

Thermodynamics

Thermo \rightarrow heat & dynamics \rightarrow motion

- ∴ Thermodynamics means motion of heat i.e. flow of heat
 - \rightarrow deals \bar{c} relationship b/w heat & work.
 - \rightarrow It deals \bar{c} the interconversion of one kind of energy such as heat energy, electrical energy etc into another.
 - \rightarrow predicts whether the rxn is spontaneous or non-spontaneous
 - \rightarrow does not tell how fast rxn can proceed by but can tell whether rxn can take place or not.
 - \rightarrow Deals \bar{c} four fundamental law.
- [
- Zeroth law \rightarrow deals \bar{c} thermal equilibrium among the systems which are in physical contact
 - First law \rightarrow deals \bar{c} conservation of energy i.e. conversion of heat energy to other form of energy.
It introduces internal energy & enthalpy.
 - Second law: tells whether particular process is feasible or not i.e. no heat can flow from a body of lower temp. to a body of higher temp. without the involvement of external energy in some form.
It introduces free energy, entropy & spontaneity.
 - Third law: provides a basis for the calculation of some imp. thermodynamic parameters viz., entropy]

General Terms:

System \rightarrow part of universe under investigation

Surrounding - remaining part of universe, other than system

Isolated system: system which can't exchange both matter & energy w/ its surroundings.

Closed system: system which, can exchange energy but not matter w/ its surroundings.

Open system: system which can exchange energy & matter w/ its surroundings.

Homogeneous: uniform system throughout

Heterogeneous: Not uniform throughout.

Isothermal process: process in which the temp. remains constant
 $dT = 0$

Adiabatic process: $dq = 0$, no heat can flow from into or out of the system

Isobaric process: Process which take place at const. pressure
 $dP = 0$

Isochoric process: $dV = 0$, process which take place at constant volume.

Intensive properties: properties which do not depend on the amt of the substance but depend only on the nature of substance present in the system
e.g. Temp, Press, Concⁿ, density.

Extensive properties: depend on the amt of substance in the system
e.g. Mass, Vol., Entropy, enthalpy,
(S) (H)
Internal energy (E) & free energy (G)

State of a system: Solid, liquid, Gas

Internal energy: denoted by U or E

A substance is associated with different types of energies such as Vibⁿ energy (E_v), rotⁿ energy (E_r), transitional energy (E_t), electronic energy (E_e) etc.

Actually I.E is the sum of all the possible types of energies associated with the molecule of the given system

$$E = \sum \text{all energy}$$

$$\therefore E = E_v + E_r + E_t + E_e \dots$$

The abs. value of I.E of a substance can not be determined exactly bcs it is not possible to determine exact value of various energy. But the change in I.E (ΔE) can be measured; basically ΔE depends upon on the initial & final states of the system & not on the intermediate states.

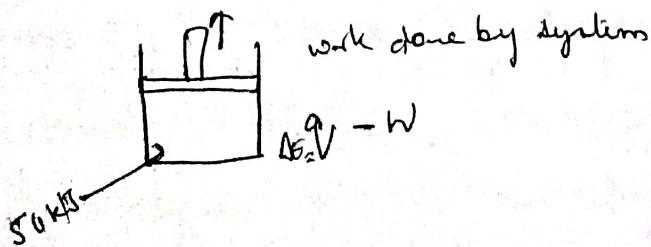
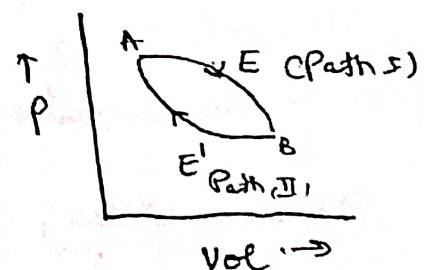
$$\therefore \Delta E = E_{\text{final state}} - E_{\text{initial state}}$$

For Chemical Rxn:

$$\Delta E = E_{\text{product}} - E_{\text{reactants}}$$

$$\Delta E = E_p - E_{R.}$$

$$\boxed{\begin{aligned} \Delta E &= A - B \text{ for Path I} \\ \Delta E' &= B - A \text{ for Path II} \end{aligned}}$$



ENTHALPY : denoted by H
heat content of a system

→ defined as the "total heat content of a system at const. pressure is equivalent to the sum of internal energy E & PV ".

