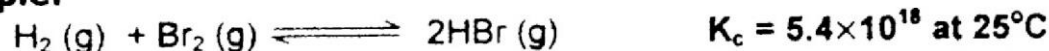
**ii. The Extent of Chemical Reaction:**

The extent of a chemical reaction can be predicated by considering the magnitude of equilibrium constant. Again there are three possibilities.

**a.  $K_c$  is very large:**

Many reactions have very large equilibrium constant.

**Example:**



If concentration of each of the reactant at equilibrium is 1 mole then concentration of HBr would be

$$\frac{[\text{HBr}]^2}{1 \times 1} = 5.4 \times 10^{18}$$

$$[\text{HBr}] = \sqrt{5.4 \times 10^{18}} \\ = 2.32 \times 10^9 \text{M}$$

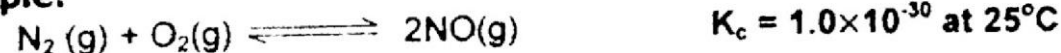
**Conclusion:**

It means that the concentration of HBr is very large as compared to that of reactants. At equilibrium the mixture will have mainly products. Thus large value of  $K_c$  indicates that the reaction goes virtually to completion.

**b.  $K_c$  is very small:**

Reactions having very small  $K_c$  do not proceed appreciably in the forward direction.

**Example:**



$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 1.0 \times 10^{-30}$$

If one mole of each of the reactant is present at equilibrium, then the concentration of NO would be

$$\frac{[\text{NO}]^2}{1 \times 1} = 1 \times 10^{-30}$$

$$[\text{NO}] = \sqrt{1 \times 10^{-30}}$$

$$[\text{NO}] = 1 \times 10^{-15} \text{ moles}$$

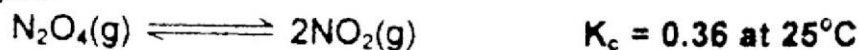
**Conclusion:**

Thus concentration of NO will be very small. Equilibrium mixture will have mainly reactants. Therefore, small value of  $K_c$  indicates that the reaction has very little tendency to move in the forward direction.

**c.  $K_c$  is neither very small nor very large:**

When  $K_c$  is neither very small nor very large, the equilibrium mixture contains appreciable amounts of both products and reactants.

**Example:**



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.36$$

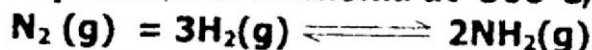
If 1 mole of  $\text{N}_2\text{O}_4$  is present at equilibrium, 0.8 mole of  $\text{NO}_2$  will be present in the equilibrium mixture.

**Conclusion:**

Hence the equilibrium mixture will contain appreciable amount of reactants and products. In such cases neither forward nor the reverse reaction go to completion.

**Example 7.8:**

For the synthesis of ammonia at  $500^\circ\text{C}$ ,  $K_c = 6.0 \times 10^{-2}$



Predict the direction in which the system will shift to attain equilibrium when the concentrations of species were found to be

$$[\text{H}_2] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{N}_2] = 1.0 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3] = 1.0 \times 10^{-3} \text{ M}$$

**Solution:**

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

$$Q = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-3})(1.0 \times 10^{-2})^3}$$

$$Q = 1.0 \times 10^3$$

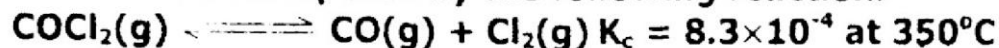
But

$$K_c = 6.0 \times 10^{-2}$$

Therefore  $Q > K_c$ . The system will shift to the left to achieve equilibrium.

## SELF-CHECK EXERCISE 7.7

Phosgene is potent chemical warfare agent and has been used in World War II. It decomposes by the following reaction.



Predict the direction in which system will shift to attain equilibrium, when the concentrations of species were found to be

$$[\text{COCl}_2] = 0.5 \text{ M}$$

$$[\text{CO}] = 2.5 \times 10^{-2} \text{ M}$$

$$[\text{Cl}_2] = 2.5 \times 10^{-2} \text{ M}$$

(Ans: Towards left)

**Solution:**

$$Q = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

$$Q = \frac{(2.5 \times 10^{-2})(2.5 \times 10^{-2})}{(0.5)} = 1.25 \times 10^{-3}$$

But

$$K_c = 8.3 \times 10^{-4}$$

Since  $Q > K_c$

Hence the system will shift towards left

## SELF-CHECK EXERCISE 7.8

White phosphorus  $\text{P}_4$  is produced by the reaction of phosphorite rock,  $\text{Ca}_3(\text{PO}_4)_2$  with coke. When exposed to air it bursts into smoke and fumes and releases a large amount of heat. Predict whether  $K_c$  for this reaction is large or small.



**Solution:**

This reaction is exothermic and when exposed to air it bursts into smoke and fumes and releases a large amount of heat. All these things show that the reaction virtually goes to completion. Thus the value of  $K_c$  will be very large and the reaction will go in forward direction.

**Q11. Define Le Chatelier's principle and how can it help us to predict the various factors which can affect the chemical equilibrium?**

**Ans:** Le Chatelier's principle

"It states that if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction which tends to reduce that change".

**Factors Affecting Equilibrium:**

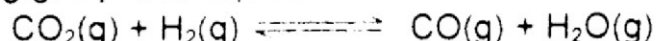
We can predict the effect of various factors such as concentration, pressure and temperature on a system at equilibrium by using Le Chatelier's principle.

### i. The Effect of a Change in Concentration:

When the concentration of one or more of the reactants or products present in equilibrium mixture is disturbed, the system will not remain at equilibrium state. According to Le Chatelier's principle, the equilibrium shifts to accommodate the substance added or removed and restore equilibrium again

#### Explanation:

Consider the following gas phase equilibrium.



- i. When  $\text{CO}_2$  is added to this equilibrium system, it is no longer in equilibrium. Higher concentration of  $\text{CO}_2$  increases the rate of forward reaction relative to the reverse reaction.
- ii. Thus more  $\text{CO}_2$  and  $\text{H}_2$  combine and more  $\text{CO}$  and  $\text{H}_2\text{O}$  form.
- iii. As time passes the concentrations of  $\text{CO}_2$  and  $\text{H}_2$  decrease, lowering the rate of forward reaction.
- iv. At the same time increased concentrations of the products accelerate the reverse reaction ultimately the two rates become equal again and equilibrium is re-established.
- v. At the new equilibrium concentrations of  $\text{CO}$  and  $\text{H}_2\text{O}$  are higher than were present before the  $\text{CO}_2$  was added.
- vi. Thus equilibrium is said to have shifted to the products side

#### Effect of increase in concentration:

In all chemical systems, an increase in concentration of any reactant shifts the equilibrium towards the formation of the products. If concentration of a product is increased, the equilibrium shifts towards the reactants. A shift towards the reactant lowers the concentration of the added product.

#### Effect of decrease in concentration:

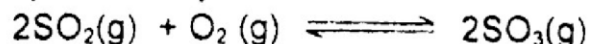
The opposite happens when we decrease the concentration of a reactant or product. If the reactant concentration is decreased, the equilibrium system shifts towards the reactants. Removal of product shifts equilibrium towards the products.

### ii. The Effect of Pressure Change:

Equilibria that contain gases are influenced by pressure changes

When pressure on a gaseous system at equilibrium is increased, the system tends to reduce the volume to undo or minimize the effect of increased pressure. This is done by decreasing the total number of gaseous molecules in the system. This is because at constant temperature and pressure, the volume of gas is directly proportional to the total number of molecules of the gas present.

Consider the following equilibrium system.



#### Increase in pressure:

When pressure increases the reaction system will reduce its volume by reducing the number of molecules present.

This means that the reaction will shift to the right, because in this direction three molecules (two of  $\text{SO}_2$  and one of  $\text{O}_2$ ) react to produce two molecules (of  $\text{SO}_3$ ), thus reducing the total number of gaseous molecules present.

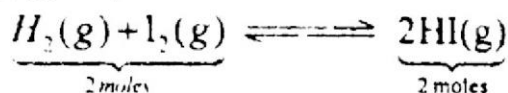
This means the equilibrium position will shift towards the side involving the smaller number of gaseous molecules in the balanced equation.

**When the pressure is reduced:**

When the pressure is reduced the system will shift so as to increase its volume.

**When number of molecules are same:**

When the total number of molecules is same on either side then.

**Example:**

Whenever the pressure is changed on such a system, neither forward nor the reverse reaction is favoured because the number of molecules is the same on each side. Such equilibria are not affected by pressure or volume changes.

**iii. The Effect of Change in Temperature:**

Chemical reactions that liberate heat are called **exothermic**.

Chemical reactions that absorb heat are called **endothermic**.

**Explanation:**

Heat is placed on the **right side of the equation** in case of exothermic reactions.

In endothermic reactions, it is placed on the **left side of the equation**.

We can use Le Chatelier's Principle to predict the direction of change.

**Endothermic process:**

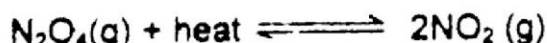
Treat heat as a reactant in the endothermic process. Predict the direction of shift in the same way as an actual reactant or product is added or removed. As an increase in temperature adding heat favours the endothermic reaction.

**Example:**

Now consider the following reaction



Because the reaction is endothermic, we can write heat on left side of equation.

**Conclusion:**

As the temperature is increased, heat enters the system and the reaction will shift from left to right. As a result of this change, concentration of  $NO_2$  will increase and that of  $N_2O_4$  will decrease. This will increase the value of  $K_c$ .

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \quad \begin{array}{l} \longleftarrow \text{increases} \\ \longleftarrow \text{decreases} \end{array}$$

That is why  $K_c$  for this reaction is  $7.7 \times 10^{-6}$  at  $0^\circ\text{C}$  and 0.4 at  $100^\circ\text{C}$ .

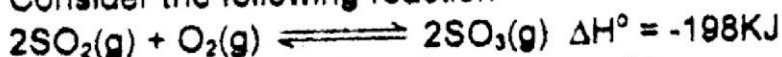
**Exothermic process:**

Treat heat as a product in the exothermic process. Predict the direction of shift in the same way as an actual reactant or product is added or removed.

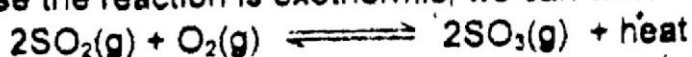
**Example:**

As decrease in temperature (removing heat) favours the exothermic reaction.

Consider the following reaction



Because the reaction is exothermic, we can write





Heat can be treated as if it were a substance involved in the reaction.

### Conclusion:

According to the Le Chatelier's Principle an increase in temperature will shift reaction from right to left in order to absorb the added heat and to counteract the temperature increase. As a result of this change concentration of  $\text{SO}_3$  will decrease and concentrations of  $\text{SO}_2$  and  $\text{O}_2$  will increase. As a result, the value of equilibrium constant will decrease.

