Chapter – 6

Equilibrium

2marks:

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

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
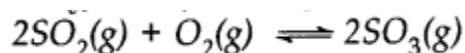
Given: $[SO_2] = 0.6\ M;\ [O_2] = 0.82\ M;\ and\ [SO_3] = 1.90\ M$

Answer:

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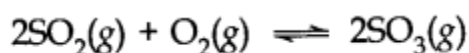
$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.9\ M) \times (1.9\ M)}{(0.6\ M) \times (0.6\ M) \times (0.82\ M)}$$

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

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

K. NO(g)+O₃ ——>NO₂(g) + O₂(g) Both the forward and reverse

reactions in the equilibrium are elementary bimolecular

reactions. What is K_c for the reverse reaction?

Answer:

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

3. Explain why pure liquids and solids can be ignored while writing the value of equilibrium constants.
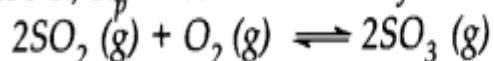
Answer: This is because molar concentration of a pine solid or liquid is independent of the amount present.

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

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

4.

At 450 K, $K_p = 2.0 \times 10^{10}$ bar^{-1} for the equilibrium reaction:
$$2SO_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2SO_3 \text{ (g)}$$,
What is K_c at this temperature?

Answer:

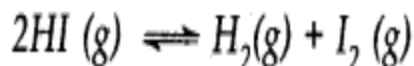$$K_p = K_c (RT)^{\Delta ng} \text{ or } K_c = \frac{K_p}{(RT)^{\Delta ng}} = K_p (RT)^{-\Delta ng}$$

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

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

$= 7.47 \times 10^{11}$ mol^{-1} L $= 7.47 \times 10^{11}$ M^{-1}

5. 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?

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

Answer:

pHI = 0.04 atm, pH$_2$ = 0.08 atm; pI$_2$ = 0.08 atm

$$K_p = \frac{pH_2 \times pI_2}{p_{HI}^2} = \frac{(0.08 \ \text{atm}) \times (0.08 \ \text{atm})}{(0.04 \ \text{atm}) \times (0.04 \ \text{atm})} = 4.0$$
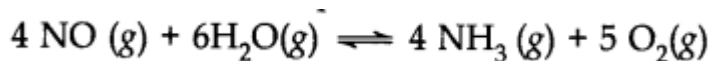
6. The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

Answer:

Balanced chemical equation for the reaction is 4

$$4 \ NO \ (g) + 6H_2O(g) \ \rightleftharpoons 4 \ NH_3 \ (g) + 5 \ O_2(g)$$

7. What is the effect of:

(i) addition of H$_2$ (ii) addition of CH$_3$OH

(iii) removal of CO (iv) removal of CH$_3$OH

On the equilibrium $2H_2 \ (g) + CO(g) \rightleftharpoons CH_3OH(g)$
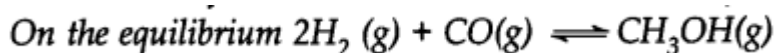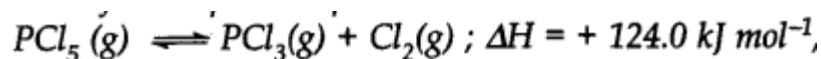
Answer:

(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.

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

$$PCl_5 (g) \rightleftharpoons PCl_3(g) + Cl_2(g) ; \Delta H = + 124.0 \ kJ \ mol^{-1},$$

(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 $K_c = \dfrac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$,

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

(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.

9. 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.

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

Answer:

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

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

or $\qquad [O_3]^2 = (2.0 \times 10^{-50}) \times (1.6 \times 10^{-2})^3$

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

11.

The reaction $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ is at equilibrium at 1300 K in a 1L flask. It also contain 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:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

According to available data

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

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

12. 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 ($HA \longrightarrow A^- + H^+$) is known as conjugate acid-base pair.

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

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

13. Which of the following are Lewis Acids?

H_2O, BF_3, H^+ and NH^{4+},

Answer:

BF_3, H^+ ions are Lewis acids.

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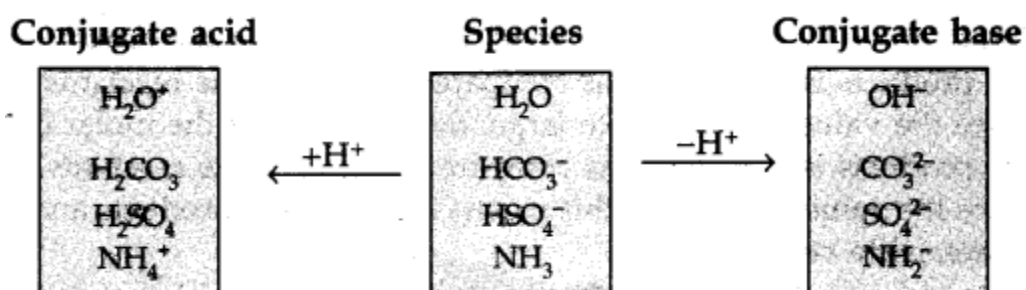
H_2SO_4 and H_2CO_3?

Answer:

Conjugate bases: F^-, HSO^-_4 , HCO^-_3.

15. Write the conjugate acids for the following Bronsted bases:

NH_2, NH_3 and $HCOO^-$

Answer: NH_3, NH_4^+ and HCOOH

16. 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:

Conjugate acid	Species	Conjugate base
H_3O^+	H_2O	OH^-
H_2CO_3 $\xleftarrow{+H^+}$	HCO_3^- $\xrightarrow{-H^+}$	CO_3^{2-}
H_2SO_4	HSO_4^-	SO_4^{2-}
NH_4^+	NH_3	NH_2^-

17. 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) BCl₃

Answer:

(a) OH^- ions can demate 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.

