Chemical Equilibrium

Introduction

Chemical reaction is a process in which one or more reactants react to produce one or more products.

Type of Chemical reaction

(a) Irreversible Reactions
(b) Reversible reactions

Concept Ladder

Physical changes can also be categorised into Reversible and Irreversible changes.

(a) Irreversible Reaction

Unidirectional reactions are known as irreversible reactions. i.e. reactants convert to produce products and where products cannot convert back to the reactants.

Ex.

(1) $BaCl_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(ppt) + 2HCl(aq)$

(2) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

(b) Reversible Reaction

Reversible reactions occur in both forward and backward directions and therefore never go on to completion.

Ex.

(1) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(2) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Rack your Brain

Does a physical change accompain a chemical change?

Note :

For any reversible reaction, container should be closed.

Equilibrium

It is defined as the state when measurable properties such as position speed, temperature, concentration and pressure do not change with time.

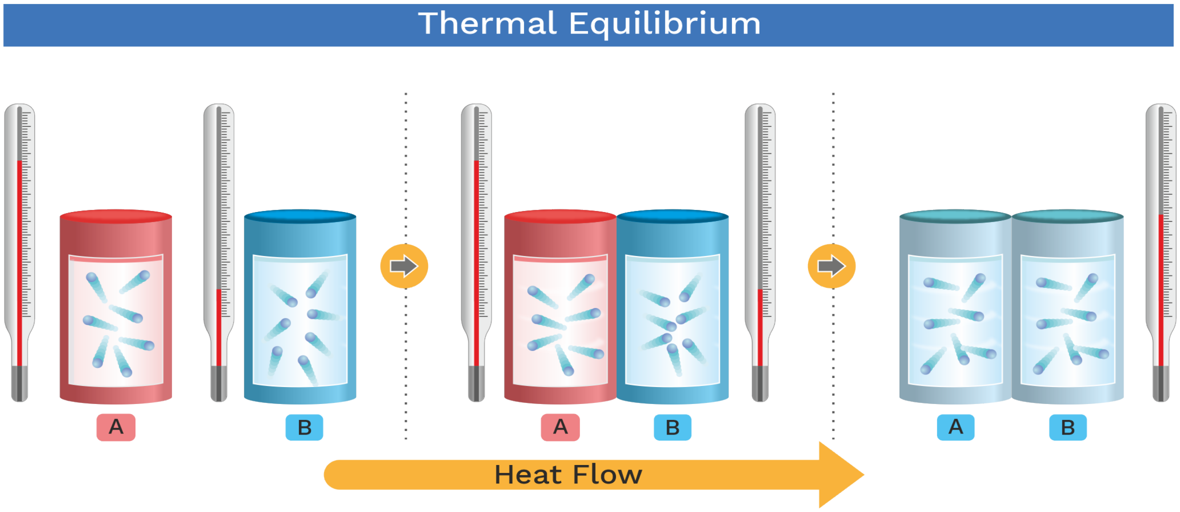
Equilibirum can be of a no. of types. For example: physical equilibrium, thermal equilibrium, mechanical equilibrium, chemical equilibrium etc.

Concept Ladder

In mechanical equilibrium, the net forces on an object is zero.

Thermal Equilibrium

It is that type of equilibrium where the thermal energy between two or more substances are equal in nature.



The above figure shows two objects A and B which are far from each other and when the come in contact then their thermal energies become equal. So, they are in thermal equilibrium with each other.

Physical Equilibrium

The type of equilibrium which develops between different phases and there is no change in chemical composition. In physical equilibrium, there is the existence of same substance in different physical states.

(1) Solid-liquid equilibrium

H_2O (solid) $\rightleftharpoons$ H_2O (liquid)

Rate of transfer of ice is equal to the rate of freezing of water

(2) Liquid-vapour equilibrium

Rate of vaporization = Rate of condensation,

H_2O(liquid) $\rightleftharpoons$ H_2O(vapour)

Concept Ladder

Solid-Liquid-Gaseous equilibrium can be seen in it's three states. The point at which these three exist for H_2O is known as triple point of water. Triple point of water is 273.15K

Conditions necessary for a Liquid-Vapour Equilibrium

(i) The system must be a closed system.

(ii) The system must be at a constant temperature.

(iii) The visible properties of the system should not change with time.

(3) Solid-vapour equilibrium

Certain solid substances on heating get converted directly into vapour without passing through the liquid phase. This process is called sublimation. The vapour when cooled, gives back the solid, it is called deposition or desublimation or sublimation.

$$NH_4Cl\,(solid) \overset{Heat}{\rightleftharpoons} NH_4Cl\,(vapour)$$

For example, Ammonium chloride when. heated sublimes.

(4) Equilibrium between a solid and its solution

If a solid solute is in contact with the saturated solution, there exits a dynamic equilibrium between the solid and the solution phase.

Solid substance $\rightleftharpoons$ Solution of the substance

Example : Sugar and sugar solution. In a saturated solution, a dynamic is equilibrium is established between dissolved sugar and solid sugar.

Sugar (solid) $\rightleftharpoons$ Sugar (aqueous)

Rate of dissolution on of solid sugar =Rate of precipitation of sugar from the solution.

At the equilibrium state, the no. of sugar molecules going into the soln from the solid sugar is equal to the no. of molecules precipitating out from the soln, i.e., at equilibrium.

(5) Equilibrium between a gas & its solution in a liquid.

Gases mixed in liquids. The dependent factors for solubility of a gas in any liquid are :

Concept Ladder

For any pure liquid at 1 atm pressure, the temperature at which the liquid and vapor are at equilibrium is called normal boiling point of liquid.

Rack your Brain

When a solution becomes supersaturated will you be able to observe equilibrium?

Concept Ladder

The number of precipitating molecules at equilibrium state is equal to the number of molecules dissolving in the solution.

(a) Nature of the gas and liquid.
(b) Temp. of the liquid.
(c) Pressure (P) of the gas over the surface of the solution.

This equilibrium is defined by Henry's law, which explains that the mass of a gas mixed in a known mass of solvent at a temp. is proportional to the solvent's pressure of the given gas. It decreases with increases of temperature.

Chemical Equilibrium

In chemical equilibrium, concentration of the reactants and products do not change with time and the system does not show any further change in properties.

In case of chemical equilibrium, rate of forward reaction becomes equal to the rate of backward reaction. i.e. Rate (forward reaction) = Rate (backward reaction)

Forward reaction (In an open glass container)

$$3Fe(s) + 4H_2O(g) \xrightarrow{\Delta} 3Fe(s) + 4H_2O(g)$$

If the container tube is closed, both the reactions take place simultaneously and hence reaction become reversible.

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

Other example may include

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

Characteristics of Equilibrium State

- A reaction (or a process) is said to be in equilibrium when the rate of forward reaction (process) becomes equal to the rate of backward reaction (process).
- An equilibrium is dynamic in nature and not static i.e., even after equilibrium is attained, the forward as well as the backward reaction take place but at equal speeds.
- A chemical equilibrium can be established only if none of the products is allowed to escape out.

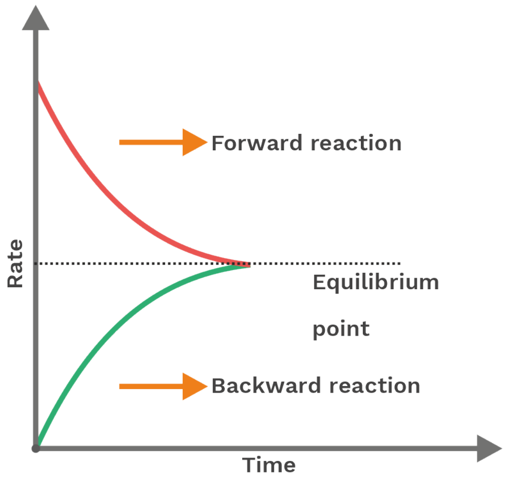
Concept Ladder

When the condition is changed at equilibrium state, the equilibrium changes.

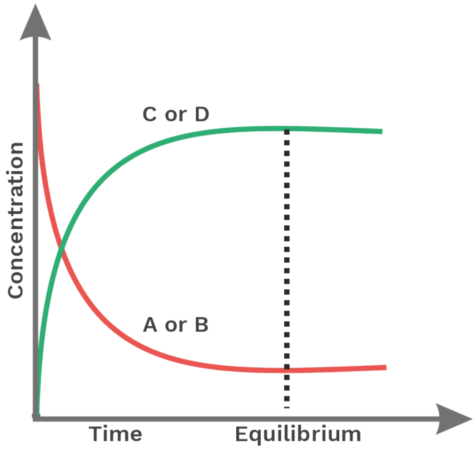
When temperature of a solution of gas is increased, the rate of dissolution of gas decreases.

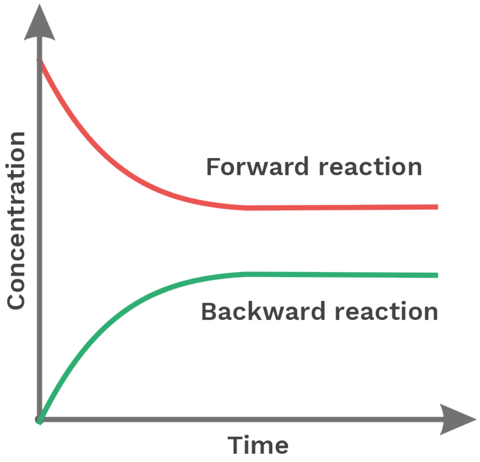
Rack your Brain

Equilibrium state is dynamic in nature. Why it is not static?



- At equilibrium, the concentration of each of the reactants and products become constant.





- When reaction attains equilibrium at certain temperature and pressure, $\Delta G = 0$
- Chemical equilibrium can be achieved from either direction.

Law of Mass Action

The rate of a reaction is proportional to the product of the active masses of the reactants, in which each term is raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation.

$$aA + bB + cC + \ldots\ldots$$

Rate of reaction is directly proportional to

$[A]^a\ [B]^b\ [C]^c$

Law of Chemical Equilibrium is a result obtained by applying the Law of Mass Action to a reversible reaction in equilibrium.

$$A + B \rightleftharpoons C + D$$

Rate of the forward reaction $\propto [A]\ [B]$

$= k_f\ [A]\ [B]$

Rate of the backward reaction $\propto [C]\ [D]$

$= k_b\ [C]\ [D]$

At equilibrium,

Rate of forward rxn = Rate of backward rxn

Rack your Brain

Does spontaneity play any role in equilibrium being attained?

Concept Ladder

In chemical kinetics for a reaction of the type

$aA + bB \longrightarrow cC + dD$

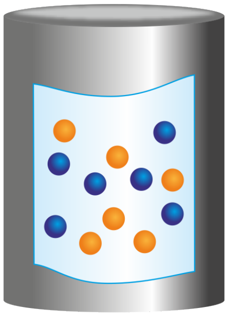
Rate of reaction = $K[A]^a[B]^b$

where K depends upon temperature.

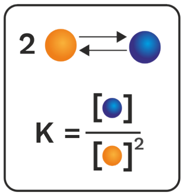
$$k_f[A][B] = k_b[C][D] \text{ or } \frac{[C][D]}{[A][B]} = \frac{k_f}{k_b} = K$$

At constant temperature, k_f and k_b are constant, therefore, $\frac{k_f}{k_b} = K$ is also constant at constant temperature and is called 'Equilibrium constant'.

The product of the molar concentrations of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar concentrations of the reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temperature and is called Equilibrium constant.



EQUILIBRIUM CONSTANT



EQUILIBRIUM CONSTANT 'K'

For a General Reaction of the type

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant expression is

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

where K_c is Equilibrium constant

Q.1 The rate constant for a forward reaction in a reversible reaction ($K_{eq} = 10^8$) is 10^4. Calculate the rate constant for the backward reaction.