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

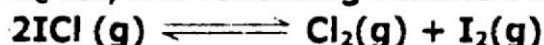
$\xleftarrow{\text{increases}}$   
 $\xleftarrow{\text{decreases}}$

That is why  $K_c = 2.8 \times 10^2$  at 1000K whereas at 298K the value of  $K_c = 1 \times 10^{26}$ . The equilibrium production of  $\text{SO}_3$  is favoured at lower temperature. This is because  $K_c$  is much larger at 298K than at 1000K.

### iv. The Effect of Addition of Catalyst:

A catalyst added to a reaction mixture speeds up both the forward and the reverse reaction to the same degree. Thus catalyst has no effect on the equilibrium concentrations of reaction mixture. However, the catalyst is important in enhancing the rate at which equilibrium is established.

**Example 7.9:**  $K_c$  for the following reaction is  $1.0 \times 10^{-3}$  at  $230^\circ\text{C}$



1.6 moles of ICl, 0.05 mole of  $\text{I}_2$  and 0.05 mole of  $\text{Cl}_2$  is present in the equilibrium mixture in  $2\text{dm}^3$  container at  $230^\circ\text{C}$ . Determine the equilibrium concentrations of  $\text{I}_2$ ,  $\text{Cl}_2$  and ICl when the equilibrium is restored after the addition of another mole of ICl.

**Solution:**

On adding one mole of ICl into the equilibrium mixture will shift equilibrium in the forward direction. Thus the concentration of ICl will decrease and concentration of  $\text{I}_2$  and  $\text{Cl}_2$  will increase by  $x$  whereas concentration of ICl will decrease by  $2x$ .

	$2\text{ICl}(\text{g}) \rightleftharpoons \text{Cl}_2(\text{g}) + \text{I}_2(\text{g})$		
Initial Conc.	$1.6 + 1 = 2.6$	0.05	0.05
(in moles)			
Conc. at new	$2.6 - 2x$	$0.05 + x$	$0.05 + x$
Equilibrium			
(in moles)			
Eq. Conc in	$\frac{2.6 - 2x}{2}$	$\frac{0.05 + x}{2}$	$\frac{0.05 + x}{2}$
Moles $\text{dm}^{-3}$			

$$K_c = \frac{[\text{Cl}_2][\text{I}_2]}{[\text{ICl}]^2}$$

$$1.0 \times 10^{-3} = \frac{\left(\frac{0.05 + x}{2}\right)\left(\frac{0.05 + x}{2}\right)}{\left(\frac{2.6 - 2x}{2}\right)^2}$$

Taking square root of both the sides

$$\sqrt{1.0 \times 10^{-3}} = \sqrt{\frac{(0.05+x)}{2} \cdot \frac{2.6-2x}{2}}$$

$$3.1 \times 10^{-3} = \frac{0.05-x}{2.6-2x}$$

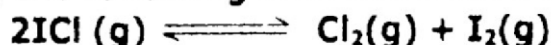
$$x = 0.029 \text{ moles dm}^{-3}$$

$$\begin{aligned} [\text{ICl}] &= 2.6 - 2x \\ &= 2.6 - 2 \times 0.029 \\ &= 2.571 \text{ moles dm}^{-3} \end{aligned}$$

$$\begin{aligned} [\text{I}_2] &= [\text{Cl}_2] = 0.05 + x \\ &= 0.05 + 0.029 \\ &= 0.079 \text{ moles dm}^{-3} \end{aligned}$$

## SELF-CHECK EXERCISE 7.9

$K_c$  for, the following reaction is  $1.0 \times 10^{-3}$  at  $230^\circ\text{C}$



1.6 moles of ICl, 0.05 mole of  $\text{I}_2$  and 0.05 mole of  $\text{Cl}_2$  is present in the equilibrium mixture in  $2\text{dm}^3$  container at  $230^\circ\text{C}$ . Determine the equilibrium concentrations of  $\text{I}_2$ ,  $\text{Cl}_2$  and ICl when the equilibrium is restored after the removal of one mole of ICl.

(Ans: 0.00478M, 0.00478, 0.6904M)

**Solution:**

When we add ICl into the equilibrium mixture will shift equilibrium in the forward direction. Therefore the concentration of ICl will decrease while the concentration of  $\text{I}_2$  and  $\text{Cl}_2$  will increase

	$2\text{ICl}(\text{g})$	$\rightleftharpoons$	$\text{Cl}_2(\text{g}) + \text{I}_2(\text{g})$
<i>Initial Concentration</i> (in moles)	1.6 + 1 = 2.6		0.05      0.05
<i>Concentration at new equilibrium.</i> (in moles)	2.6 - 2x		0.05 + x    0.05 + x
<i>Equation concentration</i> (in mole $\text{dm}^{-3}$ )	$\frac{2.6 - 2x}{2}$		$\frac{0.05 + x}{2}$ $\frac{0.05 + x}{2}$

$$\begin{aligned} K_c &= \frac{[\text{Cl}_2][\text{I}_2]}{[\text{ICl}]^2} \\ 1.0 \times 10^{-3} &= \frac{\left(\frac{0.05+x}{2}\right)\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)^2} \end{aligned}$$

$$1.0 \times 10^{-3} = \frac{\left(\frac{0.05+x}{2}\right)^2}{\left(\frac{2.6-2x}{2}\right)^2}$$

Taking squar root of both the sides

$$\sqrt{1.0 \times 10^{-3}} = \sqrt{\frac{\left(\frac{0.05+x}{2}\right)^2}{\left(\frac{2.6-2x}{2}\right)^2}}$$

$$\sqrt{1.0 \times 10^{-3}} = \frac{\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)}$$

$$0.0316 = \frac{0.05+x}{2.6-2x}$$

$$0.05+x = 0.0316(2.6-2x)$$

$$0.05+x = 0.0822 - 0.0632x$$

$$x + 0.0632x = 0.0822 - 0.05$$

$$1.0632x = 0.0322$$

$$x = \frac{0.0322}{1.0632} = 0.030 \text{ mole dm}^{-3}$$

$$[ICl] = 2.6 - 2x$$

$$= 2.6 - 2x \times 0.030 = 2.54 \text{ mole dm}^{-3}$$

$$[I_2] = [Cl_2] = 0.05 + x$$

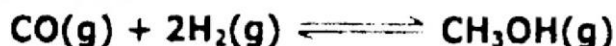
$$= 0.05 + 0.030 = 0.080 \text{ mole dm}^{-3}$$

**Do you know?**

Cigarette smoke is a major source of CO. Smokers inhale it directly through burning cigarette, even non-smoker also inhale CO when they are exposed to cigarette smoke of others. CO combines with hemoglobin to form carboxy-hemoglobin. Because carboxy-hemoglobin is unable to transport oxygen, the heart must pump more blood to get the needed oxygen. Also heavy smokers do not give their hemoglobin much opportunity to recover. Thus chronic exposure to CO from smoking is believed to cause heart disease and heart attacks. Other substances in cigarette smoke can cause lung cancer and respiratory problems. Infact, smoking is a habit with many higher risks.

## SELF-CHECK EXERCISE 7.10

The formation of methanol is an important industrial reaction in the processing of new fuels



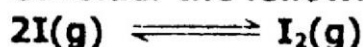
A student decreases pressure over the system in an attempt to increase the yield of methanol. Is this approach reasonable? Explain.

**Solution:**

There is present one molecule of CO and two molecules of H<sub>2</sub> on reactant side (total three molecules), while one molecule of CH<sub>3</sub>OH is present on product side. Thus, total number of molecules of products is less than that of reactants. Hence, if pressure is decreased, the system will increase its volume and it will shift in backward direction. Therefore, the approach of the student is not correct. In order to increase the yield of methanol, the equilibrium must shift in forward direction. This is done by increasing the pressure.

**SELF-CHECK EXERCISE 7.11**

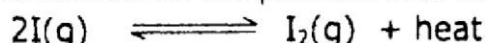
- Consider the following equilibrium



**What would be the effect on the position of equilibrium when temperature is decreased?**

**Solution:**

As the reaction is exothermic it is favoured at low temperature and in exothermic reactions heat is written on the product side as a product.

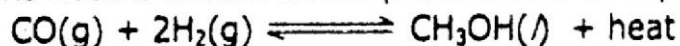


According to the Le-Chatelier's Principle decrease in temperature will shift the reaction in forward direction.

**Predict the effect of increasing the temperature on the amount of product in the following reaction.**

**Solution:**

As the reaction is exothermic it is favoured at low temperature and in exothermic reactions heat is written on the product side as a product.



According to the Le-Chatelier's Principle an increase in temperature will shift this reaction in backward direction in order to absorb the added heat and to compensate the added heat.

**Q12. Define and explain the solubility product.**

**Ans: Solubility Product:**

It is defined as the product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balanced equation.

**Explanation:**

When an excess of slightly soluble ionic compound is mixed with water. Some of it dissolves and remaining compound settle at the bottom. Dynamic equilibrium is established between undissolved solid compound and its ions in the saturated solution.

**Example:**

For example when CaF<sub>2</sub> is mixed with water. Following equilibrium is established.



**Mathematically:**

$K_C$  for this equilibrium can be written as

$$K_C = \frac{[Ca^{+2}][F^{-}]^2}{[CaF_2]}$$

Since  $CaF_2$  is slightly soluble salt its concentration almost remains constant.

Therefore,

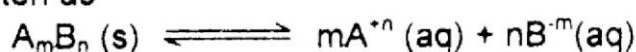
$$K_C [CaF_2] = [Ca^{+2}] [F^{-}]^2$$

$$K_{SP} = [Ca^{+2}] [F^{-}]^2$$

Where  $K_{SP}$  is a constant known as the solubility product constant.

**General,  $K_{SP}$  expression:**

In general,  $K_{SP}$  expression of any slightly soluble ionic compound  $A_mB_n$  can be written as



$$K_{SP} = [A^{+n}]^m [B^{-m}]^n$$

**Conclusion:**

This means that the solubility product constant is equal to the product of the equilibrium concentration of ions each raised to a power equal to the number of such ions in the formula unit of the compound.

**Q13. Define and explain precipitation reactions.****Ans: Precipitation Reactions:**

An aqueous reaction that takes place when two or more solution are mixed together, yielding a solid insoluble substance is called precipitation reaction.

**Explanation:**

Consider the reverse process i.e the formation of a solid from solution. For the prediction whether a precipitate will form when two solutions are mixed. We will use the term ion product ( $Q'$ ). It is obtained by substituting initial concentrations instead of equilibrium concentrations in the expression for  $K_{SP}$ .

**Example:**

For example, ion product expression for solid  $CaF_2$  is given by

$$Q' = [\text{Initial conc. of } Ca^{+2}] [\text{Initial conc. of } F^{-}]^2$$

If we add a solution containing  $Ca^{+2}$  ions to a solution containing  $F^{-}$  ions, precipitate may or may not form. To predict whether a precipitation will occur, we compare  $Q'$  and  $K_{SP}$ . There are two possibilities.

