Thermodynamics

Thermo → heat
Dynamics → motion

→ It is the branch of science that deals with the study of flow of heat or any other form of energy between system and surroundings during any physical or chemical change.

→ system + surrounding ⇒ universe

→ **System** :- The object which is under consideration or investigation and we measure any physcial and chemical change is called system.

→ **surrounding** : It is the part of universe except system

→ system is limited but surrounding is unlimited. Boundry is that seperates system from surrounding.

* Types of thermodynamic system :-

① **Open system**

→ The system which allow exchange of both matter and energy Eg :- water in beaker.

② **Closed system**

→ allows exchange of energy only
Eg :- water in beaker with lid

③ **Isolated system**

→ doesn't allows exchange of both matter and energy
Eg :- water in thermos flask.

→ There is no perfect isolated system.

* Properties of system

① Extensive properties

→ The properties which depends upon amount of system is called extensive properties

→ Eg:- mass, weight, Enthalpy, Entropy, volume, area etc.

② Intensive properties

→ Does not depends upon amount of system

→ Depends upon nature of system

Eg:- density, refractive index, sp. Heat capacity, surface tension, viscosity, concn, temp etc.

* State of system :-

→ The condition of system which can be described by measurable properties like pressure, tempr, volume etc is called state of the function.

→ If one of the variable changes, state of system also changes.

* State variables / state function

→ State variables which are dependent upon only the state of the system but not the path followed by ~~them~~ which that state has been attained are called state function.

Reversible process	Irreversible process.
A reversible process is a process that can be reversed in order to obtain the initial state of a system.	An irreversible process is a thermodynamic process that cannot be reversed in order to obtain the initial state of a system
Infinite small change occur in the system.	Finite change occur in the system.
There is equilibrium between the initial state and the final state of the system	There is no equilibrium in the system.
Workdone is more than that of irreversible process	workdone is less than that of reversible process.

Internal Energy [E or U] (IMP)

The sum of all kind of energies associated with the substance of system is called Internal Energy. For eg:- KE, PE, nuclear energy etc---.

Its characterstics are

- It is state Function (Initial and Final step dependen)
- It is Extensive property (value depends on quantity)
- It's absolute value can't be determined since it's very complex process to calculate all the energy associated with substance
- change in E/U is given by

$$\Delta E = E_2 - E_1$$

final — initial

Mode of Exchange of Energy.

Thermodynamic process are accompanied by exchange of energy that takes place btn system and surrounding.

Energy is exchanged in two forms

i) In the form of heat.

If the system and surrounding differs in tempeature, then energy exchanges between them is in form of heat.

$q = +ve$ → (absorbed by system)

$q = -ve$ → (lost by system).

ii) In the form of workdone

$$\text{At two different pressure}\begin{cases} \rightarrow W = +ve :- \text{workdone on system} \\ \rightarrow W = -ve :- \text{workdone by system} \end{cases}$$

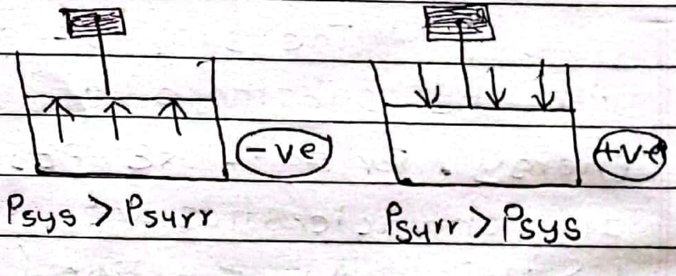
(pressure-voln workdone)

$W = P\Delta V$

$= P(V_2 - V_1)$

In Physics, $V_1 > V_2 = -ve$

$V_2 > V_1 = +ve$



First law of thermodynamics (IMP)

↳ It is based upon law of conservation of energy

↳ It states that "The total energy in the universe always remains constant.

↳ Energy can neither be created nor be destroyed.