A.1

$$K_{eq} = \frac{K_f}{K_b}$$

Where; K_f = Rate constant for forward reaction.
K_b = Rate constant for backward reaction.
K_{eq} = Equilibrium constant.
Now. $K_{eq} = 10^8$; $K_f = 10^4$.
Therefore, from equation (1)

$$K_b = \frac{K_f}{K_{eq}} = \frac{10^4}{10^8} = 10^{-4}$$

Importants Point about Equilibrium Constant

- If the reaction is reversed, the value of equilibrium constant is inversed e.g.,

  $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$ $K_c = K$,

  then for

  $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$, $K_c = 1/K$

Equilibrium Constant on Inversion of Reaction

$$aA + bB \underset{K'_c}{\overset{K_c}{\rightleftharpoons}} cC + dD$$

Then at constant temperature,

The equilibrium constant K_c for forward reaction

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \longleftarrow \boxed{\text{Forward Product}}$$

$$K'_c = \frac{[A]^a\,[B]^b}{[C]^c\,[D]^d} = \frac{1}{K_c} \longleftarrow \boxed{\text{Backward Product}}$$

- If the reaction is divided by 2, equilibrium constant is the square root of the original e.g.,

  For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $K_c = K$

  then for;

  $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$, $K_c = \sqrt{K}$

  If then reaction is multiplied by 2, equilibrium constant is the square of the original. Equilibrium constatns of the step reactions e.g., if for

  $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$,

  equilibrium constant = K

Previous Year's Question

If the equilibrium constant for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is K, the equilibrium constant for $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$ will be **[NEET]**

(1) $\frac{1}{2}K$
(2) K
(3) K^2
(4) K^{X_2}

(1) $NO_2(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, $K_c = K_1$

(2) $NO_2(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, $K_c = K_2$

then, $K = K_1 \times K_2$

- Effect of temperature:

  According to Van't Hoff equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Where K_1 and K_2 are the equilibrium constants at temperature T_1 and T_2 respectively and ΔH is the molar enthalpy change in the temperature range T_1 to T_2.

Note:

- For exothermic reaction, as temperature increases K decreases.
- For endothermic reaction, as temperature increases K increases.

Previous Year's Question

The equilibrium constants of the following are

$N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1

$N_2 + O_2 \rightleftharpoons 2NO$; K_2

$N_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$; K_3

The equilibrium constant (K) of the reaction will be:

$$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$$

[NEET]

(1) $K_2K_3^3 / K_1$ (2) K_2K_3 / K_1

(3) $K_2^3K_3 / K_1$ (4) $K_1K_3^3 / K_2$

Q.2 For the reactions,

$A \rightleftharpoons B$ $K_C = 1$

$B \rightleftharpoons C$ $K_c = 3$

$C \rightleftharpoons D$ $K_c = 5$

Find K_C for the reaction $A \rightleftharpoons D$ is

(1) 15 (2) 5 (3) 3 (4) 1

A.2 For $A \rightleftharpoons D$

$$\frac{[B]}{[A]} = K_1 = 1;$$

$$\frac{[C]}{[B]} = K_2 = 3;$$

$$\frac{[D]}{[C]} = K_3 = 5$$

$$K = K_1 \times K_2 \times K_3$$

$$\frac{[D]}{[A]} = 1 \times 3 \times 5 = 15$$

[Multiplying all the three]

Q.3 The equilibrium constants of the reactions

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

and $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

are K_1 and K_2, respectively. The relationship between K_1 and K_2 is

(1) $K_1 = K_2$	(2) $K_2^2 = K_1$
(3) $K_1^2 = K_2$	(3) $K_2 = \sqrt{K_1}$

A.3 $$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g); \quad \therefore K_1 = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$$

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g): \quad \therefore K_2 = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$\therefore K_2 = K_1^2$$

Q.4 The rate at which a substance reacts, depends on its

(1) Active mass	(2) Molecular mass
(3) Equivalent mass	(4) Total volume

A.4 Active mass

Q.5 For the reaction:

$$2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$$

Two moles each of A and B were taken into a flask. The following must always be true when the system attained equilibrium

(1) [A] = [B]	(2) [A] < [B]
(3) [B] = [C]	(4) [A] > [B]

A.5 For the reaction $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$ 2 mol of A reacts with 1 mol of B to give products. Hence, the concentration of A will be lesser than that of B at equilibrium.

Q.6 The equilibrium constant for the reaction

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

At a particular temperature is 100. Determine the values of equilibrium constants for the following reactions.

$2NO_2 \rightleftharpoons N_2 + 2O_2$ ....(1)

$NO_2 \rightleftharpoons 1/2\,N_2 + O_2$ ....(2)

A.6 The equilibrium constant for the reaction

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

$$K_c = \frac{[NO_2]^2}{[N_2][O_2]^2} = 100 \qquad \text{........(a)}$$

The equilibrium constant equation for reaction (1)

$$K_1 = \frac{[N_2][O_2]^2}{[NO_2]^2} \qquad \text{........(b)}$$

This equation is reciprocal of equation (a)

$$\text{So } K_1 = \frac{1}{K_c} = \frac{1}{100} = 1 \times 10^{-2}$$

The equilibrium constant equation for reaction (2)

$$K_2 = \frac{[N_2]^{1/2}[O_2]}{[NO_2]} \qquad \text{........(c)}$$

Comparing equation (a) and (c),

$$K_2 = \sqrt{K_1} = \sqrt{10^{-2}} = 10^{-1} = 0.1$$

Q.7 Given:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); K_1$$

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g); K_2$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g); K_3$$

The equilibrium constant for $2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$

will be

(1) $K_1K_2K_3$ (2) $\frac{K_1K_2}{K_3}$ (3) $\frac{K_1K_3^2}{K_2}$ (4) $\frac{K_2K_3^3}{K_1}$

A.7 $K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}; K_2 = \frac{[NO]^2}{[N_2][O_2]}; K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}}$

The equilibrium constant for

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

Will be

$$K = \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = \frac{K_2 \times K_3^3}{K_1}$$

Q.8 For a system, $A + 2B \rightleftharpoons C$, the equilibrium concentration are [A] = 0.06, [B] = 0.12, and [C] = 0.216. The K_c for the reaction is

(1) 120 (2) 400

(3) 4×10^{-3} (4) 250

A.8 $A + 2B \rightleftharpoons C$

$$K = \frac{[C]}{[A][B]^2} \Rightarrow \frac{(0.216)}{(0.06)(0.012)^2} = 250$$

Homogeneous Equilibrium

When all the reactant and the products are in the same phase for a homogeneous system. This phenomenon is termed as homogenous equilibrium. For example, in the gaseous reaction, $CaCO_3(\text{solid}) \xrightarrow{\Delta} CaO(\text{solid}) + CO_2(\text{gas})$, reactants and products are in the homogeneous phase.

Similarly, for the reactions,

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

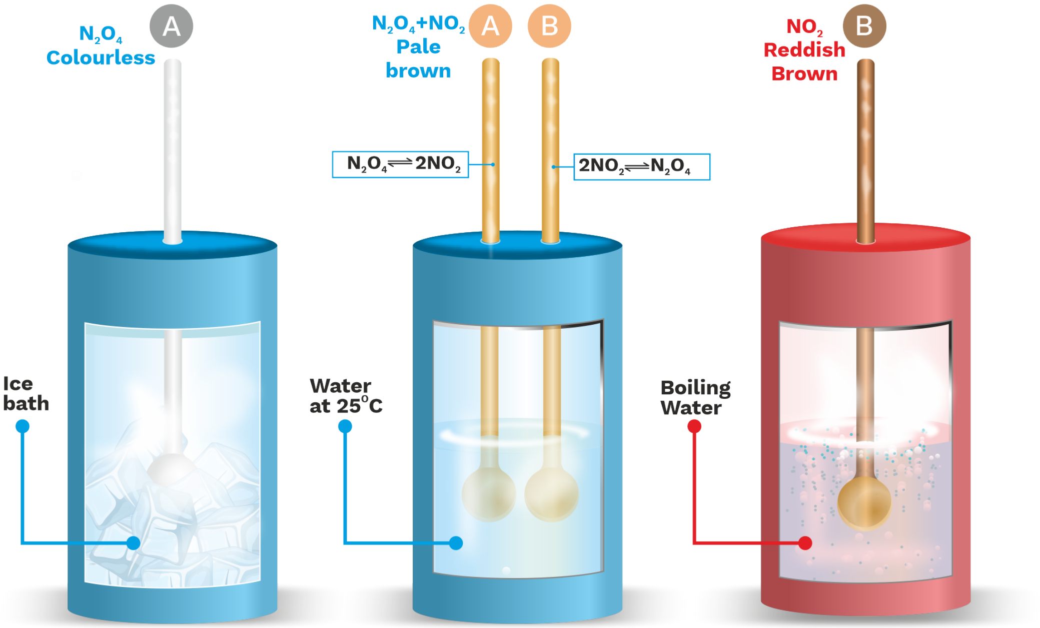
$$Fe^{3+}(aq) + SCBN^-(aq) \rightleftharpoons Fe(SCN^{2+})(aq)$$

Equilibrium constant in gaseous reaction

For gaseous reactions, equilibrium constant is expressed in terms of partial pressure. For example the decomposition of N_2O_4 into NO_2 in close container is gaseous reaction at equilibrium.

Concept Ladder

Is case of Homogeneous equilibrium of gases both the pressure and concentration of gases can be used to represent liquid and equilibrium states.



Ideal gas equation; $PV = nRT$

$$P = \frac{n}{V}RT \qquad \text{......(1)}$$

Where, P = Pressure of gas in "Bar"
n = number of moles of gas in mol
V = volume of gas in liter
T = absolute temperature in Kelvin "K"
R = 0.0831 bar L mol^{-} K^{-1}

Now form equation (1)

$$P = C.R.T. \text{ or } P = [gas]\ RT; \qquad \text{where } C = \frac{n}{V}$$

At constant temperature, pressure of gas is proportional to its concentration i.e.,

$$P \propto [gas]$$

for general reaction in equilibrium

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

or $$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Concept Ladder

R can have different units also.

R = 0.0821 atm. L $mol^{-1}K^{-1}$

$$= \frac{8.314\,J}{mol\ K}$$

$$= \frac{2\ cal}{mol\ K}$$

Equilibrium constant in terms of mole fraction

Consider a general reaction in equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

Amount of $A = X_A$ (mole fraction of A)

Amount of $B = X_B$ (mole fraction of B)

Amount of $C = X_C$ (mole fraction of C)

Amount of $D = X_D$ (mole fraction of D)

Now equilibrium constant in term of mole fraction

$$K_X = \frac{(X_C)^c (X_D)^d}{(X_A)^a (X_B)^b}$$

Relationship between K_c, K_p and K_X

(a) Relation between K_p and K_X

Consider a general reaction in equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

according to Raoult's Law

$$p_A = X_A.P$$

Where, p_A = partial pressure of gas A

X_A = mole fraction of gas A

P = Total pressure.

similarity; $p_B = X_B\,P$

$p_C = X_C\,P$

$p_D = X_D\,P$

Now; $$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

$$K_p = \frac{(X_C)(X_D)\,P^{(c+d)-(a+b)}}{(X_A)(X_B)}$$

$$K_p = K_X.P^{\Delta n}$$

where, $\Delta n_g = (c+d)-(a+b)$

(b) Relation between K_p and K_c

Consider a general reaction in equilibrium

$$aA + bB \rightleftharpoons cC + dD \quad \text{.........} \ (1)$$

$$p = \frac{n}{V}RT = CRT \text{ where } C = \frac{n}{V}$$

Concept Ladder

Active mass of a solid substance is taken as unity during calculations.

