

CH7 – EQUILIBRIUM

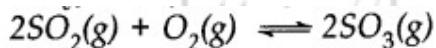
Question 1. A liquid is in equilibrium with its vapours in a sealed container at a fixed temperature. The volume of the container is suddenly increased, (i) What is the initial effect of the change on the vapour pressure? (ii) How do the rates of evaporation and condensation change initially? (iii) What happens when equilibrium is restored finally and what will be the final vapour pressure?

Answer: (i) On increasing the volume of the container, the vapour pressure will initially decrease because the same amount of vapours are now distributed over a larger space.

(ii) On increasing the volume of the container, the rate of evaporation will increase initially because now more space is available. Since the amount of the vapours per unit volume decrease on increasing the volume, therefore, the rate of condensation will decrease initially.

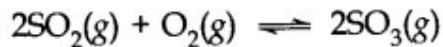
(iii) Finally, equilibrium will be restored when the rates of the forward and backward processes become equal. However, the vapour pressure will remain unchanged because it depends upon the temperature and not upon the volume of the container.

Question 2. What is K_c for the following reaction in state of equilibrium?



Given: $[SO_2] = 0.6\text{ M}$; $[O_2] = 0.82\text{ M}$; and $[SO_3] = 1.90\text{ M}$

Answer:



$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{(1.9\text{ M}) \times (1.9\text{ M})}{(0.6\text{ M}) \times (0.6\text{ M}) \times (0.82\text{ M})}$$

$$= 12.229\text{ M}^{-1} = 12.229\text{ L mol}^{-1}$$

Question 3.

At a certain temperature and total pressure of 10^5 Pa , iodine vapours contain 40% by volume of iodine atoms in the equilibrium $I_2(g) \rightleftharpoons 2I(g)$. Calculate K_n for the equilibrium.

Answer:

According to available data:

Total pressure of equilibrium mixture = 10^5 Pa

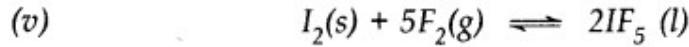
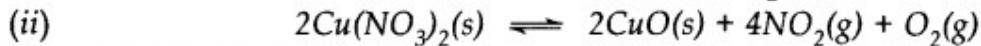
$$\text{Partial pressure of iodine atoms (I)} = \frac{40}{100} \times (10^5 \text{ Pa}) = 0.4 \times 10^5 \text{ Pa}$$

$$\text{Partial pressure of iodine molecules (I}_2\text{)} = \frac{60}{100} \times (10^5 \text{ Pa}) = 0.6 \times 10^5 \text{ Pa}$$



$$K_p = \frac{p_{I_2}}{p_I} = \frac{(0.4 \times 10^5 \text{ Pa})^2}{(0.6 \times 10^5 \text{ Pa})} = 2.67 \times 10^4 \text{ Pa}$$

Question 4. Write the expression for the equilibrium constant for each of the following reactions



Answer:

$$(i) \quad K_c = \frac{[\text{NO}(g)]^2 [\text{Cl}_2(g)]}{[\text{NOCl}(g)]^2}$$

$$(ii) \quad K_c = \frac{[\text{CuO}(g)]^2 [\text{NO}_2(g)]^4 [\text{O}_2(g)]}{[\text{Cu}(\text{NO}_3)_2(s)]^2} = [\text{NO}_2(g)]^4 [\text{O}_2(g)]$$

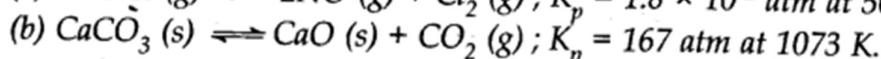
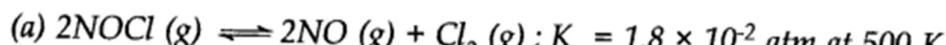
$$(iii) \quad K_c = \frac{[\text{CH}_3\text{COOH}(aq)][\text{C}_2\text{H}_5\text{OH}(aq)]}{[\text{CH}_3\text{COOC}_2\text{H}_5(aq)][\text{H}_2\text{O}(l)]}$$

$$= \frac{[\text{CH}_3\text{COOH}(aq)][\text{C}_2\text{H}_5\text{OH}(aq)]}{[\text{CH}_3\text{COOC}_2\text{H}_5(aq)]}$$

$$(iv) \quad K_c = \frac{[\text{Fe(OH)}_3(s)]}{[\text{Fe}^{3+}(aq)][\text{OH}^-(aq)]^3} = \frac{1}{[\text{Fe}^{3+}(aq)][\text{OH}^-(aq)]^3}$$

$$(v) \quad K_c = \frac{[\text{IF}_5(l)]^2}{[\text{I}_2(s)][\text{F}_2(g)]^5} = \frac{[\text{IF}_5(l)]^2}{[\text{F}_2(g)]^5}$$

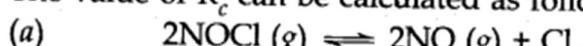
Question 5. Find the value of K_c for each of the following equilibria from the value of K



Answer:

K_p and K_c are related to each other as $K_p = K_c (RT)^{\Delta n g}$

The value of K_c can be calculated as follows:

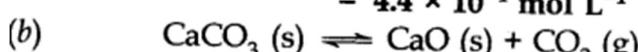


$$K_p = 1.8 \times 10^{-2} \text{ atm,}$$

$$\Delta n g = 3 - 2 = 1 ; R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1} ; T = 500 \text{ K}$$

$$\therefore K_c = \frac{K_p}{(RT)^{\Delta n g}} = \frac{(1.8 \times 10^{-2} \text{ atm})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 500 \text{ K})^1}$$

$$= 4.4 \times 10^{-4} \text{ mol L}^{-1}$$



$$K_p = 167 \text{ atm, } \Delta n g = 1$$

$$R = 0.0821 \text{ liter atm K}^{-1} \text{ mol}^{-1} ; T = 1073 \text{ K}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n g}} = \frac{(167 \text{ atm})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 1073 \text{ K})^1}$$

$$= 1.9 \text{ mol L}^{-1}$$

Question 6. For the following equilibrium, $K = 6.3 \times 10^{14}$ at 1000

$\text{NO}(\text{g}) + \text{O}_3 \rightleftharpoons \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c for the reverse reaction?

Answer:

$$\text{For the reverse reaction } K_c = \frac{1}{K_p} = \frac{1}{6.3 \times 10^{14}} = 1.59 \times 10^{-15}.$$

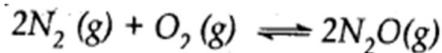
Question 7. Explain why pure liquids and solids can be ignored while writing the value of equilibrium constants.

Answer: This is because molar concentration of a pure solid or liquid is independent of the amount present.

$$\text{Molar concentration} = \frac{\text{No. of moles}}{\text{volume}} \times \frac{\text{Mass}}{\text{volume}} \times \text{Density}$$

Since density of pure liquid or solid is fixed and molar mass is also fixed. Therefore molar concentration are constant.

Question 8. Reaction between nitrogen and oxygen takes place as follows:



If a mixture of 0.482 mol of N_2 and 0.933 mol of O_2 is placed in a reaction vessel of volume 10 L and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of the equilibrium mixture.

Answer: Let x moles of $N_2(g)$ take part in the reaction. According to the equation, $x/2$ moles of $O_2(g)$ will react to form x moles of $N_2O(g)$. The molar concentration per litre of different species before the reaction and at the equilibrium point is:

	$2N_2(g)$	$+ O_2(g)$	$\rightleftharpoons 2N_2O(g)$
Initial mole/litre:	$\frac{0.482}{10}$	$\frac{0.933}{10}$	Zero
Mole/litre at eqm. point:	$\frac{0.482-x}{10}$	$\frac{0.933-\frac{x}{2}}{10}$	$\frac{x}{10}$

The value of equilibrium constant (2.0×10^{-37}) is extremely small. This means that only small amounts of reactants have reacted. Therefore, is extremely small and can be omitted as far as the reactants are concerned.

$$\text{Applying Law of Chemical Equilibrium } K_c = \frac{[N_2O(g)]^2}{[N_2(g)]^2 [O_2(g)]}$$

$$2.0 \times 10^{-37} = \frac{\left(\frac{x}{10}\right)^2}{\left(\frac{0.482}{10}\right)^2 \times \left(\frac{0.933}{10}\right)} = \frac{0.01 x^2}{2.1676 \times 10^{-4}}$$

$$x^2 = 43.352 \times 10^{-40} \quad \text{or} \quad x = 6.6 \times 10^{-20}$$

As x is extremely small, it can be neglected.

