CH#08 CHEMICAL EQUILIBRIUM

▷ **Irreversible Reaction:-** (complete reaction)

↳ The reaction in which reactants are completely consumed & converted into product are called irreversible reaction.

↳ Reactant ⟶ Product

$C + O_2 \longrightarrow CO_2$

↳ Indicated by single headed arrow.

↳ This reaction proceeds in one direction only.

↳ This reaction will stop when limiting reactant is consumed completely.

▷ **Reversible Reaction:-** (incomplete reaction)

↳ A reversible reaction is one in which the products once formed can react together to reform the original reactant.

↳ Reactant ⇌ Product

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

↳ Indicated by double headed arrow.

↳ This reaction proceeds in both directions i.e forward & backward direction.

↳ This reaction never undergoes completion.

Difference between Reversible And IRREVERSIBLE Reaction

Reversible reaction	Irreversible reaction
Definition	
Reversible reaction is the one in which products once formed can react together to reform reactant.	The reaction in which reactants are completely consumed and converted into products.
Direction	
It is a bi-directional reaction.	It is a uni-directional reaction.
Arrow representation	
$\rightleftharpoons$	$\longrightarrow$
Completion	
It never undergoes completion.	It undergoes completion
Equilibrium	
Equilibrium exists here.	Equilibrium doesn't exist.
limiting reactant	
Reaction does not stop even if limiting reactant is consumed.	Reaction is stopped when limiting reactant is consumed.
Examples	
$N_2 + 3H_2 \rightleftharpoons 2NH_3$	$CaCO_3 \longrightarrow CaO + CO_2$
$N_2 + O_2 \rightleftharpoons 2NO$	$C + O_2 \longrightarrow CO_2$
	$Na + H_2O \longrightarrow NaOH + H_2$

MACROSCOPIC EVENTS:-

Macroscopic events refer to phenomenon that can be observed with the naked eye without considering the individual particles involved in the process.

Examples: ① Change in colour
② Evolution/absorption of heat
③ Formation of precipitates
④ Change in volume / pressure
⑤ Change in Physical State.

MICROSCOPIC EVENTS:-

Microscopic events refer to phenomenon that cannot be observed with naked eye but can be observed with microscope.

Examples: ① Collision between molecules
② Breaking & formation of bonds
③ Rearrangement of molecule
④ Direction of reaction.
⑤ Structure of atom / molecule / compound.

Equilibrium State:- (Dynamic Equilibrium)

State at which rate of forward reaction reaction become equal to rate of backward reaction.

State at which concentration of reactant & product

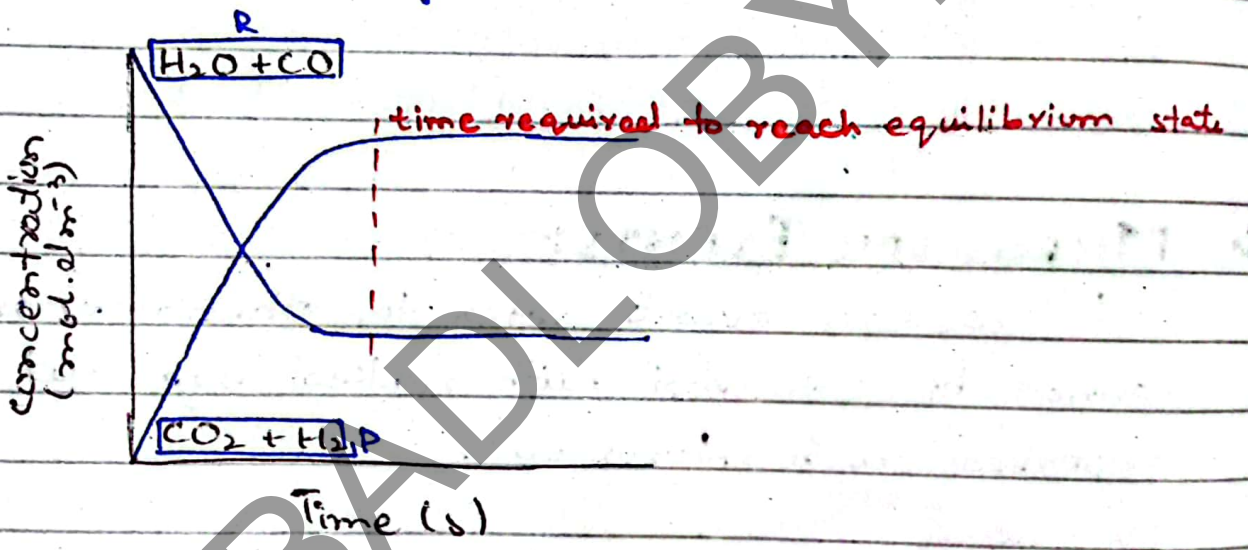
become constant.

