Thermodynamics

* Limitations of Thermodynamic
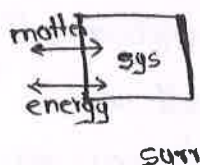
  → Mechanism of reaction (cannot explain)

  → Microscopic particle (not applicable)

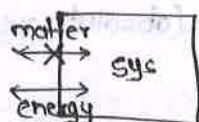 → Cannot say rate of reaction

* Basic Terms and Concepts

  → System :- Part of universe in which observations are made.

  → Surroundings :- Rest of the universe.

  ∴ System + Surrounding = Universe

  → Boundary :- The wall that separate system from surrounding which may be,

    (i) real or imaginery

    (ii) rigid or flexible
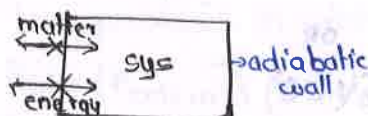
    (iii) diathermic or adiabatic

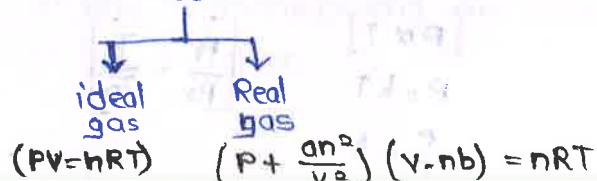* Types of system

  (1) Open system   (2) Closed system

matter, energy, sys, surr

matter, energy, sys

  (3) Isolated system

matter, energy, sys → adiabatic wall

* State of system

Gases
  ↓   ↓
ideal   Real
gas   gas
$(PV = nRT)$ $\left(P + \frac{an^2}{V^2}\right)(V-nb) = nRT$

A system can be described by parameters such as n, V, P, T, U, H, s and G.

↓

known as state of a system

* Thermodynamic (TD) functions

(1) State functions (SF)

  TD functions which depends only on initial and final stage of system but not on the path followed.

  Eg: Volume, Temperature, Pressure

(2) Path Function (PF)

  TD functions which depends only on the path followed and on the initial and final stage of system.

  Eg: Heat and Work
       (q)   (w)
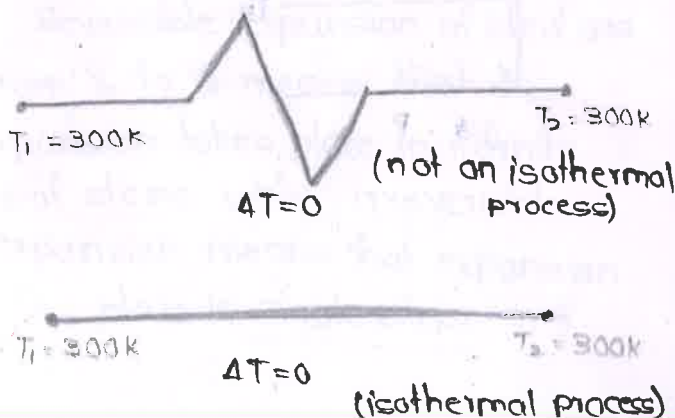
* Thermodynamic process

(1) Isothermal process

  Process taking place at constant temperature.

  ie, $(\Delta T = T_2 - T_1 = 0)$

  but the most appropriate condition is,

  $(\delta T = 0)$

$T_1 = 300K$ $T_2 : 300K$
$\Delta T = 0$ (not an isothermal process)

$T_1 = 300K$ $T_2 = 300K$
$\Delta T = 0$ (isothermal process)

The connecting law for an isothermal process is <u>Boyle's law</u>. (P.V relation)

At constant T and n,

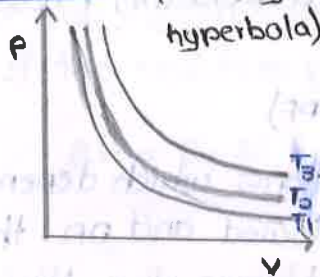$$\boxed{P \propto \frac{1}{V}}$$

$$P = k \frac{1}{V}$$

$$\therefore PV = k$$

$$\boxed{P_1 V_1 = P_2 V_2}$$

$$\boxed{\frac{P_1}{P_2} = \frac{V_2}{V_1}}$$
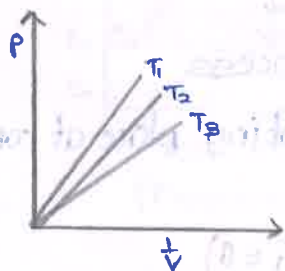
<u>P Vs V graph</u> (rectangular hyperbola)

$\left\{ \begin{array}{l} T_3 > T_2 > T_1 \\ \text{Higher curve} \\ = \text{high } T \end{array} \right\}$

<u>P Vs $\frac{1}{V}$ graph</u>

(straight line through origin)

$P \propto \frac{1}{V}$

$P = k \frac{1}{V}$

$\underset{y}{} \underset{m}{} \underset{x}{\phantom{\frac{1}{V}}}$

$\{T_1 > T_2 > T_3\}$

<u>PV Vs P graph</u>

(straight line with slope = 0)

slope = 0
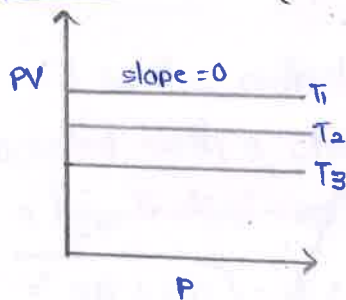
$\{T_1 > T_2 > T_3\}$

(2) <u>Isobaric process</u>

$$\left(\Delta P = 0 \right)$$

$$P_2 - P_1 = 0 \implies P_1 = P_2$$

OR

$$\left(\delta P = 0 \right)$$

Connecting law is <u>Charles law</u>,

At constant P and n,

$$\boxed{V \propto T}$$

$$V = kT$$

$$\frac{V}{T} = k$$

$$\boxed{\frac{V_1}{V_2} = \frac{T_1}{T_2}}$$

<u>V Vs T graph</u>

$\{P_3 > P_2 > P_1\}$

$-273 \cdot 15\,^\circ\text{C}$
or
OK
(absolute zero)
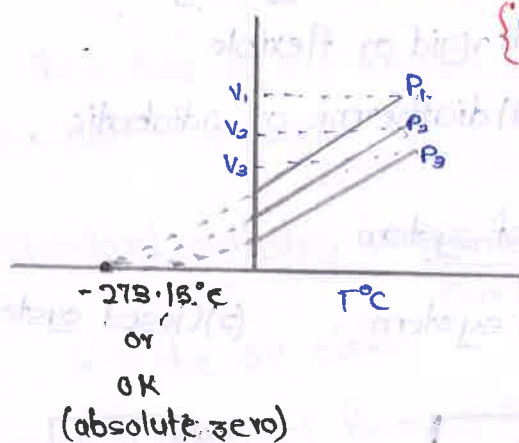
(3) <u>Isochoric process</u>

$$\left(\Delta V = 0 \right)$$

$$V_2 - V_1 = 0 \implies V_1 = V_2$$

OR

$$\left(\delta V = 0 \right)$$

Connecting law is <u>Gay Lussac's law</u>

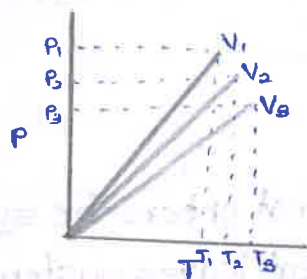At constant V and n,

$$\boxed{P \propto T}$$

$$P = kT$$

$$\frac{P}{T} = k$$

$$\boxed{\frac{P_1}{P_2} = \frac{T_1}{T_2}}$$
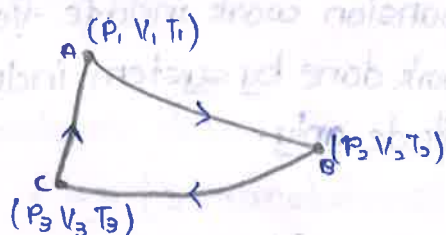
Vs T graph

$$\{V_1 < V_2 < V_3\}$$

(4) Adiabatic process

Process in which there is no transfer of heat btw system and surrounding.

$$(q = 0)$$

(5) Cyclic process

Here,

$$\left(\Delta \text{state function} = 0\right)$$
$$w \neq 0 \text{ (path function)}$$

eg: $\Delta H = 0$, $\Delta U = 0$, $\Delta P = 0 \cdots$

★ Thermodynamic process

(On the basis of way the process are carried out)

(1) Reversible process

→ It is a process in which the driving force ($P_{external}$) must be greater or less than opposing force ($P_{internal}$)

→ These process can be reversed at any moment during the course of the reaction.

→ It involves infinite no. of steps and therefore, it is a very slow process.

→ For reversible compression of an ideal gas, P_{ext} must be infinitisimally greater than P_{int}.

ie, $$\left\{\begin{array}{l} P_{ext} > P_{int} \\ P_{ext} = P_{in} + dp \end{array}\right\}$$

Similarly, for reversible expansion of an ideal gas,

ie, $$\left\{\begin{array}{l} P_{ext} < P_{int} \\ P_{ext} = P_{in} - dp \end{array}\right\}$$

∴ for any reversible process,

$$\boxed{P_{ext} = P_{in} \pm dp}$$

(2) Irreversible process

Process other than reversible are irreversible.

→ All naturally occuring process are irreversible.

→ Sudden change and single step process.

→ Finite time of completion.

NOTE

Reversible expansion of ideal gas from V_1 to V_2 means that the expansion takes place in infinite no. of steps while irreversible expansion means that expansion takes place in single step.

* Thermodynamic property

(1) Extensive property : depends upon the amount of substance.

　　eg : no. of moles, mass, heat capacity, volume, internal energy, Gibb's free energy, entropy...

(2) Intensive property : independent of the amount.

　　eg : density, pressure, temperature, concentration, Electrode potential, refractive index, viscocity, P_H^H molar volume

V=50ml T=100°C	V=50ml T=100°C

T=100°C
V = 100 ml
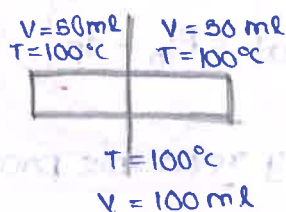
NOTE

$$\left(\frac{extensive}{extensive} = intensive\right)$$

✓density $= \dfrac{mass}{volume}$

✓molar volume $= \dfrac{volume}{mole}$

✓Pressure $= \dfrac{Force}{Area}$

* Modes of energy exchange

⇒ Heat (q) : It is the mode of energy exchange due to temperature difference

⇒ Work (w) : It is the mode of energy exchange due to pressure difference.

* IUPAC sign convention about heat and work

Heat (q)

　　q = +ve ⟶ heat enters the system
　　q = -ve ⟶ heat leaves system

Work (w)

　　w = +ve ⟶ workdone on system
　　　　　(compression work)

　　w = -ve ⟶ workdone by system
　　　　　(expansion work)

NOTE

　　Expansion work include -ve sign but work done by system include magnitude only.

* Internal energy (U)

　　It is defined as total amount of energy available within system.

$$U = E_{KE} + E_{PE} + E_{vibrational} + \cdots$$

Since the individual measurement of different kinds of energy is very difficult, the determination of absolute value U is not possible. But we can calculate change in internal energy ΔU.

$$\boxed{\Delta U = U_2 - U_1}$$

Internal energy can be changed by the following ways :

(i) Matter enters of leaves the system
(ii) Heat enters or leaves the system
(iii) Work done by the system

$$\Delta U \longrightarrow \begin{cases} \text{+ve} \quad \uparrow U \\ \text{-ve} \quad \downarrow U \end{cases}$$

When measured under standard condition of 298 K and 1 bar, ΔU is designated as, standard $(\Delta \overset{\ominus}{U}, \Delta^\circ u)$

By considering degree of freedom, (rotational and translational only), internal energy u can be calculated by equation,

$$\boxed{U = \frac{f}{2} nRT}$$

For 1 mol,

$$\boxed{U = \frac{f}{2} RT}$$

Monoatomic atom,

$f = 3$ (3 translational).