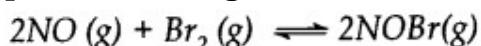
Thus, in the equilibrium mixture

$$\text{Molar conc. of } N_2 = 0.0482 \text{ mol L}^{-1}$$

$$\text{Molar conc. of } O_2 = 0.0933 \text{ mol L}^{-1}$$

$$\begin{aligned} \text{Molar conc. of } N_2O &= 0.1 \times x = 0.1 \times 6.6 \times 10^{-20} \text{ mol L}^{-1} \\ &= 6.6 \times 10^{-21} \text{ mol L}^{-1} \end{aligned}$$

Question 9. Nitric oxide reacts with bromine and gives nitrosyl bromide as per reaction given below:



When 0.087 mole of NO and 0.0437 mole of Br₂ are mixed in a closed container at constant temperature, 0.0518 mole of NOBr is obtained at equilibrium. Determine the compositions of the equilibrium mixture.

Answer: The balanced chemical equation for the reaction is:

According to the equation, 2 moles of NO (g) react with 1 mole of Br₂ (g) to form 2 moles of NOBr (g). The composition of the equilibrium mixture can be calculated as follows:

No. of moles of NOBr (g) formed at equilibrium = 0.0518 mol (given)

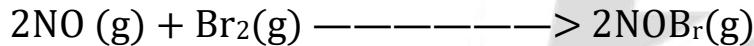
No. of moles of NO (g) taking part in reaction = 0.0518 mol

No. of moles of NO (g) left at equilibrium = 0.087 - 0.0518 = 0.0352 mol

No. of moles of Br₂ (g) taking part in reaction = 1/2 x 0.0518 = 0.0259 mol

No. of moles of Br₂ (g) left at equilibrium = 0.0437 - 0.0259 = 0.0178 mol

The initial molar concentration and equilibrium molar concentration of different species may be represented as:

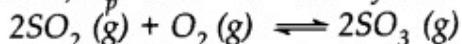


Initial moles 0.087 0.0437 0

Moles at eqm. point: 0.0352 0.0178 0.0518

Question 10.

At 450 K, $K_p = 2.0 \times 10^{10} \text{ bar}^{-1}$ for the equilibrium reaction:



What is K_c at this temperature?

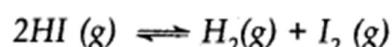
Answer:

$$K_p = K_c (RT)^{\Delta n_g} \text{ or } K_c = \frac{K_p}{(RT)^{\Delta n_g}} = K_p (RT)^{-\Delta n_g}$$

$$K_p = 2.0 \times 10^{10} \text{ bar}^{-1}; R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}; T = 450 \text{ K}; \Delta n_g = 2 - 3 = -1$$

$$K_c = (2.0 \times 10^{10} \text{ bar}^{-1}) \times [(0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K})]^{-(-1)} \\ = 7.47 \times 10^{11} \text{ mol}^{-1} \text{ L} = 7.47 \times 10^{11} \text{ M}^{-1}$$

Question 11. A sample of HI (g) is placed in a flask at a pressure of 0.2 atm. At equilibrium partial pressure of HI (g) is 0.04 atm. What is K_p for the given equilibrium?

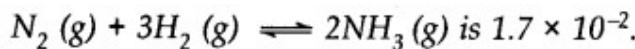


Answer:

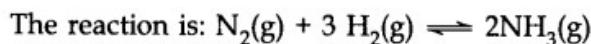
$$p\text{HI} = 0.04 \text{ atm}, p\text{H}_2 = 0.08 \text{ atm}; p\text{I}_2 = 0.08 \text{ atm}$$

$$K_p = \frac{p\text{H}_2 \times p\text{I}_2}{p\text{HI}^2} = \frac{(0.08 \text{ atm}) \times (0.08 \text{ atm})}{(0.04 \text{ atm}) \times (0.04 \text{ atm})} = 4.0$$

Question 12. A mixture of 1.57 mol of N_2 , 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant K_c for the reaction



Is this reaction at equilibrium? If not, what is the direction of net reaction?

Answer:

$$\text{Concentration quotient (Q}_c\text{)} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(8.13/20 \text{ mol L}^{-1})^2}{(1.57/20 \text{ mol L}^{-1}) \times (1.92/20 \text{ mol L}^{-1})^3} \\ = 2.38 \times 10^3$$

The equilibrium constant (K_c) for the reaction = 1.7×10^{-2}

As $Q_c \neq K_c$; this means that the reaction is not in a state of equilibrium.

Question 13. The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^4 [\text{H}_2\text{O}]^6}$$

Write the balanced chemical equation corresponding to this expression.

Answer: Balanced chemical equation for the reaction is 4



Question 14. If 1 mole of H_2O and 1 mole of CO are taken in a 10 litre vessel and heated to 725 K, at equilibrium point 40 percent of water (by mass) reacts with carbon monoxide according to equation.



Calculate the equilibrium constant for the reaction.

Answer: Number of moles of water originally present = 1 mol

Percentage of water reacted = 40%

Number of moles of water reacted = $1 \times 40/100 = 0.4 \text{ mol}$

Number of moles of water left = $(1 - 0.4) = 0.6 \text{ mole}$ According to the equation, 0.4 mole of water will react with 0.4 mole of carbon monoxide to

form 0.4 mole of hydrogen and 0.4 mole of carbon dioxide.

Thus, the molar cone, per litre of the reactants and products before the reaction and at the equilibrium point are as follows:

	$\text{H}_2\text{O}(g)$	+	$\text{CO}(g)$	\rightleftharpoons	$\text{H}_2(g)$	+	$\text{CO}_2(g)$	
Initial moles/litre	$\frac{1}{10}$				$\frac{1}{10}$		0	0

Mole/litre at the equilibrium point

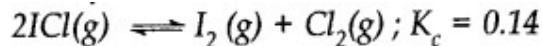
$$\frac{1-0.4}{10} = \frac{0.6}{10} \quad \frac{1-0.4}{10} = \frac{0.6}{10} \quad \frac{0.4}{10} \quad \frac{0.4}{10}$$

Applying law of chemical equilibrium,

$$\text{Equilibrium constant } (K_c) = \frac{[\text{H}_2(g)][\text{CO}_2(g)]}{[\text{H}_2\text{O}(g)][\text{CO}(g)]} = \frac{\left(\frac{0.4}{10} \text{ mol L}^{-1}\right) \times \left(\frac{0.4}{10} \text{ mol L}^{-1}\right)}{\left(\frac{0.6}{10} \text{ mol L}^{-1}\right) \times \left(\frac{0.6}{10} \text{ mol L}^{-1}\right)}$$

$$= \frac{0.16}{0.36} = 0.44$$

Question 15. What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?



Answer:

Suppose at equilibrium, the molar concentration of both $\text{I}_2(g)$ and $\text{Cl}_2(g)$ is $x \text{ mol L}^{-1}$.

	$2\text{ICl}(g)$	\rightleftharpoons	$\text{I}_2(g)$	+	$\text{Cl}_2(g)$	
Initial molar conc.	0.78 M		0		0	
Eqn. molar conc.	$(0.78 - 2x)$ M		x		x	

$$K_c = \frac{[\text{I}_2(g)][\text{Cl}_2(g)]}{[\text{ICl}(g)^2]} = \frac{(x) \times (x)}{(0.78 - 2x)^2}$$

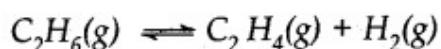
$$\frac{x}{(0.78 - 2x)} = (0.14)^{1/2} = 0.374 \quad \text{or} \quad x = 0.374 (0.78 - 2x)$$

$$x = 0.292 - 0.748x \quad \text{or} \quad 1.748x = 0.292; x = \frac{0.292}{1.748} = 0.167$$

$$[\text{ICl}] = (0.78 - 2 \times 0.167) = (0.78 - 0.334) = 0.446 \text{ M}$$

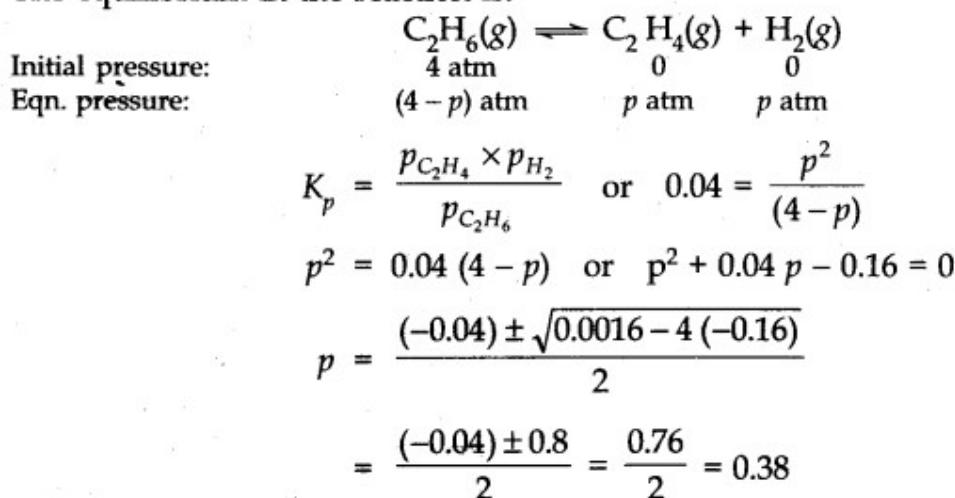
$$[\text{I}_2] = 0.167 \text{ M}; [\text{Cl}_2] = 0.167 \text{ M}$$

Question 16. $K = 0.04 \text{ atm}$ at 898 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4 atm pressure, and allowed to come to equilibrium.