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

Answer:

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

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

Answer:

$pH = -\log[H^+]$ or $\log[H^+] = -pH = -3.76 = \overline{4}.24$

.·. $[H^+] = $ Antilog $\overline{4}.24 = 1.738 \times 10^{-4} = 1.74 \times 10$-4 M

20. The ionization constant of HF, HCOOH and HCN at 298 K are is 6.8 x 10^{-4} , 1.8 x 10^{-4} and 4.8 x 10^{-9} respectively, Calculate the ionization constant of the corresponding conjugate base.
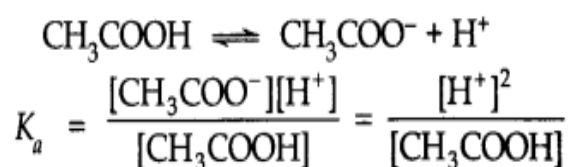
Answer:

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

21. The ionization constant of acetic acid is 1.74 x 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:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

or $\quad [H^+] = \sqrt{K_a[CH_3COOH]} = \sqrt{(1.74 \times 10^{-5})(5 \times 10^{-2})} = 9.33 \times 10^{-4}$ M

$[CH_3COO^-] = [H^+] = 9.33 \times 10^{-4}$ M

$pH = -\log(9.33 \times 10^{-4}) = 4 - 0.9699 = 4 - 0.97 = $ **3.03**

22. 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:

$$HA \rightleftharpoons H^+$$
$$pH = -\log [H^+] \quad \text{or} \quad \log [H^+] = -4.15 = \bar{5}.85$$
∴
$$[H^+] = 7.08 \times 10^{-5} M = 7.08 \times 10^{-5} M$$
$$[A^-] = [H^+] = 7.08 \times 10^{-5} M$$
$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{10^{-2}} = 5.0 \times 10^{-7}$$
$$pK_a = -\log K_a = -\log (5.0 \times 10^{-7}) = 7 - 0.699 = 6.301$$

23. 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:

(a) $HCl + aq \rightarrow H^+ + Cl^-$, ∴ $[H^+] = [HCl] = 3 \times 10^{-3} M$, $pH = -\log (3 \times 10^{-3}) = 2.52$

(b) $NaOH + aq \rightarrow Na^+ + OH^-$
∴ $[OH^-] = 5 \times 10^{-3} M$, $[H^+] = 10^{-14}/(5 \times 10^{-3}) = 2 \times 10^{-12} M$
$pH = -\log (2 \times 10^{-12}) = 11.70$

(c) $HBr + aq \rightarrow H^+ + Br^-$, ∴ $[H^+] = 2 \times 10^{-3} M$, $pH = -\log (2 \times 10^{-3}) = 2.70$

(d) $KOH + aq \rightarrow K^+ + OH^-$,
∴ $[OH^+] = 2 \times 10^{-3} M$, $[H^+] = 10^{-14}/(2 \times 10^{-3}) = 5 \times 10^{-12}$
$pH = -\log (5 \times 10^{-12}) = 11.30$

4marks:

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.

2.

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

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

Partial pressure of iodine molecules $(I_2) = \dfrac{60}{100} \times (10^5 \text{ Pa}) = 0.6 \times 10^5$ Pa

$$
\begin{array}{ccc}
I_2\ (g) & \rightleftharpoons & 2I\ (g) \\
(0.6 \times 10^5 \text{ Pa}) & & (0.4 \times 10^5 \text{ Pa})
\end{array}
$$

$$K_p = \dfrac{p_{I^2}}{p_I} = \dfrac{(0.4 \times 10^5 \text{Pa})^2}{(0.6 \times 10^5 \text{Pa})} = \mathbf{2.67 \times 10^4}\ \textbf{Pa}$$

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

(a) $2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$; $K_p = 1.8 \times 10^{-2}$ atm at 500 K
(b) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$; $K_p = 167$ atm at 1073 K.

Answer:

K_p and K_c are related to each other as $K_p = K_c\ (RT)^{\Delta ng}$
The value of K_c can be calculated as follows:

(a) $\qquad 2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2$

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

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

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

$\qquad\qquad = \mathbf{4.4 \times 10^{-4}}\ \textbf{mol L}^{-1}$

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

$\qquad\qquad K_p = 167$ atm, $\quad \Delta ng = 1$

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

$\qquad\qquad K_c = \dfrac{K_p}{(RT)^{\Delta ng}} = \dfrac{(167 \text{ atm})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 1073 \text{ K})^1}$

$\qquad\qquad = \mathbf{1.9}\ \textbf{mol L}^{-1}$

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

$$2NO \, (g) + Br_2 \, (g) \rightleftharpoons 2NOBr(g)$$
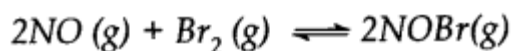
When 0.087 mole of NO and 0.0437 mole of Br₂ are mixed in a closed container at constant temperature, 0.0518 mole of NOB$_r$ is obtained at equilibrium. Determine the compositions of the equilibrium mixture.

Answer:

The balanced chemical equation for the reaction is:

According to the equation, 2 moles of NO (g) react with 1 mole of Br_2 (g) to form 2 moles of NOB$_r$ (g). The composition of the equilibrium mixture can be calculated as follows:

No. of moles of NOB$_r$ (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 Br_2 (g) taking part in reaction = 1/2 x 0.0518 = 0.0259 mol

No. of moles of Br_2 (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:

2NO (g) + Br₂(g) ──────────> 2NOB$_r$(g)

Initial moles 0.087 0.0437 0

Moles at eqm. point: 0.0352 0.0178 0.0518

5. A mixture of 1.57 mol of N₂, 1.92 mol of H₂ and 8.13 mol of NH₃is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant Kc for the reaction

$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$ is 1.7×10^{-2}.
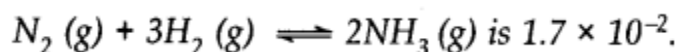
Is this reaction at equilibrium? If not, what is the direction of net reaction?

