THERMODYNAMICS

Thermodynamic processes :

- 1.Isothermal process :T = constant
dT = 0
 $\Delta T = 0$ 2.Isochoric process :V = constant
dV = 03.Isobaric process :P = constant
dP = 0
 $\Delta P = 0$
- 4. Adiabatic process :

aV = 0 $\Delta V = 0$ P = constant dP = 0 $\Delta P = 0$ q = 0

or heat exchange with the surrounding = 0(zero)

IUPAC Sign convention about Heat and Work :

Work done on the system = Positive Work done by the system = Negative

1st Law of Thermodynamics

 $\Delta \mathsf{U} = (\mathsf{U}_2 - \mathsf{U}_1) = \mathsf{q} + \mathsf{w}$

Law of equipartion of energy :

$$U = \frac{f}{2} nRT$$
 (only for ideal gas)

$$\Delta \mathsf{E} = \frac{\mathsf{f}}{2} \mathsf{nR} (\Delta \mathsf{T})$$

where f = degrees of freedom for that gas. (Translational + Rotational)

- f = 3 for monoatomic
 - = 5 for diatomic or linear polyatmic
 - = 6 for non linear polyatmic

Calculation of heat (q) : Total heat capacity :

$$C_{T} = \frac{\Delta q}{\Delta T} = \frac{dq}{dT} = J/°C$$

Molar heat capacity :

$$C = \frac{\Delta q}{n\Delta T} = \frac{dq}{ndT} = J \text{ mole}^{-1} \text{ K}^{-1}$$
$$C_{p} = \frac{\gamma R}{\gamma - 1} \qquad C_{v} = \frac{R}{\gamma - 1}$$

Specific heat capacity (s) :

$$S = \frac{\Delta q}{m\Delta T} = \frac{dq}{mdT} = J \text{ gm}^{-1} \text{ K}^{-1}$$

WORK DONE (w) :

Isothermal Reversible expansion/compression of an ideal gas : $W = -\,nRT\, ln\, (V_f/V_i)$

Reversible and irreversible isochoric processes.

Since dV = 0So $dW = -P_{ext} \cdot dV = 0$.

Reversible isobaric process :

 $\mathsf{W} = \mathsf{P} (\mathsf{V}_{\mathsf{f}} - \mathsf{V}_{\mathsf{i}})$

Adiabatic reversible expansion :

$$\Rightarrow T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

Reversible Work:

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} = \frac{nR (T_2 - T_1)}{\gamma - 1}$$

Irreversible Work :

W =
$$\frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{nR(T_2 - T_1)}{\gamma - 1} = nC_v(T_2 - T_1) = -P_{ext}(V_2 - V_1)$$

and use
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Free expansion–Always going to be irrerversible and since $P_{ext} = 0$ so $dW = -P_{ext}$. dV = 0If no. heat is supplied q = 0then $\Delta E = 0$ so $\Delta T = 0$.

Application of Ist Law :

 $\Delta U = \Delta Q + \Delta W \qquad \Rightarrow \qquad \Delta W = -P \Delta V$ $\therefore \quad \Delta U = \Delta Q - P \Delta V$

Constant volume process

Heat given at constant volume = change in internal energy

 $\therefore du = (dq)_v$ $du = nC_v dT$ $C_v = \frac{1}{n} \cdot \frac{du}{dT} = \frac{f}{2} R$

Constant pressure process :

H = Enthalpy (state function and extensive property) H = U + PV

 \Rightarrow C_p – C_v = R (only for ideal gas)

Second Law Of Thermodynamics :

 $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ for a spontaneous process.