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

Forward reaction's rate: Reactant decrease
highest at start of rxn
Product increase

Backward reaction's rate: Reactant increase
highest during the rxn.
Product decrease

Equilibrium State: Rate of forward rxn = Rate of backward rxn



Difference between Macroscopic and Microscopic Events

Macroscopic Events	Microscopic Events
Definition	
Refer to chemical phenomenon that occurs at a large scale, observable with the naked eye or with minimal instrumentation.	Refer to chemical phenomenon that occurs at a molecular or atomic level, requiring specialized instruments for observation.

Characteristics	
Involve changes in bulk properties of a substance, such as colour, texture, temperature, volume.	Involve interactions between individual molecules or atoms, influencing chemical reactions and material properties.
Scale	
Occur at a scale measurable in meters, liters, or grams etc.	Occur at a scale measurable in nanometers or angstroms etc.
Observation Methods	
Observed using everyday instruments such as thermometer, balances, spectrophotometer	Observed using specialized instruments such as electron microscopes, AFM etc.
Examples	
Boiling water, precipitation, rust formation etc.	Atomic orbital overlap, electron transfer, molecular shape changes

THE LAW OF MASS ACTION

C.M Guldberg & P. Wage in 1864 proposed The law of mass action.

↳ The rate at which a substance react is proportional to it's active mass, & rate of chemical reaction is proportional to the product of Active Mass of reacting substance.

▷ **Active Mass** represents concentration of reactant & product in $mol.dm^{-3}$ & represented by "[ ]" square brackets.

Derivation of Equilibrium Constant (K_c)

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

reactants ⇌ products

Consider a Hypothetical Situation at room temperature 25°.

rate of forward reaction $\propto [A]^a [B]^b$

rate of forward reaction $= K_f [A]^a [B]^b$ ——— (i)

rate of reverse reaction $\propto [C]^c [D]^d$

rate of reverse reaction $= K_r [C]^c [D]^d$ ——— (ii)

At equilibrium State:-

rate of forward rxn = rate of reverse rxn

$K_f [A]^a [B]^b = K_r [C]^c [D]^d$

Rearranging: $\frac{K_f}{K_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

$$\therefore \frac{K_f}{K_r} = K_c$$

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

K_c = "Equilibrium constant is defined as the ratio of the product of concentration of products to the product of concentration of reactants, each raised to power equal to the coefficients in the balanced chemical equation"

Derive K_c for the following Reactions

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

Rate of forward rxn $\propto [N_2][H_2]^3$

rate of forward rxn $= K_f [N_2][H_2]^3$

Rate of reverse rxn $\propto [NH_3]^2$

Rate of reverse rxn $= K_r [NH_3]^2$

At equilibrium: Rate of forward rxn = Rate of reverse rxn

$$K_f [N_2][H_2]^3 = K_r [NH_3]^2$$

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

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

▷ CONDITIONS FOR EQUILIBRIUM :-

① K_c applies only at Equilibrium state. "c" indicates concentration of reactant & product in $mol.dm^3$ at Equilibrium.