Thermodynamic process

① Isothermal process

↳ Tempeature of the system remains constant throughout the state change i.e. $\Delta T = 0$

(Initial) $P_1V_1T_1 \longrightarrow P_2V_2T_1$ (final)

② Isobaric process

↳ Pressure of the system remains constant.

i.e. $\Delta P = 0$ $\quad P_1V_1T_1 \longrightarrow P_1V_2T_2$

(Initial) (Final)

③ Isochoric process

↳ vol. of system remain constant

i.e $\Delta V = 0$

$P_1V_1T_1 \longrightarrow P_2V_1T_2$

(Initial) (Final)

④ Adiabatic process

↳ No Flow of heat From system ⇌ surrounding.

i.e $\Delta q = 0$

⑤ cyclic process

↳ system passes through no. ~~internal~~ of intermediate change and return to its initial state.

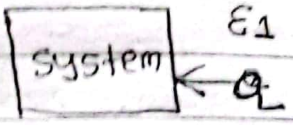
↳ In this process,

$\Delta E = 0$ (Internal energy)

$\Delta W = 0$

First law, (Mathmatical interpretation)

↳ Let us suppose a system whose internal energy in it's initial state is ε_1. Heat 'q' is absorbed by the system, work 'W' is done by the system. Then let it's energy be ε_2 in final state.



Then, $\varepsilon_2 = \varepsilon_1 + q - W$ (q → +ve absorbed by system)

or $\varepsilon_2 - \varepsilon_1 = q - W$

or, $\Delta E = q - W$ (mathmatical form of 1st law)

or, $dq = \Delta E + W$ ($W = F.S = P.\Delta V$)

or $dq = dE + Pdv$

↳ In isothermal process, $\Delta t = 0$ so, $\Delta E = 0$

so, $q = P\Delta V$

↳ In isochoric process, $\Delta V = 0$ then $P\Delta V = 0$

$\therefore q = \Delta E$

↳ In adiabatic process, $q = 0$

$\therefore \Delta E + P\Delta V = 0$

or, $\Delta E = -P\Delta V$

or $\Delta E = -W$

Imp

Limitations

↳ Doesn't tell about direction of energy flow.

↳ Doesn't tell about extent of convertablity of energy from one form to another.

↳ Doesn't tell about the direction of change of state.

Statement + limitation

Imp

Enthalpy (H)

- Generally thermal changes are carried out in constant pressure (in open vessel) rather than in close vessel (at constant volume).
- So pressure is constant but volume changes due to expansion and contraction but this workdone is not considered by Internal energy. So new term is introduced called Enthalpy.

" Heat contained of the system at constant pressure is called Enthalpy".

i.e. $H = E + PV$

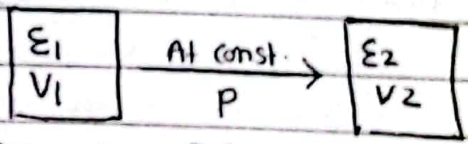
- It is State Function. (path independent)
- It is extensive property. (E value can't be measured
- It's absolute value is unknown approximately that's why)

Then, $\Delta H = H_2 - H_1$

$\Delta H = E_2 + PV_2 - E_1 - PV_1$

$\Delta H = E_2 - E_1 + P(V_2 - V_1)$

$\Delta H = \Delta E + P\Delta V$ ✳



$H_1 = E_1 + PV_1$

$H_2 = E_2 + PV_2$

Also from 1st law of thermodynamics

$\Delta q = \Delta E + P\Delta V$

$\boxed{\text{So, } \Delta H = q}$

- For the rxn involving solid and liquid system,

$\Delta V = 0$

So, $\Delta E = \Delta H$

↳ Suppose a gaseous system and its rxn :-

Initial state	Final state
$P\ V_1\ n_1$	$P\ V_2\ n_2$

From ideal gas equation,

$$PV = nRT$$

For initial state $PV_1 = n_1RT$ ——— ①

For Final state $PV_2 = n_2RT$ ——— ⑪

subtracting ① From ⑪ we get

$$P(V_2 - V_1) = RT(n_2 - n_1)$$

$\boxed{P\Delta V = \Delta nRT}$ when all are in gaseous Form

Enthalpy change of chemical reactions (Heat of Reaction)

↳ The amount of heat either absorbed or released during chemical reaction is called enthalpy change or Heat of reaction.

