CHEMICAL KINETICS

➤ **Rate of reaction** (ROR) $= \dfrac{\text{Rate of disappearance of reactant (appearance of products)}}{\text{Stoichiometric coefficient of reactant (products)}}$
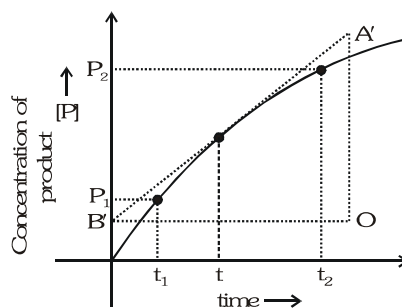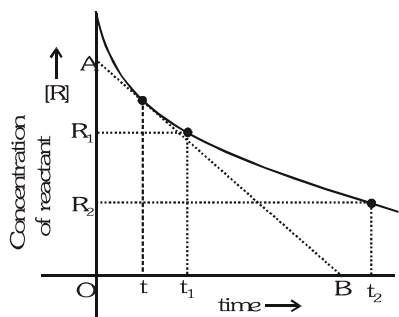
➤ **For a reaction :**

$aA + bB \longrightarrow cC + dD$

➤ **Instantaneous rate :** $-\dfrac{1}{a}\left(\dfrac{d[A]}{dt}\right) = -\dfrac{1}{b}\left(\dfrac{d[B]}{dt}\right) = \dfrac{1}{c}\left(\dfrac{d[C]}{dt}\right) = \dfrac{1}{d}\left(\dfrac{d[D]}{dt}\right)$

Relationship between rate of reaction and rate of disappearence of reactant (rate of appearance of product).

◆ **Average rate :** $-\dfrac{1}{a}\left(\dfrac{\Delta[A]}{\Delta t}\right) = -\dfrac{1}{b}\left(\dfrac{\Delta[B]}{\Delta t}\right) = \dfrac{1}{c}\left(\dfrac{\Delta[C]}{\Delta t}\right) = \dfrac{1}{d}\left(\dfrac{\Delta[D]}{d\Delta t}\right)$

⇒ Graphical method for determining rate :

Avg. Rate $= -\left(\dfrac{[R]_2 - [R]_1}{t_2 - t_1}\right) = \dfrac{([P]_2 - [P]_1)}{t_2 - t_1}$

Instantaneous rate $= -\left(\dfrac{OA}{OB}\right) = +\dfrac{OA'}{OB'} = \pm$ slope of tangent

➤ **Important kinetic expression for reaction of type A $\longrightarrow$ B :**

Order	Zero	1st	2nd	nth
Differential rate law	Rate = k	Rate= k[A]	Rate = $k[A]^2$	Rate = $k[A]^n$
Integrated rate law	$[A_0]-[A]= kt$	$kt = \ln\dfrac{[A]_0}{[A]}$	$kt = \dfrac{1}{[A]} - \dfrac{1}{[A]_0}$	$kt = \dfrac{1}{(n-1)}\left[\dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A]_0^{n-1}}\right]$
Half life ($t_{1/2}$)	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{\ln 2}{k}$	$t_{1/2} = \dfrac{1}{[A]_0 k}$	$t_{1/2} = \dfrac{1}{k(n-1)}\left[\dfrac{2^{n-1}-1}{[A_0]^{n-1}}\right]$
($t_{3/4}$)	$t_{3/4}=1.5\, t_{1/2}$	$t_{3/4}= 2\, t_{1/2}$	$t_{3/4} = 3\, t_{1/2}$	$t_{3/4}= (2^{n-1} + 1)\, t_{1/2}$

➢ **Graphs of various order**

Order	Rate vs [A]	[A] vs t	log [A] vs t	$\dfrac{1}{[A]}$ vs t
Zero order				
First order				
Second order				

Where

$[A]_0 \Rightarrow$ initial concentration

$[A] \Rightarrow$ concentration at time t

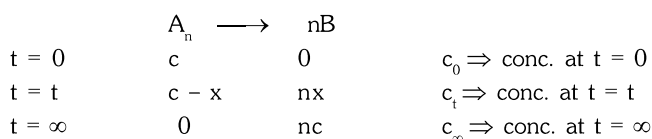$t_{1/2} \Rightarrow$ time taken for initial concentration of reactant to finish by 50%

$t_{3/4} \Rightarrow$ time taken for initial concentration of reactant to finish by 75%

➢ **Monitoring Kinetics Experimently :**

The kinetics of reaction can be followed (i.e. order, rate constant etc. can be established) by measuring a property which changes with time.

e.g. (i) Total pressure in a gaseous reaction.

