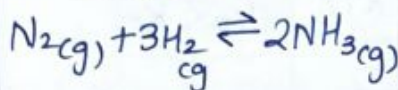


CHEMICAL EQUILIBRIUM

Types of Reaction

Reversible Reaction

Product can be converted into reactant.



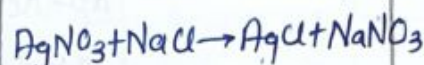
Proceeds in forward as well as backward direction.

Attain eq^m state and Rxⁿ never complete.

Closed Container

Irreversible Reaction

Product can't be converted into reactant.



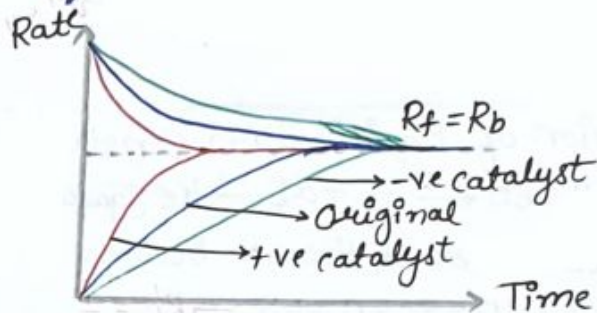
Proceeds only in one direction.

Do not attain eq^m, Rxⁿ completes.

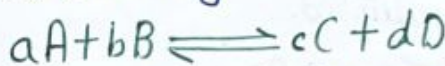
Open container also

Use of Catalyst in Equilibrium

Catalyst alter rate of approach of equilibrium but do not change state of eq^m.



Law of Mass Action and Eq^m Const
Rate of chemical Rxⁿ at particular temp. is \propto to product of active mass of reactant raised to the power of their stoichiometry.



$$R_f \propto [\text{A}]^a [\text{B}]^b \quad R_b \propto [\text{C}]^c [\text{D}]^d$$

$$R_f = K_f [\text{A}]^a [\text{B}]^b \quad R_b = K_b [\text{C}]^c [\text{D}]^d$$

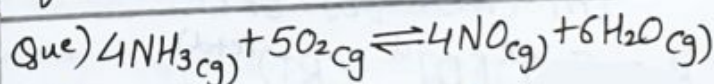
at eq^m $R_f = R_b$, So \rightarrow

$$K_f [\text{A}]^a [\text{B}]^b = K_b [\text{C}]^c [\text{D}]^d$$

$$\left(\frac{K_f}{K_b} \right) = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

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

equilibrium constant



Solⁿ $\rightarrow K_c = \frac{[\text{NO}]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^5}$

Equilibrium Constant

K_p

When partial pressure of reactant and product is used.

K_c

When conc. of reactant and product is used.

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Equilibrium

Static

Dynamic

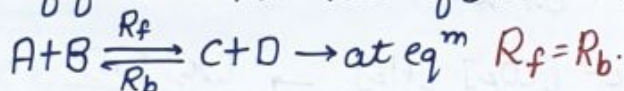
Physical eq^m

Chemical eq^m

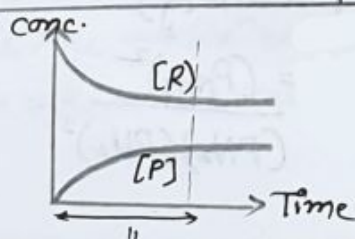
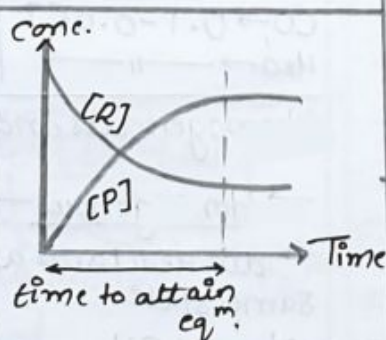
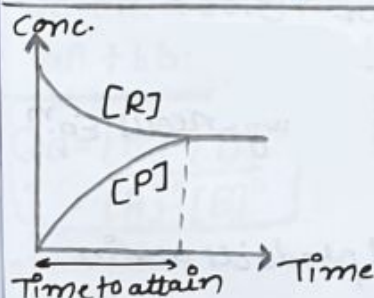
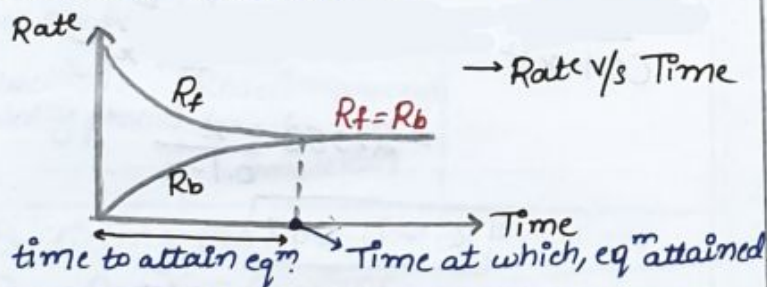
Chemical Equilibrium