**Conditions for precipitation:**

- If  $Q' > K_{SP}$ , precipitation occurs and will continue until the concentration satisfy  $K_{SP}$ .
- If  $Q' < K_{SP}$ , precipitation does not occur.

**Example 7.10:**

50cm<sup>3</sup> of 0.001M NaOH is mixed with 150cm<sup>3</sup> of 0.01M  $MgCl_2$ . Will  $Mg(OH)_2$  precipitate?  $K_{SP}$  for  $Mg(OH)_2 = 2 \times 10^{-11}$ .

**Solution:**

First we will determine the concentrations of the ions present after mixing

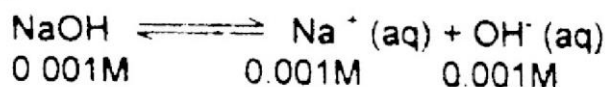
Total volume of solution



$$= 50\text{cm}^3 + 150\text{cm}^3$$

$$= 200\text{ cm}^3$$

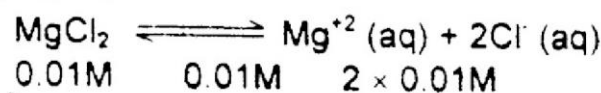
$$= 0.2\text{dm}^3$$



$$50\text{cm}^3 \text{ NaOH solution} = 0.05\text{dm}^3$$

$$[\text{OH}^-] = \frac{0.05\text{dm}^3 \times 0.001\text{M}}{0.2\text{dm}^3}$$

$$= 2.5 \times 10^{-4}\text{M}$$



$$150\text{cm}^3 \text{ MgCl}_2 \text{ solution} = 0.15\text{dm}^3$$

$$[\text{Mg}^{+2}] = \frac{0.05\text{dm}^3 \times 0.001\text{M}}{0.2\text{dm}^3}$$

$$= 7.5 \times 10^{-3}\text{M}$$

Now

$$Q' = [\text{Mg}^{+2}] [\text{OH}]^2$$

$$= (7.5 \times 10^{-3}) (2.5 \times 10^{-4})^2$$

$$= 47 \times 10^{-11}$$

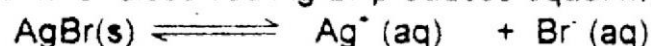
As  $Q' > K_{\text{SP}}$  therefore precipitation will occur.

### Example 7.11:

The solubility of Ag Br is  $7.1 \times 10^{-7}\text{M}$  at  $25^\circ\text{C}$ . Calculate its  $K_{\text{SP}}$ .

**Solution:**

$7.1 \times 10^{-7}\text{M}$  of dissolved Ag Br produces equal moles of  $\text{Ag}^+$  and  $\text{Br}^-$  ions.



$$7.1 \times 10^{-7}\text{M} \quad 7.1 \times 10^{-7}\text{M} \quad 7.1 \times 10^{-7}\text{M}$$

$$K_{\text{SP}} = [\text{Ag}^+][\text{Br}^-]$$

$$K_{\text{SP}} = (7.1 \times 10^{-7}) (7.1 \times 10^{-7})$$

$$K_{\text{SP}} = 5.0 \times 10^{-15}$$

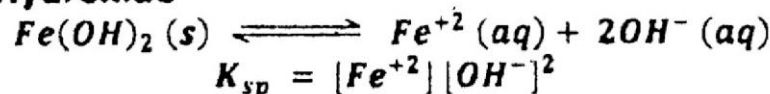
## SELF-CHECK EXERCISE 7.12

i. Write  $K_{\text{SP}}$  expressions for

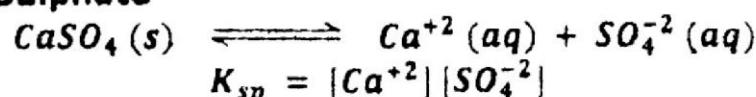
- Iron(II)Hydroxide
- Calcium Sulphate

**Solution:**

- Iron(II)Hydroxide



- Calcium Sulphate



- ii. Lead(II)Sulphate is used as white pigment. What is the solubility of  $PbSO_4$ ?  $K_{sp} = 1.96 \times 10^{-8}$  at  $25^\circ C$  (Ans:  $1.4 \times 10^{-4} M$ )

**Solution:**

	$PbSO_4 (s)$	$\rightleftharpoons$	$Pb^{+2} (aq)$	$+ SO_4^{-2} (aq)$
Initial Concentration. (in moles)	$a$		0	0
Concentration at equilibrium. (in moles)	$a - x$		$x$	$x$

$$K_{sp} = [Pb^{+2}] [SO_4^{-2}]$$

$$K_{sp} = [x \times x] = 1.96 \times 10^{-8}$$

$$x^2 = 1.96 \times 10^{-8}$$

Taking square root on both sides

$$\sqrt{x^2} = \sqrt{1.96 \times 10^{-8}}$$

$$x = 1.40 \times 10^{-4} M$$

- iii. Phosphate in natural water often precipitates as insoluble  $Ca_3(PO_4)_2$ . In Indus river concentration of  $Ca^{+2}$  and  $PO_4^{-3}$  ions is  $1.0 \times 10^{-9} M$  each. Will calcium phosphate precipitate?  $K_{sp} = 1.2 \times 10^{-29}$  at  $25^\circ C$  (Ans: No)

**Solution:**

$$K_{sp} = 1.2 \times 10^{-29} \text{ at } 25^\circ C$$

$$\text{Concentration of } Ca^{+2} \text{ ions} = 1.0 \times 10^{-9} M$$

$$\text{Concentration of } PO_4^{-3} \text{ ions} = 1.0 \times 10^{-9} M$$

$$Ca_3(PO_4)_2 \text{ ionizes in water as}$$

$$Ca_3(PO_4)_2 (s) \rightleftharpoons 3Ca^{+2} (aq) + 2PO_4^{-3} (aq)$$

$$\text{Its ion product is given as}$$

$$Q' = [Ca^{+2}]^3 [PO_4^{-3}]^2$$

$$= (1.0 \times 10^{-9})^3 (1.0 \times 10^{-9})^2$$

$$= 1.0 \times 10^{-45}$$

Since  $Q' < K_{sp}$ , Hence, the precipitation will not occur.

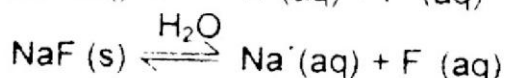
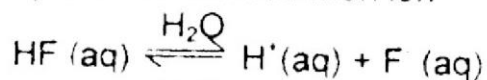
**Q14. Define and explain the Common Ion Effect.**

**Ans: Common Ion Effect:**

"The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of highly soluble electrolyte containing a common ion is called common ion effect"

**Explanation:**

Consider a solution of weak acid, hydrofluoric acid  $K_a = 7.2 \times 10^{-4}$ , its salt sodium fluoride produces the common ion



- Since HF is a weak electrolyte it slightly dissociates
- NaF being strong electrolyte breaks up completely into its ions
- The common ion  $F^-$  is produced by NaF will upset its equilibrium

- iv. This will increase concentration of  $F^-$  ions.
- v. According, to the Le Chatelier's principle, the equilibrium will shift to the left to use some of  $F^-$  ions.
- vi. This will decrease the dissociation of HF. Thus dissociation of HF will decrease in the presence of dissolved NaF.
- vii. This means as a result of equilibrium shift, the concentration of HF will increase.
- viii. Similarly when a highly soluble salt is added to the saturated solution of less soluble salt containing a **common ion**.
- ix. The degree of dissociation of less soluble salt decreases. Therefore it causes to decrease its solubility.

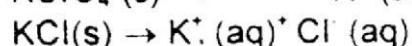
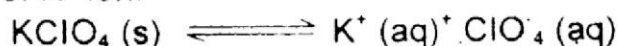
**Q15. Give the different applications of common ion effect.**

**Ans: Applications of common ion effect:**

The term common ion effect is used to describe the **behaviour of a solution** in which **same ion** is produced by two different compounds.

**i. Precipitation of Potassium per chlorate ( $KClO_4$ ):**

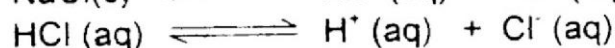
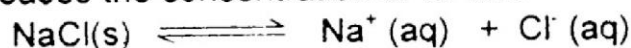
Potassium per chlorate  $KClO_4$  is moderately soluble in water. When highly soluble KCl is added to the saturated solution of  $KClO_4$ . It causes to increase the concentration of  $K^+$  ion.



According to the Le Chatelier's principle  $K^+$  ions will react with  $ClO_4^-$  ions to form  $KClO_4(s)$ . This will suppress, the ionization of  $KClO_4$ . Thus it will precipitate out.

**ii. Precipitation of pure NaCl:**

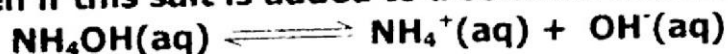
When HCl gas is passed through the saturated solution of NaCl (Brine), it causes to increase the concentration of  $Cl^-$  ion.



According to Le Chatelier's principle  $Cl^-$  ions will combine with  $Na^+$  ions to form precipitate of pure NaCl.

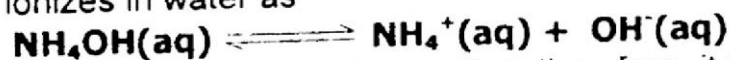
### SELF-CHECK EXERCISE 7.13

**i. Ammonium Chloride,  $NH_4Cl$  is a water soluble salt. What will happen if this salt is added to a solution containing ammonium hydroxide.**



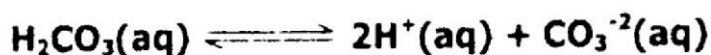
**Solution:**

$NH_4Cl$  ionizes in water as



Since,  $NH_4Cl$  is highly soluble in water, therefore, it increases the concentration of  $NH_4^+$  ions in the solution. According to the Le Chatelier's principle,  $NH_4^+$  ions will react with  $OH^-$  ions to form  $NH_4OH$ . Thus, it will suppress the ionization of  $NH_4OH$  and concentration of  $OH^-$  ions is decreased in the solution.

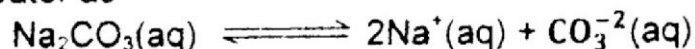
**ii. Carbonic acid is a weak acid. It ionizes in water as follows**



**What will happen if a strong electrolyte such as  $\text{Na}_2\text{CO}_3$  is added to a solution containing carbonic acid.**

**Solution:**

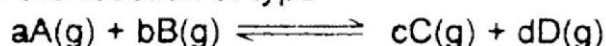
$\text{Na}_2\text{CO}_3$  ionizes in water as



Since,  $\text{Na}_2\text{CO}_3$  is more soluble in water than  $\text{H}_2\text{CO}_3$ , therefore, it increases the concentration of  $\text{CO}_3^{2-}$  in the solution. According to the Le-Chatelier's principle,  $\text{CO}_3^{2-}$  ions will react with  $\text{H}^+$  ions to form  $\text{H}_2\text{CO}_3$ . Thus, it will suppress the ionization of  $\text{H}_2\text{CO}_3$  and concentration of  $\text{H}^+$  ions is decreased in the solution.

