7

Equilibrium

Multiple Choice Questions (MCQs)

Q. 1 We know that the relationship between K_c and K_p is

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

What would be the value of Δn for the reaction?

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HI(g)$$

(a) 1 (b) 0.5 (c) 1.5 (d) 2

Ans. *(d)* The relationship between K_p and K_c is

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

where, Δn = (number of moles of gaseous products) – (number of moles of gaseous reactants)

For the reaction,

$$NH_4Cl\ (s) \rightleftharpoons NH_3(g) + HCl\ (g)$$

$$\Delta n = 2 - 0 = 2$$

Q. 2 For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2\ HI\ (g)$, the standard free energy is $\Delta G^\ominus > 0$. The equilibrium constant (K) would be

(a) $K = 0$ (b) $K > 1$ (c) $K = 1$ (d) $K < 1$

Ans. *(d)* $\Delta G^\ominus$ and K are related as

$$\Delta G^\ominus = -RT \text{ In } K_c$$

when $G^\ominus > 0$ means $\Delta G°$ is positive. This can be so only if In K_c is negative *i.e.*, $K_c < 1$.

Q. 3 Which of the following is not a general characteristic of equilibria involving physical processes?

(a) Equilibrium is possible only in a closed system at a given temperature
(b) All measurable properties of the system remain constant
(c) All the physical processes stop at equilibrium
(d) The opposing processes occur at the same rate and there is dynamic but stable condition

Ans. ***(c)*** At the stage of equilibria involving physical processes like melting of ice and freezing of water etc., process does not stop but the opposite processes *i.e.*, forward and reverse process occur with the same rate.

Q. 4 $PCl_{5,}$ $PCl_{3,}$ and Cl_2 are at equilibrium at 500 K in a closed container and their concentrations are $0 \cdot 8 \times 10^{-3}$ mol L^{-1}, 1.2×10^{-3} mol L^{-1} and 1.2×10^{-3} mol L^{-1}, respectively. The value of K_c for the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2\ (g) \text{ will be}$$

(a) 1.8×10^3 mol L^{-1}
(b) 1.8×10^{-3}
(c) 1.8×10^{-3} mol^1 L
(d) 0.55×10^4

Ans. ***(b)*** For the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

At 500 K in a closed container, $[PCl_5] = 0.8 \times 10^{-3}$ mol L^{-1}

$$[PCl_3] = 1.2 \times 10^{-3} \text{ mol } L^{-1}$$

$$[Cl_2] = 1.2 \times 10^{-3} \text{ mol } L^{-1}$$

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{(1.2 \times 10^{-3}) \times (1.2 \times 10^{-3})}{(0.8 \times 10^{-3})}$$

$$= 1.8 \times 10^{-3}$$

Q. 5 Which of the following statements is incorrect?

(a) In equilibrium mixture of ice and water kept in perfectly insulated flask, mass of ice and water does not change with time
(b) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate
(c) On addition of catalyst the equilibrium constant value is not affected
(d) Equilibrium constant for a reaction with negative ΔH value decreases as the temperature increases

Ans. ***(b)*** In the reaction, $Fe^{3+} + SCN^- \rightleftharpoons \underset{\text{(Red)}}{FeSCN^{2+}}$

When oxalic acid is added it combines with Fe^{3+} ions, then, equilibrium shifts towards backward direction and intensity of red colour decreases.

Q. 6 When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information mark the correct answer.

$$\underset{\text{(Pink)}}{[Co\ (H_2O_6)]^{3+}}\ (aq) + 4Cl^-\ (aq) \rightleftharpoons \underset{\text{(Blue)}}{[CoCl_4]^{2-}}\ (aq) + 6H_2O\ (l)$$

(a) $\Delta H > 0$ for the reaction
(b) $\Delta H < 0$ for the reaction
(c) $\Delta H = 0$ for the reaction
(d) The sign of ΔH cannot be predicted on the basis of this information

Ans. ***(a)*** In the reaction,

$$\underset{\text{(Pink)}}{[Co\ (H_2O)_6]^{3+}}(aq) + 4Cl^-(aq) \rightleftharpoons \underset{\text{(Blue)}}{[CoCl_4]^{2-}}(aq) + 6H_2O\ (l)$$

On cooling, the equilibrium shifts backward direction or on heating, the equilibrium shifts forward direction. Hence, reaction is endothermic. *i.e.,* $\Delta H > 0$.

Q. 7 The pH of neutral water at 25°C is 7.0. As the temperature increases, ionisation of water increases, however, the concentration of H^+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C?

(a) Equal to 7.0 (b) Greater than 7.0 (c) Less than 7.0 (d) Equal to zero

Ans. ***(c)*** The pH of neutral water at 25°C is 7.0.

At 25°C, $[H^+] = [OH^-] = 10^{-7}$

and $K_w = [H^+]\,[OH^-] = 10^{-14}$

On heating, K_w increases, *i.e.*, $[H^+]\,[OH^-] > 10^{-14}$

As $[H^+] = [OH^-]$ or, $[H^+]^2 >= 10^{-14}$

or, $[H^+] > 10^{-7}M$

$\therefore$ $pH < 7.$

With rise in temperature, pH of pure water decreases and it become less than 7 at 60°C.