(ii) Volume of a reagent (Acidic, Basic, oxidising or reducing agent)

(iii) Volume of a gaseous mixture (V)

(iv) Optical rotation (R)

For a Reaction -

$$A_n \longrightarrow nB$$

t = 0	c	0	$c_0 \Rightarrow$ conc. at t = 0
t = t	c – x	nx	$c_t \Rightarrow$ conc. at t = t
t = ∞	0	nc	$c_\infty \Rightarrow$ conc. at t = ∞

For any measurable property X proportional to the concentration of reaction mixture at various times, following relations can be expressed.

In terms of -

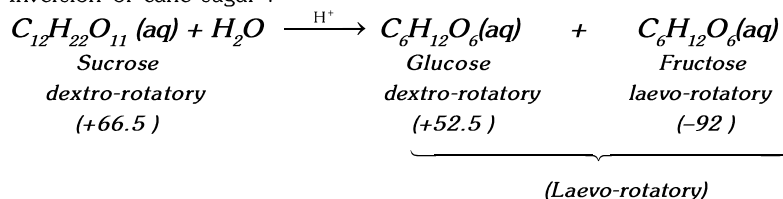| (i) X_0 and x	(ii) X_0 and X_t	(iii) X_∞ and X_t	(iv) X_0, X_t, and X_∞
$k = \dfrac{1}{t}\ln\dfrac{X_0}{X_0 - x}$	$k = \dfrac{1}{t}\ln\dfrac{(n-1)X_0}{nX_0 - X_t}$	$k = \dfrac{1}{t}\ln\dfrac{(n-1)X_\infty}{n(X_\infty - X_t)}$	$k = \dfrac{1}{t}\ln\left(\dfrac{X_\infty - X_0}{X_\infty - X_t}\right)$

where

x $\Rightarrow$ amount of reactant reacted in time 't'.

$X_0 \Rightarrow$ measured property at t = 0

$X_t \Rightarrow$ measured property at t = t

$X_\infty \Rightarrow$ measured property at t = ∞

➢ *Examples : (For Monitoring Kinetics Experimently)*

(i) Inversion of cane sugar :

$$C_{12}H_{22}O_{11}\ (aq) + H_2O \xrightarrow{\ H^+\ } C_6H_{12}O_6(aq) \quad + \quad C_6H_{12}O_6(aq)$$

Sucrose	Glucose	Fructose
dextro-rotatory	dextro-rotatory	laevo-rotatory
(+66.5)	(+52.5)	(–92)

(Laevo-rotatory)
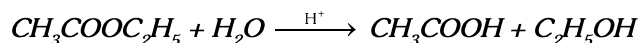
$$k = \frac{2.303}{t} log\left(\frac{r_\infty - r_0}{r_\infty - r_t}\right)$$

$r_0 = $ rotation at time, t = 0

$r_t = $ rotation at time, t = t

$r_\infty = $ rotation at time, t = ∞

(ii) *Acidic hydrolysis of ethyl acetate* :

$$CH_3COOC_2H_5 + H_2O \xrightarrow{\ H^+\ } CH_3COOH + C_2H_5OH$$

$$k = \frac{2.303}{t} log\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

$V_0 = $ Volume of NaOH solution used at time, t = 0

$V_t = $ Volume of NaOH solution used at time, t = t

$V_\infty = $ Volume of NaOH solution used at time, t = ∞

Note : Here NaOH acts as a reagent. Acetic acid is one of the product the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as catalyst, also reacts with NaOH solution.

