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 equipartion of energy :

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

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

where f = degrees of freedom for that gas. (Translational + Rotational)
f = 3 for monoatomic
= 5 for diatomic or linear polyatmic
= 6 for non - linear polyatmic

Calculation of heat (q) :

Total heat capacity :

$$C_T = \frac{\Delta q}{\Delta T} = \frac{dq}{dT} = \text{J/ºC}$$

Molar heat capacity :

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

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

Specific heat capacity (s) :

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

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) :

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

Entropy calculation for an ideal gas undergoing a process :

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

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.

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

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 :

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

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

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 $H_{products} > H_{reactants}$

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

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

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

Enthalpy change of a reaction :

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

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

= 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

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

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 :

$$\Delta H°_{resonance} = \Delta H°_{f,\ experimental} - \Delta H°_{f,\ calclulated}$$
$$= \Delta H°_{c,\ calclulated} - \Delta H°_{c,\ experimental}$$

CHEMICAL EQUILIBRIUM

At equilibrium :

(i) Rate of forward reaction = rate of backward reaction

(ii) Concentration (mole/litre) of reactant and product becomes constant.

(iii) $\Delta G = 0$.

(iv) $Q = K_{eq.}$

Equilibrium constant (K) :

$$K = \frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}} = \frac{K_f}{K_b}.$$

Equilibrium constant in terms of concentration (K_C) :

$$\frac{K_f}{K_b} = K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Equilibrium constant in terms of partial pressure (K_P) :

$$K_P = \frac{[P_C]^c\ [P_D]^d}{[P_A]^a\ [P_B]^b}$$

Equilibrium constant in terms of mole fraction (K_x) :

$$K_x = \frac{x_C^c x_D^d}{x_A^a x_B^b}$$

Relation between K_p & K_C :

$K_p = K_c.(RT)^{\Delta n}$.

Relation between K_p & K_x :

$K_P = K_x (P)^{\Delta n}$

* $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$; ΔH = Enthalpy of reaction

Relation between equilibrium constant & standard free energy change :

$\Delta G^o = -\ 2.303\ RT \log K$

Reaction Quotient (Q) :

The values of expression $Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

Degree of Dissociation (α) :

α = no. of moles dissociated / initial no. of moles taken

= fraction of moles dissociated out of 1 mole.

Note : % dissociation = α x 100

Observed molecular weight and Observed Vapour Density of the mixture :
Observed molecular weight of A_n(g)

$$= \frac{\text{molecular weight of equilibrium mixture}}{\text{total no. of moles}}$$

$$\alpha = \frac{D - d}{(n-1) \times d} = \frac{M_T - M_o}{(n-1)M_0}$$

External factor affecting equilibrium :

<u>Le Chatelier's Principle:</u>

If a system at equilibrium is subjected to a disturbance or stress that changes any of the factors that determine the state of equilibrium, the system will react in such a way as to minimize the effect of the disturbance.

Effect of concentration :

* If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .

* If the concentration of product is increased then equilibrium shifts in the backward direction

Effect of volume :

* If volume is increased pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.

* If volume is increased then, for

$\Delta n > 0$	reaction will shift in the forward direction
$\Delta n < 0$	reaction will shift in the backward direction
$\Delta n = 0$	reaction will not shift.

Effect of pressure :

If pressure is increased at equilibrium then reaction will try to decrease the pressure, hence it will shift in the direction in which less no. of moles of gases are formed.

Effect of inert gas addition :

(i) Constant pressure :

If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

$\Delta n > 0$ reaction will shift in the forward direction

$\Delta n < 0$ reaction will shift in the backward direction

$\Delta n = 0$ reaction will not shift.

(ii) Constant volume :

Inert gas addition has no effect at constant volume.

Effect of Temperature :

Equilibrium constant is only dependent upon the temperature.

If plot of ℓnk vs $\frac{1}{T}$ is plotted then it is a straight line with slope = $-\frac{\Delta H^\circ}{R}$,

and intercept = $\frac{\Delta S^\circ}{R}$

- * For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature
- * For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature
- * For $\Delta H > 0$, reaction shiffts in the forward direction with increase in temperatutre
- * For $\Delta H < 0$, reaction shifts in the backward direction with increases in temperature.
- * If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .
- * If the concentration of product is increased then equilibrium shifts in the backward direction

Vapour Pressure of Liquid :

Relative Humidity = $\dfrac{\text{Partial pressure of } H_2O \text{ vapours}}{\text{Vapour pressure of } H_2O \text{ at that temp.}}$

Thermodynamics of Equilibrium :

$$\mathbf{\Delta G = \Delta G^0 + 2.303\, RT \log_{10} Q}$$

Vant Hoff equation- $\log\left(\dfrac{K_1}{K_2}\right) = \dfrac{\Delta H^0}{2.303R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$