

## Exercise

### Multiple choice questions

Choose the Correct Answer.

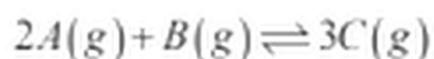
1.  $K_c$  is independent of

- |                                   |              |
|-----------------------------------|--------------|
| (a) Temperature                   | (b) Pressure |
| (c) Both Temperature and Pressure | (d) $K_p$    |

2. 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) $3(g) \rightleftharpoons 2C(g)$ |

3. For the following reaction



We can write

- |                     |                      |
|---------------------|----------------------|
| (a) $K_c > K_p$     | (b) $K_c < K_p$      |
| (c) $K_p - K_c = 0$ | (d) $K_p - K_c = -1$ |

4. When a catalyst is added to an equilibrium mixture, it decreases

- |                                       |                          |
|---------------------------------------|--------------------------|
| (a) Reverse reaction                  | (b) Forward reaction     |
| (c) Concentration of reaction mixture | (d) Enthalpy of reaction |
| (e) it has no effect                  |                          |

5. 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) None of these

6. NaCl can be purified by passing HCl gas through the \_\_\_\_\_ solution of NaCl

(a) Dilute

(b) Concentrated

(c) Hot

(d) Cold

7.  $K_c = K_p$ , when  $n$  is equal to

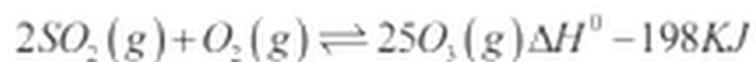
(a) Zero

(b) +1

(c) -1

(d) -2

8. Consider the following reaction:



Yield of sulphur trioxide can be increased

(a) Increasing Pressure

(b) increasing temperature

(c) adding catalyst

(d) increasing concentration of oxygen

### Answer

1. d	2. c	3. c	4. e
5. b	6. b	7. a	8. d

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 dm<sup>3</sup> 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 coefficient 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 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 a physical property of the reaction mixture. This physical property is measured during the course of reaction without removing the saturation of the 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  $N_2O_4$ - $NO_2$ , system can be determined by the spectrophotometer.



$N_2O_4$ , is a colorless gas whereas  $NO_2$  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  $NO_2$

At equilibrium spectrometer will show constant value of absorbance. Suppose reaction is started with "a" mole of  $N_2O_4$ , at  $100^\circ C$ , and x moles of it is converted to  $NO_2$ . By applying stoichiometry, the amount of  $NO_2$  present 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



Initial Conc (in mole)	a	zero
Eq. Conc (in mole)	$a - x$	$2x$
Eq Conc (mole/dm <sup>3</sup> )	$\frac{a - x}{V}$	$\frac{2x}{V}$

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

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

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

### b. Chemical Method:

In this method, the amount of a reactant or product is determined by a b) 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,



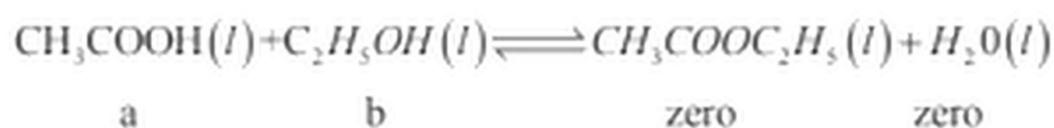
Suppose this reaction is started by taking 'a' mole of acetic acid and 'b' moles of ethanol in a stoppered flask at room temperature. A small amount of mineral acid is added in the mixture to catalyze the reaction

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 NaOH using phenolphthalein as indicator. Concentration of acetic acid will decrease until equilibrium is attained. Suppose x moles of acetic acid has been reacted with ethanol, since one mole of acetic reacts with one mole of ethanol, the amount of ethanol reacted with acetic acid will also be x moles. As one mole of each of the product is formed, at equilibrium x moles of ethyl acetate and x moles of water are produced.

### Mathematically:

Reaction initial Conc (in mole)



Eq Conc (in mole)



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

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

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

**4. Describe the microscopic events that occur when a chemical system is in equilibrium.**

**Ans: Microscopic events:**

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

- i. The rate of chemical reaction depends on the numbers of effective collisions between the reacting molecules.
- ii. 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.

