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Thermodynamics & Thermochemistry

Thermodynamics

Branch of physical chem. which deals with energy change that can take place during any physical or chem. change.

Basic Terminology

1) **System** — Any space/matter/vol. whose thermo. ~~prop~~ behavior is to be studied

2) **Surrounding** — (Universe) − (System)

3) **Boundary** — Anything that sep. system from surroundings.

1) It may be real or imag.

2) It may be conducting or Non-conducting

3) On basis of conductivity, system is divided into 3 categories.

3.1) Open System: Both energy & matter can exchange. b/w sys. & surr.

$\boxed{q \neq Const.}$, $\boxed{m \neq Const.}$

Eg: Tea in open cup.

Eg: Human body.

3.2) Closed System: Only energy exchange b/w sys. & surr.

$\boxed{q \neq Const.}$, $\boxed{m = Const.}$

Eg: Refrigirator, fridge, Bulb, ...
gas gas

3.3) **Isolated System** : Nothing exchange.

$\boxed{q = Const.}$, $\boxed{m = Const.}$

Eg: Tea in thermos flask.

4) Thermodynamic State Variables —

They define ThD state of system.

They are P, V, T

5) ThD Qty —

Those qty. whose value depends on ThD state variables.

Eg: Internal Energy (E/U),
Enthalpy (H),
Work (W),
Heat (q),
Entropy (S),
Gibb's free energy (G), ...

ThD Process —

Change in at least 1 ThD ~~P~~ state variable
i.e. at least 1 of P, V, T must change.

Any system can undergo ∞ no. of ThD process.

But at a certain cond^{n}s, we have defined special process names for such

6.1) Isothermal : $\boxed{\Delta T = 0}$

i.e. Temp. = Const.

Eg : Phase change

6.2) Isobaric : $\boxed{\Delta P_{int} = 0}$

i.e. P_{int} = Const.

Eg : Any activity in open atmosphere.

6.3) Isochoric : $\boxed{\Delta V = 0}$

i.e. V = Const.

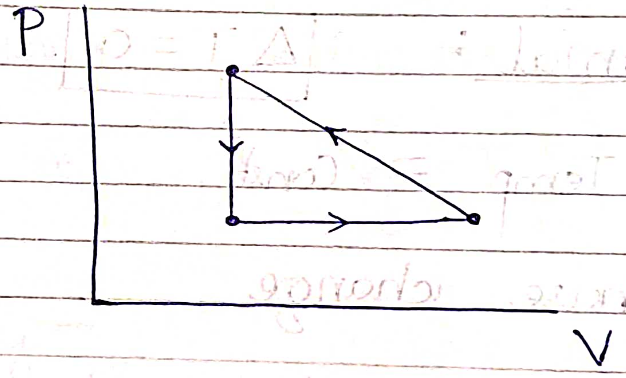
Eg : Heating gas in closed container.

6.4) Adiabatic : $\boxed{\Delta q = 0}$

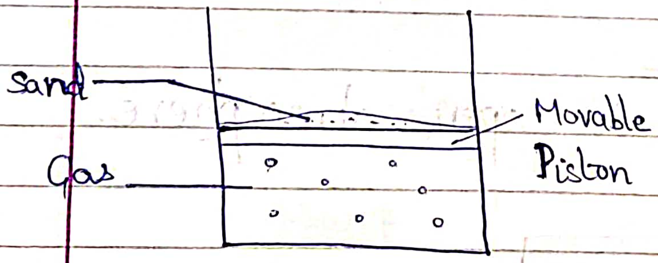
i.e. no heat change.

Eg: Sudden change such as bomb blast, explosion of cylinder, ...

6.5) Cyclic : System undergoes ~~many~~ many changes but ultimately returns to orig. state.

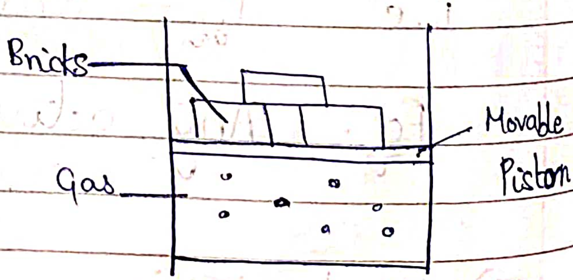


6.6) Reversible :



Before process starts ~~Initially~~, $P_{ext} = P_{gas}$

6.7) Irreversible :



~~Initially~~, Before process starts. $P_{ext} = P_{gas}$

Now, remove 1 sand particle.

⇒ $P_{\substack{\cancel{gas}\\ ext}}$ change.

⇒ $P'_{\substack{\cancel{gas}\\ ext}} = P_{ext} \pm \underset{(0)}{\cancel{\Delta P}}$

As very very small change

⇒ $P'_{gas} \approx P_{gas} = P_{ext} \approx P'_{ext}$

⇒ $P'_{gas} = P'_{ext}$

Repeating this many times.

In each step, system & surrounding ~~remain~~ are in equilibrium.

⇓

We can reverse the process!

Now, remove 1 brick

⇒ $P_{\substack{\cancel{gas}\\ ext}}$ change

⇒ $P'_{\substack{\cancel{gas}\\ ext}} = P_{ext} \pm \Delta P$

This is large change

We can't neglect it.

⇓

We can NOT reverse the process!

In each step, system & surrounding NOT in equilibrium.

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7) <u>ThD Fx</u>

7) **ThD Fx^{n}s** — Any change in ThD qty. during ThD process.

7.1) **State Fx^{n}s** : Value depends on init. & final state of system

Eg: ΔE, ΔH, ΔG, ΔS, ...

7.2) **Path Fx^{n}s** : Value depends on path followed by the system.

Eg: q, W, ...

8) **Therm. Prop^{t}s** —

8.1) **Extensive** : Mass dependent

Eg: Mass (m), Vol. (V), Internal Energy (ΔE), ΔH, mole (n), ...

8.2) **Intensive** : Mass independent

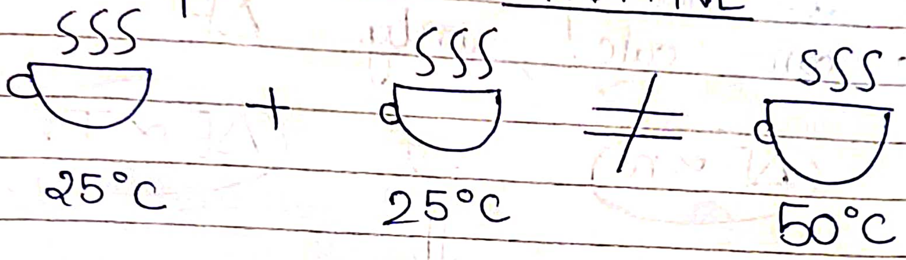
Eg: T (Temp), ρ (density) [Solid/Liq.], B.P., M.P., Refractive Index (μ), Surface Tension, Viscosity, Vapor Pressure, ...

☆ ‡ $\left(\frac{\text{Extensive Prop}^t}{\text{Extensive Prop}^t}\right) = (\text{Intensive Prop}^t)$.

☆ Intensive Prop^ts are <u>NON ADDITIVE</u>

Extensive Prop^ts are <u>ADDITIVE</u>

Eg :



☆ <u>Density of Gas</u> —

At const. P ⟶ Intensity

At const. V ⟶ Extensive

<u>Reason</u> : ‡ $\rho_{gas} = \left(\frac{P\overset{\text{Molar Mass}}{M}}{RT}\right)$

✓ Const. P ⇒ ‡ ρ const.

✓ Const. V ⇒ (n↑ ⇒ P↑)

⇒ ρ change

☆ Consider a collection of particles. Suppose we want to find if prop^t P is int^n. or ext^n.