Answer:

The reaction is: $N_2(g) + 3\ H_2(g) \rightleftharpoons 2NH_3(g)$
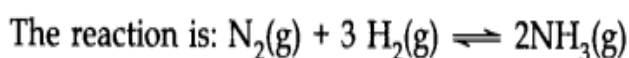
Concentration quotient $(Q_c) = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = \dfrac{(8.13/20\ mol\ L^{-1})^2}{(1.57/20\ mol\ L^{-1}) \times (1.92/20\ mol\ L^{-1})^3}$

$= 2.38 \times 10^3$

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

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

6. If l mole of H₂0 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.

$H_2O + CO(g) \rightleftharpoons H_2\ (g) + CO_2(g)$

Calculate the equilibrium constant for the reaction.
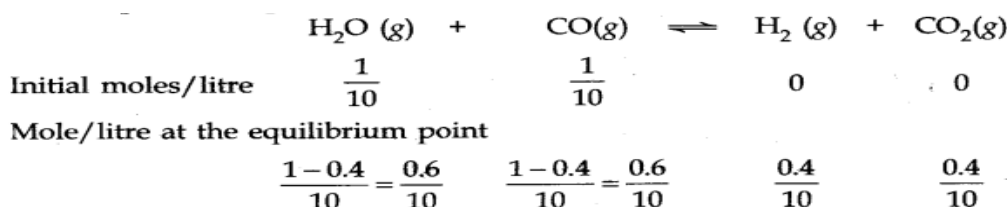
Answer:

Number of moles of water originally present = 1 mol

Percentage of water reacted =40%

Number of moles of water reacted = 1 x 40/100 = 0.4 mol

Number of moles of water left = (1 – 0.4) = 0.6 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:

$$H_2O\ (g) \quad + \quad CO(g) \quad \rightleftharpoons \quad H_2\ (g) \quad + \quad CO_2(g)$$

Initial moles/litre $\quad\quad \dfrac{1}{10} \quad\quad\quad \dfrac{1}{10} \quad\quad\quad 0 \quad\quad\quad 0$

Mole/litre at the equilibrium point

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

Applying law of chemical equilibrium,

$$\text{Equilibrium constant } (K_c) \ = \ \frac{[H_2(g)][CO_2(g)]}{[H_2O(g)][CO(g)]} \ = \ \frac{\left(\dfrac{0.4}{10}\text{ mol L}^{-1}\right) \times \left(\dfrac{0.4}{10}\text{ mol L}^{-1}\right)}{\left(\dfrac{0.6}{10}\text{ mol L}^{-1}\right) \times \left(\dfrac{0.6}{10}\text{ mol L}^{-1}\right)}$$

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

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

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

Partial pressure of iodine molecules (I_2) $= \dfrac{60}{100} \times (10^5\text{ Pa}) = 0.6 \times 10^5$ Pa

$$I_2\ (g) \quad\quad \rightleftharpoons \quad\quad 2I\ (g)$$
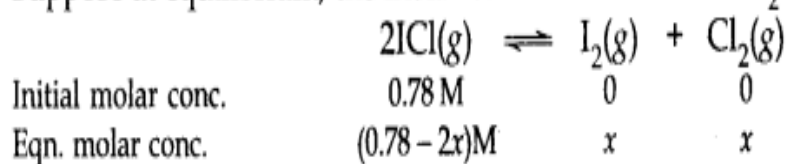$$(0.6 \times 10^5\text{ Pa}) \quad\quad\quad\quad (0.4 \times 10^5\text{ Pa})$$

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

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

$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g) ; K_c = 0.14$
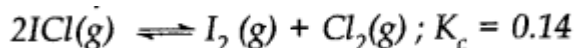
Answer:

Suppose at equilibrium, the molar concentration of both $I_2(g)$ and $Cl_2(g)$ is x mol L^{-1}.

$$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$$

Initial molar conc.	0.78 M	0	0
Eqn. molar conc.	(0.78 – 2x)M	x	x

$$K_c = \frac{[I_2(g)][Cl_2(g)]}{[ICl(g)^2]} = \frac{(x) \times (x)}{(0.78 - 2x)^2}$$

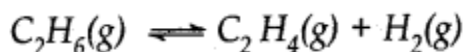$$\frac{x}{(0.78 - 2x)} = (0.14)^{1/2} = 0.374 \quad \text{or} \quad x = 0.374 \,(0.78 - 2x)$$

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

$[ICl] = (0.78 - 2 \times 0.167) = (0.78 - 0.334) = \textbf{0.446 M}$
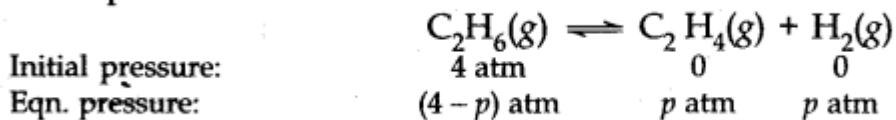
$[I_2] = 0.167 \text{ M} ; [Cl_2] = \textbf{0.167 M}$

8. K =0.04 atm at 898 K for the equilibrium shown below. What is the equilibrium concentration ok C_2H_6 when it is placed in a flask

at 4 atm pressure, and allowed to come to equilibrium.

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

Answer:

The equilibrium in the reaction is:

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

Initial pressure:	4 atm	0	0
Eqn. pressure:	$(4-p)$ atm	p atm	p atm

$$K_p = \frac{p_{C_2H_4} \times p_{H_2}}{p_{C_2H_6}} \quad \text{or} \quad 0.04 = \frac{p^2}{(4-p)}$$

$$p^2 = 0.04\,(4-p) \quad \text{or} \quad p^2 + 0.04\,p - 0.16 = 0$$

$$p = \frac{(-0.04) \pm \sqrt{0.0016 - 4\,(-0.16)}}{2}$$

$$= \frac{(-0.04) \pm 0.8}{2} = \frac{0.76}{2} = 0.38$$

Equilibrium pressure or concentration of $C_2H_6 = (4 - 0.38)$ **= 3.62 atm.**

9. A sample of pure PCl₅ was introduced into an evacuated vessel at 473 K. After equilibrium was reached, the concentration of PCl₅ was found to be 0.5 x 10⁻¹ mol L⁻¹. If K꜀ is 8.3 x 10⁻³ what are the concentrations of PCl₃ and Cl₂ at equilibrium?