## SUMMARY

- Chemical Equilibrium is a dynamic state in which the reaction proceeds with equal rates in both the directions.
- At equilibrium state reactants are converted continuously into products and vice versa, as molecules collide with each other.
- The law of mass action is a general description of the equilibrium condition. It states that for the reaction of type



The equilibrium equation is given by 
$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

where  $K_c$  is equilibrium constant

- The equilibrium can be expressed in terms of the equilibrium partial pressure of gases as  $K_p$ .
- The reaction quotient  $Q$  has the same form as the equilibrium constant expression, but it applies to the reaction that may not be at equilibrium.  
If  $Q > K_c$ , the reaction will proceed from right to left to achieve equilibrium.  
If  $Q < K_c$ , the reaction will proceed from left to right to achieve equilibrium.  
If  $Q = K_c$ , the reaction is at equilibrium.
- There is only value of  $K_c$  for each reaction at a given temperature. However, there are infinite numbers of equilibrium positions. An equilibrium position is defined as a particular set of equilibrium concentrations that satisfies the equilibrium expressions.
- The concentration of pure solids, pure liquids and solvents are constant and do not appear in equilibrium constant expression of a reaction.
- Le Chatelier's Principle allows us to predict the effect of changes in concentration, pressure and temperature on a system at equilibrium. It states that when a change is imposed on system equilibrium, the equilibrium position will shift in a direction that tends to undo the effect of imposed change
- Only a change in temperature changes the value of  $K_c$  for a particular reaction.

- The addition of catalyst has no effect on the equilibrium concentrations of reactants and products. However, it decreases time to achieve equilibrium state.
- The principle of equilibrium can also be applied when an excess of solid is added to form a saturated solution.

## EXERCISE

### MULTIPLE CHOICE QUESTIONS

**1. Choose the Correct Answer.**

- (i)  **$K_c$  is independent of**  
 (a) Temperature (b) Pressure  
 (c) Both temperature and pressure (d)  $K_p$
- (ii) **For which of the following reactions,  $K_c$  has units of concentration.**  
 (a)  $2A(g) \rightleftharpoons B(g)$  (b)  $A(g) \rightleftharpoons B(g)$   
 (c)  $A(g) \rightleftharpoons 2B(g)$  (d)  $3(g) \rightleftharpoons 2C(g)$
- (iii) **For the following reaction**  
 $2A(g) + B(g) \rightleftharpoons 3C(g)$   
**We can write**  
 (a)  $K_c > K_p$  (b)  $K_c < K_p$   
 (c)  $K_p - K_c = 0$  (d)  $K_p - K_c = -1$
- (iv) **When a catalyst is added to an equilibrium mixture, it decreases**  
 (a) Reverse reaction (b) Forward reaction  
 (c) Concentrations of reaction mixture (d) Enthalpy of reaction  
 (e) It has not effect
- (v) **If  $K_{sp} = [M^{+2}]^3 [X^{-3}]^2$ , the chemical formula of compound is**  
 (a)  $MX_2$  (b)  $M_2X_3$   
 (c)  $M_3X_2$  (d)  $M_1X_2$  (e) None of these
- (vi) **NaCl can be purified by passing HCl gas through the \_\_\_\_\_ solution of NaCl.**  
 (a) Dilute (b) Concentrated (c) Hot (d) Cold
- (vii)  **$K_c = K_p$  when  $\Delta n$  is equal to**  
 (a) Zero (b) +1 (c) -1 (d) -2
- (viii) **Consider the following reaction:**  
 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^\circ = -198 \text{ KJ}$   
**Yield of sulphur trioxide can be increased by**  
 (a) increasing pressure (b) increasing temperature  
 (c) adding catalyst (d) increasing concentration of oxygen
- 1 a. b

- The addition of catalyst has no effect on the equilibrium concentrations of reactants and products. However, it decreases time to achieve equilibrium state.
- The principle of equilibrium can also be applied when an excess of solid is added to form a saturated solution.

## EXERCISE

### MULTIPLE CHOICE QUESTIONS

1. Choose the Correct Answer.

- (i)  $K_c$  is independent of  
 (a) Temperature (b) Pressure  
 (c) Both temperature and pressure (d)  $K_p$
- (ii) For which of the following reactions,  $K_c$  has units of concentration.  
 (a)  $2A(g) \rightleftharpoons B(g)$  (b)  $A(g) \rightleftharpoons B(g)$   
 (c)  $A(g) \rightleftharpoons 2B(g)$  (d)  $3(g) \rightleftharpoons 2C(g)$
- (iii) For the following reaction  
 $2A(g) + B(g) \rightleftharpoons 3C(g)$   
 We can write  
 (a)  $K_c > K_p$  (b)  $K_c < K_p$   
 (c)  $K_p - K_c = 0$  (d)  $K_p - K_c = -1$
- (iv) When a catalyst is added to an equilibrium mixture, it decreases  
 (a) Reverse reaction (b) Forward reaction  
 (c) Concentrations of reaction mixture (d) Enthalpy of reaction  
 (e) It has not effect
- (v) If  $K_{sp} = [M^{+2}]^3 [X^{-3}]^2$ , the chemical formula of compound is  
 (a)  $MX_2$  (b)  $M_2X_3$   
 (c)  $M_3X_2$  (d)  $M_1X_2$  (e) None of these
- (vi) NaCl can be purified by passing HCl gas through the \_\_\_\_\_  
 solution of NaCl.  
 (a) Dilute (b) Concentrated (c) Hot (d) Cold
- (vii)  $K_c = K_p$  when  $\Delta n$  is equal to  
 (a) Zero (b) +1 (c) -1 (d) -2
- (viii) Consider the following reaction:  
 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^\circ = -198 \text{ KJ}$   
 Yield of sulphur trioxide can be increased by  
 (a) increasing pressure (b) increasing temperature  
 (c) adding catalyst (d) increasing concentration of oxygen



2. a, b, c
3. a, b, c, d
4. a, d

### Answers

i. d	ii. c	iii. c	iv. e	v. b	vi. b	vii. a	viii. 4
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#### 2. Define chemical equilibrium?

##### Ans. Chemical Equilibrium:

"It is the state of a reversible reaction at which composition of the reaction mixture do not change and the rate of both forward and reverse reaction is same that stage of reaction is called chemical equilibrium."

#### 3. State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.

##### Ans: Conditions for Equilibrium:

Important features of equilibration constant expression are as follows:

- i.  $K_c$  applies only at equilibrium. The subscript c indicates the concentrations of reactants and products are in moles per  $\text{dm}^3$  at equilibrium state.
- ii.  $K_c$  is independent of initial concentrations of reactants and products but depends upon temperature. At a given temperature, it has only one value. Whether we start reaction with pure reactants or pure products or any composition in between, the value of  $K_c$  remains unchanged.
- iii.  $K_c$  is related to the coefficients of the balanced equation. The concentrations of the products are placed in the numerator and those of reactants in the denominator. Each concentration is raised to a power equal to its coefficient in the balanced equation.
- iv. The magnitude of  $K_c$  indicates the position of equilibrium. When  $K_c$  is less than 1, the denominator is greater in magnitude than the numerator. This means the concentration of the reactants are greater than those of products when the equilibrium is established. Whereas, when  $K_c$  is greater than 1, the numerator is greater in magnitude than the denominator. This means the concentrations of the products are greater than those of the reactants at equilibrium.

#### Ways to Recognize Equilibrium and Determination of Equilibrium Constant:

Equilibrium constant expression can be determined by two methods:

- a) Physical Method (spectrometric method)
- b) Chemical Method

##### a) Physical Method (spectrometric method):

This method is based on the measurement of a physical property of the reaction mixture. This physical property is measured during the course of reaction without removing the sample from the reaction mixture.

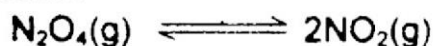
#### Explanation:

This method is applicable if a reactant or product absorbs ultraviolet, visible or infrared radiation. The concentration can be determined by measuring the amount of radiation absorbed.

#### Example:



Equilibrium constant for  $\text{N}_2\text{O}_4 - \text{NO}_2$  system can be determined by the spectrophotometer.



$\text{N}_2\text{O}_4$  is a colourless gas whereas  $\text{NO}_2$  is reddish brown gas. The progress of the reaction can be studied by measuring the absorbance at regular interval. Absorbance is proportional to the concentration of  $\text{NO}_2$ .

At equilibrium spectrometer will show constant value of absorbance. Suppose reaction is started with "a" moles of  $\text{N}_2\text{O}_4$  at  $100^\circ\text{C}$ . and x moles of it is converted to  $\text{NO}_2$ . By applying stoichiometry, the amount of  $\text{NO}_2$  present in equilibrium will be  $2x$ , which is measured by the spectrophotometer.

#### Mathematically:

Suppose the volume of the reaction mixture is  $V \text{ dm}^3$ , then we can write.

	$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	
Initial Conc	a	zero
(in moles)		
Eq. Conc	$a - x$	$2x$
(in moles)		
Eq. Conc	$\frac{a - x}{V}$	$\frac{2x}{V}$
(mole/ $\text{dm}^3$ )		

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

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

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

#### b) Chemical Method:

In this method, the amount of a reactant or product is determined by a suitable chemical reaction

#### Explanation:

Consider the reaction between acetic acid and ethanol to form ethyl acetate and water. It is an example of reversible reaction in the solution state



Suppose this reaction is started by taking 'a' moles of acetic acid and 'b' moles of ethanol in a stoppered flask at room temperature. A small amount of mineral acid is added in the mixture to catalyse the reaction.

The progress of the reaction can be studied by determining the concentration of acetic acid after regular intervals. For this purpose small portion of mixture is withdrawn

The concentration of acetic acid is determined by titrating it against a standard solution of  $\text{NaOH}$  using phenolphthalein as indicator. Concentration of



using initial concentrations or concentrations at any particular time instead of equilibrium concentration.

$$Q = \frac{[\text{Products}]}{[\text{reactant}]}$$

The value  $Q$  leads to one of the following possibilities.

**a.  $Q < K_c$**

This indicates that more product is needed to acquire equilibrium. Therefore system must shift to the right until equilibrium is attained.

**b.  $Q > K_c$**

This indicates that less product or more reactant is needed to acquire equilibrium. Therefore system must shift to the left until equilibrium is reached

**c.  $Q = K_c$**

This shows that reaction is at equilibrium. No shift will occur

**(ii) Solubility product:**

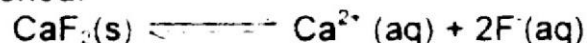
It is defined as the product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balanced equation.

**Explanation:**

When an excess of slightly soluble ionic compound is mixed with water. Some of it dissolves and remaining compound settle at the bottom. Dynamic equilibrium is established between undissolved solid compound and its ions in the saturated solution.

**Example:**

For example when  $\text{CaF}_2$  is mixed with water. Following equilibrium is established.