Pick a small part of collection. If prop^t P same for part as for whole ⇒ $\boxed{\text{Int}^n}$.

If prop^t is <u>NOT</u> same for part & whole ⇒ $\boxed{\text{Ext}^n}$

Internal Energy (E/U)

Sum of all energies associated with the system. It is temp. dependent.

It is not possible to calc. E.
We can calc. only ΔE.

$\Delta E \propto n$ & $\Delta E \propto T$

$$\Downarrow$$

$$\boxed{\Delta E = n C_{v,m} \Delta T}$$

(Mol. heat cap. at const. vol.)

This is applicable if rx^n NOT happening
i.e. # mol. NOT change.

For liq. & solids, $\boxed{\Delta E = m C_s \Delta T}$

(Specific heat cap.)

Heat (q)

Mode of energy tranfer b/w system & surroundings during ThD process.

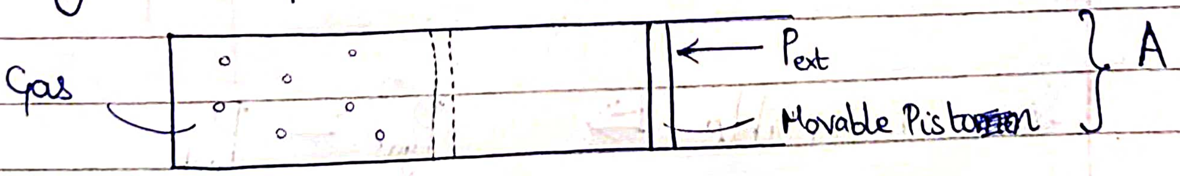
Sign Convention —

(Heat Loss by System) < 0

(Heat GAIN by System) > 0

Work (W) (Specifically, ThD work)

Mode of energy ~~tranfer~~ as work done by or on system against External pressure during expansion or contraction. resp.



$$(\text{Work done}) = \vec{F}\cdot d\vec{s} = F\,ds\,\cos(180^\circ)$$

$$= -P_{ext}\,A\,ds$$

$$\Rightarrow \boxed{dW = -P_{ext}\,dV}$$

$$\Rightarrow \quad \boxed{W = \int_{V_1}^{V_2} -P_{ext}\, dV}$$

Its mag. is equal to $\boxed{\text{area under P-V Curve.}}$ (This is ext. P)
with sign.

Sign Convention —

$(\text{Compression}) \Rightarrow (\text{Work done}) \underset{>}{\cancel{\leq}} 0$

$(\text{Expansion}) \Rightarrow (\text{Work done}) < 0$

Work done in Reversible Isothermal Process

$$W = \int_{V_1}^{V_2} -P_{ext}\, dV$$

Since reversible $\Rightarrow \quad P_{gas} = P_{ext}$.

$$\Rightarrow \quad W = \int_{V_1}^{V_2} -P_{gas}\, dV$$

$$\Rightarrow \quad W = (-nRT) \int_{V_1}^{V_2} 1/V\, dV$$

$$\Rightarrow \boxed{W = (nRT)\ln\left(\frac{V_1}{V_2}\right) = (nRT)\ln\left(\frac{P_2}{P_1}\right)}$$

Work done in Irreversible Process

(Since sudden change) ⇒ (P_{ext} remains same)

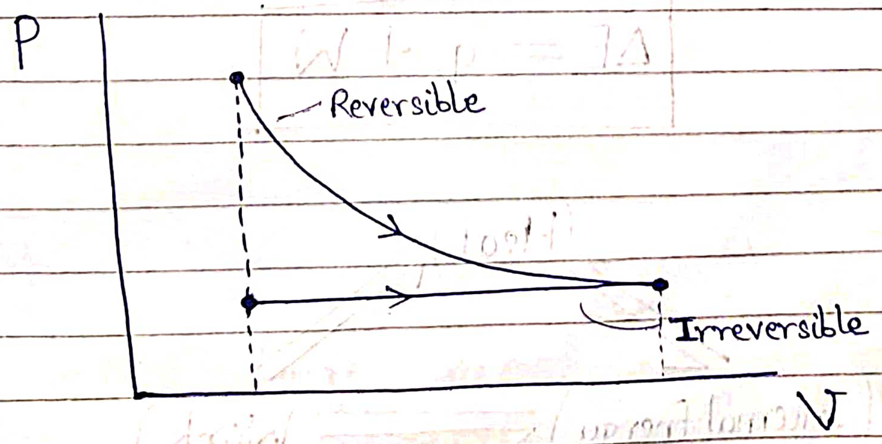
(first change, then)

(during process)

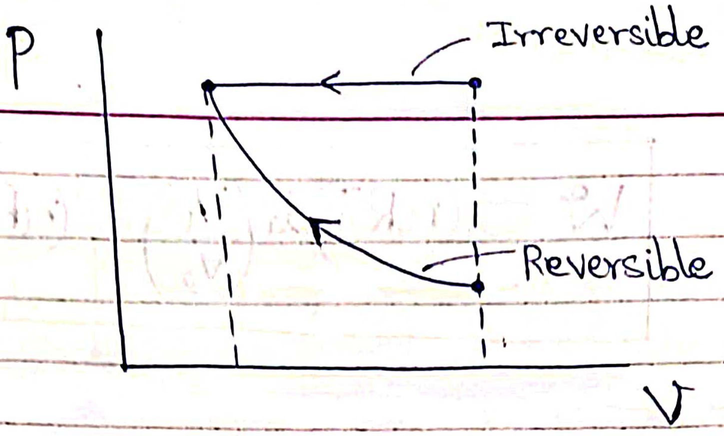
$$W = \int_{V_1}^{V_2} \underbrace{-P_{ext}}_{\text{const.}} \, dV = (-P_{ext})\int_{V_1}^{V_2} dV$$

$$\Rightarrow \boxed{W = (-P_{ext})(\Delta V)}$$

~~We make~~ P – V graphs (for Isothermal)



For expansion, $\boxed{\left|\text{Work in Reversible}\right| > \left|\text{Work in Irreversible}\right|}$



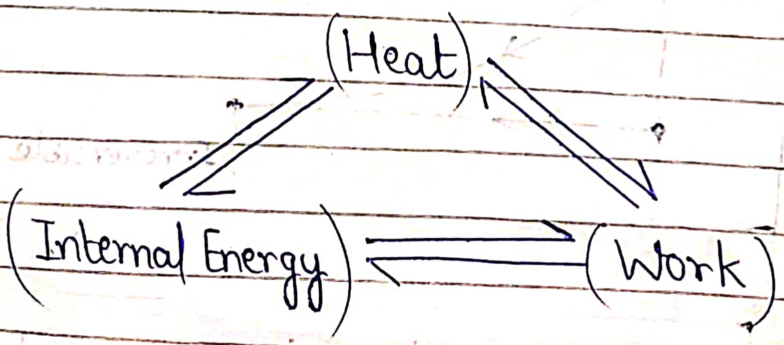
$$\boxed{\left|\text{Work in Reversible}\right| < \left|\text{Work in Irreversible}\right|}$$

☆ Initial state reversible aur irreversible main alag hai kyun ki initial state P_{ext} change ke just baad lete hain, aur irreversible main change bahut jyada hota hai. Final state same hai kyun ki gas tab tak expand/contract karge jab tak $P_{ext} = P_{gas}$ na ho jaye.

First Law of ThD

Energy can neither be created nor be destroyed. It can only transform from one form to another.

$$\boxed{\Delta E = q + W}$$



Q) 2 L of $N_2(g)$ at 0°C & 5 atm ~~are~~ is expanded isothermally against a const. ext. P of 1 atm, until P_{gas} reaches 1 atm. Find work done during expansion.

