Question 7.21:

Equilibrium constant, K_c for the reaction

$N_2(g) + 3H_2(g) \longleftrightarrow 2NH_3(g)$ at 500 K is 0.061.

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

Answer 7.21:

The given reaction is:

	$N_{2(g)}$ +	$3H_{2(g)} \longleftrightarrow$	$2NH_{3(g)}$
At a particular time:	3.0 mol L^{-1}	2.0 mol L^{-1}	0.5 mol L^{-1}

Now, we know that,

$$Q_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
$$= \frac{(0.5)^2}{(3.0)(2.0)^3}$$
$$= 0.0104$$

It is given that $K_c = 0.061$.

Since $Q_C \neq K_c$, the reaction is not at equilibrium.

Since $Q_C < K_c$, the reaction will proceed in the forward direction to reach equilibrium.

Question 7.22:

Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium:

$$2BrCl\,(g) \longleftrightarrow Br_2\,(g) + Cl_2\,(g)$$

for which K_c= 32 at 500 K.

If initially pure BrCl is present at a concentration of 3.3×10^{-3} $molL^{-1}$, what is its molar concentration in the mixture at equilibrium?

Answer 7.22:

Let the amount of bromine and chlorine formed at equilibrium be *x*. The given reaction is:

	$2BrCl_{(g)}$	$\longleftrightarrow$	$Br_{2(g)}$	+	$Cl_{2(g)}$
Initial conc.	3.3×10^{-3}		0		0
At equilibrium	$3.3\times10^{-3}-2x$		x		x

Now, we can write,

$$\frac{[Br_2][Cl_2]}{[BrCl]^2}=K_C$$

$$\Rightarrow \frac{x\times x}{\left(3.3\times10^{-3}-2x\right)^2}=32$$

$$\Rightarrow \frac{x}{3.3\times10^{-3}-2x}=5.66$$

$$\Rightarrow x=18.678\times10^{-3}-11.32x$$

$$\Rightarrow 12.32x=18.678\times10^{-3}$$

$$\Rightarrow x=1.5\times10^{-3}$$

Therefore, at equilibrium,

$$[BrCl]=3.3\times10^{-3}-\left(2\times1.5\times10^{-3}\right)$$

$$=3.3\times10^{-3}-3.0\times10^{-3}$$

$$=0.3\times10^{-3}$$

$$=3.0\times10^{-4}\ \text{molL}^{-1}$$

Question 7.23:

At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass

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

Calculate K_c for this reaction at the above temperature.

Answer 7.23:

Let the total mass of the gaseous mixture be 100 g.

Mass of CO = 90.55 g

And, mass of CO_2 = (100 – 90.55) = 9.45 g

Now, number of moles of CO, $n_{CO} = \frac{90.55}{28} = 3.234 \text{ mol}$

Number of moles of CO_2, $n_{CO_2} = \frac{9.45}{44} = 0.215 \text{ mol}$

Partial pressure of CO,

$$p_{CO} = \frac{n_{CO}}{n_{CO} + n_{CO_2}} \times p_{total}$$
$$= \frac{3.234}{3.234 + 0.215} \times 1$$
$$= 0.938 \text{ atm}$$

Partial pressure of CO_2,

$$p_{CO_2} = \frac{n_{CO_2}}{n_{CO} + n_{CO_2}} \times p_{total}$$
$$= \frac{0.215}{3.234 + 0.215} \times 1$$
$$= 0.062 \text{ atm}$$

$$\text{Therefore, } K_p = \frac{[CO]^2}{[CO_2]}$$
$$= \frac{(0.938)^2}{0.062}$$
$$= 14.19$$

For the given reaction,

$$\Delta n = 2 - 1 = 1$$

We know that,

$$K_p = K_c (RT)^{\Delta n}$$
$$\Rightarrow 14.19 = K_c (0.082 \times 1127)^1$$
$$\Rightarrow K_c = \frac{14.19}{0.082 \times 1127}$$
$$= 0.154 \text{(approximately)}$$

Question 7.24:

Calculate

a) $\Delta G°$ and

b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K

$$NO\,(g) + \tfrac{1}{2}O_2\,(g) \longleftrightarrow NO_2\,(g)$$

Where:

$\Delta_f G°\,(NO_2) = 52.0$ kJ/mol

$\Delta_f G°\,(NO) = 87.0$ kJ/mol

$\Delta_f G°\,(O_2) = 0$ kJ/mol

Answer 7.24:

(a) For the given reaction,

$\Delta G° = \Delta G°(\text{ Products}) - \Delta G°(\text{ Reactants})$

$\Delta G° = 52.0 - \{87.0 + 0\}$

$= -35.0$ kJ mol^{-1}

(b) We know that,

$\Delta G° = RT \log K_c$

$\Delta G° = 2.303\, RT \log K_c$

$$K_c = \frac{-35.0\times10^{-3}}{-2.303\times8.314\times298}$$
$$= 6.134$$
$$\therefore K_c = \text{antilog}\,(6.134)$$
$$= 1.36\times10^{6}$$

Hence, the equilibrium constant for the given reaction K_c is 1.36×10^6

Question 7.25:

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?

(a) $PCl_5\,(g) \longleftrightarrow PCl_3\,(g) + Cl_2\,(g)$

(b) $CaO(s) + CO_2(g) \longleftrightarrow CaCO_3(s)$

(c) $3Fe(s) + 4H_2O(g) \longleftrightarrow Fe_3O_4(s) + 4H_2(g)$

Answer 7.25:

(a) The number of moles of reaction products will increase. According to Le Chatelier's principle, if pressure is decreased, then the equilibrium shifts in the direction in which the number of moles of gases is more. In the given reaction, the number of moles of gaseous products is more than that of gaseous reactants. Thus, the reaction will proceed in the forward direction. As a result, the number of moles of reaction products will increase.

(b) The number of moles of reaction products will decrease.

(c) The number of moles of reaction products remains the same.

Question 7.26:

Which of the following reactions will get affected by increasing the pressure?

Also, mention whether change will cause the reaction to go into forward or backward direction.

(i) $COCl_2(g) \longleftrightarrow CO(g) + Cl_2(g)$

(ii) $CH_4(g) + 2S_2(g) \longleftrightarrow CS_2(g) + 2H_2S(g)$

(iii) $CO_2(g) + C(s) \longleftrightarrow 2CO(g)$

(iv) $2H_2(g) + CO(g) \longleftrightarrow CH_3OH(g)$

(v) $CaCO_3(s) \longleftrightarrow CaO(s) + CO_2(g)$

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

Answer7.26:

The reactions given in (i), (iii), (iv), (v), and (vi) will get affected by increasing the pressure.

The reaction given in (iv) will proceed in the forward direction because the number of moles of gaseous reactants is more than that of gaseous products.

The reactions given in (i), (iii), (v), and (vi) will shift in the backward direction because the number of moles of gaseous reactants is less than that of gaseous products.

Question 7.27:

The equilibrium constant for the following reaction is 1.6 ×10^5 at 1024 K.

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

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

Answer 7.27:

Given,

K_p for the reaction i.e., $H_{2(g)} + Br_{2(g)} \longleftrightarrow 2HBr_{(g)}$ is 1.6×10^5.

Therefore, for the reaction $2HBr_{(g)} \longleftrightarrow H_{2(g)} + Br_{2(g)}$, the equilibrium constant will be,

$$K'_p = \frac{1}{K_p}$$

$$= \frac{1}{1.6\times10^5}$$

$$= 6.25\times10^{-6}$$

Now, let p be the pressure of both H_2 and Br_2 at equilibrium.

	$2HBr_{(g)}$	$\longleftrightarrow$	$H_{2(g)}$	+	$Br_{2(g)}$
Initial conc.	10		0		0
At equilibrium	$10-2p$		p		p

Now, we can write,

$$\frac{p_{HBr}\times p_{_2}}{p^2_{HBr}} = K'_p$$

$$\frac{p\times p}{(10-2p)^2} = 6.25\times10^{-6}$$

$$\frac{p}{10-2p} = 2.5\times10^{-3}$$

$$p = 2.5\times10^{-2} - (5.0\times10^{-3})p$$

$$p + (5.0\times10^{-3})p = 2.5\times10^{-2}$$

$$(1005\times10^{-3})p = 2.5\times10^{-2}$$

$$p = 2.49\times10^{-2}\text{ bar} = 2.5\times10^{-2}\text{ bar (approximately)}$$

Therefore, at equilibrium,

$$[H_2] = [Br_2] = 2.49 \times 10^{-2} \text{ bar}$$
$$[HBr] = 10 - 2 \times (2.49 \times 10^{-2}) \text{ bar}$$
$$= 9.95 \text{ bar} = 10 \text{ bar (approximately)}$$

Question 7.28:

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

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

(a) Write as 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 7.28:

(a) For the given reaction,

$$K_p = \frac{p_{CO} \times p_{H_2}^3}{p_{CH_4} \times p_{H_2O}}$$

(b)

(i) According to Le Chatelier's principle, the equilibrium will shift in the backward direction.