Previous Year's Question

Equilibrium constant K_p for the following reaction

$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$

[NEET]

(1) $K_p = P_{CO_2}$

(2) $K_p = P_{CO_2}\left(\frac{P_{CO_2} P_{MgO}}{P_{MgCO_3}}\right)$

(3) $K_p = \left(\frac{P_{CO_2} P_{MgO}}{P_{MgCO_3}}\right)$

(4) $K_p = \frac{P_{MgCO_3}}{P_{CO_2} \times P_{MgO}}$

for an ideal 'A', $p_A = C_A.RT$ .... (2)

where; p_A = Partial pressure of gas 'A'
C_A = concentration of gas 'A'
R = gas constant
T = absolute temperature

Similarly for gas 'B'

$$p_B = C_B.RT \quad ....(3)$$

$$p_C = C_C.RT \quad ....(4)$$

$$p_D = C_D.RT \quad ....(5)$$

Now K_p for the reaction (1) is

$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \quad .....(6)$$

Now put the values of (2), (3), (4) and (5) in the given equation (6), will get

$$K_p = \frac{[C]^c [D]^d (RT)^{(c+d)}}{[A]^a [B]^b (RT)^{(a+b)}}$$

Here R and T are constants

$$\text{Now,} \quad K_p = \frac{[C]^c [D]^d (RT)^{(c+d)-(a+b)}}{[A]^a [B]^b} \quad ....(7)$$

$$\text{where;} \quad K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Now above equation (7) becomes

Concept Ladder

$$K_P = K_C (RT)^{\Delta n_g}$$

where Δn_g = no. of moles of gaseous product no. of moles of gaseous reactant.
If $\Delta n_g > 0$, then $K_P > K_C$
If $\Delta n_g < 0$, then $K_P < K_C$
If $\Delta n_g = 0$, then $K_P = K_C$

Previous Year's Question

In which of the following equilibrium K_C and K_P are not equal? **[NEET]**

(1) $2NO(g) \rightleftharpoons N_2(g) + O_2 g$
(2) $SO(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
(3) $H_2(g) + I_2(g) \rightleftharpoons 2H(g)$
(4) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$

Relation Between K_p and K_c

$$K_P = \frac{[P_C]^C [P_D]^C}{[P_A]^a [P_B]^b} = \frac{[C]^c [P]^d}{[A]^a [B]^b} \; \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

Where $\Delta n_g = (c+d)-(a+b)$

$K_p = K_c(RT)^{\Delta n_g}$
if $\Delta n_g = 0$, then $K_P = K_C$

Δn_g = no. of moles of gaseous products-no. of moles of gaseous reactants

Units of equilibrium constant

Unit of $K_p = (atm)^{\Delta n_g}$

Unit of K_c = $(mol\ L^{-1})^{\Delta n}$

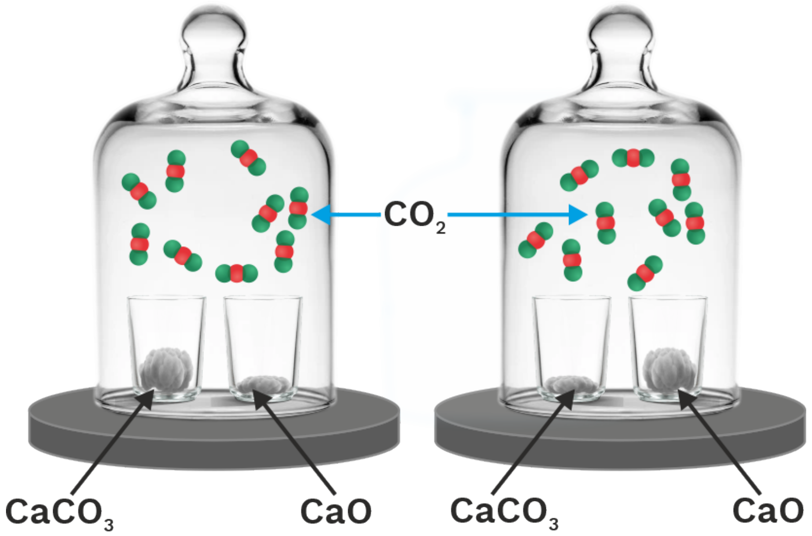
Unit of K_{X_c} = unit less

Heterogeneous Equilibrium

In a heterogeneous system, all the reactants and products are in different phases. For example, in the given reaction, $CaCO_3\,(solid) \overset{\Delta}{\rightleftharpoons} CaO\,(solid) + CO_2\,(gas)$, reactants and products are in the heterogeneous phase.

Rack your Brain

A reaction which is unimolecular w.r.t to forward reaction and bimolecular w.r.t backward reaction has 2 and 4 moles respectively what would be the relationship between K_p & K_C?



Aa long as some $CaCO_3$ or CaO remain in the system, the amount of CO_2 above the solid will remain the same.

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

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

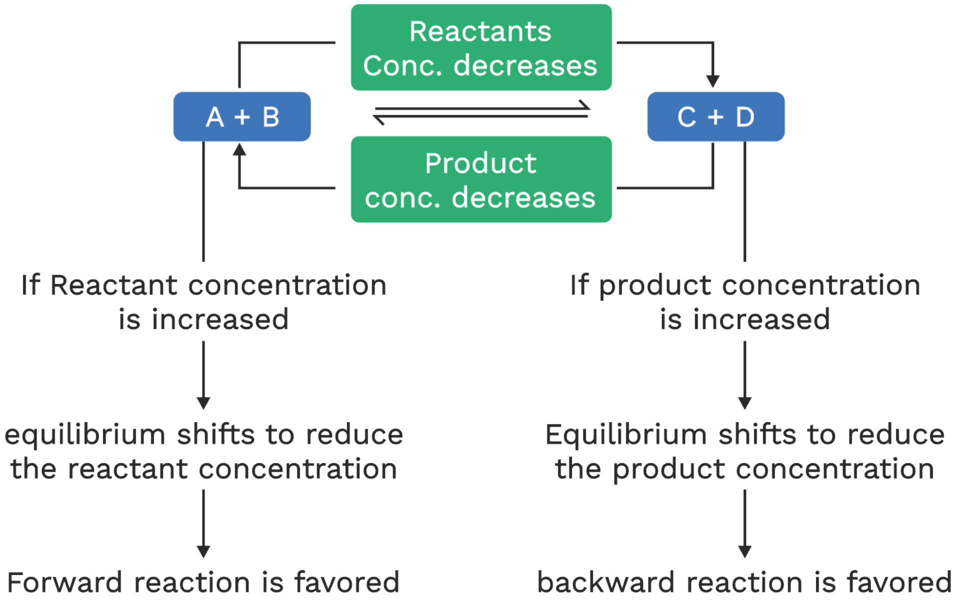
Similarly, for the reactions,

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_3(g)$$

Factors influencing equilibrium

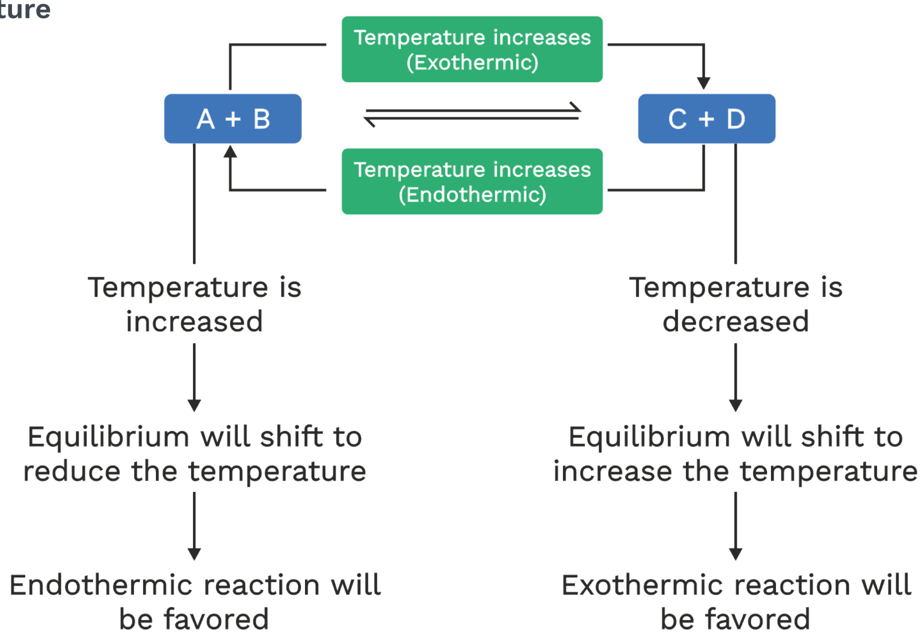
(a) Concentration



Note:

Increasing concentration of one side favours the other side.

(b) Temperature



Note :

- If the forward reaction exothermic then backward reaction will be endothermic and vice-versa.

- For exothermic reaction as temperature increases K decreases; for endothermic reaction as temperature increases K increases.

  According to van't Hoff equation

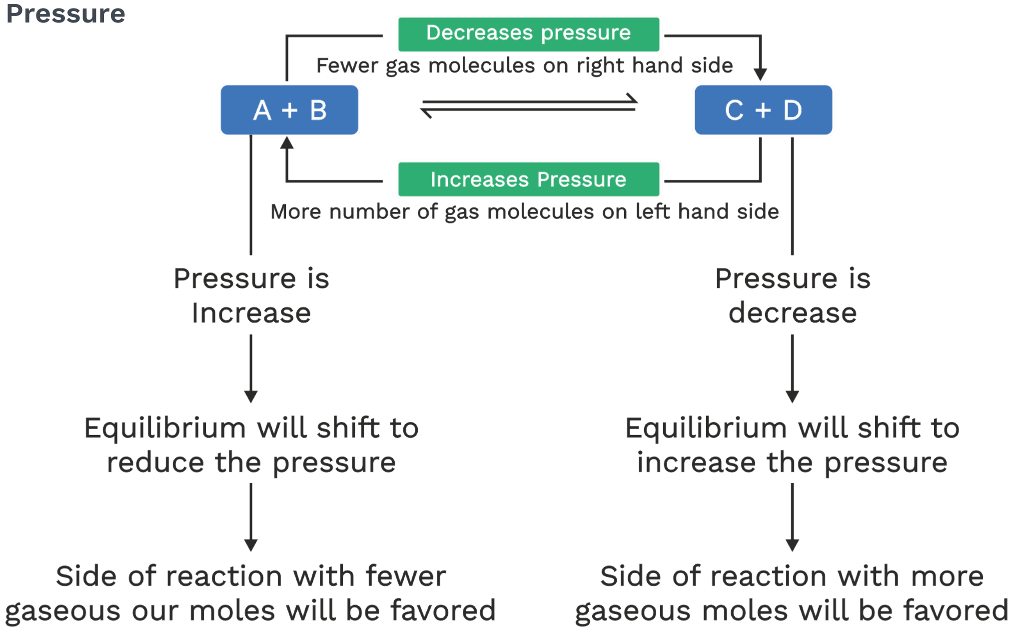
  $$\log\frac{K_2}{K_1}=\frac{\Delta H}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

  Where K_1 and K_2 are the equilibrium constants at temperature T_1 and T_2 respectively and ΔH is the molar enthalpy change in the temperature T_1 to T_2.

Concept Ladder

When the value of ethalpy change for the reaction would be zero than the value of K is independent of temperature.

(c) Pressure



Note:

If the number of gas molecules is the same on either side, then changing of pressure will have no effect.

Q.9 The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[N_2] = 1.5 \times 10^{-2}$M, $[H_2] = 3.0 \times 10^{-2}$M, and $[NH_3] = 1.2 \times 10^{-2}$M. calculate the equilibrium constant.