Mathematically,
$$H = E + PV$$

As internal energy, enthalpy also can not be measured, but change in enthalpy (ΔH) can be measured from the diff. in the enthalpy of initial & final state of the system.

$$\Delta H = H_f - H_i$$

for Chem. Ran. $\Delta H = H_p - H_R$

or
$$\Delta H = \Delta E - P \cdot \Delta V$$

Enthalpy Change in Rns

Let $A + B \rightarrow C + D$, As we know

$$\Delta H = \sum H_p - \sum H_R$$

Two cases $\Rightarrow \sum H_p < \sum H_R$

$\therefore \Delta H = +ve$

$$\sum H_R > \sum H_p$$

$$\Delta H = -ve$$

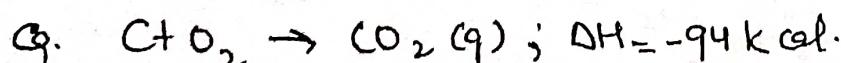
proceed via absorption of heat energy ↓

endothermic rxn.



proceed via evolution of heat energy ↓

exothermic rxn.



Heat of Rxn :

→ when Chem. Rxn carried at const vol; ($\Delta V=0$)

$$\downarrow$$

then Heat of Rxn = ΔE (change in int. energy)

→ If Chem. Rxn carried at const Pressure

$$\left\{ \begin{array}{l} \Delta H = \Delta E + P \cdot \Delta V \\ \Delta H = \Delta E \end{array} \right.$$

then Heat of Rxn = ΔH (change in enthalpy)

first Law of Thermody: → Energy can never be created nor destroyed, but converted from one form to another.

Limitations: → unable to explain why it is not possible to convert heat energy completely into equivalent amt of work.

→ unable to predict feasibility of a process in a particular dir^n.

→ unable to explain whether a gas can diffuse from low pressure to high pressure or water itself can flow uphill.

Second Law of Thermody: Explains the spontaneity or feasibility of phys. & chemical processes.

→ Introduces two new thermody. functions entropy & free energy

Entropy (S): is a measure of degree of disorder or randomness in a mol. structure. It is also defined as the "measure of unusable energy".

When system goes from a more orderly to less orderly state, randomness ↑'s & hence entropy also ↑'s.

eg. solid → liquid	entropy ↑'s	$\Delta S > 0$ sys + ΔS_{un}
solidification	entropy ↓'s	$\Delta S > 0$ spontaneous
ice melted	entropy ↑'s	$\Delta S < 0$ non-sp.
		$\Delta S = 0$ equilibrium

$$\Delta G = \frac{q_{rev}}{T}$$

Significance of entropy: (indicate heat if ^{reversible} _{slowly})

i) Entropy & Unavailable energy: When heat is supplied to the system, some portion of this heat is used to do some work, which is known as available energy. The remaining portion of heat is left as unavailable energy.

∴ Second law of thermodynamics states that the entropy is a measure of unavailable energy ∴

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temp}}$$

(ii) Entropy & Randomness: → measure of randomness in a system. ↑ in entropy means change from an orderly state to disordered state. for eg. all natural processes are spontaneous process.

Spontaneous process: A rxn that does occur of its own under a given set of cond's. is a spontaneous rxn.

e.g.; water freezes automatically below 0°C & melts above 0°C

No one by force makes this happen.

→ Heat flows from hot end of metal rod to the cold end spontaneously by ~~but~~

→ A gas let out, diffuses air to atm. spontaneously, but never the opposite

→ Corrosion of iron into rust

All rxns are unidirectional and spontaneous in nature.

③

Spontaneous process can be chemical or physical
 $\Delta G = \Delta H - T\Delta S$ if $\Delta G = -ve \rightarrow$ Spontaneous
 $\Delta G = +ve \rightarrow$ non-spont

FREE ENERGY: In order to express the spontaneity of process more directly, free energy has been introduced. As we know, from 2nd law of thermodynamics that total energy is not completely converted into work & a part of it used to increase the randomness, which is the unavailable part of energy.

The energy converted into work is termed as available energy to do useful work is precisely known as "free energy". There are two free energy functions

(1) Helmholtz free function (2) Gibbs free energy function.

