**INTRODUCTION**

Chemical reaction: Symbolic representation of any chemical change in terms of reactants and products is called chemical reaction.

Ex. \[ N_2 + 3H_2 \rightleftharpoons 2NH_3 \]

**TYPES OF CHEMICAL REACTION:**

<table>
<thead>
<tr>
<th>Homogeneous reaction</th>
<th>Heterogeneous reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>All reactants and products are in same phase</td>
<td>Reactants and products are in more than one phase</td>
</tr>
<tr>
<td>( N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) )</td>
<td>( Zn(s) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g) )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reversible reaction</th>
<th>Irreversible reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Chemical reaction in which products can be converted back into reactants</td>
<td>(i) Chemical reaction in which products cannot be converted back into reactants.</td>
</tr>
<tr>
<td>( N_2 + 3H_2 \rightleftharpoons 2NH_3 )</td>
<td>( AgNO_3 + NaCl \rightarrow AgCl + NaNO_3 )</td>
</tr>
<tr>
<td>( 3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2 )</td>
<td>( NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl )</td>
</tr>
<tr>
<td>( H_2 + I_2 \rightleftharpoons 2HI )</td>
<td>( Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 )</td>
</tr>
<tr>
<td>(ii) Proceed in forward as well as backward direction.</td>
<td>(ii) Proceed only in one direction (forward).</td>
</tr>
<tr>
<td>(iii) To obtain reversible reactions, if anyone of the reactant or product is in gaseous state, then the reaction should be carried out in closed vessel.</td>
<td>(iii) Generally possible in open container.</td>
</tr>
<tr>
<td>( CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \uparrow )</td>
<td></td>
</tr>
<tr>
<td>(iv) These attain equilibrium.</td>
<td>(iv) These do not attain equilibrium.</td>
</tr>
<tr>
<td>(v) Reactants are never completely converted into products.</td>
<td>(v) Reactants are completely converted into products.</td>
</tr>
<tr>
<td>(vi) Generally thermal decomposition in closed vessel.</td>
<td>(vi) Generally thermal decomposition in open vessel.</td>
</tr>
<tr>
<td>( PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) )</td>
<td>( PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g) )</td>
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</table>

<table>
<thead>
<tr>
<th>On the basis of speed.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast reactions</td>
</tr>
<tr>
<td>(i) Generally these reactions are ionic reactions.</td>
</tr>
<tr>
<td>( HCl + NaOH \rightarrow NaCl + H_2O )</td>
</tr>
</tbody>
</table>
On the basis of heat

<table>
<thead>
<tr>
<th>Exothermic reaction</th>
<th>Endothermic reaction</th>
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<tbody>
<tr>
<td>(i) Heat is evolved in these chemical reaction</td>
<td>(i) Heat is absorbed in these chemical reaction</td>
</tr>
<tr>
<td>R → P + x kcal</td>
<td>R + x kcal → P</td>
</tr>
<tr>
<td>or R → P - x kcal</td>
<td></td>
</tr>
<tr>
<td>(ii) Change in heat energy</td>
<td>(ii) Change in heat energy</td>
</tr>
<tr>
<td>ΔQ = (+) ve</td>
<td>ΔQ = (-) ve</td>
</tr>
<tr>
<td>(iii) Change in enthalpy</td>
<td>(iii) Change in enthalpy</td>
</tr>
<tr>
<td>ΔH = (-) ve</td>
<td>ΔH = (+) ve</td>
</tr>
<tr>
<td>[ ΔH = -ΔQ ]</td>
<td></td>
</tr>
<tr>
<td>Eg. : Formation reaction</td>
<td>Eg. : Dissociation reaction</td>
</tr>
<tr>
<td>Exception ( N_2 + O_2 \rightarrow 2NO/ N_2O/ NO_2 )</td>
<td></td>
</tr>
<tr>
<td>( O_2 + F_2 \rightarrow O_2F_2/OF_2 )</td>
<td></td>
</tr>
</tbody>
</table>

**Active mass**: The term active mass means the concentration of the reactants & products expressed in moles per litre (molar concentration). Active mass is usually expressed by enclosing the symbol of the reactant in square bracket [   ]

\[
\text{Active mass} = \frac{\text{moles}}{\text{Volume in litres}} = \frac{\text{grams}(w)}{\text{mol.wt.}(M_w) \times \text{Volume in litres}(V)} = \frac{w \times 1000}{M_w \times V(\text{mL})}
\]

The active mass of solids and pure liquids is a constant quantity (unity) and solvent (excess) is considered as one. Because there is no change in activity with the change in quantity or volume of vessel.

Molar concentration \( = \frac{w}{M_w \times V_{\text{lit.}}} = \frac{\rho}{M_w} \) (\( \rho \) = density in g/lit)

\[
= \frac{\text{density of the substance}}{\text{molecular mass of the substance}}
\]

as density of pure solids and liquids is constant and molecular mass is also constant.

But this is not applicable to the substance in aqueous solution or gaseous state because their amount in a given volume can vary.

Following other names of active mass can also be use:

(i) mole/lit.  (ii) gram mole/lit.  (iii) gram molecules/lit.
(iv) molarity  (v) Concentration  (vi) Effective concentration
(vii) active quantity  (viii) n/v  (ix) C
(x) \( M \)  (xi) [ ]

**Examples**:

(a) 25.4 g of iodine is present in 2 litres of solution

\[ \left[ I_2 \right] = \frac{25.4}{254 \times 2} = 0.05 \text{ mole/litre} \]

(b) 8.5 g ammonia is present in a vessel of 0.5 litre capacity then

\[ \left[ \text{NH}_3 \right] = \frac{8.5}{17 \times 0.5} = 1 \text{ mole/litre} \]

(c) Active mass of C (s) or S(s) or Zn(s) is equal to 1.
RATE OF REACTION:
The change in concentration of reactants or products per mole in unit time is known as rate of the reaction.

\[ \text{Rate of reaction} = \frac{(-) \text{ change in concentration of reactants}}{\text{time}} = -\left(\frac{dc}{dt}\right)_{\text{reactants}}. \]

Here negative sign indicate that concentration of reactants decrease with time.

\[ \text{Rate of reaction} = \frac{(+ \text{ change in concentration of products}}{\text{time}} = +\left(\frac{dc}{dt}\right)_{\text{products}}. \]

Here positive sign indicate that concentration of products increase with time.

Note: The concentration change may be positive or negative but the rate of reaction is always positive.

Unit of rate of reaction = \( \frac{\text{mole/lit.}}{\text{sec}} = \text{mole/lit/sec} = \text{mole lit}^{-1} \text{sec}^{-1} \)

For example A \( \rightarrow \) B

For reactant \( \rightarrow -\frac{d[A]}{dt} \) [concentration decreases with time]

For product \( \rightarrow +\frac{d[B]}{dt} \) [concentration increases with time]

Ex. \( 2A + 3B \rightleftharpoons C + 4D \)

Rate of disappearance of A = \( -\frac{d[A]}{dt} \)

Rate of disappearance of B = \( -\frac{d[B]}{dt} \)

Rate of appearance of C = \( +\frac{d[C]}{dt} \)

Rate of appearance of D = \( +\frac{d[D]}{dt} \)

Rate of reaction (ROR) = \( -\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = +\frac{d[C]}{dt} = +\frac{1}{4}\frac{d[D]}{dt} \)

Note: Rate of reaction is always for per mole.

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

Rate of reaction = \( -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt} \)

Ex. For the reaction \( 2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 \)

rate of reaction is \( 2.5 \times 10^{-4} \text{ moles/lit.sec} \) then find out the rate of disappearance of \( \text{SO}_2 \).

Ans. \( \text{ROR} = -\frac{1}{2}\frac{d[\text{SO}_2]}{dt} = -\frac{d[\text{O}_2]}{dt} = 2.5 \times 10^{-4} \text{ mole/lit.sec.} \)

\( -\frac{d[\text{SO}_2]}{dt} = 5 \times 10^{-4} \text{ mole/lit.sec.} \)
FACTORS AFFECTING RATES OF REACTIONS:
(a) **State of matter**: The decreasing order of rate of reaction in gas, liquid and solid state are—
g > l > s
(b) **Temperature**: Rate of reaction α temperature
(c) **Concentration**: Rate of reaction α concentration.
(d) **Catalyst**: Positive catalyst increases the rate of reaction.

CHEMICAL EQUILIBRIUM:
The state of the reversible chemical reaction at which rate of forward reaction becomes equal to rate of backward reaction.

\[ A + B \xrightarrow{R_f} C + D \quad R_f = \text{forward rate of reaction} \]
\[ \quad R_b = \text{backward rate of reaction} \]

i.e. \[ R_f = R_b \]

or The state of the reversible chemical reaction at which the measurable properties of the system like temperature, concentration, colour, density etc. don’t undergo any change with time at the given set of conditions is said to be chemical equilibrium conditions. Rate of forward reaction decreases as the concentration of products increases, rate of backward reaction also starts increasing.

At a certain stage, rate of forward reaction becomes equal to rate of backward reaction called equilibrium state.

AT EQUILIBRIUM STATE:
Rate of forward reaction = Rate of backward reaction

✦ At this state of equilibrium forward and backward reactions proceeds with same speed.
✦ The stage of the reversible reaction at which the concentrations of the reactants and products do not change with time is called the equilibrium state.
✦ The equilibrium state is dynamic in nature.
✦ The reaction does not stop, but both the opposing reactions are going on continuously with same speeds.

CHARACTERISTICS OF EQUILIBRIUM:
(a) Chemical equilibrium is dynamic in nature means the reaction, although appears to be stopped, but actually takes place in both the directions with the same speed.
(b) To obtain equilibrium, if anyone of the reactant or product is in gaseous state then the reaction should be carried out in closed vessel.
(c) At a given temperature and pressure of equilibrium the properties like concentration, colour, density remains constant.
(d) In a reversible chemical reaction the equilibrium state can be attained in lesser time by the use of positive catalyst.
   A catalyst doesn’t change the equilibrium state because it increases the rate of both forward and backward reaction simultaneously by changing the path of reaction and it helps in attaining equilibrium rapidly.
(e) In order to prevent escape of products, equilibrium is reached in only in closed vessels in reversible reactions.
(f) Homogeneous equilibrium is the equilibrium in which the reactants and products are in the same phase.
   \[ \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(l) + \text{C}_2\text{H}_5\text{OH}(l) \]
(g) Heterogeneous equilibrium is the equilibrium in which the reactants and products are in two or more phases.
   \[ \text{Zn(s)} + \text{CO}_2(g) \rightleftharpoons \text{ZnO(s)} + \text{CO(g)} \]
Note:
(i) Whenever question doesn't ask about direction, then we take forward direction only.
(ii) In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice versa.

**TYPES OF EQUILIBRIA:**

There are two types of equilibria:

1. **Physical equilibria:**
   
   If in a system only physical state (phase) is changed and then equilibrium is established, (i.e. there is no chemical change) the equilibrium is called physical equilibrium.
   
   e.g. Fusion of ice, evaporation of water, dissolution of salts and absorption of gases in liquid etc.
   
   Following are the types of common physical equilibria:
   
   (i) **Liquid-Vapour equilibria**: In a closed vessel, the vapours above the liquid are in equilibrium at given temperature.
   
   Ex. \( \text{H}_2\text{O (l) } \underset{\text{H}_2\text{O (g)}}{\rightleftharpoons} \)
   
   (ii) **Solid-Liquid equilibria**: This equilibrium can be established only at melting point of solid. At this stage solid and liquid phases exist simultaneously in equilibrium.
   
   Ex. \( \text{H}_2\text{O (s) } \underset{\text{H}_2\text{O (l) at melting point}}{\rightleftharpoons} \)
   
   (iii) **(Solute-Solvent), Saturated solution equilibria**: If the rate of dissolution of solids in liquid is equal to the rate of crystallization of solid from solution i.e. solution is saturated with respect to solid then saturated solution equilibrium established, provided temperature is constant.
   
   Ex. \( \text{NaI (s) } \underset{\text{Na}^+ (aq.) + \text{I}^- (aq.)}{\rightleftharpoons} \)
   
   **Note**: Above example is of solubility of sparingly soluble salt, which only depends on temperature.
   
   (iv) **(Gas + Solvent), Saturated solution equilibria**: In such equilibriums, solvents is saturated with respect to gas i.e. rate of entering of gas molecules in solvent is equal to rate of escaping of gas molecules from solvents. Above phenomenon can be observed in closed container at definite temperature.
   
   Ex. Dissolved CO\(_2\) in cold drinks. Dissolved O\(_2\) in water etc.

**Note**:
(i) The solubilities of gases in liquid is a function of pressure of gas over liquid.
(ii) Henry's law can be applied on such system, that states, the mass of gas dissolved in a given mass of solvent at any temperature is proportional to the pressure of the gas above the solvent.

\[ C_g \propto P_g \quad \text{or} \quad C_g = k P_g \]

where \( k = \text{Henry's constant} \)

\( C_g = \text{Solubility of gas in the solution (mol L}^{-1}) \)

\( P_g = \text{Pressure of the gas} \)

(iii) One should not compare it with liquid vapour equilibria.

2. **Chemical equilibria**:

When chemical change occur in a reversible reaction i.e. reactants convert into products and products also convert into reactants under similar conditions of pressure and temperature, the reaction is said to be in chemical equilibria.

(i) \( \text{H}_2\text{ (g) + I}_2\text{ (g) } \underset{\text{2HI (g) (formation of HI)}}{\rightleftharpoons} \)

(ii) \( \text{SO}_2\text{ (g) + Cl}_2\text{ (g) } \underset{\text{SO}_2\text{Cl}_2\text{ (g) (formation of SO}_2\text{Cl}_2)}{\rightleftharpoons} \)

(iii) \( \text{PCl}_3\text{ (g) + Cl}_2\text{ (g) } \underset{\text{PCl}_5\text{ (g) (formation of PCl}_5\text{)}}{\rightleftharpoons} \)

(iv) \( 2\text{NH}_3\text{ (g) } \underset{\text{N}_2\text{ (g) + 3H}_2\text{ (g) (Decomposition of NH}_3\text{)}}{\rightleftharpoons} \)
EXAMPLES:

Ex. Chemical equilibrium is a condition:
(A) where all species have same concentration
(B) where all species have constant concentration with respect to time.
(C) where all species have concentration = 1
(D) all of above

Sol. (B)
Chemical equilibrium defined as when all species have constant concentration with respect to time.

Ex. Example of physical equilibria, is:
(A) \( \text{H}_2 (g) + \text{I}_2 (g) \rightleftharpoons 2\text{HI} (g) \)
(B) \( \text{CaCO}_3 (s) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (g) \)
(C) \( \text{H}_2\text{O} (s) \rightleftharpoons \text{H}_2\text{O} (l) \)
(D) \( \text{PCl}_5 (g) \rightleftharpoons \text{PCl}_3 (g) + \text{Cl}_2 (g) \)

Sol. (C)
Physical equilibria does not include any chemical change.

Ex. At equilibrium:
(A) the energy of system is minimum
(B) the entropy of system is maximum
(C) the energy of system is maximum
(D) the entropy of system is minimum

Sol. (A,B)
It is the compromising stage of minimum energy and maximum entropy.

LAW OF MASS ACTION OR LAW OF CHEMICAL EQUILIBRIUM:
The law of mass action is given by Guldberg and Waage.
According to them at a given temperature rate of reaction is proportional to product of active masses of reactants at that instant raised to the powers which are numerically equal to the number of their respective molecule in the stoichiometric equation describing the reaction.

Derivation of equilibrium constant:
Consider a reversible homogeneous reaction which has attained equilibrium state at particular temperature:

\[ \text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \]

Let the active masses of \( \text{A} \), \( \text{B} \), \( \text{C} \) and \( \text{D} \) be \( [\text{A}] \), \( [\text{B}] \), \( [\text{C}] \) & \( [\text{D}] \) are respectively.