Entropy (S):

$$\Delta S_{\text{system}} = \int_{A}^{B} \frac{dq_{\text{rev}}}{T}$$

Entropy calculation for an ideal gas undergoing a process :

State A
$$\xrightarrow{\text{irr}} \Delta S_{\text{irr}}$$
State BP_1, V_1, T_1P_2, V_2, T_2 $\Delta S_{\text{system}} = nc_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ (only for an ideal gas)

Third Law Of Thermodynamics :

The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

Gibb's free energy (G): (State function and an extensive property)

$$G_{system} = H_{system} - TS_{system}$$

Criteria of spontaneity :

- (i) If ΔG_{system} is (-ve) < 0 \Rightarrow process is spontaneous (ii) If ΔG_{system} is > 0 \Rightarrow process is non spontaneous
- (iii) If $\Delta G_{system}^{optiment} = 0 \implies system is at equilibrium.$

Physical interpretation of ΔG :

 \rightarrow The maximum amount of non-expansional (compression) work which can be performed.

 $\Delta G = dw_{non-exp} = dH - TdS.$

Standard Free Energy Change (ΔG°) :

- 1. $\Delta G^{\circ} = -2.303 \text{ RT} \log_{10} \text{K}$
- 2. At equilibrium $\Delta G = 0$.
- 3. The decrease in free energy $(-\Delta G)$ is given as :

$$-\Delta G = W_{net} = 2.303 \text{ nRT} \log_{10} \frac{V_2}{V_1}$$

- 4. ΔG_{f}° for elemental state = 0
- 5. $\Delta G_{f}^{\circ} = G_{products}^{\circ} G_{Reactants}^{\circ}$

Thermochemistry :

Change in standard enthalpy

$$\Delta \mathsf{H}^{\circ} = \mathsf{H}^{\mathsf{0}}_{\mathsf{m},2} - \mathsf{H}^{\mathsf{0}}_{\mathsf{m},1}$$

= heat added at constant pressure.

 $= C_{P} \Delta T.$

If $H_{products} > H_{reactants}$

→ Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products

and if H_{products} < H_{reactants}

→ Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

Enthalpy change of a reaction :

$$\begin{array}{l} \Delta \mathsf{H}_{\mathsf{reaction}} = \mathsf{H}_{\mathsf{products}} - \mathsf{H}_{\mathsf{reactants}} \\ \Delta \mathsf{H}^{\circ}_{\mathsf{reactions}} = \mathsf{H}^{\circ}_{\mathsf{products}} - \mathsf{H}^{\circ}_{\mathsf{reactants}} \\ = \mathsf{positive} - \mathsf{endothermic} \\ = \mathsf{negative} - \mathsf{exothermic} \end{array}$$

Temperature Dependence Of ΔH : (Kirchoff's equation) :

For a constant pressure reaction $\Delta H_2^{\circ} = \Delta H_1^{\circ} + \Delta C_P (T_2 - T_1)$ where $\Delta C_P = C_P (\text{products}) - C_P (\text{reactants})$. For a constant volume reaction

$$\Delta E_2^0 = \Delta E_1^0 + \int \Delta C_V \,.dT$$

Enthalpy of Reaction from Enthalpies of Formation :

The enthalpy of reaction can be calculated by $\Delta H_r^{\circ} = \Sigma v_B \Delta H_f^{\circ}$, products $-\Sigma v_B \Delta H_f^{\circ}$, reactants v_B is the stoichiometric coefficient.

Estimation of Enthalpy of a reaction from bond Enthalpies :

 $\Delta H = \begin{pmatrix} \text{Enthalpy required to} \\ \text{break reactants into} \\ \text{gasesous atoms} \end{pmatrix} - \begin{pmatrix} \text{Enthalpy released to} \\ \text{form products from the} \\ \text{gasesous atoms} \end{pmatrix}$

Resonance Energy :

$$\begin{split} \Delta H^{\circ}_{\text{resonance}} &= \Delta H^{\circ}_{\text{f, experimental}} - \Delta H^{\circ}_{\text{f, calclulated}} \\ &= \Delta H^{\circ}_{\text{c, calclulated}} - \Delta H^{\circ}_{\text{c, experimental}} \end{split}$$