\downarrow
work function

\downarrow
net work.

As we know, that

Total energy = Isothermally + Isothermally available energy unavailable energy
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And entropy is a measure of unavailable energy per unit temp.

\therefore when entropy is multiplied by T, the product (TS) gives amt of unavailable energy, which cannot be converted into work.

then out of total energy heat absorbed by a system (q), -ve

amt less by TS will give the unavailable amt of heat which can be converted into useful work.

\therefore Useful work = Heat absorbed - Unavailable energy

$$X = q - TS$$

when heat is absorbed at const. Vol V, then q is replaced by E & when heat is absorbed at const. Pressure P, then q \leftarrow \leftarrow \leftarrow H

\therefore X will be given as $E - TS$ & $H - TS$ depending upon exp "Const"; To describe these two forms of energy terms.

$$\Delta = E - TS$$

$$\Delta' = H - TS$$

where A = Isothermally available internal energy
 ΔA or A is called Helmholtz free energy work function

ΔB = Isothermally available enthalpy ΔB or B is Gibbs free energy.

Significance of work function (A)

The work function is given by

$$A = E - TS \quad \text{--- (1)}$$

For a small change in a reversible system at const. temp.,

$$\Delta A = \Delta E - T \cdot \Delta S \quad \text{--- (2)}$$

But entropy change ΔS is given by

$$\Delta S = \frac{q_{rev}}{T}$$

$$\therefore q_{rev} = T \cdot \Delta S \quad \text{--- (3)}$$

Eq (2) becomes

$$\Delta A = \Delta E - q_{rev} \quad \text{--- (4)}$$

Acc. to first law of thermodynamics $q = \text{heat absorbed} - \text{work done}$

$$\Delta E = q - w$$

$$\text{or } -w = \Delta E - q \quad \text{--- (5)}$$

\therefore Eq (4) becomes -

$$\Delta A = -w \quad \text{or} \quad \boxed{\Delta A = -w_{\text{non}}} \quad \text{--- (6)}$$

Eq 6 defines that decrease in work function during the process at const. temp. ^{& const volume} gives a max. work obtained from the system.

Significance of Gibb's free energy (G)

Free energy or Gibb's free energy is the total energy present in a reversible system at const. T & P as useful work. It is given by

$$G = H - TS \quad \text{--- (1)}$$

For small change in rev. procs system at const T.

$$\boxed{\Delta G = \Delta H - T \cdot \Delta S} \quad \text{--- (2)}$$

We know enthalpy change $\Delta H = \Delta E + P \cdot \Delta V \quad \text{--- (3)}$

∴ Eq (2) becomes →

$$\Delta G = \Delta E + P \cdot \Delta V - T \cdot \Delta S$$

$$\text{or } \Delta G = (\Delta E - T \cdot \Delta S) + P \cdot \Delta V$$

$$\Delta G = \Delta A + P \cdot \Delta V$$

$$\left\{ \text{As } \Delta A = \Delta E - T \cdot \Delta S \right\}$$

$$\therefore \Delta G = -W_{\max} + P \cdot \Delta V$$

$$\left\{ \because \Delta A = -W_{\max} \right\}$$

$$\text{or } -\Delta G = W_{\max} - P \cdot \Delta V \quad \text{--- (4)}$$

Here W_{\max} = Maximum work that is obtol from the system

2 $P \cdot \Delta V$ = work done by expansion or work wasted against the confining pressure.

$$\therefore W_{\text{useful}} = W_{\max} - P \cdot \Delta V \quad \text{--- (5)}$$

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

∴ Decrease in free energy is equal to useful work obtol from a rev. procn. at const T & P.

free energy & spontaneity:

$$\text{As we know } \Delta G = \Delta H - T \cdot \Delta S$$

For all natural process or spontaneous rxn's $\Delta S = +ve$

if ΔS is very high such that $\Delta H < T \cdot \Delta S$

\downarrow
 ΔG will be $-ve$.