② K_c does not depend upon initial concentration of reactant & product but depend on Temperature.

③ K_c is related to coefficient of balanced chemical equation. Product is in numerator, Reactant is in denominator.

④ Magnitude of K_c indicate position of equilibrium.

$K_c < 1$; Reactant is greater ; Forward direction.

$K_c > 1$; Product is greater ; Reverse direction.

$K_c = 1$; R = P ; Equilibrium state

⑤ Container should be closed if any reactant or product is in gaseous state.

⑥ Pressure, temperature, volume must be kept constant.

WRITING EQUILIBRIUM CONSTANT EXPRESSION

$$K_c = \frac{[\text{product}]}{[\text{Reactant}]}$$

Example 8.1

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

reactant product

$$K_c = \frac{[\text{product}]}{[\text{reactant}]}$$

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

Example 8.2

$$CO + 1/2\ O_2 \rightleftharpoons CO_2$$

$$K_c = \frac{[CO_2]}{[CO][O_2]^{1/2}}$$

Example 8.3

$$A_2 + B_2 \rightleftharpoons 2AB$$

$$\downarrow \quad \downarrow \quad \downarrow$$

0.399M 1.197M 0.203 M

Calculate K_c :-

$$K_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{[0.203]^2}{[0.399][1.197]}$$

$$K_c = 0.0824$$

UNIT OF K_c

↳ When moles of reactant = moles of product

There will be no unit

$$1H_2 + 1Cl_2 \rightleftharpoons 2HCl$$

$1 + 1 = 2$

$2 = 2$ ⟶ No unit

$$K_c = \frac{[HCl]^2}{[H_2][Cl_2]}$$

$$= \frac{(mol.dm^{-3})^2}{(mol.dm^{-3})(mol.dm^{-3})}$$

= No unit.

↳ When moles of reactant ≠ moles of product

K_c will have unit

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

$1 + 3 \neq 2$

$4 \neq 2$ ⟶ K_c will have unit

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

$$= \frac{(mol.dm^{-3})^2}{(mol.dm^{-3})(mol.dm^{-3})^3}$$

$$K = mol^{-2}\,dm^6$$

TYPES OF EQUILLIBRIUM

There are two types:

① Homogenous Equilibria

② Heterogenous Equilibria.

▷ Homogenous Equilibria:-

The type of equilibrium in which physical state of reactant & product are same.

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

$$SO_{2(g)} + O_{2(g)} \rightleftharpoons SO_{3(g)}$$

▷ Heterogenous Equilibria:-

The type of equilibria in which physical state of reactant & product is different.

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

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

$$I_{2(s)} \rightleftharpoons I_{2(g)}$$

Difference between Homogenous And Heterogenous Equilibria

Homogenous equilibria	Heterogeneous equilibria
Definition	
It occurs when all reactants and products are in same phase (solid, liquid, or gas)	It occurs when reactants and products are present in different phases.
Phase Involvement	
All substances involved are in a single phase, such as all gases or all solutions.	Substances exist in more than one phase, like solid-liquid or solid-gas systems.
Type of mixture	
This equilibrium exists is solutions.	This equilibrium exists in suspensions or colloids.
Equilibrium Expression	
The concentrations of all reactants & products are included in equilibrium constant expression.	Only the concentration of gaseous & aqueous species are included; pure solids & liquids are not.
Catalysis	
Catalysts, if used, are in the same phase as the reactants.	Catalysts are typically in a different phase than the reactants eg., solid catalyst in a gas-phase reaction.
Applications	
Gas-phase reaction, solution	Decomposition of solids, surface

Chemistry (acid-base, redox reactions.)

catalysis, eg many industrial processes. e.g., catalytic converters.

Reaction in Solution

Reactions can occur entirely in solutions, where all reactants & products dissolve.