Diatomic atom,

$f = 3 + 2 = 5$ (3 translational, 2 rotational)

From above eq,

$$\boxed{U \propto T}$$

∴ For an isothermal process, U remains constant.

$$\boxed{\Delta U = 0}$$

WORK (W)

★ Work done for isothermal process

$\Delta T = 0$

$\Delta U = 0$

Boyle's law

$P_1 V_1 = P_2 V_2$

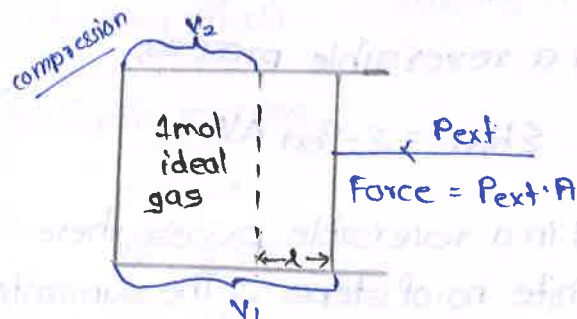$\dfrac{V_1}{V_2} = \dfrac{P_2}{P_1}$

Irreversible work

→ single step
→ finite time of complete
→ sudden change
→ compression / expansion against constant external pressure.

$$\begin{aligned} W &= F \times l \\ &= P_{ext} \, A \times l \\ &= P_{ext} \, \Delta V \\ W &= P_{ext} (V_2 - V_1) \end{aligned}$$

For compression (irr)

$$\boxed{W = - P_{ext} \, \Delta V} \quad \text{IUPAC}$$

P-V Graph

expansion
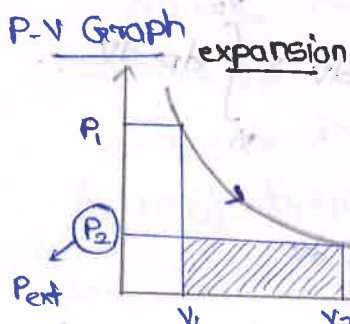
Work done ⇒ Area of rectangular strip.

$$\boxed{W = -ve}$$

compression
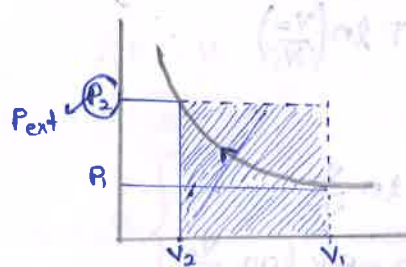
Work done ⇒ Area of rectangular strip

$$\boxed{W = +ve}$$

* Workdone for isothermal reversible process

→ multistep
→ slow change
→ infinite time of completion

$$W_{rev} = \sum W_{irr} =$$

For a reversible process,

$$W_{rev} = \sum W_{irr} = \sum -P_{ext}\, \Delta V$$

But in a reversible process, there are infinite no. of steps. ∴ The summation is very difficult.

$$W_{rev} = \int_{V_1}^{V_2} W_{irr} = -\int_{V_1}^{V_2} P_{ext}\, dv$$

For rev process, $P_{ext} = P_{in} \pm dp$

$$W_{rev} = -\int_{V_1}^{V_2} (P_{in} \pm dp)\, dv$$

$$= -\int_{V_1}^{V_2} P_{in}\, dv \pm \int_{V_1}^{V_2} dp\, dv$$

$$= -\int_{V_1}^{V_2} \frac{nRT}{V}\, dv$$

$$= -nRT \left[\ln \right]_{V_1}^{V_2}$$

$$= -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\left\{ \begin{array}{l} W_{rev} = -nRT \ln \frac{V_2}{V_1} \\ = -2.303\, nRT \log \frac{V_2}{V_1} \end{array} \right.$$

According to Boyle's law, $\frac{V_2}{V_1} = \frac{P_1}{P_2}$

$$\left\{ \begin{array}{l} W_{rev} = -nRT \ln \frac{P_1}{P_2} \\ = -2.303\, nRT \log \frac{P_1}{P_2} \end{array} \right.$$

P-V Graph

isothermal reversible process

→ expansion
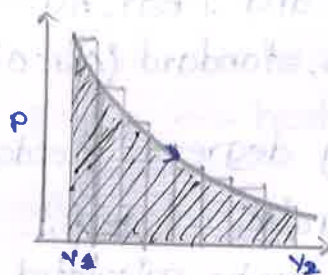
→ compression
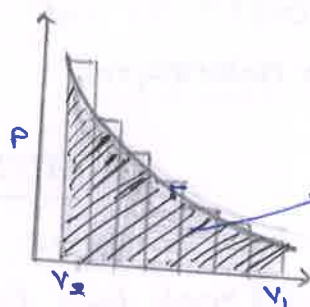
Work done
⇒ Area under curve

* Max Work done

For expansion, max work done when it reversible and for compression, when it is irreversible (obtain from P-V graph)

SI unit of Work ⇒ Joule

$$1\, Cal = 4.184\, J$$
$$1\, Latm = 101.3\, J$$
$$1\, L\, bar = 100.2\, J$$

These unit conversions are possible with different values of R.

R (Workdone per kelvin per mol)

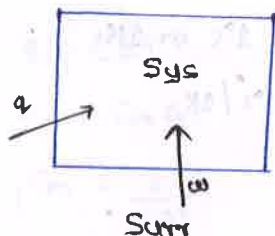* First Law of Thermodynamic (FLOT)

Law of conservation of energy

According to FLOT, energy of an isolated system remains constant. *

Mathematical expression

$$U_2 = U_1 + q + \omega$$
$$U_2 - U_1 = q + \omega$$
$$\boxed{\Delta U = q + \omega}$$

FLOT for :

(1) Isothermal

$$\Delta T = 0 \quad \therefore \Delta U = 0$$

$$\Delta U^{0} = q + W$$

$$\boxed{q = -W}$$

For an isothermal process, if q amount of heat is absorbed, U increases, $\therefore$ T also increases. But inorder to prevent the increase in T, an equal amount of work should be done by the system on its surrounding.

(2) Isochoric

$$\Delta V = 0 \qquad \therefore \omega = 0 \text{ (whether}$$
$$\Delta U = q + \omega^{0} \qquad \text{it is reversible}$$
$$\text{on irreversible)}$$

$$\boxed{\Delta U = q_V} \quad \text{heat transfered at constant volume}$$

(3) Adiabatic

$$q = 0$$
$$\Delta U = q^{0} + \omega$$

$$\boxed{W_{ad} = \Delta U}$$

$$W_{ad} = \Delta U$$

$W_{ad} = +ve$
(adiabatic compression)
$\Delta U = +ve$
$\boxed{U \uparrow \quad T \uparrow}$
(heating effect)

$W_{ad} = -ve$
(adiabatic expansion)
$\Delta U = -ve$
$\boxed{U \downarrow \quad T \downarrow}$
(cooling effect)

(4) Cyclic process

$$\Delta SF = 0$$
$$\Delta U^{0} = q + \omega$$
$$\boxed{q = -\omega}$$

(5) Isobaric process

$$\Delta P = 0 \implies P_1 = P_2$$

$$\Delta U = q + \omega$$

At constant external Pressure,

$$\omega = \omega_{irr} = -P\Delta V$$

q_p : heat transfered at constant P

$$\Delta U = q_p - P\Delta V$$
$$U_2 - U_1 = q_p - P(V_2 - V_1)$$
$$U_2 - U_1 = q_p - PV_2 + PV_1$$
$$(U_2 + PV_2) - (U_1 + PV_1) = q_p$$

Here,

$U + PV = H$ (heat content of the system known as enthalpy)

$$\therefore H_2 - H_1 = q_p$$

$$\boxed{\Delta H = q_p}$$

* Isothermal free expansion of an ideal gas

$$\begin{cases} \Delta T = 0 \\ \Delta U = 0 \end{cases}$$

Free expansion means expansion of ideal gas x vaccum.
where $P_{ext} = 0$. $\therefore \omega = 0$

$$\Delta U = \cancel{q} + \cancel{w}^{0}$$

$$\cancel{\Delta U}^{0} = q + \cancel{w}^{0}$$

$$\therefore \boxed{q = 0} \Rightarrow \text{Adiabatic}$$

Isothermal free expansion of an ideal gas must be adiabatic and viceversa.

✶ Enthalpy (H)

$$\boxed{H = U + PV}$$

↓   ↓

internal   pressure
energy   volume energy

The absolute value of H cannot be measured, but we can calculate ΔH.

$$\Delta H = \Delta U + \Delta PV$$

$$= \Delta U + P\Delta V + V\Delta P$$

At const P, $\Delta P = 0$

$$\boxed{\Delta H = \Delta U + P\Delta V}$$

✶ Relation b/w heat of reaction at constant volume ($q_V = \Delta U$) and at constant pressure ($q_p = \Delta H$)

$$aA_{(g)} + bB_{(g)} \longrightarrow cC_{(g)} + dD_{(g)}$$

Calculation of change in no. of moles is more convenient than that of volume change.

∴ At constant temperature and pressure,

$$PV_1 = n_1 RT$$

$$PV_2 = n_2 RT$$

$$P(V_2 - V_1) = (n_2 - n_1)RT$$

$$P\Delta V = \Delta n_g RT \quad ; \Delta n_g : \text{no. of moles}$$

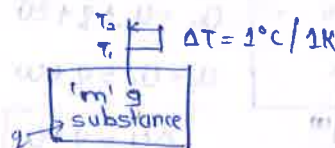$$\left\{ \Delta n_g = \Sigma n_{P_g} - \Sigma n_{R_g} \right\}$$

$$\Delta H = \Delta U + P\Delta V$$

$$\left(\Delta H = \Delta U + \Delta n_g RT \right)$$

$$\left(q_p = q_v + \Delta n_g RT \right)$$

✶ Total Heat Capacity (c)

It is the amount of heat energy required to increase temperature of an object through 1°c or 1K.

$$q \propto \Delta T$$

$$q = C \Delta T$$

$$\left(C = \frac{q}{\Delta T} \right)$$

unit : $J K^{-1}$

✶ Specific heat Capacity (s)

Heat capacity for unit mass of a substance.

$$q = C\Delta T$$

Here,

$$mg \equiv C$$

$$\Delta g \equiv \frac{C}{m} \equiv s$$

$$C = ms$$

$$q = C\Delta T \Rightarrow q = ms\Delta s$$

$$q = ms\Delta T$$

$$\left(s = \frac{q}{m\Delta T} \right)$$

unit : $J K^{-1} kg^{-1}$

Note

$$s_{H_2O} = 1 \text{ cal}$$

$$= 4.184 J$$

Molar heat capacity (C_m)

Heat capacity for 1 mole of a substance.

We know,

$$q = C\Delta T$$

$$C_m = \frac{C}{n}$$

$$C = n C_m$$

$$q = C\Delta T$$

$$q = n C_m \Delta T$$

$$\left(C_m = \frac{q}{n \Delta T} \right)$$

unit : $JK^{-1}mol^{-1}$

$$\left(q = C\Delta T = ms\Delta T = nC_m\Delta T \right)$$

$$\left(C = ms = nC_m \right)$$

* Different types of heat capacities can be defined for,

(1) Isochoric process

$$C_v \qquad S_v \qquad C_{mv}$$
$$\downarrow$$
Total HC at const V

(2) Isobaric process

$$C_p \qquad S_p \qquad C_{mp}$$
Total H.C at const P

For an isochoric process,

$$\left[\Delta U = q_v = C_v\Delta T = mS_v\Delta T = nC_{mv}\Delta T \right.$$

$$\left. \Delta H = q_p = C_p\Delta T = mS_p\Delta T = nC_{mp}\Delta T \right\}$$

∴ enthalpy can be defined at constant pressure and temperature.

$$q_v = C_v\Delta T$$

$$\left\{ C_v = \frac{q_v}{\Delta T} = \frac{\Delta U}{\Delta T} = \left(\frac{dU}{dT}\right)_v \right\}$$

$$q_p = C_p\Delta T$$

$$\left\{ C_p = \frac{q_p}{\Delta T} = \frac{\Delta H}{\Delta T} = \left(\frac{dH}{dT}\right)_p \right\}$$

* Relation b/w C_p and C_v (Mayer's relation)

For n moles of an ideal gas,

$$H = U + PV$$

$$H = U + nRT$$

$$\Delta H = \Delta U + nR\Delta T$$

$$q_p = q_v + nR\Delta T$$

$$C_p\Delta T = C_v\Delta T + nR\Delta T$$

$$\boxed{C_p - C_v = nR} \qquad C_p > C_v$$
for ideal gas

* C_p/C_v ratio (γ)

Mayer's relation,

$$C_p - C_v = nR$$

$$\frac{C_p}{C_v} - 1 = \frac{nR}{C_v}$$

$$\gamma - 1 = \frac{nR}{C_v}$$

$$\left(\gamma = 1 + \frac{nR}{C_v} \right)$$

Also, $\left(\gamma = \frac{C_p}{C_v} \right)$

Monoatomic gas (He)

For 1 mol,

$$U = \frac{f}{2}RT = \frac{3}{2}RT$$

$$\left(\frac{dU}{dT}\right)_v = \frac{3}{2}R$$

$$C_v = \frac{3}{2}R$$

For 1 md,

$C_P - C_V = R$

$C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$

$$\left(\gamma_{mono} = \frac{C_P}{C_V} = \frac{5}{3}\right)$$

Diatomic gas (H_2)

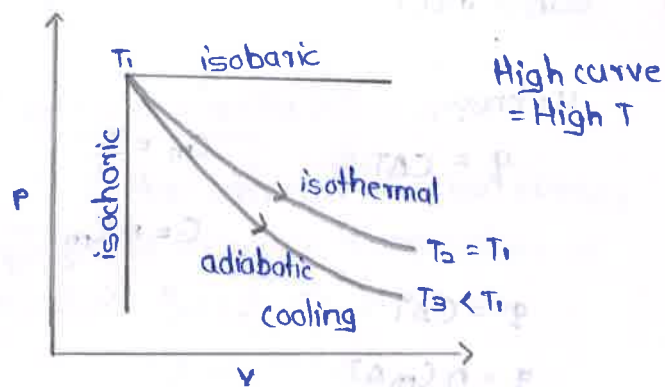$U = \frac{5}{2}RT$

$C_V = \frac{5}{2}RT$

$C_P = \frac{7}{2}RT$

$$\left(\gamma_{dia} = \frac{C_P}{C_V} = \frac{7}{5}\right)$$

* Workdone during adiabatic expansion

$q = 0$

$\Delta U = q + \omega$

$W_{ad} = \Delta U = q_v = C_V \Delta T$

$\qquad\qquad C_V = \frac{nR}{\gamma - 1}$

```
    ↓            ↓
  W=+ve       W=-ve
ad·compr     ad·exp
```