Q. 8 The ionisation constant of an acid, K_a is the measure of strength of an acid. The K_a values of acetic acid, hypochlorous acid and formic acid are 1.74×10^{-5}, $3 \cdot 0 \times 10^{-8}$ and $1 \cdot 8 \times 10^{-4}$ respectively. Which of the following orders of pH of $0 \cdot 1$ mol dm^{-3} solutions of these acids is correct?

(a) Acetic acid > hypochlorous acid > formic acid

(b) Hypochlorous acid > acetic acid > formic acid

(c) Formic acid > hypochlorous acid > acetic acid

(d) Formic acid > acetic acid > hypochlorous acid

Thinking Process

This problem is based upon the relationship between ionisation constant (K_a) and pH i.e, $K_a \propto \frac{1}{pH}$. Greater the K_a lesser the value of pH and vice-versa.

Ans. ***(d)*** As the acidity or K_a value increases, pH decreases, thus, the order of pH value of the acids is

$$\underset{(3.8 \times 10^{-8})}{\text{Hypochlorous acid}} < \underset{(1.74 \times 10^{-5})}{\text{Acetic acid}} < \underset{(18 \times 10^{-4})}{\text{Formic acid}}$$

Q. 9 K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.

$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{2-}$$
$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

The correct relationship between K_{a_1}, K_{a_2}, K_{a_3} is

(a) $K_{a_3} = K_{a_1} \times K_{a_2}$

(b) $K_{a_3} = K_{a_1} + K_{a_2}$

(c) $K_{a_3} = K_{a_1} - K_{a_2}$

(d) $K_{a_3} = K_{a_1} / K_{a_2}$

Thinking Process

To find out the correct relationship between three ionisation constants (K_{a_1}, K_{a_2} and K_{a_3}) this must be keep in mind that when two reactions are added, their equilib

Ans. *(a)* For the reaction,

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$K_{a_1} = \frac{[H^+]\,[HS^-]}{[H_2S]}$$

For the reaction,

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

$$K_{a_2} = \frac{[H^+]\,[S^{2-}]}{[HS^-]}$$

When, the above two reactions are added, their equilibrium constants are multiplied, thus

$$K_{a_3} = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]} = K_{a_1} \times K_{a_2}$$

Hence, $K_{a_3} = K_{a_1} \times K_{a_2}$

Q. 10 Acidity of BF_3 can be explained on the basis of which of the following concepts?

(a) Arrhenius concept

(b) Bronsted Lowry concept

(c) Lewis concept

(d) Bronsted Lowry as well as Lewis concept

Ans. *(c)* GN Lewis in 1923 defined an acid as a species which accepts an electron pair and base which donates an electron pair. As BF_3 is an electron deficient compound, hence, it is a Lewis acid.

Q. 11 Which of the following will produce a buffer solution when mixed in equal volumes?

(a) 0.1 mol dm^{-3} NH_4OH and 0.1mol dm^{-3} HCl

(b) 0.05 mol dm^{-3} NH_4OH and 0.1mol dm^{-3} HCl

(c) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl

(d) 0.1 mol dm^{-3} CH_4COONa and 0.1mol dm^{-3} NaOH

Ans. *(c)* When the concentration of NH_4OH (weak base) is higher than the strong acid (HCl), a mixture of weak base and its conjugate acid is obtained, which acts as basic buffer.

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

Initially	0.1 M	0.05M	0
After reaction	0.05 M	0	0.05 M

Q. 12 In which of the following solvents is silver chloride most soluble?

(a) 0.1 mol dm^{-3} $AgNO_3$ solution

(b) 0.1 mol dm^{-3} HCl solution

(c) H_2O

(d) Aqueous ammonia

Ans. *(d)* Among the given solvent, AgCl is most soluble in aqueous ammonia solution. AgCl react with aqueous ammonia to form a complex, $[Ag(NH_3)_2]^+Cl^-$.

Q. 13 What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH ($K_a = 1.74 \times 10^{-5}$)?

(a) 3.4 (b) 3.6 (c) 3.9 (d) 3.0

Ans. *(a)* Given that, $K_a = 1.74 \times 10^{-5}$

Concentration of CH_3COOH = 0.01 mol dm^{-3}

$$[H^+] = \sqrt{K_a \cdot C}$$

$$= \sqrt{1.74 \times 10^{-5} \times 0.01} = 4.17 \times 10^{-4}$$

$$pH = -\log [H^+]$$

$$= -\log (4.17 \times 10^{-4}) = 3.4$$

Q. 14 K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5}. The pH of ammonium acetate will be

(a) 7.005 (b) 4.75 (c) 7.0 (d) Between 6 and 7

Ans. *(c)* Given that, K_a for $CH_3COOH = 1.8 \times 10^{-5}$

K_b for $NH_4OH = 1.8 \times 10^{-5}$

Ammonium acetate is a salt of weak acid and weak base. For such salts

$$pH = 7 + \frac{pK_a - pK_b}{2}$$

$$= 7 + \frac{[-\log 1.8 \times 10^{-5}] - [-\log 1.8 \times 10^{-5}]}{2}$$

$$= 7 + \frac{4.74 - 4.74}{2} = 7.00$$

Q. 15 Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$?

(a) $\Delta G^\ominus = 0$ (b) $\Delta G^\ominus > 0$ (c) $\Delta G^\ominus < 0$ (d) $\Delta G^\ominus = -RT \ln K$

Ans. *(a)* As we know that

$$\Delta G^\ominus = -RT \ln K$$

At the stage of half completion of the reaction,

$$A \rightleftharpoons B, [A] = [B]$$

Therefore, $K = 1.$

Thus, $\Delta G^\ominus = 0$

Q. 16 On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le-Chatelier's principle. Consider the reaction,

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

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(a) K will remain same

(b) K will decrease

(c) K will increase

(d) K will increase initially and decrease when pressure is very high

Ans. ***(a)*** In the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

If the total pressure at which the equilibrium is established, is increased without changing the temperature, *K* will remain same. *K* changes only with change in temperature.