Reactions may involve substances that are insoluble, where at least one component remains undissolved.

Examples

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

$I_{2(s)} \rightleftharpoons I_{2(g)}$

$SO_{2(g)} + O_{2(g)} \rightleftharpoons SO_{3(g)}$

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

D CONCEPT ASSESSMENT 8.1:-

1.(i) $SO_2 + O_2 \rightleftharpoons SO_3$

Balancing:- $2SO_2 + O_2 \rightleftharpoons 2SO_3$

K_c expression:- $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

(ii) $NH_3 + O_2 \rightleftharpoons NO + H_2O$

Balancing:- $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$

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

(iii) $CH_4 + H_2O \rightleftharpoons CO + H_2$

Balancing:- $CH_4 + H_2O \rightleftharpoons CO + 3H_2$

K_c expression:- $K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$

2. $K_c = \frac{[CH_3OH]}{[CO][H_2]^2}$

$K_c = \frac{[product]}{[reactant]}$

Balanced equation:- $CO + 2H_2 \rightleftharpoons CH_3OH$

$K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$

Balanced equation:- $2NO + 2H_2 \rightleftharpoons N_2 + 2H_2O$

Relationship of K_c with K_p, K_n And K_x

$aA + bB \longrightarrow cC + dD$

$K_c = \frac{[product]}{[reactant]}$

Henry Law

$P_{gas} \propto [Gas]$

"At constant temperature, partial pressure of a gas is directly proportional to it's molar concentration."

∴ K_p = Equilibrium constant of partial pressure

$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ ——— ① Equilibrium constant

Writing K_p for the reaction:-

$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$ ——— ② Partial pressure of gas

R = ideal gas constant → 0.0821 $dm^3 atm K^{-1} mol^{-1}$

T = Temperature

$\Delta n = n_2 - n_1$ = product − reactant

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

Relationship b/w K_p & K_c.

When equilibrium concentration of reactant & product are expressed in terms of their moles then equilibrium constant K_c is represented by K_n.

moles (3) $$K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}$$

n_A, n_B, n_C, n_D are no. of moles of A, B, C, D respectively.

Relationship between K_n & K_p

$$K_p = K_n \left(\frac{P}{n}\right)^{\Delta N}$$

ΔN = product moles − reactant moles

P = Pressure n = no. of moles.

Mole fraction (X) = no. of moles of compound / Total no. of moles

A reactant = X_A = no. of moles of A / Total no. of moles.

When equilibrium concentration of R & P are expressed in mole fraction, the equilibrium constant is represented by K_x

mole fraction (4) $$K_x = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b}$$

X_A, X_B, X_C, X_D are mole fractions of A, B, C, D.

Relationship between K_x & K_p

$K_p = K_x (P)^{\Delta n}$ P = pressure

$\Delta n = n_2 - n_1$

no. of moles of product − no. of moles of reactant

Concept Assessment 8.2:-

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Calculate K_p?

$[SO_2] = 0.59\,M$

$[O_2] = 0.05\,M$

$[SO_3] = 0.259\,M$

$\Delta n = 2 - 3$

$= -1$

$T = 450 + 273$

$= 723\,K$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[0.259]^2}{[0.59]^2[0.05]}$$

$$\boxed{K_c = 3.854\ mol^{-1}dm^3}$$

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

$= 3.854 (0.0821 \times 723)^{-1}$

$$\boxed{K_p = 0.0648\ atm^{-1}}$$

$K_p = K_c (RT)^{\Delta n}$ ——— (1)

$K_p = K_n \left(\frac{P}{N}\right)^{\Delta n}$ ——— (2)

$K_p = K_x (P)^{\Delta n}$ ——— (3)

Relating eq (1) (2) & (3)

$$K_p = K_c (RT)^{\Delta n} = K_n \left(\frac{P}{N}\right)^{\Delta n} = K_x (P)^{\Delta n} \quad \text{——— (4)}$$