$= m s_v \Delta T$

$= n C_{mv} \Delta T$

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

$= \frac{nR}{\gamma - 1}\left(\frac{P_2 V_2}{nR} - \frac{P_1 V_1}{nR}\right)$

$= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$

$$\left(W_{ad} = \frac{\Delta(PV)}{\gamma - 1}\right)$$

For any adiabatic reversible process

$$\left\{\begin{array}{l} PV^{\gamma} = k \\ TV^{\gamma - 1} = k \\ TP^{\frac{1-\gamma}{\gamma}} = k \end{array}\right\}$$

* Graphical representation of thermodynamic process

$$\left\{\begin{array}{l} W_{isothermal} > W_{adiabatic} \\ \Delta U_{iso} = 0 \\ \Delta U_{ad} = -ve \ (Cooling \ T\downarrow U\downarrow) \end{array}\right\}$$

STUDY material

① option (3)

② option (2)

③ $W_{irr} = -P_{ext} \Delta V$

$= -10^5 \ Nm^{-2}(10^{-2}m^3 - 10^{-3}m^3)$

$= -10^5 \ Nm^{-2} \times 10^{-3} m \ (0.9)$

$= -0.9 \times 10^2 J$

$= -0.9 \ KJ$

④ option (3)

⑤ $C_7H_{16} + 11O_2 \longrightarrow 7CO_2 + 8H_2O$

$\quad (1) \qquad (9) \qquad\qquad (9) \qquad (8)$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta H - \Delta U = \Delta n_g RT$

$\Delta H - \Delta U = -4RT$

$\Delta n_g = 7 - 11$
$= -4$

⑪ 300J

④ $W_{ABCD} = W_{AB} + W_{BC} + W_{CD}$

$\quad = W_{AB_{ITT}} + W_{BC_{TEV}} + W_{CD_{ITY}}$

$\quad = (-P_{ext} \Delta V)_{AB} + \left(-nRT \ln \frac{V_2}{V_1}\right)_{BC}$

$\quad\quad + (-P_{ext} \Delta V)_{CD}$

$\quad = -P_o(2V_o - V_o) - nRT \ln \frac{4V_o}{2V_o}$

$\quad\quad -\frac{P_o}{2}(4V_o - 4V_o)$

boyle's law
$P_o \ 2V_o \to 4V_o$
$P_o \to \frac{P_o}{2}$

$\quad = P_o V_o - P_o 2V_o \ln 2$

$\quad\quad + P_o V_o$

$\quad = -2P_o V_o \ln 2$

$\quad = -2P_o V_o \ln 2$

⑮ $W_{ITT} = -P_{ext} \Delta V$

$\quad = -4 Nm^{-2}(1m^3 - 5m^3)$

$\quad = 16 J$

$\Delta v^{0} = q + \omega$
isothermal

$q = -\omega$

$q = -16 J$ (16J of heat is released into 1 mol Al)

$q = nC_m \Delta T$

$16 = 1 \times 24 \times \Delta T$

$\Delta T = \frac{16}{24} = \frac{2}{3} K$

⑯ (A)   free expansion $\to P_{ext} = 0$
isothermal
$T \to constant$

⑲ Work done = Area of circle

$\quad = \pi \left(\frac{P_2 - P_1}{2}\right)^2$

$\quad = \pi \left(\frac{V_2 - V_1}{2}\right)^2$

$\quad = \pi \left(\frac{P_2 - P_1}{2}\right)\left(\frac{V_2 - V_1}{2}\right)$

$\quad = \frac{\pi}{4}(P_2 - P_1)(V_2 - V_1)$

---

* Thermochemistry
(Application of FLOT)

Measurement of ΔH and ΔU
(calorimetry)

$\Rightarrow$ Measurement of ΔU (q_v)

since, $\Delta U = q_v$

We need a constant volume calorimeter such as bomb calorimeter in which bomb is steel closed vessel immersed in m gram water (specific heat of water = 1 Cal = 4.184J).

The water present inside calorimeter is associated with a thermometer (to measure ΔT) and a stirrer (uniform distribution of heat).

Assuming the heat of reaction completely absorbed by bomb or completely transferred into water.

Then,

$\begin{cases} \Delta U = q_v = -C_v \Delta T \\ \quad\quad\quad or \\ \Delta U = q_v = -ms \Delta T \end{cases}$

If a part of heat still absorbed by the bomb, then,

$q_{reaction} = q_{bomb} + q_{water}$

(Energy conservation)

$\Delta U = q_v = -[C_v \Delta T + ms \Delta T]$

$\boxed{\Delta U = q_v = -[C_v + ms] \Delta T}$

$C_v \to$ heat capacity
of bomb calorimeter

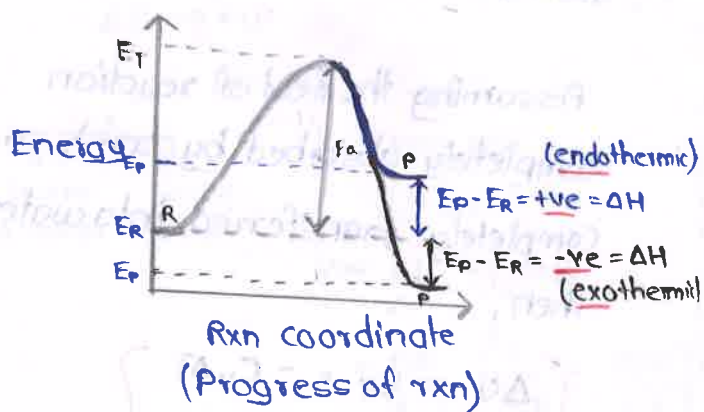ΔU is always reported for 1 mole unless otherwise mentioned.

⇒ **Measurement of ΔH (q_p)**

Since $\Delta H = q_p$, heat transferred at constant pressure, we need constant pressure calorimeter such as coffee cup calorimeter usually made up of polystyrene.

By knowing the value of C_p for coffee cup calorimeter, we can calculate ΔH of the reaction by the equation,
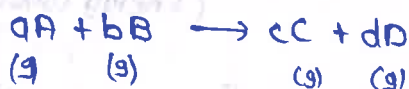
$$\boxed{\Delta H = C_p \Delta T}$$

* Endothermic and Exothermic rxn

Rxn coordinate
(Progress of rxn)

$E_p - E_R = +ve = \Delta H$ (endothermic)

$E_p - E_R = -ve = \Delta H$ (exothermic)

* Enthalpy of a rxn ($\Delta_r H$)

It is the enthalpy change associated with a chemical rxn. For a hypothetical rxn,

$$aA + bB \longrightarrow cC + dD$$
$$\text{(g)} \quad \text{(g)} \qquad \text{(g)} \quad \text{(g)}$$

$$\boxed{\Delta_r H = \Sigma H_P - \Sigma H_R} \quad —— ①$$

Under standard conditions,

$$\boxed{\Delta_r H^\ominus = \Sigma H_P^\ominus - \Sigma H_R^\ominus} \quad —— ②$$

+ve (endo)   −ve (exo)

Variation of ΔH for a reaction at two different temperatures T_1 and T_2 given by eq,

$$\boxed{\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_p \Delta T}$$

$$\Delta C_p = \Sigma C_{P_P} - \Sigma C_{P_R}$$

$$\boxed{\Delta U_{T_2} - \Delta U_{T_1} = \Delta C_V \Delta T}$$

$$\Delta C_V = \Sigma C_{V_P} - \Sigma C_{V_R}$$

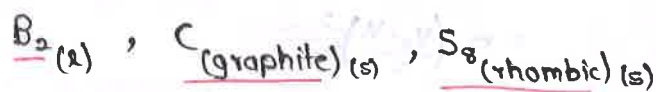These two eq are known as Kirchoff's equation.

* Standard enthalpy of formation ($\Delta_f H$) (1)

[can be −ve or +ve]

It is the ΔH when

1 mole of product formed from their constituent elements in their standard or reference state.

Standard or reference state of some elements

$F_{2(g)}$, $I_{2(s)}$, $Fe_{(s)}$, $Hg_{(l)}$,

$B_{2(l)}$, $C_{(graphite)(s)}$, $S_{8(rhombic)(s)}$

↓

$\Delta H = 369$

$$\left\{ \Delta_f H^{\ominus} \begin{bmatrix} \text{element in their} \\ \text{standard state} \end{bmatrix} = 0 \right\}$$
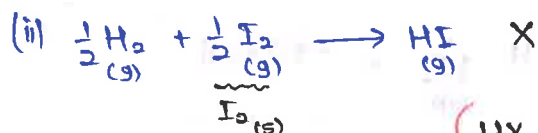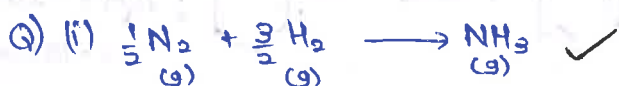
ie, If $\Delta_f H^{\ominus}$ is 0, the element in their standard reference state.
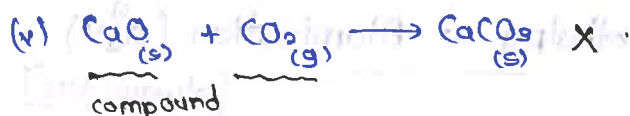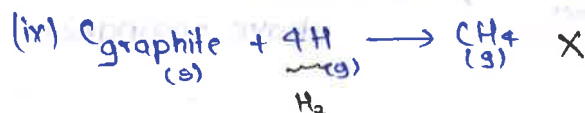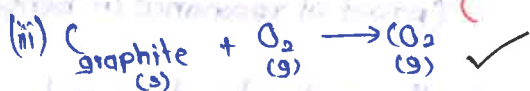
Note

$\Rightarrow$ Even though, red phosphorus is more stable than white, Thermodynamically most stable form of phosphorus is black.

Byut, $\Delta_f H^{\ominus}$ is 0 for white.

$\Rightarrow \Delta H_f^{\ominus} (H^+_{aq}) = 0$

Q) (i) $\frac{1}{2} N_2{}_{(g)} + \frac{3}{2} H_2{}_{(g)} \longrightarrow NH_3{}_{(g)}$ ✓

(ii) $\frac{1}{2} H_2{}_{(g)} + \frac{1}{2} \underbrace{I_2{}_{(g)}}_{I_2{}_{(s)}} \longrightarrow HI_{(g)}$ ✗

$\left. \begin{array}{c} \\ \\ \end{array} \right\}$ HX$_{(g)}$ except HF$_{(\ell)}$
$\downarrow$
H-bonding

(iii) $C_{graphite}{}_{(s)} + O_2{}_{(g)} \longrightarrow CO_2{}_{(g)}$ ✓

(iv) $C_{graphite}{}_{(s)} + \underbrace{4H_{(g)}}_{H_2} \longrightarrow CH_4{}_{(g)}$ ✗

(v) $\underbrace{CaO_{(s)}}_{compound} + \underbrace{CO_2{}_{(g)}}_{} \longrightarrow CaCO_3{}_{(s)}$ ✗
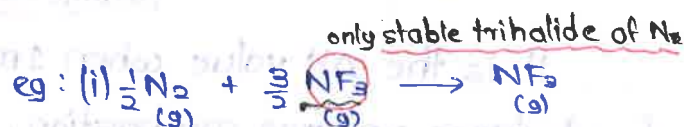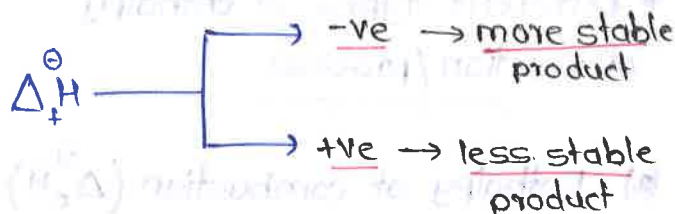
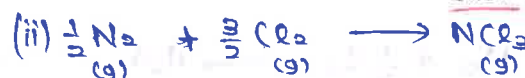If $\Delta_f H^{\ominus}$ of products and reactants are given,

$$\left\{ \Delta_r H^{\ominus} = \sum \Delta_f H_P^{\ominus} - \sum \Delta_f H_R^{\ominus} \right\}$$

For eq (i) and (iii),

$\Delta_r H^{\ominus} = \Delta_f H_P^{\ominus}$

$\Delta_f H \left[\begin{array}{c} \\ \end{array} \right]$
→ −ve → more stable product
→ +ve → less stable product

only stable trihalide of N₂

eg: (i) $\frac{1}{2} N_2{}_{(g)} + \frac{3}{2} F_2{}_{(g)} \longrightarrow \overset{\text{only stable trihalide of N}_2}{NF_3{}_{(g)}}$