Q. 17 What will be the correct order of vapour pressure of water, acetone and ether at 30°C? Given that among these compounds, water has maximum boiling point and ether has minimum boiling point?

(a) Water < ether < acetone (b) Water < acetone < ether

(c) Ether < acetone < water (d) Acetone < ether < water

Ans. ***(b)*** *The given compounds are*

$$\underset{\text{(Maximum b.p)}}{\text{Water}}, \text{ acetone}, \underset{\text{(Minimum b.p)}}{\text{ether}}$$

Greater the boiling point, lower is the vapour pressure of the solvent. Hence, the correct order of vapour pressure will be

Water < acetone < ether.

Q. 18 At 500 K, equilibrium constant, K_c, for the following reaction is 5.

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

What would be the equilibrium constant K_c for the reaction?

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

(a) 0.04 (b) 0.4 (c) 25 (d) 2.5

Ans. ***(a)*** For the reaction, $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$

$$K_c = \frac{[HI]}{[H_2]^{1/2}\,[I_2]^{1/2}} = 5$$

Thus, for the reaction, $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

$$K_{c_1} = \frac{[H_2]\,[I_2]}{[HI]^2} = \left(\frac{1}{K_c}\right)^2 = \left(\frac{1}{5}\right)^2 = \frac{1}{25} = 0.04$$

Q. 19 In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?

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

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

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

(d) The equilibrium will remain unaffected in all the three cases

Thinking Process

At constant volume, the equilibrium remain unaffected on addition of small amount of inert gas like argon, nean, Kruspton, etc.

Ans. ***(d)*** In these reactions, at constant volume

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The equilibrium constant (*K*) remains unaffected on addition of inert gas in all the three cases.

Multiple Choice Questions (More Than One Options)

Q. 20 For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2\ (g)$, the value of K is 50 at 400 K and 1700 at 500 K. Which of the following option(s) is/are correct?

(a) The reaction is endothermic

(b) The reaction is exothermic

(c) If $NO_2\ (g)$ and $N_2O_4(g)$ are mixed at 400 K at partial pressures 20 bar and 2 bar respectively, more $N_2O_4(g)$ will be formed

(d) The entropy of the system increases

Ans. ***(a, c, d)***

For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2\ (g)$

At 400 K, $K = 50$

At 500 K, $K = 1700$

(a) As the value of K increase with increase of temperature and $K = \dfrac{K_f}{K_b}$, this means that K_f increases, *i.e.,* forward reaction is favoured. Hence, reaction is endothermic.

(c) Since, number of moles of gaseous products are greater than the number of moles of gaseous reactants. Thus, higher pressure favours the backward reaction, *i.e.*, more $N_2O_4(g)$ will be obtained, if $P_{\text{product}} > P_{\text{reactant}}$.

(d) As reaction is accompanied by increase in the number of moles, entropy increases.

Q. 21 At a particular temperature and atmospheric pressure, the solid and liquid phases of a pure substance can exist in equilibrium. Which of the following term defines this temperature?

(a) Normal melting point

(b) Equilibrium temperature

(c) Boiling point

(d) Freezing point

Ans. ***(a, d)***

At a particular temperature and atmospheric pressure, the solid and liquid phases of a pure substance can exist as Solid $\rightleftharpoons$ liquid.

They exists at normal melting point or normal freezing point.

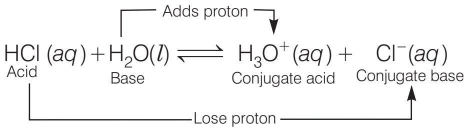
Short Answer Type Questions

Q. 22 The ionisation of hydrochloric acid in water is given below

$$HCl\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Cl^-\ (aq)$$

Label two conjugate acid-base pairs in this ionisation.

Ans.



$$\underset{\text{Acid}}{HCl\ (aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+(aq)} + \underset{\text{Conjugate base}}{Cl^-(aq)}$$

Note *If Bronsted acid is a strong acid then its conjugate base is a weak base and vice-versa. Generally, the conjugate acid has one extra proton and each conjugate base has one less proton.*

Q. 23 The aqueous solution of sugar does not conduct electricity. However, when sodium chloride is added to water, it conducts electricity. How will you explain this statement on the basis of ionisation and how is it affected by concentration of sodium chloride?

Ans. *Explanation for the given statement on the basis of ionisation and effect upon the concentration of sodium chloride is given below*

(i) Sugar being a non-electrolyte does not ionise in water whereas NaCl ionises completely in water and produces Na^+ and Cl^- ion which help in the conduction of electricity.

(ii) When concentration of NaCl is increased, more Na^+ and Cl^- ions will be produced. Hence, conductance or conductivity of the solution increases.

Q. 24 BF_3 does not have proton but still acts as an acid and reacts with $\ddot{N}H_3$. Why is it so? What type of bond is formed between the two?