➢ *Important characteristics of first order reaction :*

◆ $t_{1/2}$ is independent of initial concentration.

◆ In equal time interval, reactions finishes by equal fraction.

	t = 0	t = t	t = 2t	t = 3t ....
Reactant conc.	a_0	a_0x	a_0x^2	a_0x^3........

x = fraction by which reaction complete in time 't'.

◆ Graph of ln[A] vs t is straight line with slope = $\dfrac{k}{2.303}$

◆ Graph of [A] vs t is exponentially decreasing.

➢ *Zero order :*

• $t_{1/2}$ of zero order is directly proportional to initial concentration.

• In equal time interval, reaction finishes by equal amount.

t = 0	t = t	t = 2t	t = 3t .....
C_0	$C_0 - x$	$C_0 - 2x$	$C_0 - 3x$ ....

• Graph of [A] vs t is straight line.

A zero order reaction finishes in $\boxed{t = \dfrac{[A]_0}{k}}$

➢ *Temperature dependence :*

– Arrhenious equation : $k = A.e^{-Ea/RT}$

– E_a = minimum energy over and above the avg. energy of reactant which must be possesed by reacting molecule for collision to be succesful.

– A = frequency factor - proportional to number of collisions per unit volume per second.

– $e^{-E_a/RT}$ = Fraction of collision in which energy is greater than E_a.

– A and E_a are constant i.e. do not vary with temperature

$$\ln k = \ln A - \frac{E_a}{RT}$$
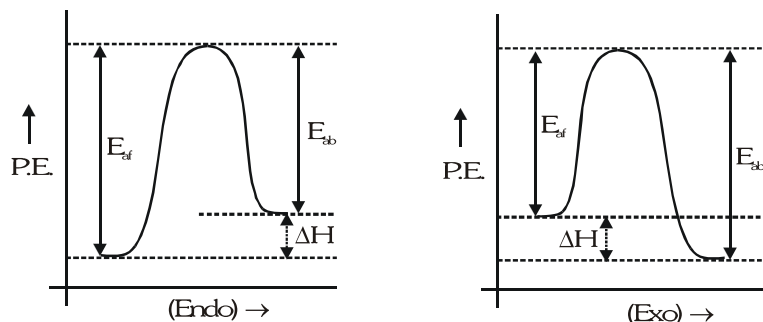
Graph : Graphical determination of E_a.
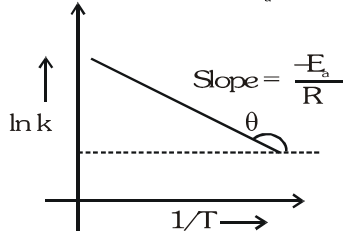
Temperature coefficient $= \dfrac{k_{T+10}}{k_T}$

By default T = 298 K

Variation of rate constant with temparture $\Rightarrow \ln \dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

➢ *Endothermic and exothermic reactions :*

(Endo) $\rightarrow$ (Exo) $\rightarrow$

$$\boxed{\Delta H = E_{af} - E_{ab}}$$

➢ *Parallel reaction :* $A \underset{k_2}{\overset{k_1}{\longrightarrow}} \begin{matrix} B \\ C \end{matrix}$

(i)   Rate = $(k_1 + k_2)$ [A] - (differential rate law)

(ii) $\dfrac{k_1}{k_2} = \dfrac{[B]}{[C]}$

(iii) $t_{1/2} = \dfrac{0.693}{k_1 + k_2}$

(iv)   % of B = $\dfrac{k_1}{k_1 + k_2} \times 100$; % of C = $\dfrac{k_2}{k_1 + k_2} \times 100$

(v) $[A] = [A]_0\, e^{-(k_1 + k_2)t}$

➢ *Pseudo-order reaction :*

Rate law $\rightarrow$ rate = $k\, [A]^m\, [B]^n$

Pseudo rate law :

rate = $k_1\, [A]^m$

[B] assumed constant in two cases :