↳ The energy change in chemical reaction are due to breaking of old bonds (energy absorbed) and formation of new bonds. (Released. E)

↳ $A + B \longrightarrow C + D$

$\Delta H = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

→ The value of ΔH can either be positive, negative or zero.

If $\Delta H_r > \Delta H_p$, ΔH is negative [Exothermic]

$\Delta H_p > \Delta H_r$, ΔH is +ve [Endothermic]

$E_{Abs} > E_{res} \rightarrow$ Endo , ΔH +ve

$E_{Res} > E_{Abs} \rightarrow$ EXO , ΔH −ve

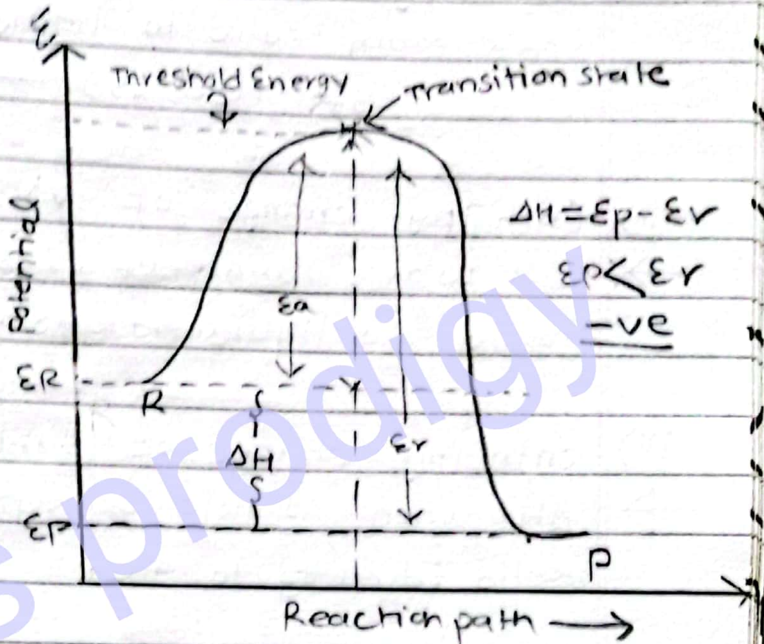
Exothermic Reactions

↳ Those reactions which are accompanied by the release of heat energy are called exothermic reactions.

Here, Energy released is greater than Energy absorbed so, the rxn is Exothermic and

$\Delta H = E_P - E_R$

$= -ve$ H



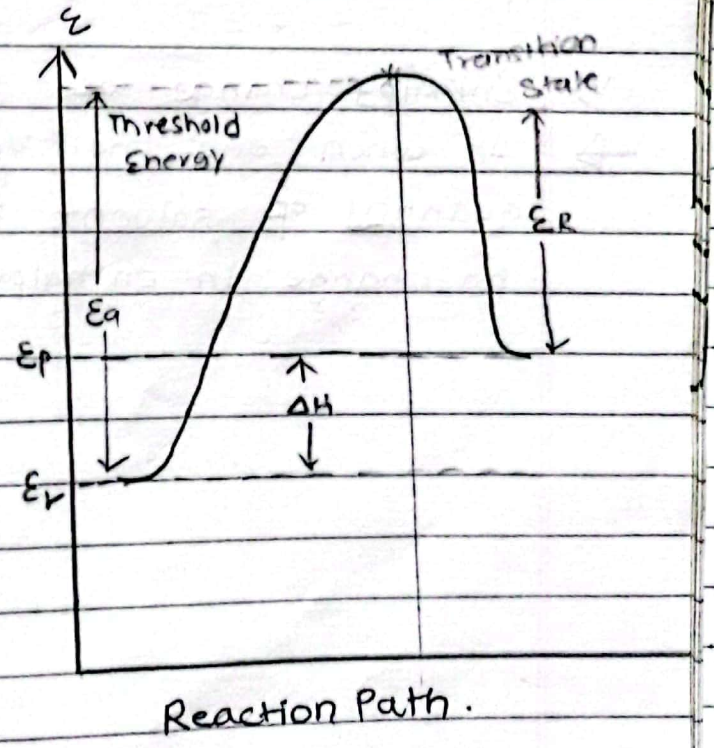
Endothermic Reactions :