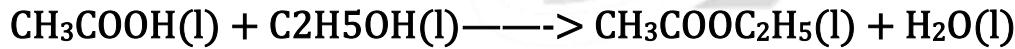
Answer:

The equilibrium in the reaction is:



Equilibrium pressure or concentration of $C_2H_6 = (4 - 0.38) = 3.62 \text{ atm}$.

Question 17. The ester, ethyl acetate is formed by the reaction of ethanol and acetic acid and the equilibrium is represented as:



(i) Write the concentration ratio (concentration quotient) Q for this reaction. Note that water is not in excess and is not a solvent in this reaction.

(ii) At 293 K, if one starts with 1.000 mol of acetic acid and 0.180 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.50 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after some time. Has equilibrium been reached?

Answer:

(i) The concentration ratio (Concentration quotient) Q_c for the reaction is:

$$Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5(l)][\text{H}_2\text{O}(l)]}{[\text{CH}_3\text{COOH}(l)][\text{C}_2\text{H}_5\text{OH}(l)]}$$

(ii)	$\text{CH}_3\text{COOH}(l) + \text{C}_2\text{H}_5\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$
Initial molar conc.	1.0 mol
Molar conc. at equilibrium point	(1 - 0.17l) = 0.829 mol

Applying Law of Chemical equilibrium,

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

$$= \frac{(0.171 \text{ mol}) \times (0.171 \text{ mol})}{(0.829 \text{ mol}) (0.009 \text{ mol})} = 3.92$$

(iii)	$\text{CH}_3\text{COOH}(l) + \text{C}_2\text{H}_5\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$
Initial molar conc.	1.0 mol
Molar conc. at equilibrium	1.0 - 0.214 = 0.786 mol

$$Q_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5(l)][\text{H}_2\text{O}(l)]}{[\text{CH}_3\text{COOH}(l)][\text{C}_2\text{H}_5\text{OH}(l)]}$$

$$= \frac{(0.214 \text{ mol}) \times (0.214 \text{ mol})}{(0.786 \text{ mol}) (0.286 \text{ mol})} = 0.204$$

Since Q_c is less than K_c this means that the equilibrium has not been reached. The reactants are still taking part in the reaction to form the products.

Question 18. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was reached, the concentration of PCl_5 was found to be $0.5 \times 10^{-1} \text{ mol L}^{-1}$. If K_c is 8.3×10^{-3} what are the concentrations of PCl_3 and Cl_2 at equilibrium?

Answer: Let the initial molar concentration of PCl_5 per litre = $x \text{ mol}$

Molar concentration of PCl_5 at equilibrium = 0.05 mol

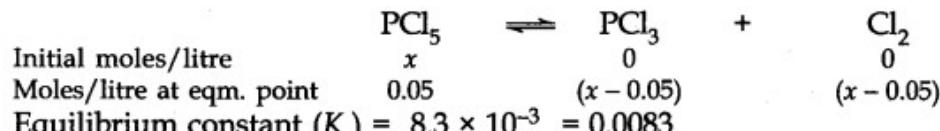
∴ Moles of PCl_5 decomposed = $(x - 0.05) \text{ mol}$

Moles of PCl_3 formed = $(x - 0.05) \text{ mol}$

Moles of Cl_2 formed = $(x - 0.05) \text{ mol}$

The molar conc./litre of reactants and products before the reaction and at

the equilibrium point are:



Applying Law of chemical equilibrium,

$$\begin{aligned}
 K_c &= \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} ; \quad 0.0083 = \frac{(x - 0.05) \times (x - 0.05)}{0.05} \\
 (x - 0.05)^2 &= 0.0083 \times 0.05 = 4.15 \times 10^{-4} \\
 (x - 0.05) &= (4.15 \times 10^{-4})^{1/2} = 2.037 \times 10^{-2} = 0.02 \text{ moles} \\
 x &= 0.05 + 0.02 = 0.07 \text{ mol}
 \end{aligned}$$

The molar concentration per litre of PCl_3 at eqm. = $0.07 - 0.05 = 0.02 \text{ mol}$

The molar concentration per litre of Cl_2 at eqm. = $0.07 - 0.05 = 0.02 \text{ mol}$.

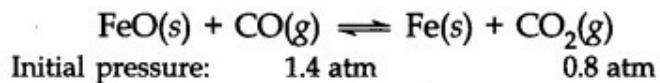
Question 19. One of the reactions that takes place in producing steel from iron ore is the reduction of iron

(II) oxide by carbon monoxide to give iron metal and CO_2



What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial pressures are: $P_{\text{CO}} = 1.4 \text{ atm}$ and $P_{\text{CO}_2} = 0.80 \text{ atm}$?

Answer:



$$Q_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \frac{(0.8 \text{ atm})}{(1.4 \text{ atm})} = 0.571$$

Since $Q_p > K_p (0.265)$, this means that the reaction will move in the backward direction to attain the equilibrium. Therefore, partial pressure of CO_2 will decrease while that of CO will increase so that the equilibrium may be attained again. Let $p \text{ atm}$ be the decrease in the partial pressure of CO_2 . Therefore, the partial pressure of CO will increase by the same magnitude i.e., $p \text{ atm}$.

$$p_{\text{CO}_2} = (0.8 - p) \text{ atm}; p_{\text{CO}}(\text{g}) = (1.4 + p) \text{ atm}$$

$$\text{At equilibrium, } K_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \frac{(0.8 - p) \text{ atm}}{(1.4 + p) \text{ atm}} = \frac{(0.8 - p)}{(1.4 + p)}$$

$$\text{or } 0.265 = \frac{(0.8 - p)}{(1.4 + p)}$$

$$0.371 + 0.265 p = 0.8 - p \text{ or } 1.265 p = 0.8 - 0.371 = 0.429$$

$$p = 0.429/1.265 = 0.339 \text{ atm}$$

$$(p_{\text{CO}})_{\text{eq}} = (1.4 + 0.339) = 1.739 \text{ atm}$$

$$(p_{\text{CO}_2})_{\text{eq}} = (0.8 - 0.339) = 1.461 \text{ atm}$$

Question 20.

Equilibrium constant K_c for the reaction, $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ at 500 K is 0.061.

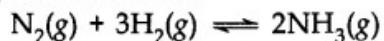
At particular time, the analysis shows that the composition of the reaction mixture is:

3.0 mol L⁻¹ of N_2 ; 2.0 mol L⁻¹ of H_2 ; 0.50 mol L⁻¹ of NH_3 . Is the reaction at equilibrium?

If not, in which direction does the reaction tend to proceed to reach the equilibrium?

Answer:

The given reaction is:



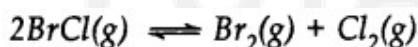
According to available data.

$$\text{N}_2 = [3.0]; \text{H}_2 = [2.0]; \text{NH}_3 = [0.50]$$

$$Q_c = \frac{[\text{NH}_3(g)]^2}{[\text{N}_2(g)][\text{H}_2(g)]^3} = \frac{[0.50]^2}{[3.0][2.0]^3} = \frac{0.25}{24} = 0.0104.$$

Since the value of Q_c is less than that of K_c (0.061), the reaction is not in a state of equilibrium. It will proceed in the **forward direction** till Q_c becomes the same as K_c .

Question 21. Bromine monochloride (BrCl) decomposes into bromine and chlorine and reaches the equilibrium:



The value of K_c is 32 at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L⁻¹ what is its molar concentration in the mixture at equilibrium?

Answer: Let x moles of BrCl decompose in order to attain the equilibrium. The initial molar concentration and the molar concentration at equilibrium

point of different species may be represented as follows:

	2BrCl (g)	\rightleftharpoons	Br ₂ (g)	+	Cl ₂ (g)
Initial moles/litre	0.0033		0		0
Moles/litre at eqm. point	0.0033 - x		x/2		x/2

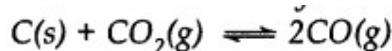
$$\text{Applying Law of chemical equilibrium, } K_c = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} \text{ or } 32 = \frac{(x/2) \times (x/2)}{(0.0033 - x)^2}$$

$$\text{On taking the square root, } 5.656 = \frac{x/2}{(0.0033 - x)}$$

$$\frac{x}{(0.0033 - x)} = 11.31 \text{ or } 12.31x = 0.037 ; x = \frac{0.037}{12.31} = 0.003$$

$$\therefore \text{Molar concentration of BrCl at equilibrium point} = 0.0033 - 0.003 \\ = 0.0003 \text{ mol l}^{-1} = 3 \times 10^{-4} \text{ mol l}^{-1}$$

Question 22. At 1127 K and 1 atmosphere pressure, a gaseous mixture of CO and CO₂ in equilibrium with solid carbon has 90.55% CO by mass.