A.9 The equil. const. for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ can be written as

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = \frac{\left(1.2 \times 10^{-2}\right)^2}{\left(1.5 \times 10^{-2}\right)\left(3.0 \times 10^{-2}\right)^3} = 3.55 \times 10^2$$

Q.10 For the equilibrium,

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ K_c is 3.75×10^{-6} at 1069K. Calculate the K_p for this reaction at this temperature.

A.10 $K_p = K_c [RT]^{\Delta n}$

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

$K_p = 3.75 \times 10^{-6}(0.0831 \times 1069)^1 = 0.033$

Q.11 The equation constants of the dissociation of various oxides of an elements A are given at constant temperature:

(1) $2A_2O(g) \rightleftharpoons 2A_2(g) + O_2(g); K_C = 4.0 \times 10^{30}$

(2) $2AO(g) \rightleftharpoons A_2(g) + O_2(g); K_C = 2.0 \times 10^{27}$

(3) $2AO_2(g) \rightleftharpoons A_2(g) + 2O_2(g); K_C = 7.0 \times 10^{13}$

(4) $2A_2O_5(g) \rightleftharpoons 2A_2(g) + 5O_2(g); K_C = 1.0 \times 10^{31}$

Write the stability of these oxides in increasing order.

A.11 $A_2O_5 < A_2O < AO < AO_2$

At higher rate constant, the reaction will have more tendency to go on completion.

In this case, metal oxide dissociates in forward direction. Therefore, the metal oxide with lesser value of equilibrium constant will be stable.

Q.12 At a certain temperature, the equilibrium constant (K_c) is 16 for the reaction:

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If we take one mole of each of the four gases in one litre container, what would be the equilibrium concentration of NO and NO_2?

A.12

$$SO_2(g) + \quad NO_2(g) \quad \rightleftharpoons \quad SO_3(g) + NO(g)$$

Initial conc.	1	1	1	1
Equilibrium conc.	1-x	1-x	1+x	1+x

Applying the law of mass action,

$$K_C = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = 16$$

$$\frac{1+x}{1-x} = 4 \qquad \text{or } 1 + x = 4 - 4x$$

Concentration of NO_2 at equilibrium = (1 – 0.6) = 0.4 mol.

Concentration of NO at equilibrium = (1 + 0.6) = 1.6 mol.

Q.13 For an ideal gas reaction

$$2A + B \rightleftharpoons C + D$$

the value of Kp will be

(1) $K_p = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{V}{RT^2}$

(2) $K_p = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{V}{RT}$

(3) $K_p = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{RT}{V}$

(4) $K_p = \frac{n_C n_D}{4 n_A^2 n_B} \cdot \frac{V}{RT}$

A.13 $2A + B \rightleftharpoons C + D$

$$K_p = \frac{p_C \cdot p_D}{p_A^2 \cdot p_B} = \frac{\frac{n_C RT}{V} \cdot \frac{n_D RT}{V}}{\left(\frac{n_A RT}{V}\right)^2 \left(\frac{n_B RT}{V}\right)} = \frac{n_C n_D}{n_A^2 n_B} \cdot \frac{V}{RT}$$

Q.14 Prove that the pressure necessary to obtain 50% dissociation of PCl_5 at 250°C is numerically three times of K_p.

A.14

$$\begin{array}{lcccc} & PCl_5 & \rightleftharpoons & PCl_3 & + & Cl_2 \\ \text{(Inital mole)} & 1 & & 0 & & 0 \\ \text{(Mole at equilibrium)} & (1-0.5) & & 0.5 & & 0.5 \end{array}$$

Total mole of equilibrium = (1-0.5) + 0.5 + 0.5 = 1.5

$$K_p = \frac{p_{PCl_3} \cdot p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{0.5}{1.5}P\right)\left(\frac{0.5}{1.5}P\right)}{\left(\frac{0.5}{1.5}P\right)} \qquad \text{(where; } P = \text{inital pressure)}$$

$$\text{or } K_p = \frac{1}{3}P$$

$$\text{or } P = 3K_p$$

Q.15 At 700K, the equilibrium constant K_p for the reaction

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

is 1.80×10^{-3} kPa. What is the numerical value of K_c in moles per litre for this reaction at the same temperature?

A.15 Given

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

1 atm = 10^5 Pa; $\Delta n = 1$

$$K_p = 1.8 \times 10^{-3} \text{KPa} = 1.8\,\text{Pa} = 1.8 \times 10^{-5}\,\text{atm}$$

$$T = 700\,K$$

$$R = 0.082\,\text{lit.atm}$$

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

$$K_c = \frac{K_p}{RT}$$

$$K_c = \frac{1.8 \times 10^{-5}}{700 \times 0.0821} = 0.031 \times 10^{-5} = 3.1 \times 10^{-7}\,\text{mol}\,L^{-1}$$

Q.16 Write the expressions for equilibrium constant for the following reactions. If the concentrations are expressed in mol L^{-1}, give the units in each case.

(1) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(2) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

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

(4) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(5) $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$

A.16 (1) $K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$, units = mol L

(2) $K_c = \dfrac{[NO]^4\,[H_2O]^6}{[NH_3]^4\,[O_3]}$, units = mol L^{-1}

(3) $K_c = \dfrac{[NO]^4\,[H_2O]^6}{[NH_3]^4\,[O_3]}$, units = mol^{-2}L^{2}

(4) $K_c = \dfrac{[H_2][I_2]}{[HI]^2}$, no units

(5) $K_c = \dfrac{[NO_2]^4\,[O_2]}{[N_2O_4]^2}$; units = mol^{3}L^{-3}

Applications of Equilibrium constant

(1) It can predict the extent of reaction on the basis of its magnitude.

(2) Predicting the extent of a reaction

High value of equilibrium constant indicates that products concentration is high and its low value indicates that concentration of the products in equilibrium mixture is low

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

$$K_P = \frac{(p_{HBr})^2}{(p_{H_2})(p_{Br_2})} = 5.4 \times 10^{18}$$

The large volume of equilibrium constant indicates that concentration of the product,

Previous Year's Question

If the value of equilibrium constant for a particular reaction is 1.6 × 10^{12}, then at equilibrium the system will contain **[NEET]**

(1) Mostly products

(2) Similar amount of reactants and products

(3) All reactants

(4) Mostly reactants.

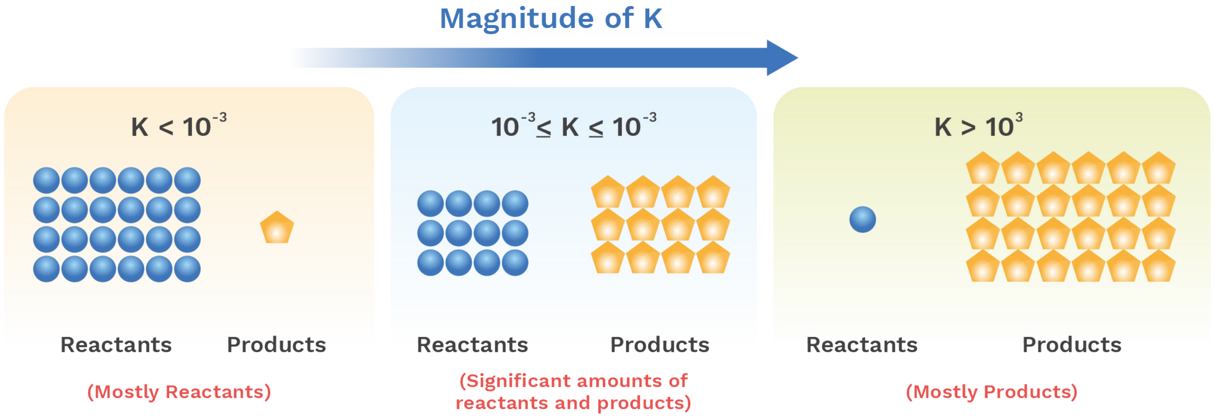
HBr is very high and reaction goes nearly to completion.

Similarly, equilibrium constant for [$H_2(g) + Cl_4(g) \rightleftharpoons 2\ HCl\ (g)$] is very high and reaction goes virtually to completion.

$$K_C = \frac{[HCl]^2}{[H_2][Cl_2]} = 4.0 \times 10^{31}$$

Rack your Brain

An equilibrium reaction has the value of rate constant as 3.8 × 10^{21}. What will happen to the reaction.



- The reaction of hydrogen with oxygen at 500 K temperature has a very large equilibrium constant,
  $K_c = 2.4 \times 10^{47}$
- When H_2O is decomposed into H_2 and O_2 at 500K, it has a very small equilibrium constant, $K_c = 4.1 \times 10^{-48}$

Note:

large value of K_p, or K_C (larger than about 10^3), favour the products strongly. For intermediated values of K (approximately in the range of 10^{-3} to 10^3), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than 10^{-3})., favour the reactants strongly.

At 298 K for reaction,

$$N_2,(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$K_C = \frac{[NO]^2}{[N_2][O_2]} = 4.8 \times 10^{-31}$$

Previous Year's Question

In Haber process, 30 litres of dihydrogen and 30 litres of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end? **[AIIMS]**

(1) 20 litres ammonia, 20 litres nitrogen, 20 litres hydrogen
(2) 10 litres ammonia, 25 litres nitrogen, 15 litres hydrogen
(3) 20 litres ammonia, 10 litres nitrogen, 30 litres hydrogen
(4) 20 litres ammonia, 25 litres nitrogen, 15 litres hydrogen

The very small value of. implies that reactants N_2, and O_2, will be the predominant species in the reaction mixture at equilibrium

(ii) Predicting the direction of the reaction.

The equilibrium constant is also used to find in which direction the reaction will proceed fora given concentration of reactants and products. For this purpose, we calculate the Reaction Quotient (Q). The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_c, or with partial pressure to give Q_P) at any stage of reaction. Fora general reaction:

$$n_1A + n_2B \rightleftharpoons m_1C + m_2D$$

$$Q_C = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}$$

Note:

If $Q_C > K_C$ the reaction will proceed in the backward direction

If $Q_c < K_c$, the reaction will move in the forward direction

If $Q_c = K_C$ then reaction will be in equilibrium.

(a) K>>1	If **K>>1,** the reaction is product-favoured; product predominates at **Equilibrium.**
(b) K>>1	If **K>>1,** the reaction is product-favoured; product predominates at **Equilibrium.**
(c) K=1	The reaction lies in the middle (mix of reactants and products)

Previous Year's Question

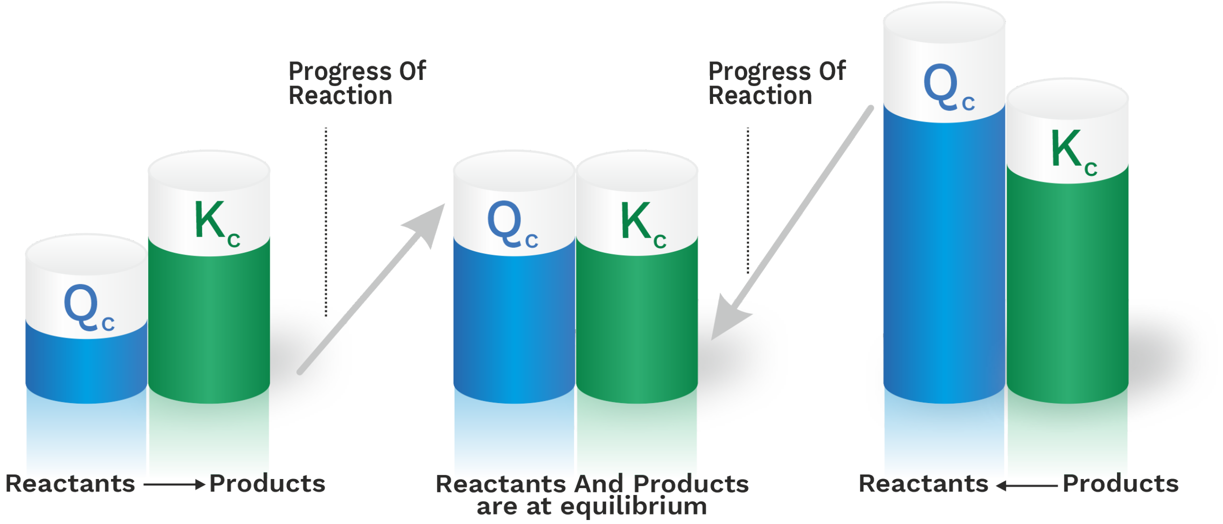
The reaction quotient (Q) for the reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

is given by $Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed from right to left if. **[AIPMT]**

(1) $Q = K_C$ (2) $Q < K_C$

(3) $Q > K_C$ (4) $Q = 0$



For example,

In the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, if the molar concentration of H_2, I_2 and HI are 0.1 mol L^{-1} respectively at 783K, then reaction quotient at this stage of the reaction is

$$Q_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

K_C for this reaction at 783 K at 46 and we find that $Q_C < K_C$. The reaction, therefore, will move to right i.e. more H_2 and I_2 will react to form more HI and their concentration will decrease till $Q_C = K_c$.