A) Const. ext P ⇒ Irreversible Process.

$W = -P(\Delta V) = (-1)(V_2 - 2)$

For gas, ${}^{gas}P_1 V_1 = {}^{gas}P_2 V_2 \Rightarrow 5 \cdot 2 = 1 \cdot V_2$

$\Rightarrow \boxed{V_2 = 10}$

$\Rightarrow W = -(10-2)$ atm L

$\Rightarrow \boxed{W = (-8)\text{ atm L} = (-800)\text{ J}}$

☆ $\boxed{1 \text{ atmL} = 101.3 \text{ J} \approx 100 \text{ J}}$

Enthalpy (H)

Generally, rxn's are carried out in open atmosphere i.e. isobaric condn's.

☆ A system, with no rx^n can have max energy = H.

for mathematical convenience, we define

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

$$\Rightarrow \quad \Delta H = \Delta E + \Delta(PV)$$

$$\Rightarrow \quad \boxed{\Delta H = \Delta E + (P_2V_2 - P_1V_1)}$$

(in general if $P \neq$ const.

Now, $\quad \Delta H = \Delta E + (\Delta P)V + (\Delta V)P$

If $P =$ Const. $\Rightarrow \quad \boxed{\Delta H = \Delta E + P\Delta V}$

By 1st Law of ThD, $\quad \Delta E = q + W$

$$\Rightarrow \quad \Delta E = q_P - P\Delta V$$

$\because$ if P const.

$$\Rightarrow \quad \boxed{\Delta H = q_P}$$

Hence, ΔH is heat change at const. P.

Heat change at Const. V — $\quad \boxed{\Delta E = q_V}$

Derivation :

By 1st Law of ThD, $\Delta E = q + W$

At const. vol., $\boxed{\Delta E = q_v}$ (as $W = 0$)

Rel^n b/w q_p & q_v (for Reversible Process)

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Rightarrow \Delta H = \Delta E + \Delta(nRT)$$

If (Temp. = Const.), $\boxed{\Delta H = \Delta E + RT(\Delta n_g)}$

$$\Rightarrow \boxed{q_p = q_v + RT(\Delta n_g)}$$

$$\Rightarrow \boxed{\Delta H = \Delta E + RT(\Delta n_g)}$$

Here, reversible process $\Rightarrow P_{ext.} = P_{gas} = \frac{nRT}{V}$

$$\Rightarrow \boxed{PV = nRT}$$

If $\Delta n_g = 0$ $\Rightarrow$ $\boxed{q_p = q_v}$

☆ Before this topic, everything has been defined/derived for processes W/O Rx^n.

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Q) Ethyl chloride (C_2H_5Cl) is made as follows —

$C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g)$, $\Delta H = -72.3$ k

What is ~~ΔE~~ ΔU if 70 g ethylene & 73 g of HCl are allowed to react at 300 K.

A) $$\Delta H = \Delta E + RT(\Delta n_g)$$

$$\Rightarrow -72.3 = \Delta E + \frac{25}{3} \cdot 300 \cdot 10^{-3} \cdot (-1)$$

$$\Rightarrow \boxed{\Delta E = -69.8 \text{ kJ mol}^{-1}}$$

$n_{C_2H_4} = 2.5$ $n_{HCl} = 2$ mol.

$\min\{2.5, 2\} = 2 \Rightarrow$ $\boxed{\text{HCl is L.R.}}$

$\cancel{\frac{n_{C_2H_4}}{1} = 2} \Rightarrow \left(\frac{n_{C_2H_5Cl}}{1}\right) = 2 \Rightarrow \boxed{n_{C_2H_5Cl} = 2}$

2 mol product formed! $\Rightarrow$ $\Delta E = 2 \times \Delta E_{(\text{per mol})}$

$$\Rightarrow \Delta E = \underset{(2\text{ mol})}{\cancel{2}} \times (-69.8 \text{ kJ mol}^{-1})$$

$$\Rightarrow \boxed{\Delta E = (-139.6) \text{ kJ}}$$

Heat Capacity (C)

Amt. of heat req. to raise temp. of any substance by 1°C.

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

✓ Unit – J/°C, J/K, ...

✓ It is extensive propt. as mass is NOT specified.

$C_p = \left(\text{Heat cap. at Const. } P\right)$

$C_V = \left(\text{Heat cap. at Const. } V\right)$

Specific Heat Capacity (C_s)

Amt. of heat req. to raise temp. of 1g of substance by 1°C.

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

✓ ~~Ut~~ Unit – $J\,g^{-1}\,K^{-1}$

✓ It is Intensive propt.

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Molar Heat Capacity (C_m)

Amt. of heat req. to raise temp. of 1 mol of substance by 1°C.

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

✓ Unit - $J\,mol^{-1}K^{-1}$ ✓ It is Intensive prop.

Molar Heat cap. at const. P — $C_{p,m} = \left(\frac{q_p}{n\Delta T}\right)$

$$\Rightarrow \boxed{\Delta H = nC_{p,m}\Delta T}$$

Molar Heat cap. at const. V — $C_{v,m} = \left(\frac{q_v}{n\Delta T}\right)$

$$\Rightarrow \boxed{\Delta E = nC_{v,m}\Delta T}$$

☆ Heat Capacity is ∞ for Isothermal process.

Rel^n b/w $C_{p,m}$ & $C_{v,m}$ (for Reversible Process)

$$H = E + PV$$

$$\Rightarrow H = E + nRT$$

$$\Rightarrow \left(\frac{dH}{\cancel{dt}\;dT}\right) = \left(\frac{dE}{dT}\right) + nR$$

Now, $\Delta H = nC_{p,m}\Delta T \Rightarrow \left(\frac{dH}{dT}\right) = nC_{p,m}$

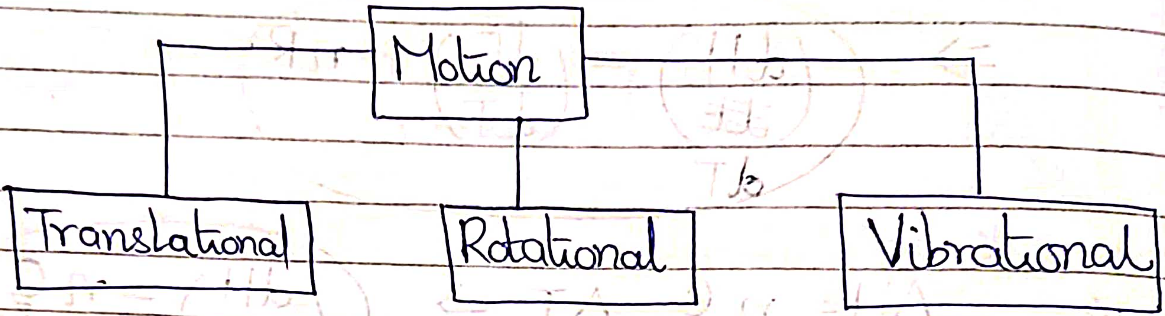
$\Delta E = nC_{v,m}\Delta T \Rightarrow \left(\frac{dE}{dT}\right) = nC_{v,m}$

$$\Rightarrow nC_{p,m} = \cancel{E}\; nC_{v,m} + nR$$

$$\Rightarrow \boxed{C_{p,m} - C_{v,m} = R}$$

Degree of Freedom :

No. of independent ways in which the system can exchange energy.



