

THERMODYNAMICS

Thermodynamic processes :

1. **Isothermal process :** $T = \text{constant}$
 $dT = 0$
 $\Delta T = 0$
2. **Isochoric process :** $V = \text{constant}$
 $dV = 0$
 $\Delta V = 0$
3. **Isobaric process :** $P = \text{constant}$
 $dP = 0$
 $\Delta P = 0$
4. **Adiabatic process :** $q = 0$
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

$$\Delta U = (U_2 - U_1) = q + w$$

Law of equipartition of energy :

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

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

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

$f = 3$ for monoatomic

$= 5$ for diatomic or linear polyatomic

$= 6$ for non-linear polyatomic

Calculation of heat (q) :

Total heat capacity :

$$C_T = \frac{\Delta q}{\Delta T} = \frac{dq}{dT} = J/^{\circ}C$$

Molar heat capacity :

$$C = \frac{\Delta q}{n\Delta T} = \frac{dq}{ndT} = J \text{ mole}^{-1} K^{-1}$$

$$C_P = \frac{\gamma R}{\gamma - 1} \quad C_V = \frac{R}{\gamma - 1}$$

Specific heat capacity (s) :

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

Isothermal Reversible expansion/compression of an ideal gas :

$$W = -nRT \ln (V_f/V_i)$$

Reversible and irreversible isochoric processes.

$$\text{Since } dV = 0$$

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

Reversible isobaric process :

$$W = P (V_f - V_i)$$

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 :

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

$$\text{and use } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Free expansion—Always going to be irreversible and since $P_{\text{ext}} = 0$

$$\text{so } dW = -P_{\text{ext}} \cdot dV = 0$$

$$\text{If no. heat is supplied } q = 0$$

$$\text{then } \Delta E = 0 \quad \text{so} \quad \Delta T = 0.$$

Application of 1st Law :

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

$$\therefore \Delta U = \Delta Q - P \Delta V$$

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 :

$H \equiv$ Enthalpy (state function and extensive property)

$$H = U + PV$$

$$\Rightarrow C_p - C_v = R \text{ (only for ideal gas)}$$

Second Law Of Thermodynamics :

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

Entropy (S) :

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

Entropy calculation for an ideal gas undergoing a process :

$$\begin{array}{ccc} \text{State A} & \xrightarrow[\Delta S_{\text{irr}}]{\text{irr}} & \text{State B} \\ P_1, V_1, T_1 & & P_2, V_2, T_2 \end{array}$$

$$\Delta S_{\text{system}} = nc_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad (\text{only for an ideal gas})$$

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)

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

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 $\Delta G_{\text{system}} = 0$ | \Rightarrow | system is at equilibrium. |

Physical interpretation of ΔG :

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

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

Standard Free Energy Change (ΔG°) :

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

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

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

Thermochemistry :

Change in standard enthalpy $\Delta H^\circ = H_{m,2}^0 - H_{m,1}^0$
= heat added at constant pressure.
= $C_p \Delta T$.

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

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

and if $H_{\text{products}} < H_{\text{reactants}}$

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

Enthalpy change of a reaction :

$$\begin{aligned}\Delta H_{\text{reaction}} &= H_{\text{products}} - H_{\text{reactants}} \\ \Delta H_{\text{reactions}}^\circ &= H_{\text{products}}^\circ - H_{\text{reactants}}^\circ \\ &= \text{positive} - \text{endothermic} \\ &= \text{negative} - \text{exothermic}\end{aligned}$$

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

$$\Delta H_r^\circ = \sum v_B \Delta H_f^\circ, \text{products} - \sum v_B \Delta H_f^\circ, \text{reactants}$$

v_B is the stoichiometric coefficient.

Estimation of Enthalpy of a reaction from bond Enthalpies :

$$\Delta H = \left(\text{Enthalpy required to break reactants into gaseous atoms} \right) - \left(\text{Enthalpy released to form products from the gaseous atoms} \right)$$

Resonance Energy :

$$\begin{aligned}\Delta H_{\text{resonance}}^\circ &= \Delta H_{f, \text{experimental}}^\circ - \Delta H_{f, \text{calculated}}^\circ \\ &= \Delta H_{c, \text{calculated}}^\circ - \Delta H_{c, \text{experimental}}^\circ\end{aligned}$$