Q Prove that $K_p = K_c = K_n = K_x$

If $\Delta n = 0$

i.e., the reaction in which no. of moles of reactant is equal to no. of moles of product.

eg:- $\Delta n = P - R$ $\quad N_2 + O_2 \rightleftharpoons 2NO$

$= 2 - 2$ $\quad 1 + 1 = 2$

$\Delta n = 0$ $\quad 2 = 2$

when $\Delta n = 0$, equation ④ will be

$K_p = K_c (RT)^{\circ} = K_n \left(\frac{P}{N}\right)^{\circ} = K_x (P)^{\circ}$

$= K_c (1) = K_n (1) = K_x (1)$

$K_p = K_c = K_n = K_x$ Proved!

All constants are equal when $\Delta n = 0$

$N_2 + O_2 \rightleftharpoons 2NO$

$2 = 2$

$K_p = K_c$

$NO_2 + CO \rightleftharpoons NO + CO_2$

$2 = 2$

$K_p = K_c$

- When $\Delta n < 0$ (negative):-

$K_p < K_c$

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$4 = 2$

$\Delta n = 2 - 4$

$\Delta n = -2$ $\quad K_p < K_c$

- When $\Delta n > 0$ (positive):-

$K_p > K_c$

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

1 : 2

$\Delta n = 2 - 1$

$\boxed{\Delta n = 1}$ $K_p > K_c$

In order to write K_c, K_p, K_n, K_x only consider gaseous substances

Concept Assessment 8.3:-

(i) $Fe_2O_{3(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}$

$K_c = \frac{[CO_2]}{[CO]}$ $K_n = \frac{n_{CO_2}}{n_{CO}}$

$K_p = \frac{P_{CO_2}}{P_{CO}}$ $K_x = \frac{X_{CO_2}}{X_{CO}}$

(ii) $P_{4(s)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$

$K_c = \frac{1}{[O_2]^5}$ $K_n = \frac{1}{n_{O_2}^5}$

$K_p = \frac{1}{P_{O_2}^5}$ $K_x = \frac{1}{X_{O_2}^5}$

(iii) $CH_{4(g)} + 4Cl_{2(g)} \rightleftharpoons CCl_{4(l)} + 4HCl_{(g)}$

$K_c = \frac{[HCl]^4}{[CH_4][Cl_2]^4}$ $K_n = \frac{n_{HCl}^4}{n_{CH_4} \cdot n_{Cl_2}^4}$

$K_p = \frac{P_{HCl}^4}{P_{CH_4} \cdot P_{Cl_2}^4}$ $K_x = \frac{X_{HCl}^4}{X_{CH_4} \cdot X_{Cl_2}^4}$

WAYS TO RECOGNIZE EQUILIBRIUM

Physical methods | Chemical methods

a) **Physical Method:-** (Spectrometric method)

The physical property is measured during the reaction without removing sample from the reaction mixture.

E.g.: $N_2O_4 \underset{}{\overset{\text{radiation}}{\rightleftharpoons}} 2NO_2$

colourless — reddish brown

The reactant or Product absorb radiation (UV, IR, visible light).

$K_c \propto$ Amount of radiations

Q. **What is importance of Physical method in recognizing equilibrium?**

① Reactant can be used and re-used.

② Reactant or Product have ability to absorb radiation.

③ It helps to find value of K_c through radiation absorbed.

$N_2O_4 \underset{}{\overset{\text{radiation absorbed}}{\rightleftharpoons}} 2NO_2$

colourless — reddish brown

$K_c \propto$ Amount of radiations

b) Chemical Method:-

Amount of reactant by product is determined by a suitable chemical reaction.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
at $t=0$ (time interval)	"a" amount of CH_3COOH	"b" amount of C_2H_5OH	0 amount of $CH_3COOC_2H_5$	0 amount of H_2O
at $t=eq$ (time required to reach equilibrium)	$a-x$	$b-x$	x	x
Concentration Mol/V	$\frac{a-x}{V}$	$\frac{b-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

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

$$K_c = \frac{(x/V)(x/V)}{(a-x/V)(b-x/V)}$$

$$K_c = \frac{x^2}{V^2} \times \frac{V^2}{(a-x)(b-x)}$$

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

This method is used when concentrations are not given.