In degree of freedom, we do <u>NOT</u> take vibrational motion.

$$\boxed{f_T = f_t + f_R + \cancel{f_V}^{(0)}}$$

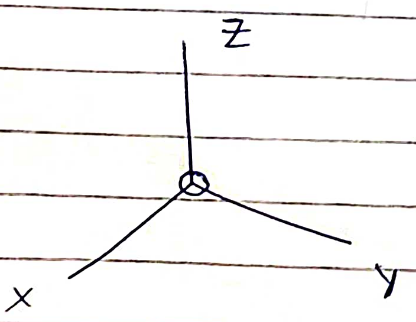
(Degree of Freedom)

(due to trans.)

(due to rot.)

For Monoatomic,

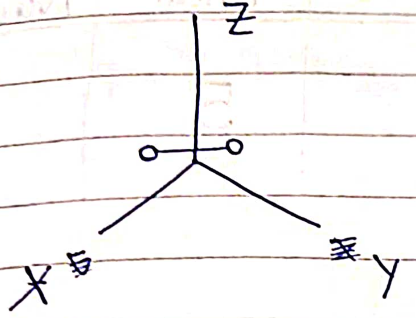
☆ We only consider axis abt. which KE ≠ 0 i.e. (Moment of Inertia) ≠ 0

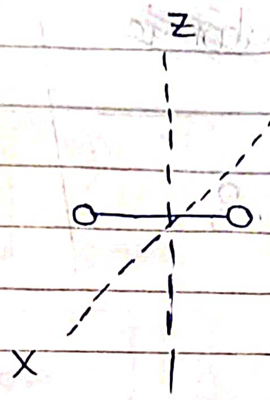


(No axis)

$3 + 0 = \boxed{3}$

for ~~diato~~ Diatomic, —



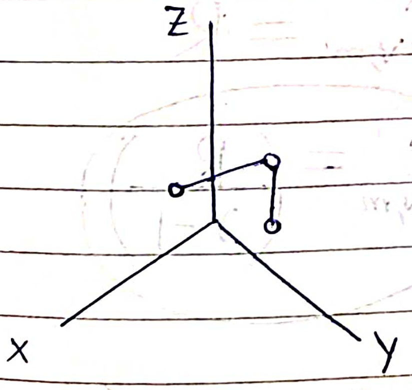


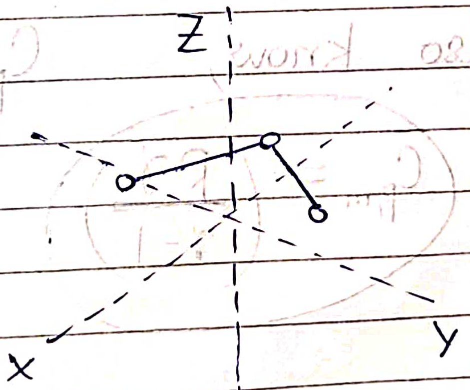
3 + 2 = ⑤

for Triatomic, —

if linear ⇒ Same as diatomic ⇒ ⑤

if Non-linear,





3 + 3 = ⑥

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Molecule	Monoatomic ~~Diatomic~~	Diatomic	Triatomic	
			Linear	Non-linear
Degree of Freedom	3	5	5	6

Poisson's Ratio

$$\boxed{\gamma = \left(\frac{C_{p,m}}{C_{v,m}}\right)}$$ ← This is def^n of γ.

Poisson's ratio

&

$$\boxed{\gamma = 1 + \left(\frac{2}{F}\right)}$$ Degree of freedom

We also know, $C_{p,m} - C_{v,m} = R$

$$\Rightarrow \quad C_{p,m} = \left(\frac{R\gamma}{\gamma - 1}\right) \qquad C_{v,m} = \left(\frac{R}{\gamma - 1}\right)$$

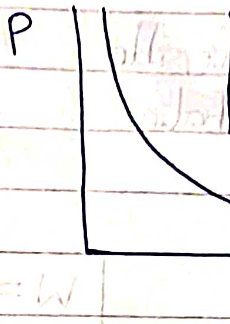
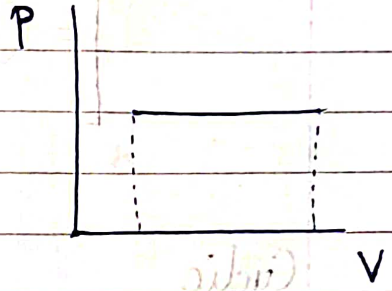
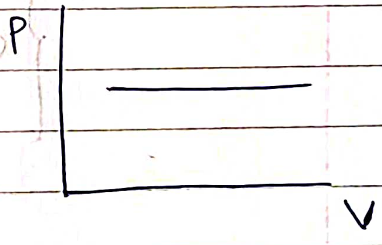
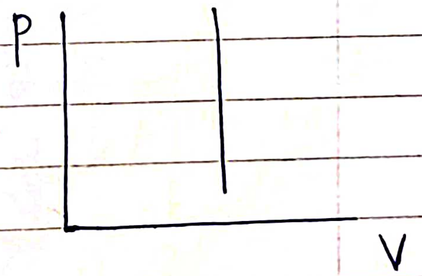
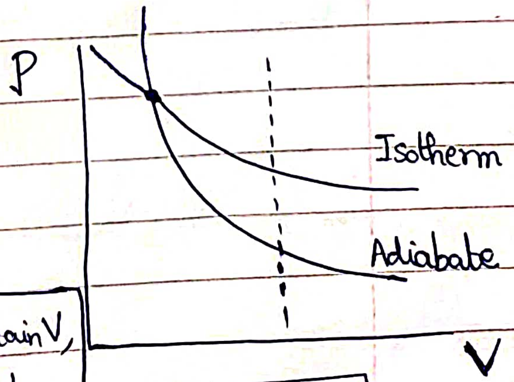
Atomicity	F_t	F_R	γ	$C_{p,m}$	$C_{v,m}$
Mono.	3	0	5/3	5R/2	3R/2
Di.	3	2	7/5	7R/2	5R/2
Tri (Linear)	3	2	7/5	7R/2	5R/2
Tri (NON linear)	3	3	4/3	4R	3R

for a mix. of gases —

$$C_{p,m} = \left[\frac{\sum\left(n_i\,(C_{p,m})_i\right)}{\sum n_i}\right] ; \quad C_{v,m} = \left[\frac{\sum\left(n_i\,(C_{v,m})_i\right)}{\sum n_i}\right]$$

$$\boxed{\gamma = \left(\frac{C_{p,m}}{C_{v,m}}\right)}$$

Process	W	q
Reversible Isothermal	$-nRT\ln(V_2/V_1)$ $-nRT\ln(P_1/P_2)$	$nRT\ln(V_2/V_1)$ $nRT\ln(P_1/P_2)$ $(\Delta E = q + W)$
Irreversible Isothermal	$-P(V_2 - V_1)$	$P(V_2 - V_1)$ $(\Delta E = q + W)$
Isobaric	$-P(V_2 - V_1)$ $-nR(T_2 - T_1)$	$n\,C_{p,m}\,\Delta T$
Isochoric	0	$n\,C_{v,m}\,\Delta T$
Reversible Adiabatic	$\left(\frac{nR}{\gamma - 1}\right)(\Delta T)$ $\left(\frac{P_2V_2 - P_1V_1}{\gamma - 1}\right)$ $(\Delta E = q + W)$ $(\Delta E = nC\ \Delta T)$	0

ΔE	ΔH	Graph
0 $(\Delta E = nC_{v,m}\Delta T)$	0 $(\Delta H = nC_{p,m}\Delta T)$	 $\boxed{\text{Slope} = \left(\frac{-P}{V}\right)}$
0 $(\Delta E = nC_{v,m}\Delta T)$	0 $(\Delta H = nC_{p,m}\Delta T)$	
$nC_{v,m}\Delta T$	q ~~$nC_{p,m}\Delta T$~~	
q ~~$nC_{v,m}\Delta T$~~	$nC_{p,m}\Delta T$	
W	$nC_{p,m}\Delta T$	