$\Delta_f H^{\ominus} = -ve$
(stable)
exothermic compd

(ii) $\frac{1}{2} N_2{}_{(g)} + \frac{3}{2} Cl_2{}_{(g)} \longrightarrow NCl_3{}_{(g)}$

$\Delta_f H^{\ominus} = +ve$
(less stable)
endothermic compd

* Thermochemical equation

Chemical equations in balanced form with all the reactants and products are in their respective physical state along with thermodynamic data.

eg: $CH_4{}_{(g)} + 2O_2{}_{(g)} \longrightarrow CO_2{}_{(g)} + 2H_2O_{(\ell)}$

$\Delta H = -890.3$ KJ/mol

$A_{(g)} \longrightarrow B_{(g)}$ $\Delta H^{\ominus} = a \times$ KJ —①

① $\times n$; $nA_{(g)} \longrightarrow nB$ $\Delta H^{\ominus} = nx$ KJ

① $\div n$; $\frac{1}{n}A_{(g)} \longrightarrow \frac{1}{n}B_{(g)}$ $\Delta H^{\ominus} = \frac{x}{n}$ KJ

①$^{-1}$; $B_{(g)} \longrightarrow A_{(g)}$ $\Delta H^{\ominus} = -x$ KJ

also,

$B_{(g)} \longrightarrow C_{(g)} + D_{(g)}$: $\Delta H^{\ominus} = -y$ KJ —②

①+②, $A_{(g)} \longrightarrow C_{(g)} + D_{(g)}$ $\Delta H^{\ominus} = x+y$ KJ
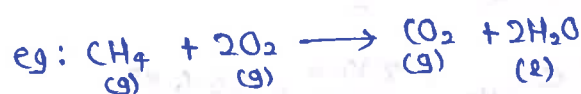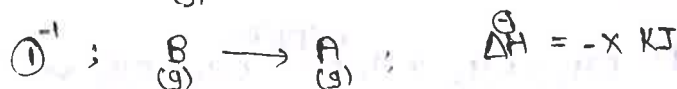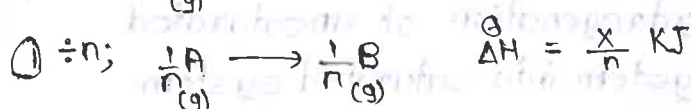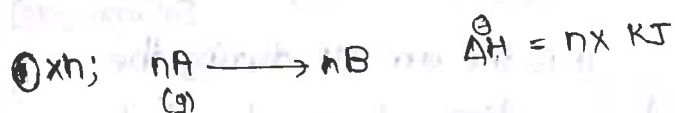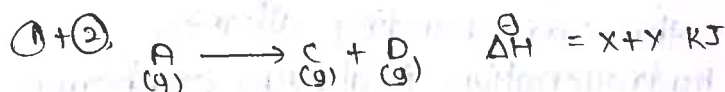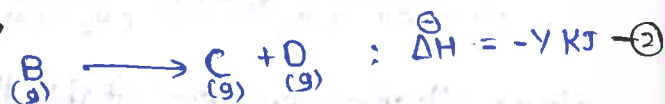
* **Different types of enthalpy of reaction / process**

$$\left\{ \Delta_h H^{\ominus} \propto \frac{1}{\text{stability of alkenes}} \right\}$$

(1) Enthalpy of combustion $(\Delta_c H^{\ominus})$
[always -ve]

It is the ΔH value when 1 mole of substance undergo combustion.
[exothermic (always -ve)].

eg: $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$

$$\Delta_c H^{\ominus} = -286 \text{ KJ/mol}$$

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$$\Delta_c H^{\ominus} = -890.3 \text{ KJ/mol}$$
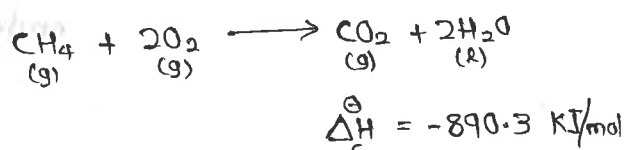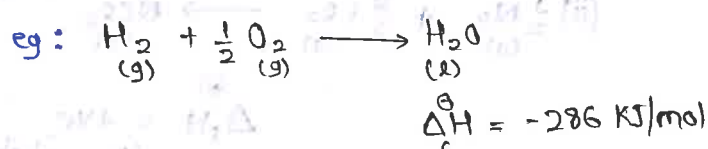
Calorific Value / Fuel Value

$$\left\{ CV = \frac{|\Delta_c H^{\ominus}|}{\text{molar mass}} \right\}$$

eg: $CV_{H_2} = \frac{286}{2} = 143 \text{ KJ}$

$CV_{CH_4} = \frac{890.3}{16} = 55.6 \text{ KJ}$

[Efficiency of fuel $\propto$ CV value]

(3) Enthalpy of Hydrogenation $(\Delta_h H^{\ominus})$
[always -ve]

It is the an ΔH during the hydrogenation of unsaturated system into saturated system.

eg: $\underset{\substack{\text{unsaturated}\\\text{(less stable)}}}{CH_2=CH_2} + H_2 \xrightarrow{Ni/Pd/Pt} \underset{\substack{\text{unsaturated}\\\text{(more stable)}}}{CH_3-CH_3}$ ✓
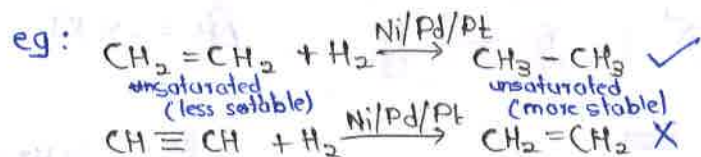
$CH \equiv CH + H_2 \xrightarrow{Ni/Pd/Pt} CH_2=CH_2$ ✗

since alkenes are less stable than the corresponding alkanes, hydrogenation is always exothermic

$$\left\{ \begin{array}{l} \text{Stability of alkene } \propto \text{ no. of} \\ \text{hyperconjugation} \\ \text{ano. of } \alpha\text{-H} \end{array} \right\}$$

Resonance Enthalpy $(\Delta_{res} H^{\ominus})$
[always -ve]

$$\left(\Delta_{res} H^{\ominus} = \underset{\text{theoretical}}{\Delta_h H^{\ominus}} - \underset{\text{experimental}}{\Delta_h H^{\ominus}} \right)$$

eg:

 $+ H_2 \longrightarrow$; $\Delta_h H^{\ominus} = -25$ KCal

 $+ 3H_2 \longrightarrow$; $\Delta_h H^{\ominus} = -25\times3$
$= -75$ KCal
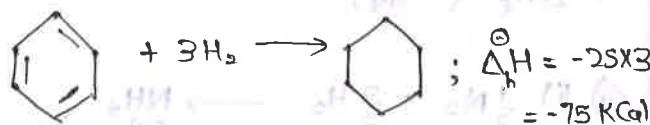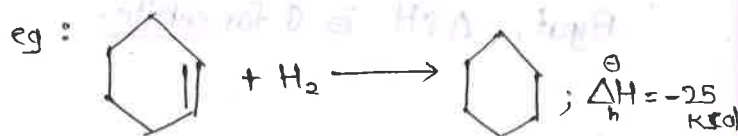
$\Delta_h H^{\ominus}$ $_{exp} = -40$ Kcal

$\Delta_{res} H^{\ominus} = -75 - (-40) = -35$ Kcal

(proof of resonance in benzene)

If $\Delta_{res} H^{\ominus} = 0$, the molecule does not have resonance

(4) Enthalpy of Atomisation $(\Delta_a H^{\ominus})$
[always +ve]

$$\Delta_a H^{\ominus}$$

sublimation enthalpy	Bond dissociation enthalpy
$(\Delta_{sub} H^{\ominus})$	$(\Delta_{bond} H^{\ominus} / BDE)$

eg: $Na(s) \longrightarrow Na(g)$

$\Delta_{sub} H^{\ominus} = +108.3 \text{ KJ}$

eg: $H-H(g) \longrightarrow 2H(g)$

$\Delta_{bond} H^{\ominus} = +435.8 \text{ KJ/mol}$
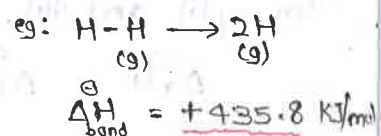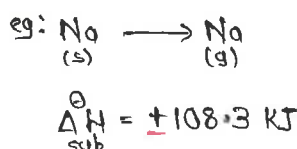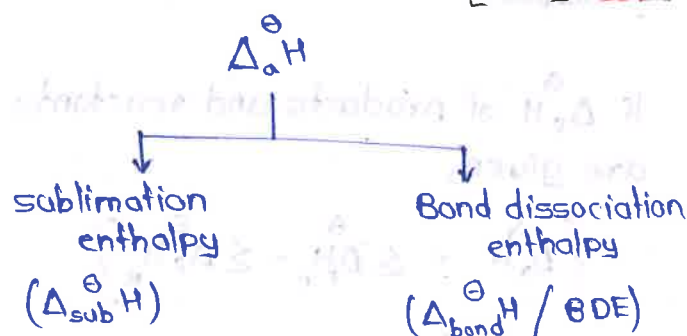
For polyatomics, the term average or mean bond enthalpy is used because the different bonds present in a polyatomic molecule shows different bond enthalpy due to different electronic environment.

eg: CH_4.

$a \neq b \neq c \neq d$

$(CH_4 \xrightarrow{(g)} C_{(g)} + 4H_{(g)})$; $\Delta_{bond}^{\ominus} H = 1660 \, kJ/mol$
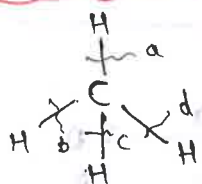
$$\text{Average/Mean BE} = \frac{1660}{4}$$
(for polyatomic)
$$= 415 \, kJ\,mol^{-1}$$

V.IMP

If BE are given,

$$\left(\Delta_r H^{\ominus} = \Sigma BE_R - \Sigma BE_P \right)$$

If $\Delta_c H^{\ominus}$ of reactants and products are given,

$$\left(\Delta_r H^{\ominus} = \Sigma \Delta_c H_R^{\ominus} - \Sigma \Delta_c H_P^{\ominus} \right)$$

eg: $N_2 + 3H_2 \longrightarrow 2NH_3$

OR

$N \equiv N + 3[H-H] \longrightarrow 2 \; \ddot{N}$
$\qquad\qquad\qquad\qquad / | \backslash$
$\qquad\qquad\qquad\qquad H \; H \; H$

$$\Delta_r H^{\ominus} = \left[1 \times BE_{N \equiv N} + 3 \times BE_{H-H} \right] - \left[2 \times 3 \times BE_{N-H} \right]$$

(5) Enthalpy of Allotropic transformation $(\Delta_{allo}^{\ominus} H)$

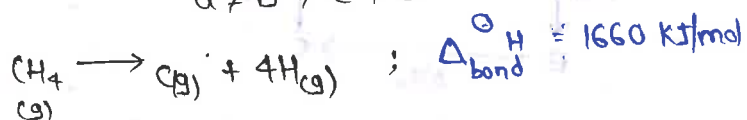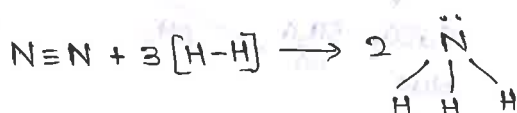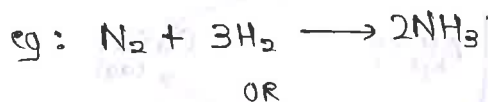[may be +ve or -ve]

eg: $C_{graphite,s} \longrightarrow C_{diamond,s}$; $\Delta H = +ve$
more stable   less stable

$C_{diamond,s} \longrightarrow C_{graphite,s}$; $\Delta H = -ve$
less stable   more stable
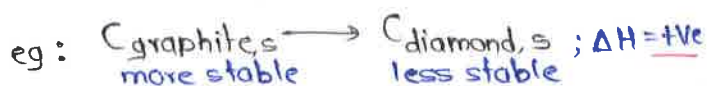
(6) Enthalpy of Phase Transitions

[always +ve]

(i) Enthalpy of fusion $(\Delta_{fus}^{\ominus} H)$

It is the ΔH during the fusion of 1 mole of solid into its liquid form at its normal melting point. (melting point measured at 1 atm).

