

Thermodynamics

- * Extensive properties → depend upon matter contained in the system. e.g., mass, volume, all energies (entropy, enthalpy, gibbs free energy), no. of molec, force, area, etc.
- * Intensive Properties → doesn't depend upon matter contained in the system. e.g., Temp., viscosity, refractive index, all conc. terms, pressure, density, etc.



Extensive = Intensive
Extensive

Path function → Heat, Work only
(Q) (W)

State function → Volume, Temp, Internal energy, etc.
(ΔV)

Adiabatic Process

$$Q = 0$$

- Adiabatic Expansion → Temp. decreases.
- Adiabatic Compression → Temp. increases.

Reversible Process → very slow & at all steps in equilibrium

Irreversible Process → very fast

ESTIMATE

Heat (q) :- $q = m s \Delta T$

For Isothermal Process, $\Delta S = \infty$

Specific heat of substance

Work (w) :- $W = -P_{ext} \Delta V$

- Expansion = $\Delta V = +ve$, $W = -ve$, i.e., Work is done by the system.
- Compression = $\Delta V = -ve$, $W = +ve$ i.e., Work is done on the system.

First Law of Thermodynamics

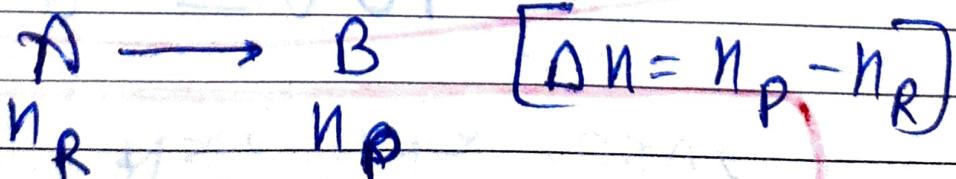
$$\Delta U = q + w$$

Enthalpy (H) :- Heat change at constant pressure

$$\Delta H = \Delta U + P \Delta V$$

$$\Delta H = \Delta U + nR\Delta T / \Delta n_{\text{g}} RT$$

$$\Delta n_{\text{g}} = n_p(g) - n_R(g)$$



If $n_p > n_R \Rightarrow \Delta n = +ve$ [i.e., endothermic]

If $n_p < n_R \Rightarrow \Delta n = -ve$ [i.e., exothermic]

$$dU = nC_V \Delta T$$

$$dH = nC_p \Delta T$$

$$\Delta n = \int_{T_1}^{T_2} \frac{C_p \Delta T}{T}$$

Work done in P-V graph =

Area under curve

Bar Tach

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

$$C_p - C_V = R$$

$$\gamma = \frac{C_p}{C_V}$$

Adiabatic Process

$$PV^\gamma = \text{const.}, \quad TV^{\gamma-1} = \text{const.}$$

$$P \propto T^{\gamma/(\gamma-1)}$$

* Reversible Isothermal

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

In vacuum, $P_{\text{ext}} = 0$

$$\therefore W = \Delta U = \Delta n = 0$$

* Reversible Adiabatic

ESTIMATE

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

$$W = \frac{1}{\gamma - 1} R T$$

Formula of ΔH

$$\Delta H_{\text{atom}} = \Delta H_{\text{vap}} + \Delta E$$

$$\Delta H = \sum \Delta H_{\text{(products)}} - \sum \Delta H_{\text{(Reactants)}}$$

Applied everywhere except

$$\Delta H = \sum (B \cdot E)_{\text{Reactants}} - \sum (B \cdot E)_{\text{products}}$$

$$\Delta H = \sum (\Delta H)_{\text{combustion of Reactants}} - \sum (\Delta H)_{\text{comb. of products}}$$

Enthalpy of Neutralisation

When 1 mole of acid & base completely neutralise then,

$$\Delta H_N = -57.1 \text{ KJ}$$

Bomb Calorimeter [heat released during combustion of organic compound]

$$\Delta H = \text{Heat absorbed by } \text{H}_2\text{O} + \text{Heat absorbed by bomb calorimeter} \times \frac{\text{no. of moles of org. comp.}}{1}$$

$$\Delta H = \left(M_{H_2O + N_2O} + \text{Heat Capacity of Bomb Calorimeter} \right) \times \Delta T$$