Q $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Find K_c through chemical method?

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

	N_2	$3H_2$	$2NH_3$
at $t=0$	"a"	"b"	0
at $t=eq$	$a-x$	$b-3x$	$2x$
Concentration Mol/V	$\frac{a-x}{V}$	$\frac{b-3x}{V}$	$\frac{2x}{V}$

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

$$K_c = \frac{(2x/v)^2}{(a-x/v)(b-3x/v)^3}$$

$$= \frac{x^2}{v^2} \times \frac{v^3 \cdot v}{(a-x)(b-3x)^3}$$

$$= \frac{4x^2}{v^2} \times \frac{v^4}{(a-x)(b-3x)^3}$$

$$\boxed{K_c = \frac{4x^2 v^2}{(a-x)(b-3x)^3}}$$

FACTORS AFFECTING EQUILIBRIUM

Equilibrium is disturbed whether we change:

① Temperature ② Pressure ③ Concentration of reactant & product

④ Collision between reactant & product molecules.

Le Chatelier's Principle :-

If a change is imposed on a system at equilibrium, the position of equilibrium (forward or reverse) will shift in a direction that tends to reduce the change.

A Effect of change in concentration

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$ at equilibrium

⊙ When reactant's concentration is increased, the reaction will shift in forward direction (→ right)

Reactant increased ↑ $[CO_2]$ → forward direction → after sometime greater amount of product will be produced. ↑ $[CO]$ & $[H_2O]$

New equilibrium will be established after sometime ← High concentration of reactant by product.

⊙ When reactant's concentration is decreased, the reaction will shift in backward direction (← left)

Reactant decreased ↓ $[CO_2]$ → Backward direction → after sometime greater amount of reactants will be produced.

low concentration of reactant by product will be achieved. ← New equilibrium will be established

Rate of reaction ∝ no. of effective collision

∴ At equilibrium

Effective collision of reactant = Effective collision of product

Reactant increase → effective collision of reactant increase → forward direction

Example #8.5 :-

K_c for following reaction is 1×10^{-3} at 230°C.

$$2\,ICl_{(g)} \rightleftharpoons Cl_{2(g)} + I_{2(g)} \quad \rightarrow \text{volume} = 2\,dm^3$$

1.6 0.05 0.05

Required: $[I_2] = ?$ $[Cl_2] = ?$ $[ICl] = ?$

When equilibrium is restored after addition of 1 mole of ICl.

Solution:

	$2\,ICl \rightleftharpoons$	Cl_2	+ I_2
→ Initial conc:	1.6	0.05	0.05
Adding → 1 mole ICl, new conc:	1.6 + 1 = 2.6	0.05 + x	0.05 + x
At equilibrium	2.6 − 2x	0.05 + x	0.05 + x
→ Equilibrium concentration ($mol\,dm^{-3}$) :	$\frac{2.6-2x}{2}$	$\frac{0.05+x}{2}$	$\frac{0.05+x}{2}$

$$K_c = \frac{[Cl_2][I_2]}{[ICl]^2}$$

$$1 \times 10^{-3} = \frac{\left(\frac{0.05+x}{2}\right)\left(\frac{0.05+x}{2}\right)}{\left(\frac{2.6-2x}{2}\right)^2}$$