\downarrow
 Rxn is spontaneous in forward dir?

if $\Delta G_r = -ve \rightarrow$ proc is spontaneous

$\Delta G_r = 0 \rightarrow$ proc in equilibrium

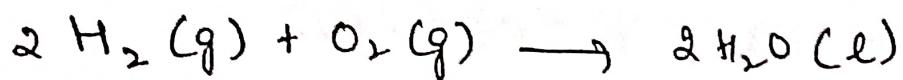
$\Delta G_r = +ve \rightarrow$ proc non-spontaneous

In terms of Entropy, enthalpy & free energy change terms:

<u>ΔH</u>	<u>ΔS</u>	<u>$\Delta G_r = \Delta H - T \Delta S$</u>	<u>Conclusion</u>
- (Exothermic)	+	-	spontaneous
- (Exothermic)	-	- (at low Temp) + (at high Temp)	spontaneous Non-spontaneous
+ (endothermic)	+	+ (at low temp) - (high Temp)	non-spontaneous spontaneous
+ (endothermic)	-	+ (at high temp)	Non-spontaneous

Explain how Gibb's free energy for water form is determined?

Let us look the rxn of water form



The Gibb's free energy relates the spontaneity of various rxn's by looking at the change in enthalpy, entropy & temp.

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$$

from the rxn, it is clear it is exothermic rxn.
Bonds are being formed as hydrogen gas & Oxygen gas form water. Moles of gas is decreasing and liquid is formed
so entropy is also decreases.

As formation of H_2O is spontaneous process \rightarrow so ΔG must be -ve.

\therefore Rxn must be run at temp, where ~~that~~ where the diff. of enthalpy & product's entropy & temp must be < 0

$$\Delta H^\circ - T \cdot \Delta S^\circ < 0$$

\rightarrow Gibb's free energy is a state function, so.

$$\Delta G^\circ = \sum_{\text{rxn}} \Delta G^\circ_{\text{product}} - \sum_{\text{reactants}} \Delta G^\circ_{\text{reactants}}$$

Both H_2 & O_2 gas are in std state, \therefore ~~Gibb's~~ Gibb's free energy is 0.

& from Std thermody. data at 25°C $\text{H}_2\text{O(l)}$ has gibb's free energy of $-237.13 \text{ kJ mol}^{-1}$

$$\therefore \Delta G^\circ_{\text{rxn}} = -237.13 - 0 = -237.13 \text{ kJ mol}^{-1}$$

Gibb's Helmholtz Equation :

→ Helps to determine the value of ΔG at any temp -

As we know

$$G = H - TS \quad \& \quad H = E + PV$$

Gibb's free energy

$$\therefore G = E + PV - TS$$

Enthalpy

for infinitesimal change,

$$dG = dE + PdV + VdP - TdS - SdT \quad \text{--- (2)}$$

According to first law of Thermodynamics -

$$E = q - w \quad \text{or} \quad E = q - PV$$

$$\text{or } dE = dq - PdV$$

--- (3)

and from entropy concept ..

$$\Delta S = \frac{q_{rev}}{T}$$

$$\text{or } dS = \frac{dq_{rev}}{T} \quad \text{or} \quad dq_{rev} = T \cdot dS \quad \text{--- (4)}$$

Substitute (3 & 4) in eq (2) -

$$dG = dq_{rev} - PdV + PdV + VdP - dq_{rev} - SdT$$

$$\therefore dG = VdP - SdT \quad \text{--- (5)}$$

At const Pressure $dP=0$, eq becomes,

$$(dG)_P = - SdT \quad \text{--- (6)}$$

$$\left(\frac{\partial G}{\partial T} \right)_P = - S \quad \text{--- (7)}$$

~~Gibb's Helmholtz eqⁿ~~:

→ Helps to determine value of ΔG at any temp.

as we know $\Delta G = \Delta H + T \cdot \Delta S$

and $\Delta H = \Delta E + P \cdot \Delta V$

Substitute (7) in $G = H - TS$, we get

$$G = H + T \left(\frac{\partial G}{\partial T} \right)_P$$

or $\boxed{G - T \left(\frac{\partial G}{\partial T} \right)_P = H}$ — (8)

This is one form of Gibb's Helmholtz eqⁿ.

for any two states of the system the eq (8) becomes

if $dG_1 = -S_1 dT$ (Initial state)

$$dG_2 = -S_2 dT \quad (\text{Final state})$$

To get the change

$$dG_2 - dG_1 = -S_2 dT - (-S_1 dT)$$

$$d\Delta G = -\Delta S dT \quad — (9a)$$

$$\therefore \left(\frac{d\Delta G}{dT} \right)_P = -\Delta S \quad — (9b)$$

But acc to def. of free energy.