**5. Define and explain the following terms:**

- i. **Common ion effect**
- ii. **Reaction quotient**
- iii. **Solubility product**
- iv. **Ion product**

**Ans: (i). 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.

**$Q < K_c$**

This indicates that more product is needed to acquire equilibrium.

Therefore, system must shift to the right until equilibrium is attained

**$Q > K_c$**

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

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

**(ii) Solubility product:**

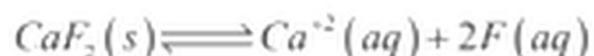
It is defined as the product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balanced equation.

**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 the 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.

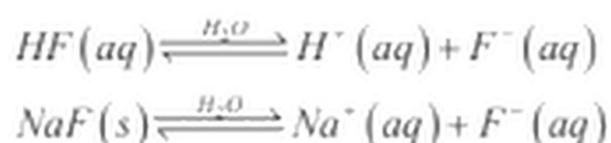
### iii. Common ion effect:

#### Common ion effect:

The phenomenon in when the degree of ionization or solubility of an electrolyte 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  $K_a = 7.2$  sodium fluoride produces the common ion.



- Since HF is a weak electrolyte, slightly dissociates
- NaF being strong electrolyte breaks up completely into its ions.
- The common ion F is produced by NaF will upset its equilibrium
- This will increase concentration of F ions
- According, to the Le Chatellier's principle, the equilibrium will shift to the left use some of F ions
- This will decrease the dissociation of HF Thus dissociation of HF will decrease in the presence of dissolved NaF

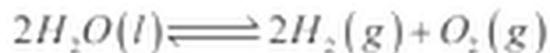
- This means as a result of equilibrium shift, the concentration of HF will increase
- Similarly, when a highly soluble salt is added to the saturated solution of less soluble salt containing a common ion
- The degree of dissociation of less soluble salt decreases. Therefore, it causes to decrease its solubility

**iv. Heterogeneous equilibrium:**

Equilibrium 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



$$K_c = [H_2]^2 [O_2]$$

$$\text{and } K_p = p_{H_2}^2 \times p_{O_2}$$

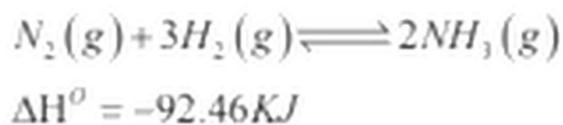
**v. Ion product:**

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 Chatellier's principle using Haber's process as an example.**

**Ans: Industrial Application of Le Chatellier'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 favor the formation of ammonia the suitable temperature is 400°C

**ii. High Pressure:**

Since four molecules (one of  $N_2$  and three of  $H_2$ ) react to produce two molecules of  $NH_3$ . Thus high pressure will shift the equilibrium to the right side i.e. formation of  $NH_3$ . 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%  $NH_3$  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 cm<sup>3</sup> of acetic acid (d = 1.049 gcm<sup>-3</sup>) is mixed with 50 cm<sup>3</sup> of ethanol (d=0.789 gcm<sup>-3</sup>) what is the equilibrium composition of the mixture at 25°C (K<sub>C</sub>=4). (Ans:CH<sub>3</sub>COOH=31.68 g, C<sub>2</sub>H<sub>5</sub>OH=32.506 g, CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> =30.448 g, H<sub>2</sub>O= 6.22 g)

**Solution:**

Equilibrium constant = K<sub>C</sub> = 4 at 25°C

Volume of acetic acid = 50 cm<sup>3</sup>

Density of acetic acid = 1.049 g cm<sup>-3</sup>

Mass of acetic acid = density x Volume = 1.049x50 = 52.45 g

Molar mass of acetic acid = 60 g mole

Number of moles of CH<sub>3</sub>COOH =  $\frac{52.45}{60} = 0.874$  mole

Number of moles of C<sub>2</sub>H<sub>5</sub>OH =  $\frac{52.45}{60} = 0.858$  mole



Initial concentration (in moles)

0.874                  0.858                  zero                  zero

Equation concentration (in moles)

0.874-x                  0.858-x                  x                  x

K<sub>C</sub> will be

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

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

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

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

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

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

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

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

**Taking negative sign common on both side**

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

**Using quadratic formula**

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

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

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

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

Thus

$$x = \frac{6.928 + \sqrt{11.997}}{6}, \quad \text{or} \quad x = \frac{6.928 - \sqrt{11.997}}{6}$$