Degree of Dissociation

Degree of dissociation is the ratio of a mole of the reactant dissociated to the reactant present initially. It is represented by ‘α’

$$\alpha = \frac{\text{no. of moles of reactant dissociated}}{\text{no. of moles of reactant present initially}}$$

For example,

For reversible reaction

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

	$NH_3(g)$	$\frac{1}{2}N_2(g)$	$\frac{3}{2}H_2(g)$
Moles initially	a	0	0
At equilibrium;	$a(1-\alpha)$	$\frac{a\alpha}{2}$	$\frac{3a\alpha}{2}$

Here, α represented the degree of dissociation.

The process of formation of ammonia takes place by combination of nitrogen and hydrogen gases in the presence of molybdenum as promoter and iron as catalyst.

This process is known as Haber’s process. The reactants and products are in equilibrium phase with each other.

This process takes place at a temperature range 400 - 450 °C and pressure range of 150 - 200 atm.

Rack your Brain

The value of Q_C for a reaction is determined on the basis of active mass. Why not some other term is considered to calculate it?

Previous Year’s Question

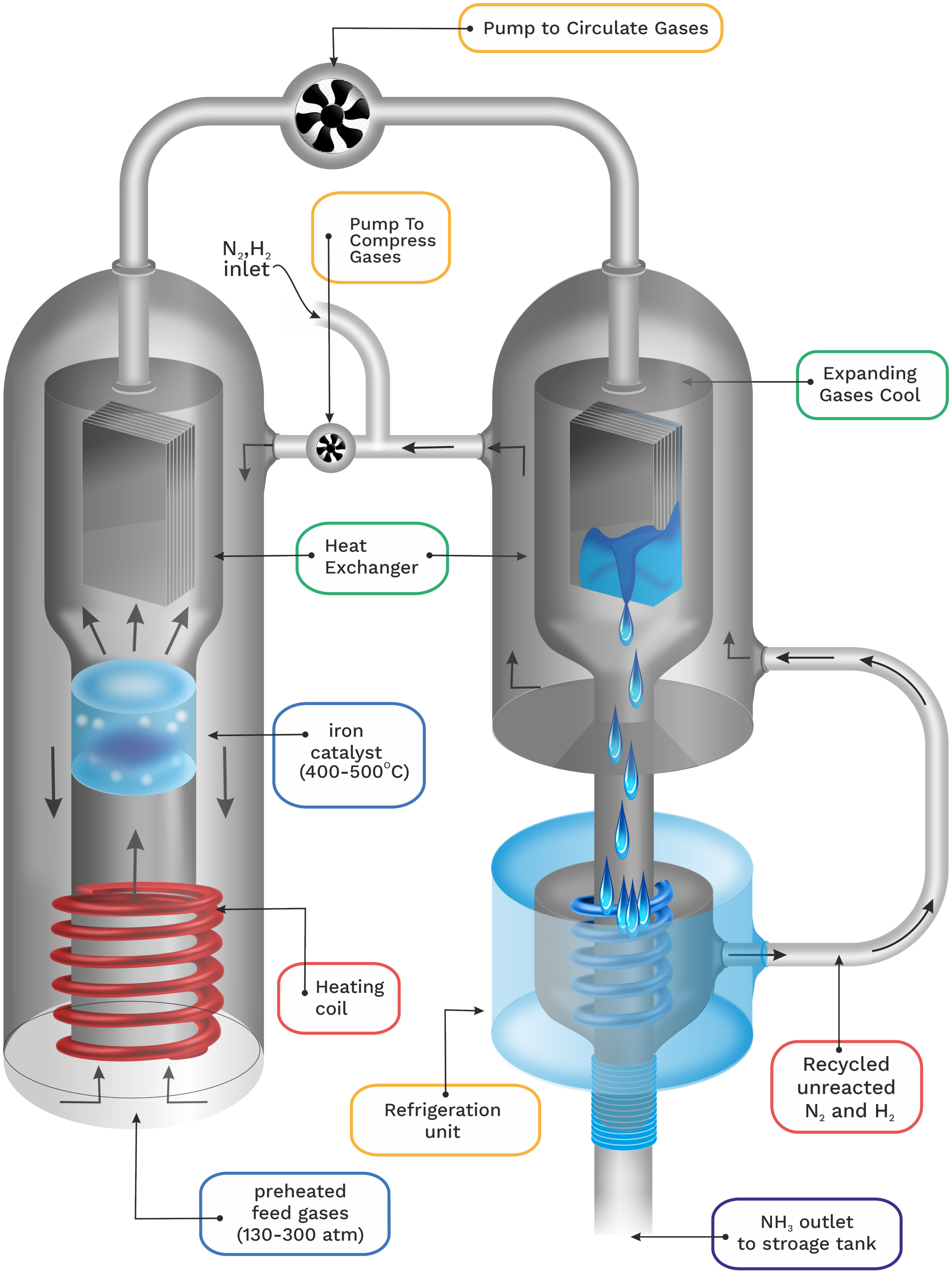
If α is dissociation constant, then the total number of moles for the reaction, $2HI \longrightarrow H_2 + I_2$ will be **[AIPMT]**

(1) 1 (2) 1-α

(3) 2 (4) 2-α

Definitions

Degree of dissociation is the fraction of molecules dissociated at any given time.


Pump to Circulate Gases
Pump To Compress Gases
N_2,H_2 inlet
Expanding Gases Cool
Heat Exchanger
iron catalyst (400-500°C)
Heating coil
Refrigeration unit
Recycled unreacted N_2 and H_2
preheated feed gases (130-300 atm)
NH_3 outlet to stroage tank

Q.17 2.56 gm of sulphur $S_8(s)$ is taken which is in equilibrium with its vapour according to reaction, If vapour occupies 960 mL at 1 atm and 273 K then the degree of dissociation of $S_8(s)$ will be

(1) 0.5
(2) 0.55
(3) 0.4
(4) 0.44

A.17 $$n_{S_8} = \frac{2.56}{8 \times 32} = 0.01$$

$$S_8(s) \rightleftharpoons 8S(g)$$

$$0.01(1-\alpha) \qquad 8 \times 0.1 \times \alpha$$

$$1 \times \frac{960}{1000} = (0.01 \times 8 \times \alpha) \times 0.08 \times 273$$

$$\alpha = 0.55$$

Q.18 For the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

The degree of dissociation (α) of HI(g) is related to equilibrium constant K_p by the expression.

(1) $\dfrac{1+2\sqrt{K_p}}{2}$
(2) $\sqrt{\dfrac{1+2K_p}{2}}$
(3) $\sqrt{\dfrac{2K_p}{1+2K_p}}$
(4) $\dfrac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

A.18

	$2HI(g) \rightleftharpoons$	$H_2(g) +$	$I_2(g)$
Initial	1	0	0
At equilibrium	$1-\alpha$	$\alpha/2$	$\alpha/2$

$$K_p = \frac{\left(\frac{\alpha}{2}P_T\right)^2}{(1-\alpha)^2 P_T^2} \qquad \left(\because K_p = \frac{P_{I_2} \times P_{H_2}}{(P_{HI})^2}\right)$$

$$\frac{\alpha}{1-\alpha} = 2\sqrt{K_p} \qquad \alpha = \frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$$

Q.19 For the dissociation reaction $N_2O \rightleftharpoons 2NO_2\left(g\right)$, the equilibrium constant K_P is 0.120 atm at 298K and total pressure of system is 2 atm. Calculate the degree of dissociation of N_2O_4.

A.19 For the reaction $N_2O \rightleftharpoons 2NO_2\left(g\right)$

Initial 1 0

At equilibrium (1-α) 2α

Let α be the degree of dissociation and P is the total pressure, then

Total number of moles $= 2\alpha + 1 - \alpha = 1 + \alpha$

$\therefore P_{N_2O} = \text{moles of } N_2O \times P_{\text{total}}$

$$= \left(\frac{1-\alpha}{1+\alpha}\right)P$$

and $P_{NO_2} = \left(\frac{2\alpha}{1+\alpha}\right)P$

$$\therefore K_P = \frac{\left(P_{NO_2}\right)^2}{P_{N_2O}} = \frac{\left[\left(\frac{2\alpha}{1+\alpha}\right)P\right]^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P}$$

$$= \frac{4\alpha^2P^2}{1+\alpha} \times \frac{1+\alpha}{\left(1-\alpha\right)P} = \frac{4\alpha^2P}{1-\alpha^2} \qquad \text{....... (i)}$$

Given atm; K_P = 0.120 atm; P = 2 atm

Substituting all the values in equation (i), we get

$$0.120 = \frac{4\alpha^2\left(2\right)}{\left(1-\alpha^2\right)} = \frac{8\alpha^2}{\left(1-\alpha^2\right)}$$

$$\Rightarrow 0.120\left(1-\alpha^2\right) = 8\alpha^2$$

Degree of dissociation, $\alpha = \left(\frac{0.120}{8.12}\right)^{1/2} = 0.121$

Calculation of K_P and K_C

(a) Homogeneous equilibrium in gaseous phase
(b) Homogeneous equilibrium in solution phase
(c) Equilibrium constant for various heterogeneous equilibrium

(a) Homogeneous equilibrium in gaseous phase

Formation of Nitric Oxide : ($\Delta n = 0$)

1. Calculation of K_C :–

Suppose the initial concentration of N_2 and O_2 is a and b respectively. x is the degree of dissociation.

	N_2 +	$O_2 \rightleftharpoons$	$2NO$
Initial moles	a	b	0
Moles at equilibrium	(a – x)	(b – x)	2x
Active mass (mol l^{-1})	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$

Here, V is the vol. of container in litre.

According to the law of mass action

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

Substitution the values in the above equation

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

$$\boxed{K_C = \frac{4x^2}{(a-x)(b-x)}}$$

K_C for this reaction is independent of V of the reaction container.