According to law of mass action:
rate of forward reaction \( \alpha [\text{A}] [\text{B}] \)
rate of backward reaction \( \alpha [\text{C}] [\text{D}] \)

\[ R_f = K_f [\text{A}] [\text{B}] \quad R_b = K_b [\text{C}] [\text{D}] \]

Where \( K_f \) and \( K_b \) are forward and backward rate constants respectively.

At equilibrium
\[ R_f = R_b \]
\[ K_f [\text{A}] [\text{B}] = K_b [\text{C}] [\text{D}] \]

\[ \frac{K_f}{K_b} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \]

\[ K_c = \frac{K_f}{K_b} \]

\( K_c \) is known as equilibrium constant \( K_c \) has a definite value for every chemical reaction at particular temperature.
For a general reaction

\[ m_1A + m_2B + m_3C \rightleftharpoons n_1M + n_2N + n_3O \]

\[ r_i \propto [A]^{m_1} [B]^{m_2} [C]^{m_3} \]

\[ r_i = K_i [A]^{m_1} [B]^{m_2} [C]^{m_3} \quad [K_i = \text{forward rate (velocity) constant}] \]

\[ r_b \propto [M]^{n_1} [N]^{n_2} [O]^{n_3} \]

\[ r_b = K_b [M]^{n_1} [N]^{n_2} [O]^{n_3} \quad [K_b = \text{backward rate (velocity) constant}] \]

At equilibrium

\[ r_i = r_b \]

\[ K_c = \frac{K_i}{K_b} = \frac{[M]^{n_1} [N]^{n_2} [O]^{n_3}}{[A]^{m_1} [B]^{m_2} [C]^{m_3}} \]

The equilibrium constant, at a given temperature, is the ratio of the rate constants of forward and backward reactions.

**Ex.** Write down the equilibrium constant for the following reactions.

(a) \( N_2 + 3H_2 \rightleftharpoons 2NH_3 \)

(b) \( \text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2 \)

(c) \( 3A + 2B \rightleftharpoons C + 4D \)

(d) \( \text{CaCO}_3 (s) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (g) \)

(e) \( 2\text{KClO}_3(s) \rightleftharpoons 2\text{KCl}(s) + 3\text{O}_2(g) \)

(f) \( \text{CH}_3\text{COOH} (l) + \text{C}_2\text{H}_5\text{OH} (l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 (l) + \text{H}_2\text{O} (l) \)

(g) \( \text{NH}_3 (aq) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ (aq) + \text{OH}^- (aq) \)

(h) \( \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_2\text{O} (g) \)

**Ans.**

(a) \( K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \)

(b) \( K = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \)

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

(d) \( K = [\text{CO}_2] \quad (\text{Active mass of solid is 1}) \)

(e) \( K = [\text{O}_2]^3 \)

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

(g) \( K = \frac{[\text{NH}_3][\text{OH}^-]}{[\text{NH}_3]} \)

(h) \( K = [\text{H}_2\text{O}]_{\text{aq}} \)

The equilibrium constant, at a given temperature, is the ratio of the rate constants of forward and backward reactions.

For reactants, stability increases when value of \( K \) decreases.

For products, stability increases when value of \( K \) increases.

(more is the value of equilibrium constant, more is the formation of product means more is the stability of product.)

Time taken to attain equilibrium increases when value of \( K \) decreases.
FORMS OF EQUILIBRIUM CONSTANT:

There are two forms.

(i) Concentration form \((K_c)\)  
(ii) Partial pressure form \((K_p)\)

**Partial pressure:** The individual pressure exerted by the gases substance of the total pressure is called partial pressure of the gases substance.

\[
\text{Partial pressure} = \frac{\text{Moles of substance}}{\text{Total moles}} \times P_{\text{total}} \Rightarrow \frac{\text{Moles of substance}}{\text{Total moles}} = \text{Mole fraction}
\]

Let \(n_1 + n_2 + n_3 + n_4 = N\)

\[
P_A = \frac{n_1}{N} P_t, \quad P_B = \frac{n_2}{N} P_t, \quad P_C = \frac{n_3}{N} P_t, \quad P_D = \frac{n_4}{N} P_t
\]

**Q.** A vessel contains 5 moles of A & 10 moles of B. If total pressure is 18 atm. Find out partial pressure of gases.

**Ans.**

\[
P_A = \frac{5}{15} \times 18 = 6 \text{ atm}
\]

\[
P_B = \frac{10}{15} \times 18 = 12 \text{ atm}
\]

When the reactants and products are in gaseous state then partial pressure can be used instead of concentration. At a definite temperature, as the partial pressure of a substance is proportional to its concentration in the gas phase.

\[
m_1 A + m_2 B \rightleftharpoons n_1 C + n_2 D
\]

If partial pressure of A, B, C and D at equilibrium are \(P_A', P_B', P_C', P_D'\) respectively, then

\[
K_p = \frac{(P_C')^{n_1} (P_D')^{n_2}}{(P_A')^{m_1} (P_B')^{m_2}}
\]

**RELATION BETWEEN** \(K_p\) **AND** \(K_c\) **:**

This relation can be established for reaction not involving liquids because \(k_p\) is not defined for liquids.

Consider a reversible reaction

\[
m_1 A + m_2 B \rightleftharpoons n_1 C + n_2 D
\]

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

\[
K_p = \frac{(P_C')^{n_1} (P_D')^{n_2}}{(P_A')^{m_1} (P_B')^{m_2}}
\]

For an ideal gas \(PV = nRT\)

\[
P = \frac{n}{V} \times RT = \text{active mass} \times RT
\]

\[
\therefore n = \text{number of mole and } V = \text{Volume in litre}
\]

So \(\frac{n}{V}\) = molar concentration or active mass

\[
P = \left[ \right] \times RT
\]

at constant temperature \(P \propto \left[ \right]\)
\[ P_A = [A] \text{RT}, \quad P_B = [B] \text{RT}, \quad P_C = [C] \text{RT}, \quad P_D = [D] \text{RT} \]
\[ R = \text{gas constant} \]
\[ = 0.0821 \text{lit. atm. K}^{-1} \text{mol}^{-1} \]
\[ = 8.314 \text{ J K}^{-1} \text{mol}^{-1} \]
\[ = 1.98 \approx 2 \text{ Cal K}^{-1} \text{mol}^{-1} \]

So \[ K_p = \frac{[C]^n [D]^m}{[A]^r [B]^s} \]

\[ K_p = \frac{[C]^n [D]^m}{[A]^r [B]^s} \]

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

\[ \Delta n = (n_1 + n_2) - (m_1 + m_2) \]

= total number of gaseous molecules of products - total number of gaseous molecules of reactants.

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

Ex. Find the values of \( K_c \) for each of the following equilibria from the value of \( K_p \).

(a) \[ 2\text{NOCl} (g) \rightleftharpoons 2\text{NO} (g) + \text{Cl}_2 (g) \quad K_p = 1.8 \times 10^{-2} \text{ at 600 K} \]

(b) \[ \text{CaCO}_3 (g) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (g) \quad K_p = 167 \text{ at 1173 K} \]

Sol.

(a) \[ 2\text{NOCl} (g) \rightleftharpoons 2\text{NO} (g) + \text{Cl}_2 (g) \]

\[ K_p = 1.8 \times 10^{-2} \]

\[ \Delta n_g = 3 - 2 = 1 \]

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

\[ \therefore \quad K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-2}}{0.0821 \times 600} = 3.65 \times 10^{-4} \]

(b) \[ K_p = 167 \]

\[ \Delta n_g = 1 \]

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

\[ \therefore \quad K_c = \frac{K_p}{RT} = \frac{167}{0.0821 \times 1173} = 1.734 \]

Ex. At 540 K, 0.10 moles of \( \text{PCl}_5 \) are heated in 8 litre flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate \( K_p \) and \( K_c \) for the reaction.

Sol.

\[ \text{PCl}_5 (g) \rightleftharpoons \text{PCl}_3 (g) + \text{Cl}_2 (g) \]

0.1 0 0

\[ (0.1-x) \quad x \quad x \]

\[ K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{x/8 \times x/8}{(0.1-x)/8} = \frac{x^2}{8(0.1-x)} \quad \ldots \ldots \text{(i)} \]

From gas law

\[ PV = nRT \]

\[ \Rightarrow 1 \times 8 = (0.1 + x) \times 0.082 \times 540 \]

\[ \therefore \quad x = 0.08 \quad \ldots \ldots \text{(ii)} \]

From eqs. (i) and (ii)

\[ K_c = \frac{0.08 \times 0.08}{8 \times (0.1 - 0.08)} = 4 \times 10^{-2} \text{ mol L}^{-1} \]

\[ K_p = K_c (RT)^{\Delta n_g} \quad (\Delta n_g = +1) \]
At a given temperature and a total pressure of 1.0 atm for the homogeneous gaseous reaction, \( \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \), the partial pressure of \( \text{NO}_2 \) is 0.5 atm.

(a) Calculate the value of \( K_p \).

(b) If the volume of the vessel is decreased to half of its original volume, at constant temperature, what are the partial pressures of the components of the equilibrium mixture?

**Sol.**

For equilibrium system, \( \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2 \), the total pressure is 1.0 atm.

\[ \text{Total pressure} = P_{\text{N}_2\text{O}_4} + P_{\text{NO}_2} = 1 \]

\[ P_{\text{N}_2\text{O}_4} = 0.5 \text{ atm and } P_{\text{NO}_2} = 0.5 \text{ atm} \]

(i) \[ K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(0.5)^2}{0.5} = 0.5 \text{ atm} \]

(ii) As volume is decreased to half its original volume, equilibrium is disturbed and the new initial conditions for the re-establishment of new equilibrium are:

\[ P_{\text{N}_2\text{O}_4} = 1.0 \text{ atm and } P_{\text{NO}_2} = 1.0 \text{ atm} \]

According to Le Chatelier’s principal, when volume is decreased, the system moves in that direction where there is decrease in number of moles. Hence, the system (here will moves in reverse direction, as there is a decrease in mole \( \Delta n = 2 - 1 = 1 \), i.e. \( \text{NO}_2 \) will be converted into \( \text{N}_2\text{O}_4 \).

Let, the decrease in pressure of \( \text{NO}_2 \) be \( x \) atm.

\[
\begin{align*}
\text{N}_2\text{O}_4 & \rightleftharpoons 2\text{NO}_2 \\
\text{Initial pressure (atm)} & = 1 \quad 1 \\
\text{At equilibrium} & = 1 + x/2 \quad 1 - x
\end{align*}
\]

\[ K_p = \frac{(1 - x)^2}{(1 + x/2)} = 0.5 \Rightarrow 4x^2 - 9x + 2 = 0 \]

\[ x = 2 \text{ or } 0.25 \quad (x \neq 2 \text{ as initial pressure } = 1.0) \Rightarrow x = 0.25 \]

\[ P_{\text{N}_2\text{O}_4} = 1 + \frac{x}{2} = 1.125 \text{ atm and } P_{\text{NO}_2} = 1 - x = 0.75 \text{ atm} \]

At temperature \( T \), a compound \( \text{AB}_2(g) \) dissociates according to the reaction, \( 2\text{AB}_2(g) \rightleftharpoons 2\text{AB} (g) + \text{B}_2(g) \) with degree of dissociation \( \alpha \), which is small compared to unity. Deduce the expression for \( \alpha \) in terms of the equilibrium constant \( K_p \) and the total pressure \( P \).

**Sol.**

\[
\begin{align*}
2\text{AB}_2 (g) & \rightleftharpoons 2\text{AB} (g) + \text{B}_2 (g) \\
\text{Initial (mole)} & = 1 \quad 0 \quad 0 \\
\text{At eq. (mole)} & = 1 - \alpha \quad \alpha \quad \alpha/2 \\
\text{Total moles at equilibrium} & = (1 + \alpha/2)
\end{align*}
\]

\[
\begin{align*}
\text{At eq. (p.p)} & = P \left( \frac{1 - \alpha}{1 + \alpha/2} \right) \quad P \alpha/2 \quad P \alpha/2 \\
K_p & = \frac{P_{\text{AB}}^2 P_{\text{Br}_2}}{P_{\text{AB}_2}^2} \\
K_p & = \left( \frac{P \alpha}{1 + \alpha/2} \right)^2 \left( \frac{P \alpha/2}{1 + \alpha/2} \right) \\
K_p & = \frac{P \alpha^3}{2(1 - \alpha)^2 (1 + \alpha/2)} \\
\text{But } 1 & >> \alpha \quad \therefore K_p = \frac{P \alpha^2}{2}
\end{align*}
\]
\[ \alpha = \left( \frac{2K_p}{P} \right)^{1/3} \]

The \( K_c \) is expressed by the units (mole liter\(^{-1}\)) and \( K_p \) by (atm)\(^2\).

In terms of mole fraction, equilibrium constant is denoted by \( K_X \).

For general reaction \( aA + bB \rightleftharpoons mC + nD \)

\[ K_X = \frac{(X_C)^m(X_D)^n}{(X_A)^a(X_B)^b} \]

\[ K_p = K_X (RT)^{\Delta n_g} \]

\( \Delta n_g = (m + n) - (a + b) \)

When \( \Delta n_g = 0 \), \( K_p = K_c = K_X \)

### Some General Equilibrium Expressions:

(a) \[ \text{H}_2 (g) + \text{I}_2 (g) \rightleftharpoons 2\text{HI} (g) \]

Initially \( \begin{array}{c} a \\ b \\ 0 \end{array} \)

At equilibrium \( \begin{array}{c} (a-x) \\ (b-x) \\ 2x \end{array} \)

\[ K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(a-x)(b-x)} = \frac{4x^2}{(a-x)(b-x)} \]

\[ K_p = \frac{(p_{\text{HI}})^2}{p_{\text{H}_2} \times p_{\text{I}_2}} = \frac{(a+b)^2}{(a-x)(b-x)} = \frac{4x^2}{(a-x)(b-x)} \]

So \( K_c = K_p \) \( (\Delta n = 0) \)

(b) \[ 2\text{NO} (g) \rightleftharpoons \text{N}_2 (g) + \text{O}_2 (g) \]

Initially \( \begin{array}{c} a \\ 0 \\ 0 \end{array} \)

At equilibrium \( \begin{array}{c} (a-x) \\ x/2 \\ x/2 \end{array} \)

\[ K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2} = K_p \] \( (\Delta n = 0) \)

(c) \[ \text{CH}_3\text{COOH}(_{(l)}) + \text{C}_2\text{H}_5\text{OH}(_{(l)}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(_{(l)}) + \text{H}_2\text{O}(_{(l)}) \]

Initially \( \begin{array}{c} a \\ b \\ 0 \\ 0 \end{array} \)

At equilibrium \( \begin{array}{c} (a-x) \\ (b-x) \\ x \\ x \end{array} \)

\[ K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{x^2}{(a-x)(b-x)} \]

\( K_p \) should not be given for this reaction

(d) \[ \text{PCl}_5 (g) \rightleftharpoons \text{PCl}_3 (g) + \text{Cl}_2 (g) \]

Initially \( \begin{array}{c} a \\ 0 \\ 0 \end{array} \)

At equilibrium \( \begin{array}{c} (a-x) \\ x \\ x \end{array} \)

Active mass \( \begin{array}{c} (a-x) \\ x \\ x \end{array} \)

\[ K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{x \times x}{(a-x)v} = \frac{x^2}{(a-x)v} \]
\[
K_p = \frac{p_{PCl} \times p_{Cl}}{p_{PCl}} = \left(\frac{x}{a+x}\right)P \times \left(\frac{x}{a+x}\right)P = \frac{x^2P}{(a+x)(a-x)} = \frac{x^2P}{a^2-x^2}
\]

(e) \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \)

Initially \( a \quad b \quad 0 \)

At equilibrium \( (a-x) \quad (b-3x) \quad 2x \)

Active mass \( \frac{(a-x)}{v} \quad \frac{(b-3x)}{v} \quad \frac{2x}{v} \)

\[
K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \left(\frac{2x}{v}\right)^2 \left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3 = \frac{4x^2v^2}{(a-x)(b-3x)^3}
\]

\[
K_p = \frac{(p_{\text{NH}_3})^2}{p_{\text{N}_2} \times (p_{\text{H}_2})^3} = \left[\frac{2xP}{a+b-2x}\right]^2 \left[\frac{(a-x)P}{(a+b-2x)}\right] \left[\frac{(b-3x)P}{(a+b-3x)}\right]^3 = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3P^2}
\]

**Ex.** In the reaction, \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \) the concentration of \( \text{H}_2, \text{I}_2 \) and \( \text{HI} \) at equilibrium are 10.0, 6.0 and 28 moles per litre respectively. What will be the equilibrium constant?