Answer:

Let the initial molar concentration of PCl₅ per litre = x mol
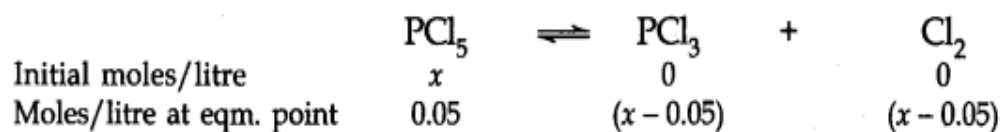
Molar concentration of PCl₅ at equilibrium = 0.05 mol

.'. Moles of PCl₅ decomposed = (x – 0.05) mol

Moles of PCl₃ formed = (x – 0.05) mol

Moles of Cl₂ formed = (x – 0.05) mol

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

at the equilibrium point are:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial moles/litre	x	0	0
Moles/litre at eqm. point	0.05	$(x-0.05)$	$(x-0.05)$

Equilibrium constant $(K_c) = 8.3 \times 10^{-3} = 0.0083$
Applying Law of chemical equilibrium,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}; \quad 0.0083 = \frac{(x-0.05) \times (x-0.05)}{0.05}$$

$$(x-0.05)^2 = 0.0083 \times 0.05 = 4.15 \times 10^{-4}$$
$$(x-0.05) = (4.15 \times 10^{-4})^{1/2} = 2.037 \times 10^{-2} = 0.02 \text{ moles}$$
$$x = 0.05 + 0.02 = 0.07 \text{ mol}$$

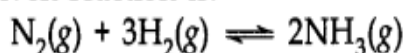The molar concentration per litre of PCl_3 at eqm. = 0.07 − 0.05 = **0.02 mol**
The molar concentration per litre of Cl_2 at eqm. = 0.07 − 0.05 = **0.02 mol.**

10.

Equilibrium constant K_c for the reaction, N_2 (g) + 3H$_2$ (g) $\rightleftharpoons$ 2NH$_3$ (g) at 500 K is 0.061. At particular time, the anaylsis 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?
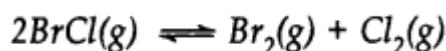
Answer:

The given reaction is:
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
According to available data.
$$N_2 = [3.0]; H_2 = [2.0]; NH_3 = [0.50]$$

$$Q_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = \frac{[0.50]^2}{[3.0][2.0]^3} = \frac{0.25}{24} = 0.0104.$$

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.
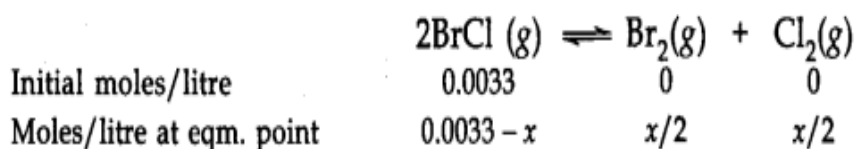
11. Bromine monochloride (B$_r$Cl) decomposes into bromine and chlorine and reaches the equilibrium:

$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$

The value of Kc is 32 at 500 K. If initially pure B$_r$Cl is present at a concentration of 3.3 x10^{-3}mol L^{-1}what is its molar concentration in the mixture at equilibrium?

Answer:

Let x moles of B$_r$Cl 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:

$$2BrCl\ (g) \rightleftharpoons Br_2(g) \ + \ Cl_2(g)$$

	2BrCl (g)	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

Applying Law of chemical equilibrium, $K_c = \dfrac{[Br_2][Cl_2]}{[BrCl]^2}$ or $32 = \dfrac{(x/2)\times(x/2)}{(0.0033-x)^2}$

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

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

∴ Molar concentration of BrCl at equilibrium point = 0.0033 – 0.003
= 0.0003 mol L^{-1} = 3 x 10^{-4} mol L^{-1}

12. 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
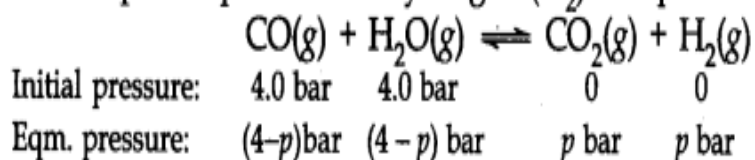
more steam in water gas shift reaction.

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

If a reaction vessel at 400°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°C.

Answer:

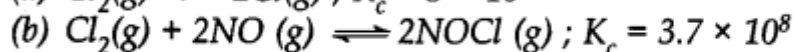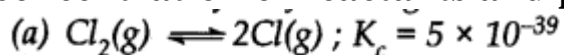Let the partial pressure of hydrogen (H_2) at equilibrium point = p bar

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Initial pressure: 4.0 bar   4.0 bar   0   0

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

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

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

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

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

13. 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.