Concept Ladder

The numerical value of equilibrium constant K_C is not influenced by catalyst. Presence of a catalyst simply helps in attaining the equilibrium earlier

Previous Year's Question

The reaction,

$2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$

is begun with the concentrations of A and B both at an initial value of 1.00 M. When equilibrium is reached, the concentration of D is measured and found to be 0.25M. The value for the equilibrium constant for this reaction is given by the expression **[AIPMT]**

(1) $\left[(0.75)^3(0.25)\right] \div \left[(1.00)^2(1.00)\right]$
(2) $\left[(0.75)^3(0.25)\right] \div \left[(0.50)^2(0.75)\right]$
(3) $\left[(0.75)^3(0.25)\right] \div \left[(0.50)^2(0.25)\right]$
(4) $\left[(0.75)^3(0.25)\right] \div \left[(0.75)^2(0.25)\right]$

2. Calculation of K_P

All the thing being same as above, except pressure. Let P atmosphere is the pressure at equilibrium

	N_2	+	$O_2 \rightleftharpoons$	$2NO$
Initial moles	a		b	0
At equilibrium	(a – x)		(b–x)	2x

Total no. of moles = (a – x) + (b – x) + 2x = (a + b)

$$P_{N_2} = \frac{(a-x)P}{(a+b)}$$

$$P_{O_2} = \frac{(b-x)P}{(a+b)}$$

$$P_{NO} = \frac{(2x)P}{(a+b)}$$

According to the law of mass action

$$K_P = \frac{[P_{NO}]^2}{[P_{N_2}][P_{O_2}]}$$

Substituting the value of P_{NO}, P_{N_2}, P_{O_2} in the above equation of K_P.

$$K_P = \frac{\left[\frac{(2x)P}{(a+b)}\right]^2}{\left[\frac{(a-x)P}{(a+b)}\right]\left[\frac{(b-x)P}{(a+b)}\right]}$$

$$K_P = \frac{4x^2}{(a-x)(b-x)}$$

Thermal Dissociation of Phosphorus pentachloride ($\Delta n > 0$)

Rack your Brain

The value of K_P depends upon partial pressure of gases at equilibrium. Would it depend upon degree of dissociation?

Concept Ladder

K_P and K_C are equilibrium constant of ideal gas mixture considered under reversible reaction K_P is an equilibrium constant wrt. to atmospheric pressure and the K_C is the equilibrium constant wrt. concentration expressed in molarity.

Dissociation of PCl_5

1. **Calculation of K_C :** Suppose one mole of PCl_5 is take in a closed container of V litre. Further at equilibrium x mol of PCl_5 dissociated

	PCl_5	$\rightleftharpoons$	PCl_3 +	Cl_2
Initial moles	1		0	0
Moles at equilibrium	(1 – x)		x	x
Concentration (mol l^{-1})	$\frac{1-x}{V}$		$\frac{x}{V}$	$\frac{x}{V}$

According to law of mass action

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Substituting the values in the above equation.

$$K_C = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)}$$

$$\boxed{K_C = \frac{x^2}{(1-x)V}}$$

The formula of K_C has V in the denominator, hence the equilibrium will be affected by V of the reaction container for the given reaction.

If x << 1, then, 1 – x ≈ 1

So, $$K_C = \frac{x^2}{V}$$

$$x^2 = K_C.V$$

$$x^2 \propto V$$

$$\boxed{x \propto \sqrt{V}}$$

If we increase the volume, the dissociation x is also increased.

Previous Year's Question

The dissociation equilibrium of a gas AB_2 can be represented as:

$2AB_{2(g)} \rightleftharpoons 2AB_{(g)} + B_{2(g)}$

the degree of dissociation is x and is small compared to 1. the expression relating the degree of dissociation (x) with equilibrium constant K_P and total pressure P is **[AIPMT]**

(1) $(2K_P/P)^{1/2}$
(2) (K_P/P)
(3) $(2K_P/P)$
(4) $(2K_P/P)^{1/3}$

Concept Ladder

The numerical value of K_C is independent of initial concentration of reactants and product.

2. **Calculation of K_p**

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Initial moles 1 0
0

Moles at equilibrium (1 – x) x
x

total no. of moles at equilibrium,

$(1-x)+x+x=(1+x)$ moles

According to law of mass action

$$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

At equilibrium $P_{PCl_3} = \dfrac{x \times P}{(1+x)}$

$$P_{Cl_2} = \frac{x \times P}{(1+x)}$$

$$P_{PCl_5} = \frac{(1-x)P}{(1+x)}$$

Substituting the values in the above equation of K_P –

$$K_P = \frac{\left(\dfrac{x \times P}{1+x}\right)\left(\dfrac{x \times P}{1+x}\right)}{\dfrac{(1-x) \times P}{(1+x)}}$$

The equation of K_P is not independent of pressure.

Suppose, x<<1, then, $1 - x^2 \approx 1$

$$K_P = x^2 P$$

$$x^2 = \frac{K_P}{P}$$

$$\boxed{x \propto \frac{1}{\sqrt{P}}}$$

The degree of dissociation of PCl_5 is inversely proportional to the square root of pressure so, decrease of pressure increases dissociation of PCl_5.

Rack your Brain

Why the concentration of pure solid and liquid should be ignored while writing the equilibrium constant expression?

Previous Year's Question

In which of the following equilibrium K_C and K_P are not equal? **[AIPMT]**

(1) $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$

(2) $SO_{2(g)} + NO_{2(g)} \rightleftharpoons 2HI_{(g)}$

(3) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

(4) $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

Formation of Ammonia – ($\Delta n < 0$)

1. Calculation of K_c :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Initial moles	1	3	0
moles at equilibrium	$(1-x)$	$(3-3x)$	$2x$
Active mass (mol l^{-1})	$\left(\frac{1-x}{V}\right)$	$\left(\frac{3-3x}{V}\right)$	$\left(\frac{2x}{V}\right)$

According to law of mass action

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Substituting the values in the above equation

$$K_C = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3}$$

$$K_C = \frac{4x^2V^2}{(1-x)(3-3x)^3}$$

$$K_C = \frac{4x^2V^2}{27(1-x)^4}$$

The formula of K_C has V in the numerator; hence the equilibrium will be affected by V of the reaction container.

Dependence If, $x<<1$ then, $(1-x)^4 = 1$

$$K_C = \frac{4x^2V^2}{27}$$

$$x^2 = \frac{27K_C}{4V^2}$$

$$x^2 \propto \frac{1}{V^2} \qquad \boxed{x \propto \frac{1}{V}}$$

If we increase the volume of container the degree of dissociation x is decreased.

Previous Year's Question

Equilibrium constant K_P for following reaction

$$MgCO_{3(s)} \rightleftharpoons MgO_{(s)} + CO_{2(g)}$$

[AIPMT]

(1) $K_P = P_{CO_2}$

(2) $K_P = K_{CO_2} \times \frac{P_{CO_2} \times P_{MgO}}{P_{MgCO_3}}$

(3) $K_P = \frac{P_{CO_2} \times P_{MgO}}{P_{MgCO_3}}$

(4) $K_P = \frac{P_{MgCO_3}}{P_{CO_2} \times P_{MGo}}$

2. Calculation of K_P:

	$N_2 + 3H_2 \rightleftharpoons 2NH_3$		
Initial concentration	1	3	0
moles at equilibrium	(1-x)	(3-3x)	2x

Total number of moles at equilibrium $= (1-x) + (3-3x) + 2x = (4-2x)$

According to the law of mass action

$$K_P = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right) \times \left(P_{H_2}\right)^3}$$

At equilibrium; $p_{NH_3} = \dfrac{(2x).P}{(4-2x)}$

$$p_{N_2} = \frac{(1-x).P}{(4-2x)}$$

$$p_{H_2} = \frac{(3-3x).P}{(4-2x)}$$

Substituting the values in the above equation of K_P.

$$K_P = \frac{\left(\dfrac{2x}{4-2x}.P\right)^2}{\left(\dfrac{1-x}{4-2x}.P\right)\left(\dfrac{3-3x}{4-2x}.P\right)}$$

$$K_P = \frac{4x^2(4-2x)^2}{(1-x)(3-3x)^3P^2}$$

$$\boxed{K_P = \frac{16x^2(2-x)^2}{27(1-x)^4P^2}}$$

The equation of K_P is not independent of pressure

Suppose, x << 1 then,

$$(1-x)^4 = 1$$

And $(2-x)^2 = 4$

$$K_P = \frac{64x^2}{27P^2}$$

$$x^2 \propto P^2 \qquad \boxed{x \propto P}$$

If we increase the pressure the degree of dissociation x is also increased.

Previous Year's Question

A 20 litre container at 400K contains $CO_{2(g)}$ at pressure 0.4 atm and an excees of SrO (neglect the volume of solid SrO). the volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be

(Given by: $SrCO_{3(s)} \rightleftharpoons SrO_{(s)} + CO_{2(g)}$

K_P = 1.6 atm) **[NEET]**

(1) 10 litre (2) 4 litre

(3) 2 litre (4) 5 litre

(b) Homogeneous equilibrium is solution phase

Formation of ethyl acetate

Equilibrium is represented as

$$C_2H_5(OH)(\ell) + CH_3COOH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$$

Initial moles	1	1	0	0
Moles at equilibrium	1-x	1-x	x	x

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]}$$

$$K_C = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(1-x)}{v} \times \frac{(1-x)}{v}} = \frac{x^2}{(1-x)(1-x)}$$

(c) Equilibrium constant for various heterogeneous equilibrium

Heterogenous equilibrium results from a reversible reaction involving reactants and product that are in different phases. The law of mass action is applicable to a homogeneous equilibrium and is also applicable to a heterogeneous system.

Previous Year's Question

If the concentration of HO^- ions in the reaction

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

is decreased by 1/4 times, then equilibrium concentration of Fe^{3+} will increase by **[AIPMT]**

(1) 64 times (2) 4 times

(3) 8 times (4) 16 times

1. Decomposition of solid $CaCO_3$ into solid CaO and gaseous CO_2

Let 'a' moles of $CaCO_3$ are taken in a vessel of volume 'V' litre at temperature 'T' K.

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

Moles initially	a	0	0
Moles at equilibrium	a – x	x	x

$$K_{eq} = \frac{[CaO][CO_2]}{[CaCO_3]}$$

As $CaCO_3$ and CaO(s) are pure solids, so their concentration is unity

$$\therefore K_C = \frac{P_{CO_2}}{RT}$$

$$K_C(RT) = P_{CO_2}$$

Since K_C R and T are constant, their product will also be a constant referred as K_P.

$$\therefore K_P = P_{CO_2} = \frac{xRT}{V}$$

Simultaneous Equilibrium

In simultaneous equilibrium more than one equilibrium are established in a vessel at the same time and any one of the reactant or product is common in more than one equilibrium, then the equilibrium concentration of the common species in all the equilibrium would be same.

For example, if we take $CaCO_3$(s) and C(s) together in a vessel of capacity 'V' litre and heat it at temperature 'T' K, then CaCO3 decomposes to CaO(s) and CO_2(g). further, evolved CO_2 combines with the C(s) to give carbon monoxide. Let the moles of $CaCO_3$ and carbon taken initially be 'a' and 'b' respectively.

Concept Ladder

Equilibrium concentration of common species at equilibrium are always same in case of simultaneous equilibrium.

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

Moles at equilibrium $\quad a - x \quad x \quad (x - y)$

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

Moles at equilibrium $\quad (x - y) \quad (b - y) \quad 2y$

Thus, as CO_2 is common in both the equilibrium so its concentration is same in both the equilibrium constant expression.