★ At a certain V,
iT : $PV = \text{const.}$
A : $PV^{\gamma} = \text{const.}$
& $\gamma > 1$

$\boxed{\text{Slope} = \left(\frac{-\gamma P}{V}\right)}$

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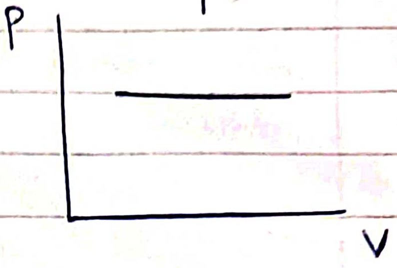
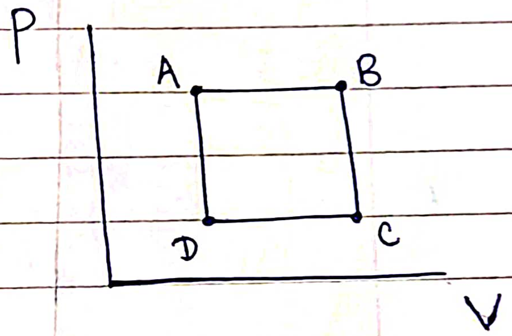
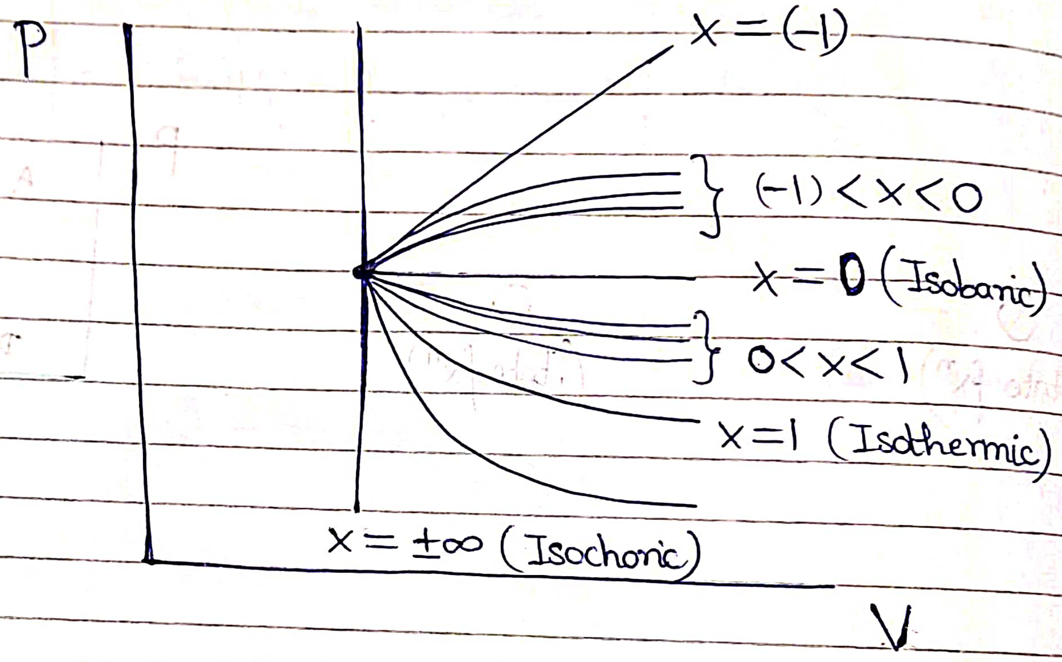
Process	W	q
Irreversible Adiabatic.	$-P_{gas,2}\left(\frac{nRT_2}{P_{gas,2}}-\frac{nRT_1}{P_{gas,1}}\right)$ $= nC_{v,m}\Delta T$ $\boxed{\begin{array}{l} W=(-P)(V_2-V_1)=\Delta E \\ =(-P_{gas,2})\left[\frac{nRT_2}{P_{gas,2}}-\frac{nRT_1}{P_{gas,1}}\right]=nC_{v,m}\Delta T \end{array}}$	0
Cyclic	(Area under P-V curve) { ↻ = +, ↺ = − }	$-W$ $(\Delta E = q + W)$

ΔE	ΔH	Graph
W	$nC_{p,m}\Delta T$	
0 (State fx^n)	0 (State fx^n)	

Polytropic Process

$$\boxed{PV^x = \text{Const.}} \quad (x \in \mathbb{R})$$



$$\boxed{W = (\text{Area under P-V curve})}$$

These ~~the~~ are all reversible!

Molar Heat Capacity –

$$PV^x = \text{Const.} = K \quad (\text{say})$$

Now, $P_{gas} V = PV = nRT$

$$\Rightarrow \quad PV^x = nRT\,V^{(x-1)}$$

$$\Rightarrow \quad V^{(1-x)} = \left(\frac{nR}{K}\right) T$$

$$\Rightarrow \quad (1-x)\,V^{-x}\left(\frac{dV}{dT}\right) = \left(\frac{nR}{K}\right)$$

$$\Rightarrow \quad \boxed{\left(\frac{P}{n}\right)\left(\frac{dV}{dT}\right) = \frac{R}{(1-x)}}$$

Acc. to 1st Law of ThD,

$$dE = q + W$$

$$\Rightarrow \quad nC_{V,m}\,dT = nC_m\,dT - PdV$$

$$\Rightarrow \quad C_{V,m} = C_m - \left(\frac{P}{n}\right)\left(\frac{dV}{dT}\right)$$

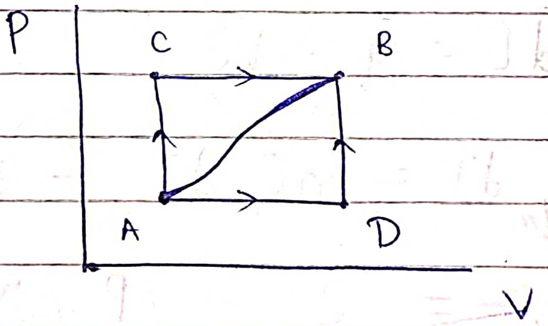
$$\Rightarrow \quad \boxed{C_m = C_{V,m} + \frac{R}{(1-x)}}$$

Q) When a system is taken from state A to B along ACB, 80 J of heat flows into system & system does 30 J of work.

a) How much heat flows into system along ADB if work done is (−10) J.

b) When sys. B→A along ~~II~~ curved portion, work done on sys. is 20 J. Find heat absorbed/released by sys.

c) If $U_D - U_A = 40\,J$, find heat absorbed in process AD & DB.