eg: $H_2O_{(s)} \rightleftharpoons H_2O_{(\ell)}$

N.B.P. at 0°C and 1 atm (at equilibrium)
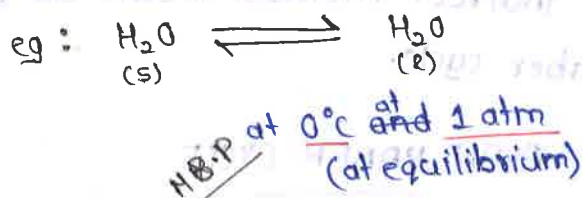
(ii) Enthalpy of vapourisation $(\Delta_{vap}^{\ominus} H)$

eg: $H_2O_{(\ell)} \rightleftharpoons H_2O_{(g)}$

B.P. at 100°C at 1 atm (equilibrium)
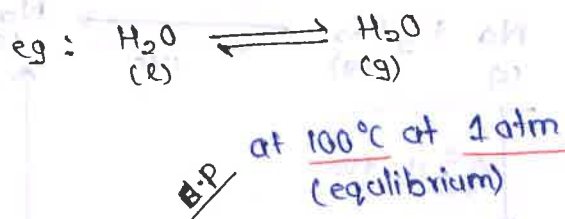
(iii) Enthalpy of sublimation $(\Delta_{sub}^{\ominus} H)$

eg: $I_{2(s)} \rightleftharpoons I_{2(g)}$

at its normal sublimation point (equilibrium)
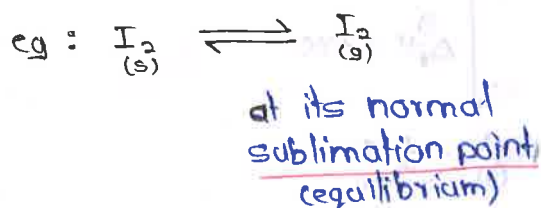
(7) Enthalpy of Solution $(\Delta_{sol}^{\ominus} H)$

[can be +ve or -ve]

Lattice enthalpy $(\Delta_{lattice}^{\ominus} H)$

+ve   -ve

eg: $NaCl_{(g)} \longrightarrow Na^+_{(g)} + Cl^-_{(g)}$

$\Delta H_{lattice}^{\ominus} = +788 \, kJ/mol$

Hydration enthalpy $(\Delta_{hyd}^{\ominus} H)$

always -ve

eg:
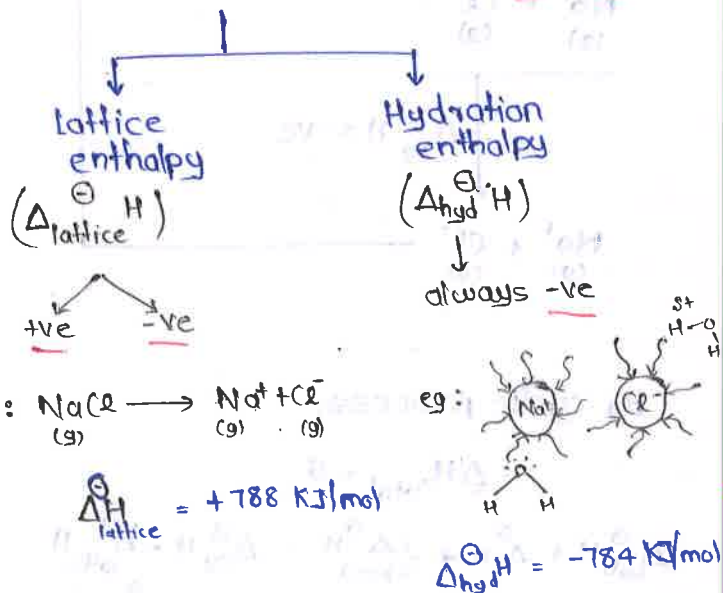
$\Delta_{hyd}^{\ominus} H = -784 \, kJ/mol$

$$\left\{ \Delta_{sol}^{\ominus} H = \Delta H_{lattice} + \Delta_{hyd}^{\ominus} H \right\}$$

$$= 788 + -784$$

$$= +4 \text{ KJ/mol (endothermic)}$$

The measurement of Lattice enthalpy is very difficult. Therefore, we adopt an indirect method known as Born Haber cycle.

BORN HABER CYCLE

eg : NaCl

$$\Delta_f H = -ve$$

$$Na_{(s)} + \tfrac{1}{2} Cl_{2 (g)} \xrightleftharpoons[+ve]{} NaCl_{(s)}$$

$$\Delta_{sub}^{\ominus} H = +ve$$

$$Na_{(g)} + \tfrac{1}{2} Cl_{2 (g)}$$

$$\Delta_i^{\ominus} H = +ve$$

$$Na^{+}_{(g)} + \tfrac{1}{2} Cl_{2 (g)}$$

$$\tfrac{1}{2} \Delta_{bond}^{\ominus} H = +ve$$

$$Na^{+}_{(g)} + Cl_{(g)}$$

$$\Delta_{eg}^{\ominus} H = -ve$$

$$Na^{+}_{(g)} + Cl^{-}_{(g)}$$
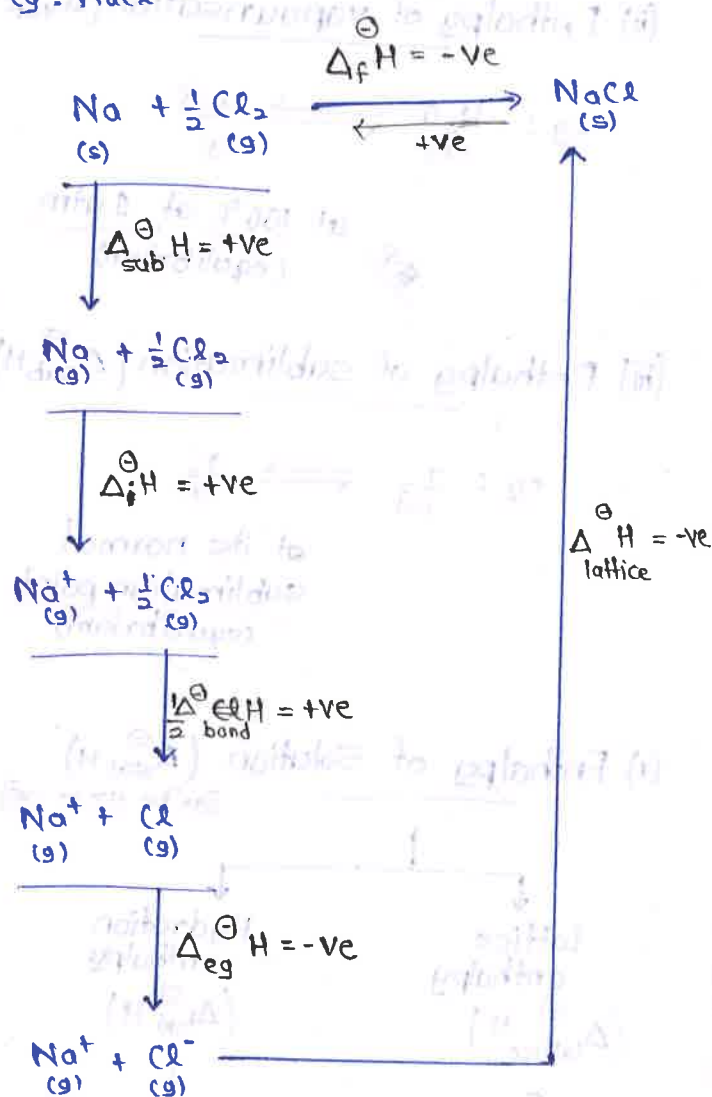
$$\Delta_{lattice}^{\ominus} H = -ve$$

By cyclic process,

$$\Delta H_{Total} = 0$$

$$\Delta_{sub}^{\ominus} H + \Delta_i^{\ominus} H + \tfrac{1}{2}\Delta_{bond}^{\ominus} H - \Delta_{eg}^{\ominus} H - \Delta_{lattic}^{\ominus} H$$

$$\ldots \Delta^{\ominus} H = 0$$

$$\left\{ \therefore \Delta_{lattice}^{\ominus} H = \Delta_{sub}^{\ominus} H + \Delta_i^{\ominus} H + \tfrac{1}{2}\Delta_{bond}^{\ominus} H - \Delta_{eg}^{\ominus} H + \Delta_f^{\ominus} H \right\}$$

HESS'S LAW OF CONSTANT HEAT SUMMATION
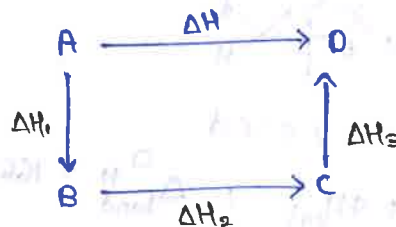
By Hess'law,

$$\boxed{\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3}$$

$$H = \Delta H_1 + H_2 + H_3 \quad \times$$

By cyclic process,

$$\Delta H_{total} = 0$$

$$\Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H = 0$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

eg :

$$CuSO_{4 (s)} \text{ white} \xrightarrow{\Delta H_1} CuSO_{4 (aq)}$$

$$\Delta_{hyd} H = ?$$

$$CuSO_4 \cdot 5H_2O_{(s)} \text{ blue} \xrightarrow{\Delta H_2}$$
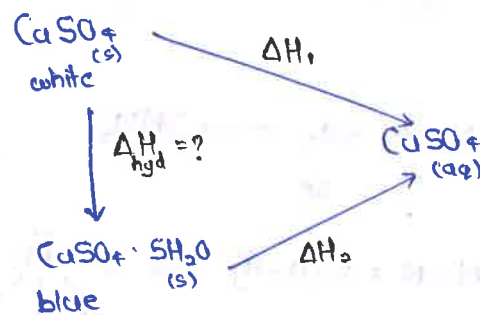
•By Hess's law,

$$\Delta H_1 = \Delta H_{hyd} + \Delta H_2$$

$$\boxed{\Delta H_{hyd} = \Delta H_1 - \Delta H_2}$$

AIM :

$$HCl \cdot 25 \, aq + 15aq \longrightarrow HCl \cdot 40aq$$
$$\Delta H = ?$$

$$\textcircled{2}^{-1} + \textcircled{3} \Rightarrow \Delta H = 72 \cdot 03 - 72 \cdot 74 \, KJ$$
$$= -0 \cdot 71 \, KJ/mol$$

$\Rightarrow$ Enthalpy of dilution depends upon :

    (i) Original concentration of stock solution.

    (ii) Amount of solvent added.

$*$ Ionisation energy and electron affinity

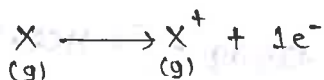Ionisation energy Vs Ionisation enthalpy
$$(IE) \qquad\qquad (\Delta_i H)$$
$$\downarrow \qquad\qquad\qquad \downarrow$$
measured at $\underline{0K}$ measured at TK
$$\qquad\qquad\qquad\qquad\quad (T \neq 0)$$

For monoatomic gas,

$$X_{(g)} \longrightarrow X^+_{(g)} + 1e^-$$

$$\cdot \; \Delta_i H = IE + \int_0^T Cp \, dT$$

    For monoatomic gas, $Cp = \frac{5}{2}R$
    but it is a function of T.

$$\left\{ \Delta_i H = IE + \int_0^T \frac{5}{2}R \, dT \right\}$$

Assuming Cp remains constant within a Temp range of 0 to T K,

$$\left(\Delta_i H = IE + \frac{5}{2}RT \right)$$

At room temperature, $\frac{5}{2}R$ is very small.

$$\boxed{\Delta_i H = IE}$$

Electron gain enthalpy Vs Electron affinity
$$(\& \Delta_{eg} H) \qquad\qquad (EA)$$
$$\downarrow \qquad\qquad\qquad \downarrow$$
$$TK \qquad\qquad\qquad 0K$$
$$(T \neq 0)$$

$$\left\{ \Delta_{eg} H = -EA - \frac{5}{2}RT \right\}$$

At room temperature,

$$\boxed{\Delta_{eg} H = -EA}$$

    (contradiction to T.D,
    energy absorption $\Rightarrow$
$$EA = -ve$$
    energy release $\Rightarrow$
$$EA = +ve$$

$*$ Limitation of FLOT

$\rightarrow$ Failed to explain whether a process is spontaneous or not.

STUDY MATERIAL

$\textcircled{6} \quad \Delta_r H = \sum \Delta_f H_P - \sum \Delta_f H_R$

$$= \& \left[\Delta_f^\ominus H \, (Al_2O_3) + \Delta_f^\ominus H_{(Cr)} \atop (s) \qquad\qquad (s) \right]$$

$$- \left[2\Delta_f^\ominus H_{(Al_s)} + \Delta_f H \, (Cr_2O_3) \atop \qquad\qquad\qquad (s) \right]$$

$$= \left[-1596 + 2\times0 \right] - \left[2\times0 - 1134 \right]$$

$$= -462 \, KJ$$

(8) Enthalpy of Neutralisation ($\Delta_n H$)

[always -ve]

1eq SA + 1eq SB ⟶ always release 57.1 KJ of heat

$$\left(\Delta_n^\ominus H_{(SA+SB)} = -57.1 \text{ KJ}\right)$$

OR

$$\left(\Delta_n^\ominus H_{(H^+ + OH^-)} = -57.1 \text{ KJ/mol of } H_2O \text{ formed}\right)$$

$$\begin{cases} N = \dfrac{n_{eq}}{V} \\ n_{eq} = N \times V \\ n_{eq} = n\text{-factor} \times \text{no. of moles} \\ N = n\text{-factor} \times M \end{cases}$$

If the neutralisation involves weak acid or weak base, the energy released after neutralisation will be less than 57.1 KJ because a part of the energy will be used for the dissociation or ionisation of weak electrolyte.