Equiliibrium constant for first equilibrium,

$$K_{C_1} = [CO_2] = \frac{x - y}{V}$$

Equilibrium constant for second equilibrium,

$$K_{C_2} = \frac{[CO]^2}{[CO_2]} = \frac{(2y)^2 V}{V^2(x-y)} = \frac{4y^2}{V(x-y)}$$

Calculation of Degree of dissociation by vapour density measurement

Reactions in which there is a change in the number of moles after dissociation, the extent of dissociation can be determined by vapour density measurement.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initially	1	0	0	
Moles at equilibrium	(1 – a)	a	a	('α' is the degree of dissociation)

Total number of moles at equilibrium; $(1-\alpha)+\alpha+\alpha=(1+\alpha)$

V is the vol. occupied by 1 mol of $PCl_5(s)$ which have vapour density is 'D' before dissociation and after dissociation is 'd'. For the same conditions, the volume occupied by (1 + a) moles at equilibrium would be (1 + a)V litre.

$$\text{Density} \propto \frac{1}{\text{Volume}}$$

$$D \propto \frac{1}{V} \quad d \propto \frac{1}{(1-\alpha)V}$$

or $$\frac{D}{d}=\frac{\frac{1}{V}}{\frac{1}{(1+\alpha)V}}=(1+\alpha)$$

or $$\alpha=\frac{D}{d}-1=\frac{D-d}{d}$$

Molecular mass = 2 × Vapour density

So $$\alpha=\frac{M_t-M_0}{M_0}$$

Where, M_t = calculated molecular mass
M_0 = observed molecular mass

Concept Ladder

For polymerization reaction

$nA(g) \rightleftharpoons A_n(g)$,

where $n \geq 2$

$$\alpha=\frac{D-d}{d\left(\frac{1}{n}-1\right)}=\frac{M_t-M_0}{M_0\left(\frac{1}{n}-1\right)}$$

Rack your Brain

In which case the degree of dissociation constant be determined by measuring vapour density?

Q.20 At 627°C and 1 atm SO_3 is partially dissociated into SO_2 and O_2 by the reaction

$$SO_3(g) \rightleftharpoons SO_2(g) + 1/2O_2(g)$$

The density of the equilibrium mixture is 0.925g L^{-1}. What is the degree of dissociation.

A.20 Let the molecular mass of the mixture at equilibrium be .
Applying the reaction

$$M_{mix} = \frac{dRT}{P} = \frac{0.925 \times 0.0821 \times 900}{1} = 63.348$$

Molecular mass of $SO_3 = 80$

Vapour density of $SO_3, D = \frac{80}{2} = 40$

Vapour density of mixture, $d = \frac{68.348}{2} = 34.174$

Let the degree of dissociation be x.

$$x = \frac{D-d}{(n-1)d} = \frac{40-34.174}{\left(\frac{3}{2}-1\right) \times 34.174} = \frac{5.826 \times 2}{34.174} = 0.34$$

or x = 34% dissociated
i.e. SO_3 is 34% dissociated.

Q.21 The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.

A.21 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Molecular mass of $N_2O_4 = (28+64) = 92$

Vapour density, $D = \frac{92}{2} = 46$

Let the degree of dissociation be x.
Given, d = 30
Applying the relationship,

$$x = \frac{D-d}{d} = \frac{(46-30)}{30} = \frac{16}{30} = 0.533$$

Degree of dissociation = 53.3%

LE-CHAPTELIER'S PRINCIPLE

How an equilibrium state relieves the external stress?

How a state in equilibrium (a stable state) adjusts to the external stress (change in Temperature, pressure or concentration of reactants/products) is generalised in Le-Chatelier's principle.

Le-Chatelier's Principal states that :

If a stress is applied on a system in equilibrium, the equilibrium condition is upset; A net reaction occurs in that direction which tends to relieve the external stress and finally a new equilibrium is attained.

To understand its application to a system, let us consider following example :

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

ΔH = -92 kJ for Forward Reaction

ΔH = +92 kJ for Backward Reaction

Note :

ΔH : Enthalpy Change is a measure of heat evolved or heat absorbed in a chemical reaction. It is negative when heat is evolved and positive when heat is absorbed during a chemical change. You will learn details of it later in the Chapter on Chemical Energetics.

Note that in the above reaction :

(a) Forward reaction is exothermic (favours formation of NH_3) and backward reaction is endothermic (favours decomposition of NH_3)

(b) Formation of NH_3 results in decrease in number of moles (from 4 total moles of N_2 and H_2 to 2 total moles of NH_3) is a decrease in volume to right (in forward reaction)

(c) Both reactants and products are gases and they will be influenced by changes in P, T and changing concentrations.

Concept Ladder

According to Le-Chatelier, to get better yield of NH_3-

(a) High pressure

(b) Low Pressure

(c) High concentration of reactants

(d) Low concentration of product

Previous Year's Question

For the reversible reaction,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + \text{heat}$$

The equilibrium shifts in forward direction **[NEET]**

(1) by increasing the concentration of $NH_{3(g)}$

(2) by decreasing the pressure

(3) by decreasing the concentrations of $N_{2(g)}$ and $H_{2(g)}$

(4) by increasing pressure and decreasing temperature.

Effect of Temperature

Temperature can be increased by adding heat and can be decreased by taking out heat from the system.

- Increase the temperature by supplying heat: According to Le-Chatelier's principle the disturbed equilibrium state will move in that direction where heat is being absorbed (where stress is relieved) i.e., in endothermic direction. In case of given situation, reverse direction will be favoured (that being endothermic) till whole of extra heat in consumed. so NH3 will decompose on increasing temperature.
- Decrease the temperature by extracting heat: According to Le Chatelier's principle, the system will go in the direction where heat is evolved i.e. in exothermic direction. In given situation, forward reaction will be favoured (i.e. formation of NH_3) till the new equilibrium is again established.

Note:

The new equilibrium state has a new value of equilibrium constant K on changing the temperature.

Effect of Pressure

- Increase in pressure would result in decrease in volume thereby increasing the concentration (mol/L). The system will shift in a direction where number of moles decreases (decreasing concentration). In given situation, there is decrease in number of moles in forward direction, so increasing pressure favours forward reaction (i.e, formation of NH_3)
- Decreasing the pressure would mean lower number of moles/L. The system will shift in a direction which will produce more moles. In given situation, there is increase is number

Previous Year's Question

Which of the following information can be obtained on the basis of Le-Chatelier's principle. **[AIIMS]**

(1) entropy change in a reaction
(2) Dissociation constant of a weak acid
(3) Equilibrium constant of a chemical reaction
(4) Shift in equilibrium position on changing value of a constant

Rack your Brain

Why formation of NO requires high temperature whereas formation of NH_3 is preferred at low temperature?

Previous Year's Question

According to Le-Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause the **[NEET]**

(1) temperature to increase
(2) temperature to decrease
(3) amount of liquid to decrease
(4) amount of solid to decrease

of moles in reverse direction, so decreasing pressure favours backward reaction (i.e., decomposition of NH_3)

Effect of Concentration:

The Concentration can be changed in two ways :

(a) By removing some of a component or

(b) By adding some more of a component.

According to Le-Chatelier's principle :

- The addition of any component to any side (reactants and products) to a reaction in equilibrium, tends the equilibrium in the direction away from that side or one can say that it tends in that direction which consumes increase in concentration.
- In given situation ; increasing amount of pure N_2 and H_2 would favour formation of NH_3 . increasing amount of NH_3 would favour decomposition of NH_3
- The removal of any component from any side (reactants and products) of a reaction in equilibrium tends the equilibrium in the direction towards that side, or one can say the equilibrium tends in that direction which causes decrease in concentration.
- In given situation : Decreasing the amount of NH_3 from right side drives the equilibrium to forward direction i.e. favours formation of NH_3 . Decreasing amount of N_2 or H_2 from left drives the equilibrium to reverse direction i.e. favours decomposition of NH_3

Effect of Catalyst:

- Catalyst will increase the rate for both forward & backward reactions simultaneously and to the same extent in a reversible reaction. By increase in both rates, it reduces the time to reach equilibrium state.

Rack your Brain

What is the effect of a catalyst in a system at equilibrim?

Concept Ladder

Solubility of NaOH increases with temperature although dissolution is exothermic (an exception).

Previous Year's Question

Which one of the following inforation can be obtained on the basis of Le-Chatelier principle? **[AIPMT]**

(1) dissociation constant of a weak acid

(2) Entropy change in a reaction

(3) Equilibrium constant of a chemical reaction

(4) Shift in equilibrium position on changing value of a constraint

- Catalyst doesn't change the relative amounts of either reactants or products, therefore it has no effect on equilibrium constant

Evaluation of K_{eq} at different temperatures:

If K_1 be the equilibrium constant at T_1 (in Kelvin) and K_2 be the equilibrium constant at T_2 (in Kelvin) ($T_2 > T_1$), the two constants (K_1 & K_2) are related by Van't Hoff equation as follows:

$$\log_{10}\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Where ΔH° is the standard heat of reaction and R is gas constant.

Le-Chatelier's principle and Physical equilibrium:

Consider the physical equilibrium of change of state:

$$\text{solid} \rightleftharpoons \text{liquid}$$

Effect of pressure on melting:

When a solid melt, there is a decrease in volume for some solids (ice, quartz, carborundum, magnesium nitride, diamond etc.) and there is an increase in volume for some solids (gold, silver, sulphur, copper, iron etc.).

Melting of ice cause decrease in volume. For this type of system where there is a decrease in volume due to melting, increase in pressure will reduce the M.P. of the system. Thus, increasing the pressure will favour the melting of ice.

Similarly, increase in volume is cause due to melting of sulphur. For this type of system where there is an increase in volume due to melting, decreasing pressure will reduce the M.P. of the system. Thus, decrease in the pressure will favor the melting of sulphur.

Rack your Brain

Water boil at high temperature in pressure cooker why?

Concept Ladder

Liquid phase of H_2O, ie., water cannot exist above 647.15K and 218 atm. these values are called critical temperature and critical pressure for water.

Previous Year's Question

For a given exothermic reaction, K_P and K'_P are the equilibrium constants at temperature T_1 and T_2, respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2 it is readily observed that **[NEET]**

(1) $K_P > K'_P$
(2) $K_P < K'_P$
(3) $K_P = K'_P$
(4) $K_P = \dfrac{1}{K'_P}$

Vapour pressure of liquids:

Considering liquid vapour equilibrium, it is an endothermic reaction towards forward direction. Therefore rise in temperature will support evaporation. This means, increasing temperature results in increase in vapour pressure of the system.

Effect of pressure on boiling point:

With increase in pressure on the system : Liquid vapour; vapours condense lowering the vapour pressure of system. This means B.P. rises with increase in pressure as to reach the pressure required for the liquid to start boiling, needs to be increased.

Effect of temperature on solubility:

Generally, formation of solution (solute in solvent) is an endothermic process. For such cases, increase in temperature, increases the solubility of solutes. In such cases, where dissolution of solute is followed by evolution of heat; increase in temperature lowers the solubility of solutes.

Solubility of gases in liquid :

With increase in temperature, the solubility of a gas decreases. This implies that with lower temperature, more gas is present in a solution as compared to a solution with higher temperature.

Effect of pressure on solubility :

There is a decrease in volume of the gas (X(g) $\rightleftharpoons$ X(aq.)) when a gas is dissolved in liquid. Therefore, increase in pressure will favour the dissolution of gas in liquid.

Rack your Brain

Why sealed soda water bottle on opening shows the evolution of gas with effervescences?