Calculate K_c for the reaction at the above temperature.

Answer:

Step I: Calculation of K_p for the reaction

Let the total mass of the gaseous mixture = 100 g

Mass of CO in the mixture = 90.55 g

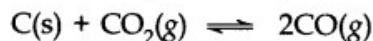
Mass of CO_2 in the mixture = $(100 - 90.55) = 9.45$ g

$$\text{No. of moles of CO} = \frac{90.55\text{g}}{(28\text{g mol}^{-1})} = 3.234 \text{ mol}$$

$$\text{No. of moles of CO}_2 = \frac{9.45}{(44\text{g mol}^{-1})} = 0.215 \text{ mol}$$

$$p_{\text{CO}} \text{ in the mixture} = \frac{(3.234 \text{ mol})}{(3.234 + 0.215)} \times 1 \text{ atm} = \frac{(3.234 \text{ mol})}{(3.449 \text{ mol})} \times 1 \text{ atm} = 0.938 \text{ atm}$$

$$p_{\text{CO}_2} \text{ in the mixture} = \frac{(0.215 \text{ mol})}{(3.449 \text{ mol})} \times 1 \text{ atm} = 0.062 \text{ atm}$$

Eqm. pressure 0.062 atm 0.938 atm

$$K_p = \frac{p^2\text{CO}}{p\text{CO}_2} = \frac{(0.938 \text{ atm})^2}{(0.062 \text{ atm})} = 14.19 \text{ atm}$$

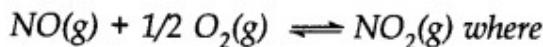
Step II. Calculation of K_c for the reaction.

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

$$K_p = 14.19 \text{ atm}, \quad R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}, \quad T = 1127 \text{ K}; \quad \Delta n_g = 2 - 1 = 1$$

$$K_c = \frac{(14.19 \text{ atm})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (1127 \text{ K})^1} = 6.46$$

Question 23. Calculate (a) ΔG^\ominus and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K



$$\Delta_f G^\ominus (\text{NO}_2) = 52.0 \text{ kJ/mol}, \quad \Delta_f G^\ominus (\text{NO}) = 87.0 \text{ kJ/mol}, \quad \Delta_f G^\ominus (\text{O}_2) = 0 \text{ kJ/mol},$$

Answer:

Step I. Calculation of ΔG^\ominus

$$\begin{aligned} \Delta G^\ominus &= \Delta_f G^\ominus (\text{NO}_2) - [\Delta_f G^\ominus (1/2\text{O}_2)] \\ &= 52.0 - (87 + 0) = -35 \text{ kJ mol}^{-1} \end{aligned}$$

Step II. Calculation of K_c

$$\Delta G^\ominus = -2.303 RT \log K_c$$

$$\log K_c = -\frac{\Delta G^\ominus}{2.303 RT} = -\frac{(-35 \times 10^3 \text{ J mol}^{-1})^3}{2.303 \times (8.314 \text{ kJ mol}^{-1}) \times (298 \text{ K})} = 6.134$$

$$K_c = \text{Antilog } 6.134 = 1.36 \times 10^6$$

Question 24. Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
 (ii) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$
 (iii) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Answer: (i) Pressure will increase in the forward reaction and number of moles of products will increase.

(ii) Pressure will increase in backward reaction and number of moles of products will decrease.

(iii) The change in pressure will have no effect on the equilibrium constant and there will be no change in the number of moles.

Question 25. Which of the following reactions will get affected by increase in pressure? Also mention whether the change will cause the reaction to go to the right or left direction.

(i) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$
 (ii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$
 (iii) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
 (iv) $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$
 (v) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$
 (vi) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

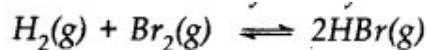
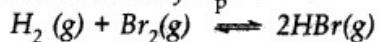
Answer: Only those reactions will be affected by increasing the pressure in which the number of moles of the gaseous reactants and products are different ($n_p \neq n_r$) (gaseous). With the exception of the reaction (1); all the remaining five reactions will get affected by increasing the pressure. In general,

- The reaction will go to the left if $n_p > n_r$.
- The reaction will go to the right if $n_r > n_p$.

Keeping this in mind,

(i) Increase in pressure will not affect equilibrium because $n_p = n_r = 3$.
 (ii) Increase in pressure will favour backward reaction because $n_p (2) > n_r (1)$
 (iii) Increase in pressure will favour backward reaction because $n_p (10) >$

nr (9)

(iv) Increase in pressure will favour forward reaction because n_p (1) < nr (2)(v) Increase in pressure will favour backward reaction because n_p (2) > nr (1)(vi) Increase in pressure will favour backward reaction because n_p (1) > nr (0).**Question 26.** The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K.Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.**Ans.****Step I. Calculation of K_p .**

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^0 \quad (\because \Delta n = 2 - 2 = \text{zero})$$

$$K_p = K_c = 1.6 \times 10^5.$$

Step II. Calculation of partial pressure of gases

	$2\text{HBr}(g)$	\rightleftharpoons	$\text{H}_2(g)$	+	$\text{Br}_2(g)$	
Initial pressure	10 bar		zero		zero	
Eqm. pressure	(10 - P) bar		P/2 bar		P/2 bar	

$$K_p' = \frac{p\text{H}_2 \times p\text{Br}_2}{p^2\text{HBr}} \text{ or } \frac{1}{1.6 \times 10^5} = \frac{P/2 \times P/2}{(10 - P)^2} = \frac{P^2}{4(10 - P)^2}$$

$$\begin{aligned} \text{On taking square root; } \frac{P^2}{4(10 - P)^2} &= \left(\frac{1}{1.6 \times 10^5} \right)^{1/2} \text{ or } \frac{2(10 - P)}{P} = (1.6 \times 10^5)^{1/2} \\ &= 4 \times 10^2 \\ 20 - 2P &= 4 \times 10^2 P \text{ or } P(4 \times 10^2 + 2) = 20 \end{aligned}$$

$$\text{or } P = \frac{20}{(400 + 2)} = \frac{20}{402} = 0.050 \text{ bar}$$

$p\text{H}_2 = 0.025 \text{ bar}$; $p\text{Br}_2 = 0.025 \text{ bar}$; $p\text{HBr} = 10 - 0.05 = 9.95 \text{ bar} \approx 10.0 \text{ bar}$.

Question 27. Hydrogen gas is obtained from the natural gas by partial oxidation with steam as per the following endothermic reaction:Write the expression for K_p for the above reactionHow will the value of K_p and composition of equilibrium mixture be affected

by:

(i) increasing the pressure, (ii) increasing the temperature, (iii) using a catalyst?

Answer: The expression for K_p for the reaction is:

$$K_p = \frac{(p\text{CO}) \times (p\text{H}_2)^3}{(p\text{CH}_4) \times (p\text{H}_2\text{O})}$$

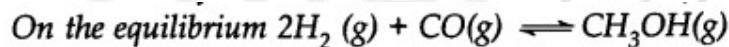
(i) By increasing the pressure, the number of moles per unit volume will increase. In order to decrease the same, the equilibrium gets shifted to the left or in the backward direction. As a result, more of reactants will be formed and the value of K_p will decrease.

(ii) If the temperature is increased, according to Le Chatelier's principle, the forward reaction will be favoured as it is endothermic. Therefore, the equilibrium gets shifted to the right and the value of K_p will increase.

(iii) The addition of catalyst will not change the equilibrium since it influences both the forward and the backward reactions to the same extent. But it will be attained more quickly.

Question 28. What is the effect of:

(i) addition of H_2 (ii) addition of CH_3OH
 (iii) removal of CO (iv) removal of CH_3OH



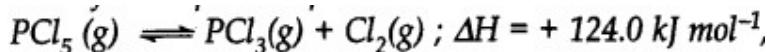
Answer: (i) Equilibrium will be shifted in the forward direction.

(ii) Equilibrium will be shifted in the backward direction.

(iii) Equilibrium will be shifted in the backward direction.

(iv) Equilibrium will be shifted in the forward direction.

Question 29. At 473 K, the equilibrium constant K_c for the decomposition of phosphorus pentachloride (PCl_5) is 8.3×10^{-3} . if decomposition proceeds as:



(a) Write an expression for K_c for the reaction
 (b) What is the value of K_c for the reverse reaction at the same temperature.
 (c) What would be the effect on K_c if
 (i) More of PCl_5 is added (ii) Temperature is increased.