**X=1.73 moles**

**or**

**x=0.577 moles**

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

X=0.577 moles

The equilibrium concentration in moles are as follows

$$[CH_3OOH] = 0.874 - x = 0.874 - 0.577 = 0.297 \text{ moles}$$

$$\text{Mass of } [CH_3COOH] \text{ in grams} = 0.297 \text{ moles} \times 60 \text{ g mole}^{-1} = 17.82 \text{ g}$$

$$[C_2H_5OH] = 0.858 - x = 0.858 - 0.577 = 0.281 \text{ moles}$$

$$\text{Mass of } [C_2H_5OH] \text{ in grams} = 0.281 \text{ moles} \times 46 \text{ g moles}^{-1} = 12.93 \text{ g}$$

$$[CH_3COOC_2H_5] = x = 0.577 \text{ moles}$$

$$\text{Mass of } [CH_3COOC_2H_5] = 0.577 \text{ moles} \times 88 \text{ g mole}^{-1} = 50.78 \text{ g}$$

$$[H_2O] = x = 0.577 \text{ moles}$$

$$\text{Mass of } [H_2O] = 0.577 \text{ moles} \times 18 \text{ g mol}^{-1} = 10.39 \text{ g}$$

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

- i.  $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$
- ii.  $H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$
- iii.  $O_3(g) \rightleftharpoons O_2(g) + O(g)$
- iv.  $O_3(g) \rightleftharpoons \frac{3}{2}O_2(g)$
- v.  $Fe_3O_4(s) + H_2(g) \rightleftharpoons 3FeO(s) + H_2O(g)$
- vi.  $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$
- vii.  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
- viii.  $C(s) + H_2O(g) \rightleftharpoons O(g) + H_2(g)$

**Solution:**

- i.  $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$   

$$K_c = \frac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}}, \text{ (and) } K_c = \frac{P_{SO_3}}{P_{SO_2} \times P_{O_2}^{\frac{1}{2}}}$$
- ii.  $H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$   

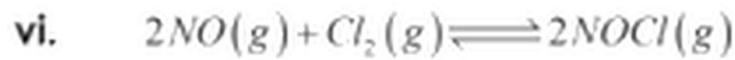
$$K_c = \frac{[HOCl]^2}{[H_2O][Cl_2O]}, \text{ (and) } K_c = \frac{P_{HOCl}^2}{P_{H_2O} \times P_{Cl_2O}}$$
- iii.  $O_3(g) \rightleftharpoons O_2(g) + O(g)$   

$$K_c = \frac{[O_2][O]}{[O_3]}, \text{ (and) } K_c = \frac{P_{O_2} \times P_O}{P_{O_3}}$$
- iv.  $O_3(g) \rightleftharpoons \frac{3}{2}O_2(g)$   

$$K_c = \frac{[O_2]^{\frac{3}{2}}}{[O_3]}, \text{ (and) } K_c = \frac{P_{O_2}^{\frac{3}{2}}}{P_{O_3}}$$
- v.  $Fe_3O_4(s) + H_2(g) \rightleftharpoons 3FeO(s) + H_2O(g)$

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

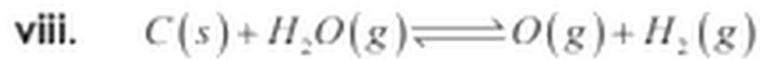
$$K_c = \frac{[H_2O]}{[H_2]}, \text{ (and) } K_p = \frac{P_{H_2O}}{P_{H_2}}$$



$$K_c = \frac{[NOCl]^2}{[NO]^2 [Cl_2]}, \text{ (and) } K_p = \frac{P_{NOCl}^2}{P_{NO}^2 \times P_{Cl_2}}$$



$$K_c = [CO_2], \text{ (and) } K_p = P_{CO_2}$$



$$K_c = \frac{[CO][H_2]}{[H_2O]}, \text{ (and) } K_p = \frac{P_{CO} \times P_{H_2}}{P_{H_2O}}$$

10.  $K_c = 2.6 \times 10^{-5}$  at  $125^\circ C$  for the reaction  $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$  calculate  $K_p$  at this temperature. (Ans:  $K_p = 284.4078$ )

**Solution:**

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

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

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

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

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 atm. Which of the following conditions corresponds to equilibrium position for the reaction.