**Mathematically:**

$K_c$  for this equilibrium can be written as

$$K_c = \frac{[\text{Ca}^{2+}][\text{F}^{-}]^2}{[\text{CaF}_2]}$$

Since  $\text{CaF}_2$  is slightly soluble salt its concentration almost remains constant.

Therefore,

$$K_c [\text{CaF}_2] = [\text{Ca}^{2+}] [\text{F}^{-}]^2$$

$$K_{sp} = [\text{Ca}^{2+}] [\text{F}^{-}]^2$$

Where  $K_{sp}$  is a constant known as the solubility product constant.

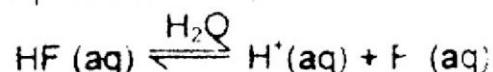
**(iii) Common Ion Effect:**

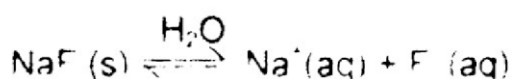
**Common Ion Effect:**

The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of highly soluble electrolyte containing a common ion is called **common ion effect**

**Explanation:**

Consider a solution of weak acid, hydrofluoric acid  $K_a = 7.2 \times 10^{-4}$ , its salt sodium fluoride produces the common ion.

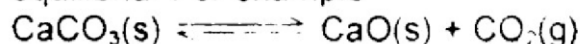




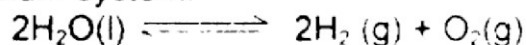
- i. Since HF is a weak electrolyte, it slightly dissociates.
- ii. NaF being strong electrolyte breaks up completely into its ions.
- iii. The common ion  $\text{F}^-$  is produced by NaF will upset its equilibrium.
- iv. This will increase concentration of  $\text{F}^-$  ions
- v. According, to the Le Chatelier's principle, the equilibrium will shift to the left to use some of  $\text{F}^-$  ions.
- vi. This will decrease the dissociation of HF. Thus dissociation of HF will decrease in the presence of dissolved NaF.
- vii. This means as a result of equilibrium shift, the concentration of HF will increase.
- viii. Similarly when a highly soluble salt is added to the saturated solution of less soluble salt containing a **common ion**.
- ix. The degree of dissociation of less soluble salt decreases. Therefore it causes to decrease its solubility

**(iv) Heterogenous equilibrium:**

Equilibria which involve more than one phases are called Heterogeneous equilibria. For example



If pure solids or pure liquids are involved in an equilibrium system, their concentrations are not included in the equilibrium constant expression. This is because the change in concentrations of any pure solid or liquid has no effect on the equilibrium system.



$$K_c = [\text{H}_2]^2 [\text{O}_2]$$

$$\text{and } K_p = p_{\text{H}_2}^2 \times p_{\text{O}_2}$$

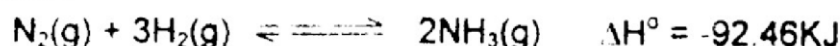
**(v) Ion product:**

It is the product of the initial concentration of ions each raised to a power equal to the co-efficient of the ion in the balanced chemical equation.

**6. Explain industrial application of Le Chatelier's principle using Haber's process as an example.**

**Ans: Industrial Application of Le Chatelier's Principle (Synthesis of Ammonia by Haber's Process):**

The manufacture of ammonia by Haber's process is represented by the following equation.



This equation provides the following information.

- i) The reaction is exothermic.
  - ii) The reaction proceeds with a decrease in number of molecules or moles.  
Le Chatelier's principle suggests three ways to get maximum yield of ammonia.
- i. Low Temperature:**

The forward reaction is exothermic therefore, low temperature will favour the formation of ammonia. The suitable temperature is  $400^{\circ}\text{C}$ .

**ii. High Pressure:**

Since four molecules (one of  $\text{N}_2$  and three of  $\text{H}_2$ ) react to produce two molecules of  $\text{NH}_3$ . Thus high pressure will shift the equilibrium to the right side i.e. formation of  $\text{NH}_3$ . The most suitable pressure is 200 – 300 atm.

**Optimum condition:**

Thus optimum condition for equilibrium production of ammonia is low temperature and high pressure. Although at low temperature yield of ammonia is high, but the rate of its formation is so slow that the process becomes uneconomical. Therefore, a catalyst is used to increase the rate of reaction. Usually a piece of iron with other metal oxides is used as catalyst. The equilibrium mixture contains 35%  $\text{NH}_3$  by volume.

**iii. Continual removal of ammonia:**

A final factor which greatly increases the production of ammonia is the continuous removal of ammonia as it is formed. This is done by liquefying ammonia.

The equilibrium mixture is cooled by refrigeration coils until ammonia condenses at  $-33.4^{\circ}\text{C}$  and is removed.  $\text{N}_2$  and  $\text{H}_2$  which do not liquefy at this temperature are recycled into the reaction chamber.

The stress caused by the continual removal of ammonia shifts the equilibrium toward the production of more ammonia. In fact the mixture needs not to be allowed to come to equilibrium at all. In this way practically 100% conversion of  $\text{N}_2$  and  $\text{H}_2$  to  $\text{NH}_3$  is possible.

**7. Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium.**

**Ans. Microscopic events:**

The microscopic events that take place in an equilibrium system are given below.

- The rate of chemical reaction depends on the numbers of effective collisions between the reacting molecules.
- At equilibrium the numbers of effective collisions for the forward and reverse reactions are equal.

**Number of effective collisions:**

Increase in concentration of reactant increases such collisions for the forward reaction. Thus equilibrium shift towards right with the formation of more molecules of products.

Therefore the number of effective collisions for the reverse process also increases. As time passes the effective collisions of reactant molecules decreased, lowering the rate of forward reaction.

Ultimately the number of effective collisions for both the processes again becomes equal and equilibrium is re-established.

- 8.  $50\text{ cm}^3$  of acetic acid ( $d = 1.049\text{ g cm}^{-3}$ ) is mixed with  $50\text{ cm}^3$  of ethanol ( $d = 0.789\text{ g cm}^{-3}$ ) what is the equilibrium composition of the mixture at  $25^{\circ}\text{C}$  ( $K_c = 4$ ). (Ans:  $\text{CH}_3\text{COOH} = 31.68\text{ g}$ ,  $\text{C}_2\text{H}_5\text{OH} = 32.506\text{ g}$ ,  $\text{CH}_3\text{COOC}_2\text{H}_5 = 30.448\text{ g}$ ,  $\text{H}_2\text{O} = 6.22\text{ g}$ )**

**Solution:**

**Equilibrium constant =  $K_c = 4$  at  $25^{\circ}\text{C}$**

Volume of acetic acid =  $50 \text{ cm}^3$

Density of acetic acid =  $1.049 \text{ g cm}^{-3}$

Mass of acetic acid =  $\text{density} \times \text{Volume} = 1.049 \times 50 = 52.45 \text{ g}$

Molar mass of acetic acid =  $60 \text{ g mole}^{-1}$

$$\text{Number of moles of } \text{CH}_3\text{COOH} = \frac{52.45}{60} = 0.874 \text{ mole}$$

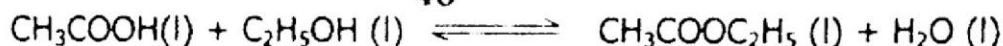
Volume of ethanol =  $50 \text{ cm}^3$

Density of ethanol =  $0.789 \text{ g cm}^{-3}$

Mass of ethanol =  $\text{density} \times \text{Volume} = 0.789 \times 50 = 39.45 \text{ g}$

Molar mass of ethanol =  $46 \text{ g mole}^{-1}$

$$\text{Number of moles of } \text{C}_2\text{H}_5\text{OH} = \frac{39.45}{46} = 0.858 \text{ mole}$$



Initial Concentration. (in moles)	0.874	0.858	zero	zero
--------------------------------------	-------	-------	------	------

Equation Concentration. (in moles)	$0.874 - x$	$0.858 - x$	$x$	$x$
---------------------------------------	-------------	-------------	-----	-----

$K_c$  will be

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

$$4 = \frac{(x)(x)}{(0.874 - x)(0.858 - x)}$$

$$x^2 = 4(0.874 - x)(0.858 - x)$$

$$x^2 = 4(0.750 - 0.874x - 0.858x + x^2)$$

$$x^2 = 4(0.750 - 1.732x + x^2)$$

$$x^2 = 3 - 6.928x + 4x^2$$

$$x^2 - 3 + 6.928x + 4x^2 = 0$$

$$-3x^2 + 6.928x - 3 = 0$$

Taking negative sign common on both side

$$3x^2 - 6.928x + 3 = 0$$

Using quadratic formula

$a = 3$ ,  $b = -6.928$  and  $c = 3$

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

$$x = \frac{-(-6.928) \pm \sqrt{(-6.928)^2 - 4(3 \times 3)}}{2 \times 3}$$

$$x = \frac{6.928 \pm \sqrt{11.997}}{6}$$

Thus,

$$x = \frac{6.928 \pm \sqrt{11.997}}{6} \text{ or } x = \frac{6.928 - \sqrt{11.997}}{6}$$

$$x = 1.73 \text{ moles} \text{ or } x = 0.577 \text{ moles}$$

$x = 1.73$  moles is not possible because it is greater than the initial concentration of reactants.

Therefore,

$$x = 0.577 \text{ moles}$$



The equilibrium concentrations in moles are as follows.

$$[\text{CH}_3\text{COOH}] = 0.874 - x = 0.874 - 0.577 = 0.297 \text{ moles}$$

$$\text{Mass of } [\text{CH}_3\text{COOH}] \text{ in grams} = 0.297 \text{ moles} \times 60 \text{ g mole}^{-1} = 17.82 \text{ g}$$

$$[\text{C}_2\text{H}_5\text{OH}] = 0.858 - x = 0.858 - 0.577 = 0.281 \text{ moles}$$

$$\text{Mass of } [\text{C}_2\text{H}_5\text{OH}] = 0.281 \text{ moles} \times 46 \text{ g mole}^{-1} = 12.93 \text{ g}$$

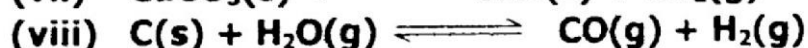
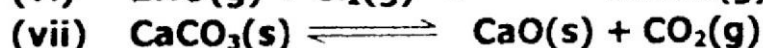
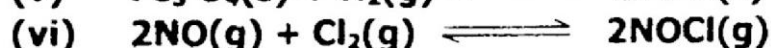
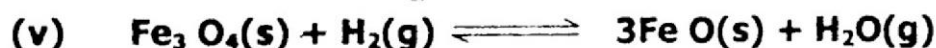
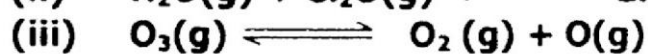
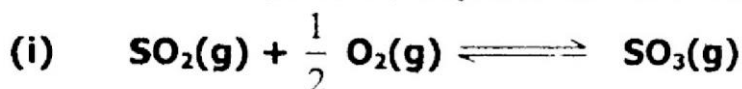
$$[\text{CH}_3\text{COOC}_2\text{H}_5] = x = 0.577 \text{ moles}$$

$$\text{Mass of } [\text{CH}_3\text{COOC}_2\text{H}_5] = 0.577 \text{ moles} \times 88 \text{ g mole}^{-1} = 50.78 \text{ g}$$