Reversible Rxⁿ in which,

Rate of forward Rxⁿ = Rate of Backward Rxⁿ

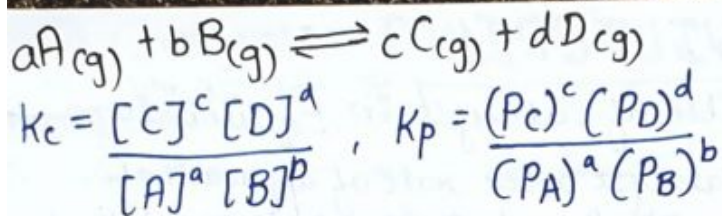


Reversible Rxⁿ in which reactant and product is constant w.r.t. time



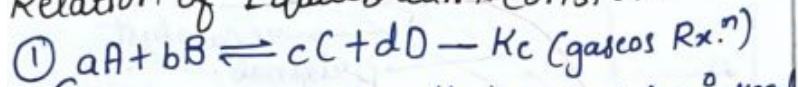
conc. vs time.

concentration becomes constant at a point.

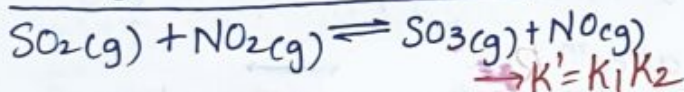
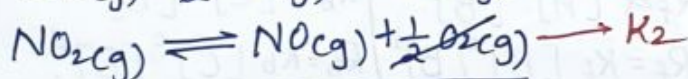
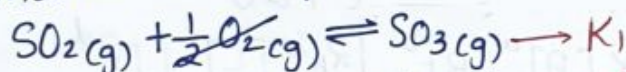
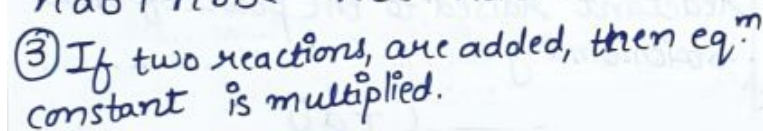
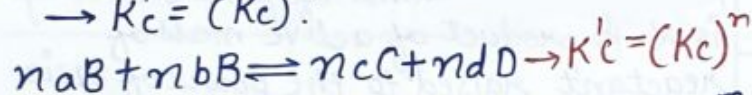
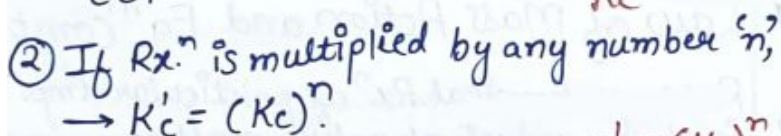
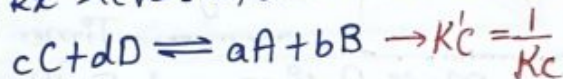


Note → Equilibrium Const. only depends on temperature, rest independent of every thing

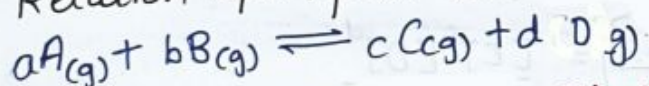
Relation of Equilibrium Constant →



If Rxn reversed, then K_c becomes reciprocal



Relation b/w K_p and K_c .



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

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

$$P = CRT$$

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

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

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

$$K_p = K_c (RT)^{(c+d)-(a+b)}$$

$$K_p = K_c (RT)^{\text{Product stoichiometry sum} - \text{Reactant stoichiometry sum}}$$

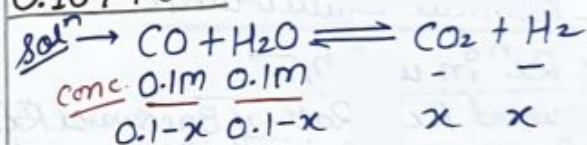
$$K_p = K_c (RT)^{\Delta n}$$

$$\text{Unit} \rightarrow K_p \rightarrow (\text{atm})^{\Delta n}$$

$$\text{Unit} \rightarrow K_c \rightarrow \left(\frac{\text{mol}}{\text{litre}}\right)^{\Delta n}$$

