Unit 4 Thermodynamics

The flow of heat from one system to another.

System
Surrounding
Boundary
Application
Work function
Internal Energy

Derivation of work function
Derivation of Gibbs
Derivation of Gibbs Helmholtz

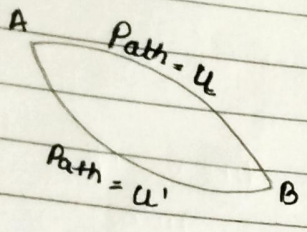
Application of thermodynamics:

1) It is applicable to vast number of molecule
2) It is applicable only to the macroscopic object not to microscopic.

S U V At Grassmant & Pallavi's House

S → Entropy
U → Internal Energy
V → volume
A → work function
G → Gibbs
P → Pressure
H → Enthalpy

Internal Energy : Energy required to complete a cycle.



Derivation of Work function / ~~and~~ Δ A

* It is the sum total of system & surrounding

$\therefore$ [Δ system + Δ surrounding]

* If it is feasible (or spontaneous when Δs is in the +ve) sign
* If Δs is in the zero then it attain the chemical equilibrium
* If we want to decide the Energy transferred from one system to the other, two parameters are needed

$$A = U - TS \quad -①$$
$$G = H - TS \quad -②$$

U, S & H → these are the three state functions which depends on temp, pressure & volume.

A & G also depends on the state of the system

$\therefore$ eq ① & ② are at initial & final stage at two temperatures are

$$A_1 = U_1 - TS_1 \quad -(3)$$
$$A_2 = U_2 - TS_2 \quad -(4)$$

Subtract the eq NO. (3) from eq. NO. (4)

$$A_2 - A_1 = U_2 - U_1 - T(S_2 - S_1)$$

$$\boxed{\Delta A = \Delta U - T\Delta S} \quad -(5)$$

But the heat absorbed by the system is given by the relation

$$\boxed{\Delta S = \frac{q_{reversable}}{T}} \quad -(6)$$

$$\boxed{T\Delta S = q_{rev}} \quad -(7)$$

sub the eq. NO. (7) in eq. no. (5)

$$\boxed{\begin{aligned} \Delta A &= \Delta U - T\Delta S \\ \Delta A &= \Delta U - q_{rev} \end{aligned}} \rightarrow (8)$$

$$\boxed{\Delta U = q_{rev} - W_{max}} \quad -(9)$$ Ist law of thermal

$$\Delta A = (q_{rev} - W_{max}) - q_{rev}$$

$$\Delta A = - W_{max}$$

$$W_{max} = - \Delta A$$

the work function deri vation feasible at Negative value.

* Gibbs free energy Derivation
* Gribbs Helmholtz derivation

$\Delta A = \Delta U - T\Delta S$
$\Delta G = \Delta H - T\Delta S$
$\Delta H = \Delta U + P\Delta V$
Remeber

Gibbs Derivation of the Free Energy derivation

* Derived in the yeaar of (1821 - 1994) by the scientist Gibbs Helmholtz Von
* German physicast who's contributed his idea in the thermodynamic optics and acheustics
* G, H, S three thermodynamics function to solve the Gibbs free Energy.

Let us consider for the initial stage of the system.

$$G = H - TS$$

initial stage $\therefore$ $\boxed{G_1 = H_1 - TS_1}$ — (1)

Simil. FOR the final stage : $\boxed{G_2 = H_2 - TS_2}$ — (2)

Subtract the eq no. (1) from eq no. (2)

$$G_2 = H_2 - TS_2$$
$$G_1 = H_1 - TS_1$$

$$(G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1)$$

$$\boxed{\Delta G = \Delta H - T\Delta S} \quad — (3)$$

at constant temp the ΔH is related to the equation

$$\boxed{\Delta H = \Delta U + P\Delta V} \quad — (4)$$

Substitute eq. (4) in eq (3)

$$\therefore \boxed{\Delta G = \Delta U + P\Delta V - T\Delta S} \quad — (5)$$

As we know that the Internal energy is related by the equation $\boxed{\Delta A = \Delta U - T\Delta S}$

$\therefore$ $\boxed{\Delta U = \Delta A + T\Delta S}$ - (6)

Substitute eq no (6) in eq. no (5)

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$
$$\Delta G = \Delta A + T\Delta S + P\Delta V - T\Delta S$$
$$\Delta G = \Delta A + P\Delta V$$

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

$$-\Delta G = W_{max} + (-P\Delta V)$$

$$\boxed{-\Delta G = (work)_{(max)} - P\Delta V}$$ Gibbs equation

Gibbs - Helmholtz Derivation

* Let G_1 be the initial stage of the gibbs function at temperature T

* Suppose if the temp. rises then it is given by $(T + dT)$ where dT is always infinitesimally small.

* Let $\boxed{G_1 + dG_1}$ is the new system for the free energy in a closed vessel at initial stage then the final stage of the new function is given by $\boxed{G_2 + dG_2}$ at ~~constant~~ temp. T the pressure remains constant, thus the equation becomes $dG_1 = -S_1\,dT$ - (1) and

$$dG_2 = -S_2\,dT \quad -(2)$$

subtract the above eq.

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

$$\therefore \boxed{\Delta G = -\Delta S\,dT} \quad -(3)$$

Differentiate the eq no. (3) with respect to temp at a constant Pressure

$$\boxed{\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\Delta S} \quad -(4)$$

$$\boxed{\Delta G = \Delta H - T\Delta S} \quad -(5)$$

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

$$\frac{\Delta G - \Delta H}{-T} = \Delta S \longrightarrow \text{eq } (6)$$

Substitute $-\Delta S$ factor in eq (4)

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

Gibbs - Helmholtz equation