↳ Those reactions which are accompanied by the absorption of heat energy are called endothermic reactions.

$E_a > E_R$ so $\Delta H = +ve$

$\Delta H = E_p - E_R$

$= +ve$



Enthalpy change in physical transformation

i) Enthalpy change of Fusion.

→ Enthalpy change when 1 mole of a system change its state from solid to liquid.

Eg:- $H_2O(s) \xrightarrow{0^\circ C} H_2O(l)$

II) Enthalpy change of vapourization.

→ ΔH when 1mole of system change it's state from liquid to gas.

iii) Enthalpy change of sublimation

→ ΔH when 1 mole of system change it's state from solid directly to gas.

iv) Enthalpy change of Transition

→ ΔH when 1 mole of system changes from one allotropic form to another allotropic form.

v) Enthalpy change of soln:

→ ΔH when one mole of substance is added to that quantity of solvent which on further addition bring no change in enthalpy.

Enthalpy change in chemical.Form.

i) Heat of combustion :

↳ Enthalpy change when one mole of substance undergoes complete combustion.

↳ Here, $\Delta H = -ve$ (always exothermic)

$$C + O_2 \xrightarrow{burn} CO_2 \; : \; \Delta H = -393.5\,kJ$$

↳ Animal get energy from combustion of Food.

↳ The amount of heat produced by 1 gm of food/Fuel on complete combustion is called calorific value of Food/Fuel.

$$\therefore \text{calorific value} = \frac{\Delta H\,(\text{combustion})}{\text{molar mass (g)}}$$

ii) Enthalpy of Formation / Heat of Formation.

↳ Enthalpy change when 1 mole of compound is formed from it's constituent elements is called enthalpy of Formation.

Eg :- $H_2(g) + Cl_2(g) \longrightarrow \underline{2HCl} \; : \; \Delta H = -44.0\,kcal$

$$\therefore HOF = \frac{-44.0}{2} = -22.0\,kcal.$$

IMP

↳ Standard heat of formation is at 25°c & 1atm pressure

↳ It is denoted by ΔH_F°.

Laws of thermochemistry

i) Lavoisier – Laplace's law

It states that, when a chemical equation is reversed, the sign of ΔH is changed.

For eg :–

$$S(s) + O_2(g) \longrightarrow SO_2(g) \quad \Delta H^\circ = -296.9 \text{ kJ mol}^{-1}$$

$$SO_2(g) \longrightarrow S(s) + O_2(g) \quad \Delta H^\circ = 296.9 \text{ kJ mol}^{-1}$$

i.e.

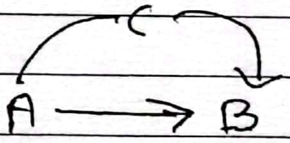
$$\boxed{\Delta H_{\text{Forward reaction}} = -\Delta H_{\text{backward rxn}}}$$

ii) Hess's law of constant heat summation

VVIMP

It states that, the enthalpy of reaction is independent of the number and nature of the intermediate steps.