Even though HF is a weak acid, The amount of energy released from the rxn btw HF and NaOH will be 68 KJ because of high hydration enthalpy of small F^- ion.
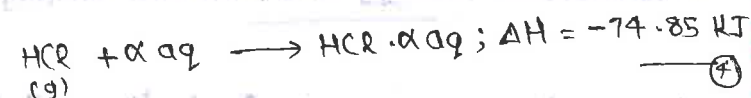
$$\underbrace{HF_{(\ell)}}_{\substack{weak \\ acid}} \quad \underbrace{HCl_{(g)} \; HBr_{(g)} \; HI_{(g)}}_{\substack{strong \\ acid}}$$
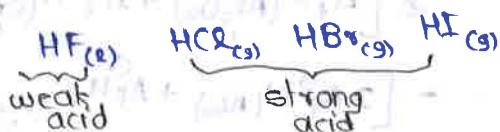
(9) Dilution Enthalpy ($\Delta_{dil} H$)

[always -ve]

It is the ΔH when a solution having particular concentration undergo dilution into solution having another concentration.

eg: Acid dilution

Preparation of stock solution:

$$HCl_{(g)} + 10\,aq \longrightarrow HCl \cdot 10\,aq \; ; \Delta H = -69.01 \text{ KJ/mol} \quad ①$$

$$HCl_{(g)} + 25\,aq \longrightarrow HCl \cdot 25\,aq \; ; \Delta H = -72.08 \text{ KJ} \quad ②$$

$$HCl_{(g)} + 40\,aq \longrightarrow HCl \cdot 40\,aq \; ; \Delta H = -72.72 \text{ KJ} \quad ③$$

$$HCl_{(g)} + \alpha\,aq \longrightarrow HCl \cdot \alpha\,aq \; ; \Delta H = -74.85 \text{ KJ} \quad ④$$

AIM :

$$HCl \cdot 10\,aq + 15\,aq \longrightarrow HCl \cdot 25\,aq \quad \Delta H = ?$$

$$①^{-1} \Rightarrow HCl \cdot 10\,aq \longrightarrow HCl_{(g)} + 10\,aq$$
$$\Delta H = +69.01 \text{ KJ} \quad —ⓐ$$

$$② \Rightarrow HCl_{(g)} + 25\,aq \longrightarrow HCl \cdot 25\,aq$$
$$\Delta H = -72.03 \text{ KJ} \quad —ⓑ$$

$$ⓐ+ⓑ \Rightarrow HCl \cdot 10\,aq + 15\,aq \longrightarrow HCl \cdot 25\,aq$$
$$\Delta H = 69.01 + -72.03$$
$$= -3.02 \text{ KJ/mol}$$
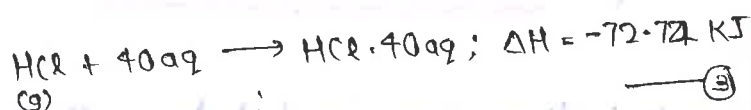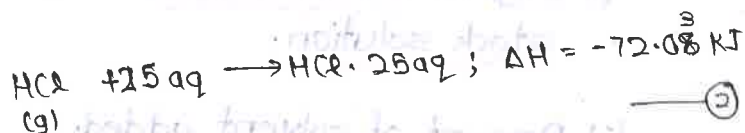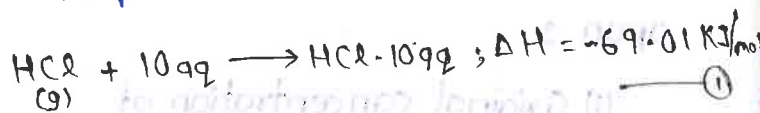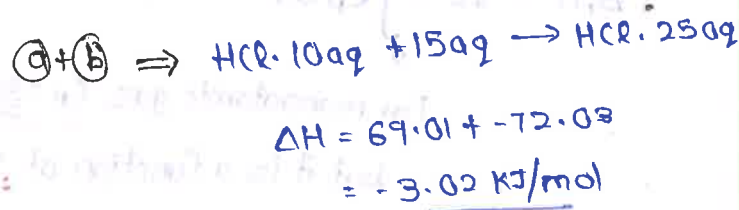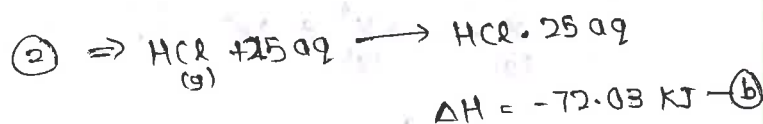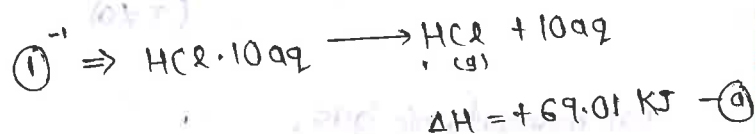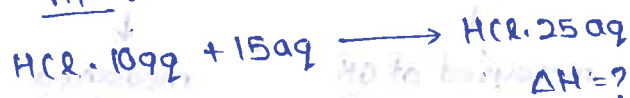
If one species is present in more than one equation, neglect it.

OR

aim: $2Al + Cr_2O_3 \longrightarrow 2Cr + Al_2O_3$

Given,

$2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3$

$\Delta H = -1596 \, KJ$

$2Cr + \frac{3}{2}O_2 \longrightarrow Cr_2O_3$

$\Delta H = -1134 \, KJ$

$① + ②^{-1} = -1596 + 1134 = -462 \, KJ$

⑦ $2C + 3H_2 \longrightarrow C_2H_6$

$\Delta H = \sum \Delta^\ominus_{comb} H \, {}_R - \sum \Delta^\ominus_{comb} H \, {}_P$

$= \left(2 \times \Delta_c^\ominus H_c + 3 \Delta_c^\ominus H_{H_2} \right)$

$- \left(\Delta_c^\ominus H_{C_2H_6} \right)$

$= \left(2 \times -393.5 + 3 \times -286 \right) - (-1560)$

$= -85 \, KJ/mol$

⑧ $\Delta_{sol}^\ominus H = 788 + -784 = 4 \, KJ/mol$

⑫ $C + O_2 \longrightarrow CO_2 \qquad \Delta H = -X \quad —①$

$CO + \frac{1}{2}O_2 \longrightarrow CO_2 \quad \Delta H = -Y \quad —②$

aim: $C + \frac{1}{2}O_2 \longrightarrow CO$
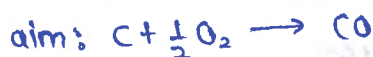
$① + ②^{-1} \Rightarrow \Delta H = -X + Y$

$= ax + by$

$a = -1, \quad b = 1$

$|a+b| = 0 /\!/$

⑬ $16g \, CH_4 = 890 \, KJ$ released

$1g \, CH_4 = \frac{890}{16} \, KJ$

$3.2g \, CH_4 = \frac{890}{16} \times 3.2 = 178 \, KJ$

⑳ $250 \, W = 250 J/s$

Power of heater $= 250 J/s$

$1s \longrightarrow 250 \, J$

$55 s \longrightarrow 250 \times 55 \, J$

$= 13750 \, J$

$= 13.75 \, KJ$

$\Delta T = 4.22°C = 4.22 K$

$\therefore q = C \Delta T$

$C = \frac{q}{\Delta T} = \frac{13750}{4.22}$

Oxidn of methanol $\Rightarrow$ combustion

$\Delta T = T_2 - T_1 = 26.77 - 22.49$

$= 4.28 °C$

$q = C \Delta T$

$= \frac{13750}{4.22} \times 4.28$

$= 13.75 \, KJ = 13.9 \, KJ$

But enthalpy change of oxidn
= enthalpy of combustion
$= -13.9 \, KJ$

Ans : (A)

㉓ (A) $\Delta_r H° = \Delta_f H°$

(B) 2 mol prdt

(C) 2 mol prdt, not constituent element

(D) monoclinic $\times$
        rhombic

㉔ $C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$
         (ℓ)   (g)   (g)   (ℓ)
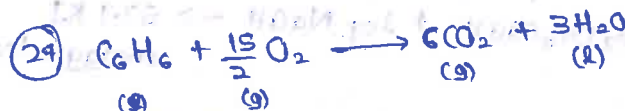
Given, $q_v = \Delta U = -321 \, KJ$
for $7.8g \, C_6H_6$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = 6 - 7.5 = \frac{-3}{2}$

$\Delta H = -327 \times 10^3 + \frac{-3}{2} \times 8.314 \times 300$

$= -327000 + -3 \times 4.157 \times 300$

$= -327000 - 3741.3$

$= -330741.3 \, J = -330.7413 \, KJ$

~~wrong~~

Magnitude $= 330.74 \, KJ$

$C_6 H_6$
$78g$

Energy released at const $V =$

$q_v = 327 \, KJ$

for $7.8g \, C_6H_6$

$\Delta U = -327 \, KJ$ for $7.8g \, C_6H_6$

$\Delta U = -3270 \, KJ$ for $78g \, C_6H_6$
(1 mol)

$\Delta H = -3270600 - \frac{3}{2} \times 8.314 \times 300$

$= -3270000 - 3741.3$

$= -3273741.3 \, J$

$= -3273.7 \, KJ$ for $1 \, mol \, (78g)$

$= -327.37 \, KJ$ for $(7.8g)$

Ans : -327.37

n-factor $=1$
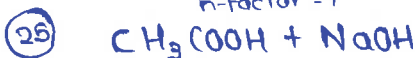
② CH$_3$COOH + NaOH
200 ML   400 mL
0.6 M   0.8 M
↓   ↓
200 mL   400 mL
$1 \times 0.6 = 0.6 N$ $1 \times 0.8 = 0.8N$

$n_{eq} = N \times V$ 400×0.8
$= 200 \times 0.6$ $= 320 \, meq$
$= 120 \, meq$
(L.R)

$1eq \, CH_3COOH + 1eq \, NaOH \Rightarrow 57.1 \, KJ$
energy release
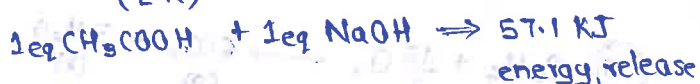
$120 \, meq \, CH_3COOH + 120 \, meq \, NaOH$
$\Rightarrow 57.1 \times 120 \times 10^{-3} \, KJ$
$= 6.852 \, KJ$
energy released

Dissociation energy of CH$_3$COOH

$= 17.1 \, KJ/mol$ for $1eq$

$= 17.1 \times 120 \times 10^{-3}$ for $120 \, meq$

⊗ $= 2.052 \, KJ$

$\Delta_n^\Theta H (CH_3COOH + NaOH) \begin{array}{l} = 6.852 - 2.052 \\ = 4.8 \, KJ \end{array}$

㉗ $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$
(g)   (g)   (g)   (g)
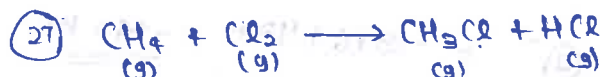
$\Delta H = -25 \, KCal$

$\Delta_r H = \sum BE_R - \sum BE_P$

$= \left[4 \times BE_{CH} + 1 BE_{Cl-Cl} \right]$

$\left(\right) - \left[3 \times BE_{C-H} + 1 \times BE_{C-Cl} \right.$

$\left. + 1 \times BE_{H-Cl} \right]$

$= \left[1 \times BE_{C-H} + 1 \times BE_{Cl-Cl} \right]$

$- \left[1 \times BE_{C-Cl} + 1 \, BE_{H-Cl} \right]$

$-25 = [x+y] - [84 + 103]$

$-25 = [x+y] - 187$

$x+y = 162$

$\frac{x}{y} = \frac{9}{5}$

$\frac{9}{5}y + y = 162$

$\frac{14y}{5} = 162$

$y = \frac{162 \times 5}{14} = 57.85 \, KJ$

* Second Law of Thermodynamics

Spontaneous and non-spontaneous process (SP) (Non-SP)

SP process is a process which can take place on its own or with an initial help.

eg: Water flows from top to bottom, heat flows from hot end to cold end, burning of coal (initial help is required)

Non-SP process cannot takes place by its own and requires an external help throughout the process.

eg: Water flows from bottom to top (motor), Electrolysis (help of battery).

All spontaneous process (naturally occuring) are thermodynamically irreversible. (SLOT)

Without the help of an external agency, spontaneous process cannot be reversed. (SLOT)

Criterion for spontaneity of a reaction

ΔH, derived from FLOT is failed to predict whether a process is spontaneous or not because spontaneous process can have $\Delta H = -ve$, $\Delta H = +ve$ or even $\Delta H = 0$.

For $\Delta H = 0$, we can take two examples,
(i) Spreading of ink drop in water.
(ii) Mixing of two ideal gases

$(\Delta H = 0, = C_p \Delta T$
$\Delta T = 0$ isothermal)

From the above two examples, we can see that the system moves in a direction where the degree of disorder increases.

∴ Condition for spontaneity may be, Low energy and high degree of disorder.

* Entropy (s)

→ It is emerged from SLOT and is defined as the measure of randomness or degree of disorder in a system.

→ S is a state function as well as an extensive property.