14. The ionization constant of phenol is 1.0 x 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:

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

Initial   0.05 M

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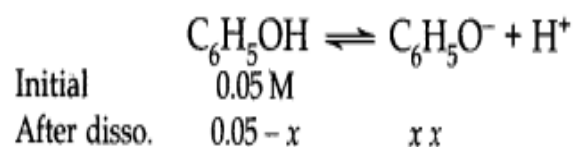
$$\therefore K_a = \frac{x \times x}{0.05 - x} = 1.0 \times 10^{-10} \text{ (Given)} \quad \text{or} \quad \frac{x^2}{0.05} = 1.0 \times 10^{-10}$$

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

In presence of 0.01 C_6H_5ONa, suppose y is the amount of phenol dissociated, then at equilibrium

$$[C_6H_5OH] = 0.05 - y \approx 0.05,$$
$$[C_6H_5O^-] = 0.01 + y \approx 0.01 \text{ M}, [H^+] = y \text{ M}$$

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

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

15. Calculate the pH of the following solutions:

(a) 2g ofTlOH dissolved in water to give 2 litre of the solution

(b) 0.3 g of Ca(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

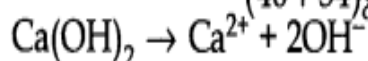**(d) l mL of 13.6 M HCl is diluted with water to give 1 litre of the solution.**

Answer:

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

$$[OH^-] = [TlOH] = 4.52 \times 10^{-3}\,M$$
$$[H^+] = 10^{-14}/\,(4.52 \times 10^{-3}) = 2.21 \times 10^{-12}\,M$$
$$\therefore \quad pH = -\log\,(2.21 \times 10^{-12}) = 12 - (0.3424) = 11.66$$

(b) Molar conc. of Ca(OH)₂ $= \dfrac{0.3\,g}{(40+34)g\,mol^{-1}} \times \dfrac{1}{0.5\,L} = 8.11 \times 10^{-3}\,M$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$
$$[OH^-] = 2[Ca(OH)_2] = 2 \times (8.11 \times 10^{-3})\,M = 16.22 \times 10^{-3}\,M$$
$$pOH = -\log\,(16.22 \times 10^{-3}) = 3 - 1.2101 = 1.79$$
$$pH = 14 - 1.79 = \mathbf{12.21}$$

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

$$[OH^-] = 3.75 \times 10^{-2}\,M$$
$$pOH = -\log\,(3.75 \times 10^{-2}) = 2 - 0.0574 = 1.43$$
$$pH = 14 - 1.43 = \mathbf{12.57}$$

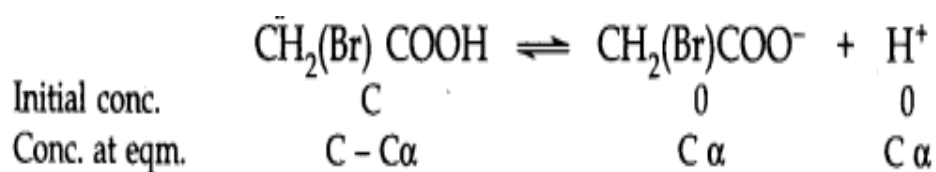(d) $M_1V_1 = M_2V_2$ $\therefore$ $13.6\,M \times 1m\,L = M_2 \times 1000\,mL$ $\therefore$ $M_2 = 1.36 \times 10^{-2}\,M$
$$[H^+] = [HCl] = 1.36 \times 10^{-2}\,M,\ pH = -\log\,(1.36 \times 10^{-2}) = 2 - 0.1335 \approx \mathbf{1.87}$$

16. 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:

$$CH_2(Br)\ COOH \rightleftharpoons CH_2(Br)COO^- + H^+$$

Initial conc.	C	0	0
Conc. at eqm.	C – Cα	C α	C α

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

$$pK_a = -\log(1.74 \times 10^{-3}) = 3 - 0.2405 = \mathbf{2.76}$$

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

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

7marks:

**1.Write the expression for the equilibrium constant for each of the following reactions**

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(v) $I_2(s) + 5F_2(g) \rightleftharpoons 2IF_5(l)$

Answer:

(i) $K_c = \dfrac{[NO(g)]^2[Cl_2(g)]}{[NOCl(g)]^2}$

(ii) $K_c = \dfrac{[CuO(g)]^2[NO_2(g)]^4[O_2(g)]}{[Cu(NO_3)_2(s)]^2} = [NO_2(g)]^4[O_2(g)]$

(iii) $K_c = \dfrac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)][H_2O(l)]}$

            $= \dfrac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)]}$

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

(v) $K_c = \dfrac{[IF_5(l)]^2}{[I_2(s)][F_2(g)]^5} = \dfrac{[IF_5(l)]^2}{[F_2(g)]^5}$

2. Reaction between nitrogen and oxygen takes place as follows:

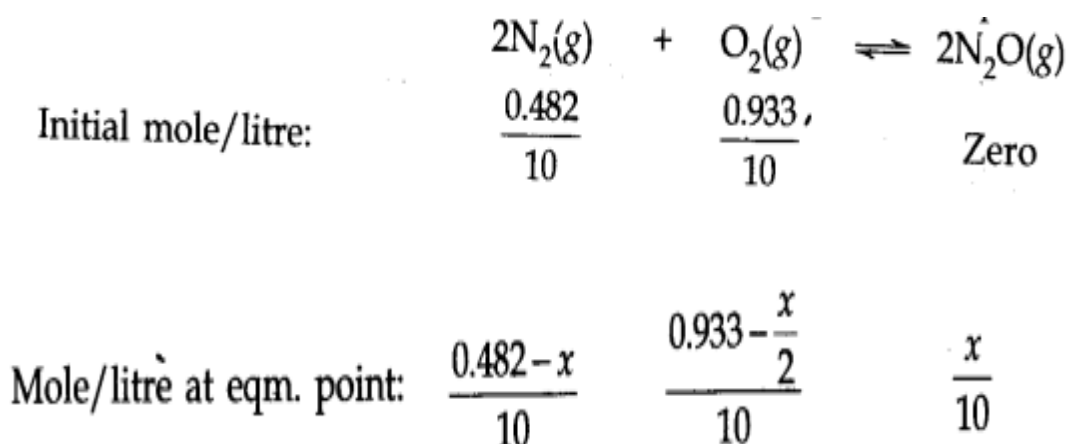$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$
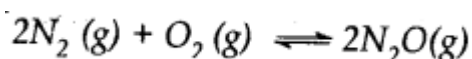
If a mixture of 0.482 mol of N₂ and 0.933 mol of O₂ is placed in a reaction vessel of volume 10 L and allowed to form N₂O at a

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:

$$2N_2(g) \quad + \quad O_2(g) \quad \rightleftharpoons \quad 2N_2O(g)$$

Initial mole/litre:
$$\frac{0.482}{10} \qquad \frac{0.933}{10} \qquad \text{Zero}$$

Mole/litre at eqm. point:
$$\frac{0.482 - x}{10} \qquad \frac{0.933 - \dfrac{x}{2}}{10} \qquad \frac{x}{10}$$

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.