case I : $A \longrightarrow B \quad \Delta H$



case II : $A \longrightarrow C \quad \Delta H_1$

$$+ \; C \longrightarrow B \quad \Delta H_2$$

$$A \longrightarrow B \quad \Delta H_1 + \Delta H_2 = \Delta H$$

Eg. $C(s) + 1/2\, O_2 \longrightarrow CO(g) \quad \Delta H = -x$ —— ①

$CO + 1/2\, O_2 \longrightarrow CO_2(g) \quad \Delta H = -y$ —— ⑪

Find the heat of reaction

$$C(s) + O_2 \longrightarrow CO_2 \quad \Delta H = ?$$

Adding ① and ⑪

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -x - y$$

Qn) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

$\Delta H_1 = -26\ kJ$

$FeO + CO \longrightarrow Fe + CO_2 \quad \Delta H_2 = -16\ kJ$

Find the ΔH of the reaction

$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$

→ Solution :-

Given reactions are :-

$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2 \quad \Delta H_1 = -26\ kJ$ —— ①

$FeO + CO \longrightarrow Fe + CO_2 \quad \Delta H_2 = -16\ kJ$ —— ②

The demanded equation is

$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2 \quad \Delta H = ?$

To get required equation, let us multiply eqn ② by ~~②~~ 2 and subtract it from equation 1 we get.

$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2 \quad \Delta H_1 = -26\ kJ$

$2FeO + 2CO \longrightarrow 2Fe + 2CO_2 \quad \Delta H_2 = -32\ kJ$

$- \quad - \quad - \quad - \quad +$

$Fe_2O_3 + CO - 2FeO \longrightarrow CO_2 \quad \Delta H = (-26+32)\ kJ$

$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2 \quad \Delta H = 6\ kJ$

is the required answer #.

Qn) The bond dissociation energy of $H_2(g)$ and $Cl_2(g)$ are 435 kJ/mol and 243 kJ/mol respectively. The enthalpy of formation of $HCl(g) = -92$ kJ/mol. calculate the bond dissociation energy of $HCl(g)$.

A. Enthalpy of formation of HCl is

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H = -92 \text{ kJ/mol}$$

Given B.E of $H_2(g) = 435$ kJ/mol

BE of $Cl_2(g) = 243$ kJ/mole

Then we have,

$$\Delta H = \frac{1}{2} \text{BE of } H_2(g) + \frac{1}{2} \text{BE of } Cl_2(g) - \text{BE of } HCl$$

or, $-92 = \frac{1}{2} \times 435 + \frac{1}{2} \times 243 - \text{BE of } HCl$

or, BE of $HCl = 217.5 + 121.5 + 92$

$= 431 \text{ kJ mol}^{-1}$ ans.

Qn) State enthalpy of combustion. If heat of formation of CO_2, H_2O and $C_6H_{12}O_6$ are -395 kJ mole^{-1}, -269.4 kJ mol^{-1} and -1109 kJ mol^{-1} respectively calculate heat of combustion of glucose.

A. Ethalpy of combustion is change in enthalpy when 1 mole of substance is completly burnt. It is exothermic.

Glucose is combusted as

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

$\Delta H = ?$

Given that

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -395\ kJ\ mol^{-1}$ ——①

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H = -269.4\ kJ\ mol^{-1}$ ——②

$6C_{(s)} + 6H_{2(g)} + 3O_{2(g)} \longrightarrow C_6H_{12}O_{6(s)}$ $\Delta H = -1169\ kJ\ mol^{-1}$ ——③

Required eqn:

$C_6H_{12}O_{6(s)} \xrightarrow{+6O_{2(g)}} 6CO_{2(g)} + 6H_2O_{(l)}$ $\Delta H = ?$

6 × eqn ① + 6 × eqn ② − eqn ③ we get

$6C_{(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)}$ $\Delta H = -2370\ kJ\ mol^{-1}$

$6H_{2(g)} + 3O_{2(g)} \longrightarrow 6H_2O_{(l)}$ $\Delta H = -1616.64\ kJ\ mol^{-1}$

$6C_{(s)} + 6H_{2(g)} + 3O_{2(g)} \longrightarrow C_6H_{12}O_{6(s)}$ $\Delta H = -1169$

(−)   (−)   (−)   (−)   (+) kJ/M

$6O_{2(g)} \longrightarrow 6CO_2 + 6H_2O - C_6H_{12}O_{6(s)}$

$\Delta H = -2817.64\ kJ\ mol^{-1}$

or $C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(l)}$

$\Delta H = -2817.64\ kJ\ mol^{-1}$

Bond dissociation energy :-

↳ It is the energy required to break the bond in one mole of gaseous covalent compound to form the product in gaseous state.

