

THERMODYNAMICS

► First Law of Thermodynamics :

$$\Delta E = Q + W$$

Expression for pressure-volume work

$$W = -P\Delta V$$

Maximum work in a reversible expansion :

$$W_{\text{rev}} = -2.303 \text{ nR} \log \frac{V_2}{V_1} = -2.303 \text{ nRT} \log \frac{P_1}{P_2}$$

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

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

Enthalpy changes during phase transformation

i. Enthalpy of Fusion

ii. Heat of Vapourisation

iii. Heat of Sublimation

► Enthalpy : $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n_{\text{m}} RT$

► Kirchoff's equation :

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

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

► Entropy(s) :

Measure of disorder or randomness

$$\Delta S = \Sigma S_p - \Sigma S_n$$

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

Entropy Changes in an Ideal Gas

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

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

► for isothermal process :

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

$$\Delta S = 2.303 \text{ nR} \log \frac{V_2}{V_1}$$

► For isobaric process :

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

► For isochoric process :

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

► For adiabatic process

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

$$\Delta S_{\text{rev}} = 0$$

$$\Delta S_{\text{irr}} = 0$$

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

► Entropy and Spontaneity

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

Case I : For a spontaneous process $\Delta S_{\text{total}} > 0$

Case II : For non spontaneous process $\Delta S_{\text{total}} < 0$

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

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

$$\Delta S_{\text{rev}} = \Delta S_{\text{irr}} = \Delta S_{\text{total}} = 0$$

► Free energy change :

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



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