(A) 30.61 \quad (B) 13.066 \quad (C) 29.40 \quad (D) 20.90

**Sol.** (B)

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \]

Applying law of mass action,

\[
K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \]

Given \( [\text{H}_2] = 10 \text{ mol L}^{-1} \)

\( [\text{I}_2] = 6.0 \text{ mol L}^{-1} \)

\( [\text{HI}] = 28.0 \text{ mol L}^{-1} \)

So,

\[
K_c = \frac{(28.0)^2}{(10) \times (6.0)} = 13.066
\]

**Ex.** For a gas phase reaction at equilibrium, \( 3\text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2\text{NH}_3(g) \), the partial pressures of \( \text{H}_2 \) and \( \text{N}_2 \) are 0.4 and 0.8 atmosphere respectively. The total pressure of the entire system is 2.4 atmosphere. What will be the value of \( K_p \) if all the pressures are given in atmosphere?

(A) 32 atm\(^{-2}\) \quad (B) 20 atm\(^{-2}\) \quad (C) 28.125 atm\(^{-2}\) \quad (D) 80 atm\(^{-2}\)

**Sol.** (C)

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g), \]

Partial pressures at equilibrium

\[
0.8 \quad 0.4 \quad [2.4 - (0.8 + 0.4) = 1.2]
\]
Applying law of mass action,

\[ K_p = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]} = \frac{1.2 \times 1.2}{0.8 \times 0.4 \times 0.4} \Rightarrow K_p = 28.125 \text{ atm}^{-2} \]

**Ex.** When ethanol and acetic acid were mixed together in equimolecular proportion 66.6% are converted into ethyl acetate. Calculate \( K_c \). Also calculate quantity of ester produced if one mole of acetic acid is treated with 0.5 mole and 4 mole of alcohol respectively.

(A) 4, 0.93, 0.43  (B) 0.93, 4, 0.43  (C) 0.43, 0.93, 4  (D) 4, 0.43, 0.93

**Sol.**

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} & \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \\
1 & \quad 1 & 0 & 0 \\
1-0.666 & 1-0.666 & 0.666 & 0.666
\end{align*}
\]

\[
K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{[0.666][0.666]}{[0.333][0.333]} = 4
\]

(a) Let \( x \) moles of ester is formed from 1 mole of acid and 0.5 mole of alcohol, then

\[
K_c = \frac{x^2}{(1-x)(0.5-x)} \Rightarrow \frac{x^2}{(1-x)(0.5-x)} = 4 \Rightarrow x = 0.43
\]

(b) \( K_c = \frac{x^2}{(1-x)(4-x)} \) or \( 4 = \frac{x^2}{(1-x)(4-x)} \) \( \Rightarrow x = 0.93 \)

**Ex.** Starting with 3 : 1 mixture of \( \text{H}_2 \) and \( \text{N}_2 \) at 450°C, the equilibrium mixture is found to be 9.6% \( \text{NH}_3 \); 22.6% \( \text{N}_2 \) and 67.8% \( \text{H}_2 \) by volume. The total pressure is 50 atm. What will be the value of \( K_p \). The reaction is -

\[
\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3
\]

(A) 3.25 \times 10^{-5} \text{ atm}^{-2}  (B) 5.23 \times 10^{-5} \text{ atm}^{-2}  (C) 6.23 \times 10^{-5} \text{ atm}^{-2}  (D) 8 \times 10^{-5} \text{ atm}^{-2}

**Sol.**

The ratio of number of moles will be the same as the ratio of volume. According to Dalton’s law, the partial pressure of a gas in a mixture is given by the product of its volume fraction and the total pressure. Therefore, the equilibrium pressure of each gas is,

\[
\begin{align*}
P_{\text{NH}_3} &= \frac{9.6}{100} \times 50 \text{ atm} = 4.8 \text{ atm} \\
P_{\text{N}_2} &= \frac{22.6}{100} \times 50 \text{ atm} = 11.3 \text{ atm} \\
P_{\text{H}_2} &= \frac{67.6}{100} \times 50 \text{ atm} = 33.9 \text{ atm}
\end{align*}
\]

Total pressure = 50 atm

\[
K_p = \frac{[P_{\text{NH}_3}]^2}{[P_{\text{N}_2}][P_{\text{H}_2}]} \; ; \; \text{Substituting the values of partial pressures,}
\]

\[
K_p = \frac{(4.80 \text{ atm})^2}{(11.3 \text{ atm})(33.9 \text{ atm})} = 5.23 \times 10^{-5} \text{ atm}^{-2}
\]

**Ex.** \( K_p \) for the reaction \( \text{A(g)} + 2\text{B(g)} \rightleftharpoons 3\text{C(g)} + \text{D(g)} \); is 0.01 atm. What will be its \( K_c \) at 1000 K in terms of \( R \)?

(A) \( \frac{1.0 \times 10^{-5}}{R} \)  (B) \( \frac{R}{5 \times 10^{-5}} \)  (C) 5 \( \times 10^{-5} R \)  (D) none of these

**Sol.**

We know that

\[
K_p = K_c (RT)^{\Delta n} \; \text{or} \; K_c = \frac{K_p}{(RT)^{\Delta n}}
\]

Here \( \Delta n = 4 - 3 = 1 \)
\(T = 1000\ \text{K},\ K_p = 0.01\)

\[K_c = \frac{0.01}{(R \times 1000)^2} = \frac{1.0 \times 10^{-5}}{R}\]

**Ex.**

0.5 mole of \(H_2\) and 0.5 mol of \(I_2\) react in 200 L flask at 448° C. The equilibrium constant \(K_c\) is 50 for \(H_2 + I_2 \rightleftharpoons 2HI\),

(a) What is the \(K_p\)?

(b) Calculate mol of \(I_2\) at equilibrium.

**Sol.**

\[H_2 + I_2 \rightleftharpoons 2HI\]

0.5 \( \text{mol} \) \( \text{H}_2\) \( \text{and} \) 0.5 \( \text{mol} \) \( \text{I}_2\) \( \text{Initial} \)

\((0.5-x)\) \( \text{mol} \) \( \text{H}_2\) \( \text{and} \) \((0.5-x)\) \( \text{mol} \) \( \text{I}_2\) \( \text{at equili.} \)

(a) Since \(\Delta n = 0\) \(\Rightarrow K_p = K_c\)

(b) \(50 = \frac{4x^2}{(0.5-x)^2}\) or \(\frac{2x}{0.5-x} = \sqrt{50}\)

\(x = 0.39\)

\(\therefore \text{mol of } I_2 = 0.5 - 0.39 = 0.11 \text{ mol}\)

\(\Rightarrow \text{Three cases may arise:}\)

(a) When \(\Delta n = 0\)
\[K_p = K_c (RT)^0 = K_c\]

For example:

\[N_2 + O_2 \rightleftharpoons 2NO\quad H_2 + I_2 \rightleftharpoons 2HI\]

\(\Rightarrow K_c\) and \(K_p\) are unit less in this case.

(b) When \(\Delta n = +ve\)

\(K_p > K_c\)

For example:

\[\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2\quad \left(\begin{array}{c} K_C \rightarrow \text{mole} \text{lit}^{-1} \\ K_P \rightarrow \text{atm} \end{array}\right)\]

\(\Delta n = 1\)

\[2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2\quad \left(\begin{array}{c} K_C \rightarrow \text{mole}^2 \text{lit}^{-2} \\ K_P \rightarrow \text{atm}^2 \end{array}\right)\]

\(\Delta n = 2\)

(c) When \(\Delta n = -ve\)

\(K_p < K_c\)

\[\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3\quad \left(\begin{array}{c} K_C \rightarrow \text{mole}^{-2} \text{lit}^2 \\ K_P \rightarrow \text{atm}^{-2} \end{array}\right)\]

\(\Delta n = -2\)

\(\Rightarrow \text{Factors affecting equilibrium constant:}\)

(a) **Mode of representation of the reaction:**

\[A + B \rightleftharpoons C + D\]

The equilibrium constant for the reaction

\[K_c = \frac{[C][D]}{[A][B]}\]

If the reaction is reversed

\[C + D \rightleftharpoons A + B\]

then,

\[K_p = \frac{[A][B]}{[C][D]}\]
The two equilibrium constant related as \( K_c = \frac{1}{K'_c} \)

**Ex.** For \( N_2 + 3H_2 \rightleftharpoons 2NH_3 \) if \( K_c = 5 \) then find \( K'_c \) for reverse reaction.

**Ans.** \( K'_c = 1/5 = 0.2 \)

**(b) Stoichiometry of the reaction :**

When a reversible reaction can be written with the help of two or more stoichiometric equation, the value of equilibrium constant will be numerically different.

For reaction \( 2NO_2 \rightleftharpoons N_2 + 2O_2 \)

\[
K_c = \frac{[N_2][O_2]^2}{[NO_2]^2}
\]

For reaction \( NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2 \)

\[
K'_c = \frac{[N_2]^2[O_2]}{[NO_2]^2}
\]

The two constants are related as \( K'_c = \sqrt{K_c} \)

**(c) Temperature :** The value of equilibrium constant changes with the change of temperature.

If \( K_1 \) and \( K_2 \) be the equilibrium constants of a reaction at absolute temperatures \( T_1 \) and \( T_2 \) and \( \Delta H \) is the heat of reaction at constant volume, then :

\[
\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2}
\]

\[
\log K_2 - \log K_1 = \frac{-\Delta H}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

(According to Vant Hoff equation)

(i) \( \Delta H = 0 \) (neither heat is absorbed or evolved)

\[
\log K_2 - \log K_1 = 0
\]

\[
\log K_1 = \log K_2
\]

\[
K_1 = K_2
\]

Thus, equilibrium constant remains the same at all temperatures

If temp. \( T_2 \) is higher than \( T_1 \)

\[
\frac{1}{T_2} - \frac{1}{T_1} < 0, \log K_2 - \log K_1 = \frac{+ve \Delta H}{2.303R}
\]

(ii) When \( \Delta H = +ve \) (endothermic reaction)

\[
\log K_2 - \log K_1 > 0
\]

or

\[
\log K_2 > \log K_1
\]

\[
K_2 > K_1
\]

The value of equilibrium constant is higher at higher temperature in case of endothermic reactions.

\[
K_c \propto T
\]

(iii) When \( \Delta H = -ve \) (exothermic reaction)

\[
\log K_2 - \log K_1 < 0
\]

\[
\log K_2 < \log K_1
\]

\[
K_2 < K_1
\]

The value of equilibrium constant is lower at higher temperature in the case of exothermic reactions.

\[
K_c \propto 1/T
\]

\[\text{u} \]

The value of equilibrium constant is independent of the following factors :-

(a) Initial concentrations of reactants.

(b) The presence of a catalyst.
(c) The direction from which the equilibrium has been attained.

(d) Presence of inert materials.

Ex. For the reaction,

\[ A \rightleftharpoons B, \ \Delta H \text{ for the reaction is } -33.0 \text{ kJ/mol.} \]

Calculate:

(i) Equilibrium constant \( K_c \) for the reaction at 300 K

(ii) If \( E_a(f) \) and \( E_a(r) \) in the ratio of 20 : 31, calculate \( E_a(f) \) and \( E_a(r) \) at 300 K.

Assuming pre-exponential factor same for forward and reverse reaction.

Sol. (i) \( \Delta H = E_{a(f)} - E_{a(r)} = -33 \text{ kJ} \)

\[ k_f = A e^{-E_{a(f)}/RT} \]

\[ k_b = A e^{-E_{a(r)}/RT} \]

\[ \therefore k_c = \frac{k_f}{k_b} = e^{\left[ E_{a(f)} - E_{a(r)} \right] / RT} \Rightarrow e^{33 \times 10^3 / 8.314 \times 300} = 5.572 \times 10^5 \text{ at 300 K} \]

(ii) \( \frac{E_{a(f)}}{E_{a(r)}} = \frac{20}{31} \)

\( E_{a(f)} - E_{a(r)} = -33 \text{ kJ} \)

\[ \therefore E_{a(r)} = \frac{33 \times 20}{11} = 60 \text{ kJ} \]

\[ E_{a(f)} = +93 \text{ kJ} \]

Ex. The equilibrium constant for the reaction \( \text{H}_2(g) + \text{S} (s) \rightleftharpoons \text{H}_2\text{S}(g) \) is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction will be:

(A) \(-68000.05 \text{ J mol}^{-1}\) (B) \(-71080.57 \text{ J mol}^{-1}\) (C) \(-80071.75 \text{ J mol}^{-1}\) (D) \(57080.75 \text{ J mol}^{-1}\)

Sol. (B)

Using the relation,

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

\[ \log \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \left[ \frac{925 - 1000}{925 \times 1000} \right] \]

\[ -0.301 = \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000} \Rightarrow \Delta H = -71080.57 \text{ J mol}^{-1}. \]

Ex. The reaction \( \text{CuSO}_4 \cdot 3\text{H}_2\text{O(s)} \rightleftharpoons \text{CuSO}_4 \cdot \text{H}_2\text{O(s)} + 2\text{H}_2\text{O (g)} \) ; the dissociation pressure is \( 7 \times 10^{-3} \text{ atm at 25 C and } \Delta H = 2750 \text{ cal.} \) What will be the dissociation pressure at 127 C?

Sol. For given reaction

\[ K_p = \left( p_{(H_2O)} \right)^2 \]

so \( K_p \) (25 C) = \( (7 \times 10^{-3})^2 \text{ atm}^2 \)

\[ = 4.9 \times 10^{-5} \text{ atm}^2 \]

Since \( \Delta H = 2750 \text{ cal, so using Vant Hoff eq.} \)
\[
\log \left[ \frac{K_p(127^\circ C)}{K_p(25^\circ C)} \right] = \frac{\Delta H^o}{2.303 \times R} \left[ \frac{400 - 298}{400 \times 298} \right]
\]
\[
\log \left[ \frac{K_p(127^\circ C)}{4.9 \times 10^{-5}} \right] = \frac{2750}{2.303 \times 2} \left[ \frac{102}{119200} \right]
\]
\[
K_p (127^\circ C) = 3.2426 \times 4.9 \times 10^{-5} = 1.58 \times 10^{-4}
\]

so \( p_{H_2O} \) at 127 = \( \sqrt{K_p(127^\circ C)} = \sqrt{1.58 \times 10^{-4}} = 1.26 \times 10^{-2} \) atm.

**Law of Mass Action as Applied to Heterogeneous Equilibrium:**

In such cases the active mass of pure solid and pure liquid is taken as unity and the value of equilibrium constant is determined by the gaseous substances only.