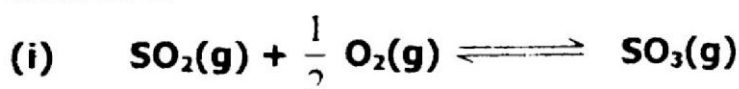
$$[\text{H}_2\text{O}] = x = 0.577 \text{ moles}$$

$$\text{Mass of } [\text{H}_2\text{O}] = 0.577 \text{ moles} \times 18 \text{ g mole}^{-1} = 10.39 \text{ g}$$

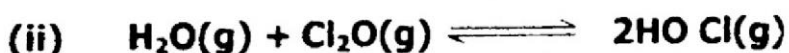
9. Write  $K_c$  and  $K_p$  expressions for the following reactions



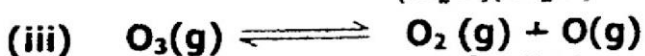
Solution:



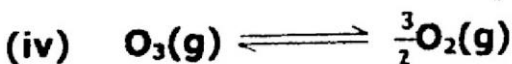
$$K_c = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{\frac{1}{2}}} \quad \text{and} \quad K_p = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} \times P_{\text{O}_2}^{\frac{1}{2}}}$$



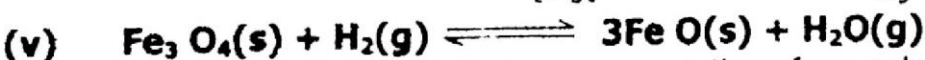
$$K_c = \frac{[\text{HOCl}]^2}{[\text{H}_2\text{O}][\text{Cl}_2\text{O}]} \quad \text{and} \quad K_p = \frac{P_{\text{HOCl}}^2}{P_{\text{H}_2\text{O}} \times P_{\text{Cl}_2\text{O}}}$$



$$K_c = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \quad \text{and} \quad K_p = \frac{P_{\text{O}_2} \times P_{\text{O}}}{P_{\text{O}_3}}$$



$$K_c = \frac{[\text{O}_2]^{\frac{3}{2}}}{[\text{O}_3]} \quad \text{and} \quad K_p = \frac{P_{\text{O}_2}^{\frac{3}{2}}}{P_{\text{O}_3}}$$

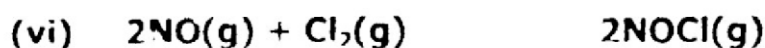


As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression.

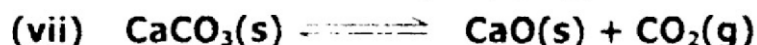
Therefore

$$K_c = \frac{[\text{H}_2\text{O}]}{[\text{H}_2]} \quad \text{and} \quad K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$$





$$K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]} \quad \text{and} \quad K_p = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 \times P_{\text{Cl}_2}}$$



As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression.

$$K_c = [\text{CO}_2] \quad \text{and} \quad K_p = P_{\text{CO}_2}$$



As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression

$$K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]} \quad \text{and} \quad K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$$

10.  $K_c = 2.6 \times 10^{-5}$  at  $125^\circ\text{C}$  for the reaction  $2\text{NH}_3\text{(g)} \rightleftharpoons \text{N}_2\text{(g)} + 3\text{H}_2\text{(g)}$   
Calculate  $K_p$  at this temperature. (Ans:  $K_p = 284.4078$ )

**Solution:**

$$T = 125^\circ\text{C} + 273 = 398 \text{ K}$$

$$K_c = 2.6 \times 10^{-5} \text{ at } 125^\circ\text{C}$$

$$\Delta n = (1 + 3) - 2 = 2$$

$$R = 0.0821 \text{ atm dm}^3 \text{ K}^{-1} \text{ mole}^{-1}$$

As we know that

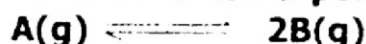
$$K_p = K_c(RT)^{\Delta n}$$

Putting values

$$K_p = 2.6 \times 10^{-5} (0.0821 \times 398)^2$$

$$K_p = 2.78 \times 10^{-2}$$

11. At a particular temperature  $K_p = 0.133 \text{ atm}$ . Which of the following conditions corresponds to equilibrium position for the reaction.

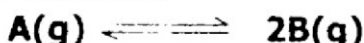


(a)  $P_B = 0.175 \text{ atm}, \quad P_A = 0.102 \text{ atm}$

(b)  $P_B = 0.064 \text{ atm}, \quad P_A = 0.0308 \text{ atm}$

(c)  $P_B = 0.144 \text{ atm}, \quad P_A = 0.156 \text{ atm} \quad (\text{Ans: b and c})$

**Solution:**



$$K_p = 0.133 \text{ atm}$$

As we know that

$$K_p = \frac{P_B^2}{P_A}$$

(a)  $P_B = 0.175 \text{ atm}, \quad P_A = 0.102 \text{ atm}$

$$K_p = \frac{P_B^2}{P_A} = \frac{(0.175)^2}{(0.102)} = 0.30 \text{ atm}$$

As this value does not correspond with the given value therefore the reaction is not at equilibrium.

(b)  $P_B = 0.064 \text{ atm}, \quad P_A = 0.0308 \text{ atm}$

$$K_p = \frac{P_B^2}{P_A} = \frac{(0.064)^2}{(0.0308)} = 0.133 \text{ atm}$$

As this value corresponds with the given value therefore the reaction is at equilibrium

(c)  $P_B = 0.144 \text{ atm}, \quad P_A = 0.156 \text{ atm}$

$$K_p = \frac{P_B^2}{P_A} = \frac{(0.144)^2}{(0.156)} = 0.133 \text{ atm}$$

As this value corresponds with the given value therefore the reaction is at equilibrium.

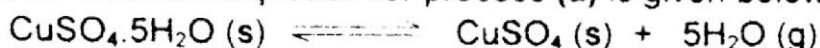
12. Write the expression for  $K_c$  and  $K_p$  for the following processes.

(a) Blue vitriol is deep blue solid copper (II) sulphate pentahydrate is heated to drive off water vapours to form white solid copper (II) sulphate.

(b) The decomposition of solid phosphorus pentachloride to gaseous phosphorus trichloride and chlorine gas.

**Solution:**

(a) The balance chemical equation for process (a) is given below.

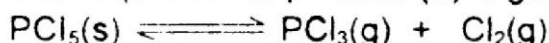


As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression

$$K_c = [\text{H}_2\text{O}]^5$$

$$K_p = P_{\text{H}_2\text{O}}^5$$

(b) The balance chemical equation for process (b) is given below

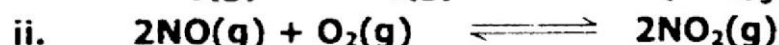
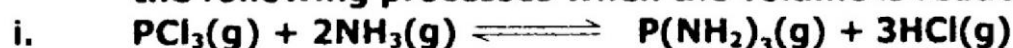


As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression.

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

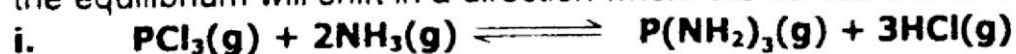
$$K_p = P_{\text{PCl}_3} \times P_{\text{Cl}_2}$$

13. Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.



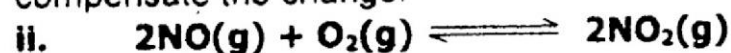
**Ans. Principle:**

According to Le-Chatlier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus the equilibrium will shift in a direction where the numbers of molecules are less.



In this reaction three molecules are present on reactant side ( $\text{PCl}_3$ ,  $2\text{NH}_3$ ) while four molecules are present on product side ( $\text{P}(\text{NH}_2)_3$ ,  $3\text{HCl}$ ).

Therefore, when the volume decreases by increasing pressure then the equilibrium will shift in backward direction to reduce the number of molecules and to compensate the change.



In this reaction three molecules are present on reactant side ( $2\text{NO}$ ,  $\text{O}_2$ ) and two molecules ( $2\text{NO}_2$ ) are present on product side

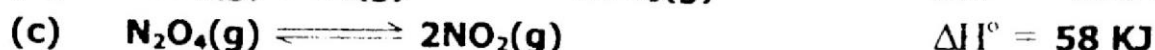
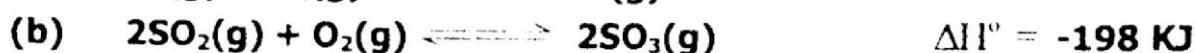
Therefore, when the volume decreases by increasing pressure then the equilibrium will shift in forward direction to reduce the number of molecules, and to compensate the change



In this reaction, nine molecules are present on reactant side ( $4\text{NH}_3$ ,  $5\text{O}_2$ ) and ten molecules are present on product side ( $4\text{NO}$ ,  $6\text{H}_2\text{O}$ ).

Therefore, when the volume decreases by increasing pressure then the equilibrium will shift in backward direction to reduce the number of molecules and to compensate the change

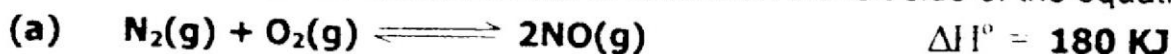
**14. For each of the following reactions, predict how the value of  $K_c$  changes as the temperature is increased.**



**Ans.**

**Principles:**

- High temperature favours endothermic reactions.
- Low temperature favours exothermic reactions.
- In exothermic reactions heat is written on the right side of the equation.
- In endothermic reactions heat is written on the left side of the equation.



As the reaction is endothermic therefore heat is written on the left side of the equation.



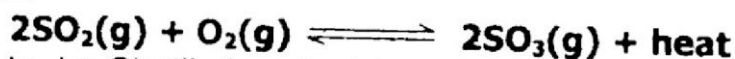
According to Le-Chatelier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat. Therefore, concentration of NO will increase while that of  $\text{N}_2$  and  $\text{O}_2$  will decrease.

$$K_c = \frac{[\text{NO}]^2 \longleftarrow \text{decrease}}{[\text{N}_2][\text{O}_2] \longleftarrow \text{increase}}$$

Hence, in this case the value of  $K_c$  will increase with increase in temperature.



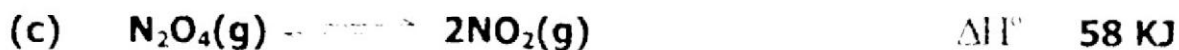
As the reaction is exothermic therefore, heat is written on the right side of the equation.



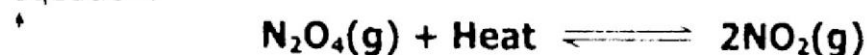
According to Le-Chatelier's principle, when temperature is increased this reaction will shift in the reverse direction in order to compensate the added heat. Thus, concentration of  $\text{SO}_2$  and  $\text{O}_2$  will increase while that of  $\text{SO}_3$  will decrease.