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

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

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

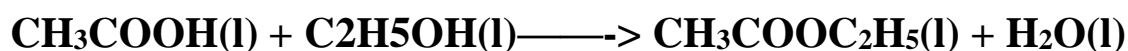As x is extremely small, it can be neglected.
Thus, in the equilibrium mixture

Molar conc. of N_2 = 0.0482 mol L^{-1}
Molar conc. of O_2 = 0.0933 mol L^{-1}
Molar conc. of N_2O = 0.1 × x = 0.1 × 6.6 × 10^{-20} mol L^{-1}
= 6.6 × 10^{-21} mol L^{-1}

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

$CH_3COOH(l) + C2H5OH(l)$——-> $CH_3COOC_2H_5(l) + H_2O(l)$

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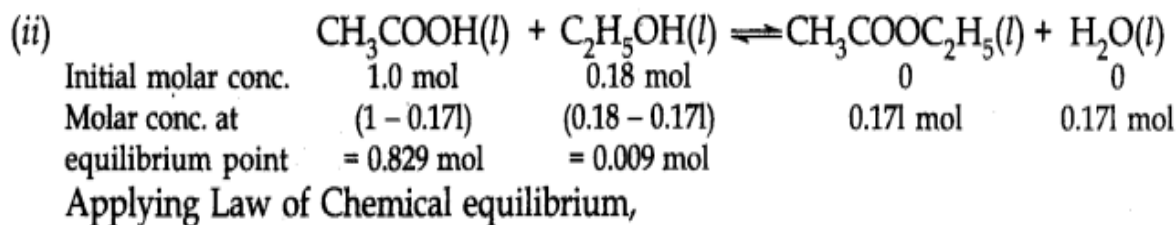
(ii) At 293 K, if one starts with 1.000 mol of acetic acid and 0.180 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting mth 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?
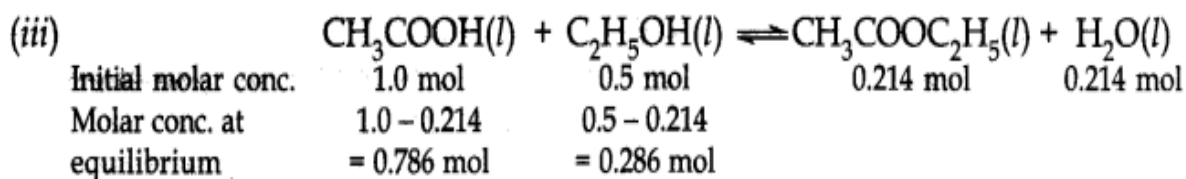
Answer:

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

$$Q_c = \frac{[CH_3COOC_2H_5(l)][H_2O(l)]}{[CH_3COOH(l)][C_2H_5OH(l)]}$$

(ii) $$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial molar conc.	1.0 mol	0.18 mol	0	0
Molar conc. at equilibrium point	(1 – 0.171) = 0.829 mol	(0.18 – 0.171) = 0.009 mol	0.171 mol	0.171 mol

Applying Law of Chemical equilibrium,

$$K_c = \frac{\left[CH_3COOC_2H_5\right](l)\left[H_2O(l)\right]}{\left[CH_3COOH(l)\right]\left[C_2H_5OH(l)\right]}$$

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

(iii) $$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial molar conc.	1.0 mol	0.5 mol	0.214 mol	0.214 mol
Molar conc. at equilibrium	1.0 – 0.214 = 0.786 mol	0.5 – 0.214 = 0.286 mol		

$$Q_c = \frac{[CH_3COOC_2H_5(l)][H_2O(l)]}{[CH_3COOH(l)][C_2H_5OH(l)]}$$

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

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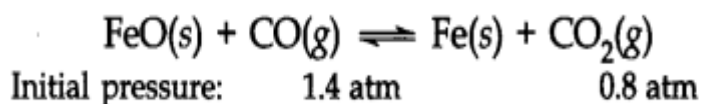
4. One of the reactions that takes place in producing steel from iron ore is the reduction of iron

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

FeO(s) + CO(g) ————>Fe(s) + CO₂(g) ; Kₚ = 0.265 atm at 1050 K

What are the equilibrium partial pressures of CO and CO₂ at 1050 K if the initial pressures are: P_{CO} = 1.4 atm and P_{CO2} = 0.80 atm?

Answer:

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

Initial pressure: 1.4 atm   0.8 atm

$$Q_p = \frac{p_{CO_2}}{p_{CO}} = \frac{(0.8 \text{ atm})}{(1.4 \text{ atm})} = 0.571$$

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 CO₂ will decrease while that of CO will increase so that the equilibrium may be attained again. Let p atm be the decrease in the partial pressure of CO₂. Therefore, the partial pressure of CO will increase by the same magnitude i.e., p atm.

$$p_{CO_2} = (0.8 - p) \text{ atm}; \quad p_{CO}(g) = (1.4 + p) \text{ atm}$$

At equilibrium, $$K_p = \frac{p_{CO_2}}{p_{CO}} = \frac{(0.8 - p) \text{ atm}}{(1.4 + p) \text{ atm}} = \frac{(0.8 - p)}{(1.4 + p)}$$
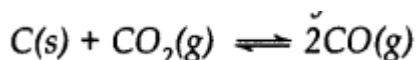
or $$0.265 = \frac{(0.8 - p)}{(1.4 + p)}$$