| Case-1 | Case-2 | Case-3 |
|---|---|---|
| $\Delta n = 0$ | $\Delta n > 0$ | $\Delta n < 0$ |
| $K_p = K_c$ | $K_p = K_c (RT)^{\Delta n}$ $K_p > K_c$ | $K_p < K_c$ |
| $H_2 + I_2 \rightleftharpoons 2HI$ (g) (g) (g) $\Delta n = 0$ | $PdCl_5 \rightleftharpoons PdCl_2 + Cl_2$ (g) (g) (g) $\Delta n = 1$ | $PdCl_2 + Cl_2 \rightleftharpoons PdCl_4$ (g) (g) (g) $\Delta n = -1$ |
| $K_p \text{ and } K_c = \text{Unitless}$ | $K_p \rightarrow \text{atm}$ $K_c \rightarrow \frac{\text{mol}}{\text{litre}}$ | $K_p \rightarrow \text{atm}^{-1}$ $K_c \rightarrow \text{mol}^{-1} \text{litre}$ |

Que) $K_c = 4.24$, $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$
 Calculate eq.^m constnations of CO_2 , H_2 , CO and H_2O if only CO and H_2O are present initially at concentrations of 0.10 M each.

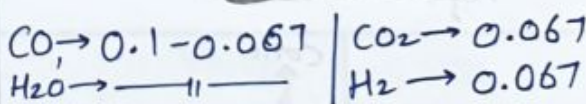


$$K_c = \frac{[CO_2] [H_2]}{[CO] [H_2O]} = \frac{[x] [x]}{[0.1-x] [0.1-x]}$$

$$K_c = \frac{x^2}{(0.1-x)^2} \rightarrow \sqrt{4.24} = \sqrt{\frac{x^2}{(0.1-x)^2}}$$

$$= 2.059 = \frac{x}{0.1-x}$$

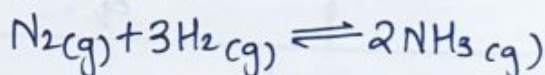
$$x = 0.067$$



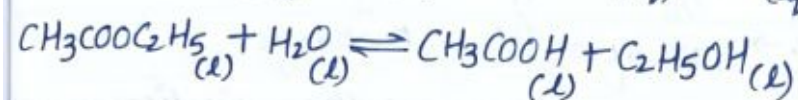
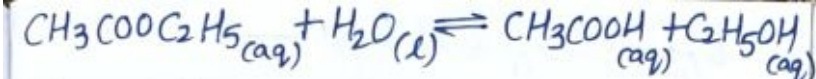
Homogeneous and Heterogeneous Eq.^m

→ Homogeneous →

→ all reactants and products are in same state.



$$K_c = \frac{[NH_3]^2}{[N_2] [H_2]^3}, \quad K_p = \frac{(P_{NH_3})^2}{(P_{N_2}) (P_{H_2})^3}$$

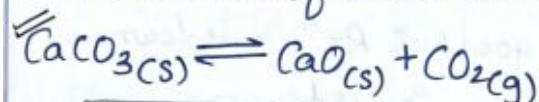


$$K_c = \frac{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5]}$$

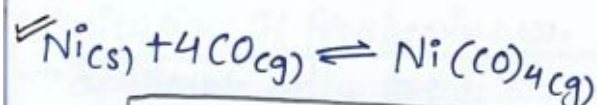
→ Heterogeneous →

→ Having more than one state.

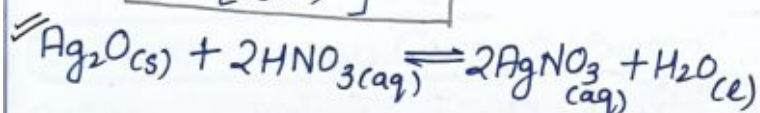
→ Active mass of Solid and liquid is unity.



$$K_c = [\text{CO}_2]$$



$$K_c = \frac{[\text{Ni}(\text{CO})_4]}{[\text{CO}]^4}$$



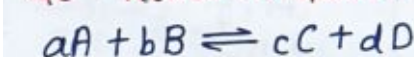
$$K_c = \frac{[\text{AgNO}_3]^2}{[\text{HNO}_3]^2}$$

Application of equilibrium Constant →

| $K_c < 10^{-3}$ | $K_c > 10^3$ | $10^{-3} < K_c < 10^3$ |
|--|---|---|
| Reactants are predominant over product | Products are predominant over reactant. | Both reactants and products are in eq. ^m . |
| Reaction hardly proceed | Reaction proceeds largely to completion | |

Predicting the direction of Reaction

$Q_c \rightarrow$ Reaction Quotient.



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

at any time

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

conc. at eq.^m
eq.^m constant.