**For example:** The dissociation of \( \text{CaCO}_3 \) in closed vessel.

\[
\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)
\]

\( K_c = [\text{CO}_2], \quad K_p = p_{\text{CO}_2} \)

\( \text{PCl}_5(s) \rightleftharpoons \text{PCl}_3(\ell) + \text{Cl}_2(g) \)

\( K_c = [\text{Cl}_2], \quad K_p = p_{\text{Cl}_2} \)

\( 2\text{H}_2\text{O}(\ell) \rightleftharpoons 2\text{H}_2(g) + \text{O}_2(g) \)

\( K_c = [\text{H}_2]^2[\text{O}_2], \quad K_p = (p_{\text{H}_2})^2(p_{\text{O}_2}) \)

\( 3\text{Fe}(s) + 4\text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_3\text{O}_4(s) + 4\text{H}_2(g) \)

\( K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}, \quad K_p = \frac{(p_{\text{H}_2})^4}{(p_{\text{H}_2\text{O}})^4} \)

**Ex.** One mole of ammonium carbamate dissociate as shown below at 500 K.

\( \text{NH}_2\text{COONH}_4(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g) \)

If the pressure exerted by the released gases is 6.0 atm, the value of \( K_p \) is -

(A) 7 atm  \quad (B) 3 atm  \quad (C) 32 atm  \quad (D) 8 atm

**Sol.** (C)

Applying the law of chemical equilibrium, we get

\( K_p = (p_{\text{NH}_3})^2(p_{\text{CO}_2}) \)

Since total pressure is 6 atm, the partial pressures of \( \text{NH}_3 \) (g) and \( \text{CO}_2 \) (g) are

\( (p_{\text{NH}_3}) = 6 \cdot \frac{2}{3} = 4 \text{ atm} \)

\( (p_{\text{CO}_2}) = 6 \cdot \frac{1}{3} = 2 \text{ atm} \)

\( K_p = [4.0]^2[2.0] = 32.0 \text{ atm} \)

**Ex.** For the reaction.

\( \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \); \( K_p = 1.16 \text{ atm} \) at 800 C. If 40 g of \( \text{CaCO}_3 \) was put into a 20 L container and heated to 800 C, what percent of \( \text{CaCO}_3 \) would remain unreacted at equilibrium.

**Sol.** \( K_p = P_{\text{CO}_2} = 1.16 \text{ atm} \)

\( n(\text{CO}_2) = \frac{PV}{RT} = \frac{1.16 \times 20}{0.0821 \times 1073} = 0.26335 \text{ mol} \)

moles of \( \text{CaCO}_3 \) initially present

\( = 40/100 = 0.4 \text{ mol} \)
So \% \text{ decomposition of CaCO}_3 = \frac{0.26335}{0.4} \times 100 = 65.83 \% \text{ decomposed}

Hence 34.17 \% remain unreacted.

Ex. For the reaction:
\text{SnO}_2 (s) + 2\text{H}_2 (g) \rightleftharpoons 2\text{H}_2\text{O} (g) + \text{Sn} (s)
Calculate \( K_p \) at 900 K where the equilibrium steam hydrogen mixture was 35 \% \text{H}_2 by volume.

Sol. \hspace{1cm} K_p = \frac{(P_{\text{H}_2\text{O}})^2}{(P_{\text{H}_2})^2}
\text{given} \ \text{H}_2 \text{ is 35\% by volume at constant temperature in closed vessel (} P \propto V \text{)}
\text{so} \ P_{\text{H}_2\text{O}} = 0.65 \ \text{atm and} \ P_{\text{H}_2} = 0.35 \ \text{atm}
\hspace{1cm} K_p = \left( \frac{0.65}{0.35} \right)^2 = 3.448

\text{LE-CHATELIER'S PRINCIPLE}:
According to this principle, if a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium is shifted in such a way as to nullify the effect of change.

(a) \text{Change in concentration} : In an equilibrium increasing the concentrations of reactants results in shifting the equilibrium in favour of products while increasing concentrations of the products results in shifting the equilibrium in favour of the reactants.

(b) \text{Change of pressure} : When the pressure on the system is increased, the volume decreases proportionately. The total number of moles per unit volume increases. According to Le-Chatelier’s principle, the equilibrium shift in the direction in which there is decrease in number of moles.

If there is no change in number of moles of gases in a reaction, a pressure change does not affect the equilibrium.

(c) \text{Change in temperature} : - If the temperature at equilibrium is increased reaction will proceed in the direction in which heat can be used. Thus increase in temperature will favour the forward reaction for endothermic reaction.

Similarly, increase in temperature will favour the backward reaction in exothermic reactions.

\text{APPLICATION OF LE-CHATELIER'S PRINCIPLE}:
(A) \text{Chemical equilibria} :
(a) \text{Formation of HI}
\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) + 3000 \text{ Cals}

(i) \text{Effect of concentration} : When concentration of \text{H}_2 \text{ or } \text{I}_2 \text{ is increased at equilibrium, the system moves in a direction in which decreases the concentration. Thus the rate of forward reaction increases thereby increasing the concentration of HI.}

(ii) \text{Effect of pressure} : - In formation of HI, there is no change in the number of moles of reactants and products \( (\Delta n = 0) \). Thus it is not affected by the change in pressure or volume.

(iii) \text{Effect of temperature} : - The formation of HI is exothermic reaction. Thus the backward reaction moves faster when temperature is increased. i.e. formation of HI is less.

In short favourable conditions for greater yield of HI : 
- High concentration of \text{H}_2 \text{ and } \text{I}_2.
- Low temperature.
- No effect of pressure

(b) \text{Formation of NO} :
\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} - 43200 \text{ cals.}

(i) \text{Effect of concentration} : When concentration of \text{N}_2 \text{ or } \text{O}_2 \text{ is increased, the system moves in a direction in}
which \( N_2 \) or \( O_2 \) is used up or rate of forward increases.

(ii) **Effect of pressure**: The formation of NO is not affected by change in pressure.

\[ \Delta n = 0. \]

(iii) **Temperature**: The formation of NO is endothermic. Thus increase in temperature favours to forward reaction.

Favourable conditions for greater yield of NO:
- High concentration of \( N_2 \) and \( O_2 \).
- High temperature.
- No effect of pressure

(c) **Dissociation of \( \text{PCl}_5 \)**:

\[ \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) - 15000 \text{ cals.} \]

(i) **Effect of concentration**: When concentration of \( \text{PCl}_5 \) is increased at equilibrium, the rate of forward reaction increases as to decrease the added concentration. Thus dissociation of \( \text{PCl}_5 \) increases.

(ii) **Effect of pressure**: The volume increases in the dissociation of \( \text{PCl}_5 \) when pressure is increased, the system moves in the direction in which there is decrease in volume. Thus high pressure does not favour dissociation of \( \text{PCl}_5 \).

(iii) **Effect of temperature**: The dissociation of \( \text{PCl}_5 \) is an endothermic reaction. Thus increase of temperature favours the dissociation.

Favourable conditions for dissociation of \( \text{PCl}_5 \) are:
- High concentration of \( \text{PCl}_5 \).
- Low pressure.
- High temperature.

(d) **Synthesis of ammonia**:

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) + 22400 \text{ Cals.} \]

The favourable conditions for greater yield of \( \text{NH}_3 \) are:
- High concentration of \( \text{N}_2 \) and \( \text{H}_2 \).
- High pressure.
- Low temperature.

(e) **Formation of \( \text{SO}_3 \)**:

\[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3 + 45200 \text{ Cals.} \]

The favourable conditions for greater yield of \( \text{SO}_3 \) are:
- High concentration of \( \text{SO}_2 \) and \( \text{O}_2 \).
- High pressure.
- Low temperature.

Ex. In reaction,

\[ \text{CO}(g) + 2\text{H}_2 \text{ (g)} \rightleftharpoons \text{CH}_3\text{OH} \text{ (g)} \quad \Delta H = - 92 \text{ kJ/mol}^{-1} \]

concentrations of hydrogen, carbon monoxide and methanol become constant at equilibrium. What will happen if:

(A) volume of the reaction vessel in which reactants and products are contained is suddenly reduced to half?
(B) partial pressure of hydrogen is suddenly doubled?

(C) an inert gas is added to the system at constant pressure?

(D) the temperature is increased?

Sol.

For the equilibrium,

\[ \text{CO (g) + 2H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH (g)} \]

\[ K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} \Rightarrow K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \times P_{\text{H}_2}^2} \]

(A) When the volume of the vessel is suddenly reduced to half, the partial pressures of various species get doubled. Therefore, \( Q_p = \frac{2P_{\text{CH}_3\text{OH}}}{2P_{\text{CO}} \times (2P_{\text{H}_2})^2} = \frac{1}{4} K_p \)

Since \( Q_p \) is less than \( K_p \), the equilibrium shift in the forward direction producing more \( \text{CH}_3\text{OH} \).

(B) When partial pressure of hydrogen is suddenly doubled, \( Q_p \) changes and is no longer equal to \( K_p \).

\[ Q_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \times (2P_{\text{H}_2})^2} = \frac{1}{4} K_p \]

Equilibrium will shift from left to right.

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

(D) By increasing the temperature, \( K_p \) will decrease and equilibrium will shift from right to left.

**SPECIAL POINTS:**

(1) Irreversible reaction proceeds in one direction and completed with time while reversible reaction proceeds in both direction and are never completed.

(2) Equilibrium is defined as the point at which the rate of forward reaction is equal to the rate of backward reaction.

(3) Chemical equilibrium is dynamic in nature and equilibrium state can be approached from both sides.

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

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

(6) If a reaction can be expressed as the sum of two or more reactions then overall \( K_c \) will be equal to the product of the equilibrium constant of individual reaction.

**Example:**

\[ \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{SO}_3(g) \rightarrow K_1 \]

\[ \text{NO}_2(g) \rightleftharpoons \text{NO(g)} + \frac{1}{2} \text{O}_2(g) \rightarrow K_2 \]

then \( \text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO(g)} \rightarrow K \)

So \( K = K_1 \times K_2 \)

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

(8) A catalyst ables the system to reach a state of equilibrium more quickly.

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

(10) If the concentration of reactants is increased and product is removed, the reaction will take place in forward direction.
Free energy change

\[ \Delta G = \Delta G^o + 2.303 \, RT \log Q \]

At equilibrium \( \Delta G = 0 \), (T is in Kelvin), \( Q = K \) so

\[ \Delta G = -2.303 \, RT \log K, \text{ where } K \text{ is equilibrium constant.} \]

**Ex.** \( \Delta G \) for \( \frac{1}{2} \mathrm{N}_2 + \frac{3}{2} \mathrm{H}_2 \rightleftharpoons \mathrm{NH}_3 \) is -16.5 kJ mol\(^{-1}\). Find out \( K_p \) for the reaction at 25°C. Also report \( K_p \) and \( \Delta G^o \) for \( \mathrm{N}_2 + 3\mathrm{H}_2 \rightleftharpoons 2\mathrm{NH}_3 \) at 25°C.

**Sol.**

\[
\log K_p = -\frac{\Delta G^o}{2.303RT} = \frac{+16.5 \times 10^3}{2.303 \times 8.314 \times 298} = 2.8917
\]

\[ K_p = \text{antilog} \, (2.8917) = 779.41 \]

Now given reaction \( \mathrm{N}_2 + 3\mathrm{H}_2 \rightleftharpoons 2\mathrm{NH}_3 \) can be obtained by multiplying eq. \( \frac{1}{2} \mathrm{N}_2 + \frac{3}{2} \mathrm{H}_2 \rightleftharpoons \mathrm{NH}_3 \) by 2.

so \( K_p' = (779.41)^2 = 6.07 \times 10^6 \)

and \( \Delta G = -2.303 \, RT \log K_p' = -2.303 \times 8.314 \times 298 \log (6.07 \times 10^6) \) J

\[ \Delta G = -32.998 \, \text{kJ mol}^{-1} \]

**Ex.** For the gaseous reaction \( \mathrm{CO} + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{CO}_2 + \mathrm{H}_2 \) the following thermodynamics data are given.

\[ \Delta H_{300 \, \text{K}} = -41.16 \, \text{kJ mol}^{-1}; \Delta S_{300 \, \text{K}} = -0.0424 \, \text{kJ mol}^{-1}. \]

\[ \Delta H_{1200 \, \text{K}} = -32.93 \, \text{kJ mol}^{-1}; \Delta S_{1200 \, \text{K}} = -0.0296 \, \text{kJ mol}^{-1}. \]

Assuming partial pressure of each component at 1 atm. determine the direction of spontaneous reaction at

(i) 300 K

(ii) 1200 K. Also calculate \( K_p \) for the reaction at each temperature.

**Sol.**

Using \( \Delta G = \Delta H - T \Delta S \)

\[ \Delta G_{300 \, \text{K}} = -41.16 - 300 (-0.0424) \]

\[ = -28.44 \, \text{kJ mol}^{-1} \]

so reaction is spontaneous in given direction since \( \Delta G \) is negative

\( \mathrm{CO} + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{CO}_2 + \mathrm{H}_2 \)

at 1200 K

\[ \Delta G_{1200 \, \text{K}} = -32.93 - 1200 (-0.0296) \]

\[ = 2.56 \, \text{kJ mol}^{-1} \]

so reaction will not be spontaneous in given direction, but reverse reaction spontaneous i.e.

\( \mathrm{CO} + \mathrm{H}_2 \rightleftharpoons \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \)

We know \( \Delta G = -2.303 \, RT \log K_p \)

so \( K_p (300 \, \text{K}) \)

\[ = \text{antilog} \left( \frac{-28.44 \times 10^3}{-2.303 \times 8.314 \times 300} \right) = 8.8 \times 10^4 \]
\[ K_p = (1200 \text{ K}) \]
\[ = \text{antilog} \left( \frac{+2.59 \times 10^3}{-2.303 \times 8.314 \times 1200} \right) = 0.77 \]

**REACTION QUOTIENT AND EQUILIBRIUM CONSTANT:**

Consider the following reversible reaction

\[ \text{A + B} \rightleftharpoons \text{C + D} \]

The reaction quotient \((Q_c)\) is ratio of the product of active masses of the products and product of active masses of the reactants, at any given time.

\[ \therefore Q_c = \frac{[C][D]}{[A][B]} \]

The concentrations are not necessarily equilibrium concentration.

[At equilibrium \(Q_c = K_c\)]

**Case I:**

If \( Q_c < K_c \) then : \([\text{Reactants}] > [\text{Products}]\)

then the system is not at equilibrium

The value of \( \frac{[\text{Product}]}{[\text{Reactant}]} \) is small

\[ \therefore \] For establishment of equilibrium the reaction will go in forward direction. \([\text{Reactants} \rightarrow \text{Products}]\)

**Case II:**

If \( Q_c = K_c \) then : The system is at equilibrium and the concentration of the species \( \text{C,D,B,A} \) are at equilibrium.

**Case III:**

If \( Q_c > K_c \) then : \([\text{Product}] > [\text{Reactants}]\)

The system is not at equilibrium.

The value of \( \frac{[\text{Product}]}{[\text{Reactant}]} \) is large

\[ \therefore \] For establishment of equilibrium the reaction will go in backward direction. \([\text{Products} \rightarrow \text{Reactants}]\)

**Ex.**

A mixture of 4.2 moles of \( \text{N}_2 \), 2.0 moles of \( \text{H}_2 \) and 10.0 moles of \( \text{NH}_3 \) is introduced into a 10.0 L reaction vessel at 500 K. At this temperature, equilibrium constant \( K_c \) is \( 1.7 \times 10^2 \), for the reaction \( \text{N}_2 (g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \)

(i) is the reaction mixture at equilibrium ?

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

**Sol.**

\[ [\text{N}_2] = \frac{4.2}{10} = 0.42 \text{ M} \]

\[ [\text{H}_2] = \frac{2.0}{10} = 0.2 \text{ M} \]

\[ [\text{NH}_3] = \frac{10}{10} = 0.1 \text{ M} \]

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

\( \text{N}_2 (g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \) is
\[ Q = \frac{[\text{NH}_4]^2}{[\text{N}_2][\text{H}_2]^2} = \frac{(0.1)^2}{(0.42) \times (0.2)^2} = 2.976 \]

But \( K_c = 1.7 \times 10^2 \)

(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.

