CHEMICAL EQUILIBRIUM

chemical equilibrium $\rightleftharpoons$

Types of chemical reaction:

(1.) Direction of chemical reaction: (2 types)

Reversible	Irreversible
- carried out in closed container.	- carried out in closed as well as open container.
- can be reversed under suitable condition.	- cannot be revert back.
- both forward and backward reactions take place simultaneously.	- it is unidirectional; proceed only in forward direction
- $R \underset{\text{rate of backward rxn}}{\overset{\text{rate of forward rxn}}{\rightleftharpoons}} P$	- $R \longrightarrow P$.
- it attains equilibrium	- it doesnot attain equilibrium
- reactant is not completely converted to product.	- reactant completely converts to product.
- comparitively it is a slow process.	- it is a fast process compared to reversible

eg: - $H_2 + I_2 \rightleftharpoons 2HI$ - combustion reactions;

hammer rxn $N_2 + 3H_2 \rightleftharpoons 2NH_3$ neutralisation reactions

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ displacement reactions

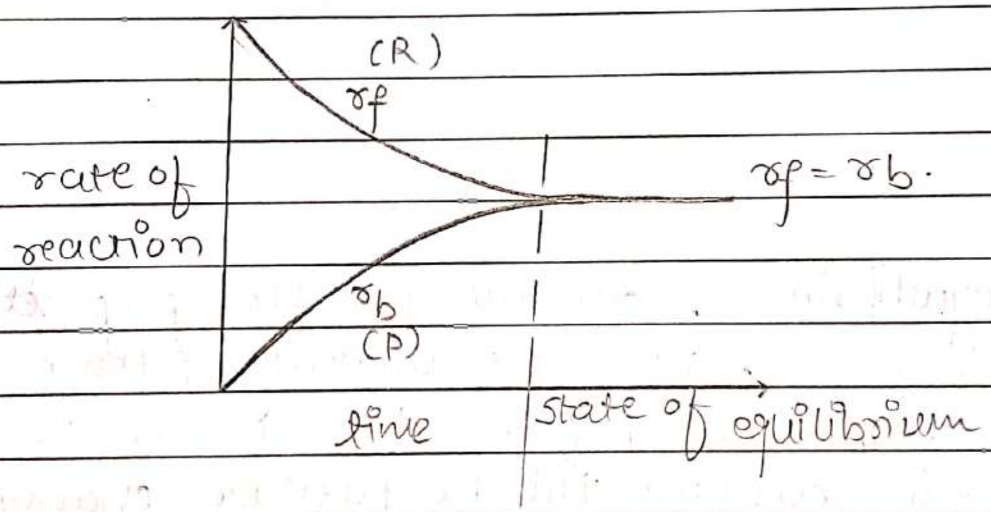
double displacement reactions.

(11.) State of equilibrium:

→ when rate of forward reaction and rate of backward reaction is equal for reversible reaction, that condition is said to be Equilibrium condition or State of equilibrium.

$$R \underset{r_b}{\overset{r_f}{\rightleftharpoons}} P$$

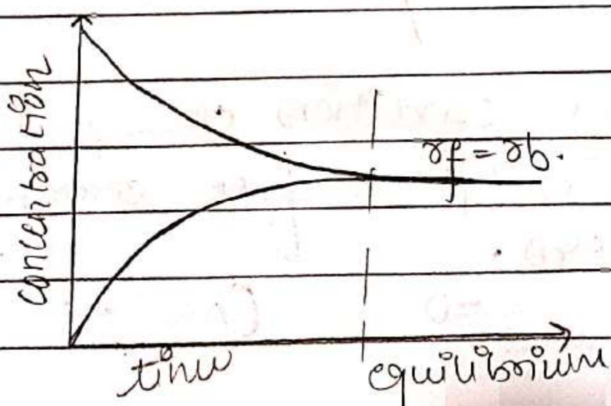
$[r_f = r_b$ (State of equilibrium)$]$



Characteristic of chemical equilibrium:

- at equilibrium condition, it isn't necessary that the amount of reactant and product becomes equal. but they become constant.