- a.  $P_B = 0.175 \text{ atm}, P_A = 0.102 \text{ atm}$   
 b.  $P_B = 0.064 \text{ atm}, P_A = 0.0308 \text{ atm}$   
 c.  $P_B = 0.144 \text{ atm}, P_A = 0.156 \text{ atm}$

**(Ans: b and c)**

**Solution:**

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

as we know that

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

- (a).**  $P_B = 0.175 \text{ atm}, P_A = 0.102 \text{ atm}$

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

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

- (b).**  $P_B = 0.064 \text{ atm}, P_A = 0.0308 \text{ atm}$

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

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

- (c).**  $P_B = 0.144 \text{ atm}, P_A = 0.156 \text{ atm}$

$$K_p = \frac{P_s^2}{P_A} = \frac{(0.144)^2}{(0.156)} = 0.113 \text{ atm}$$

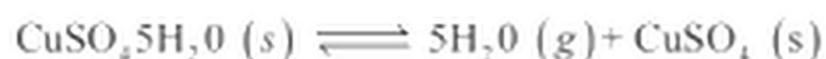
As this value correspond with the given value therefore the reaction is at equilibrium

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

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

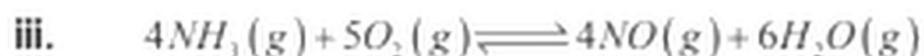
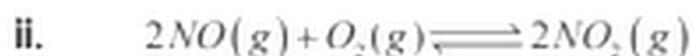
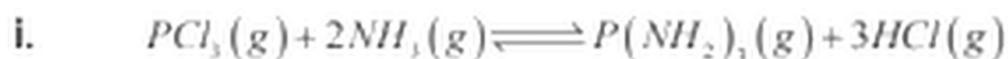


As the equilibrium is heterogeneous therefore only gas phase is included (b) equilibrium constant expression.

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

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

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



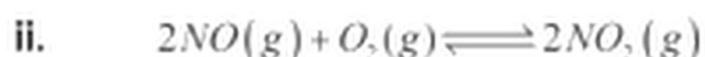
**Ans. Principle:**

According to Le-Chatellier'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.



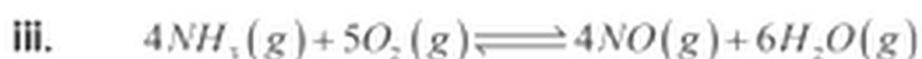
In this reaction three molecules are present on reactant side ( $PCl_3, 2NH_3$ ) while four molecules are present on product side ( $P(NH_2)_3, 3HCl$ ).

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



In this reaction three molecules are present on reactant side ( $2NO, O_2$ ) and two molecules ( $2NO_2$ ) are present on product side

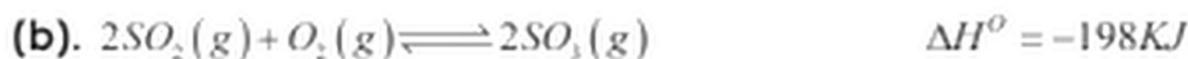
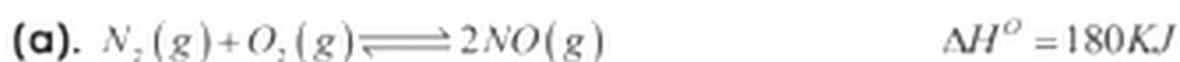
Therefore when the volume decreases by increasing pressure then the equilibrium will shift in forward direction to reduce the number of molecules, and to compensate the change



In this reaction, nine molecules are present on reactant side ( $4NH_3, 5O_2$ ) and ten molecules are present on product side ( $4NO, 6H_2O$ )

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.

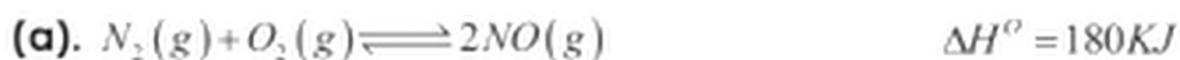
**14. For each of the following reactions, predict how the value of  $K_C$  changes as the temperature is increased.**



**Ans:**

**Principles:**

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



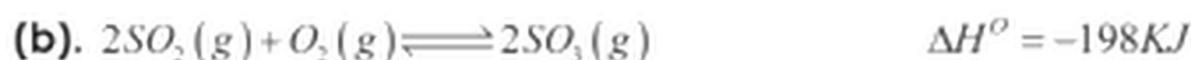
As the reaction is endothermic therefore heat is written on the left side of the equation.