Ans. BF_3 is an electron deficient compound and hence acts as Lewis acid. $\ddot{N}H_3$ has one lone pair which it can donate to BF_3 and form a coordinate bond. Hence, NH_3 acts as a Lewis base.

$$H_3N\!: \longrightarrow BF_3$$

Q. 25 Ionisation constant of a weak base MOH, is given expression

$$K_b = \frac{[M^+]\,[OH^-]}{[MOH]}$$

Values of ionisation constant of some weak bases at a particular temperature are given below

Base	Dimethylamine	Urea	Pyridine	Ammonia
K_b	5.4×10^{-4}	1.3×10^{-14}	1.77×10^{-9}	1.77×10^{-5}

Arrange the bases in decreasing order of the extent of their ionisation at equilibrium. Which of the above base is the strongest?

Ans. Given that, ionisation constant of a weak base *MOH*

$$K_b = [M^+]\,[OH^-]\,[MOH].$$

Larger the ionisation constant (K_b) of a base, greater is its ionisation and stronger the base. Hence, dimethyl amine is the strongest base.

$$K_b\ \underset{5.4\times10^{-4}}{\text{Dimethyl amine}} > \underset{1.77\times10^{-5}}{\text{ammonia}} > \underset{1.77\times10^{-9}}{\text{pyridine}} > \underset{1.3\times10^{-14}}{\text{urea}}$$

Q. 26 Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?

$$OH^-, RO^-\ CH_3COO^-, Cl^-$$

Ans. Conjugate acid of the given bases are H_2O, ROH, CH_3COOH and HCl. Order of their acidic strength is

$$HCl > CH_3COOH > H_2O > ROH$$

Hence, order of basic strength of their conjugate bases is

$$Cl^- < CH_3COO^- < OH^- < RO^-$$

Q. 27 Arrange the following in increasing order of pH.

$$KNO_3(aq), CH_3COONa\ (aq)\ NH_4Cl\ (aq), C_6H_5COONH_4(aq)$$

Ans. **(i)** KNO_3 is a salt of strong acid (HNO_3) strong base (KOH), hence its aqueous solution is neutral; pH = 7.

(ii) CH_3COONa is a salt of weak acid (CH_3COOH) and strong base (NaOH), hence, its aqueous solution is basic; pH >7.

(iii) NH_4Cl is a salt of strong acid (HCl) and weak base (NH_4OH) hence, its aqueous solution is acidic; pH< 7.

(iv) $C_6H_5COONH_4$ is a salt of weak acid, C_6H_5COOH and weak base, NH_4OH. But NH_4OH is slightly stronger than C_6H_5COOH. Hence, pH is slightly >7.

Therefore, increasing order of pH of the given salts is,

$$NH_4Cl < C_6H_5COONH_4 > KNO_3 < CH_3COONa$$

Q. 28 The value of K_c for the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 1×10^{-4}. At a given time, the composition of reaction mixture is $[HI] = 2 \times 10^{-5}$ mol, $[H_2] = 1 \times 10^{-5}$ mol and $[I_2] = 1 \times 10^{-5}$ mol. In which direction will the reaction proceed?

Ans. Given that,

$$[HI] = 2 \times 10^{-5} \text{ mol}$$
$$[H_2] = 1 \times 10^{-5} \text{ mol}$$
$$[I_2] = 1 \times 10^{-5} \text{ mol}$$

At a given time, the reaction quotient Q for the reaction will be given by the expression

$$Q = \frac{[H_2]\ [I_2]}{[HI]^2}$$
$$= \frac{1 \times 10^{-5} \times 1 \times 10^{-5}}{(2 \times 10^{-5})^2} = \frac{1}{4}$$
$$= 0.25 = 2.5 \times 10^{-1}$$

As the value of reaction quotient is greater than the value of K_c, *i.e.*, 1×10^{-4} the reaction will proceed in the reverse reaction.

Q. 29 On the basis of the equation $pH = -\log[H^+]$, the pH of 10^{-8} mol dm^{-3} solution of HCl should be 8. However, it is observed to be less than 7.0. Explain the reason.

Ans. Concentration 10^{-8} mol dm^{-3} indicates that the solution is very dilute. So, we cannot neglect the contribution of H_3O^+ ions produced from H_2O in the solution. Total $[H_3O^+] = 10^{-8} + 10^{-7}$ M. From this we get the value of pH close to 7 but less than 7 because the solution is acidic.

From calculation, it is found that pH of 10^{-8} mol dm^{-3} solution of HCl is equal to 6.96.

Q. 30 pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution a 100 times?

Ans. Given that,

$$pH = 5$$
$$[H^+] = 10^{-5} \text{ mol } L^{-1}$$

On diluting the solution 100 times $[H^+] = \frac{10^{-5}}{100} = 10^{-7} \text{ mol } L^{-1}$

On calculating the pH using the equation pH = – log $[H^+]$, value of pH comes out to be 7. It is not possible. This indicates that solution is very dilute.