Answer:

(a) The expression for $K_c = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$

(b) For reverse reaction $(K_c') = \frac{PCl_5(g)}{[PCl_3(g)][Cl_2(g)]} = \frac{1}{8.3 \times 10^{-3}} = 120.48$

(c) (i) By adding more of PCl_5 , value of K_c will remain constant because there is no change in temperature.

(ii) By increasing the temperature, the forward reaction will be favoured since it is endothermic in nature. Therefore, the value of equilibrium constant will increase.

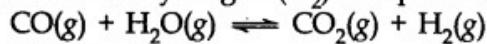
Question 30. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2 . In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction.



If a reaction vessel at $400^\circ C$ is charged with an equimolar mixture of CO and steam so that $P_{CO} = P_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? $K_p = 0.1$ at $400^\circ C$.

Answer:

Let the partial pressure of hydrogen (H_2) at equilibrium point = p bar



Initial pressure: 4.0 bar 4.0 bar

Eqm. pressure: $(4-p)$ bar $(4-p)$ bar p bar p bar

$$K_p = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} \text{ or } 0.1 = \frac{(p \text{ bar}) \times (p \text{ bar})}{(4-p) \text{ bar} \times (4-p) \text{ bar}}$$

$$\frac{p^2}{(4-p)^2} = 0.1 \text{ or } \frac{p}{(4-p)} = (0.1)^{1/2} = 0.316$$

$$p = 0.316(4-p) \text{ or } p = 1.264 - 0.316p$$

$$1.316p = 1.264 \text{ or } p = \frac{1.264}{1.316} = 0.96 \text{ bar}$$

Question 31. Predict which of the following will have appreciable concentration of reactants and products:

(a) $Cl_2(g) \rightleftharpoons 2Cl(g)$; $K_c = 5 \times 10^{-39}$
 (b) $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g)$; $K_c = 3.7 \times 10^8$
 (c) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g)$; $K_c = 1.8$.

Answer: Following conclusions can be drawn from the values of K_c .

(a) Since the value of K_c is very small, this means that the molar concentration of the products is very small as compared to that of the reactants.

(b) Since the value of K_c is quite large, this means that the molar concentration of the products is very large as compared to that of the reactants.

(c) Since the value of K_c is 1.8, this means that both the products and reactants have appreciable concentration.

Question 32. The value of K_c for the reaction $3O_2(g) \rightarrow 2O_3(g)$ is 2.0×10^{-50} at $25^\circ C$. If equilibrium concentration of O_2 in air at $25^\circ C$ is 1.6×10^{-2} , what is the concentration of O_3 ?

Answer:



$$K_c = \frac{[O_3]^2}{[O_2]^3} \quad \text{or} \quad (2.0 \times 10^{-50}) = \frac{[O_3]^2}{(1.6 \times 10^{-2})^3}$$

or $[O_3]^2 = (2.0 \times 10^{-50}) \times (1.6 \times 10^{-2})^3$
 $[O_3]^2 = 8.192 \times 10^{-56}$ or $[O_3] = (8.192 \times 10^{-56})^{1/2} = 2.86 \times 10^{-28} M$.

Question 33.

The reaction $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ is at equilibrium at 1300 K in a 1 L flask. It also contains 0.30 mol of CO , 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

Answer:



According to available data

$$K_c = \frac{[CH_4] \times [H_2O]}{[CO] \times [H_2]^3} \quad \text{or} \quad 3.90 = \frac{[CH_4] \times [0.02]}{[0.30] \times [0.1]^3}$$

$$[CH_4] = \frac{(3.9) \times (0.30) \times (0.001)}{(0.02)} = 5.85 \times 10^{-2} M$$

Question 34. What is meant by conjugate acid-base pair? Find the conjugate acid/base for the following species: HNO_2 , CH^- , HClO_4 , OH^- , CO_3^{2-} , S^{2-}

Answer: An acid-base pair which differs by a proton only ($\text{HA} \longrightarrow \text{A}^- + \text{H}^+$) is known as conjugate acid-base pair.

Conjugate acid: HCN , H_2O , HCO_3^- , HS^- .

Conjugate base: NO_2^- , ClO_4^- , O_2^-

Question 35. Which of the following are Lewis Acids?

H_2O , BF_3 , H^+ and NH_4^+ ,

Answer: BF_3 , H^+ ions are Lewis acids.

Question 36. What will be the conjugate bases for the Bronsted acids? HF , H_2SO_4 and H_2CO_3 ?

Answer: Conjugate bases: F^- , HSO_4^- , HCO_3^- .

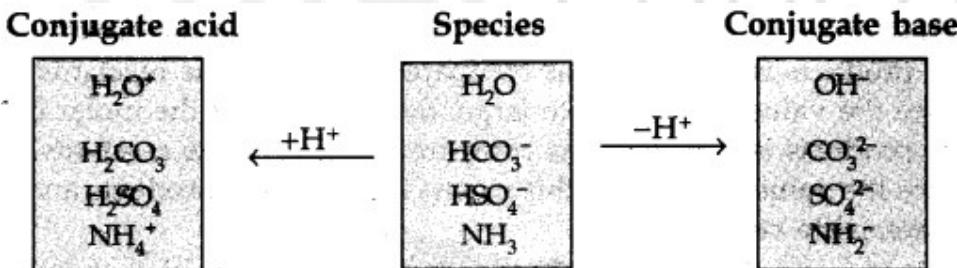
Question 37. Write the conjugate acids for the following Bronsted bases:

NH_2 , NH_3 and HCOO^-

Answer: NH_3 , NH_4^+ and HCOOH

Question 38. The species H_2O , HCO_3^- , HSO_4^- and NH_3 can act both as Bronsted acid and base. For each case, give the corresponding conjugate acid and base.

Answer:



Question 39. Classify the following species into Lewis acids and Lewis bases and show how these can act as Lewis acid/Lewis base?

(a) OH^- ions (b) F^- (c) H^+ (d) BCl_3

Answer: (a) OH^- ions can demote an electron pair and act as Lewis base.

(b) F^- ions can donate an electron pair and act as Lewis base.

(c) H^+ ions can accept an electron pair and act as Lewis acid.

(d) BCl_3 can accept an electron pair since Boron atom is electron deficient. It is a Lewis acid.

Question 40. The concentration of hydrogen ions in a sample of soft drink is 3.8×10^{-3} M. What is the pH value?

Answer: $\text{pH} = -\log [\text{H}^+] = -\log (3.8 \times 10^{-3}) = -\log 3.8 + 3 = 3 - 0.5798 = 2.4202 = 2.42$

Question 41. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Answer: $\text{pH} = -\log [\text{H}^+]$ or $\log [\text{H}^+] = -\text{pH} = -3.76 = 4.24$

$\therefore [\text{H}^+] = \text{Antilog } 4.24 = 1.738 \times 10^{-4} = 1.74 \times 10^{-4}$ M

Question 42. The ionization constant of HF, HCOOH and HCN at 298 K are 6.8×10^{-4} , 1.8×10^{-4} and 4.8×10^{-9} respectively, Calculate the ionization constant of the corresponding conjugate base.

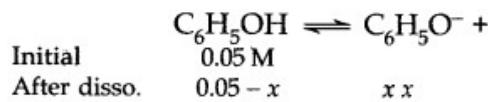
Answer: For F^- , $K_b = K_w/K_a = 10^{-14}/(6.8 \times 10^{-4}) = 1.47 \times 10^{-11} = 1.5 \times 10^{-11}$.

For HCOO^- , $K_b = 10^{-14}/(1.8 \times 10^{-4}) = 5.6 \times 10^{-11}$

For CN^- , $K_b = 10^{-14}/(4.8 \times 10^{-9}) = 2.08 \times 10^{-6}$

Question 43. The ionization constant of phenol is 1.0×10^{-10} . What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate?

Answer:



$$\therefore K_a = \frac{x \times x}{0.05 - x} = 1.0 \times 10^{-10} \text{ (Given)} \quad \text{or} \quad \frac{x^2}{0.05} = 1.0 \times 10^{-10}$$

$$\text{or} \quad x^2 = 5 \times 10^{-12} \quad \text{or} \quad x = 2.2 \times 10^{-6} \text{ M}$$

In presence of 0.01 $\text{C}_6\text{H}_5\text{ONa}$, suppose y is the amount of phenol dissociated, then at equilibrium

$$\begin{aligned} [\text{C}_6\text{H}_5\text{OH}] &= 0.05 - y \approx 0.05, \\ [\text{C}_6\text{H}_5\text{O}^-] &= 0.01 + y \approx 0.01 \text{ M}, [\text{H}^+] = y \text{ M} \end{aligned}$$

$$\therefore K_a = \frac{(0.01)(y)}{0.05} = 1.0 \times 10^{-10} \text{ (Given)} \quad \text{or} \quad y = 5 \times 10^{-10}$$

$$\therefore \alpha = \frac{y}{c} = \frac{5 \times 10^{-10}}{5 \times 10^{-2}} = 10^{-8}.$$

Question 44. The first ionization constant of H_2S is 9.1×10^{-8} . Calculate the concentration of HS^- ions in its 0.1 M solution and how will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13} , calculate the concentration of S^{2-} under both conditions.