According to Le-Chatellier'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  $N_2$  and  $O_2$  will decrease.

$$K_c = \frac{[NO]^2 \leftarrow \text{decrease}}{[N_2][O_2] \leftarrow \text{increas}}$$

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.  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + \text{heat}$

According to Le-Chatellier's principle, when temperature is increased this reaction will shift in the reverse direction in order to compensate the added heat. Thus, concentration of  $SO_2$  and  $O_2$  will increase while that of  $SO_3$  will decrease.

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

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-Chatier'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 will increase with increase in temperature



According to Le-Chatellier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat.

Therefore, concentration of 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 HBr would be

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

$$[HBr] = \sqrt{5.4 \times 10^{18}}$$

$$= 2.32 \times 10^9 M$$

**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:**



$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 1.0 \times 10^{-30}$$

If one mole of each of the reactant is present at equilibrium. Then the concentration of NO would be

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

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

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

**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.

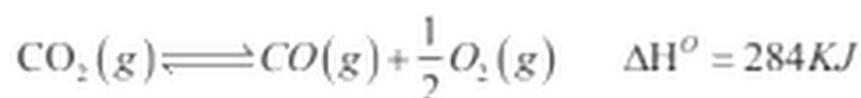
**16. Describe the behavior of the following equilibrium with the stated changes**

**(a) Increasing pressure on**



**(b) Adding  $I_2(g)$  to  $2HI(g) \rightleftharpoons I_2(g) + H_2(g)$**

**(c) Removing heat from**



**(d) Decreasing pressure on**



**Ans.**

**(a) Increasing pressure on**



According to Le-Chatellier'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.

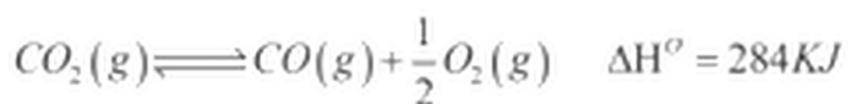
According to the given reaction, six molecules are present on reactant side ( $C_3H_8, 5O_2$ ) and seven molecules ( $3CO_2, 4H_2O$ ) are present on product side.

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.

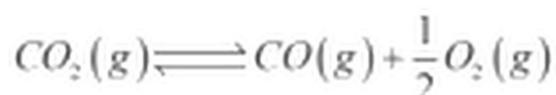
**(b) Adding  $I_2(g)$  to  $2HI(g) \rightleftharpoons I_2(g) + H_2(g)$**

According to Le-Chatellier's principle, the addition of  $I_2$  increases the concentration of product and to compensate it the equilibrium will shift in the backward reaction.

**(c) Removing heat from**



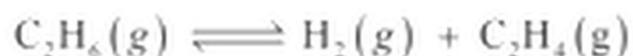
As the reaction is endothermic therefore heat is written on the left side of the equation.



According to Le-Chatellier'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  $CO$ , will decrease while that of  $CO$  and  $O_2$  will decrease.

$$K_c = \frac{[CO][O_2]^{\frac{1}{2}} \leftarrow \text{decreas}}{[CO_2] \leftarrow \text{increas}}$$

**(d) Decreasing pressure on**



In the given reaction one molecule is present on reactant side ( $C_2H_6$ ) and two molecules are present on product side ( $H_2$ ...  $C_2H_4$ .) So, when pressure is decreased, the equilibrium will shift in forward direction to compensate the change.