Hence, Total H^+ ion concentration = H^+ ions from acid + H^+ ion from water

$$[H^+] = 10^{-7} + 10^{-7} = 2 \times 10^{-7}\text{ M}$$
$$\text{pH} = -\log [2 \times 10^{-7}]$$
$$\text{pH} = 7 - 0.3010 = 6.699$$

Q. 31 **A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution (Q_{sp}) becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}. Calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4.**

Ans.
$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$
$$K_{sp} \text{ for } BaSO_4 = [Ba^{2+}]\,[SO_4^{2-}] = s \times s = s^2$$

But $s = 8 \times 10^{-4}$ mol dm^{-3}

∴ $K_{sp} = (8 \times 10^{-4})^2 = 64 \times 10^{-8}$

In the presence of 0.01MH_2SO_4, the expression for K_{sp} will be

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$
$$K_{sp} = (s).(s + 0.01) \quad (0.01\text{ M } SO_4^{2-} \text{ ions from } 0.01\text{ M } H_2SO_4)$$
$$64 \times 10^{-8} = s \cdot (s + 0.01)$$
$$s^2 + 0.01s - 64 \times 10^{-8} = 0$$
$$s = \frac{-0.01 \pm \sqrt{(0.01)^2 + (4 \times 64 \times 10^{-8})}}{2}$$
$$= \frac{-0.01 \pm \sqrt{10^{-4} + (256 \times 10^{-8})}}{2}$$
$$= \frac{-0.01 \pm \sqrt{10^{-4}(1 + 256 \times 10^{-4})}}{2}$$
$$= \frac{-0.01 \pm 10^{-2}\sqrt{1 + 0.0256}}{2} = \frac{10^{-2}(-1 \pm 1.012719)}{2}$$
$$= 5 \times 10^{-3}(-1 + 1.012719) = 6.4 \times 10^{-5} \text{ mol dm}^{-3}$$

Note *$s <<< 0.01$, so, $s + 0.01 \approx 0.01$ and $64 \times 10^{-8} = s \times 0.01$*

$$s = \frac{64 \times 10^{-8}}{0.01} = 6.4 \times 10^{-5}$$

Q. 32 **pH of 0.08 mol dm^{-3} HOCl solution is 2.85. Calculate its ionisation constant.**

Thinking Process

To solve this problem, we use two steps

Step I *Find out the concentration of hydrogen ion $[H^+]$ through the formula $-\text{pH} = \log [H^+]$*

Step II *Afterward, calculate the K_a of HOCl which is weak monobasic acid by using the formula $K_a = \frac{[H^+]^2}{C}$. where, C is concentration of the solution*

Ans. pH of HOCl $= 2.85$

But, $-\text{pH} = \log [\text{H}^+]$

$\therefore$ $-2.85 = \log [\text{H}^+]$

$\Rightarrow$ $\bar{3}.15 = \log [\text{H}^+]$

$\Rightarrow$ $[\text{H}^+] = 1.413 \times 10^{-3}$

For weak monobasic acid $[\text{H}^+] = \sqrt{K_a \times C}$

$$\Rightarrow \quad K_a = \frac{[\text{H}^+]^2}{C} = \frac{(1.413 \times 10^{-3})^2}{0.08}$$

$$= 24.957 \times 10^{-6} = 2.4957 \times 10^{-5}$$

Q. 33 Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively.

Ans. pH of solution $A = 6$. Hence, $[\text{H}^+] = 10^{-6}$ mol L^{-1}

pH of solution $B = 4$. Hence, $[\text{H}^+] = 10^{-4}$ mol L^{-1}

On mixing 1 L of each solution, molar concentration of total H$^+$ is halved.

$$\text{Total,} \quad [\text{H}^+] = \frac{10^{-6} + 10^{-4}}{2} \text{ mol L}^{-1}$$

$$[\text{H}^+] = \frac{1.01 \times 10^{-4}}{2} = 5.05 \times 10^{-5} \text{ mol L}^{-1}$$

$$[\text{H}^+] = 5.0 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{H}^+] \quad \Rightarrow \quad \text{pH} = -\log (5.0 \times 10^{-5})$$

$$\text{pH} = -[\log 5 + (-5 \log 10)] \quad \Rightarrow \quad \text{pH} = -\log 5 + 5$$

$$\text{pH} = 5 - \log 5 = 5 - 0.6990 \quad \Rightarrow \quad \text{pH} = 4.3010 \approx 4.3$$

Thus, the pH of resulting solution is 4.3.

Q. 34 The solubility product of Al(OH)_3 is 2.7×10^{-11}. Calculate its solubility in g L^{-1} and also find out pH of this solution. (Atomic mass of Al = 27 u)

Ans. Let S be the solubility of Al(OH)_3.

$$\underset{\substack{1 \\ 1-S}}{\text{Al(OH)}_3} \rightleftharpoons \underset{\substack{0 \\ S}}{\text{Al}^{3+}}(aq) + \underset{\substack{0 \\ 3S}}{3\text{OH}^-}(aq)$$

Concentration of species at $t = 0$

Concentration of various species at equilibrium

$$K_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3 = (S)(3S)^3 = 27S^4$$

$$S^4 = \frac{K_{sp}}{27} = \frac{2.7 \times 10^{-11}}{27} = 1 \times 10^{-12}$$

$$S = 1 \times 10^{-3} \text{ mol L}^{-1}$$

(i) **Solubility of Al(OH)_3**

Molar mass of Al(OH)_3 is 78 g. Therefore,

Solubility of Al(OH)_3 in g L^{-1} $= 1 \times 10^{-3} \times 78$ g L^{-1} $= 78 \times 10^{-3}$ g L^{-1}