Answer:

To calculate $[\text{HS}^-]$

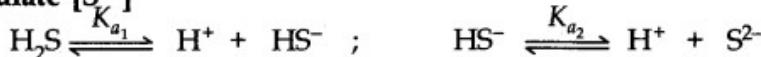
	$\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$
Initial	0.1 M
After disso.	$0.1 - x \quad x \quad x$ $\simeq 0.1$

$$K_a = \frac{x \times x}{0.1} = 9.1 \times 10^{-8} \quad \text{or} \quad x^2 = 9.1 \times 10^{-9} \quad \text{or} \quad x = 9.54 \times 10^{-5}.$$

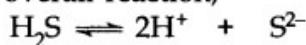
In presence of 0.1 M HCl, suppose H_2S dissociated is y . Then at equilibrium, $[\text{H}_2\text{S}] = 0.1 - y \simeq 0.1$, $[\text{H}^+] = 0.1 + y \simeq 0.1$, $[\text{HS}^-] = y$ M

$$K_a = \frac{0.1 \times y}{0.1} = 9.1 \times 10^{-8} \quad (\text{Given}) \quad \text{or} \quad y = 9.1 \times 10^{-8} \text{ M}$$

To calculate $[\text{S}^{2-}]$



For the overall reaction,



$$K_a = K_{a_1} \times K_{a_2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13} = 1.092 \times 10^{-20}$$

$$K_a = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

In the absence of 0.1 M HCl, $[\text{H}^+] = 2 [\text{S}^{2-}]$

Hence, if $[\text{S}^{2-}] = x$, $[\text{H}^+] = 2x$

$$\therefore \frac{(2x)^2 x}{0.1} = 1.092 \times 10^{-20} \quad \text{or} \quad 4x^3 = 1.092 \times 10^{-21} = 273 \times 10^{-24}$$

$$3 \log x = \log 273 - 24 = 2.4362 - 24$$

$$\log x = 0.8127 - 8 = 8.8127$$

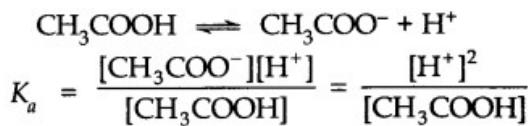
$$\text{or} \quad x = \text{Antilog } 8.8127 = 273 \times 10^{-24} = 6.497 \times 10 = 6.5 \times 10^{-8} \text{ M.}$$

In presence of 0.1 M HCl, suppose $[\text{S}^{2-}] = y$, then

$$[\text{H}_2\text{S}] = 0.1 - y \simeq 0.1 \text{ M}, \quad [\text{H}^+] = 0.1 + y \simeq 0.1 \text{ M}$$

$$K_a = \frac{(0.1)^2 \times y}{0.1} = 1.09 \times 10^{-20} \quad \text{or} \quad y = 1.09 \times 10^{-19} \text{ M.}$$

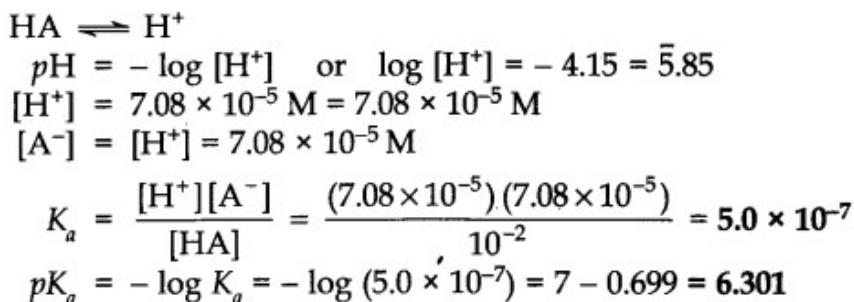
Question 45. The ionization constant of acetic acid is 1.74×10^{-5} . Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ions in the solution and its pH.

Answer:

or $[\text{H}^+] = \sqrt{K_a [\text{CH}_3\text{COOH}]} = \sqrt{(1.74 \times 10^{-5})(5 \times 10^{-2})} = 9.33 \times 10^{-4} \text{ M}$

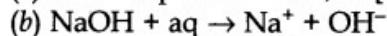
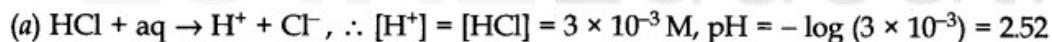
 $[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 9.33 \times 10^{-4} \text{ M}$
 $\text{pH} = -\log(9.33 \times 10^{-4}) = 4 - 0.9699 = 4 - 0.97 = 3.03$

Question 46. It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a .

Answer:

Question 47. Assuming complete dissociation, calculate the pH of the following solutions:

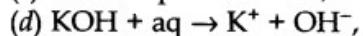
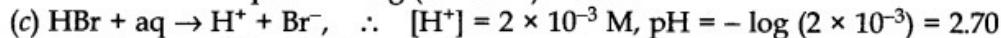
(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

Answer:

$$\therefore [\text{OH}^-] = 5 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = 10^{-14} / (5 \times 10^{-3}) = 2 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log(2 \times 10^{-12}) = 11.70$$



$$\therefore [\text{OH}^+] = 2 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = 10^{-14} / (2 \times 10^{-3}) = 5 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log(5 \times 10^{-12}) = 11.30$$

Question 48. Calculate the pH of the following solutions:

(a) 2g of TlOH dissolved in water to give 2 litre of the solution
 (b) 0.3 g of $\text{Ca}(\text{OH})_2$ dissolved in water to give 500 mL of the solution
 (c) 0.3 g of NaOH dissolved in water to give 200 mL of the solution
 (d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of the solution.

Answer:

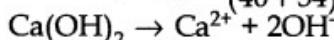
$$(a) \text{Molar conc. of TlOH} = \frac{2g}{(204 + 16 + 1) g \text{ mol}^{-1}} \times \frac{1}{2 \text{ L}} = 4.52 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = [\text{TlOH}] = 4.52 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = 10^{-14} / (4.52 \times 10^{-3}) = 2.21 \times 10^{-12} \text{ M}$$

$$\therefore \text{pH} = -\log (2.21 \times 10^{-12}) = 12 - (0.3424) = 11.66$$

$$(b) \text{Molar conc. of Ca(OH)}_2 = \frac{0.3 \text{ g}}{(40 + 34) \text{ g mol}^{-1}} \times \frac{1}{0.5 \text{ L}} = 8.11 \times 10^{-3} \text{ M}$$



$$[\text{OH}^-] = 2[\text{Ca(OH)}_2] = 2 \times (8.11 \times 10^{-3}) \text{ M} = 16.22 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log (16.22 \times 10^{-3}) = 3 - 1.2101 = 1.79$$

$$\text{pH} = 14 - 1.79 = 12.21$$

$$(c) \text{Molar conc. of NaOH} = \frac{0.3 \text{ g}}{40 \text{ g mol}^{-1}} \times \frac{1}{0.2 \text{ L}} = 3.75 \times 10^{-2} \text{ M}$$

$$[\text{OH}^-] = 3.75 \times 10^{-2} \text{ M}$$

$$\text{pOH} = -\log (3.75 \times 10^{-2}) = 2 - 0.0574 = 1.43$$

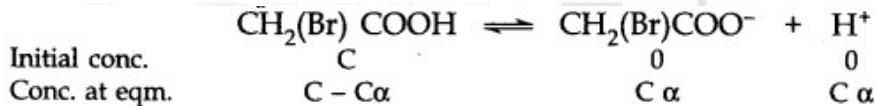
$$\text{pH} = 14 - 1.43 = 12.57$$

$$(d) M_1 V_1 = M_2 V_2 \therefore 13.6 \text{ M} \times 1 \text{ m L} = M_2 \times 1000 \text{ mL} \therefore M_2 = 1.36 \times 10^{-2} \text{ M}$$

$$[\text{H}^+] = [\text{HCl}] = 1.36 \times 10^{-2} \text{ M}, \text{pH} = -\log (1.36 \times 10^{-2}) = 2 - 0.1335 \approx 1.87$$

Question 49. The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the PK_a of bromoacetic acid.

Answer:



$$K_a = \frac{\text{C}\alpha \cdot \text{C}\alpha}{\text{C} (1 - \alpha)} = \frac{\text{C}\alpha^2}{1 - \alpha} \approx \text{C}\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$

$$\text{pK}_a = -\log (1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$$

$$[\text{H}^+] = \text{C} \alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log (1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88$$

Question 50. The pH of 0.005 M codeine ($\text{C}_{18}\text{H}_{21}\text{NO}_3$) solution is 9.95.