**17. A solution is prepared by mixing  $50cm^3$  of  $5 \times 10^{-3}M$  NaCl with  $50cm^3$  of  $2 \times 10^{-2}M$   $Pb(NO_3)_2$  . will a precipitation of  $PbCl_2$  form?  $K_{sp}$  For  $PbCl_2$  is  $1.7 \times 10^{-5}$  .**

**Solution:**

**Molarity of  $Pb(NO_3)_2$  solution =  $2 \times 10^{-2} M$**

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

**Precipitate of  $PbCl_2$  = ?**

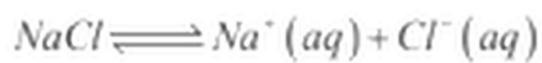
$K_{sp}$  for  $PbCl_2 = 1.7 \times 10^{-5}$

**Volume of NaCl solution =  $50 cm^3 = 0.05 dm^3$**

**Volume of  $Pb(NO_3)_2$  solution =  $50 cm^3 = 0.05 dm^3$**

**Total volume of solution =  $0.05 dm^3 + 0.05 dm^3 = 0.1 dm^3$**

**Concentration of  $Cl^-$ :**



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

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

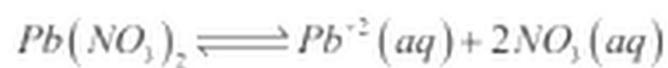
$$= 25 \times 10^{-4} \text{ moles}$$

Now total volume is 0.1  $dm^3$  therefore

0.1  $dm^3$  of total solution contains  $Cl^-$  ions =  $25 \times 10^{-4}$  moles

1 dm of total solution contains  $Cl^-$  ions =  $\frac{25 \times 10^{-4}}{0.1} = 25 \times 10^{-3}$  moles

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



1  $dm^3$  of  $Pb(NO_3)_2$  Solution contains  $Pb^{+2}$  ions  $2 \times 10^{-2}$  moles moles

0.05  $dm^3$  of  $Pb(NO_3)_2$  Solution contains  $Pb^{+2}$  ions =  $2 \times 10^{-2} \times 0.05$

$$= 1.0 \times 10^{-3} \text{ moles}$$

Now total volume is 0.1  $dm^3$  therefore

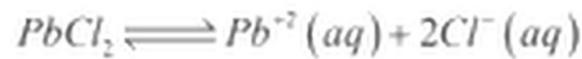
0.1  $dm^3$  of total solution contains  $Pb^{+2}$  ions =  $1.0 \times 10^{-3}$  moles

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

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

Precipitate of PbCl<sub>2</sub>

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



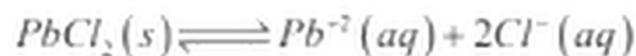
So,

$$\begin{aligned} Q' &= [Pb^{+2}][Cl^{-}]^2 \\ &= (1.0 \times 10^{-2})(2.5 \times 10^{-3})^2 = 6.25 \times 10^{-8} \\ K_{sp} &= 1.7 \times 10^{-5} \end{aligned}$$

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 x 10<sup>-2</sup> M. After this concentration is reached, excess solid remains undissolved. What is K<sub>sp</sub> for this salt? (Ans: 1.6384x10<sup>-5</sup>)**

**Solution:**



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

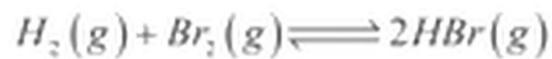
$$[Cl^{-}] = 2 \times 1.6 \times 10^{-2} M = 3.2 \times 10^{-2}$$

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

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

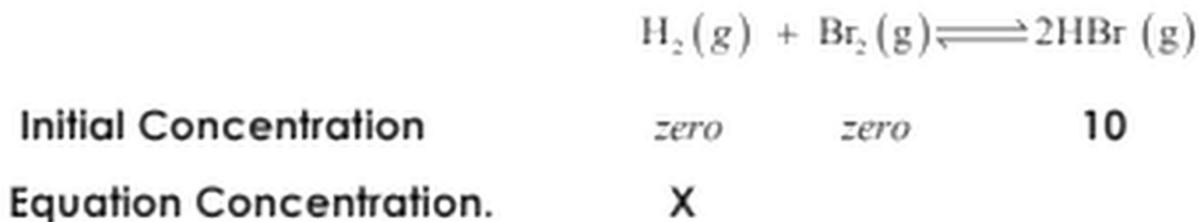
$$K_{sp} = 1.6384 \times 10^{-5}$$

**19. The equilibrium constant for the following reaction is 1.6 x 10<sup>5</sup> at 1000K**



Find the equilibrium pressures of all the gases if 10.0 atm of HBr is introduced into a sealed container at 1000K

**Solution:**



$$K_p = \frac{P_{HBr}^2}{P_{H_2} \times P_{Br_2}}$$

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

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

**Taking square root of both the sides**

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

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

$$400x = 10 - 2x$$

$$400x + 2x = 10$$

$$402x = 10$$

or

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

$$x = 0.0249$$

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

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

**20. Consider the following gas phase reaction. Describe four changes that would drive the equilibrium to left (backward direction).**



**Ans.** According to Le-Chatellier'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 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.