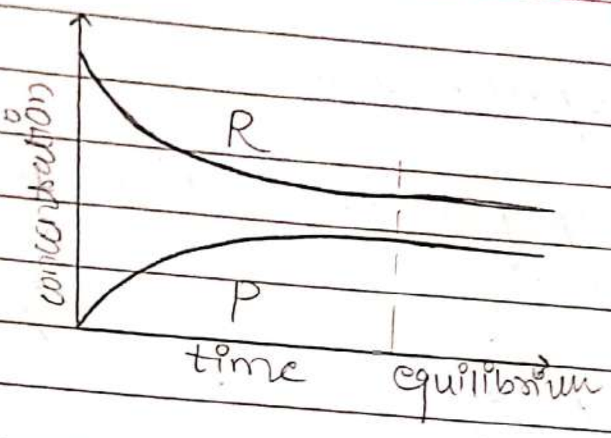
CASE: 1.



$[R]_{eq} = [R]_{eq}$.

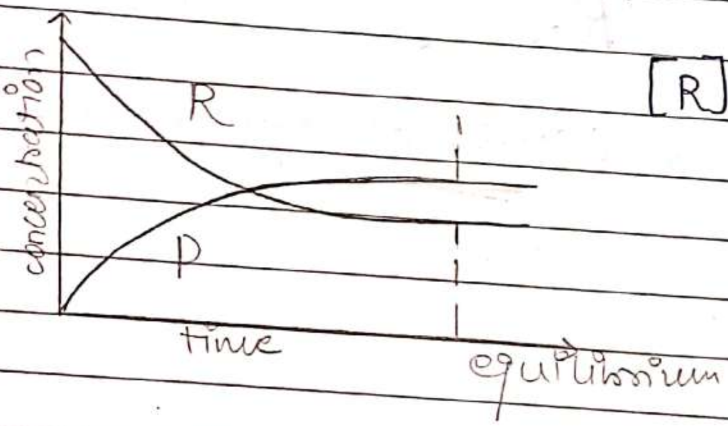
... always the means perfect to imperfect

CASE: II



$[R]_{eq} > [P]_{eq}$.

CASE: III



$[R]_{eq} < [P]_{eq}$.

- at equilibrium, all measureable properties, like mass; mole; volume; molality; temperature; pressure; density; etc. becomes constant and remain constant till no further change takes place.

- chemical equilibrium is <u>Dynamic Equilibrium</u>.

→ it means at equilibrium condition, reaction seems to be stopped as there is no change occuring but actually both the reactions are running at equal rates.

- at equilibrium condition change in Entropy (ΔS) and change in Gibb's free energy (ΔG) should always be zero.

$(\Delta S)_{universe} = 0$ $\qquad$ $(\Delta G)_{T,P} = 0$

temp $\quad$ press.

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- State of chemical equilibrium characterised by equilibrium constant (K). Equilibrium constant have constant value at a given temperature.

Law of chemical equilibrium or mass action:

- Given by Guldberg and Waage.

- according to this law, rate of forward reaction and rate of backward reaction is directly proportional to active masses of reactant and product respectively. For a general reversible reaction:

→ $$A + B \underset{r_b}{\overset{r_f}{\rightleftharpoons}} C + D$$

rate of forward reaction (r_f)
active mass of A = [A]
active mass of B = [B].

$r_f \propto [A][B]$

$$\therefore \boxed{r_f = K_f[A][B]} \quad \text{—— eq (I)}$$

similarly, $r_b \propto [C][D]$

$$\therefore \boxed{r_b = K_b[C][D]} \quad \text{—— eq (II)}$$

here,
K_f = rate ~~of~~ constant for forward reaction.
K_b = rate constant for backward reaction.
[C] = active mass of C
[D] = active mass of D.

[ ] = molar concentration.

at equilibrium reaction,

$r_f = r_b$.

$\therefore$ $\boxed{K_f[A][B] = K_b[C][D]}$

$$\frac{K_f}{K_b} = K_{eq} = \frac{[C][D]}{[A][B]}$$ equilibrium constant.

here,

$K_{eq} = K_c$

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

[K_c = equilibrium constant in terms of concentration]

{ [ ] = active mass or molar concentration } (w.r.t to any reactant/product.