Calculate the ionization constant and PK_b .

Answer:



$$\text{pH} = 9.95 \therefore \text{pOH} = 14 - 9.95 = 4.05, \text{ i.e., } -\log [\text{OH}^-] = 4.05$$

$$\text{or } \log [\text{OH}^-] = -4.05 = 5.95 \text{ or } [\text{OH}^-] = 8.913 \times 10^{-5} \text{ M}$$

$$K_b = \frac{[\text{CodH}^+][\text{OH}^-]}{[\text{Cod}]} = \frac{[\text{OH}^-]^2}{[\text{Cod}]} = \frac{(8.91 \times 10^{-5})^2}{5 \times 10^{-3}} = 1.588 \times 10^{-6}$$

$$\text{pK}_b = -\log (1.588 \times 10^{-6}) = 6 - 0.1987 = 5.8$$

MORE QUESTIONS SOLVED

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NCERT Solutions for Class 11 Chemistry Chapter 7 Very Short Answer Type Questions

Question 1. What is meant by equilibrium?

Answer: Equilibrium is a state at which rate of forward reaction is equal to the rate of backward reaction.

Question 2. State the law of mass action?

Answer: It states that the rate at which a substance reacts is directly proportional to its molar concentration.

Question 3. What is meant by reaction quotient?

Answer: It is defined as the ratio of the product of molar concentration of products to the product of molar concentration of reactants at any stage of the reaction.



$$\text{pH} = 9.95 \therefore \text{pOH} = 14 - 9.95 = 4.05, \text{ i.e., } -\log [\text{OH}^-] = 4.05$$

or $\log [\text{OH}^-] = -4.05 = 5.95 \text{ or } [\text{OH}^-] = 8.913 \times 10^{-5} \text{ M}$

$$K_b = \frac{[\text{CodH}^+][\text{OH}^-]}{[\text{Cod}]} = \frac{[\text{OH}^-]^2}{[\text{Cod}]} = \frac{(8.91 \times 10^{-5})^2}{5 \times 10^{-3}} = 1.588 \times 10^{-6}$$

$$\text{p}K_b = -\log (1.588 \times 10^{-6}) = 6 - 0.1987 = 5.8$$

Question 4. Define ionic equilibrium.

Answer: The equilibrium between ions and unionised molecules is called ionic equilibrium.

Question 5. What is meant by ionic product of water (K_w)?

Answer: It is the product of concentration of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ at a specific temperature.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$= 1.0 \times 10^{-14} \text{ at } 298 \text{ K}$$

Question 6. Define solubility product.

Answer: It is product of molar concentration of ion raised to the power of number of ions produced per compound in saturated solution.

Question 7. How does common ion affect the solubility of electrolyte?

Answer: Solubility of electrolyte decreases due to common ion effect.

Question 8. Write conjugate acid and conjugate base of H_2O ?

Answer: Conjugate acid is H_3O^+ and conjugate base is OH^- .

Question 9. Give two characteristics of a buffer solution.

Answer:

- Its pH does not change on the addition of small amount of acid or base.
- Its pH does not change on dilution or standing.

Question 10. How does a catalyst affect the equilibrium constant?

Answer: The equilibrium constant is not affected by a catalyst.

Question 11. State Ostwald's dilution law.

Answer: Ostwald's dilution law states that the degree of dissociation of weak electrolyte is inversely proportional to square root of its concentration.

$$\alpha = \sqrt{\frac{K_a}{C}}, \alpha = \sqrt{\frac{K_b}{C}}$$

Where, K_a and K_b are acid dissociation and base dissociation constants.

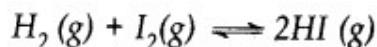
Question 12. What is basic buffer?

Answer: Basic buffer is the buffer whose pH is more than 7. It is a mixture containing weak base and its salt with a strong acid, e.g., $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$

Question 13. SO_3^{2-} is Bronsted base or acid and why?

Answer: SO_3^{2-} is Bronsted base because it can accept H^+ .

Question 14.



What is the relationship between K_p and K_c ?

Answer: $K_p = K_c$

because $\Delta n = 0$.

Question 15. Define common ion effect.

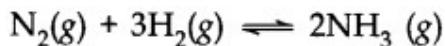
Answer: The supervision in concentration of one of the ions by adding other ion as common ion is called common ion effect.

NCERT Solutions for Class 11 Chemistry Chapter 7 Short Answer Type Questions

Question 1. The following concentration were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500 K. $[\text{N}_2(g)] = 1.5 \times 10^{-2} \text{ M}$ $[\text{H}_2(g)] = 3.0 \times 10^{-2} \text{ M}$ $[\text{NH}_3] = 1.2 \times 10^{-2} \text{ M}$. Calculate equilibrium constant.

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Answer:

$$\begin{aligned} K_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\ &= \frac{[1.2 \times 10^{-2} \text{M}]^2}{[1.5 \times 10^{-2} \text{M}][3.0 \times 10^{-2} \text{M}]^3} \\ &= 3.55 \times 10^{-2} \text{ M} \end{aligned}$$

Question 2. Write the equilibrium constant (K_c) expression for the following reactions.

(i) $\text{Cu}^{2+}(aq) + 2 \text{Ag}(s) \rightleftharpoons \text{Cu}(s) + 2\text{Ag}^+(aq)$
(ii) $4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g)$

Answer:

$$(i) \quad K_c = \frac{[\text{Ag}^+(aq)]^2}{[\text{Cu}^{2+}(aq)]}$$

$$(ii) \quad K_c = \frac{[\text{Cl}_2(g)]^2 [\text{H}_2\text{O}(g)]^2}{[\text{HCl}(g)]^4 [\text{O}_2(g)]}$$

Question 3. Given the equilibrium $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ $K=0.15$ atm at 298 K

(a) What is K_p using pressure in torr?
(b) What is K_c using units of moles per litre.

Answer:

$$(a) \quad K_p = \frac{(760 \text{ torr}) \times (0.15 \text{ atm})}{(1 \text{ atm})}$$

$$= 1.14 \times 10^2 \text{ torr}$$

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

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

$$= \frac{(0.15 \text{ atm})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})^{2-1}}$$

$$= 6.13 \times 10^{-3} \text{ mol L}^{-1}$$

Question 4. In the reaction $A + B \rightleftharpoons C + D$, what will happen to the equilibrium if concentration of A is increased?

(b) The equilibrium constant for a reaction is 2×10^{-23} at 25°C and 2×10^{-2} at 50°C . Is the reaction endothermic or exothermic?

(c) Mention at least three ways by which the concentration of SO_3 can be increased in the following reaction in a state of equilibrium.

Answer: (a) The reaction will shift in the forward direction.

(b) Endothermic

(c) (i) lowering the temperature (ii) increasing pressure.

(iii) increasing concentration of oxygen.

Question 5. (i) Define Le Chatelier's principle.

(ii) Following reactions occur in a Blast furnace.



use Le chatelier's principle to predict the direction of reaction when equilibrium mixture is disturbed by

(a) adding Fe_2O_3 (b) removing CO_2 .

(c) removing CO.

Answer: (a) When a system under equilibrium is subjected to a change in temperature, pressure or concentration, then the equilibrium shifts in such a direction so as to undo the effect of the change.

(ii) (a) On adding $\text{Fe}_2\text{O}_3(\text{s})$, the equilibrium will remain unaffected.

(b) By removing $\text{CO}_2(\text{g})$, the equilibrium will be shifted in the forward direction.

(c) By removing $\text{CO}(\text{g})$, the equilibrium will be shifted in the backward direction.

NCERT Solutions for Class 11 Chemistry Chapter 7 Long Answer Type Questions

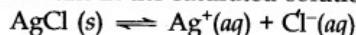
Question 1. (i) Point out the differences between ionic product and solubility product.

(ii) The solubility of AgCl in water at 298 K is 1.06×10^{-5} mole per litre. Calculate its solubility product at this temperature.

Answer: (i)

<i>Ionic Product</i>	<i>Solubility Product</i>
(a) It is applicable to all types of solutions. (b) Its value changes with the change in concentration of the ions.	(a) It is applicable to the saturated solutions. (b) It has a definite value for an electrolyte at a constant temperature.

(ii) The solubility equilibrium in the saturated solution is



The solubility of AgCl is 1.06×10^{-5} mole per litre.

$$[\text{Ag}^+(aq)] = 1.06 \times 10^{-5} \text{ mol L}^{-1}$$

$$[\text{Cl}^-(aq)] = 1.06 \times 10^{-5} \text{ mol L}^{-1}$$

$$K_{sp} = [\text{Ag}^+(aq)] [\text{Cl}^-(aq)]$$

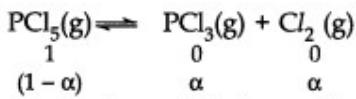
$$= (1.06 \times 10^{-5} \text{ mol L}^{-1}) \times (1.06 \times 10^{-5} \text{ mol L}^{-1})$$

$$= 1.12 \times 10^{-2} \text{ mol}^2 \text{ L}^{-2}$$

Question 2. At certain temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated at temperature remaining constant.