→ Entropy(s) will be directly proportional to temperature but change in Entropy (ΔS) will be inversely proportional to temperature.

$(S \propto T)$

$\left(\Delta S \propto \dfrac{1}{\Delta T}\right)$
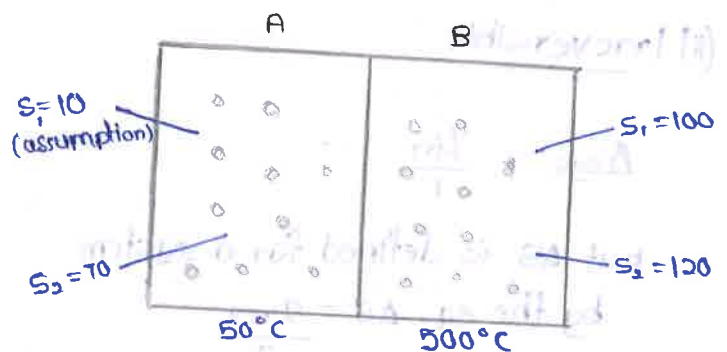
$$S_1 = 10 \text{ (assumption)} \qquad S_1 = 100$$
$$S_2 = 70 \qquad S_2 = 120$$
$$50°C \qquad 500°C$$
$$\Delta S = 60 \qquad \Delta S = 20$$
$$\Delta S \propto \dfrac{1}{\Delta T} \qquad S \propto T$$

* Entropy change (ΔS)

ΔS is defined as the ratio of heat absorbed by the system isothermally and reversibly to temperature at which absorption takes place.

$$\left(\Delta S = \frac{q_{rev}}{T} \right)$$

unit : $JK^{-1} mol^{-1}$

extensive property

Isothermal process

$\Delta T = 0 \quad \therefore \Delta U = 0$

FLOT $\Rightarrow$ $\Delta U \overset{0}{=} q + \omega$

$q = -\omega$

(i) Reversible

$\Delta S_{sys} = \dfrac{q_{sys}}{T}$

$= \dfrac{-\omega_{sys}}{T} = \dfrac{-\left(-nRT \ln \frac{V_2}{V_1} \right)}{T}$

$\Delta S_{sys} = nRT \ln \dfrac{V_2}{V_1}$

$\Delta S_{surr} = -nR \ln \dfrac{V_2}{V_1}$

$\left(\Delta S_{universe} = \Delta S_{total} = \Delta_{sys} + \Delta S_{surr} = \underline{0} \right)$

(ii) Irreversible

$\Delta_{sys} = \dfrac{q_{irr}}{T}$

but ΔS is defined for a system by the eq, $\Delta S = \dfrac{q_{rev}}{T}$

$\therefore \left\{ \begin{array}{l} \Delta_{sys} = \dfrac{q_{rev}}{T} = nR \ln \dfrac{V_2}{V_1} \\[2mm] \Delta_{surr} = \dfrac{-q_{irr}}{T} = \dfrac{-(-W_{irr})}{T} \\[2mm] \qquad\quad = \dfrac{-P_{ext} \Delta V}{T} \end{array} \right.$

$$\left(\Delta S_{universe} = \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \underset{(+ve)}{> 0} \right)$$

All spontaneous processes are accompanied by a net increase of entropy, ie, for all spontaneous processes, the total entropy change is positive. (SLOT)

Isothermal reversible and irreversible process can be distinguished by ΔS_{total} but not by ΔU ($\Delta U = 0$ for all isothermal process)

Adiabatic process

$q = 0$

FLOT $\Rightarrow$ $\Delta U = q + \omega$

$W_{ad} = \Delta U$

exp	comp
-ve	+ve
$U \downarrow T \downarrow$	$U \uparrow T \uparrow$
cooling	heating

(i) Reversible process

$\Delta S_{sys} = 0$

$\Delta S_{surr} = 0$

$\left(\Delta S_{total} = \underline{0} \right)$

(ii) Irreversible process

$\Delta S_{sys} > 0$

$\Delta S_{surr} = 0$

$\left(\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \underset{+ve}{> 0} \right)$

For expansion process, Entropy always increases.

For compression process, Entropy increases on if it is a irreversible compression because it increases the temperature. During, adiabatic irreversible compression, eventhough the volume is very small, entropy increases because of high temperature.

* Entropy of changes during phase transition

(1) Entropy of fusion : ($\Delta_{fus} S$)

$$H_2O \rightleftharpoons H_2O$$
$$(s) \qquad (l)$$

at NMP ($0°C$ and 1 atm)
equilibrium

$$\left(\Delta_{fus} S = \frac{\Delta_{fus} H}{T_{m.p}} \right)$$ more ordered state (low s)

↓

less ordered state (high s)

(2) Entropy of vapourisation : ($\Delta_{vap} S$)
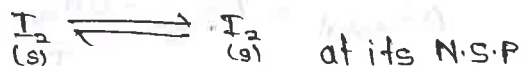
$$H_2O \rightleftharpoons H_2O$$
$$(l) \qquad (g)$$

at NBP ($100°C$ at 1 atm)
equilibrium

$$\left(\Delta_{vap} S = \frac{\Delta_{vap} H}{T_{b.p}} \right)$$

Trouten's rule

For many liquid, $\Delta_{vap} S \approx 88 JK^{-1} mol^{-1}$

(3) Entropy of sublimation : ($\Delta_{sub} S$)

$$\frac{T_2}{(s)} \rightleftharpoons \frac{T_2}{(g)} \quad \text{at its N.S.P}$$

$$\left(\Delta_{sub} S = \frac{\Delta_{sub} H}{T} \right)$$

* Spontainety in terms of entropy

$$\begin{cases} \Delta S_{total} > 0 \rightarrow \text{spontaneous} \\ \Delta S_{total} < 0 \rightarrow \text{non spontaneous} \\ \Delta S_{total} = 0 \rightarrow \text{at equilibrium} \\ \qquad \qquad \text{(s is maximum)} \end{cases}$$

eg : Consider the phase transition,

$$H_2O \longrightarrow H_2O$$
$$(l) \qquad \qquad (s)$$
more s   less s

Temp °C	ΔS_{sys}	ΔS_{surr}	ΔS_{total}
spontaneous -1	-21.85	$+21.93$	$+0.08$
equilibrium 0	-21.99	$+21.99$	0
non spontaneous $+1$	-22.13	$+22.05$	-0.08

* Entropy change for an ideal gas

(i) Temperature and Volume are variables.

$$\left(\Delta S = n C_v \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1} \right)$$

(ii) T and P are variables

$$\left(\Delta S = n C_p \ln \frac{T_2}{T_1} + n R \ln \frac{P_1}{P_2} \right)$$

* Combined form of FLOT and SLOT

$$\text{FLOT} \Rightarrow du = dq + dw = dq - pdv$$
$$\text{SLOT} \Rightarrow ds = \frac{dq}{T}$$

$$dq = Tds$$

$$\boxed{du = Tds - pdv}$$

$$H = U + pv$$
$$dH = du + pdv + Vdp$$

$$\boxed{dH = d\,Tds + Vdp}$$

Among the different statement for SLOT, the most important statement is,

"The entropy of the universe is continuosly increasing." (SLOT)

* Third Law of Thermodynamics (TLOT)

" Entropy of perfectly crystalline solids is taken as 0 at absolute 0"
But even at absolute 0 temperature, solid state associated with the small entropy known as residual entropy.

TLOT helps to calculate absolute value of entropy by adding every increment in $\frac{nC_P}{T}$ from 0K to TK.

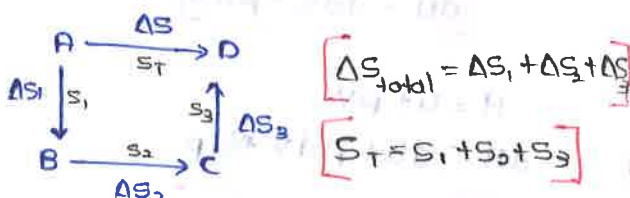$$\therefore \left\{ S_{T \to 0} = \int_0^T \frac{n C_P \, dT}{dT} \right\}$$

C_P, C_V is a function of temperature only.

$\therefore$ C_P can be considered as constant only if it is mentioned that there is no change in C_P within 0 to T temp. range.

For a chemical rxn,

$$\left(\Delta_r S = \le S_P - \le S_R \right)$$

Hess's law,

A $\xrightarrow[S_T]{\Delta S}$ D

$\Delta S_1 \Big| S_1$ $S_3 \Big| \Delta S_3$

B $\xrightarrow[\Delta S_2]{S_2}$ C

$$\boxed{\Delta S_{total} = \Delta S_1 + \Delta S_2 + \Delta S_3}$$

$$\boxed{S_T = S_1 + S_2 + S_3}$$

* Gibb's energy or Free energy (G)

→ It is a system parameter.
→ It is a state function as well as an extensive property.

→ Free energy is defined as the energy available to do some useful work.

Gibb's free energy

= Total heat content − Energy available to do non-useful work

$$\boxed{G = H - TS}$$

Helmoltz free energy,
$A = U - TS$

Absolute value of G cannot be calculated but we can calculate ΔG.

$$\Delta G = \Delta H - \Delta(TS)$$

$$\downarrow = \Delta H - T\Delta S - S\Delta T$$

Since, G is defined for isothermal process, $\Delta T = 0$;

$$\boxed{\Delta G = \Delta H - T\Delta S}$$ Gibb's equation or Gibb's Helmoltz eqn

unit : $J mol^{-1}$

* Gibb's energy and Spontaneity

For any spontaneous process,

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$$

$$= \Delta S_{sys} + \frac{\Delta H_{surr}}{T}$$

For isothermal, reversible process,

$$\Delta S_{total} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0$$

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys} > 0$$

Temperature at equilibrium,

$$\Delta G = 0$$
$$\Delta H = T\Delta S$$
$$\left(T_{eq} = \frac{\Delta H}{\Delta S} \right)$$

* Gibb's energy change for a rxn ($\Delta_r G$)
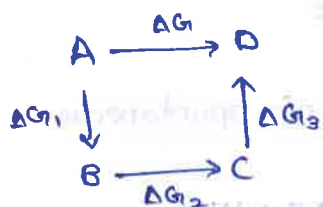
$$\Delta G = G_2 - G_1$$

For a rxn,

$$\left(\Delta_r^{\ominus} G = \sum G_P^{\ominus} - \sum G_R^{\ominus} \right)$$

If $\Delta_f^{\ominus} G$ are given,

$$\left(\Delta_r^{\ominus} G = \sum \Delta_f^{\ominus} G_P - \sum \Delta_f^{\ominus} G_R \right)$$

+ve — endoergonic

−ve — exoergonic

$A \xrightarrow{\Delta G} D$

$A \downarrow^{\Delta G_1}$ $\uparrow \Delta G_3$

$B \xrightarrow{\Delta G_2} C$

By Hess's law,

$$(\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3)$$
$$\Delta G = G_1 + G_2 + G_3 \text{ X}$$

* Gibb's energy change and chemical equilibrium

For a reversible rxn,

$$aA + bB \rightleftharpoons cC + dD$$

$$\boxed{\Delta_r G = \Delta_r^{\ominus} G + RT \ln Q}$$

Q : Rxn Quotient

At eqm, $\Delta_r G = 0$

$Q = K$ → eqm constant

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

But [ ] is not taken from eqm.

$$\boxed{\Delta_r^{\ominus} G = -RT \ln K}$$

$$\boxed{\Delta_r^{\ominus} H - T\Delta_r^{\ominus} S = -RT \ln K}$$

Note

Efficiency of fuel cell,

$$\left(\eta = \frac{|\Delta G|}{|\Delta H|} \times 100 \right)$$

$$\eta = \frac{\text{energy used for useful work}}{\text{total energy}} \times 100$$

* Zeroth law of thermodynamics

When a body A is in thermal equilibrium with C and another body B is in thermal equilibrium C, then A and B are in thermal equilibrium.

eg : Clinical thermometer.

*STUDY MATERIAL

⑨ $\Delta G = 0$

$0 = \Delta H - T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{491.1 \times 10^3 \text{ J mol}^{-1}}{198. \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$= 2480.3 \text{ K}$$

At 2480.3 K, rxn is at equilibrium.

$T = 2480.3$ K above which rxn become spontaneous.