$$1 \times 10^{-3} = \frac{(0.05+x)^2}{4} \times \frac{4}{(2.6-2x)^2}$$

$$1 \times 10^{-3} = \frac{(0.05+x)^2}{(2.6-2x)^2}$$

Taking square root on both sides

$$\sqrt{1\times10^{-3}} = \sqrt{\frac{(0.05+x)^2}{(2.6-2x)^2}}$$

$$3.1\times10^{-2} = \frac{0.05+x}{2.6-2x}$$

$$(2.6-2x)(3.1\times10^{-2}) = 0.05+x$$

$$2.6(0.031) - 2x(0.031) = 0.05+x$$

$$0.0806 - 0.062x = 0.05+x$$

$$-0.062x - x = 0.05 - 0.0806$$

$$-1.062x = -0.0306$$

$$x = \frac{-0.0306}{-1.062}$$

$$\boxed{x = 0.029}$$

$$[ICl] = 2.6 - 2x$$

$$= 2.6 - 2(0.029)$$

$$= 2.6 - 0.058$$

$$\boxed{[ICl] = 2.542 \text{ mol/dm}^3}$$

$$[I_2] = [Cl_2] = 0.05 + x$$

$$= 0.05 + 0.029$$

$$\boxed{[I_2] = [Cl_2] = 0.079 \text{ mol/dm}^3}$$

Concept Assessment 8.4:-

$$2\,ICl_{(g)} \rightleftharpoons Cl_{2(g)} + I_{2(g)}$$

$K_c = 1.0 \times 10^{-3}$ at 230°C

$ICl = 1.6$ moles $\quad Cl_2 = 0.05$ moles $\quad I_2 = 0.05$ moles

Volume = 2 dm^3

To find:- $[ICl] = ?$ $\quad [I_2] = ?$ $\quad [Cl_2] = ?$

When equilibrium is restored after removal of 1 mole of ICl.

Solution:-

	$2ICl$	$\rightleftharpoons$	Cl_2	+	I_2
Initial conc:	1.6		0.05		0.05
Removal of 1 mole ICl:	1.6 − 1		0.05 − x		0.05 − x
at equilibrium ⇒	0.6 − 2x		0.05 − x		0.05 − x
Equilibrium conc: in mol/dm^3	$\frac{0.6-2x}{2}$		$\frac{0.05-x}{2}$		$\frac{0.05-x}{2}$

$$K_c = \frac{[Cl_2][I_2]}{[ICl]^2}$$

$$1 \times 10^{-3} = \frac{\left(\frac{0.05-x}{2}\right)\left(\frac{0.05-x}{2}\right)}{\left(\frac{0.6-2x}{2}\right)^2}$$

$$1 \times 10^{-3} = \left(\frac{0.05-x}{2}\right)^2 \times \left(\frac{2}{0.6-2x}\right)^2$$

$$1 \times 10^{-3} = \frac{(0.05-x)^2}{4} \times \frac{4}{(0.6-2x)^2}$$

$$\sqrt{1\times10^{-3}} = \sqrt{\frac{(0.05-x)^2}{(0.6+2x)^2}}$$

$$3.1\times10^{-2} = \frac{0.05-x}{0.6-2x}$$

$$0.031(0.6-2x) = 0.05-x$$

$$0.0186 - 0.062x = 0.05 - x$$

$$0.0186 - 0.05 = 0.062x - x$$

$$-0.0314 = -0.938\ x$$

$$x = \pm 0.0314$$
$$\pm 0.938$$

$$\boxed{x = 0.0335}$$

$$[ICl] = 0.6 - 2x$$

$$= 0.6 - 2(0.0335)$$

$$\boxed{[ICl] = 0.533}$$

$$[I_2] = [Cl_2] = 0.05 - x$$

$$= 0.05 - 0.0335$$

$$\boxed{[I_2] = [Cl_2] = 0.0165}$$

▷ Effect of Pressure Change

Boyle's Law ⇒ $P \propto \frac{1}{V}$

▷ In a system:- [to get more product]

P increase ⟶ V decrease ⟶ ▷ decrease in total number of gas in system

Equilibrium will shift in direction of less number of moles

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

Left side: reactant = 3

right side: product = 2

less no. of moles

Thus, equilibrium will shift to right side by more product will be obtained.