A) a) $\Delta E\Big|_A^B = q_{ACB} + W_{ACB} = q_{\cancel{ABD}\,ADB} + W_{\cancel{II}\,ADB}$

$\Rightarrow 80 - 30 = q_2 - 10 \Rightarrow \boxed{q_{ADB} = 60\,J}$

$\Rightarrow \Delta E\Big|_A^B = 50$

b) $\Delta E\Big|_B^A = -50 = q_{BA,\,curve} + 20 \Rightarrow \boxed{q_{BA,\,curve} = (-70)}$

c) $\Delta E_{AD} = 40$ $\quad \Delta E_{AB} = 50$

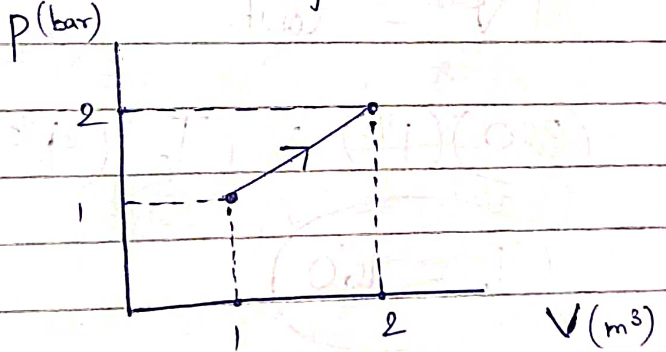
$\Rightarrow \Delta E_{DB} = 10 = q_{DB} + \overset{(0)}{\cancel{W_{DB}}}$ ~~III~~ (iV)

$\Rightarrow \boxed{q_{DB} = 10}$

Now, $q_{ADB} = q_{AD} + q_{DB}$

$\Rightarrow 60 = q_{AD} + 10 \Rightarrow \boxed{q_{AD} = 50}$

Q) What is ~~A~~ ΔE if $q = 100$ kJ



A) $W = -\left(\frac{1+2}{2}\right)(2-1) \Rightarrow W = \left(\frac{-3}{2}\right)$ bar m^3

$\Rightarrow W = \left(\frac{-3}{2}\right) \times 10^3$ bar L

$\Rightarrow W = \left(\frac{-3}{2}\right) \times 10^3 \times 10^2$ J

$\Rightarrow \boxed{W = (-150)\text{ kJ}} \Rightarrow \boxed{\Delta E = (-50)\text{ kJ}}$

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Q) 1 mol ideal gas A $\left(C_{v,m} = 3R\right)$ and 2 mol ideal gas $\left(C_{v,m} = \frac{3R}{2}\right)$ taken in container. It expanded reversibly & adiabatically from 1L to 4L starting from init. temp. = 320K. Find ΔE

A) $$\left(C_{v,m}\right)_{mix} = \left(\frac{1\cdot 3R + 2\cdot 3R/2}{1+2}\right) = 2R = \left(\frac{R}{\gamma_{mix}-1}\right)$$

$$\Rightarrow \boxed{\gamma = 3/2}$$

Now, $$TV^{\gamma-1} = \text{Const.}$$

$$\Rightarrow TV^{1/2} = \text{Const.}$$

$$\Rightarrow (320)(1^{1/2}) = (T_2)(4^{1/2})$$

$$\Rightarrow \boxed{T_2 = 160}$$

$$\Delta E = W + \cancel{q}^{(0)} = \left(\frac{nR}{\gamma-1}\right)(\Delta T) = \frac{3\cdot R}{(1/2)}\cdot(-160)$$

$$\Rightarrow \boxed{\Delta E = (-960)R}$$

Q) Calc: work done by sys. in irreversible (single step) adiabatic expansion of 2 mol of polyatomic gas ($\gamma = 4/3$) from $T = 300K$ & $P: 10 \rightarrow 1$ (atm).

A) $C_{V,m} = \frac{R}{(\gamma - 1)} \Rightarrow \boxed{C_{V,m} = 3R}$

Now, $W = \left(-P_{gas,2}\right)\left(\frac{\cancel{n}RT_2}{P_{gas,2}} - \frac{\cancel{n}RT_1}{P_{gas,1}}\right) = \cancel{n}C_{V,m}(T_2 - T_1)$

$\Rightarrow (-1)\left(\frac{\cancel{R}T_2}{1} - \frac{\cancel{R}\cdot 300}{10}\right) = (3\cancel{R})(T_2 - 300)$

$\Rightarrow (30 - T_2) = (3T_2 - 900) \Rightarrow \boxed{T_2 = \left(\frac{930}{4}\right)}$

$\Delta E = W + \cancel{q}^{(0)} = nC_{V,m}\Delta T = 2\cdot 3R\cdot\left(\frac{930}{4} - 300\right)$

$\Rightarrow$ ~~$\Delta E =$~~ $\boxed{W = (-405)R}$

Q) (N. Avasthi, L-2, Q7)

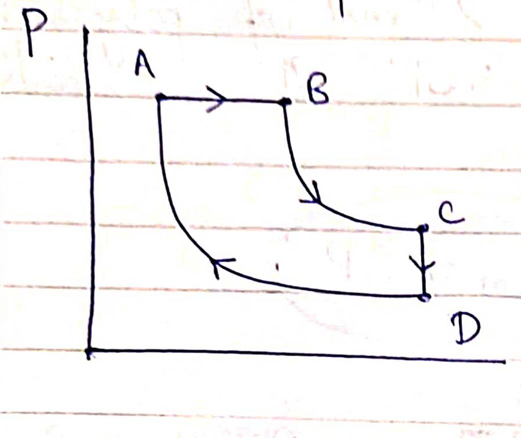
A) Graph: $3P + V = 7$ Now, $T = PV/R$

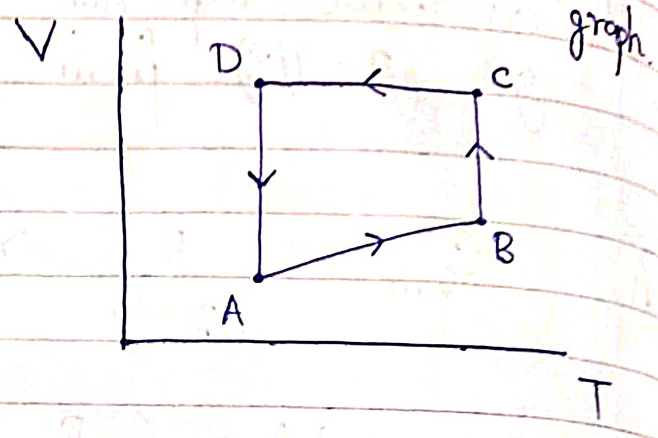
$\left(\frac{3P+V}{2}\right) = \left(\frac{7}{2}\right) \geq \sqrt{3PV} \Rightarrow PV \leq 49/12$

$\Rightarrow \boxed{T \leq \left(\frac{49}{12R}\right)}$

	AB	AC	BC
P_{max}	4	2	49/12

Q) A cyclic process ABCD is shown. Find V-T graph.





Q) 1 mol of ideal ~~monotonic~~ ~~mono~~ monoatomic gas expanded irreversibly in 2 stages. Find heat involved

$(P, V, T) : (8, 4, 300) \rightarrow (2, 16, 300) \rightarrow (1, 32, 300)$

$\uparrow$ bar $\uparrow$ L $\uparrow$ K

A) $\cancel{q_1 = -(16)(2-8) + 3}$

$$q_T = \underbrace{(2)(16-4)}_{\text{Stage 1}} + \underbrace{(1)(32-16)}_{\text{Stage 2}} \Rightarrow \boxed{q = 40 \text{ barLK}}$$

Q) What is work done by 1 mol monoatomic ideal gas in process as shown?

Limitation of Ist Law of ThD

1) Doesn't tell about dirx^n of rx^n.

(Acc. to it, EVERYTHING is possible within limits of Conservation of Energy)

2) Doesn't tell about time taken to complete rx^n.

Spontaneous Process

Processes which occurs on its own w/o any ext. support, once initiated.

Eg - Evaporation, Rusting, ...

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Non Spontaneous Process

Those process which do NOT occur or need const. ext. support.

Eg - Boiling of water, Electrolysis, ...

Driving Force (Criteria for Spontaneity)

1) Energy Factor (tendency to acquire min. energy)
2) Entropy (tendency to inc. randomness/disorder of sys.)