⑩   (B) $N_2 + 3H_2 \longrightarrow 2NH_3$

1mol + 3 mol $\longrightarrow$ 2mol

4mol $\longrightarrow$ 2 mol

entropy ↓

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

$$\left(T\Delta S_{total} = -G_{sys} > 0\right)$$

$$T\Delta S_{total} > 0, \quad -\Delta G_{sys} > 0$$

$$\therefore \Delta G_{sys} < 0!$$

For any spontaneous process,

$$\Delta G < 0 \ (-ve)$$

For any non-spontaneous process,

$$\Delta G > 0 \ (+ve)$$

At equilibrium, $\Delta G = 0$

★ Free energy change for an ideal gas

Decrease in free energy of a system indicates maximum workdone.

$$-\Delta G = W_{max}$$

$$\left(\Delta G = -W_{max}\right)$$

For isothermal process,

$$\left\{ \begin{array}{l} \Delta G = -W_{irr} \\ = P_{ext}\,\Delta V \end{array} \right\}$$

OR

$$\left\{ \begin{array}{l} \Delta G = -W_{rev} \\ = nRT \ln \dfrac{V_2}{V_1} \\ = nRT \ln \dfrac{P_1}{P_2} \end{array} \right\}$$

For Galvanic cell,

$$\Delta G = -W_{electrical;\,max}$$
$$= -charge \times potential$$
$$= -nF \times E_{cell}$$

$\downarrow$ for max work, change has to pass reversible

$$\boxed{\Delta G = -nFE_{cell}}$$

Relation btw Ext (ΔG) and Intg Ecell

★ Spontaneity from Gibb's equation

Gibb's eqn is,

$$\Delta G = \Delta H - T\Delta S$$

i) $\Delta H = +ve, \ \Delta S = +ve$

$$\Delta G = \overset{+}{\Delta H} - T\overset{+}{\Delta S} \qquad [\Delta S, \Delta H \rightarrow constant]$$

-ve $\qquad$ +ve
$T\Delta S > \Delta H$ $\qquad$ $T\Delta S < \Delta H$
at high T $\qquad$ at low T
$\downarrow$ $\qquad\qquad$ $\downarrow$
spontaneous $\qquad$ non spontaneous
at high T $\qquad$ at low T

ii) $\Delta H = +ve, \ \Delta S = -ve$

$$\Delta G = \overset{+}{\Delta H} - T\overset{-}{\Delta S}$$
$$= \Delta H + T\Delta S$$
$$= +ve$$
$\downarrow$
always non spontaneous

iii) $\Delta H = -ve, \ \Delta S = +ve$

$$\Delta G = \overset{-}{\Delta H} - T\overset{+}{\Delta S}$$
$$= -\Delta H - T\Delta S$$
$$= -ve$$
$\downarrow$
always spontaneous

iv) $\Delta H = -ve, \ \Delta S = -ve$

$$\Delta G = \overset{-}{\Delta H} - T\overset{-}{\Delta S}$$

-ve $\qquad$ +ve
if $T\Delta S < \Delta H$ $\qquad$ if $T\Delta S > \Delta H$
at low T $\qquad$ at high T
$\downarrow$ $\qquad\qquad$ $\downarrow$
spontaneous $\qquad$ non spontaneous
at low T $\qquad$ at high T

(II) adiabatic rev

$\Delta S_{sys} = 0$

$\Delta S_{surr} = 0$

$\Delta S_{total} = 0$

II → PS

(III) adiabatic free exp

$\Delta S_{sys} > 0$

$\Delta S_{surr} = 0$

III → P

(IV) Irr isothermal comp

$\Delta S_{sys} < 0$

$\Delta S_{surr} > 0$

[IV → R]

Ans : (A)

Q) [2024 ADV Paper II]

For a double strand DNA, one strand is given below,

$5'$ ⎯⏐⎯⏐⎯⏐⎯⏐⎯⏐⎯⏐⎯⏐⎯⏐⎯⏐⎯⏐⎯⏐⎯⏐⎯ $3'$

A G T C A C G T A A G T C
‖ ⫴ ‖ ⫴ ‖ ‖ ⫴ ‖ ‖ ‖ ⫴ ‖ ⫴
T C T G T G C A T T C A G
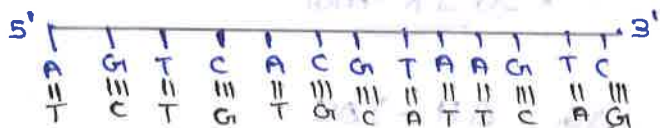
The amount of energy required to split the double strand DNA into two single strand is ___ KCal/mol

Given : Avg energy per H-bond for,

A-T base pair = 1 KCal/mol
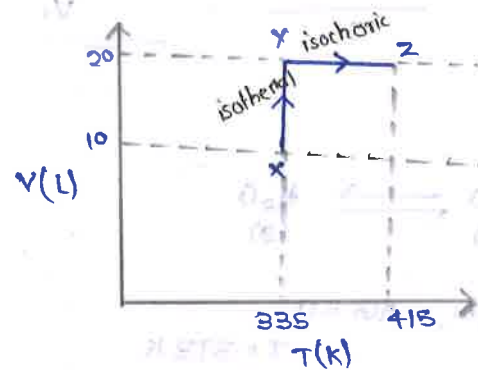
G-C base pair = 1.5 KCal/mol

A-U base pair = 1.25 KCal/mol

(Ignore electrostatic repulsion btw phosphate PO_4^{3-} group)

$BDE = \left[\text{no. of A=T pair} \times \text{no. of H-bond} \times BE_{A-T}\right]$

$+ \left[\text{no. of G≡C pair} \times \text{no. of H-bond} \times BE_{G-C}\right]$

$= \left[7 \times 2 \times 1\right] + \left[6 \times 3 \times 1.5\right]$

$= 14 + 27 = 41 \text{ KCal mol}^{-1}$

Q) [ADV 2024 Paper I]

Consider the following V-T diagram for the expansion of 5 moles of ideal monoatomic gas.

Considering only P-V work is involved, the total change in enthalpy (in J) for the transformation of state in the sequence,

$X \longrightarrow Y \longrightarrow Z$ is ___

Given, & $C_{v,m} = 12 \text{ J K}^{-1} \text{ mol}^{-1}$

$R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$

$Y \rightarrow Z$

$X \rightleftharpoons Y$,

$\Delta H = n C_p \Delta T$

$= 5 \times 20.3 \times 80$

$= 8120 \text{ J}$

$X \rightarrow Y$

$\Delta H = 0$

$C_p - C_v = R$

$C_p = 8.3 + 12$

$= 20.3 \text{ J}$ / K mol

$X \rightarrow Z \Rightarrow \Delta H = 0 + 8120 = 8120 \text{ J}$

(17) Path A
rev isothermal expansion

$$\Delta U = 0$$
$$\Delta U = q + \omega$$
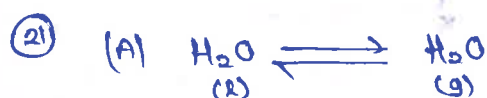$$q = -\omega = -\left(-nRT_1 \ln \frac{V_2}{V_1}\right)$$
$$= nRT_1 \ln \frac{V_2}{V_1}$$

(18) $\Delta S \left(\overset{path}{D+E}\right) = \Delta S \left(\overset{path}{A}\right)$

[Hess's law]

$$\therefore \Delta S = \frac{q_{rev}}{T}$$
$$= \frac{nRT_1 \ln \frac{V_2}{V_1}}{T_1} = nR \ln \frac{V_2}{V_1}$$

(21) (A) $H_2O \rightleftharpoons H_2O$
          (l)   (g)

At eqm, $\Delta G = 0$
$$T = 373 \, K$$
$$P = 1 \, atm$$

$T > 373 \, K \longrightarrow \Delta G < 0$
$T < 373 \, K \longrightarrow \Delta G > 0$

At 298K, backward rxn is
spontaneous.

✓ (B) True
✓ (C) True

(D) Entropy....
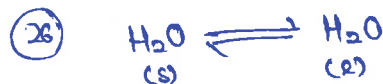
Mixing, $\Delta G = \Delta H^{\circ} - T\Delta S$

(23) $2Fe_2O_3 + 6CO \rightleftharpoons 4Fe + 6CO_2$

① + ② $\Rightarrow \Delta_r G = 1487 - 1543.2$
$$= -56.2 \, KJ$$

$$\therefore \Delta G = -28.1 \, KJ/mol$$
(D)

$\Delta G = -ve$
spontaneous

Ans: (B), (D)

(26) $H_2O \rightleftharpoons H_2O$
       (s)   (l)

$$\Delta_{fus} S = \frac{\Delta_{fus} H}{T_{m \cdot p}} = \frac{6 \times 10^3}{273} = 21.9 \, JK^{-1} \, mol^{-1}$$

(28) $H_2 + Cl_2 \longrightarrow 2HCl$
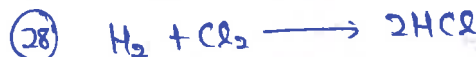
$BE = \quad 435 \quad 240 \qquad 430$

$S = \quad 131 \quad 223 \qquad 187$

$$\Delta H = \Sigma BE_R - \Sigma BE_P$$
$$= 2\times430 = [435 + 240] - (2\times430)$$
$$= -185 \, KJ \, mol^{-1}$$

$$\Delta S = \Sigma S_P - \Sigma S_R$$
$$= (131 + 223) - (2\times187)$$
$$= (2\times187) - (131+223)$$
$$= 374 - 354$$
$$= 20 \, JK^{-1} \, mol^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$
$$= -185000 - 300\times20$$
$$= -191000 \, J/mol$$
$$= -191 \, KJ/mol$$

$$|\Delta G| = 191$$
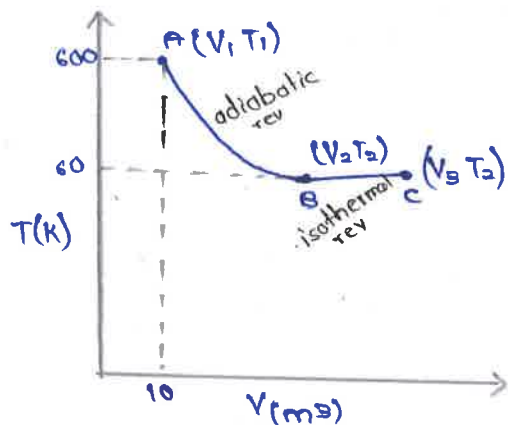
(29) (i) $\Delta S_{sys} > 0$
$$\Delta S_{surr} < 0$$
(reversible)

$I \longrightarrow Q$

Q) 1 mole of an ideal monoatomic gas undergo two reversible process, $A \longrightarrow B$, ~~then~~ $B \rightarrow C$ as shown in given fig,

$A(V_1 T_1)$
adiabatic rev

$(V_2 T_2)$
B isothermal rev C $(V_3 T_2)$

$T(K)$

$V(m^3)$

$A \rightarrow B$ adiabatic process.
If the total heat absorbed in the entire process $(A \rightarrow B; B \rightarrow c)$ is $RT_2 \ln 10$, The value of $2\log V_3$ is ___.

$\left(\text{Given, } C_{pm} = \frac{5}{2}R\right)$

$$q_{A \rightarrow B} = \cancel{nC_p \Delta T_0} = \cancel{\frac{5}{2}R}$$

$\Delta U = 0, \quad q_{B \rightarrow c} = -\left(nRT_2 \ln \frac{V_3}{V_2}\right)$

$= \left(+R \times T_2 \ln \frac{V_3}{V_2}\right)$

$RT_2 \ln\left(\frac{V_3}{V_2}\right) = RT_2 \ln 10$

$\frac{V_3}{V_2} = 10$

$V_3 = 10 V_2$

$A \longrightarrow B,$

$TV^{\gamma-1} = \text{constant}$

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ For monatomic gas, $\gamma = \frac{5}{3}$

$600 \times 10^{\gamma-1} = 60 \times V_2^{\gamma-1}$

$10 \times 10^{\frac{2}{3}-1} = V_2^{\frac{2}{3}-1}$

$10 \times 10^{-\frac{2}{3}} = V_2^{-\frac{2}{3}}$, $10^{\frac{1}{3}} = V_2^{\frac{2}{3}}$

$V_2 = \left(10^{\frac{1}{2}}\right)^{\frac{3}{2}} = 10^{\frac{3}{4}}$

$V_3 = 10 V_2$

$V_3 = 10 \times 10^{\frac{3}{4}} = 10^{\frac{7}{4}}$

$2\log V_3 = 2\log 10^{\frac{7}{4}}$

$= 2 \times \frac{7}{4} \times \log 10$

$= \frac{7}{2}$

Q) [2022 Paper 1]

Two mole of Hg (gas) undergo combustion in fixed volume bomb calorimeter with excess of O_2 at 298 K and 1 atm into $HgO_{(s)}$.
During the rxn, temperature increases from 298 K to 312.8 K. If heat capacity of bomb calorimeter and enthalpy of formation of $Hg_{(g)}$ are 20 kJ K^{-1} and 61.32 kJ mol^{-1} at 298K respectively, The calculated standard molar enthalpy of formation of $HgO_{(s)}$ at 298 K is x kJ/mol. The value of $|x|$ is ___.

$(R = 8.3)$

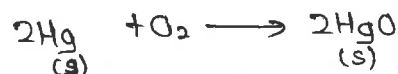$\Delta_f H_{Hg(g)} = 61.32 \text{ kJmol}^{-1}$

$C_v = 20 \text{ kJ K}^{-1}$

$\begin{array}{r} 312.8 \\ 298 \\ \hline 14.8 \end{array}$

$\Delta U = -C_v \Delta T$

$= -20 \times 14.8$

$= -296 \text{ K}$

$\underset{(g)}{2Hg} + O_2 \longrightarrow \underset{(s)}{2HgO}$

$\Delta H = \sum_f H_{HgO} - \sum_f H_{Hg}$

$\sum_f HgO = \Delta H + \sum_f H_{Hg}$