(ii) According to Le Chatelier's principle, as the reaction is endothermic, the equilibrium will shift in the forward direction.

(iii) The equilibrium of the reaction is not affected by the presence of a catalyst. A catalyst only increases the rate of a reaction. Thus, equilibrium will be attained quickly.

Question 7.29:

Describe the effect of:

a) Addition of H_2

b) Addition of CH_3OH

c) Removal of CO

d) Removal of CH_3OH on the equilibrium of the reaction:

$$2H_2(g) + CO(g) \longleftrightarrow CH_3OH(g)$$

Answer 7.29:

(a) According to Le Chatelier's principle, on addition of H_2, the equilibrium of the given reaction will shift in the forward direction.

(b) On addition of CH_3OH, the equilibrium will shift in the backward direction.

(c) On removing CO, the equilibrium will shift in the backward direction.

(d) On removing CH_3OH, the equilibrium will shift in the forward direction.

Question 7.30:

At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$$PCl_5(g) \longleftrightarrow PCl_3(g) + Cl_2(g) \quad \Delta_r H° = 124.0\ kJmol^{-1}$$

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 PCl_5 is added

(ii) pressure is increased?

(iii) The temperature is increased?

Answer 7.30:

(a) $$K_c \frac{[PCl_{3(g)}][Cl_{2(g)}]}{[PCl_{5(g)}]}$$

(b) Value of K_c for the reverse reaction at the same temperature is:

$$K'_c = \frac{1}{K_c}$$
$$= \frac{1}{8.3 \times 10^{-3}} = 1.2048 \times 10^2$$
$$= 120 - 48$$

(c) (i) K_c would remain the same because in this case, the temperature remains the same.

(ii) K_c is constant at constant temperature. Thus, in this case, K_c would not change.

(iii) In an endothermic reaction, the value of K_c increases with an increase in temperature. Since the given reaction in an endothermic reaction, the value of K_c will increase if the temperature is increased.

Question 7.31:

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,

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

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} =$ 4.0 bar, what will be the partial pressure of H_2 at equilibrium? K_p= 10.1 at 400°C

Answer 7.31:

Let the partial pressure of both carbon dioxide and hydrogen gas be p. The given reaction is:

	$CO_{(g)}$	+ $H_2O_{(g)}$	$\longleftrightarrow$	$CO_{2(g)}$	+ $H_{2(g)}$
Initial conc.	4.0 bar	4.0 bar		0	0
At equilibrium	$4.0-p$	$4.0-p$		p	p

It is given that $K_p = 10.1$.

Now,

$$\frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} = K_p$$

$$\Rightarrow \frac{p \times p}{(4.0-p)(4.0-p)} = 10.1$$

$$\Rightarrow \frac{p}{4.0-p} = 3.178$$

$$\Rightarrow p = 12.712 - 3.178p$$

$$\Rightarrow 4.178p = 12.712$$

$$\Rightarrow p = 3.04$$

Hence, at equilibrium, the partial pressure of H_2 will be 3.04 bar.

Question 7.32:

Predict which of the following reaction will have appreciable concentration of reactants and products:

a) $Cl_2\,(g) \longleftrightarrow 2\,Cl\,(g)\,; \quad K_c = 5 \times 10^{-39}$

b) $Cl_2\,(g) + 2\,NO\,(g) \longleftrightarrow 2\,NOCl\,(g)\,; \quad K_c = 3.7 \times 10^{8}$

c) $Cl_2\,(g) + 2\,NO_2\,(g) \longleftrightarrow 2\,NO_2Cl\,(g)\,; \quad K_c = 1.8$

Answer 7.32:

If the value of K_c lies between 10^{-3} and 10^{3}, a reaction has appreciable concentration of reactants and products. Thus, the reaction given in (c) will have appreciable concentration of reactants and products.