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

Hence, in this case the value of  $K_c$  will decrease with increase in temperature.



As the reaction is endothermic therefore heat is written on the left side of the equation.



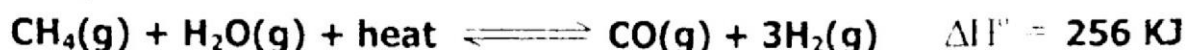
According to Le-Chatlier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat. Therefore, concentration of  $\text{NO}_2$  will increase while that of  $\text{N}_2\text{O}_4$  will decrease

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

Hence, in this case the value of  $K_c$  will increase with increase in temperature.



As the reaction is endothermic therefore heat is written on the left side of the equation.



According to Le-Chatlier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat. Therefore, concentration of  $\text{CO}$  and  $\text{H}_2$  will increase while that of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  will decrease.

$$K_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]}$$

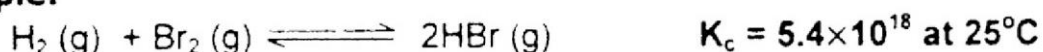
Hence, in this case the value of  $K_c$  will increase with increase in temperature.

**15. What is the difference between an equilibrium with a  $K_c$  value larger than one compared with an equilibrium that has a  $K_c$  smaller than one.**

Ans.  **$K_c$  is very large:**

Many reactions have very large equilibrium constant.

**Example:**



If concentration of each of the reactant at equilibrium is 1 mole then concentration of  $\text{HBr}$  would be

$$\frac{[\text{HBr}]^2}{1 \times 1} = 5.4 \times 10^{18}$$

$$\begin{aligned} [\text{HBr}] &= \sqrt{5.4 \times 10^{18}} \\ &= 2.32 \times 10^9 \text{ M} \end{aligned}$$

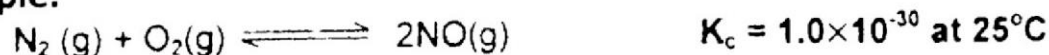
**Conclusion:**

It means that the concentration of  $\text{HBr}$  is very large as compared to that of reactants. At equilibrium the mixture will have mainly products. **Thus large value of  $K_c$  indicates that the reaction goes virtually to completion.**

**b.  $K_c$  is very small:**

Reactions having very small  $K_c$  do not proceed appreciably in the forward direction

**Example:**



$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 1.0 \times 10^{-30}$$

If one mole of each of the reactant is present at equilibrium, then the concentration of NO would be

$$\frac{[\text{NO}]^2}{1 \times 1} = 1 \times 10^{-30}$$

$$[\text{NO}] = \sqrt{1 \times 10^{-30}}$$

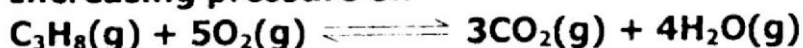
$$[\text{NO}] = 1 \times 10^{-15} \text{ moles}$$

### Conclusion:

Thus concentration of NO will be very small. Equilibrium mixture will have mainly reactants. Therefore, small value of  $K_c$  indicates that the **reaction has very little tendency to move in the forward direction.**

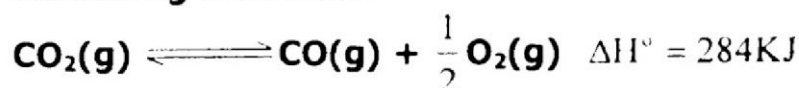
### 16. Describe the behaviour of the following equilibria with the stated changes

#### (a) Increasing pressure on



#### (b) Adding $\text{I}_2(\text{g})$ to $2\text{HI}(\text{g}) \rightleftharpoons \text{I}_2(\text{g}) + \text{H}_2(\text{g})$

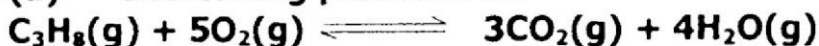
#### (c) Removing heat from



#### (d) Decreasing pressure on



### Ans. (a) Increasing pressure on



According to Le-Chatlier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus the equilibrium will shift in a direction where the numbers of molecules are less.

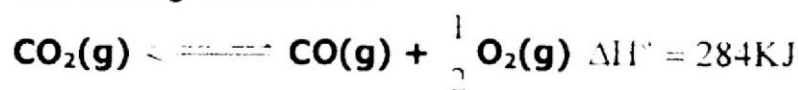
According to the given reaction, six molecules are present on reactant side ( $\text{C}_3\text{H}_8$ ,  $5\text{O}_2$ ) and seven molecules ( $3\text{CO}_2$ ,  $4\text{H}_2\text{O}$ ) are present on product side.

Therefore, when the pressure increases the volume must decrease and the equilibrium will shift in backward direction to reduce the number of molecules and to compensate the change.

#### (b) Adding $\text{I}_2(\text{g})$ to $2\text{HI}(\text{g}) \rightleftharpoons \text{I}_2(\text{g}) + \text{H}_2(\text{g})$

According to Le-Chatlier's principle, the addition of  $\text{I}_2$  increase the concentration of products and to compensate it the equilibrium will shift in the backward direction.

#### (c) Removing heat from



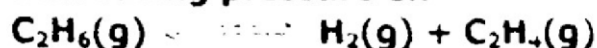
As the reaction is endothermic therefore heat is written on the left side of the equation.



According to Le-Chatelier's principle, when temperature is decreased this reaction will shift in backward direction in order to compensate the decrease in heat. Therefore, the concentration of  $\text{CO}_2$  will decrease while that of  $\text{CO}$  and  $\text{O}_2$  will increase.

$$K_c = \frac{[\text{CO}][\text{O}_2]^{\frac{1}{2}}}{[\text{CO}_2]} \quad \begin{matrix} \text{decrease} \\ \text{increase} \end{matrix}$$

(d) Decreasing pressure on



In the given reaction one molecule is present on reactant side ( $\text{C}_2\text{H}_6$ ) and two molecules are present on product side ( $\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ). So, when pressure is decreased, the equilibrium will shift in forward direction to compensate the change.

**17. A solution is prepared by mixing  $50 \text{ cm}^3$  of  $5 \times 10^{-3} \text{ M}$   $\text{NaCl}$  with  $50 \text{ cm}^3$  of  $2 \times 10^{-2} \text{ M}$   $\text{Pb}(\text{NO}_3)_2$ . Will a precipitate of  $\text{PbCl}_2$  form?  $K_{sp}$  for  $\text{PbCl}_2$  is  $1.7 \times 10^{-5}$ . (Ans: No)**

**Solution:**

Molarity of  $\text{Pb}(\text{NO}_3)_2$  solution =  $2 \times 10^{-2} \text{ M}$

Molarity of  $\text{NaCl}$  solution =  $5 \times 10^{-3} \text{ M}$

Precipitate of  $\text{PbCl}_2$  = ?

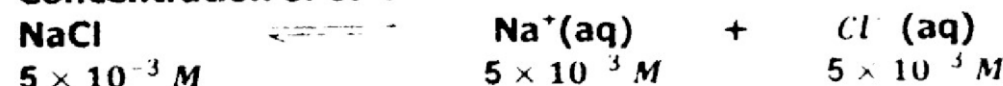
$K_{sp}$  for  $\text{PbCl}_2$  =  $1.7 \times 10^{-5}$ .

Volume of  $\text{NaCl}$  solution =  $50 \text{ cm}^3 = 0.05 \text{ dm}^3$

Volume of  $\text{Pb}(\text{NO}_3)_2$  solution =  $50 \text{ cm}^3 = 0.05 \text{ dm}^3$

Total volume of solution =  $0.05 \text{ dm}^3 + 0.05 \text{ dm}^3 = 0.1 \text{ dm}^3$

**Concentration of  $\text{Cl}^-$ :**



$1 \text{ dm}^3$  of  $\text{NaCl}$  solution contains  $\text{Cl}^-$  ions =  $5 \times 10^{-3} \text{ M}$  moles

$0.05 \text{ dm}^3$  of  $\text{NaCl}$  solution contains  $\text{Cl}^-$  ions =  $5 \times 10^{-3} \times 0.05$   
 $= 2.5 \times 10^{-4}$  moles

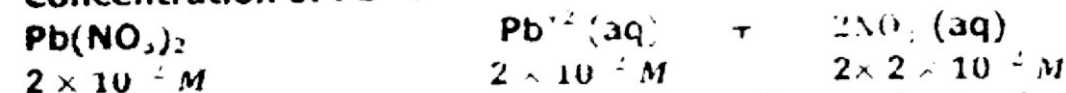
Now total volume is  $0.1 \text{ dm}^3$  therefore

$0.1 \text{ dm}^3$  of total solution contains  $\text{Cl}^-$  ions =  $2.5 \times 10^{-4}$  moles

$1 \text{ dm}^3$  of total solution contains  $\text{Cl}^-$  ions =  $\frac{2.5 \times 10^{-4}}{0.1} = 2.5 \times 10^{-3}$  moles

$[\text{Cl}^-] = 2.5 \times 10^{-3} \text{ M}$

**Concentration of  $\text{Pb}^{2+}$ :**



$1 \text{ dm}^3$  of  $\text{Pb}(\text{NO}_3)_2$  solution contains  $\text{Pb}^{2+}$  ions =  $2 \times 10^{-2}$  moles

$0.05 \text{ dm}^3$  of  $\text{Pb}(\text{NO}_3)_2$  solution contains  $\text{Pb}^{2+}$  ions =  $2 \times 10^{-2} \times 0.05$   
 $= 1.0 \times 10^{-3}$  moles

Now total volume is  $0.1 \text{ dm}^3$  therefore

$0.1 \text{ dm}^3$  of total solution contains  $\text{Pb}^{2+}$  ions =  $1.0 \times 10^{-3}$  moles

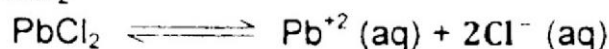


1 dm<sup>3</sup> of total solution contains Pb<sup>2+</sup> ions =  $\frac{1.0 \times 10^{-3}}{0.1} = 1.0 \times 10^{-2}$  moles

$$[\text{Pb}^{2+}] = 1.0 \times 10^{-2} \text{ M}$$

### Precipitate of PbCl<sub>2</sub>

Now for ionization of PbCl<sub>2</sub>



So

$$Q' = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

$$= (1.0 \times 10^{-2})(2.5 \times 10^{-3})^2 = 6.25 \times 10^{-8}$$

$$K_{sp} = 1.7 \times 10^{-5}$$

Since,  $Q' < K_{sp}$ , therefore precipitation will not occur.