Eg:- $H_2(g) \longrightarrow 2H(g) \quad \Delta H = +104$ Kcal

[Bond energy of H_2]

The enthalpy change is calculated as :-

NOTE

$\Delta H = H_{prod} - H_{react}$

= Heat of formation of (product − reactant)

= BE of reactant − BE of product.

Spontaneous process (Feasible process)

↳ The process which occurs on its own without the aid of any external agency is called spontaneous process.

↳ All natural process are spontaneous

Eg: Rusting of iron, melting of ice etc.

Decrease in energy and Spontaneity of process

↳ Spontaneity occurs either due to increse in energy like vaporization of water or due to decrease in energy like ~~melt~~ freezing of water. Hence energy or enthalpy is not the sole crieteria for the spontaneity of process.

↳ Spontaneous process may need some external energy to start the process.

* The spontaneity is due to following two ~~proc~~ tendencies (Imp)

↳ Tendency of a system to acquire a state of minimum energy that corresponds to maximum stablity. ✓

↳ Tendency of a system to acquire a state of maximum randomness. ✓

Entropy (S)

↳ All spontaneous process are characterized by increase in randomness or disorder of the system. To deal with this phenomena a new term entropy is introduced.

↳ It is the measure of degree of randomness

↳ It is state function.

↳ It is extensive property.

↳ It's absolute value can be determined using third law of thermodynamics.

↳ It explains the 2nd law of thermodynamics mathematically

$$S = \frac{q_{rev}}{T} = \frac{\text{heat exchange in reversible process}}{\text{absolute temp.}}$$

↳ It's SI unit is J/K.

$$\Delta S = S_2 - S_1$$

$$= \text{Final entropy} - \text{Initial entropy}$$

$$= S_{product} - S_{reactant}.$$

\# Molar entropy :- (Imp)

↳ measure of degree of randomness of 1 mole of an substance.

↳ SI unit J/K mol

physical significance.

↳ $S_{gas} >> S_{liq} > S_{solid}$.

i.e. The most random state is the gaseous state.

For the rxn

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

ΔS is +ve ore −ve?

⇒ since ΔS = $S_{product} - S_{reactant}$.

and product cointains 2 species CaO and CO_2 and CO_2 is gaseous state and gaseous state is most random state so $\Sigma_{pro} > \Sigma_R$

so ΔS will be +ve.

Entropy change and its calculation.

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$

Entropy change, $\Delta S = S_{product} - S_{reactant}$

For, $aA + bB \longrightarrow cC + dD$

$\Delta S = c \times S(C) + d \times S(D) - \{a \times S(A) + b \times S(B)\}$

$= \Sigma S(product) - \Sigma S(reactant)$

NOTE :-

For an Isolated system

$\Delta S_{system} > 0$:- Spontaneous

$\Delta S_{system} < 0$:- non-Spontaneous

$\Delta S_{system} = 0$:- Equilibrium

For open system

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

- It is not measurable in all cases since it is beyond imagination.