Combination of Entropy of System (ΔS) & Enthalpy of System (ΔH)

Enthalpy - $\Delta H < 0$ ⇒ favourable for Spontaneity

$\Delta H > 0$ ⇒ UN favourable for Spontaneity

Entropy - $\Delta S > 0$ ⇒ Favourable for Spontaneity

$\Delta S < 0$ ⇒ UN favourable for Spontaneity

ΔS \ ΔH	−	+
−	$(\lvert\Delta H\rvert > \lvert\Delta S\rvert)$ Slow, Spontaneous Eg: Rainfall, ... $(\lvert\Delta H\rvert < \lvert\Delta S\rvert)$ Slowly by ext. support, Non-Spontaneous Eg: freezing	Highly Non-Spontaneous Eg: Reverse Combustion, ...
+	Fast, Uncontrollable Highly Spontaneous Eg: Explosion, ...	$(\lvert\Delta H\rvert > \lvert\Delta S\rvert)$ Slowly by ext. support. Non-spontaneous Eg: Boiling, ... $(\lvert\Delta H\rvert < \lvert\Delta S\rvert)$ Slow & controllable, Spontaneous Eg: Melting, Evaporation, ...

Process	ΔH	ΔS
Eg: Milk → Curd	−	(Due to bio. activity, #molecules inc.) ? $(\Delta S>0)$
Eg: Curd → Milk (Highly Non Spontaneous)	+	−
Eg: Egg → Omlette	+	(Due to bio. activity, #molecules inc) ? $(\Delta S>0)$
Eg: Omlette → Egg (~~Highly~~ Non Spontaneous)	−	−

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Second Law of Therm.

For an irreversible process, entropy of universe (isolated system) always increases.

i.e. $(\Delta S)_{sys.} + (\Delta S)_{surr} > 0$, for irreversible process.

Now, $(\Delta S)_{sys} + (\Delta S)_{surr} = 0$, for reversible process.

★ [If a process inc $(\Delta S)_{universe/isolated\ system}$] $\Longleftrightarrow$ [Process is Spontaneous]

Entropy (S)

It is measure of degree of randomness, disorder, freedom.

It is a State Fx^n. Its absolute value can't be measured. Only change can be measured.

$$\boxed{\Delta S = \int dS = \int \frac{1}{T_{surr}} dq_{rev}}$$

(q is in reversible process)

Eg : S : $O_3 > O_2$

★ $\boxed{S \propto (\text{Atomicity})}$

~~Eg~~ Eg : S : Gas > Liq. > Solid

Eg : $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

$\Delta n_g > 0 \Rightarrow \boxed{\Delta S > 0}$ ★ $\boxed{S \propto \Delta n_g}$

Eg : S : $F_2 < Cl_2 < Br_2 < I_2$ (all gaseous)

★ ~~ΔS~~ $\boxed{S \propto (\text{Mass \& Size})}$

Eg : S : $CuSO_4 \cdot 5H_2O > CuSO_4 \cdot 4H_2O > CuSO_4 \cdot 3H_2O$

ΔS during Phase Change

1) Entropy of Fusion (ΔS_{fusion}) —

ΔS when 1 mol solid changes into liq.

Now, $\Delta S_{fusion} = \int \frac{1}{T_{Melt}} dq_{rev} = \left(\frac{q_{\cancel{rev}}}{T_{Melt}}\right)$ (as T = Const. during Phase Change)

$\Rightarrow \Delta S_{fusion} = \left(\frac{q_P}{T_{Melt}}\right)$ (as obj. melting under atm P)

$$\Rightarrow \boxed{\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{Melt\ pt.}}}$$

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2) Entropy of Vaporisation (ΔS_{vap}) —

$$\boxed{\Delta S_{vap.} = \left(\frac{\Delta H_{vap}}{T_{Boil.pt.}}\right)}$$

3) Entropy of Sublimation (ΔS_{sub}) —

$$\boxed{\Delta S_{Sub} = \left(\frac{\Delta H_{Sub.}}{T_{Sub.pt.}}\right)}$$

ΔS for Ideal Gas during ThD Process

This is for (sys.)

$$\Delta S = \int \frac{1}{T_{surr}} \, dq_{rev.} \quad — ①$$

Now,

$$dE = dq + dW$$

$$\Rightarrow nC_{V,m} \, dT = dq - P \, dV$$

$$\Rightarrow dq = nC_{V,m} \, dT + P \, dV \quad — ②$$

Substitute into ①,

$$\Rightarrow \quad \Delta S = \int \frac{n C_{v,m}}{T_{surr}}\, dT + \int \frac{P}{T_{surr}}\, dV$$

for ideal gas & reversible process, $P_{gas} = P$, $T_{gas} = T_{surr}$

$$\Rightarrow \quad P/T_{surr} = P_{gas}/T_{\cancel{surr}\,gas} \Rightarrow \boxed{P/T_{surr} = nR/V} \; - ③$$

Into above,

$$\Delta S = \int \frac{n C_{v,m}}{T}\, dT + \int \frac{nR}{V}\, dV$$

$$\Rightarrow \quad \boxed{\Delta S = n C_{v,m} \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)}$$

Since ΔS is a State Fx^n $\Rightarrow$ This formula valid for both irreversible & reversible.

Now,

$$\Delta S = n C_{v,m} \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{P_1}{P_2} \cdot \frac{T_2}{T_1}\right)$$

$$= \left(n C_{v,m} + nR\right) \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{P_1}{P_2}\right)$$

$$\Rightarrow \quad \boxed{\Delta S = n C_{p,m} \ln\left(\frac{T_2}{T_1}\right) \cancel{+} - nR \ln\left(\frac{P_2}{P_1}\right)}$$

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Process	$(\Delta S)_{sys.}$	$(\Delta S)_{surr.}$
Reversible Isothermal	$-nR\ln(P_2/P_1)$ $nR\ln(V_2/V_1)$	$nR\ln(P_2/P_1)$ $-nR\ln(V_2/V_1)$
Irreversible Isothermal	$-nR\ln(P_2/P_1)$ $nR\ln(V_2/V_1)$	$-P(V_2-V_1)/T_{surr}$ $\{\Delta E = 0 = q + w\}$ Now, $(\Delta S)_{surr} = \left(\frac{q_{surr}}{T_{surr}}\right) = \left(\frac{-q_{sys}}{T_{sys}}\right)$ $= \left(w/T_{surr}\right) = -P\Delta V/T_{surr}$
Reversible Isochoric	$nC_{v,m}\ln\left(\frac{T_2}{T_1}\right)$	$-nC_{v,m}\ln\left(\frac{T_2}{T_1}\right)$
Irreversible Isochoric	$nC_{v,m}\ln\left(\frac{T_2}{T_1}\right)$	$-nC_{v,m}(T_2-T_1)/T_{surr.}$ $\Delta E = q + \cancel{w}^{(0)}$ Now, $(\Delta S)_{surr} = \left(\frac{q_{surr}}{T_{surr}}\right) = \left(\frac{-q_{sys}}{T_{surr}}\right) = \left(\frac{-\Delta E}{T_{surr}}\right)$ $\Rightarrow (\Delta S)_{surr} = -nC_{v,m}\Delta T/T_{surr.}$
Reversible Isobaric	$nC_{p,m}\ln\left(\frac{T_2}{T_1}\right)$	$-nC_{p,m}\ln\left(\frac{T_2}{T_1}\right)$
Irreversible Isobaric.	$nC_{p,m}\ln\left(\frac{T_2}{T_1}\right)$	$-nC_{p,m}(T_2-T_1)/T_{surr.}$ $\Delta H = q_p.$ & $(\Delta S)_{surr} = (q_{surr}/T_{surr})$ $\Rightarrow (\Delta S)_{surr} = -\Delta H/T_{surr}$ $\Rightarrow (\Delta S)_{surr} = -nC_{p,m}\Delta T/T_{surr}$

Reversible Adiabatic	0	0
Irreversible Adiabatic	~~0~~ $\left[nC_{V,m}\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)\right]$	0

Gibb's Free Energy (G)

Max. energy available with sys. to do useful ~~energy~~ work.