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

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

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

$$(p_{CO_2})_{eq} = (0.8 - 0.339) = \textbf{1.461 atm}$$

5. At 1127 K and 1 atmosphere pressure, a gaseous mixture of CO and C0₂ in equilibrium with solid carbon has 90.55% CO by mass.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

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
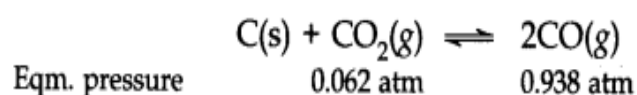
Mass of CO in the mixture = 90.55 g

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

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

$$\text{No. of moles of } CO_2 = \frac{9.45}{(44g \, mol^{-1})} = 0.215 \, mol$$

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

$$p_{CO_2} \text{ in the mixture} = \frac{(0.215 \, mol)}{(3.449 \, mol)} \times 1 \, atm = 0.062 \, atm$$

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Eqm. pressure   0.062 atm   0.938 atm

$$K_p = \frac{p^2CO}{pCO_2} = \frac{(0.938 \, atm)^2}{(0.062 \, atm)} = 14.19 \, atm$$

Step II. Calculation of K_c for the reaction.

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

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

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

6. 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) $> n_r$ (9)

(iv) Increase in pressure will favour forward reaction because n_p (1) $<$
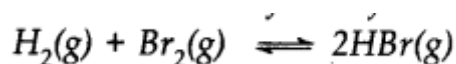
n_r (2)

(v) Increase in pressure will favour backward reaction because n_p (2) > n_r(1)

(vi) Increase in pressure will favour backward reaction because n_p (1) > n_r (0).
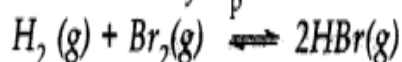
7. The equilibrium constant for the following reaction is 1.6 x 10^5 at 1024 K.

Find the equilibrium pressure of all gases if 10.0 bar of HB_r is introduced into a sealed container at 1024 K.

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Answer:

Step I. Calculation of K_p.

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

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

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

Step II. Calculation of partial pressure of gases

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$$

Initial pressure	10 bar	zero	zero
Eqm. pressure	(10 – P) bar	P/2 bar	P/2 bar

$$K_p' = \frac{pH_2 \times pBr_2}{p^2HBr} \quad \text{or} \quad \frac{1}{1.6 \times 10^5} = \frac{P/2 \times P/2}{(10-P)^2} = \frac{P^2}{4(10-P)^2}$$

On taking square root; $\dfrac{P^2}{4(10-P)^2} = \left(\dfrac{1}{1.6 \times 10^5}\right)^{1/2}$ or $\dfrac{2(10-P)}{P} = (1.6 \times 10^5)^{1/2}$

$= 4 \times 10^2$

$20 - 2P = 4 \times 10^2\,P$ or $P(4 \times 10^2 + 2) = 20$

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

$pH_2 = 0.025$ bar; $pBr_2 = \mathbf{0.025}$ **bar**: $pHBr = 10 - 0.05 = 9.95$ bar ≈ 10.0 bar.

8. The-first ionization constant of H_2S is 9.1 x 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 x 10⁻¹³, calculate the concentration of S^{2-} under both conditions.

Answer:

To calculate [HS⁻]

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

Initial	0.1 M		
After disso.	0.1 − x	x	x
	≈ 0.1		
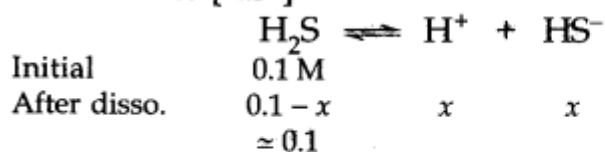
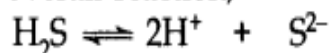$K_a = \dfrac{x \times x}{0.1} = 9.1 \times 10^{-8}$ or $x^2 = 9.1 \times 10^{-9}$ or $x = \mathbf{9.54 \times 10^{-5}}$.

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

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

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

$$H_2S \xrightleftharpoons{K_{a_1}} H^+ + HS^- \ ; \qquad HS^- \xrightleftharpoons{K_{a_2}} H^+ + S^{2-}$$
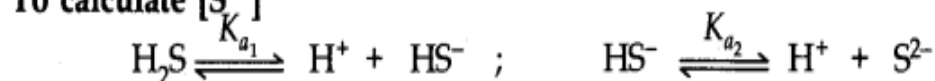
For the overall reaction,

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

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

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

In the absence of 0.1 MHCl, $[H^+] = 2 [S^{2-}]$
Hence, if $[S^{2-}] = x$, $[H^+] = 2x$

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

$$3 \log x = \log 273 - 24 = 2.4362 - 24$$
$$\log x = 0.8127 - 8 = \bar{8}.8127,$$

or $\qquad x = $ Antilog $\bar{8}.8127 = 273 \times 10^{-24} = 6.497 \times 10 = \mathbf{6.5 \times 10^{-8}}$ **M.**

In presence of 0.1 M HCl, suppose $[S^{2-}] = y$, then
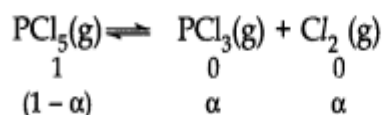$$[H_2S] = 0.1 - y \simeq 0.1 \text{ M}, \quad [H^+] = 0.1 + y \simeq 0.1 \text{ M}$$

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

9. At certain temperature and under a pressure of 4 atm, PCl₅ is 10% dissociated. Calculate the pressure at which PCl₅ will be

20% dissociated at temperature remaining constant.

Answer:

Calculation of K_p

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

$$
\begin{array}{ccc}
1 & 0 & 0 \\
(1-\alpha) & \alpha & \alpha
\end{array}
$$

Total no. of moles in the equilibrium mixture $= 1 - \alpha + \alpha + \alpha$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad = (1 + \alpha)$ mol.