- 18.** When solid PbCl<sub>2</sub> is added to pure water at 25°C, the salt dissolves until the concentration of Pb<sup>2+</sup> reaches  $1.6 \times 10^{-2}$  M. After this concentration is reached, excess solid remains undissolved. What is  $K_{sp}$  for this salt? (Ans:  $1.6384 \times 10^{-5}$ )

**Solution:**  $\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$

$$[\text{Pb}^{2+}] = 1.6 \times 10^{-2} \text{ M}$$

$$[\text{Cl}^{-}] = 2 \times 1.6 \times 10^{-2} \text{ M} = 3.2 \times 10^{-2}$$

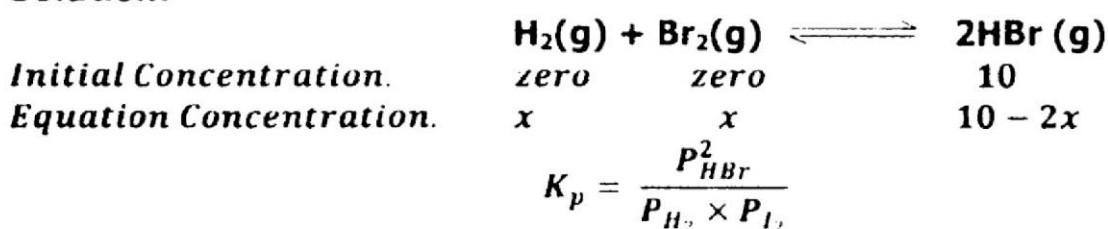
$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

$$K_{sp} = (1.6 \times 10^{-2})(3.2 \times 10^{-2})^2$$

$$K_{sp} = 1.6384 \times 10^{-5}$$

- 19.** The equilibrium constant for the following reaction is  $1.6 \times 10^5$  at 1000K  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$   
Find the equilibrium pressures of all the gases if 10.0 atm of HBr is introduced into a sealed container at 1000K.

**Solution:**



$$1.6 \times 10^5 = \frac{(10-2x)^2}{(x)(x)}$$

$$1.6 \times 10^5 = \frac{(10-2x)^2}{x^2}$$

Taking square root of both the sides

$$\sqrt{1.6 \times 10^5} = \frac{(10-2x)}{x}$$

$$400 = \frac{10-2x}{x}$$

$$10 - 2x = 400x$$

$$10 = 400x + 2x$$

$$10 = 402x$$

$$\text{or } x = \frac{10}{402}$$



$$x = 0.0249$$

$$P_{H_2} = P_{Br_2} = x = 0.0249 \text{ atm}$$

$$P_{HBr} = 10 - 2x = 10 - 2 \times 0.0249 = 9.9502 \text{ atm}$$

**20. Consider the following gas phase reaction.**

**Describe four changes that would derive the equilibrium to left (backward direction).**



**Ans.** According to Le-Chatlier's Principle following are the four changes that will drive the equilibrium in the reverse direction.

**(i) Continual removal of reactants:**

When any of the reactant is removed the equilibrium will shift in the reverse direction to compensate the change

**(ii) Low Pressure:**

According to the given equation, two molecules are present on reactant side ( $SO_2$ ,  $Cl_2$ ) and one molecule is present on product side ( $SO_2Cl_2$ ). Thus when pressure decreased, the equilibrium will shift in the reverse direction to compensate the change.

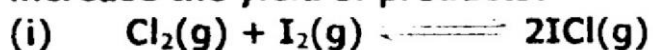
**(iii) High Temperature:**

As the reaction is exothermic therefore, high temperature will not favour it and hence the reaction will proceed in the reverse direction with the increase in temperature.

**(iv) Addition of products:**

Addition of products increases their concentration and the reaction will shift in the reverse direction to compensate this change i.e. from right to left

**21. How would you change the volume of the following reactions to increase the yield of products?**



**Ans. (i)**  $Cl_2(g) + I_2(g) \rightleftharpoons 2ICl(g)$

According to Le-Chatlier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus the equilibrium will shift in a direction where the numbers of molecules are less.

According to the given reaction, two molecules are present on both the reactant and the product side ( $Cl_2$ ,  $I_2$ ,  $2ICl$ )

Thus the change in volume will not affect the equilibrium position.

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

According to Le-Chatlier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus the equilibrium will shift in a direction where the numbers of molecules are less.

According to the given equation, two molecules are present on reactant side ( $2NO_2$ ) and one molecule is present on product side ( $N_2O_4$ )

When we reduce volume by increasing pressure then the equilibrium will shift in forward direction and thus the yield increases

## Think Tank

**22. A figurine device used to predict weather condition is blue on dry, sunny days and pink on damp, rainy days. These figurines are coated with substances containing chemical species that undergo following equilibrium.  $2[\text{Co}(\text{H}_2\text{O})_6]^{+2} + 4\text{Cl}^- \rightleftharpoons \text{Co}[\text{CoCl}_4]^{-2} + 12\text{H}_2\text{O}$**

- (a) Identify the blue substance**
- (b) Identify the pink substance**
- (c) How is Le Chatelier's Principle applied here.**

**Ans.** (a) Blue substance =  $\text{Co}[\text{CoCl}_4]^{-2}$   
 (b) Pink substance =  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$   
 Applying Le Chatelier's Principle

### **Rainy days:**

According to the reaction water is the product. On damp, rainy days the concentration of water is more in the surrounding and hence according to Le-Chatlier's principle, the equilibrium will shift in the reverse direction. Thus the concentration of  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  increases and the colour of figurine becomes pink.

### **Sunny days:**

According to the reaction water is the product. On a sunny day the concentration of water is low in the surrounding and therefore according to Le-Chatlier's principle, the equilibrium will shift in forward direction. Thus the formation of  $\text{Co}[\text{CoCl}_4]^{-2}$  increases and the colour of figurine become blue.

**23. The combination of oxygen with hemoglobin (Hb) molecule, which carries oxygen through the blood, is a complex reaction. For our purpose it can be represented by the simplified equation.**

**$\text{Hb}(\text{aq}) + \text{O}_2(\text{aq}) \rightleftharpoons \text{HbO}_2(\text{aq})$  where  $\text{HbO}_2$  is oxyhaemoglobin that actually transport oxygen to tissues. The equilibrium constant expression is  $K_c = \frac{[\text{HbO}_2]}{[\text{Hb}][\text{O}_2]}$**

**Scaling a 3km mountain can cause headache, nausea, extreme fatigue and other discomforts. Give possible explanation for it.**

**Ans:**  $\text{Hb}(\text{aq}) + \text{O}_2(\text{aq}) \rightleftharpoons \text{HbO}_2(\text{aq})$

External pressure low on high mountains and thus the concentration of  $\text{O}_2$  in the atmosphere also decreases. Hence, according to Le-Chatlier's principle, the given equilibrium will shift in reverse direction.

As a result, the concentration of  $\text{HbO}_2$  decreases in order to give Hb and  $\text{O}_2$  and to compensate the change. Therefore, supply of oxygen to body is also decreased. This can cause headache, nausea, extreme fatigue and other discomforts.

**24. Baking Soda undergoes thermal decomposition as follows**



**Would we obtain more  $\text{CO}_2$  by adding extra baking soda to the reaction mixture in (a) a closed vessel (b) an open vessel.**

**Ans.** As pressure has very little effect on volume of solids so they almost remain same but pressure can affect the volume of gases.

**(a) Closed vessel:**

In close vessel volume does not change and therefore we can not obtain more carbon dioxide gas by adding extra baking soda to the reaction mixture.

**(b) Open vessel:**

According to the reaction, there are two gaseous molecules on the product side ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ). Thus in this case according to Le-Chatlier's principle, when the volume increases then the equilibrium will shift in forward direction. Therefore, by adding baking soda more  $\text{CO}_2$  will produce in an open vessel.

- 25. Potassium dichromate solution has beautiful clear orange colour. This is due to the colour of dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$ . When a salt is dissolved in water, the following equilibrium is setup, on heating solution.**
- $$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{CrO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq})$$
- (orange) (yellow)

**What will happen if:**

- i. dilute Sodium hydroxide is added to this solution.**
- ii. this is followed by dilute hydrochloric acid addition.**

**Ans.**

- i. Dilute Sodium hydroxide is added to this solution.**

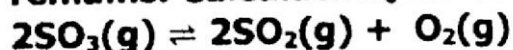
$\text{NaOH}$  is a base and it produces  $\text{OH}^-$  ions which will react with  $\text{H}^+$  ion to form water.

Therefore the concentration of  $\text{H}^+$  ions decreases and according to Le-Chatlier's principle, to compensate that change the dichromate/chromate equilibrium will shift in forward direction. As a result more orange  $\text{Cr}_2\text{O}_7^{2-}$  ions react with  $\text{H}_2\text{O}$  to give yellow  $\text{CrO}_4^{2-}$  ions and the colour of solution changes from orange to yellow.

- ii. This is followed by dilute hydrochloric acid addition.**

$\text{HCl}$  is a strong acid and it produces  $\text{H}^+$  ions in the solution due to which a concentration of  $\text{H}^+$  ion increases. Thus, according to Le-Chatliers' principle, to compensate this change the equilibrium will shift in backward direction. Thus, more yellow  $\text{CrO}_4^{2-}$  ions react with  $\text{H}^+$  ions to give orange  $\text{Cr}_2\text{O}_7^{2-}$  ions and the colour of solution changes from yellow to orange.

- 26. If 0.350 moles of  $\text{SO}_3$  is placed in a  $1.00 \text{ dm}^3$  flask and allowed to come to equilibrium at a high temperature, 0.207 mole of  $\text{SO}_3$  remains. Calculate  $K_c$  for the reaction. (Ans: 14.64)**



**Solution:**

	$2\text{SO}_3(\text{g})$	$\rightleftharpoons$	$2\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$
<b>Initial Concentration.</b> (in moles $\text{dm}^{-3}$ )	0.350		zero		zero
<b>Equation Concentration.</b> (in moles $\text{dm}^{-3}$ )	$0.350 - 2x$		$2x$		$x$

**Given that at equilibrium, 0.207 moles of  $\text{SO}_3$  remains**

$$\begin{aligned}0.350 - 2x &= 0.207 \\ -2x &= 0.207 - 0.350 \\ -2x &= -0.143\end{aligned}$$

$$\text{Or } x = \frac{0.143}{2} = 0.0715$$

**Equilibrium concentrations:**

$$[SO_3] = 0.207 \text{ moles dm}^{-3}$$

$$[O_2] = x = 0.0715 \text{ moles dm}^{-3}$$

$$[SO_2] = 2x = 2 \times 0.0715 = 0.143 \text{ moles dm}^{-3}$$

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

**Putting values**

$$K_c = \frac{(0.143)^2 (0.0715)}{(0.207)^2} = 0.0341$$

27. For the reaction between hydrogen and Iodine to form hydrogen Iodide, the value of  $K_c$  is 794 at 298K but 54 at 700K what can you deduce from this information?

**Ans.**



Given that the value of  $K_c$  decreased with the increase in temperature from 794 at 298K to 54 at 700K.

**Conclusion:**

Thus this indicates that the reaction is **exothermic** and is not favoured by high temperature. Therefore the concentration of HI is decreased and that of  $H_2$  and  $I_2$  is increased by increase in temperature.

$$K_c = \frac{[HI]^2 \longleftarrow \text{decrease}}{[H_2][I_2] \longleftarrow \text{increase}}$$