**CALCULATION OF DEGREE OF DISSOCIATION FROM VAPOUR DENSITY MEASUREMENT:**

**Degree of dissociation:**

Degree of dissociation of a substance at a particular temperature is defined as the fraction of total number of moles dissociated into simpler molecules at that particular temperature.

\[
\text{Degree of dissociation (} \alpha \text{)} = \frac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}}
\]

Degree of dissociation can be calculated from vapour density measurements for those substance which are accompanied by change in the number of moles. e.g.

\[
\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2
\]

<table>
<thead>
<tr>
<th>Initial moles</th>
<th>1</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of moles after dissociation</td>
<td>((1-\alpha))</td>
<td>(\alpha)</td>
<td>(\alpha)</td>
</tr>
</tbody>
</table>

Total number of moles = \(1 - \alpha + \alpha + \alpha = (1 + \alpha)\)

Let, volume occupied by the vapour per mole = \(V\) litres.

Initial vapour density = \(D\)

Vapour density after dissociation = \(d\)

As, vapour density \(\propto \frac{1}{V}\)

\[ \therefore D \propto \frac{1}{V} \]

\[ d \propto \frac{1}{(1+\alpha)V} \]

\[ \therefore \frac{D}{d} = \frac{1}{(1+\alpha)V} = (1 + \alpha) \]

\[ \Rightarrow \alpha = \frac{D}{d} - 1 = \frac{(D - d)}{d} \]

As, mol. wt. = 2 vapour density

Also, \( \alpha = \frac{M_i - M_o}{M_o} \)

\( M_i \) = theoretical molecular mass

\( M_o \) = observed (experimental) molecular mass

\( M_o \) can be calculated from the mass of definite volume of the vapour at particular temperature.

Also, \( PV = nRT = \frac{W}{M_o}RT \)

\[ M_o = \frac{W \times RT}{v} = \frac{\rho RT}{P} \]

where \( \rho = \text{density of the vapour.} \)
In general, if one mole dissociates to give \( n \) moles of products, then

\[
\begin{align*}
A & \rightarrow nB \\
1 & \quad 0 \\
(1 - \alpha) & \quad n\alpha
\end{align*}
\]

Total no. of moles = \( 1 - \alpha + n\alpha = 1 + (n - 1)\alpha \)

\[
\therefore \frac{D}{d} = 1 + (n - 1)\times \alpha \quad \Rightarrow \quad \alpha = \frac{(D - d)}{(n - 1)\times d}
\]

Also, \( \alpha = \frac{M_1 - M_o}{(n - 1)\times M_o} \)

Let us consider the reaction, \( 2\text{NH}_3 (g) \leftrightarrow \text{N}_2(g) + 3\text{H}_2(g) \)

If the initial moles of \( \text{NH}_3(g) \) be 'a' and \( x \) moles of \( \text{NH}_3 \) dissociated at equilibrium.

\[
2\text{NH}_3 (g) \leftrightarrow \text{N}_2 (g) + 3\text{H}_2 (g)
\]

Initial moles

\[
\begin{array}{ccc}
a & 0 & 0 \\
\end{array}
\]

At equilibrium

\[
\begin{array}{ccc}
a - x & \frac{x}{2} & \frac{3x}{2} \\
\end{array}
\]

Degree of dissociation (\( \alpha \)) of \( \text{NH}_3 \) is defined as the number of moles of \( \text{NH}_3 \) dissociated per mole of \( \text{NH}_3 \).

\[
\therefore \text{If } x \text{ moles dissociate from 'a' moles of } \text{NH}_3 \text{ then, the degree of dissociation of } \text{NH}_3 \text{ would be } \frac{x}{a}.
\]

We can also look at the reaction in the following manner.

\[
2\text{NH}_3 (g) \leftrightarrow \text{N}_2 (g) + 3\text{H}_2 (g)
\]

Initial moles

\[
\begin{array}{ccc}
a & 0 & 0 \\
\end{array}
\]

At equilibrium

\[
\begin{array}{ccc}
a(1 - \alpha) & \frac{a\alpha}{2} & \frac{3a\alpha}{2} \\
\end{array}
\]

or

\[
\begin{array}{ccc}
a - 2x' & x' & 3x' \\
\end{array}
\]

where \( \alpha = \frac{2x'}{a} \)

Here, total number of moles at equilibrium is \( a - 2x' + x' + 3x' = a + 2x' \)

Mole fraction of \( \text{NH}_3 \) = \( \frac{a - 2x'}{a + 2x'} \)

Mole fraction of \( \text{N}_2 \) = \( \frac{x'}{a + 2x'} \)

Mole fraction of \( \text{H}_2 \) = \( \frac{3x'}{a + 2x'} \)

The expression of \( K_p \) is

\[
K_p = \frac{\left( \frac{x'}{a + 2x'} \right) P_x \times \left( \frac{3x'}{a + 2x'} \right)^3 \times P_T^3}{\left( \frac{a - 2x'}{a + 2x'} \right) \times P_T^2} = \frac{27x'^4}{(a - 2x')^2} \times \frac{P_T^2}{(a + 2x')^2}
\]

In this way, you should find the basic equation. So, it is advisable to follow the below mentioned steps while solving the problems.

* Write the balanced chemical reaction (mostly it will be given).
* Under each component write the initial number of moles.
* Do the same for equilibrium condition.
* Then derive the expression for \( K_p \) and \( K_c \) accordingly.
Ex. Vapour density of the equilibrium mixture NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} is found to be 42 for the reaction, N\textsubscript{2}O\textsubscript{4} \rightleftharpoons 2NO\textsubscript{2}. Find
(a) Abnormal molecular weight
(b) Degree of dissociation
(c) Percentage of NO\textsubscript{2} in the mixture

Sol. (a) For the reaction, N\textsubscript{2}O\textsubscript{4} \rightleftharpoons 2NO\textsubscript{2}
   Observed value of vapour density = 42
   Abnormal molecular weight = 42 \times 2 \quad (d = 42)
(b) Theoretical molecular weight = 92
   \[ 2 \times D = 92 \]
   \[ \therefore D = \frac{92}{2} = 46 \]
   \[ \therefore \alpha = \frac{D - d}{d} = \frac{46 - 42}{42} = 0.095 \]
(c) N\textsubscript{2}O\textsubscript{4} \rightleftharpoons 2NO\textsubscript{2}
   1 \quad 0
   (1 - \alpha) \quad 2\alpha
   0.905 \quad 0.19
Total moles at equilibrium = 1 + \alpha = 1 + 0.095
   \[ \therefore \% \text{ of NO}_2 = \frac{2\alpha}{1 + \alpha} \times 100 = \frac{0.19}{1.095} \times 100 = 17.35 \% \]

Ex. The equilibrium constant of the reaction A\textsubscript{2}(g) + B\textsubscript{2}(g) \rightleftharpoons 2AB (g) at 50°C is 50. If one litre flask containing one mole of A\textsubscript{2} is connected to a two litre flask containing two moles of B\textsubscript{2}, how many moles of AB will be formed at 323 K.

Sol. A\textsubscript{2}(g) + B\textsubscript{2}(g) \rightleftharpoons 2AB (g) ; K\textsubscript{c} = 50
   Initial mole 1 2 0
   At eq. mole 1 - x 2 - x 2x
   At eq. conc. \[ \frac{1 - x}{3} \quad \frac{2 - x}{3} \quad \frac{2x}{3} \]
   \[ K\textsubscript{c} = \left( \frac{2x}{3} \right)^2 \times \left( \frac{1 - x}{3} \right) \times \left( \frac{2 - x}{3} \right) = 50 \Rightarrow 23x^2 - 75x + 50 = 0 \]
   \[ x = 0.934 \text{ or } 2.326 \]
   Only 0.934 values is permissible
   So, moles of AB = 1.868

Ex. Calculate the % age dissociation of H\textsubscript{2}S (g) if 0.1 mole of H\textsubscript{2}S is kept in a 0.4 L vessel at 900 K. The value of K\textsubscript{c} for the reaction, 2H\textsubscript{2}S (g) \rightleftharpoons 2H\textsubscript{2}(g) + S\textsubscript{2}(g), is 1.0 \times 10^4.

Sol. 2H\textsubscript{2}S \rightleftharpoons 2H\textsubscript{2} + S\textsubscript{2}
   Volume of vessel = V = 0.4 L
   Let, x be the degree of dissociation
Moles

\[ 2H_2S \rightleftharpoons 2H_2 + S_2 \]

Initially

\[ 0.1 \quad 0 \quad 0 \]

At equilibrium

\[ 0.1 - 0.1x \quad 0.1x \quad 0.1x/2 \]

\[ K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{(0.01x)^2 (0.01)}{0.01 - 0.01x} = 10^4 \Rightarrow x = 0.02 \quad or \quad 2\% \text{ dissociation of } H_2S \]

**Ex.**

The degree of dissociation of HI at a particular temperature is 0.8. Find the volume of 1.5 M sodium thiosulphate solution required to react completely with the iodine present at equilibrium in acidic condition, when 0.135 mol each of \( H_2 \) and \( I_2 \) are heated at 440 K in a closed vessel of capacity 2.0 L.

**Sol.**

First find the value of \( K_c \) for dissociation of HI from its degree of dissociation

\[ \text{2HI} \rightleftharpoons H_2 + I_2 \text{ (degree of dissociation is 0.8)} \]

**Concentrations**

\[ \text{Initially} \quad 1.0 \quad 0 \quad 0 \]

\[ \text{At new equilibrium} \quad 1.0 - 0.8 \quad 0.4 \quad 0.4 \]

\[ K_e = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.4)(0.4)}{0.2^2} = 4 \]

Now, we have to start with 0.135 mol each of \( H_2 \) and \( I_2 \) and the following equilibrium will be established.

\[ \text{H}_2 + \text{I}_2 \rightleftharpoons \text{2HI} \]

**Concentrations**

\[ \text{Initially} \quad 0.135 \quad 0.135 \quad 0 \]

\[ \text{At new equilibrium} \quad 0.135 - x \quad 0.135 - x \quad 2x \]

\[ \Rightarrow K_e = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(0.135 - x)(0.135 - x)} = \frac{1}{4} \]

\[ \Rightarrow x = 0.135/5 = 0.027 \text{ moles} \]

Now, find the moles of \( I_2 \) left unreacted at equilibrium.

\[ n_{I_2} = 0.135 - 0.027 = 0.108 \text{ moles} \]

\( I_2 \) reacts with sodium thiosulphate (Na\(_2\)S\(_2\)O\(_3\)) as follows:

\[ 2\text{Na}_2\text{S}_2\text{O}_3 + I_2 \rightleftharpoons \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]

Applying mole concept, we have 2 moles of Na\(_2\)S\(_2\)O\(_3\) = 1 mole of \( I_2 \)

\[ \Rightarrow 0.108 \text{ moles of } I_2 = 2 \quad 0.108 = 0.216 \text{ moles of } \text{Na}_2\text{S}_4\text{O}_6 \text{ are used up} \]

\[ \Rightarrow \text{Moles} = MV_n \text{ (M = Molarity, } V_n = \text{ volume in litres)} \]

\[ \Rightarrow 0.216 = 1.5 \quad V \]

\[ \Rightarrow V = 0.144 \text{ lt = 144 mL.} \]
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reaction</th>
<th>$\Delta n$</th>
<th>Relation between $K_p$ &amp; $K_c$</th>
<th>values of $K_c$</th>
<th>values of $K_p$</th>
<th>Unit of $K_c$</th>
<th>Unit of $K_p$</th>
<th>Relation between amount of dissociation (volume and pressure)</th>
<th>$\Delta H$</th>
<th>Conditions for obtaining more product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$H_2 + I_2 \rightarrow 2HI$</td>
<td>0</td>
<td>$K_p = K_c(RT) , ^\circ$</td>
<td>$K_p = K_c$</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>$-ve$ (exo-thermic)</td>
<td>$\hspace{0.5cm}$</td>
<td>Low temperature No pressure High concentration</td>
</tr>
<tr>
<td>2.</td>
<td>$2HI \rightarrow H_2 + I_2$</td>
<td>0</td>
<td>$K_p = K_c(RT) , ^\circ$</td>
<td>$K_p = K_c$</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>$+ve$ (endo-thermic)</td>
<td>$\hspace{0.5cm}$</td>
<td>High temperature No pressure High concentration</td>
</tr>
<tr>
<td>3.</td>
<td>$PCl_5 \rightarrow PCl_3+Cl_2$</td>
<td>$+1$</td>
<td>$K_p = K_c(RT) , ^\circ$</td>
<td>$K_p &gt; K_c$</td>
<td>gram mol$^{-1}$ (Atm. press.$)^{-1}$ or</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High temperature Low pressure High concentration</td>
</tr>
<tr>
<td>4.</td>
<td>$N_2O_4 \rightarrow 2NO_2$</td>
<td>$+1$</td>
<td>$K_p = K_c(RT) , ^\circ$</td>
<td>$K_p &gt; K_c$</td>
<td>gram mol$^{-1}$ (Atm. press.$)^{-1}$ or</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High temperature Low pressure High concentration</td>
</tr>
<tr>
<td>5.</td>
<td>$2NH_3 \rightarrow N_2+3H_2$</td>
<td>$+2$</td>
<td>$K_p = K_c(RT) , ^\circ$</td>
<td>$K_p &gt; K_c$</td>
<td>gram mol$^{-2}$ (Atm. press.$)^{-2}$ or</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High temperature Low pressure High concentration</td>
</tr>
<tr>
<td>6.</td>
<td>$N_2+3H_2 \rightarrow 2NH_3$</td>
<td>$-2$</td>
<td>$K_p = K_c(RT) , ^\circ$</td>
<td>$K_p &lt; K_c$</td>
<td>gram mol$^{-2}$ (Atm. press.$)^{-2}$ or</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Low temperature High pressure High concentration</td>
</tr>
<tr>
<td>7.</td>
<td>$PCl_3+Cl_2 \rightarrow PCl_5$</td>
<td>$-1$</td>
<td>$K_p = K_c(RT) , ^\circ$</td>
<td>$K_p &lt; K_c$</td>
<td>gram mol$^{-1}$ (Atm. press.$)^{-1}$ or</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Low temperature High pressure High concentration</td>
</tr>
<tr>
<td>8.</td>
<td>$2SO_2+O_2 \rightarrow 2SO_3$</td>
<td>$-1$</td>
<td>$K_p = K_c(RT) , ^\circ$</td>
<td>$K_p &lt; K_c$</td>
<td>gram mol$^{-1}$ (Atm. press.$)^{-1}$ or</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Low temperature High pressure High concentration</td>
</tr>
</tbody>
</table>
1. **Law of mass action.** It was put forward by Guldberg and Waage. It states that the rate at which a substance reacts is directly proportional to its active mass and hence the rate at which substances react together is directly proportional to the product of their active masses. Active mass means molar concentration.

2. **Law of chemical equilibrium.** For the reaction \( aA + bB \xrightleftharpoons{} xX + yY \), the equilibrium constant which is constant for a reaction at constant temperature is \( K = \frac{[X]^x[Y]^y}{[A]^a[B]^b} \).

3. **Equilibrium constant in terms of concentrations (K) is** \( K_c = \frac{[X]^x[Y]^y}{[A]^a[B]^b} \).
   
   Equilibrium constant in terms of pressures is \( K_p = \frac{P_xP_y}{P_A^aP_B^b} \).

4. **Relation between \( K_p \) and \( K_c \).** \( K_p \) and \( K_c \) are related to each other as \( K_p = K_c (RT)^{\Delta n_g} \) where \( \Delta n_g = (n_p - n_r) \) gaseous.

5. **Concentration Quotient condition or Reaction Quotient (Q).** For the reaction \( aA + bB \xrightleftharpoons{} xX + yY \), at any other than the stage of equilibrium, the expression \( \frac{[X]^x[Y]^y}{[A]^a[B]^b} = Q \) is called concentration quotient or reaction quotient.
   
   (i) If \( Q = K \), the reaction is in equilibrium.
   
