

THERMODYNAMICS

➤ First Law of Thermodynamics :

$$\Delta E = Q + W$$

Expression for pressure volume work

$$W = -P\Delta V$$

Maximum work in a reversible expansion :

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

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

➤ $q_p = C_p \Delta T = \Delta U$, $q_p = C_p \Delta T = \Delta H$

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 :

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

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

➤ Entropy(s) :

Measure of disorder or randomness

$$\Delta S = \sum S_p - \sum S_r$$

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

Entropy Changes in an Ideal Gas

$$\Delta S = 2.303 n C_p \log \frac{T_2}{T_1} + 2.303 n R \log \frac{P_1}{P_2}$$

$$\Delta S = 2.303 n C_v \log \frac{T_2}{T_1} + 2.303 n R \log \frac{V_2}{V_1}$$

1. for isothermal process :

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

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

2. For isobaric process :

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

3. For isochoric process :

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

4. For adiabatic process

$$q = 0 \quad \text{so} \quad \Delta S = 0$$

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

$$\Delta S_{sur} = 0$$

$$\Delta S_{total} = 0$$

➤ Entropy and Spontaneity

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

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 $q = 0$,

$$\Delta S_{sys} = \Delta S_{sur} = \Delta S_{total} = 0$$

➤ Free energy change :

$$\Delta G = \Delta H - T\Delta S, \Delta G^\circ = nFE^\circ_{cell} - \Delta G =$$

$$W(\text{maximum}) - P\Delta V, \Delta G_{system} = -T\Delta S_{total}$$



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G Psacharopoulos



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