$\Delta S_{tot} > 0$: Spontaneous
" < 0 : non- "
$= 0$: Eqbr^n

- Since Entropy tells us about spontanity but it is not ~~only~~ possible to measure in all cases so to express spontanity new term is expressed called GiFF'S Free Energy.
- It measures the available energy to do useful work.
- Mathmatically,

$$\underbrace{G}_{\text{useful work.}} = \underbrace{H}_{\text{supplied Energy}} - \underbrace{TS}_{\text{unavailable Energy}}$$

- It is State Function & Extensive property.
- $\Delta G = G_2 - G_1$

$$\begin{tikzcd} \boxed{\begin{matrix} H_1 \\ S_1 \end{matrix}} \arrow[r, "\text{At constant}", "\text{tempeature}"'] & \boxed{\begin{matrix} H_2 \\ S_2 \end{matrix}} \end{tikzcd}$$

$$\begin{aligned} \Delta G &= (H_2 - TS_2) - (H_1 - TS_1) \\ &= (H_2 - H_1) - TS_2 + TS_1 \\ &= \Delta H - T(S_2 - S_1) \end{aligned}$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

Relationship btn ΔG and ΔS total :-

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

$$= \Delta S_{system} + \frac{\Delta H_{surrounding}}{T}$$

or $T\Delta S_{total} = T\Delta S_{system} - \Delta H_{system}$

$[\Delta H_{surrounding} = -\Delta H_{system}]$

or, $T\Delta S_{total} = (T\Delta S - \Delta H)_{system}$

or, $T\Delta S_{total} = -(\Delta H - T\Delta S)_{system}$

or, $T\Delta S_{total} = -\Delta G$

or $\Delta G = -T\Delta S_{total}$ Lt

NOTE :-

$\Delta S_{total} = +ve$, $\Delta G = -ve$:- Spontaneous

$\Delta S_{total} = -ve$, $\Delta G = +ve$:- non-spontaneous

$\Delta S_{total} = 0$, $\Delta G = 0$:- Equilibrium.

↳ Difficult to calculate ↳ Easy

Qn) Melting of Ice above 0°c takes place spontaneously. Justify this statement

↳ $$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

$$= \frac{\Delta H_{system}}{T_{system}} + \frac{\Delta H_{surrounding}}{T_{surrounding}}$$

$$= \frac{\Delta H_{system}}{T_{system}} - \frac{\Delta H_{system}}{T_{surrounding}}$$

$\because T_{surrounding} > T_{system}$

$\therefore \Delta S_{total} = +ve$

i.e the process is spontaneous.

NOTE :-

ΔG should be -ve to process be spontaneous.

$$\Delta G = \Delta H - T\Delta S$$

W.IMP

S.N	ΔH	ΔS	Tempr	ΔG	Nature.
1)	-ve (Exothermic)	a) +ve	a) at all temp^r	-ve	Spontaneous
		b) -ve	a) at low temp^r	-ve	spontaneous
			b) at high tempr	+ve	Non spontaneous
2)	+ve Endothermic	a) +ve	a) at low	-ve	spontaneous
			b) at high	+ve	Non-spontaneous
		b) -ve	at all tempr	+ve	non spontaneous

Relation Between ΔG and W_{useful} or W_{net}

Imp

From 1st law, we have

$$\Delta q = E + W_{total}$$

$$\Delta q = \underbrace{E + P\Delta V} + W_{useful}$$

$$\Delta q = \Delta H + W_{useful}$$

$$\left[\begin{array}{l} \Delta S = \frac{q}{T} \\ q = T\Delta S \end{array}\right]$$

$$T\Delta S = \Delta H + W_{useful}$$

$$W_{useful} = T\Delta S - \Delta H$$

$$W_{useful} = -(\Delta H - T\Delta S)$$

$$W_{useful} = -\Delta G$$

i.e. decrease in Giff's Free Energy is measure of useful workdone.

For a Electrochemical cell

$$\Delta G = -nFE \qquad \left[\begin{aligned} W &= qE \\ &= nFE \end{aligned} \right]$$

$$\begin{aligned} \Delta G &= -\text{useful workdone} \\ &= -(W) \\ &= -(qE) \\ &= -(nFE) \end{aligned}$$

Note :-

$$\left\{ \begin{aligned} &E^\circ_{cell} :- +ve :- \text{Spontaneous} \\ &E^\circ_{cell} :- -ve :- \text{non-spontaneous} \end{aligned} \right\}$$