   (ii) If \( Q < K \), Q will tend to increase till it becomes equal to K. Hence, reaction proceeds in the forward direction.

   (iii) If \( Q > K \), Q will tend to decrease. As a result, the reaction will proceed in the backward direction.

6. **Effect of temperature on \( K \).** For \( aA + bB \xrightleftharpoons{} C + D \), \( K = \frac{k_f}{k_i} \).
   
   For exothermic reaction, \( k_f \) decreases with increase of temperature, so \( K \) decreases.

   For endothermic reaction, \( k_f \) increases with increase of temperature, so \( K \) increases.

7. **Effect of adding inert gas at equilibrium.**
   
   (i) For reactions in which \( n_p = n_r \), there is no effect of adding an inert gas at constant volume or at constant pressure on the equilibrium.

   (ii) For reaction in which \( n_p > n_r \) (e.g. \( \text{PCl}_4 \xrightleftharpoons{} \text{PCl}_3 + \text{Cl}_2 \)), there is no effect of adding inert gas on the equilibrium at constant volume but at constant pressure, equilibrium shifts in the forward direction.

8. **Le Chatelier's principle** states that "if a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction so as to undo the effect of the change imposed."

9. **Van't Hoff reaction isotherm.** It is an equation which gives the relationship between standard free energy change (\( \Delta G \)) of a reaction and its equilibrium constant (\( K_p \))
   
   i.e. \( \Delta G = -RT \ln K_p \)

   This equation helps to calculate \( \Delta G \) of a reaction at temperature T if its equilibrium constant at this temperature is known or vice-versa.

10. **Van't Hoff equation.** This equation gives the variation of equilibrium constant of a reaction with temperature. The equation is
\[ \frac{d \ln K}{dT} = \frac{\Delta H^o}{RT^2} \]

The integrated form of this equation is

\[ \log \frac{K_2}{K_1} = \frac{\Delta H^o}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \]

where \( \Delta H \) = enthalpy change of the reaction (assumed to be constant in the temperature range \( T_1 \) to \( T_2 \)).

11. Units of equilibrium const. = (mol L\(^{-1}\))\(^{(x + y) - (a + b)}\) or (atm)\(^{(x + y) - (a + b)}\)

12. Degree of dissociation of PCl\(_5\) or N\(_2\)O\(_4\) is given by

\[ \alpha = \frac{D - d}{d} = \frac{M_t - M_o}{M_o} \]

where \( D = \) theoretical vapour density and \( d = \) vapour density after dissociation (observed V.D.), \( M_t = \) theoretical (calculated) molecular mass and \( M_o = \) observed molecular mass.

13. From integrated form of van't Hoff equation, viz.

\[ \log \frac{K_2}{K_1} = \frac{\Delta H^o}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \]

We may conclude that

(i) If \( \Delta H = 0 \), i.e. no heat is evolved or absorbed in the reaction.

\[ \log (K_2/K_1) = 0, \text{ i.e. } K_2/K_1 = 1 \text{ or } K_2 = K_1. \]

So, equilibrium constant does not change with temperature.

(ii) If \( \Delta H = +ve \), i.e. heat is absorbed in the reaction, then

\[ \log (K_2/K_1) = +ve \text{ or } \log K_2 > \log K_1 \text{ or } K_2 > K_1. \]

So, equilibrium constant increases with increase in temperature.

(iii) If \( \Delta H = -ve \), i.e. heat is evolved in the reaction, then

\[ \log (K_2/K_1) = -ve, \text{ i.e. } \log K_2 < \log K_1 \text{ or } K_2 < K_1. \]

So, equilibrium constant decreases with increase in temperature.
Ex. 1  
(i) Consider the heterogeneous equilibrium
\[ \text{CaCO}_3 (s) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (s) \quad K_p = 4 \times 10^{-2} \text{ atm} \quad \text{........(i)} \]
\[ \text{C} (s) + \text{CO}_2 (g) \rightleftharpoons 2\text{CO} (g) \quad K_p' = 4.0 \text{ atm} \quad \text{........(ii)} \]

Calculate the partial pressure of CO (g) when CaCO\(_3\) and C are mixed and allowed to attain equilibrium at the temperature for which the above two equilibria have been studied.

(ii) Calculate the pressure of CO\(_2\) gas at 700 K in the heterogeneous equilibrium reaction.
\[ \text{CaCO}_3 (s) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (g) \]
If \(\Delta G^\circ\) for this reaction is 120.2 kJ/mol.

**Sol.**
(i) For Eq. (i), \(K_p = P_{\text{CO}_2}\)

From Eq. (ii), \(K_p' = P_{\text{CO}_2}^2 / P_{\text{CO}_2}\)

\[ \therefore K_p \cdot K_p' = (P_{\text{CO}_2})^3 = 4 \times 10^{-2} \cdot 4 = 16 \times 10^{-2} \text{ atm}^2 \]

\[ \therefore P_{\text{CO}_2} = \sqrt{16 \times 10^{-2} \text{ atm}^2} = 0.4 \text{ atm} \]

(ii) \(\Delta G = -2.303 \text{ RT log } K_p\)

\[ \therefore \log K_p = -\frac{\Delta G}{2.303 \times R \times T} = -\frac{120.2 \times 10^3 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (700 \text{ K})} \]

\[ \therefore K_p = 1.00 \times 10^{-9} \text{ atm} = P_{\text{CO}_2} \]

Ex. 2  
For the dissociation reaction \(\text{N}_2\text{O}_4 (g) \rightleftharpoons 2\text{NO}_2 (g)\)

derive the expression for the degree of dissociation in terms of \(K_p\) and total pressure \(P\).

**Sol.**

\[ \text{N}_2\text{O}_4 (g) \rightleftharpoons 2\text{NO}_2 (g) \]

Let initial no. of moles \(1\) \(0\)

Moles at equilibrium \((1-\alpha)\) \(2\alpha\)

\[ K_p = \left( \frac{n_{\text{NO}_2}}{n_{\text{N}_2\text{O}_4}} \right)^2 \frac{P}{\sum n} \]

\[ = \left( \frac{2\alpha}{1-\alpha} \right)^2 \frac{P}{(1-\alpha+2\alpha)} \]

\[ = \frac{4\alpha^2}{(1-\alpha)} \left( \frac{P}{1+\alpha} \right) = \frac{4\alpha^2}{(1-\alpha^2)} \times P \]

\[ \therefore \frac{4P}{K_p} = \frac{(1-\alpha^2)}{\alpha^2} = \frac{1}{\alpha^2} - 1 \]

\[ \frac{1}{\alpha^2} = \left( 1 + \frac{4P}{K_p} \right) = \frac{4P + K_p}{K_p} \quad \Rightarrow \quad \alpha^2 = \frac{K_p}{4P + K_p} \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_p}{4P + K_p}} \]
Ex. 3  The value of $K_p$ is $1 \times 10^{-3}$ atm$^{-1}$ at 25°C for the reaction, $2\text{NO} + \text{Cl}_2 \rightleftharpoons 2\text{NOCl}$. A flask contains NO at 0.02 atm and 25°C. Calculate the moles of Cl$_2$ that must be added if 1% of NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 moles of the gas produce 1 atm pressure at 25°C (ignore the probable association of NO to N$_2$O$_2$).

**Sol.** Let, initial pressure of added Cl$_2$ is $p$ atm.

\[
\begin{align*}
2\text{NO} & \rightleftharpoons 2\text{NOCl} \\
\text{Initial} & : 0.02 \text{ atm} & p \text{ atm} & 0 \\
\text{At equilibrium} & : \left(0.02 - \frac{0.02}{100}\right) & \left(p - \frac{0.01}{100}\right) & \frac{0.02}{100} \\
& = 2 \times 10^{-4} (100 - 1) & = p - 10^{-4} \text{ atm} & = 2 \times 10^{-4} \text{ atm} \\
& = 198 \times 10^{-4} \text{ atm}
\end{align*}
\]

\[
K_p = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}} \times P_{\text{Cl}_2}}
\]

\[
\Rightarrow 10^{-3} = \frac{(2 \times 10^{-4})^2}{(198 \times 10^{-4})^2 \times (p - 10^{-4})}
\]

\[
\Rightarrow p - 10^{-4} = \frac{4}{(198)^2 \times 10^{-3}} = 0.102
\]

\[
\therefore p = 0.102 + 0.0001 = 0.1021 \text{ atm}
\]

Volume of the vessel can be calculated as follows,

\[
P V = nRT
\]

or

\[
V = \frac{nRT}{P} = \frac{0.2 \times 0.082 \times 298}{1} = 4.887 \text{ L}
\]

Again applying, \((PV = nRT)\) we can calculate the number of moles of Cl$_2$

\[
n_{\text{Cl}_2} = \frac{PV}{RT} = \frac{0.1021 \times 4.887}{0.082 \times 298} = 0.0204 \text{ mol.}
\]

Ex. 4  When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate \(\Delta G^\circ\) for the following equilibria.

\[
\text{B} \rightleftharpoons \text{A} \quad \Delta G_1^\circ = ?
\]

\[
\text{B} \rightleftharpoons \text{C} \quad \Delta G_2^\circ = ?
\]

From the calculated value of \(\Delta G_1^\circ\) and \(\Delta G_2^\circ\) indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

**Sol.**

\[
\text{Pentyne} \overset{\text{KOH}}{\rightleftharpoons} \text{2-Pentyne} + 1,2\text{-Pentadiene}
\]

\[(\text{A}) \quad (\text{B}) \quad (\text{C})\]

At eqm.% 1.3 95.5 3.5

\[
K_1 = \frac{[\text{B}][\text{C}]}{[\text{A}]} = \frac{95.2 \times 3.5}{1.3} = 256.31
\]

\[\therefore \text{(i)}\]

From eqn. B \(\rightleftharpoons\) A

\[
K_1 = \frac{[\text{A}]}{[\text{B}]}
\]

From Eqs. (i) and (ii), \(K_1 = \frac{[\text{C}]}{K_1} = \frac{3.5}{256.31} = 0.013 \quad \therefore \text{(ii)}\)

\[
\Delta G = -2.303 RT \log_{10} K_1
\]

\[
= -2.303 \times 8.314 \times 448 \log_{10} 0.013
\]

\[
= 16178.4
\]

\[
= 16.1784 \text{ kJ}
\]
Stability order for A and B is $B > A$

Similarly, $B \xrightarrow{\text{C}} C$

$$K_2 = \frac{[C]}{[B]} = \frac{K_c \times [A]}{[B]^2} = \frac{256.31 \times 3.1}{95.2 \times 95.2} = 0.0876$$

$\therefore \Delta G_2 = -2.303 \text{ RT } \log_{10} K_2$

$$= -2.303 \times 8.314 \times 448 \log_{10} 0.0876$$

$$= 9068.06 \text{ J} = 9.068 \text{ kJ}$$

Thus, stability order for B and C is $B > C$

Total order of stability is $B > C > A$.

**Ex. 5**

The density of an equilibrium mixture of $N_2O_4$ and NO$_2$ at 1 atm is 3.62 g/L at 288 K and 1.84 g/L at 348 K. Calculate the entropy change during the reaction at 348 K.

**Sol.**

$$N_2O_4 \xrightarrow{2NO_2}$$

**Case (i)**

$$PV = nRT = \frac{w}{m_{\text{mix}}}RT$$

$$\Rightarrow m_{\text{mix}} = \frac{w}{V} \times \frac{RT}{P} = \frac{dRT}{P} = 3.62 \text{ 0.082 288} = 85.6$$

Let, a mole of $N_2O_4$ and $(1-a)$ mole of NO$_2$ exist at equilibrium

$\therefore a \times 92 + (1 - a) \times 46 = 85.6$

$\therefore a = 0.86$

$\therefore n_{N_2O_4} = 0.86 \text{ mol}, \ n_{NO_2} = 0.14 \text{ mol}$

$$K_p = \frac{0.14 \times 0.14}{0.86 \times 1} = 0.0228 \text{ atm at 288 K.}$$

**Case (ii)**

$$m_{\text{mix}} = \frac{dRT}{P} = 1.84 \text{ 0.0821 348} = 52.57$$

Let, $a'$ mol of $N_2O_4$ and $(1-a')$ mol of NO$_2$ exist at equilibrium

$\therefore a' \times 92 + (1 - a') \times 46 = 52.57$

$\therefore a' = 0.14$

$\therefore n_{N_2O_4} = 0.14 \text{ mol}, \ n_{NO_2} = 0.86 \text{ mol}$

$\therefore K_p = \frac{0.86 \times 0.86}{0.14 \times 1} = 5.283 \text{ atm at 348 K}$

$$\log_{10} \left( \frac{K_p}{K_{p_i}} \right) = \frac{\Delta H}{2.303R} \left[ \frac{T_2 - T_1}{T_1T_2} \right]$$

$$\Rightarrow \log_{10} \left( \frac{5.283}{0.0228} \right) = \frac{\Delta H}{2 \times 2.303} \left[ \frac{348 - 288}{348 \times 288} \right]$$

$\therefore \Delta H = 18195.6 \text{ cal} = 18.196 \text{ Kcal}$

$$\Delta G = -2.303 \text{ RT } \log K_p$$

$$= -2.303 \times 2 \times 348 \times \log 5.283$$

$$= -1158.7 \text{ cal.}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{18195.6 + 1158.7}{348} = 55.62 \text{ cal}$$
Ex. 6  For the reaction, $[\text{Ag(CN)}_2^-] \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$, the equilibrium constant, $K_c$, at 27°C is $4.0 \times 10^{-19}$.

To find the silver ion concentration in a solution which is originally 0.10 M in KCN and 0.03 M in AgNO$_3$.

**Sol.**  
$\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag(CN)}_2^-]$

$$K'_c = \frac{[\text{Ag(CN)}_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = \frac{1}{K_c} = 2.5 \times 10^{20} \quad ........(i)$$

Very high value of $K'_c$ show that complex forming equilibrium is spontaneous and almost all the Ag$^+$ ion would have reacted leaving xM in solution:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag(CN)}_2^-]$</td>
<td>0.03M</td>
<td>-xM</td>
<td>(0.1 - 0.03x)M</td>
</tr>
<tr>
<td></td>
<td>0.1M</td>
<td>-2xM</td>
<td>0.03M</td>
</tr>
</tbody>
</table>

$$K'_c = 2.5 \times 10^{20} = \frac{0.03}{x(0.1 - 0.03 \times 2x)^2}$$

$\therefore x = [\text{Ag}^+] = 7.5 \times 10^{-18}$ M

Ex. 7  In an experiment, 5 moles of HI were enclosed in a 10 litre container. At 817 K equilibrium constant for the gaseous reaction, $2\text{HI} (g) \rightleftharpoons \text{H}_2 (g) + \text{I}_2 (g)$, is 0.025. Calculate the equilibrium concentrations of HI, H$_2$ and I$_2$. What is the fraction of HI that decomposes?

**Sol.**  
Let, 2n be the number of moles of HI which is decomposed, the number of moles of H$_2$ and I$_2$ produced will be n mole each. Then molar concentrations of various species at equilibrium are

$$[\text{HI}] = \frac{(5-2n)}{10} \text{ mol/L}, \quad [\text{H}_2] = \frac{n}{10} \text{ mol/L}, \text{ and } [\text{I}_2] = \frac{n}{10} \text{ mol/L}$$

Also, $K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{n \times n}{10 \times 10} \left(\frac{5-2n}{10}\right)^2$

$$0.025 = \frac{n^2}{(5-2n)^2}$$

Solving for n, we get n = 0.6

$\therefore [\text{HI}] = \frac{5-2 \times 0.6}{10} = \frac{3.8}{10} = 0.38 \text{ mol/L}$

$[\text{H}_2] = \frac{0.6}{10} = 0.06 \text{ mol/L}$

$[\text{I}_2] = \frac{0.6}{10} = 0.06 \text{ mol/L}$

Fraction of HI decomposed = $\frac{2 \times 0.6}{5} = 0.24$ or 24%
0.5 moles of $N_2$ and 3 moles of $PCl_5$ are placed in a 100 litre container heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation of $PCl_5$ and value of $K_p$ for its dissociation.