▷ In a system:- [to get less yield]

⇒ P decrease ⟶ V increase ⟶ increase in total no. of gas in system

Equilibrium will shift ⟵ in direction of more no. of moles.

$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$

Left side: 3 (reactant)

right side: 1 (product)

more no. of moles

Thus, equilibrium will shift to left side and less product will be obtained.

V ∝ no. of mole
increase increase
decrease decrease

⇒ $O_{3(g)} \rightleftharpoons O_{2(g)} + O_{(g)}$

moles: 1 2

For this reaction, pressure decrease, volume will increase, the number of gas molecules will increase by so equilibrium will shift in forward direction by more product will be obtained.

=> $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

moles = 3 2

For this reaction, pressure will be increased, volume will decrease, gas molecules will decrease, and so equilibrium will shift in forward direction, more NO_2 will be produced.

$H_2 + I_2 \rightleftharpoons 2HI$

moles = 2 2

Change in pressure or volume will not effect the equilibrium because number of moles is same on both sides. Equilibrium will not shift to forward or reverse direction. We have to change other factors for such reactions.

Effect of Change in Temperature

Exothermic Reaction → heat is released → enthalpy (ΔH) -ive

Endothermic Reaction → heat is absorbed → enthalpy +ive

① Endothermic + temp increased → Equilibrium shift forward (Product)

Endothermic + temp decreased → Equilibrium shift reverse (Reactant)

② Exothermic + temp increased → Equilibrium shift reverse (Reactant)

Exothermic + temp decreased → Equilibrium shift forward (Product)

$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \Delta H^\circ = -198kJ$

(a) Temp increase (b) Temp decrease

Yield maximum SO_3

As, Exothermic + decreased Temperature → Equilibrium shift forward (Product)

$N_2O_4 \rightleftharpoons 2NO_2 \quad \Delta H^\circ = +57.2kJ$

(a) Temp increase (b) Temp decrease

Maximum NO_2 yield

As, Endothermic + increased Temperature → Equilibrium shift Forward (Product)

Exothermic rxn (temp inc) → equilibrium shift to left (reactant) → Amount of reactant increase → K_c will decrease

As, $K_c = \frac{[product]}{[reactant]}$

$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \Delta H^\circ = -198\ KJ$

$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ (dec) (inc)

low temp → product

For exothermic, $K_c \propto \frac{1}{T}$

$K_c = 2.8 \times 10^2$ at 1000 K

$K_c = 1 \times 10^{26}$ at 298 K

K_c increases at low temp so product also increases

※ $N_2O_4 \rightleftharpoons 2NO_2$ $\Delta H^\circ = +57.2$ KJ

Endothermic rxn → equilibrium shift → K_c will increase
(temp inc) to right (product)

$K_c \propto$ Temperature

(inc) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$ (inc)

$K_c = 7.7 \times 10^{-5}$ at 0°C

$K_c = 0.4$ at 1000°C

K_c increases at high temp ∴ product also increases

- **Effect of addition of catalyst**

No effect of catalyst because catalyst speeds up both forward & reverse reaction equally.

APPLICATIONS OF LE CHATELIER

Haber's Process

※ $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta H^\circ = -92.46$ KJ

moles: 4 → 2

1. Temperature decrease (exothermic)
2. Pressure increase (less no. of moles: forward)
3. Continuous removal of NH_3.

} More yield of NH_3 (Ammonia)

Contact Process

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H^\circ = -198\ kJ$$

moles: 3 → 2

(1) Temperature decrease (exothermic)
(2) Pressure increase (less no. of moles: forward)
(3) Addition of excess oxygen.
(4) Continuous removal of SO_3.

} More yield of SO_3 (Sulphur trioxide)