$Q_c < K_c \rightarrow \text{Rx}^n$ forward.

$Q_c > K_c \rightarrow \text{Rx}^n$ backward.

$Q_c = K_c \rightarrow \text{No net Rx}^n$

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Relation b/w eq.^m Constant K , Reaction Quotient Q , and Gibbs free energy (ΔG).

$$\Delta G = \Delta G^\circ + RT \ln Q$$

at eq.^m →

$$\Delta G = 0, Q = K_c$$

$$0 = \Delta G^\circ + RT \ln K_c$$

$$\Delta G^\circ = -RT \ln K_c$$

$$\ln K_c = -\frac{\Delta G^\circ}{RT}$$

$$K_c = e^{-\Delta G^\circ/RT}$$

$\Delta G < 0 \rightarrow K_c > 1 \rightarrow \text{Rx}^n$ Spontaneous.

→ product is dominant.

$\Delta G > 0 \rightarrow K_c < 1 \rightarrow \text{Rx}^n$ Non-Spontaneous

→ Reactant is dominant.

Degree Of Dissociation (α)

$$\alpha = \frac{\text{no. of moles dissociated}}{\text{initial moles}}$$

$$\% \alpha = \frac{\text{no. of moles dissociated}}{\text{Initial moles}} \times 100$$

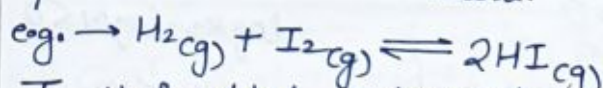
Lechatelier Principle

If eq.^m is subjected to change of conc., pressure, temp. then eq.^m is shifted in such a way to counter the effect of change and new eq.^m established.

① Concentration →

$[\text{reactant}] \uparrow \rightarrow \text{Rx}^n$ forward.

$[\text{product}] \uparrow \rightarrow \text{Rx}^n$ backward.

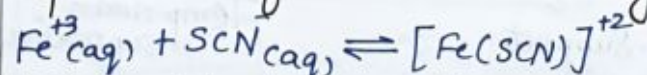


If H_2 is added → forward.

If I_2 ——— → forward.

If HI ——— → backward.

Experiment of Concentration Change.



Yellow colourless deep red

→ addition of potassium thiocyanate → Colour intensity ↑
 Rx^n forward.

→ addition of Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) → Red colour ↓
 Rx^n Backward

Addition of $HgCl_2 \rightarrow$ Red Colour Intensity \downarrow
 $Hg^{+2} + SCN^- \rightarrow [Hg(SCN)_4]^{2-}$ (rxn backward)

② Effect of pressure Change \rightarrow

$P \uparrow, V \downarrow, C \uparrow, n \uparrow \rightarrow$ rxn shift in direction of lower no. of moles $\uparrow C = \frac{n}{V} \downarrow$

e.g. $- CO_2(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$
 $P \uparrow \rightarrow$ Rxn forward (lower mole)

e.g. $- C(s) + CO_2(g) \rightleftharpoons 2CO(g)$
 $P \uparrow \rightarrow$ Rxn backward (lower mole)

③ Inert Gas Addition

at constant Vol. \rightarrow No effect

at constant Pressure \rightarrow $V \propto n$

$n \uparrow, V \uparrow, C \downarrow, n \uparrow \rightarrow$ eqm shift towards higher number of moles. $PV = nRT$

$\Delta n > 0 \rightarrow$ Rxn forward

$\Delta n < 0 \rightarrow$ Rxn backward

$\Delta n = 0 \rightarrow$ no effect

④ Temperature

Endothermic

$\Delta H = +ve$

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

$$T \uparrow \log \frac{K_2}{K_1} > 0$$

$$\log K_2 - \log K_1 > 0$$

$$K_2 > K_1$$

$T \uparrow \rightarrow$ Rxn forward

Temp. Supporter

Exothermic

$\Delta H = -ve$

$$T \uparrow \rightarrow \log \frac{K_2}{K_1} < 0$$

$$\log K_2 - \log K_1 < 0$$

$$K_2 < K_1$$

$$T \uparrow \rightarrow$$

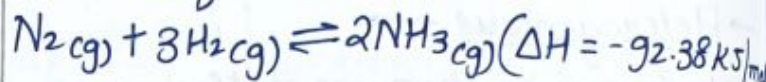
Rxn backward

Temp non-supportive

Effect Of Catalyst \rightarrow

\rightarrow State of eqm do not change.

\rightarrow Catalyst decreases the activation energy and hence, rate of approach of eqm becomes faster.



Low Temp., High Pressure.

\hookrightarrow NH_3 yield is good but Rxn slows down
 So, Iron Catalyst is Used.

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