**Sol.**

Dissociation of $PCl_5$ is written as

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

Let, $x$ be the no. of moles of $PCl_5$ decomposed at equilibrium

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

Initial moles

\[
\begin{array}{ccc}
3 & 0 & 0 \\
\end{array}
\]

Moles at eqm.

\[
\begin{array}{ccc}
3-x & x & x \\
\end{array}
\]

Now, total gaseous moles in the container = $n_T$

\[n_T = \text{moles of (PCl}_5 + \text{PCl}_3 + \text{Cl}_2) + \text{moles of N}_2\]

\[n_T = 3 - x + x + x + 0.5 = 3.5 + x\]

The mixture behaves ideally, hence $PV = n_TRT$

Let us calculate no. of moles by using gas equation

\[n_T = \frac{PV}{RT} = \frac{2.05 \times 100}{0.0821 \times 400} \implies n_T = 5\]

Now, equating the two values of $n_T$, we have

\[3.5 + x = 5 \implies x = 1.5 \implies \text{degree of dissociation} = \frac{1.5}{3} = \frac{1}{2} = 0.5\]

Now, $K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}^3}$

\[P_{PCl_5} = \frac{3-x}{3.5+x} P = \frac{1.5}{5} \times 2.05 = 0.615 \text{ atm}\]

\[P_{PCl_3} = \frac{1.5}{5} \times 2.05 = 0.615 \text{ atm}\]

\[P_{Cl_2} = \frac{1.5}{5} \times 2.05 = 0.615 \text{ atm}\]

\[K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}^3} \implies K_p = \frac{0.615 \times 0.615}{0.615} = 0.615 \text{ atm}\]

\[K_p = 0.615 \text{ atm}\]

**Note:**

The inert gases like $N_2$ or noble gases (He, Ne etc.) though do not take part in the reaction, but still they affect the degree of dissociation and equilibrium concentrations for the reactions in which $\Delta n \neq 0$. They add to the total pressure of the equilibrium mixture ($p \propto n$).

**Ex. 9**

For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $K = 0.059$ atm at 1000 K. 1 g of $CaCO_3$ is placed in a 10 litre container at 1000 K to reach the equilibrium. Calculate the mass of $CaCO_3$ left at equilibrium.

**Sol.**

At equilibrium

\[
\begin{array}{ccc}
a - x & x & x \\
\end{array}
\]

Here, $a =$ initial moles of $CaCO_3$

\[K_p = P_{CO_2} = 0.059\]

\[n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{0.059 \times 10}{0.082 \times 1000} = 7.2 \times 10^{-3} \text{ moles}\]

Moles of $CaCO_3$ left = 0.01 - 0.0072 = 0.0028

Mass of $CaCO_3$ left = 0.28 g
Ex. 10

The value of $K_p$ for the reaction, $2H_2O (g) + 2Cl_2 (g) \rightleftharpoons 4HCl (g) + O_2 (g)$ is 0.035 atm at 500°C, when the partial pressures are expressed in atmosphere. Calculate $K_c$ for the reaction,

$$\frac{1}{2}O_2 (g) + 2HCl (g) \rightleftharpoons Cl_2 (g) + H_2O (g)$$

**Sol.**

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

$\Delta n =$ moles of products – moles of reactants = 5 – 4 = 1

$R = 0.0821$ L atm/mol/K, $T = 500 + 273 = 773$ K

$\therefore K_p = K_c (0.0821 \times 773)$

$K_c = 5.515 \times 10^{-4}$ mol L$^{-1}$

$\therefore K_c$ for the reverse reaction would be

$$K_c' = \frac{1}{K_c}$$

$$K_c' = \frac{1}{5.515 \times 10^{-4}} = 1813.24 \text{ (mol L}^{-1})^{-1}$$

When a reaction is multiplied by any number n (integer or a fraction) then $K_c'$ or $K_p'$ becomes $(K_c)^n$ or $(K_p)^n$ of the original reaction.

$\therefore K_c$ for $\frac{1}{2}O_2 (g) + 2HCl (g) \rightleftharpoons Cl_2 (g) + H_2O (g)$

is $\sqrt{1813.24} = 42.58$ (mol L$^{-1}$)$^{-\frac{1}{2}}$

Ex. 11

$K_p$ for the reaction $N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$ is 0.66 at 46°C. Calculate the percent dissociation of $N_2O_4$ at 46°C and a total pressure of 0.5 atm. Also calculate the partial pressure of $N_2O_4$ and NO$_2$ at equilibrium.

**Sol.**

This problem can be solved by two methods.

**Method 1:** Let, the number of moles of $N_2O_4$ initially be 1 and $\alpha$ is the degree of dissociation of $N_2O_4$,

$$N_2O_4 \rightleftharpoons 2NO_2$$

Initial moles 1 0

Moles at equilibrium $1 - \alpha$ 2$\alpha$

Total moles at equilibrium $1 - \alpha + 2\alpha = 1 + \alpha$

$$p_{N_2O_4} = \frac{1 - \alpha}{1 + \alpha} \times P_T$$

$$p_{NO_2} = \frac{2\alpha}{1 + \alpha} \times P_T$$

$\therefore K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{4\alpha^2P_T}{(1 - \alpha)(1 + \alpha)} = 4\alpha^2 \times 0.5 \times \frac{1}{1 - \alpha^2}$

$\alpha = 0.5$, i.e. 50% dissociation

Hence, partial pressure of $N_2O_4 = 0.167$ atm.

and partial pressure of NO$_2$ = 0.333 atm.

**Method 2:** Let, the partial pressure of NO$_2$ at equilibrium be $p$ atm, then the partial pressure of $N_2O_4$ at equilibrium will be $(0.5 - p)$ atm.

$\therefore K_p = \frac{p^2}{(0.5 - p)} = 0.66$

$p^2 + 0.66p - 0.33 = 0$

On solving, $p = 0.333$ atm.

$\therefore p_{NO_2} = 0.333$ atm and $p_{N_2O_4} = 0.167$ atm.
Ex.12 Ammonium hydrogen sulphide dissociated according to the equation,
\[ \text{NH}_4\text{HS (s)} \rightleftharpoons \text{NH}_3 (g) + \text{H}_2\text{S (g)} \] If the observed pressure of the mixture is 2.24 atm at 106°C, what is the equilibrium constant \( K_p \) of the reaction?

**Sol.** The reaction is \( \text{NH}_4\text{HS (s)} \rightleftharpoons \text{NH}_3 (g) + \text{H}_2\text{S (g)} \).

If \( \alpha \) is the degree of dissociation of equilibrium,
Total moles of \( \text{NH}_3 \) and \( \text{H}_2\text{S} \) at equilibrium = \( 2\alpha \).

Partial pressure = \( \frac{\text{Moles of substance}}{\text{Total pressure}} \times \text{Total no. of moles} \)

\[ \therefore p_{\text{NH}_3} = \frac{\alpha}{2\alpha} P = 0.5 P \quad p_{\text{H}_2\text{S}} = \frac{\alpha}{2\alpha} P = 0.5 P \]

\[ K_p = p_{\text{NH}_3} \times p_{\text{H}_2\text{S}} = 0.5 P \times 0.5 P = 0.25 P^2 \]

Substituting the value of \( P = 2.24 \text{ atm} \).

\[ K_p = 0.25 \times 2.24 \times 2.24 = 1.2544 \text{ atm}^2 \]

Alternatively:
At equilibrium \( p_{\text{NH}_3} + p_{\text{H}_2\text{S}} = 2.24 \text{ atm} \)
As \( p_{\text{NH}_3} = p_{\text{H}_2\text{S}} \)

\[ \therefore p_{\text{NH}_3} = \frac{2.24}{2} = 1.12 \text{ atm} \]

\[ K_p = 1.12 \times 1.12 = 1.2544 \text{ atm}^2 \]

Ex.13 In a mixture of \( \text{N}_2 \) and \( \text{H}_2 \), initially they are in a mole ratio of 1 : 3 at 30 atm and 300°C, the percentage of ammonia by volume under the equilibrium is 17.8%. Calculate the equilibrium constant \( K_p \) of the mixture, for the reaction, \( \text{N}_2 (g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3 (g) \).

**Sol.** Let, the initial moles \( \text{N}_2 \) and \( \text{H}_2 \) be 1 and 3 respectively (this assumption is valid as \( K_p \) will not depend on the exact number of moles of \( \text{N}_2 \) and \( \text{H}_2 \)). One can even start with \( x \) and 3\( x \)

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

Initially 1  3  0
At equilibrium 1-x  3-3x  2x

Since % by volume of a gas is same as % by mole,

\[ \therefore \frac{2x}{4-2x} = 0.178 \]
\[ \therefore x = \frac{4 \times 0.178}{(2+2 \times 0.178)} = 0.302 \]

\[ \therefore \text{Mole fraction of } \text{H}_2 \text{ at equilibrium} = \frac{3-3x}{4-2x} = 0.6165 \]

Mole fraction of \( \text{N}_2 \) at equilibrium = \( 1 - 0.6165 - 0.178 = 0.2055 \)

\[ \therefore K_p = \frac{(X_{\text{NH}_3} \times P)^2}{(X_{\text{N}_2} \times P)(X_{\text{H}_2} \times P)^3} = \frac{(0.178 \times 30)^2}{(0.2055 \times 30)(0.6165 \times 30)^3} \]

\[ K_p = 7.31 \times 10^{-4} \text{ atm}^{-2} \]

Ex.14 Given below are the values of \( \Delta H \) and \( \Delta S \) for the reaction at 27°C, \( \text{SO}_2 (g) + \frac{1}{2}\text{O}_2 (g) \longrightarrow \text{SO}_3 (g) \)
\( \Delta H = 98.32 \text{ kJ/mol} \quad \Delta S = -95 \text{ J/mol} \). Calculate the value of \( K_p \) for the reaction.

**Sol.**
\[ \log_{10} K_p = \frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303 \times R} \]
\[ \therefore \log_{10} K_p = \frac{98320}{2.303 \times 8.314 \times 300} - \frac{95}{2.303 \times 8.314} \Rightarrow K_p = 1.44 \times 10^{12} \text{ atm}^{-\frac{1}{2}} \]
**SOLVED EXAMPLES**

**Ex. 1**  The volume of a closed reaction vessel in which the equilibrium:

\[ 2\text{SO}_2 (g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3 (g) \] is halved. Now -

(A) the rates of forward and backward reactions will remain the same.

(B) the equilibrium will not shift.

(C) the equilibrium will shift to the left.

(D) the rate of forward reaction will become double that of reverse reaction and the equilibrium will shift to the right.

**Sol.**  (D)

In the reaction

\[ 2\text{SO}_2 (g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3 (g) \]

In this reaction three moles (or volumes) of reactants are converted into two moles (or volumes) of products i.e. there is a decrease in volume and so if the volume of the reaction vessel is halved the equilibrium will be shifted to the right i.e. more product will be formed and the rate of forward reaction will increase i.e. double that of reverse reaction.

**Ex. 2**  The equilibrium constant of the reaction \[ \text{A}_2 (g) + \text{B}_2(g) \rightleftharpoons 2\text{AB} (g) \] at 100°C is 50. If one litre flask containing one mole of \( \text{A}_2 \) is connected to a 3 litre flask containing two moles of \( \text{B}_2 \) the number of moles of \( \text{AB} \) formed at 373 K will be -

(A) 1.886  
(B) 2.317  
(C) 0.943  
(D) 18.86

**Sol.**  (A)

The equilibrium is represented as:

\[ \text{A}_2 (g) + \text{B}_2(g) \rightleftharpoons 2\text{AB} (g) \]

Initial concentration  

<table>
<thead>
<tr>
<th>( \text{A}_2 )</th>
<th>( \text{B}_2 )</th>
<th>( \text{AB} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

Moles at equilibrium  

<table>
<thead>
<tr>
<th>( \text{A}_2 )</th>
<th>( \text{B}_2 )</th>
<th>( \text{AB} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-x</td>
<td>2-x</td>
<td>2x</td>
</tr>
</tbody>
</table>

Total volume = 1 + 3 = 4 litres

\[ [\text{A}_2] = \frac{1-x}{4}, \quad [\text{B}_2] = \frac{2-x}{4} \quad \text{and} \quad [\text{AB}] = \frac{2x}{4} \]

\[ K = \frac{[\text{AB}]^2}{[\text{A}_2][\text{B}_2]} = \frac{\left(\frac{2x}{4}\right)^2}{\left(\frac{1-x}{4}\right)\left(\frac{2-x}{4}\right)} = 50 \]

On solving we get \( 23x^2 - 75x + 50 = 0 \)

\[ \therefore x = 2.31 \text{ or } 0.943, \quad \text{since } x \text{ can't be more than } 1 \]

so, \( x = 0.943 \)

\[ \therefore \text{ moles of AB formed } = 2 \times 0.943 = 1.886 \]

**Ex. 3**  \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI} (g) \)

When 92 g of \( \text{I}_2 \) and 1g of \( \text{H}_2 \) are heated at equilibrium at 450°C, the equilibrium mixture contained 1.9 g of \( \text{I}_2 \). How many moles of \( \text{I}_2 \) and \( \text{HI} \) are present at equilibrium.

(A) 0.0075 & 0.147 moles  
(B) 0.0050 & 0.147 moles  
(C) 0.0075 & 0.7094 moles  
(D) 0.0052 & 0.347 moles

**Sol.**  (C)

moles of \( \text{I}_2 \) taken = \( \frac{92}{254} = 0.3622 \)
moles of H\textsubscript{2} taken = \frac{1}{2} = 0.5

moles of I\textsubscript{2} remaining = \frac{1.9}{254} = 0.0075

moles of I\textsubscript{2} used = 0.3622 - 0.0075 = 0.3547

moles of H\textsubscript{2} used = 0.3547

moles of H\textsubscript{2} remaining = 0.5 - 0.3547 = 0.1453

moles of HI formed = 0.3547 \times 2 = 0.7094

At equilibrium

moles of I\textsubscript{2} = 0.0075 moles

moles of HI = 0.7094 moles

Ex. 4 When 1.0 mole of N\textsubscript{2} and 3.0 moles of H\textsubscript{2} was heated in a vessel at 873 K and a pressure of 3.55 atm. 30\% of N\textsubscript{2} is converted into NH\textsubscript{3} at equilibrium. Find the value of K\textsubscript{p} for the reaction.

(A) 3.1 \times 10^{-2} atm^{-2} (B) 4.1 \times 10^{-2} atm^{-2} (C) 5.1 \times 10^{-2} atm^{-2} (D) 6.1 \times 10^{-2} atm^{-2}

Sol. (C)

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

1 mole 3 moles 0 Initial moles
1–0.3 3.0 – 0.9 0.6 moles at equilibrium
= 0.7 moles = 2.1 moles

Total no. of moles at equilibrium = 3.4

\[ K_p = \frac{(0.6)^2}{(3.4 \times 3.55)^3} = 5.1 \times 10^{-2} \text{ atm}^{-2} \]

Ex. 5 2SO\textsubscript{2} (g) + O\textsubscript{2} (g) \rightleftharpoons 2SO\textsubscript{3} (g)

If the partial pressure of SO\textsubscript{2}, O\textsubscript{2} and SO\textsubscript{3} are 0.559, 0.101 and 0.331 atm respectively. What would be the partial pressure of O\textsubscript{2} gas, to get equal moles of SO\textsubscript{2} and SO\textsubscript{3}.