$= 7.8 \times 10^{-2}$ g L^{-1}

(ii) **pH of the solution** $S = 1 \times 10^{-3}$ mol L^{-1}

$$[\text{OH}^-] = 3S = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$$

$$\text{pOH} = 3 - \log 3$$

$$\text{pH} = 14 - \text{pOH} = 11 + \log 3 = 11.4771$$

Q. 35 Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution.

(K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$, atomic mass of $Pb = 207u$)

Ans. Suppose, solubility of $PbCl_2$ in water is s mol L^{-1}

$$\underset{(1-s)}{PbCl_2(s)} \rightleftharpoons \underset{s}{Pb^{2+}}(aq) + \underset{2s}{2Cl^-}(aq)$$

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

$$K_{sp} = [s]\,[2s]^2 = 4s^3$$

$$3.2 \times 10^{-8} = 4s^3$$

$$s^3 = \frac{3.2 \times 10^{-8}}{4} = 0.8 \times 10^{-8}$$

$$s^3 = 8.0 \times 10^{-9}$$

Solubility of $PbCl_2$, $s = 2 \times 10^{-3}$ mol L^{-1}

Solubility of $PbCl_2$ in $gL^{-1} = 278 \times 2 \times 10^{-3} = 0.556$ g L^{-1}

($\because$ Molar mass of $PbCl_2 = 207 + (2 \times 35.5) = 278$)

0.556 g of $PbCl_2$ dissolve in 1 L of water.

$\therefore$ 0.1 g of $PbCl_2$ will dissolve in $= \frac{1 \times 0.1}{0.556}$ L of water

$= 0.1798$ L

To make a saturated solution, dissolution of 0.1g $PbCl_2$ in 0.1798 L $\approx$ 0.2 L of water will be required.

Q. 36 A reaction between ammonia and boron trifluoride is given below.

$$:NH_3 + BF_3 \longrightarrow H_3N{:}BF_3$$

Identify the acid and base in this reaction. Which theory explains it? What is the hybridisation of B and N in the reactants?

Ans. Although BF_3 does not have a proton but acts as Lewis acid as it is an electron deficient compound. It reacts with NH_3 by accepting the lone pair of electrons from NH_3 and complete its octet. The reaction can be represented by

$$BF_3 + :NH_3 \longrightarrow BF_3 \leftarrow NH_3$$

Lewis electronic theory of acids and bases can explain it. Boron in BF_3 is sp^2 hybridised where N in NH_3 is sp^3 hybridised.

Q. 37 Following data is given for the reaction

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

$$\Delta_f H^\ominus [CaO(s)] = -635.1 \text{kJ mol}^{-1}$$

$$\Delta_f H^\ominus [CO_2(g)] = -393.5 \text{kJ mol}^{-1}$$

$$\Delta_f H^\ominus [CaCO_3(s)] = -1206.9 \text{kJ mol}^{-1}$$

Predict the effect of temperature on the equilibrium constant of the above reaction.

Ans. Given that,

$$\Delta_f H^\ominus [CaO(s)] = -635.1 \text{kJ mol}^{-1}$$

$$\Delta_f H^\ominus [CO_2(g)] = -393.5 \text{kJ mol}^{-1}$$

$$\Delta_f H^\ominus [CaCO_3(s)] = -1206.9 \text{kJ mol}^{-1}$$

In the reaction,

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

$$\Delta_f H^\ominus = \Delta_f H^\ominus\,[CaO(s)] + \Delta_f H^\ominus\,[CO_2(g)] - \Delta_f H^\ominus\,[CaCO_3(s)]$$

$$\therefore \quad \Delta_f H^\ominus = -\,635.1 + (-\,393.5) - (-\,1206\,.\,9) = 178.3 \text{ kJmol}^{-1}$$

Because ΔH value is positive, so the reaction is endothermic. Hence, according to Le-Chatelier's principle, reaction will proceed in forward direction on increasing temperature. Thus, the value of equilibrium constant for the reaction increases.

Matching The Columns

Q. 38 Match the following equilibria with the corresponding condition.

A.	Liquid $\rightleftharpoons$ Vapour	1.	Saturated solution
B.	Solid $\rightleftharpoons$ Liquid	2.	Boiling point
C.	Solid $\rightleftharpoons$ Vapour	3.	Sublimation point
D.	Solute $(s) \rightleftharpoons$ Solute (solution)	4.	Melting point
		5.	Unsaturated solution

Ans. **A.** → (2) **B.** → (4) **C.** → (3) **D.** → (1)

A. Liquid $\rightleftharpoons$ Vapour equilibrium exists at the boiling point.
B. Solid $\rightleftharpoons$ Liquid equilibrium exists at the melting point.
C. Solid $\rightleftharpoons$ Vapour equilibrium exists at the sublimation point.
D. Solute $(s) \rightleftharpoons$ Solute (solution) equilibrium exists at saturated solution.

Q. 39 For the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\text{Equilibrium constant, } K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

Some reactions are written below in Column I and their equilibrium constants in terms of K_c are written in Column II. Match the following reactions with the corresponding equilibrium constant.

