7. Thermodynamics

- **First Law of Thermodynamcis :**

  $\Delta E = Q + W$

  Expression for pressure volume work

  $W = -P\Delta V$

  Maximum work in a reversible expansion :

  $$W = -2.303\ n\ RT \log \frac{V_2}{V_1} = -2.303\ nRT \log \frac{P_1}{P_2}$$

  $W_{rev} \geq W_{irr}$

- $q_v = c_v\Delta T = \Delta U$, $q_p = c_p\Delta T = \Delta H$

Enthalpy changes during phase transformation

i. Enthalpy of Fusion

ii. Heat of Vapourisation

iii. Heat of Sublimation.

- **Enthalpy :** $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n_g RT$
- **Kirchoff's equation** :

$$\Delta E_{T_2} = \Delta E_{T_1} + \Delta C_V(T_2 - T_1) \text{ [constant V]}$$

$$\Delta H_{T_2} = \Delta E_{T_1} + \Delta C_P(T_2 - T_1) \text{ [contant P]}$$

- **Entropy(s) :**

Meassure of disorder or randomness

$\Delta S = \Sigma S_P = -\Sigma S_R$

$$\Delta S = \frac{q_{rev}}{T} = 2.03nR \log \frac{V_2}{V_1} = 2.303\ n\ R \log \frac{P_1}{P_2}$$

Entropy Changes in an Ideal Gas

$$\Delta S = 2.303nC_p \log \frac{T_2}{T_1} + 2.303nR \log \frac{P_1}{P_2}$$

$$\Delta S = 2.303nC_V \log \frac{T_2}{T_1} + 2.303nR \log \frac{V_2}{V_1}$$

1. for isothermal process :

$$\Delta S = 2.303nR \log_{10} \frac{P_1}{P_2} \quad \text{or}$$

$$\Delta S = 2.303nR \log_{10} \frac{V_2}{V_1}$$

2. For isobaric process :

$$\Delta S = 2.303nC_P \log\left(\frac{T_2}{T_1}\right)$$

3. For isochoric process :

$$\Delta S = 2.303nC_V \log\left(\frac{T_2}{T_1}\right)$$

4. For adiabatic process

- **q = 0 so $\Delta S = 0$**

  $\Delta S_{sys} = 0$

  $\Delta S_{surr.} = 0$

  $\Delta S_{Total} = 0$

- **Entropy and Spotaneity**

  $\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings}$

Case I : For a spontaneous process **$\Delta S_{Total} > 0$**

Case II : For non spontaneous process **$\Delta S_{Total} < 0$**

Case III : When process is at equilibrium **$\Delta S_{Total} = 0$**

In a reversible adiabatic process, as **q = 0**,

$\Delta S_{sys} = \Delta S_{surr} = \Delta S_{Total} = 0$

- **Free energy change :**

$\Delta G = \Delta H - T\Delta S$, $\Delta G^\circ = nFE^\circ_{cell} - \Delta G =$ $W(\text{maximum}) - P\Delta V$, $\Delta G_{system} = -T\Delta S_{total}$

ΔH	ΔS	ΔG	Reaction characteristics
–	+	Alwasy negative	Reaction is spontaneous at all temperature
+	–	Alwasy positive	Reaction is nonspontaneos at all temperature
–	–	Negative at low temp.	Spontaneous at high temp. but positive at high temp.
+	+	Positive at low temp. but negative at high temp	Non spontaneous at low temp. & spontaneous at high temp.

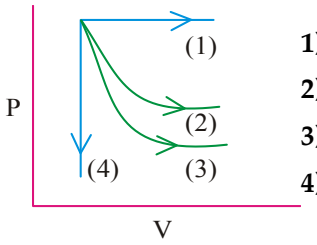
➢ Isothermal process

1. $\Delta T = 0$ 2. $\Delta U = 0$
3. $q \neq 0$ 4. $\Delta H = 0$

➢ Adiabatic process

1. $\Delta T \neq 0$ 2. $\Delta U \neq 0$
3. $q = 0$ 4. $\Delta H \neq 0$

➢ Graphical representation of **thermodynamic** processes



1) Isobaric process
2) Isothermal process
3) Adiabatic process
4) Isochoric process

for expansion:

$W_{Isobaric} > W_{Isothermal} > W_{Adiabatic} > W_{Isochoric}$

for compression :

$W_{Isobaric} > W_{Adiabatic} > W_{Isothermal} > W_{Isochoric}$

➢ Work for Osothermal Process

For expansion	for compression
1. $V_2 > V_1$	1. $V_1 > V_2$
2. W = – ve	2. W = +ve
3. $W = -P_{ext.}(V_2 - V_1)$	3. $W = +P_{ext.}(V_1 - V_2)$
4. $W = -P_{ext.}\Delta V$	4. $W = +P_{ext.}\Delta V$
5. $W_{max.} \propto$ no. of moles	

➢ Characteristics of Internal energy

Ideal gas	Real gas
U = f(T) only	U =f (T, P or V)
When T is constant	When T is constant
$\Delta U = 0, \Delta H = 0$	$\Delta U \neq 0, \Delta H \neq 0$
$\left(\frac{dU}{dV}\right)_T = 0$	$\left(\frac{dU}{dV}\right)_T \neq 0$

➢ Concept of Heat Capacity

Heat Capacity (s) $C = \frac{q}{\Delta T}$

Specific Heat Capacity (s) $s = \frac{q}{m\Delta T}$

Molar Heat Capacity (C_m) $C_m = \frac{q}{n\Delta T}$

➢ Work Done in Adiabatic Process

As q = 0

$\Delta U = W = nC_V\Delta T$

$W = nC_V(T_2 - T_1)$

$W = \frac{nR}{\gamma - 1}(T_2 - T_1)$

➢ Relation between C_P and C_V :

$C_P - C_V = R$