(A) 0.188 atm (B) 0.288 atm (C) 0.388 atm (D) 0.488 atm

Sol. (B)

2SO\textsubscript{2} (g) + O\textsubscript{2} (g) \rightleftharpoons 2SO\textsubscript{3} (g)

\[ K_p = \frac{[P_{SO_2}]^2}{[P_{SO_3}]^3} = \frac{(0.331)^2}{(0.331)^3} = 3.47 \]

If SO\textsubscript{2} and SO\textsubscript{3} have same number of moles, their partial pressure will be equal and

\[ P_{SO_3} = P_{SO_2} \Rightarrow P_{O_2} = \frac{1}{3.47} = 0.288 \text{ atm} \]

Ex. 6 A\textsubscript{2} (g) and B\textsubscript{2} (g) at initial partial pressure of 98.4 and 41.3 torr, respectively were allowed to react at 400 K. At equilibrium the total pressure was 110.5 torr. Calculate the value of K\textsubscript{p} for the following reaction at 400 K.

\[ 2A\textsubscript{2}(g) + B\textsubscript{2}(g) \rightleftharpoons 2A\textsubscript{2}B (g) \]

(A) 124 (B) 134 (C) 154 (D) 174

Sol. (B)
The given reaction is,

\[ 2A_2(g) + B_2(g) \rightleftharpoons 2A_B(g) \]

Initial pressure (torr) 98.4 41.3 0

At equilibrium 98.4–x 41.3–\(\frac{x}{2}\) x

Total pressure at equilibrium = 110.5 torr.

\[
(98.4 - x) + (41.3 - \frac{x}{2}) + x = 110.5 \\
\therefore x = 58.4 \text{ torr} \quad (760 \text{ torr} = 1 \text{ atm})
\]

\[
P(A_2B) = 58.4 \text{ torr} = 7.68 \times 10^{-2} \text{ atm}
\]

\[
P(A_2) = 98.4 - 58.4 = 40 \text{ torr} = 5.26 \times 10^{-2} \text{ atm}
\]

\[
P(B_2) = 41.3 - \frac{58.4}{2} = 12.1 \text{ torr} = 1.59 \times 10^{-2} \text{ atm}
\]

Ex. 7 \(K_p\) for the reaction \(N_2 + 3H_2 \rightleftharpoons 2NH_3\) at 400 C is \(3.28 \times 10^{-4}\). Calculate \(K_c\).

(A) 0.3 mole \(^{-2}\) litre \(^2\) \quad (B) 0.4 mole \(^{-2}\) litre \(^2\) \quad (C) 1.0 mole \(^{-2}\) litre \(^2\) \quad (D) 0.6 mole \(^{-2}\) litre \(^2\)

Sol. (C)

\[
N_2 + 3H_2 \rightleftharpoons 2NH_3
\]

\(\Delta n = -2\) and \(K_p = K_c (RT)^n\)

\[
3.28 \times 10^{-4} = K_c (0.0821 \times 673)^2
\]

and \(K_c = 1.0 \text{ mole}^{-2} \text{ litre}^2\).

Ex. 8 0.96 g of HI were heated to attain equilibrium \(2HI \rightleftharpoons H_2 + I_2\). The reaction mixture on titration requires 15.7 mL of N/20 hypo. Calculate % dissociation of HI.

(A) 18.9% \quad (B) 19.9% \quad (C) 10.46% \quad (D) 21.9%

Sol. (C)

\[
2HI \rightleftharpoons H_2 + I_2
\]

Initial moles

\[
\frac{0.96}{128} \quad 0 \quad 0
\]

= 7.5 \times 10^{-3}

Moles at equilibrium \(7.5 \times 10^{-3} - x\) \(x/2\) \(x/2\)

Now Meq. of \(I_2\) formed at equilibrium = Meq. of hypo used

\[
\frac{W}{E} \times 1000 = 15.7 \times \frac{1}{20} \quad \text{or} \quad \frac{W}{E} \text{ of } I_2 = 0.785 \times 10^{-3}
\]

\[
\therefore \text{Moles of } I_2 \text{ formed at equilibrium} = \frac{0.785 \times 10^{-3}}{2} = 0.3925 \times 10^{-3}
\]

or \(\frac{x}{2} = 0.3925 \times 10^{-3}\) \text{ or } \(x = 0.785 \times 10^{-3}\)

\[
\therefore \text{degree of dissociation of } HI = \frac{\text{moles dissociated}}{\text{initial moles}} = \frac{x}{7.5 \times 10^{-3}}
\]

\[
\alpha = \frac{0.785 \times 10^{-3}}{7.5 \times 10^{-3}} = 0.1046 = 10.46\%
\]
Ex. 9 A mixture of $H_2$ and $I_2$ in molecular proportion of 2 : 3 was heated at 444°C till the reaction $H_2 + I_2 \rightleftharpoons 2HI$ reached equilibrium state. Calculate the percentage of iodine converted into HI. ($K_c$ at 444°C is 0.02)

(A) 3.38%  (B) 4.38%  (C) 5.38%  (D) 6.38%

**Sol.** (C)

\[
\begin{align*}
H_2 & \quad + \quad I_2 & \rightleftharpoons & \quad 2HI \\
\text{Initial moles} & \quad 2 & \quad 3 & \quad 0 \\
\text{Equi.conc.} & \quad \frac{2-x}{v} & \quad \frac{3-x}{v} & \quad \frac{2x}{v}
\end{align*}
\]

\[
K_c = \frac{4x^2}{(2-x)(3-x)} = 0.02
\]

199 $x^2 + 5x - 6 = 0$

$x = 0.1615$

Out of 3 moles, 0.1615 moles $I_2$ is converted into HI.

\[
\text{Percentage of } I_2 \text{ converted to HI} = \frac{0.1615 \times 100}{3} = 5.38%
\]

Ex. 10 The equilibrium composition for the reaction is:

\[
\begin{align*}
\text{PCl}_3 & \quad + \quad \text{Cl}_2 & \rightleftharpoons & \quad \text{PCl}_5 \\
\text{0.20} & \quad \text{0.05} & \quad \text{0.40 moles/litre}
\end{align*}
\]

If 0.25 moles of Cl$_2$ is added at same temperature. Find equilibrium concentration of PCl$_5$ ($K_c = 20$)

(A) 0.48 moles/litre  (B) 0.38 moles/litre  (C) 0.56 moles/litre  (D) 1.20 moles/litre

**Sol.** (A)

\[
\begin{align*}
\text{PCl}_3 & \quad + \quad \text{Cl}_2 & \rightleftharpoons & \quad \text{PCl}_5 \\
\text{0.20} & \quad \text{0.05} & \quad \text{0.40 moles/litre}
\end{align*}
\]

If 0.25 moles of Cl$_2$ is added then at equilibrium [Let $V = 1L$]

\[
\begin{align*}
0.20 - x & \quad 0.30-x & \quad 0.40 +x \\
20 = & \frac{0.40 + x}{(0.20 - x)(0.30 - x)} & \text{or } x = 0.08
\end{align*}
\]

[PCl$_5$] = 0.4 + 0.08 = 0.48 moles/litre

Ex. 11 The equilibrium constant $K$, for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is $1.64 \times 10^{-4}$ atm$^{-2}$ at 300°C. What will be the equilibrium constant at 400°C, if heat of reaction in this temperature range is $-105185.8$ Joules.

(A) $0.64 \times 10^{-5}$ atm$^{-2}$  (B) $6.4 \times 10^{-3}$ atm$^{-2}$  (C) $0.64 \times 10^{-3}$ atm$^{-2}$  (D) $0.64 \times 10^{-1}$ atm$^{-2}$

**Sol.** (A)

\[
K_p = 1.64 \times 10^{-4} \text{ atm}^{-2}, \quad K_{p_2} = ?
\]

$T_1 = 300 + 273 = 573$ K

$T_2 = 400 + 273 = 673$ K

$\Delta H = -105185.8$ Joules

$R = 8.314$ J/K/mole

Applying equation

\[
\log K_{p_2} - \log K_{p_1} = \frac{\Delta H}{2.303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)
\]

\[
\log K_{p_2} - \log 1.64 \times 10^{-4} = -\frac{105185.8}{2.303 \times 8.314} \left( \frac{673 - 573}{673 \times 573} \right)
\]

or $K_{p_2} = 0.64 \times 10^{-5}$ atm$^{-2}$
**Ex.12** In an experiment at 500 K, the concentration of different species are \([\text{NH}_3] = 0.105 \text{ mol dm}^{-3}\), \([\text{N}_2] = 1.10 \text{ mol dm}^{-3}\) and \([\text{H}_2] = 1.50 \text{ mol dm}^{-3}\) then find the followings:-

(a) values of \(K_C\) and \(K_P\) for the reaction 

\[\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3\]

(b) value of \(K'_C\) for the reaction - 

\[2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2\]

**Sol.** (a) For the reaction \(\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3\)

\[K_C = \left(\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}\right)\]

\([\text{NH}_3] = 0.105 \text{ mol dm}^{-3}\), \([\text{N}_2] = 1.10 \text{ mol dm}^{-3}\) and 

\([\text{H}_2] = 1.50 \text{ mol dm}^{-3}\)

\[K_C = \frac{(0.105 \text{ mol dm}^{-3})^2}{(1.10 \text{ mol dm}^{-3}) \times (1.50 \text{ mol dm}^{-3})^3} = 2.97 \times 10^{-3} \text{ mol}^2\text{dm}^6\]

Now \(K_P = K_C \times (RT)^{\Delta n}\)

\(\Delta n = -2\),

\(R = 0.082 \text{ atm dm}^3\text{ K}^{-1}\text{ mol}^{-1}\), \(T = 500 \text{ K}\)

\[K_P = (2.97 \times 10^{-3} \text{ mol}^2\text{dm}^6) \times (0.082 \text{ atm dm}^3\text{ K}^{-1}\text{ mol}^{-1}) \times (500 \text{ K})^2\]

\[= 1.76 \times 10^{-6} \text{ atm}^2\]

(b) The equilibrium constant \(K_C\) for the reverse reaction is related to the equilibrium constant \(K_C\) for the forward reaction as:

\[K'_C = \frac{1}{K_C} = \frac{1}{2.97 \times 10^{-3} \text{ mol}^2\text{dm}^6} = 3.37 \times 10^{-2} \text{ mol}^2\text{dm}^6\]

**Ex.13** The equilibrium pressure of \(\text{NH}_4\text{CN (s)} \rightleftharpoons \text{NH}_3(g) + \text{HCN (g)}\) is 0.298 atm. Calculate \(K_P\). If \(\text{NH}_4\text{CN (s)}\) is allowed to decompose in presence of \(\text{NH}_3\) at 0.50 atm then calculate partial pressure of HCN at equilibrium.

**Sol.**

\(\text{NH}_4\text{CN (s)} \rightleftharpoons \text{NH}_3(g) + \text{HCN (g)}\)

Pressure at equilibrium = \(P\)

\(\therefore\) Total pressure at equilibrium = \(2P = 0.298\) atm

\(\therefore P = 0.149\) atm

\(\therefore K_P = P_{\text{NH}_3} \times P_{\text{HCN}} = 0.149 \times 0.149 = 0.0222\) atm²

If dissociation is made in presence of \(\text{NH}_3\) at 0.5 atm

\(\text{NH}_4\text{CN (s)} \rightleftharpoons \text{NH}_3(g) + \text{HCN (g)}\)

Initial pressure = 0.50 atm

Pressure at equil. = \((0.50 + P')\)

Also \(K_P = P' (0.50 + P')\)

or \(0.0222 = P' (0.50 + P')\)

\(\therefore P' = 0.1656\) atm
**Ex. 14** The value of $K_c$ for the reaction,

\[ N_2 + 2O_2 \rightleftharpoons 2NO_2 \]

at a certain temperature is 900. Calculate the value of equilibrium constant for

(i) \[ 2NO_2 \rightleftharpoons N_2 + 2O_2 \]

(ii) \[ \frac{1}{2} N_2 + O_2 \rightleftharpoons NO_2 \]

**Sol.** Equilibrium constant ($K_c$) for the reaction

\[ N_2 + 2O_2 \rightleftharpoons 2NO_2 \]

is

\[ K_c = \frac{[NO_2]^2}{[N_2][O_2]^2} = 900 \]

(i) For the reaction \[ 2NO_2 \rightleftharpoons N_2 + 2O_2 \], \[ K'_{c} = \frac{[N_2][O_2]^2}{[NO_2]^2} = \frac{1}{K_c} \]

\[ K'_{c} = \frac{1}{900} = 0.0011 \text{ mole litre}^{-1} \]

(ii) For the reaction \[ \frac{1}{2} N_2 + O_2 \rightleftharpoons NO_2 \]

\[ K''_{c} = \frac{[NO_2]}{[N_2][O_2]} = \sqrt{K_c} \]

\[ K''_{c} = \sqrt{900} = 30 \text{ litre}^{\frac{1}{2}} \text{ mol}^{\frac{1}{2}} \]

**Ex. 15** Ice melts slowly at higher altitude, why?

**Sol.** According to Le Chatelier principle, the melting of ice is favoured at high pressure because the forward reaction ice $\rightarrow$ water shows a decrease in volume. At higher altitude atmospheric pressure being low and thus ice melts slowly.

**Ex. 16** Both metals Mg and Fe can reduce copper from a solution having Cu$^{2+}$ ion according to equilibria.

\[ \text{Mg (s)} + \text{Cu}^{2+} \rightleftharpoons \text{Mg}^{2+} + \text{Cu (s)} ; K_1 = 5 \times 10^{90} \]

\[ \text{Fe (s)} + \text{Cu}^{2+} \rightleftharpoons \text{Fe}^{2+} + \text{Cu (s)} ; K_2 = 2 \times 10^{26} \]

Which metal will remove cupric ion from the solution to a greater extent.

**Sol.** Since $K_1 > K_2$, the product in the first reaction is much more favoured than in the second one. Mg thus removes more Cu$^{2+}$ from solution than Fe does.

**Ex. 17** The equilibrium constant $K_c$ for Y (g) $\rightleftharpoons$ Z (g) is 1.1. Which gas has molar concentration greater than 1.

**Sol.** For Y (g) $\rightleftharpoons$ Z (g)

\[ K_c = \frac{[Z]}{[Y]} = 1.1 \]

if $Z = 1$ ; $[Y] = 0.91$

Case I $0.9 < [Y] < 1$ only $Z = 1$

Case II $[Y] > 1$ both $[Y]$ and $[Z] > 1$
**Ex.18** When S in the form of S\(_8\) is heated 800 K, the initial pressure of 1 atmosphere falls by 30 % at equilibrium. This is because of conversion of some S\(_8\) to S\(_2\). Calculate the K\(_p\) for reaction.

**Sol.**

\[ S_8(g) \rightleftharpoons 4 \text{ S}_2(g) \]

<table>
<thead>
<tr>
<th>Initial pressure</th>
<th>1 atm</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium pressure</td>
<td>(1–0.30) atm</td>
<td>4 0.30 atm</td>
</tr>
<tr>
<td></td>
<td>0.70 atm</td>
<td>1.2 atm</td>
</tr>
</tbody>
</table>

Now, \( K_p = \frac{P^{4}_{S_2}}{P_{S_8}} = \frac{(1.2)^4}{0.70} = 2.9622 \text{ atm}^3 \)

**Ex.19** A vessel at 1000 K contains CO\(_2\) with a pressure of 0.6 atm. some of the CO\(_2\) is converted into CO on addition of graphite. Calculate the value of K, if total pressure at equilibrium is 0.9 atm.

**Sol.**

\[ \text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2 \text{CO}(g) \]

<table>
<thead>
<tr>
<th>Initial pressure</th>
<th>0.6 atm</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium pressure</td>
<td>(0.6–x) atm</td>
<td>2x atm</td>
</tr>
</tbody>
</table>

From question, (0.6 – x) + 2x = 0.9 hence, x = 0.3 atm.

Now, \( K_p = \frac{P^{2}_{CO}}{P_{CO_2}} = \frac{(2x)^2}{(0.6-x)} = 1.2 \text{ atm} \).