Column I (Reaction)		Column II (Equilibrium constant)	
A.	$2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$	1.	$2K_c$
B.	$2NH_3(g) \rightleftharpoons 2N_2(g) + 3H_2(g)$	2.	$K_c^{1/2}$
C.	$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$	3.	$\frac{1}{K_c}$
		4.	K_c^2

Ans. **A.** → (4) **B.** → (3) **C.** → (2)

For the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\text{Equilibrium constant } K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

A. The given reaction $[2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)]$ is twice the above reaction.
Hence, $K = K_c^2$

B. The reaction $[2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)]$ is reverse of the above reaction.
Hence, $K = \frac{1}{K_c}$

C. The reaction $\left[\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)\right]$ is half of the above reaction.
Hence, $K = \sqrt{K_c} = K_c^{\frac{1}{2}}$.

Q. 40 Match standard free energy of the reaction with the corresponding equilibrium constant.

A. $\Delta G^\ominus > 0$	1. $K > 1$
B. $\Delta G^\ominus < 0$	2. $K = 1$
C. $\Delta G^\ominus = 0$	3. $K = 0$
	4. $K < 1$

Ans. **A.** → (4) **B.** → (1) **C.** → (2)

As we know that, $\Delta G^\ominus = -RT \ln K$

A. If $\Delta G^\ominus > 0$, *i.e.*, ΔG° is positive, then $\ln K$ is negative *i.e.*, $K < 1$.

B. If $\Delta G^\ominus < 0$, *i.e.*, ΔG° is negative then $\ln K$ is positive *i.e.*, $K > 1$.

C. If $\Delta G^\ominus = 0$, $\ln K = 0$, *i.e.*, $K = 1$.

Q. 41 Match the following species with the corresponding conjugate acid.

Species	Conjugate acid
A. NH_3	1. CO_3^{2-}
B. HCO_3^-	2. NH_4^+
C. H_2O	3. H_3O^+
D. HSO_4^-	4. H_2SO_4
	5. H_2CO_3

Ans. **A.** → (2) **B.** → (5) **C.** → (3) **D.** → (4)

As conjugate acid → Base $+H^+$

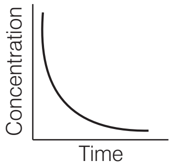
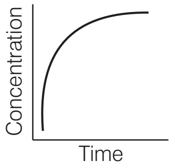
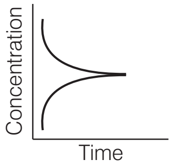
A. $NH_3 + H^+ \longrightarrow NH_4^+$

B. $HCO_3^- + H^+ \longrightarrow H_2CO_3$

C. $H_2O + H^+ \longrightarrow H_3O^+$

D. $HSO_4^- + H^+ \longrightarrow H_2SO_4$

Q. 42 Match the following graphical variation with their description.

A		B
A.		1. Variation in product concentration with time
B.		2. Reaction at equilibrium
C.		3. Variation in reactant concentration with time

A. → (3) **B.** → (1) **C.** → (2)

A. Graph (A) represents variation of reactant concentration with time.

B. Graph (B) represents variation of product concentration with time.

C. Graph (C) represents reaction at equilibrium.

Q. 43 Match the Column I with Column II.

Column I	Column II
A. Equilibrium	1. $\Delta G > 0, K < 1$
B. Spontaneous reaction	2. $\Delta G = 0$
C. Non-spontaneous reaction	3. $\Delta G^{\ominus} = 0$
	4. $\Delta G < 0, K > 1$

Ans. **A.** → (2, 3) **B.** → (4) **C.** → (1)

A. ΔG ($\Delta G^{\ominus}$) is 0, reaction has achieved equilibrium: at this point, there is no longer any free energy left to drive the reaction.

B. If $\Delta G < 0$, then $K > 1$ which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.

C. If $\Delta G > 0$, then $K < 1$, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

Assertion and Reason

In the following questions a statement of Assertion (A) *followed by a statement of Reason* (R) *is given. Choose the correct option out of the choices given below in each question.*

Q. 44 Assertion (A) Increasing order or acidity of hydrogen halides is HF < HCI < HBr < HI.

Reason (R) While comparing acids formed by the elements belonging to the same group of periodic table, H—A bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

(a) Both A and R are true R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

Ans. *(a)* Both assertion and reason are true and reason is the correct explanation of assertion.

In the hydrogen halides, the HI is strongest acid while HF is the weak acid. It is because while comparing acids formed by the elements belonging to the same group of periodic table, H — A bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

Q. 45 Assertion (A) A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on addition of small amounts of acid or alkali.

Reason (R) A solution containing a mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

Ans. *(a)* Both assertion and reason are true and reason is correct explanation of assertion.

A solution containing a mixture of acetic acid and the sodium acetate acts as a buffer solution as it maintains a constant value of pH (= 4.75) and its pH is not affected on addition of small amounts of acid or alkali.

Q. 46 Assertion (A) The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.

Reason (R) Hydrogen sulphide is a weak acid.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

Ans. *(b)* Both assertion and reason are true but reason is not correct explanation of assertion.

HCl gives the common H^+ ions and hence ionisation equilibrium $H_2S \rightleftharpoons 2H^+ + S^{2-}$ is suppressed.

Q. 47 Assertion (A) For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason (R) Equilibrium constant is independent of temperature.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

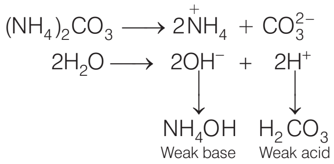
Ans. *(c)* Assertion is true but reason is false.
Equilibrium constant of a reaction depends upon temperature.