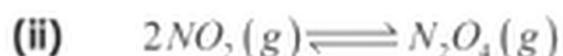
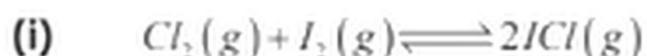
**(iii) High Temperature:**

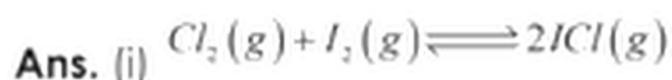
As the reaction is exothermic therefore, high temperature will not favor it and hence the reaction will proceed in the reverse direction with the increase in temperature

**(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?**

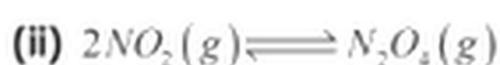




According to Le-Chatellier's principle when pressure increases then the system will reduce its volume by reducing the number of molecules present Thus the equilibrium will shift in a direction where the numbers of molecules are less.

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



(.....  
 .....**pge#299**.....  
 .....)

According to the given equation, two molecules are present un 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.**



- a. Identify the blue substance
- b. Identify the pink substance
- c. How is Le Chatellier's Principle applied here.

**Ans.**



Applying Le Chatellier's Principle

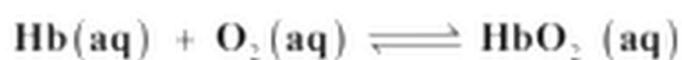
**Rainy days:**

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-Chatellier'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 color 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-Chatellier's principle, the equilibrium will shift in forward direction. Thus the formation of  $\text{Co}[\text{CoCl}_4]^{-2}$  increases and the color 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.**

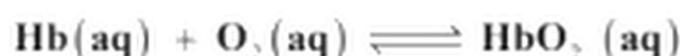


**where  $\text{HbO}_2$  is oxyhemoglobin that actually transport oxygen to tissues. The equilibrium constant**

$$\text{expression is } K_c = \frac{[HbO_2]}{[Hb][O_2]}$$

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

**Ans:**



External pressure low on high mountains and thus the concentration of  $O_2$  in the atmosphere also decreases. Hence, according to Le-Chatellier's principle, the given equilibrium will shift in reverse direction.

As a result, the concentration of  $HbO_2$  decreases in order to give Hb and  $O_2$  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  $CO_2$  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.

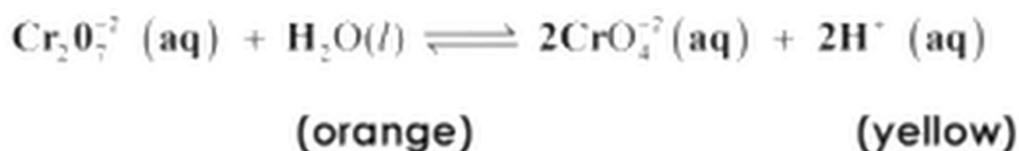
**(a) Closed vessel:**

In close vessel volume does not change and therefore we cannot 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-Chatellier'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.**



**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.**

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-Chatellier'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.**

HCl is a strong acid and it produces  $\text{H}^+$  ions in the solution due to which anases. Thus, according to Le-Chatellier's principle, to the equilibrium will shift in backward direction. Thus, more yellow  $\text{CrO}_4^{2-}$  ions react with  $\text{H}^+$  ions to give orange  $\text{CrO}_4^{2-}$  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:**

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

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

$$0.350 - 2x = 0.207$$

$$-2x = 0.207 - 0.350$$

$$-2x = -0.143$$

or

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

**Equilibrium concentrations:**

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

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

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

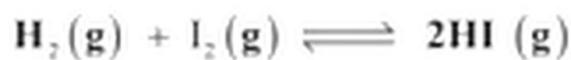
$$K_c = \frac{[SO_2]^2 [O_2]}{[SO_3]^2}$$

**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 favored by high temperature. Therefore, the concentration of HI is decreased and that of  $H_2$  and  $I_2$  is increased by increase in temperature.

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