- for another general reversible reaction like:

→ $aA + bB \rightleftharpoons cC + dD$

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

Equilibrium constant:

(1.) in terms of Partial pressure (Kp):

→ $PV = nRT$

$P = \left(\frac{n}{V}\right) RT$

$P = [gas]\ RT.$ or $P \propto [gas]$

$$\boxed{K_p = \frac{P_C^{\,c} \times P_D^{\,d}}{P_A^{\,a} \times P_B^{\,b}}}$$

[RT are constant at equilibrium]

here,
P_A = partial pressure of gas A
P_B = partial pressure of gas B.

→ Keq → Kc (Equilibrium constant in term of concentration) (for aqueous & gases)
→ Kp (Equilibrium constant in term of P. pressure) (for gases only)

Q:1 write the rev. reaction in terms of Kc and Kp:-

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

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

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

→ not possible. $K_c = [CO_2]$ $K_p = [P_{CO_2}]$

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NOTE:

- for a particular reversible reaction any type of equilibrium constant depends only upon temperature.
- it means, for a reversible reaction value of Kc and Kp are independent of any factor except temperature.

Unit of Kc & Kp:

- it depends upon Nature of reversible reaction.

$$\left[\frac{mole}{litre}\right]^{\Delta ng} = \text{unit of Kc.}$$

here,

Δng: no. of mole of gas. prod. − no. of mole gas. react.

- for Kp = $(atm)^{\Delta ng}$

Reversible rxn	Δng	unit of Kc	unit of Kp
$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$	$2-1 = \underline{1}$	mol / ltr.	atm,
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	$\underline{-2}$	$(mol/ltr)^{-2}$	atm^{-2}
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	$\underline{0}$	no unit	unitless

Mode of representation of equilibrium constant if stoichiometric number is different:

CASE: I

$$A + B \rightleftharpoons C + D \quad (K_1)$$
$$C + D \rightleftharpoons A + B \quad (K_2)$$

then, $\boxed{K_2 = \frac{1}{K_1}}$

CASE: II

$$A + B \rightleftharpoons C + D \quad (K_1)$$
$$nA + nB \rightleftharpoons nC + nD \quad (K_2)$$

then, $\boxed{K_2 = [K_1]^n}$

CASE: III

if addition of 2 different equilibrium equation occurs then final equilibrium reaction, equilibrium constant is equal to multiplication of both the reactions.

$$A \rightleftharpoons B \quad K_1$$
$$C \rightleftharpoons D \quad K_2$$

then,

$\therefore$, $A + C \rightleftharpoons B + D$. $\boxed{K_3 = K_1 \times K_2}$

CASE: IV

$$A \rightleftharpoons B \quad K_1$$
$$-C \rightleftharpoons -D \quad K_2$$

then,

$\rightarrow$ $A - C \rightleftharpoons B - D$

$\therefore$, $A + D \rightleftharpoons B + C$ $\boxed{K_3 = \frac{K_1}{K_2}}$

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CASE: V

$$A \rightleftharpoons B \quad K_1$$
$$B \rightleftharpoons C \quad K_2$$
$$C \rightleftharpoons D \quad K_3$$

then, $K_4 = \boxed{K_1 \times K_2 \times K_3}$

$\therefore$ $A \rightleftharpoons D \quad K_4$

CASE: VI

$$A \rightleftharpoons B \quad K_1$$
$$C \rightleftharpoons B \quad K_2 \quad \text{inverse } B \rightleftharpoons C$$
$$C \rightleftharpoons D \quad K_3$$

then, $\boxed{K_4 = \dfrac{K_1 \times K_3}{K_2}}$

$\therefore$ $A \rightleftharpoons D \quad K_4$

Q:2 $HI(g) \rightleftharpoons \frac{1}{2} H_2(g) + \frac{1}{2} I_2$ $\quad K = 8.0$.

find for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

$\Longrightarrow$ $K_2 = [K_1]^n$, 8.0,

$$= \frac{[H_2][I_2]}{[HI]^2} \rightarrow \frac{1}{[8]^2} = \frac{1}{64}$$

Q:3 $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\quad K_1 \quad 1/K_1$

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $\quad K_2 \quad 1/K_2$

find K for $NO_2(g) \rightleftharpoons \frac{1}{2} N_2(g) + O_2(g)$.

$\rightarrow$ K_2 inverse of K_1 (here) $\therefore$ $K_2 = \dfrac{1}{K_1}$.

$\therefore$ $K^3 = \dfrac{K_1}{K_2} \Longrightarrow \dfrac{1}{[K_1 K_2]^{1/2}}$