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

$$\text{or } -\Delta S = \frac{\Delta G - \Delta H}{T} \quad — (10)$$

Substitute in (9b), we get -

$$\frac{\Delta G - \Delta H}{T} = \left[\frac{\partial \Delta G}{\partial T} \right]_P$$

or $\Delta G - \Delta H = T \left(\frac{\partial \Delta G}{\partial T} \right)_P$

or $\therefore \Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_P$

— (11)

Similarly

$$\Delta A = \Delta E + T \left(\frac{\partial \Delta A}{\partial T} \right)_V$$

may be derived
— (12)

(11) & (12) are the alternative forms of Gibbs-Helmholtz eqn.

Another alternative form of Gibbs-Helmholtz eqn can be obtld by making some changes in (11) & (12) -

From eq (11) - $\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_P$

divide both sides by $(\frac{1}{T^2})$ - we get

$$-\frac{\Delta G}{T^2} = -\frac{\Delta H}{T^2} - \frac{1}{T} \left(\frac{\partial \Delta G}{\partial T} \right)_P$$

or $-\frac{\Delta G}{T^2} + \frac{1}{T} \left(\frac{\partial \Delta G}{\partial T} \right)_P = -\frac{\Delta H}{T^2}$ — (13)

Putting $\frac{\partial}{\partial T} \left(\frac{1}{T} \right) = -\frac{1}{T^2}$ in (13) -

$$\Delta G \left[\frac{\partial}{\partial T} \left(\frac{1}{T} \right) \right]_P + \frac{1}{T} \left(\frac{\partial \Delta G}{\partial T} \right)_P = -\frac{\Delta H}{T^2}$$

Note $\frac{\partial}{\partial T} \frac{1}{T} = -\frac{1}{T^2}$

$\therefore dx^n = nx^{n-1}$

i. The above eqn is in the form
 $udv + vdu$ which is $d(uv)$

$\therefore \left[\frac{\partial}{\partial T} \left(\frac{\Delta G}{T} \right) \right]_P = -\frac{\Delta H}{T^2}$ — (14)

Similarly,

$$\left[\frac{\partial}{\partial T} \left(\frac{\Delta A}{T} \right) \right]_V = - \frac{\Delta E}{T^2} \quad \rightarrow (15)$$

Applications of Gibbs's Helmholtz eqn:

(1) Calculation of Enthalphy change for cell & Galvanic cell

If a cell yields nF coulombs of electricity in a reversible manner, it must be equal to the decrease in the free energy, then -

$$-\Delta G = nFE$$

where n = No. of e⁻s involved in process

F = Faraday constant = 96500 coulombs

E = Energy in volts

According to Gibbs's Helmholtz eqn -

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_P$$

$$\text{or } -nFE = \Delta H + T \left[\frac{\partial (-nFE)}{\partial T} \right]_P$$

$$\text{or } -nFE = \Delta H - nFT \left(\frac{\partial E}{\partial T} \right)_P \quad \rightarrow (16)$$

divide both side by $-nF$, we get -

$$\text{or } E = -\frac{\Delta H}{nF} + T \left(\frac{\partial E}{\partial T} \right)_P \quad \rightarrow (17)$$

$$\text{or } \Delta H = -nF \left[E - T \left(\frac{\partial E}{\partial T} \right)_P \right] \quad \rightarrow (18)$$

② Calculation of EMF of the cell:

Eq (6) helps in calculating EMF of the cell -

$$E = \frac{-\Delta H}{nF} + T \left(\frac{\partial E}{\partial T} \right)_P$$

③ Calculation of Entropy change (ΔS):

As we know $\Delta G = \Delta H - T\Delta S$. ~~see~~ (Q)

$$\text{from eq (16)} \quad -nFE = \Delta H - nFT \left(\frac{\partial E}{\partial T} \right)_P \quad \rightarrow (16)$$

we ~~already~~ know

$$\Delta G = -nFE$$

on comparing (a) & (b) we get

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

where $\left(\frac{\partial E}{\partial T}\right)_p$ is the temp. coefficient of emf of the cell.