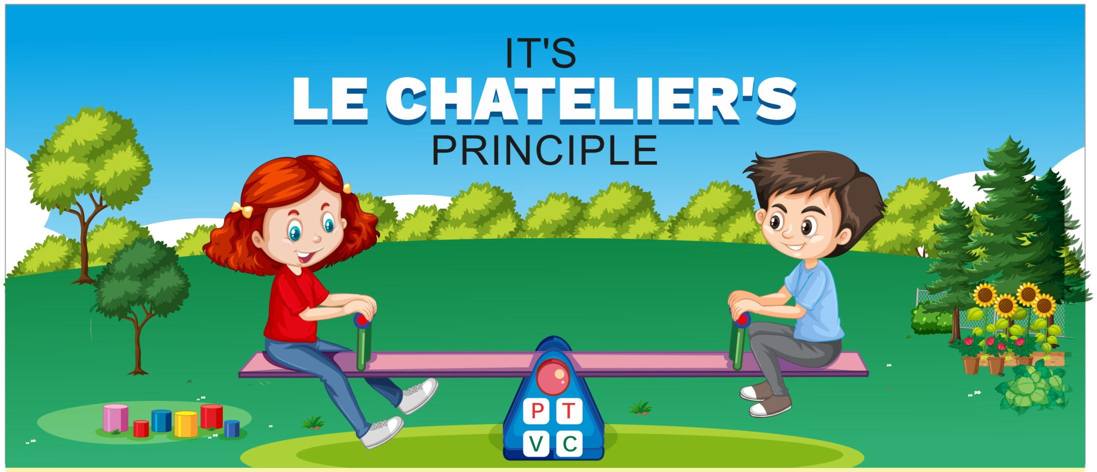
Concept Ladder

The solubility of NH_3 in water also involves H-bonding and thus, solubiliy of NH_3 in water depends on pressure as well as tendency to show H-bonding.

Rack your Brain

Ice melts slowly at higher altitude, Why?

IT'S LE CHATELIER'S PRINCIPLE



I WILL DESTROY YOUR EQUILIBRIUM

I WILL RE- ESTABLISH IT

Reactants	Products
Change a A + b B	c C + d D Counteract
I Will Increase Reactant Concentration	Then I Will Shift The Reaction Forward
I Will Steal Products	I Will Shift The Reaction Forward
I Will Increase Pressure	I Will Reduce Number Of Moles
I Will Decrease Pressure	Then I'll Increase Number Of Moles
I Will Heat Up Your Exothermic Reaction	I'll Shift The Reaction Backward
I Will Put Your Endothermic Reaction In Ice	I'll Warm It Up By Forward Reaction
I Will Catalyze Your Reaction	Hahaha.. It Won't Disturb My Equilibrium
I Will Add Noble Gases To Your Reaction	Hahaha.. It Won't Disturb My Equilibrium

How Did You Bypass My Tricks?

It's Le Chatelier's Principle Dear!

Q.22 What should be the respective active masses of methyl alcohol and carbon tetrachloride, if their densities are 0.5 and 1.2 g/mL?

(1) 15.62 and 7.79
(2) 16.65 and 7.40
(3) 15.46 and 7.80
(4) 15.40 and 6.50

A.22 (1)

Active mass = $\dfrac{\text{Density} \times 1000}{\text{Molecular weight}}$ (when density in g/mL)

(a) $[CH3OH] = \dfrac{0.5 \times 1000}{32} = 15.62 \text{ g mol L}^{-1}$

[Molecular weight of CH_3OH = 12 + 3 + 16 + 1 = 32]

(b) $[CCl4] = \dfrac{1.2 \times 1000}{154} = 7.79 \text{ g mol L}^{-1}$

[Molecular weight of CCl_4 = 12 + 35.5 × 4 = 12 + 142 = 154]

Q.23 Write down the equilibrium constant for the following reactions:

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(b) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(c) $3A + 2B \rightleftharpoons C + 4D$
(d) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(e) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$
(f) $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons$ CH¬3$COOC_2H_5(l) + H_2O(l)$
(g) $NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
(h) $H_2O(l) \rightleftharpoons H_2O(g)$

A.23 (a) $K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(b) $K = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

(c) $K = \dfrac{[C][D]^4}{[A]^3[B]^2}$

(d) $K = [CO_2]$ (Active mass of solid is 1)

(e) $K = [O_2]^3$

(f) $K = \dfrac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ (here H_2O is not in excess)

(g) $K = \dfrac{[NH_4^+][OH^+]}{[NH_3]}$ (here H_2O is in excess (solvent) so its concentration doesn't change.)

(h) $K = [H_2O](g)$

Q.24 If 0.5 mol of H_2 is reacted with 0.5 mol of I_2 in a 10 L container at 444°C and at same temperature value of equilibrium constant KC is 49, the ratio of [HI] and $[I_2]$ will be

(1) 7 (2) $\frac{1}{7}$ (3) $\sqrt{\frac{1}{7}}$ (4) 49

A.24 (1)

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$K_C = \frac{[HI]}{[H_2][I_2]} \text{ if } [H_2] = [I_2]$$

$$K_C = \frac{[HI]^2}{[I_2]^2}$$

$$\text{or} \quad \frac{[HI]}{[I_2]} = \sqrt{K_C} = \sqrt{49} = 7$$

Q.25 One mole of ammonium carbamate dissociate as shown below at 500 K.

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

If the pressure exerted by the released gases is 3.0 atm, the value of K_P is

(1) 7 atm (2) 3 atm (3) 4 atm (4) 8 atm

A.25 (3)

On applying the law of chemical equilibrium,

$$K_P = (P_{NH_3})^2(P_{CO_2})$$

Since total pressure is 3 atm, the partial pressure of $NH_3(g)$ and $CO_2(g)$ are

$$\left[P_{NH_3}\right] = 3 \times \frac{2}{3} = 2 \text{ atm}$$

$$\left[P_{CO_2}\right] = 3 \times \frac{1}{3} = 1 \text{ atm}$$

$$K_P = [2.0]^2 [1.0] = 4.0 \text{ atm}$$

Q.26 K_p for the reaction $A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$; is 0.05 atm. What will be its K_c at 1000 K in terms of R:

(1) $\dfrac{5\times10^{-5}}{R}$ (2) $\dfrac{R}{5\times10^{-5}}$ (3) $5 \times 10^{-5}R$ (4) None of these

A.26 (1)

We know that

$K_P = K_C\,(RT)^{\Delta n}$

or, $K_C = \dfrac{K_P}{(RT)^{\Delta n}}$

Here, $\Delta n = 4 - 3 = 1$

$T = 1000$ K, $K_P = 0.05$

$$K_C = \frac{0.05}{(R\times1000)^1} = \frac{5\times10^{-5}}{R}$$

Q.27 For $N_2O_3 \rightleftharpoons NO + NO_2$, if total pressure is P atm and amount of dissociation is 50%, the value of K_p will be:

(1) 3 P (2) 2 P (3) $\dfrac{P}{3}$ (4) $\dfrac{P}{2}$

A.27 (3)

	N_2O_3	$\rightleftharpoons$	NO	+	NO_2
Initial mol	1		0		0
at equilibrium	1 – 0.5		0.5		0.5

$$K_P = \frac{x^2P}{(1+x)(1-x)} = \frac{x^2P}{1-x^2}$$

$$K_P = \frac{0.5\times0.5\times P}{1.5\times0.5} = \frac{P}{3}$$

Q.28 The equilibrium constant for the reaction $H_2(g) + S(s) \rightleftharpoons H_2S(g)$; is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction will be:
(1) −68000.05 J mol^{-1}(2) −71080.57 J mol^{-1}
(3) −80071.75 J mol^{-1} (4) 57080.75 J mol^{-1}

A.28 (2)

Using the relation,

$$\log\frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{9.25}{18.5} = \frac{\Delta H}{2.303\times 8.314}\times\frac{75}{925\times 1000}$$

$$-0.301 = \frac{\Delta H}{2.303\times 8.314\times 925\times 1000} \Rightarrow \quad \Delta H = -71080.57 \text{ J mol}^{-1}$$

Q.29 In reaction,
$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta H° = -92$ kJ/mol^{-1}
concentrations of hydrogen, carbon monoxide and methanol become constant at equilibrium. What will happen if:
(1) Volume of the reaction vessel containing reactant and product is suddenly reduced to half?
(2) Partial pressure of hydrogen is suddenly doubled?
(3) An noble gas is added to the system at constant pressure?
(4) The temperature is increased?

A.29 For the equilibrium
$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

$$K_C = \frac{[CH_3OH]}{[CO][H_2]^2} \Rightarrow K_P = \frac{P_{CH_3OH}}{P_{CO}\times P_{H_2}^2}$$

(1) When the volume of the vessel is suddenly reduced to half, the partial pressure of various species gets doubled. Therefore,

$$Q_P = \frac{2P_{CH_3OH}}{2P_{CO}\times(2P_{H_2})^2} = \frac{1}{4}K_P$$

Since QP is less than KP, the equilibrium shift in the forward direction producing more CH_3COH.

(2) When partial pressure of hydrogen is suddenly, Q_P changes and is no longer equal to K_P.

$$Q_P = \frac{2P_{CH_3OH}}{P_{CO} \times (2P_{H_2})^2} = \frac{1}{4} K_P$$

Equilibrium will shift from left to right.

(3) When an noble gas is added to the system at constant pressure, equilibrium shifts from lower number of moles to higher number of moles (in backward direction).

(4) By increasing the temperature, K_P will decrease the equilibrium will shift from right to left.

Q.30 A mixture of 4.2 moles of N_2, 2.0 moles of H_2 and 10.0 moles of NH_3 is introduced into a 10.0 L reaction vessel at 500 K. At this temperature, equilibrium constant K_C is

1.7 × 102, for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(i) is the reaction mixture at equilibrium?

(ii) if not, what is the direction of the reaction?

A.30

$$[N_2] = \frac{4.2}{10} = 0.42 \text{ M}$$

$$[H_2] = \frac{2.0}{10} = 0.2 \text{ M}$$

$$[NH_3] = \frac{10}{10} = 0.1 \text{ M}$$

For the concentration, reaction quotient (Q) for the reaction

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

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.1)^2}{(0.42) \times (0.2)^3} = 2.976$$

But KC = 1.7 × 102

(i) Since $Q \neq K_C$, hence reaction is not at equilibrium.

(ii) Also $Q < K_C$, the reaction will proceed from left to right.

Chapter Summary

1. Equilibrium is termed as the point at which the rate of forward reaction is equal to the rate of backward reaction.

2. Chemical equilibrium is dynamic in nature and equilibrium state can be approached from both sides.

3. Active mass is molar concentration of the substance. Active mass of solid and pure liquid is taken as unity.

4. Equilibrium constant has definite value for every chemical reaction at a given temperature. It is independent of concentration and catalyst.

5. Overall K_C is equal to the product of equilibrium constant of individual reaction when a reaction is presented as the sum of two or more reactions.

6. Non-affecting factors of the equilibrium constant : The value of equilibrium constant is independent of the following factors :
   (a) Concentration of reactants and products.
   (b) Pressure
   (c) Volume
   (d) The presence of a catalyst.
   (e) Presence of inert materials

7. Degree of Dissociation

   $$\alpha = \frac{x}{a} \Rightarrow \% \, \alpha = \frac{x}{a} \times 100$$

   Where α = Degree of dissociation in percentage
   x = Number of dissociates moles
   a = Initial no. of moles

8. It is not necessary that all the types of equilibrium constants are defined for every reaction for eg. for a reaction involving only solutions K_p is not defined.

9. If inert gas mixed at constant temperature and constant volume in an equilibrium chemical reaction then total number of moles of gases are present in a container, increases i.e. total pressure of gases increases but concentration in terms of moles/litre and partial pressure of reacting substances are unchanged so dissociation (x) unchanged.

10. $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \rightarrow K_1$

$NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2}O_2(g) \rightarrow K_2$

then $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g) \rightarrow K$

So $K = K_1 \times K_2$

11. Change in temperature, pressure or concentration favours one of the reactions and thus shift the equilibrium point in one direction.

12. A catalyst allows the system to reach a state of equilibrium more quickly.

13. Pressure and volume has no effect on the reaction in which there is no change in the number of moles.

14. If the concentration of reactants is increased and product is removed, the reaction will take place in forward direction.

15. Free energy change

$\Delta G = \Delta G° + 2.303\ RT \log Q$ At equilibrium $\Delta G = 0$, (T is in Kelvin), $Q = K$ so

$\Delta G° = -2.303\ RT \log K$, where K is equilibrium constant.