Question 7.33:

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

Answer 7.33:

The given reaction is:

$$3O_{2(g)} \longleftrightarrow 2O_{3(g)}$$

$$\text{Then, } K_c = \frac{\left[O_{3(g)}\right]^2}{\left[O_{2(g)}\right]^3}$$

It is given that $K_C = 2.0 \times 10^{-50}$ and $\left[O_{2(g)}\right] = 1.6 \times 10^{-2}$.

Then, we have,

$$2.0 \times 10^{-50} = \frac{\left[O_{3(g)}\right]^2}{\left[1.6 \times 10^{-2}\right]^3}$$

$$\Rightarrow \left[O_{3(g)}\right]^2 = 2.0 \times 10^{-50} \times \left(1.6 \times 10^{-2}\right)^3$$

$$\Rightarrow \left[O_{3(g)}\right]^2 = 8.192 \times 10^{-56}$$

$$\Rightarrow \left[O_{3(g)}\right] = 2.86 \times 10^{-28}\ \text{M}$$

Hence, the concentration of O_3 is 2.86×10^{-28} M.

Question 7.34:

The reaction, $CO(g) + 3H_2(g) \longleftrightarrow CH_4(g) + H_2O(g)$ 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 7.34:

Let the concentration of methane at equilibrium be *x*.

$$\begin{array}{lcccc} & CO_{(g)} & + \; 3H_{2(g)} & \longleftrightarrow \; CH_{4(g)} & + \; H_2O_{(g)} \\ \text{At equilibrium} & \frac{0.3}{1} = 0.3M & \frac{0.1}{1} = 0.1M & x & \frac{0.02}{1} = 0.02M \end{array}$$

It is given that $K_c = 3.90$.

Therefore,

$$\frac{[CH_{4(g)}][H_2O_{(g)}]}{[CO_{(g)}][H_{2(g)}]^3} = K_c$$

$$\Rightarrow \frac{x \times 0.02}{0.3 \times (0.1)^3} = 3.90$$

$$\Rightarrow x = \frac{3.90 \times 0.3 \times (0.1)^3}{0.02}$$

$$= \frac{0.00117}{0.02}$$

$$= 0.0585\,M$$

$$= 5.85 \times 10^{-2}\,M$$

Hence, the concentration of CH_4 at equilibrium is 5.85×10^{-2} M.

Question 7.35:

What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:

$$HNO_2, CN^-, HClO_4, F^-, OH^-, CO_3^{2-}, \text{and}\, S^-$$

Answer 7.35:

A conjugate acid-base pair is a pair that differs only by one proton.
The conjugate acid-base for the given species is mentioned in the table below.

Species	Conjugate acid-base
HNO_2	NO_2^- (base)
CN^-	HCN (acid)
$HClO_4$	ClO_4^- (base)
F^-	HF (acid)
OH^-	H_2O (acid) /O^{2-} (base)
CO_3^{2-}	HCO_3^- (acid)
S_{2-}	HS^- (acid)

Question 7.36:

Which of the followings are Lewis acids? H_2O, BF_3, H^+, and NH_4^+

Answer 7.36:

Lewis acids are those acids which can accept a pair of electrons. For example, BF_3, H^+, and NH_4^+ are Lewis acids.

Question 7.37:

What will be the conjugate bases for the Brönsted acids: HF, H_2SO_4 and HCO_3?

Answer 7.37:

The table below lists the conjugate bases for the given Bronsted acids.

Bronsted acid	Conjugate base
HF	F^-
H_2SO_4	HSO_4^-
HCO_3^-	CO_3^{2-}

Question 7.38:

Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

Answer 7.38:

The table below lists the conjugate acids for the given Bronsted bases.

Bronsted base	Conjugate acid
NH_2^-	NH_3
NH_3	NH_4^+
$HCOO^-$	$HCOOH$

Question 7.39:

The species: H_2O, HCO_3^-, HSO_4^-, and NH_3 can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

Answer 7.39:

The table below lists the conjugate acids and conjugate bases for the given species.

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

Question 7.40:

Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base:

(a) OH^-

(b) F^-

(c) H^+

(d) BCl_3.

Answer 7.40:

(a) OH^- is a Lewis base since it can donate its lone pair of electrons.

(b) F^- is a Lewis base since it can donate a pair of electrons.

(c) H^+ is a Lewis acid since it can accept a pair of electrons.

(d) BCl_3 is a Lewis acid since it can accept a pair of electrons.