(i) B in large excess   (ii) B $\rightarrow$ CATALYST

➤ **All nuclear reactions are first order :**

Two types of nuclear reaction : **(a)** Artifical radioactivity **(b)** Radioactivity (spont.)
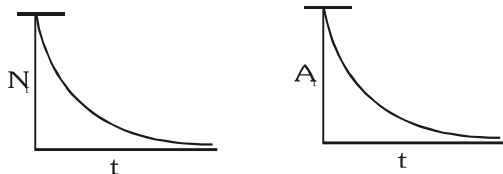
First order

$$\lambda t = 2.303 \log \frac{N_0}{N_t}$$ $\lambda \rightarrow$ Decay constant

$N_0 \rightarrow$ Initial nuclei
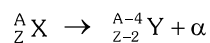
$N_t \rightarrow$ Nuclei at 't'

$$\text{Activity} = A_t = \frac{-dN_t}{d_t} = \lambda N_t \; ; \; \text{Nuclei/sec.}$$
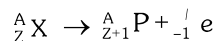
A_t = Rate of decay

$$\Rightarrow \qquad t_{\frac{1}{2}} = \frac{\ln 2}{\lambda}$$

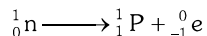➤ **α decay** $= {}^4_2\text{He}$ Particles at high velocity

$${}^A_Z X \rightarrow {}^{A-4}_{Z-2} Y + \alpha$$

To $\downarrow$ size of large nuclei

➤ **β decay** $= {}^0_{-1}e$ at high velocity

$${}^A_Z X \rightarrow {}^A_{Z+1} P + {}^{/}_{-1} e$$

To $\downarrow \dfrac{n}{P}$ ratio.

Nuclear change in β decay

$${}^1_0 n \longrightarrow {}^1_1 P + {}^0_{-1} e$$

➤ **γ-decay :**

Photons from excited nuclei after α – or β – decay

No effect on n/p ratio

High energy e/m radiation.

Mean life , $t_{avg} = \dfrac{1}{\lambda}$

➤ **Parallel decay :**

t = 0 N_0
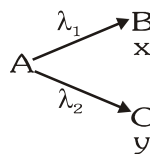
t = t $N_0 - x - y$

$\lambda_{eff.} = \lambda_1 + \lambda_2$

$$\frac{1}{t_{eff.}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}$$

$\lambda \rightarrow$ No dependence on temp.

THERMODYNAMICS

➤ **THERMODYNAMICS :**

◆ Study of heat and work interaction between system and surrounding.

◆ A macroscopic science.

◆ Thermodynamic laws are experimentally verified.

➤ **Important terms and concepts in thermodynamics.**

◆ System - Portion of universe under investigation.

◆ Surrounding - Anything apart from system.

◆ Boundary - Real or hypothetical line or surface between system and surrounding.

◆ Wall - A real boundary.

Rigid wall - Immovable wall (w = 0)

Non-rigid wall - Movable wall (w ≠ 0)

Adiabatic wall - Insulated wall (q = 0)

Diathermic wall - Non-insulated wall (q ≠ 0)

◆ State variable - Variable which defines state of system.

◆ State of system - A condition defined by fixed value of state variables.

◆ State of thermodynamic equilibrium - A condition in which state variables do not vary with time.

➤ **Extensive state variable :** State variable whose value depends upon size of system.

Examples - mass, volume, charge, mole etc.

➤ **Intensive state variable :** State variable whose value does not depends upon size of system.

Examples - concentration, density, temperature etc.

➤ **Path variable :**

◆ **Heat :** Mode of energy transfer between system and surrounding due to temperature difference.

◆ **Work :** Mode of energy transfer between system and surrounding due to difference in generalized force.(Net force).

THE FIRST LAW

(i) Energy of universe is conserved

(ii) Internal energy (U) of a system is state function.