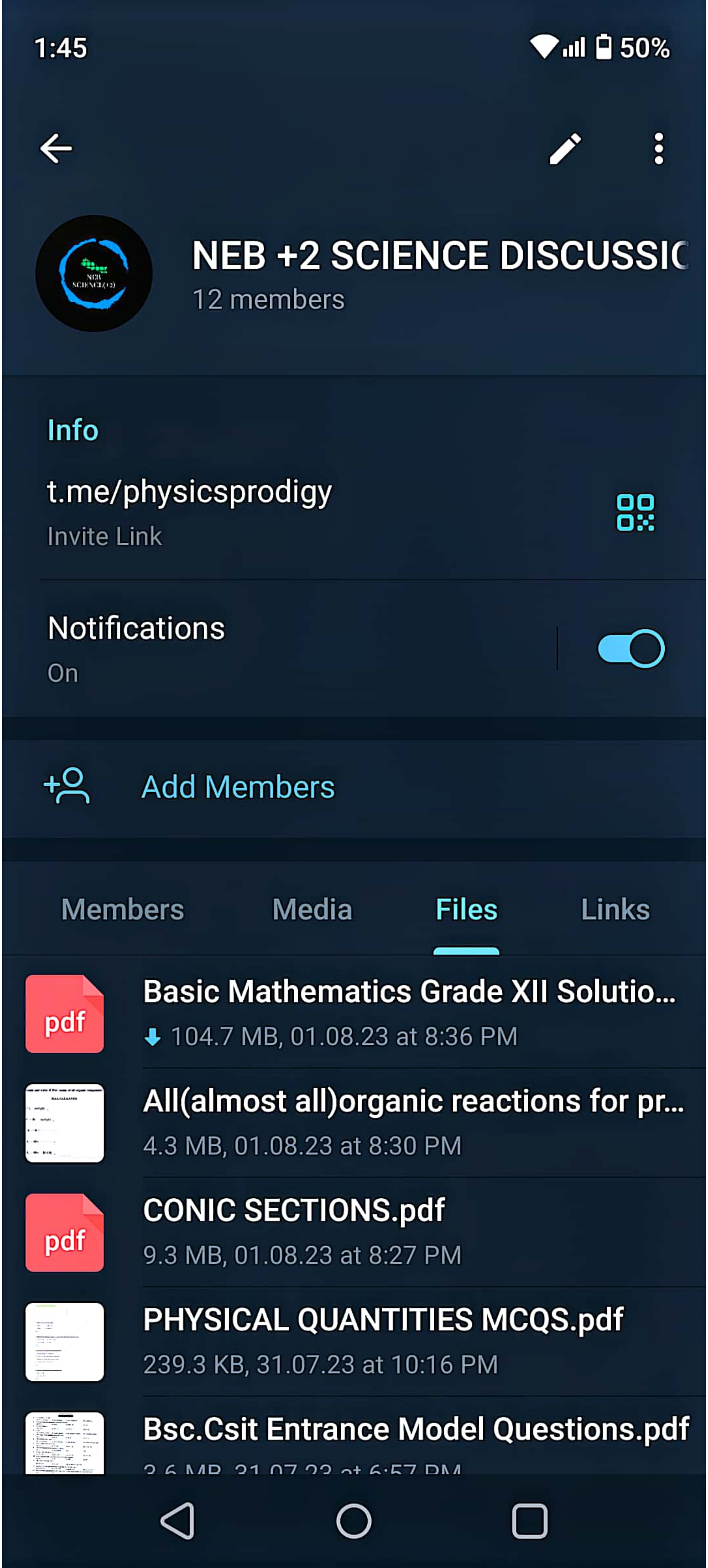
For Electrochemistry :- Remember !!!

Rxn लिखो ध अने ध्यसैवाट Anode र cathode इंदाउने || [change in oxidation state hereafter]

नत्ता मत्ता Given value वाद इंदाउने !!

Relation between ΔG and K equllibrium.

$$\boxed{\Delta G = -RT \ln (K_{eq})}$$



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