THERMODYNAMICS - I

1) Extensive property (Mass dependent):

V, Q, W, Internal energy (E), Enthalphy (H), Entropy (S), Gibbs free energy (G), Helmontz Free Energy or Work function (A), Mass

2) Intensive property (Mass independent):

P, T, (C_p & C_v), Density or concentration (c), n.i (n), Dipole moment (μ), Molar enthalphy ($\bar{H}$), molar internal energy ($\bar{E}$), molar energy ($\bar{G}$), chemical pot^{n} ($\bar{\mu}$).

3) Path function: (Depend upon path)

Heat energy (Q), Work (W)

4) State function: (does not depend upon path, dependent upon state)

Internal Energy (E), H, S, free energy (G)

5) Cyclic Rule:

$$\left(\frac{dz}{dx}\right)_y \left(\frac{dx}{dy}\right)_z \left(\frac{dy}{dz}\right)_x = -1$$

6) Condition of Perfect differential (Eular's Reciprocity Relation):

$$\frac{d^2z}{dx\,dy} = \frac{d^2z}{dy\,dx}$$

7) Zeroth law of thermodynamics:

If two systems are separately in thermal equilibrium with its third system, then ofcourse there must be a thermal equilibrium between the first two.

If $T_A = T_C$ & $T_B = T_C$, then $T_A = T_B$

8) First law of Thermodynamics :

Energy cannot be created nor destroyed, only transformation of energy is possible.

$$q = \Delta E + P.\Delta V \quad \text{---(I)} \quad \text{(Integrated form)}$$

$$dq = dE + P.dV \quad \text{---(II)} \quad \text{(Differential form)}$$

9) Heat & Work are inexact function. ← does not follow Eular's reciprocity

$$\frac{d^2q}{dT\,dp} \neq \frac{d^2q}{dp\,dT} \text{ : Heat} \quad , \quad \frac{d^2V}{dp\,dT} \neq \frac{d^2V}{dT\,dp} \text{ : Work}$$

* All state functions are exact function & follow Eular's Reciprocity

10) Enthalpy (H) or Heat content :

$$\boxed{H = E + PV}$$

For Isobaric changes (constant P), $\boxed{dH_p = dq_p}$

11) Heat is an inexact function but Heat change at constant pressure (dq_p) is an exact function.

12) Heat capacities (C_p & C_v) :

i) $C_p = n\bar{C}_p$ & $C_v = n.\bar{C}_v$ ← molar

ii) $$\bar{C}_p = \left(\frac{dq}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p = V(1-\alpha T)$$

$$\bar{C}_v = \left(\frac{dq}{dT}\right)_v = \left(\frac{dE}{dT}\right)_V$$

iii) For ideal gas, $\boxed{C_p - C_v = R}$

For Real gas, $\boxed{C_p - C_v = R\left[1 + \frac{2a}{R^2T^2}\right]}$

13) **Irreversible Work:**

Any spontaneous process which occurs suddenly. Since irreversible work occurs at once, it does not maintain thermodynamic equilibrium.

Natural processes are irreversible

$$W_{irr.} = \text{opposing force} \times \text{displacement}$$
$$= \text{opp. Pressure} \times \text{change in Volume}$$

i) **Isothermal Irreversible expansion:**

$$W_{irr.} = P_2 (V_2 - V_1)$$

ii) **Isothermal Irreversible compression:**

$$W_{irr}' = -P_1 (V_2 - V_1)$$

$\because P_1 > P_2$, (-)ve sign indicates work done upon the system by the surroundings.

iii) $|W_{irr}'| > |W_{irr}|$, i.e work for compression is much higher than that for expansion.

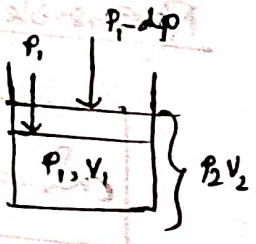
14) **Reversible Work:**

If a process is carried out slowly from one state to another in minute quantities & the whole change is done by infinite no. of stages & each stage maintain thermodynamic equilibrium, then the change is called reversible change.

These reversible change is practically impossible, it is purely a concept.

i) Total reversible work is the sum of work of each stages.

$$W_r = \int_{(P_1,V_1)}^{(P_2,V_2)} P \cdot dV = \int_{(P_1,V_1)}^{(P_2,V_2)} \frac{nRT}{V} \cdot dV$$



ii) Work for Isothermal Reversible expansion:

$$W_r = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

$\{ P_1V_1 = P_2V_2 \quad \frac{P_1}{P_2} = \frac{V_2}{V_1}$

iii) Work for Isothermal Reversible Compression

$$W_r' = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$$

(-)Ve Sign indicates Work done upon the system.

iv) Both W_r & W_r' are equal in magnitude but opposite in Sign. i.e., $|W_r| = |W_r'|$

15) Isothermal Irreversible Work for ideal gas:

$$W_{ir} = P_{opp.}(V_{final} - V_{initial})$$

$$W_{ir.} = P_2 \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$$

$$W_{ir} = nRT (1 - P_2/P_1)$$

16) Adiabatic Irreversible Work for Ideal gas,

$$W_{ir.} = P_2 \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$W_{ir.} = nR (T_2 - T_1 \cdot P_2/P_1)$$

17) Reversible Work is greater than irreversible Work.