No. of mole of org. compound

Spontaneous Process → done by themselves

Non-spontaneous II → done by external force

Entropy (S)

$$\Delta S = \frac{Q_{\text{exp}} \cdot 10^3 \text{ J}}{T} \text{ J K}^{-1}$$

but if unit of entropy

$\text{J K}^{-1} \text{ mol}^{-1}$ or $\text{J K}^{-1} \text{ g}^{-1}$ → Now $\text{J} \text{ K}^{-1}$ is standard

Note :- More the no. of gaseous molecules → more is the entropy

$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

Randomness factor
entropy factor

Exception :- In boiling of an egg
entropy incr. due to denaturation of protein

* Biggest is the size of gas molecules more is the entropy

$$\Delta S_{\text{total or Universe}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}}$$

ESTIMATE

* For Spontaneous process,

$$(\Delta S)_{\text{total}} = +\text{ve} \text{ (Always)}$$

For diff. Processes

1) For Isothermal Reversible \rightarrow

$$\Delta S_{\text{sys.}} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$$

$$\Delta S_{\text{sur.}} = -\Delta S_{\text{sys.}}$$

2) For Adiabatic Reversible \rightarrow

$$\Delta S_{\text{sys.}} = \Delta S_{\text{sur.}} = 0$$

3) For Isobaric Process \rightarrow

$$\Delta S_{\text{sys.}} = nC_p \ln \frac{T_2}{T_1}$$

4) For Isochoric Process \rightarrow

$$\Delta S_{\text{sys.}} = nC_v \ln \frac{T_2}{T_1}$$

* If both temp. & vol. are changed \rightarrow

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

* If both temp. & pressure are changed

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

(a) Entropy of fusion (ΔS_{fusion})

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_m} \rightarrow \text{enthalpy of fusion}$$

(b) Entropy of Vapourisation

$$\Delta S_{\text{Vapourisation}} = \frac{\Delta H_{\text{vap.}}}{T_B} \rightarrow \text{B.p.}$$

Gibb's free Energy

↳ energy of the system which can be converted into useful work

$$\Delta G = W_{\text{maximum}}$$

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

$$R \xrightarrow{\text{P}} G_p = \frac{\partial G}{\partial P} = \frac{\partial (H - TS)}{\partial P} = V \frac{\partial P}{\partial T}$$

$$\Delta G = \sum G_p - \sum G_g$$

$$\Delta G^\circ = \sum \Delta G_{\text{formation}}^\circ \text{ of products} - \sum G_{\text{formation}}^\circ \text{ of reactants}$$

* Elements in elementary state have $\Delta G_{\text{formation}}^\circ = 0$

ESTIMATE

* For Spontaneous Rxn.

$$\Delta H = -ve$$

* For non-spontaneous $\Rightarrow \Delta H = +ve$

If $\Delta H = 0 \Rightarrow$ Rxn. is at equil.

Temp.
at
which
 $\Delta H = 0$

$$T = \frac{\Delta H}{\Delta S}$$

- Above this temp. rxn. is spontaneous
- Below this temp. rxn. is non-spontaneous

$$\Delta G = -T \Delta S_{total}$$

- * For spontaneous rxn $\Rightarrow \Delta S_{total} = +ve$
* For non-spontaneous rxn $\Rightarrow \Delta S_{total} = -ve$

Cases of

- 1) $\Delta S = +ve, \Delta H = -ve \Rightarrow$ Rxn. is spontaneous at all temp.
- 2) $\Delta S = -ve, \Delta H = -ve \Rightarrow$ On incr. temp. spontaneity decr.
- 3) $\Delta S = +ve, \Delta H = +ve \Rightarrow$ On incr. temp. spontaneity incr.
- 4) $\Delta S = -ve, \Delta H = +ve \Rightarrow$ Rxn. is non-spontaneous at all temp.

3rd Law of Thermodynamics

Perfectly crystalline substance have zero entropy at zero Kelvin