THERMODYNAMICS

Thermodynamic processes :

1. **Isothermal process :** T = constant
   $dT = 0$
   $\Delta T = 0$
2. **Isochoric process :** V = constant
   $dV = 0$
   $\Delta V = 0$
3. **Isobaric process :** P = 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 :

$$U = \frac{f}{2} nRT$$ (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 polyatmic
= 6 for non - linear polyatmic

Calculation of heat (q) :

Total heat capacity :

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

Molar heat capacity :

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

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

Specific heat capacity (s) :

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

WORK DONE (w) :

Isothermal Reversible expansion/compression of an ideal gas :

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

Reversible and irreversible isochoric processes.

Since $dV = 0$

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

Reversible isobaric process :

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

Adiabatic reversible expansion :

$$\Rightarrow \quad T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$$

Reversible Work :

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{nR(T_2 - T_1)}{\gamma - 1}$$

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 $dW = -P_{ext} . dV = 0$

If no. heat is supplied $q = 0$

then $\Delta E = 0$ so $\Delta T = 0.$

Application of Ist Law :

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

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

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 $\equiv$ 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) :

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

Entropy calculation <u>for an ideal gas</u> undergoing a process :

$$\text{State A} \xrightarrow[\Delta S_{irr}]{irr} \text{State B}$$

P_1, V_1, T_1 $\qquad$ P_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)

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

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 :

→ 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^o) :

1. $\Delta G^o = -2.303\ RT \log_{10} K$
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. $\Delta G_f^\circ = G^\circ_{\text{products}} - G^\circ_{\text{Reactants}}$

Thermochemistry :

Change in standard enthalpy $\Delta H^\circ = H^0_{m,2} - H^0_{m,1}$

= 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 :

$\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$

$\Delta H^\circ_{\text{reactions}} = H^\circ_{\text{products}} - H^\circ_{\text{reactants}}$

= positive – endothermic

= negative – exothermic

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 $\Delta C_P = C_P$ (products) – C_P (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

$\Delta H_r° = \Sigma\, \nu_B\, \Delta H_f°{,}_{\text{products}} - \Sigma\, \nu_B\, \Delta H_f°{,}_{\text{reactants}}$

ν_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 :

$$\begin{aligned}\Delta H°_{\text{resonance}} &= \Delta H°_{\text{f, experimental}} - \Delta H°_{\text{f, calclulated}} \\ &= \Delta H°_{\text{c, calclulated}} - \Delta H°_{\text{c, experimental}}\end{aligned}$$