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 :

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

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

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 :

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

Molar heat capacity :

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

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

Specific heat capacity (s) :

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

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 :

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

Reversible Work :

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

Irreversible Work :

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{nR\ (T_2 - T_1)}{\gamma - 1}\ nC_v\ (T_2 - T_1) = -P_{ext}\ (V_2 - V_1)\ \text{and use}\ \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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

Constant volume process

Heat given at constant volume = change in internal energy
$\therefore du = (dq)_v$
$du = nC_vdT$

$$C_v = \frac{1}{n}.\frac{du}{dT} = \frac{f}{2}R$$

Constant pressure process :

H ≡ Enthalpy (state function and extensive property)

H = U + PV

⇒ **C$_p$ – C$_v$ = R (only for ideal gas)**

Second Law Of Thermodynamics :

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

Entropy (S) :

$$\Delta S_{system} = \int_{A}^{B} \frac{dq_{rev}}{T}$$

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

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

P$_1$, V$_1$, T$_1$ P$_2$, V$_2$, T$_2$

$$\Delta S_{system} = nc_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$ (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)

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

Criteria of spontaneity :

(i) If ΔG_{system} is (–ve) < 0 ⇒   process is spontaneous

(ii) If ΔG_{system} is > 0   ⇒   process is non spontaneous

(iii) If ΔG_{system} = 0   ⇒   system is at equilibrium.

Physical interpretation of ΔG :

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

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

Standard Free Energy Change (ΔG°) :

1. $\Delta G° = -2.303 \, RT \log_{10} K$

2. At equilibrium $\Delta G = 0$.

3. The decrease in free energy (–ΔG) is given as :

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

4. $\Delta G_f°$ for elemental state = 0

5. $\Delta G_f° = G_{products}° - G_{Reactants}°$

Thermochemistry :

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

$\qquad$ = heat added at constant pressure. = $C_P \Delta T$.

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

$\rightarrow$ $\qquad$ Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products

$\qquad$ and if $\quad H_{products} < H_{reactants}$

$\rightarrow$ $\qquad$ Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

$\qquad$ Enthalpy change of a reaction : $\qquad \Delta H_{reaction} = H_{products} - H_{reactants}$

$\Delta H°_{reactions}$ $\qquad$ = $H°_{products} - H°_{reactants}$

$\qquad\qquad\qquad\qquad$ = positive $\qquad$ – $\qquad$ endothermic

$\qquad\qquad\qquad\qquad$ = negative $\qquad$ – $\qquad$ exothermic

Temperature Dependence Of ΔH : (Kirchoff's equation) :

For a constant volume reaction

$\Delta H_2° = \Delta H_1° + \Delta C_P (T_2 - T_1)$

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

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

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

$\qquad\qquad\quad = \Delta H°_{c, calclulated} - \Delta H°_{c, experimental}$