<https://loyaleducation.org>

Answer: Calculation of K_p



$$\begin{aligned} \text{Total no. of moles in the equilibrium mixture} &= 1 - \alpha + \alpha + \alpha \\ &= (1 + \alpha) \text{ mol.} \end{aligned}$$

Let the total pressure of equilibrium mixture = p atm

Partial pressure of PCl_5

$$p_{\text{PCl}_5} = \frac{1-\alpha}{1+\alpha} \times p \text{ atm}$$

$$\text{Partial pressure of } \text{PCl}_3 = \frac{\alpha}{1+\alpha} \times p \text{ atm}$$

Partial pressure of Cl_2

$$p_{\text{Cl}_2} = \frac{\alpha}{(1+\alpha)} \times p \text{ atm}$$

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

$$= \frac{\left(\frac{\alpha}{1+\alpha} p \text{ atm}\right) \times \left(\frac{\alpha}{1+\alpha} p \text{ atm}\right)}{\frac{1-\alpha}{1+\alpha} p \text{ atm}} = \frac{\alpha^2 p}{1-\alpha^2} \text{ atm}$$

$$P = 4 \text{ atm and } \alpha = 10\% = \frac{10}{100} = 0.1$$

$$\begin{aligned} K_p &= \frac{(0.1) \times (0.1) \times (4 \text{ atm})}{1 - (0.1)^2} \\ &= \frac{0.04}{0.99} = 0.04 \text{ atm.} \end{aligned}$$

Calculation of P under new condition

$$\alpha = 0.2, K_p = 0.04 \text{ atm.}$$

$$\begin{aligned} K_p &= \frac{\alpha^2 p}{1-\alpha^2} \text{ or } p = \frac{K_p(1-\alpha^2)}{\alpha^2} \\ &= \frac{(0.04 \text{ atm})[(1-(0.2)^2)]}{(0.2)^2} = \frac{0.04 \text{ atm} \times 0.96}{0.04} \\ &= 0.96 \text{ atm.} \end{aligned}$$

NCERT Solutions for Class 11 Chemistry Chapter 7 Multiple Choice Questions

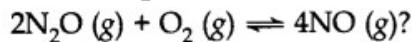
Question 1. The equilibrium expression, $K_c = [CO_2]$ represents the reaction.

(a) $C(s) + O_2(g) \rightleftharpoons CO_2(g)$ (b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
 (c) $CO(g) + \frac{1}{2} O_2(g) \rightleftharpoons CO_2(g)$ (d) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

Question 2. Hydrogen molecule (H_2) can be dissociated into hydrogen atoms (H). Which one of the following changes will not increase the number of atoms present at equilibrium?

(a) adding H atoms (b) increasing the temperature
 (c) increasing the total pressure (d) increasing the volume of the container

Question 3. What is the expression for K_{eq} ? for the reaction



(a) $\frac{[N_2][O_2]}{[NO]}$ (b) $\frac{[NO]^4}{[N_2O]^2}$ (c) $\frac{[NO]^4}{[N_2O]^2 [O_2]}$ (d) $\frac{[N_2O]^2 [O_2]}{[NO]^4}$

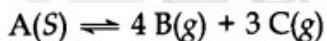
Question 4. A catalyst will increase the rate of a chemical reaction by

(a) shifting the equilibrium to the right (b) shifting the equilibrium to the left (c) lowering the activation energy (d) increasing the activation energy

Question 5. What is the correct expression for the representation of the solubility product constant of Ag_2CrO_4 ?

(a) $[Ag^+]^2 [CrO_4^{2-}]$ (b) $[2Ag^+] [CrO_4^{2-}]$ (c) $[Ag^+] [CrO_4^{2-}]$ (d) $[2Ag^+]^2 [CrO_4^{2-}]$

Question 6. In a closed system



If partial pressure of C is doubled, then partial pressure of B will be

(a) $2\sqrt{2}$ times the original value (b) $\frac{1}{2}$ times the original value
 (c) 2 times of the original value (d) $\frac{1}{2\sqrt{2}}$ times of the original value

Question 7. $H_2 + S \rightleftharpoons H_2S + \text{energy}$.

In this reversible reaction, select the factor which will shift the equilibrium to the right.

(a) adding heat (b) adding H_2S
 (c) blocking hydrogen gas reaction (d) removing hydrogen sulphide gas

Question 8. What effect does a catalyst have on the equilibrium position of a reaction?

- (a) a catalyst favours the formation of products
- (b) a catalyst favours the formation of reactants
- (c) a catalyst does not change the equilibrium position of a reaction
- (d) a catalyst may favour reactants or product formation, depending upon the direction in which the reaction is written.

Question 9. A chemist dissolves an excess of BaSO_4 in pure water at 25°C if its $K_{\text{sp}} = 1 \times 10^{-10}$ what is the concentration of barium in the water?

- (a) 10^{-4} M
- (b) 10^{-5} M
- (c) 10^{-15} M
- (d) 10^{-6} M

Question 10. If in a mixture where $Q = k$ is combined, then what happens?

- (a) the reaction shift towards products
- (b) the reaction shift towards reactants
- (c) nothing appears to happen, but forward and reverse are continuing at the same rate
- (d) nothing happens

Answer: 1.(b) 2.(c) 3.(c) 4.(c) 5.(a)

6.(d) 7.(a) 8.(c) 9.(c) 10.(c)

NCERT Solutions for Class 11 Chemistry Chapter 7 HOTS Questions

Question 1. For the equilibrium $2 \text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$ the value of the equilibrium constant K_c is 3.75×10^{-6} at 1069 K . Calculate the K_p for the reaction at this temperature?

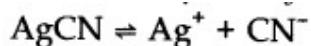
Answer: We know that $K_p = K_c(RT)^{\Delta n}$

For the above reaction, $\Delta n = (2 + 1) - 2 = 1$ $K_p = 3.75 \times 10^{-6} (0.0831 \times 1069)$

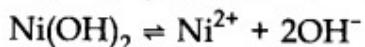
$K_p = 0.033$.

Question 2. The values of K_{sp} of two sparingly soluble salts Ni(OH)_2 and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble? Explain.

Answer:



$$K_{\text{sp}} = [\text{Ag}^+][\text{CN}^-] = 6 \times 10^{-17}$$



$$K_{\text{sp}} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 2 \times 10^{-15}$$

$$\text{Let } [\text{Ag}^+] = S_1, \text{ then } [\text{CN}^-] = S_1$$

$$\text{Let } [\text{Ni}^{2+}] = S_2, \text{ then } [\text{OH}^-] = 2S_2$$

$$S_1^2 = 6 \times 10^{-17}, S_1 = 7.8 \times 10^{-9}$$

$$(S_2)(2S_2)^2 = 2 \times 10^{-15}, S_2 = 0.58 \times 10^{-4}$$

Ni(OH)_2 is more soluble than AgCN .

Question 3. The value of K_c for the reaction $2\text{A} \longrightarrow \text{B} + \text{C}$ is 2×10^{-3} . At a given time, the composition of reaction mixture is $[\text{A}] = [\text{B}] = [\text{C}] = 3 \times 10^{-4} \text{ M}$. In which direction the reaction will proceed?

Answer: For the reaction the reaction quotient Q_c is given by $Q_c = [\text{B}][\text{C}]/[\text{A}]^2$ as $[\text{A}] = [\text{B}] = [\text{C}] = 3 \times 10^{-4} \text{ M}$ $Q_c = (3 \times 10^{-4})(3 \times 10^{-4})/(3 \times 10^{-4})^2 = 1$

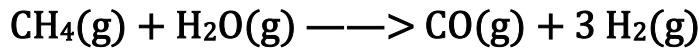
as $Q_c > K_c$, so, the reaction will proceed in the reverse direction.

Question 4. PCl_5 , PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59M PCl_5 1.59M Cl_2 and 1.41M PCl_3 . Calculate K_c for the reaction $\text{PCl}_5 \longrightarrow \text{PCl}_3 + \text{Cl}_2$

Answer: The equilibrium constant K_c for the above reaction can be written as:

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \\ = \frac{(1.59)^2}{1.41} = 1.79$$

Question 5. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:



(a) Write an expression for K_p for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be

affected by (i) increasing the pressure (ii) increasing the temperature (iii) using a catalyst?

Answer:

$$(a) K_p = \frac{[p_{CO}][p_{H_2}]^3}{[p_{CH_4}][p_{H_2O}]}$$

(b) (i) value of K_p will not change, equilibrium will shift in backward direction.
(ii) value of K_p will increase and reaction will proceed in forward direction.
(iii) no effect.

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