(iii) $\Delta U = q + w$

ΔU = Increase in internal energy of system.
q = Heat absorbed by the system
w = work done on the system

(iv) In a cyclic process $\boxed{\sum_{Cyclic} \Delta U = 0}$

If a cyclic process involves n steps with heat absorbed and work done on the system, q_i and w_i respectively, then -

$$\sum_{Cyclic} \Delta U = \sum_{i=1}^{i=n}(q_i + w_i) = \sum_{i=1}^{i=n} q_i + \sum_{i=1}^{i=n} w_i = 0$$

⇒ $Q_{net} = -W_{net}$ (in a cyclic process)

(v) If two states 1 and 2 are connected by n paths involving q_i and w_i, heat and work respectively, then

$$\Delta U = q_1 + w_1 = q_2 + w_2 = \ldots\ldots\ldots\ldots q_n + w_n$$

(vi) q and w are path dependent quantities (indefinite quantities) but there sum is a definite quantity (ΔU).

◆ **Enthalpy :** A state function defined by first law

$$H = U + PV$$

(i) Enthalpy is (pressure volume energy + internal energy of system)

(ii) Enthalpy is also called heat content of system.

◆ **Heat absorbed at constant volume and constant pressure.**

$\boxed{q_V = \Delta U}$ Heat absorbed by a system in isochoric process is equal to change in internal energy of system.

$\boxed{q_p = \Delta H}$ Heat absorbed at constant pressure by a system is equal to change in enthalpy.

◆ **Enthalpy change :**

For General process -

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1 \qquad\qquad\ldots\ldots\ldots(i)$$

For Isobaric change -

$$\Delta H = \Delta U + P\Delta V \qquad\qquad\ldots\ldots\ldots(ii)$$

For Isochoric change -

$$\Delta H = \Delta U + V(\Delta P) \qquad\qquad\ldots\ldots(iii)$$

For a differential change

$$dH = dU + PdV + VdP \qquad\qquad\ldots\ldots(iv)$$

➤ **Ideal gas processes : (See table page no. 11)**

◆ **Enthalpy of phase transition**

ΔH_{vap} = heat absorbed at constant temperature and pressure to convert one mole liquid into it's vapours.
= molar enthalpy of vapourisation.

ΔH_{fusion} = heat absorbed at constant temperature and pressure to convert one mole solid into liquid.
= molar enthalpy of fusion.

$\Delta H_{sublimation}$ = heat absorbed at constant temperature and pressure to convert one mole solid into it's vapours.
= molar enthalpy of sublimation.

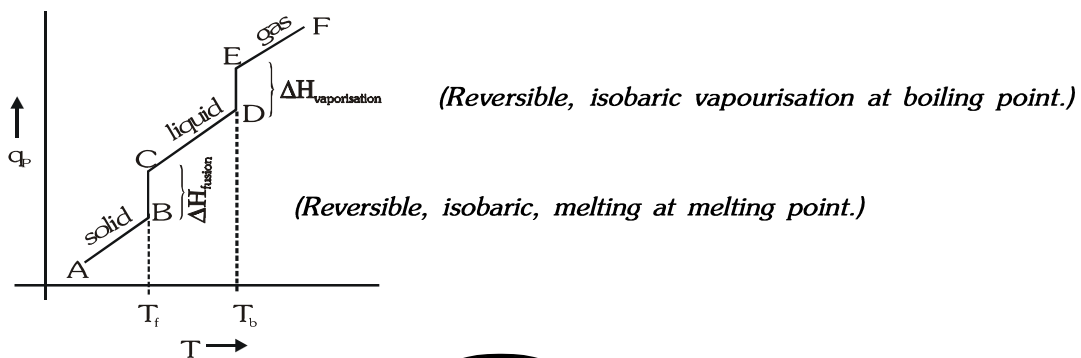$\Delta H = \Delta U + P(V_f - V_i)$ since phase transtions are isobaric and isothermal processes.

◆ **Relationship between ΔH and ΔU for phase transtions.**

For vapourisation $\Delta H_{vap} = \Delta U_{vap} + RT$

For sublimation $\Delta H_{sublimation} = \Delta U_{sublimation} + RT$

For fusion $\Delta H_{fusion} \cong \Delta U_{fusion}$

◆ **Heating curve at constant pressure :**

(Reversible, isobaric vapourisation at boiling point.)