Q. 48 Assertion (A) Aqueous solution of ammonium carbonate is basic.

Reason (R) Acidic/basic nature of a salt solution of a salt of weak acid and weak base depends on K_a and K_b value of the acid and the base forming it.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

Ans. *(a)* Both assertion and reason are true and reason is the correct explanation of assertion.



$$(NH_4)_2CO_3 \longrightarrow 2\overset{+}{N}H_4 + CO_3^{2-}$$

$$\begin{array}{cccc} 2H_2O \longrightarrow & 2OH^- & + & 2H^+ \\ & \downarrow & & \downarrow \\ & NH_4OH & & H_2CO_3 \\ & \text{Weak base} & & \text{Weak acid} \end{array}$$

If K_b of $NH_4OH > K_a$ of H_2CO_3
The solution is basic.
or, if K_a of $H_2CO_3 > K_b$ of NH_4OH; the solution is acidic.

Q. 49 Assertion (A) An aqueous solution of ammonium acetate can act as a buffer.

Reason (R) Acetic acid is a weak acid and NH_4OH is a weak base.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is false but R is true
(d) Both A and R are false

Ans. *(b)* Both assertion and reason are true but reason is not correct explanation of assertion.
Ammonium acetate is a salt of weak acid (CH_3COOH) and weak base (NH_4OH).

Q. 50 Assertion (A) In the dissociation of PCl_5 at constant pressure and temperature the addition of helium at equilibrium increases the dissociation of PCl_5.

Reason (R) Helium removes Cl_2 from the field of action.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

Ans. *(c)* Assertion is true but reason is false.

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

At constant pressure, when helium is added to the equilibrium, volume increases. Thus, in order to maintain the K constant, degree of dissociation of PCl_5 increases. Helium is unreactive towards chlorine gas.

Long Answer Type Questions

Q. 51 How can you predict the following stages of a reaction by comparing the value of K_c and Q_c?

(i) Net reaction proceeds in the forward direction.
(ii) Net reaction proceeds in the backward direction.
(iii) No net reaction occurs.

Ans. *Prediction of the following stages of a reaction by comparing the value of K_c and Q_c are*

(i) If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction).
(ii) If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).
(iii) If $Q_c = K_c$, the reaction mixture is already at equilibrium.

Q. 52 On the basis of Le-Chatelier principle explain how temperature and pressure can be adjusted to increase the yield of ammonia in the following reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\ \Delta H = -92.38 \text{ kJ mol}^{-1}$$

What will be the effect of addition of argon to the above reaction mixture at constant volume?

Ans.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ \Delta H = -92.38 \text{ kJ mol}^{-1}$$

It is an exothermic process as ΔH is negative.

Effect of temperature According to Le-Chatelier's principle, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction. So, optimum temperature 700 K is favourable in attainment of equilibrium.

Effect of pressure Similarly, high pressure about 200 atm is favourable for high yield of ammonia. On increasing pressure, reaction goes in the forward direction because the number of moles decreases in the forward direction.

Addition of argon At constant volume addition of argon does not affect the equilibrium because it does not change the partial pressures of the reactants or products involved in the reaction and the equilibrium remains undisturbed.

Q. 53 A sparingly soluble salt having general formula $A_x^{p+}\,B_y^{q-}$ and molar solubility S is in equilibrium with its saturated solution. Derive a relationship between the solubility and solubility product for such salt.

Ans. A sparingly soluble salt having general formula $A_x^{p+}\,B_y^{q-}$. Its molar solubility is S mol L^{-1}.

Then,
$$A_x^{p+}\,B_y^{q-} \rightleftharpoons \underset{x}{xA^{p+}}\,(aq) + \underset{y}{yB^{q-}}\,(aq)$$

S moles of A_xB_y dissolve to give x moles of A^{P+} and y moles of B^{q-}.

Therefore, solubility product
$$(K_{sp}) = [A^{P+}]^x\,[B^{q-}]^y$$
$$= [xS]^x\,[yS]^y$$
$$= x^x y^y\,S^{x+y}$$

Q. 54 Write a relation between ΔG and Q and define the meaning of each term and answer the following.

(a) Why a reaction proceeds forward when $Q < K$ and no net reaction occurs when $Q = K$?

(b) Explain the effect of increase in pressure in terms of reaction quotient Q.

For the reaction, $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Ans. The relation between ΔG and Q is
$$\Delta G = \Delta G^{\ominus} + RT\ln Q$$

ΔG = change in free energy as the reaction proceeds.

$\Delta G^{\ominus}$ = standard free energy

Q = reaction quotient

R = gas constant

T = absolute temperature in K

(a) Since, $\Delta G^{\ominus} = -RT\ln K$

∴ $\Delta G = -RT\ln K + RT\ln Q$

$$\Delta G = RT\ln\frac{Q}{K}$$

If $Q < K$, ΔG will be negative and the reaction proceeds in the forward direction.

If $Q = K$, $\Delta G = 0$ reaction is in equilibrium and there is no net reaction.

(b)
$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$
$$K_c = \frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3}$$

On increasing pressure, volume decreases. If we doubled the pressure, volume will be halved but the molar concentrations will be doubled. Then,
$$Q_c = \frac{2[CH_4]\cdot 2[H_2O]}{2[CO]\,\{2[H_2]\}^3} = \frac{1}{4}\frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3} = \frac{1}{4}K_c$$

Therefore, Q_c is less than K_c, so Q_c will tend to increase to re-establish equilibrium and the reaction will go in forward direction.