Let the total pressure of equilibrium mixture $= p$ atm

Partial pressure of PCl_5

$$p_{PCl_5} = \frac{1-\alpha}{1+\alpha} \times p \text{ atm}$$

Partial pressure of $PCl_3 = \frac{\alpha}{1+\alpha} \times p$ atm

Partial pressure of Cl_2

$$p_{Cl_2} = \frac{\alpha}{(1+\alpha)} \times p \text{ atm}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

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

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

$$K_p = \frac{(0.1) \times (0.1) \times (4 \text{ atm})}{1-(0.1)^2}$$

$$= \frac{0.04}{0.99} = 0.04 \text{ atm.}$$

Calculation of P under new condition

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

$$K_p = \frac{\alpha^2 p}{1-\alpha^2} \text{ or } p = \frac{K_p(1-\alpha^2)}{\alpha^2}$$

$$= \frac{(0.04 \text{ atm})[(1-(0.2)^2]}{(0.2)^2} = \frac{0.04 \text{ atm} \times 0.96}{0.04}$$

$$= 0.96 \text{ atm.}$$

Fill in the blanks:

1.In a chemical reaction at equilibrium, the rates of the forward and _____ reactions are equal.

Answer: reverse

2.The equilibrium constant (Kc) expression for the reaction aA + bB ⇌ cC + dD is given by _____.

Answer: [C]^c [D]^d / [A]^a [B]^b

3.Le Chatelier's Principle states that if a system at equilibrium is disturbed, it will adjust to counteract the _____.

Answer: disturbance

4.The value of the equilibrium constant (Kc) gives information about the extent of the reaction at a given _____.

Answer: temperature

5.The reaction quotient (Q) is calculated using the same expression as the equilibrium constant (Kc), but with _____ concentrations.

Answer: initial or non-equilibrium

6.A catalyst affects the _____ of a reaction but has no effect on the position of the equilibrium.

Answer: rate

7.The position of equilibrium can be shifted by changing the _____ of reactants or products.

Answer: concentration

8.The equilibrium constant (Kc) is unitless when concentrations are expressed in _____.

Answer: molarity

9.According to Le Chatelier's Principle, if the pressure is increased, the equilibrium will shift toward the side with _____ moles of gas.

Answer: fewer

10.The reaction quotient (Q) helps predict the direction in which a reaction will proceed to reach ____

Answer: equilibrium

Multiple choice:

1.In a chemical reaction at equilibrium, which statement is true?

a) Only the forward reaction is occurring

b) The rate of the forward reaction equals the rate of the reverse reaction

c) The rate of the forward reaction is greater than the rate of the reverse reaction

d) The concentration of reactants is zero

Answer:

b) The rate of the forward reaction equals the rate of the reverse reaction

2.What does the equilibrium constant (Kc) express for a given reaction?

a) The rate of the reaction

b) The concentration of products at equilibrium

c) The ratio of reactant concentrations at equilibrium

d) The speed of the reaction

Answer:

c) The ratio of reactant concentrations at equilibrium

3.According to Le Chatelier's Principle, if the concentration of a reactant is increased, the equilibrium will shift:

a) Toward the side with more products

b) Toward the side with fewer products

c) It will not affect the equilibrium

d) Randomly

Answer:

b) Toward the side with fewer products

4.How does an increase in temperature generally affect an endothermic reaction at equilibrium?

a) Shifts the equilibrium to the left

b) Shifts the equilibrium to the right

c) No effect on the equilibrium position

d) It depends on the specific reaction

Answer:

b) Shifts the equilibrium to the right

5.What is the relationship between the equilibrium constant (Kc) and the reaction quotient (Q)?

a) Kc is always greater than Q

b) Kc is always equal to Q

c) Kc is always less than Q

d) Kc and Q are equal only at the beginning of the reaction

Answer:

b) Kc is always equal to Q

6.A catalyst affects the equilibrium position by:

a) Increasing the rate of the forward reaction

b) Increasing the rate of the reverse reaction

c) Shifting the equilibrium to the left

d) Shifting the equilibrium to the right

Answer:

a) Increasing the rate of the forward reaction

7.What happens to the equilibrium constant (Kc) when the coefficients of a balanced chemical equation are multiplied by a factor?

a) Kc remains unchanged

b) Kc is squared

c) Kc is raised to the power of the factor

d) Kc is divided by the factor

Answer:

c) Kc is raised to the power of the factor

8.The common unit for the equilibrium constant (Kc) is:

a) M/s

b) mol/L

c) L/mol

d) Unitless

Answer:

d) Unitless

9.According to Le Chatelier's Principle, if pressure is increased, what happens to the equilibrium position for a reaction involving gaseous reactants and products?

a) Shifts toward the side with more moles of gas

b) Shifts toward the side with fewer moles of gas

c) No effect on the equilibrium

d) Depends on the specific reaction

Answer:

a) Shifts toward the side with more moles of gas

10.What is the effect of adding an inert gas at constant volume to a system at equilibrium?

a) It increases the pressure, shifting the equilibrium to the left

b) It decreases the pressure, shifting the equilibrium to the right

c) It has no effect on the equilibrium position

d) It depends on the nature of the inert gas

Answer:

c) It has no effect on the equilibrium position

<u>Summary:</u>

The study of chemical equilibrium forms a cornerstone in understanding the behaviour of reversible reactions and the dynamic interplay between reactants and products. At equilibrium, the rates of the forward and reverse reactions reach a state of balance, resulting in a consistent concentration of both reactants and products. A critical aspect of this equilibrium is expressed through the equilibrium constant (K_c), which quantifies the ratio of product to reactant concentrations. Le Chatelier's Principle further enriches our comprehension by asserting that any disturbance to a system at equilibrium prompts a response that counteracts the disturbance, ultimately restoring the system to its balanced state.

This principle is crucial in predicting how changes in concentration, temperature, or pressure influence the position of equilibrium. Thus, the chapter provides a comprehensive insight into the intricacies of chemical equilibrium, offering a fundamental framework for understanding the dynamic nature of chemical reactions.