(Reversible, isobaric, melting at melting point.)

- **Enthalpy of reaction ($\Delta_r H$) :** The enthalpy of reaction is heat exchanged at constant pressure and temperature to convert the stoichiometric amount of reactant into product with specified physical state according to balanced chemical reaction at constant temperature and pressure.

  for $aA + bB \longrightarrow cC + dD$

  $\Delta_r H = q_P$ = enthalpy of reaction

  $\Delta_r H = (cH_C + dH_D - aH_A - bH_B)$ where H_A, H_B, H_C, H_D are molar enthalpies of A,B,C and D.

- **Relationship between $\Delta_r H$ and $\Delta_r U$**

  $\Delta_r H = \Delta_r U + \Delta n_g RT$ (for ideal gas)

  $\Delta_r H = \Delta_r U + P(V_f - V_i)$ (for non ideal conditions)

- **The stoichiometric coefficient of solids and liquids in not considered in calculation of Δn_g (because $V_S \sim V_L << V_g$)**

- **Standard state for**

  (i) Ideal gas : 1 bar pressure ; any temperature.

  (ii) Solid / Liquid : 1 bar pressure ; any temperature.

  (iii) Solute : Molar concentration of 1 mole/L at P = 1 bar.

  Standard enthalpy, internal energy change for reaction.

  $\Delta_r H$ and $\Delta_r U$ are change in thermodynamics function of a system under standard conditions.

SECOND LAW

➢ **Spontaneous process :**

- A process which takes place on it's own without any external help.

- Spontaneous process ≡ Irreversible process ≡ Natural process.

➢ **Second law :** During a spontaneous process.

- $\Delta S_{universe} > 0$

⇒ $\Delta S_{system} + \Delta S_{surr.} > 0$

- S is a state function. S is measure of disorder of a system.

(A) Change in entropy of system is given by :

$$dS_{system} = \frac{dq_{rev.}}{T}$$

(i) Entropy change for ideal gas process :

- $\Delta S = nC_v \ln \dfrac{T_2}{T_1} + nR \ln \dfrac{V_2}{V_1}$

(ii) Entropy change for system in phase transition :
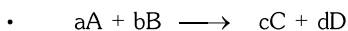
- $\Delta S_{vap.} = \dfrac{\Delta H_{vap.}}{T_b}$

- $\Delta S_{fusion.} = \dfrac{\Delta H_{fusion}}{T_f}$

- $\Delta S_{sublimation} = \dfrac{\Delta H_{sublimation}}{T_{Sub.}}$

(iii)   Entropy change of system for a chemical reaction :

For a reaction -

• $aA + bB \longrightarrow cC + dD$

$$\boxed{\Delta_r S = cS_c + dS_D - aS_A - bS_B}$$

S_A, S_B, S_C and S_D are molar absolute entropies which is obtained by third law.

(B)   Entropy change in surrounding :

(i)   Ideal gas process : $\Delta S_{surr.} = \dfrac{-q_{actual}}{T}$

(ii)   Phase transition : $\Delta S_{surr.} = \dfrac{-\Delta H}{T}$

(iii)   Chemical reaction : $\Delta S_{surr.} = -\dfrac{\Delta_r H}{T}$

$$\boxed{\begin{array}{c} \text{For reversible processes : } \Delta S_{system} + \Delta S_{surr.} = 0 \\ \Delta S_{system} = -\Delta S_{surr.} \end{array}}$$

$$\boxed{\begin{array}{c} \text{For irreversible processes : } \Delta S_{system} + \Delta S_{surr.} > 0 \\ \Delta S_{total} \geq 0 \end{array}}$$

◆   *Prediction of sign of $\Delta_r S$ from inspection :*

(i)   If $\Delta n_g > 0$; $\Delta_r S > 0$.

(ii)   If Solid $\longrightarrow$ liquid

           liquid $\longrightarrow$ gas $\Big\}$ $\Delta_r S > 0$

(iii)   If cyclisation taken place $\Delta_r S < 0$.

➢   *Gibb's function : $G = H - TS$*

     $\Delta G = \Delta H - T\Delta S$ → *For isobaric change*

     $\Delta G = -T(\Delta S_{Total})$

⇒ $(\Delta G)_{T,P} \leq 0$ → *Process spontaneous*

(A)   Change in ΔG for phase transition :

(i)   For reversible phase transitions : $\Delta G = 0$.

(ii)   For irreversible phase transition : $\Delta G_{P,T} = \Delta H_{P,T} - T\Delta S_{P,T}$

(B)   Change in ΔG for chemical reaction :

         $aA + bB \longrightarrow cC + dD$
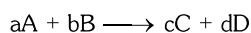
$\Delta_r G = cG_C + dG_D - aG_A - bG_B$ .....(i)

$\Delta_r G = \Delta_r H - T\Delta_r S$ .....(ii)

$\Delta_r G = \Delta_r G^\circ + RT \ln Q$ .....(iii)

Where, $Q \equiv$ Reaction quotient

➢ $\Delta G / \Delta G$ *and state of chemical equilibrium :*

At equilibrium :

-    $\Delta G = 0 \Rightarrow G_{product} = G_{reactant}$

-    $\Delta G = -RT \ln K_{eq.}$

-    At equilibrium the system gibb's function is at minimum value.

➢   *Difference between* $\Delta_r G$ *and* $\Delta_r G$:

$\Delta_r G$ = change in Gibb's function when all the reactants and products have arbitrary activities.

$\Delta_r G$ = change in Gibb's function when all the reactants and products are at unit activities.

$\Rightarrow$ All gases at 1 bar pressure.

$\Rightarrow$ All solute at molar concentration 1 M.

➢   *Factors on which* $\Delta_r G$ *depends* -

(i)   Stoichiometric coefficients of a balanced chemical reaction.

(ii)   the temperature.

(iii)   the $\Delta_r G$ is independent of actual pressure or concentration of reactants or products.

➢   *Gibb's function and non-PV work :*

$$- (\Delta G)_{T,\,P} = W_{max}$$

decrease in Gibb's function at constant temperature and pressure is equal to maximum non-PV work obtainable from system reversibly.

$$- \Delta_r G = - \Delta_r H + T\Delta_r S$$

Decrease in Gibb's function = heat given out to surrounding + $T\Delta_r S$.

Process	Expression for w	Expression for q	ΔU	ΔH	Work on PV-graph
Reversible isothermal process	$w = -nRT \ln \dfrac{V_2}{V_1}$ $= -nRT \ln \dfrac{P_1}{P_2}$	$q = nRT \ln\left(\dfrac{V_2}{V_1}\right)$ $q = nRT \ln\left(\dfrac{P_1}{P_2}\right)$	*0*	*0*	
Irreversible isothermal process	$w = -P_{ext}(V_2 - V_1)$ $= -P_{ext}\left(\dfrac{nRT}{P_2} - \dfrac{nRT}{P_1}\right)$	$q = P_{ext}(V_2 - V_1)$	*0*	*0*	
Isobaric process	$w = -P_{ext}(V_2 - V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_P\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Isochoric process	$w = 0$	$q = \Delta U = nC_V\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Reversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \dfrac{P_2V_2 - P_1V_1}{\gamma - 1}$	$q = 0$ $PV^\gamma = $constant $TV^{\gamma-1} = $constant $TP^{1-\gamma/\gamma} = $constant	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Irreversible adiabatic process	$w = nC_V(T_2 - T_1)$ $\dfrac{P_2V_2 - P_1V_1}{\gamma - 1}$				
Polytropic process	$w = \dfrac{P_2V_2 - P_1V_1}{n - 1}$ $w = \dfrac{R(T_2 - T_1)}{(n - 1)}$	$q = \displaystyle\int_{T_1}^{T_2} C_V dT$ $+ \displaystyle\int_{T_1}^{T_2} \dfrac{R}{1 - n} dT$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	

$V_2 = $ Final volume $\qquad$ $V_1 = $ Initial volume
$P_2 = $ Final pressure $\qquad$ $P_1 = $ Final pressure