$$\boxed{\underbrace{\overset{\text{(of sys.)}}{G}}_{\text{Energy available to do useful work}} = \underbrace{\overset{\text{(of sys)}}{H}}_{\text{Max. energy}} - \underbrace{\overset{\text{(of surr)}}{T}\overset{\text{(of sys.)}}{S}}_{\text{Energy of freedom}}}$$

☆ G is defined ONLY for sys.

$$\boxed{\left(\text{Max. efficiency of a system}\right) = \left(\frac{G}{H}\right) \times 100\%}$$

Now,

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

$$\Rightarrow \Delta G = \Delta H - (\Delta S)T - (\Delta T)S.$$

Now, $\Delta H = \Delta E + \Delta(PV)$

$$\Rightarrow \boxed{\Delta G = \Delta E + (\Delta P)V + (\Delta V)P \cancel{+} - (\Delta T)S - (\Delta S)T}$$

At const. P & T,

$$(\Delta G)_{P,T} = (\Delta E)_{P,T} + P(\Delta V) - T(\Delta S)$$

$$\Rightarrow \boxed{\underbrace{(\Delta G)_{P,T}}_{\text{of sys.}} = \underbrace{(\Delta H)_{P,T}}_{\text{of sys.}} - \underbrace{T}_{\text{of surr}}\underbrace{(\Delta S)}_{\text{of sys.}}}$$

Rel^n b/w $(\Delta G)_{P,T}$ & $(\Delta S)_{universe}$

$$\Delta S_{universe} = \Delta S_{sys.} + \Delta S_{surr.}$$

$$= \Delta S_{sys.} + \frac{q_{surr}}{T_{surr}}$$

$$= \Delta S_{sys} - \frac{q_{sys.}}{T_{surr}}$$

At const. P, $\Delta S_{universe} = \Delta S_{sys} - \dfrac{q_P}{T_{surr}}$

$$\Rightarrow \Delta S_{universe} = \Delta S_{sys} - \frac{\Delta H}{T_{surr}}$$

$$\Rightarrow \Delta S_{universe} = \left(\frac{-1}{T_{surr}}\right)\left(\Delta H - T_{surr}(\Delta S_{sys})\right)$$

$$\Rightarrow \boxed{(\Delta G)_{P,T} = (-T_{surr})(\Delta S_{universe})}$$

We know, $(\Delta S)_{universe} > 0 \Longleftrightarrow$ Spontaneous
$(\Delta S)_{universe} < 0 \Longleftrightarrow$ Non spontaneous
$(\Delta S)_{universe} = 0 \Longleftrightarrow$ Equilibrium

$$\Downarrow$$

☆

$$\boxed{\begin{array}{lcl} \Delta G < 0 & \Longleftrightarrow & \text{Spontaneous} \\ \Delta G = 0 & \Longleftrightarrow & \text{Equilibrium} \\ \Delta G > 0 & \Longleftrightarrow & \text{Non-spontaneous} \end{array}}$$

Since we had taken $P_{surr.}$ & $T_{surr.}$, these rel^n are valid for all process that generally occur. P_{sys} & T_{sys} CAN change.

for $Rx^{n}s$

ΔH	ΔS	$(\Delta G)_{P,T}$	Remark
−	+	Always −	Always Spontaneous
+	−	Always +	Always Non-Spontaneous
+	+	Low T : + High T : −	Non Spontaneous Spontaneous
−	−	Low T : − High T : +	Spontaneous Non spontaneous

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Change in ΔG with P, V, T (for Reversible Proc

$$G = H - TS$$

$$\Rightarrow G = E + PV - TS$$

$$\Rightarrow \boxed{dG = dE + VdP + PdV - SdT - TdS} \quad \text{—①}$$

Now, $dE = q + dW = q - PdV$

$$\Rightarrow \boxed{dE + PdV = q}$$

Also, $\boxed{dS = q/T}$

Hence, $dG = q + VdP - q - SdT$

$$\Rightarrow \boxed{dG = VdP - SdT} \quad \text{—②}$$

Case 1

If ~~Iso~~ T = const. $\Rightarrow$ $dG = V\,dP$

$$\Rightarrow dG = \left(\frac{nRT}{P}\right) dP$$

$$\Rightarrow \boxed{\Delta G = nRT \ln\left(\frac{P_2}{P_1}\right)}$$

~~Obse~~ Case 2

If P= Const. ⇒ $dG = (-S)\,dT$

⇒ ~~dS~~ $\boxed{\left(\frac{dG}{dT}\right) = (-S)}$

Rel^n b/w ΔG & Q for any rx^n

Consider a homogenous reversible rx^n,

$$aA(g) + bB(g) \rightarrow cC(g) + dD(g)$$

Now,

$$\underset{\substack{\uparrow \\ \text{(at any inst.)}}}{\Delta G} = \underset{\substack{\uparrow \\ \text{(at } 25^\circ\text{C, 1 atm} \\ \text{when rx}^n\text{ just)}}}{\Delta G^\circ} + RT \ln(\underset{\substack{\uparrow \\ \text{(Rx}^n\text{ quotient)*}}}{Q})$$

At Eq., $Q = K_{eq}$ & $\Delta G = 0$

⇒ $\boxed{\Delta G^\circ = (-RT)\ln(\underset{\text{(Eq. const.)*}}{K_{eq}})}$

* Observe we have Q & K_{eq} inside ln(). For this we need them to be unitless. Hence, we take $P_{Products}$ & $P_{Reactant}$ wrt. Standard P.

(i.e. if $P_C = 2$ ~~bar~~ atm, in rx^n quotient take P_C as 2)

3rd Law of Therm

At temp: $\boxed{T = 0\,K}$, all motion ceases.
Hence, entropy becomes Const.

$$\Delta S = \int \frac{dq_{rev.}}{T}$$

$$\Rightarrow \quad (S_T - S_0) = \int \frac{dq_{rev.}}{T}$$

for convenience, we assume $\boxed{S_0 = 0}$.

$$\Rightarrow \quad \boxed{S_T = \int \frac{dq_{rev}}{T}}$$

Q) P ~~of~~ 10 mol ideal gas changed from 2 atm to 1 atm against const. ext. P w/o change in temp. If $T_{surr} = 300\,K$ & P = 1 atm, calc. $(\Delta S)_{universe}$ in given process.

A) $(\Delta S)_{sys.} = nR \ln\left(\frac{P_1}{P_2}\right) = (10)\left(\frac{25}{3}\right) \ln\left(\frac{2}{1}\right) = \boxed{250 \ln(2)/3}$

$(\Delta S)_{surr} = \left(\frac{-P(V_2 - V_1)}{T_{surr.}}\right) = (-P_{2,gas})\left[\frac{nRT_2}{P_{2,gas}} - \frac{nRT_1}{P_{1,gas}}\right]\left(\frac{1}{T_{surr}}\right)$

$$= (-1)(10)(R)(\cancel{300})\left(\frac{1}{1}-\frac{1}{2}\right)\left(\frac{1}{\cancel{300}}\right) = \boxed{-5R}$$

$$(\Delta S)_{universe} = \left(\frac{250\ln(2)}{3}\right)\frac{J}{K} - 5R_{mol/K}$$

$$= \left(\frac{250\ln(2)}{3} - \frac{5\cdot 25}{3}\right) J/K$$

$$\approx \left(\frac{25}{3}\right)\left[10.(0.69) - 5\right] J/K$$

$$\Rightarrow \boxed{(\Delta S)_{universe} = 16.6\ J/K}$$

Q) Standard entropy of X_2, Y_2 & XY_3 are 60, 40, 50 J/mol K, resp. ~~for rx^n~~.

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3 \; ; \quad \Delta H = (-30)\ kJ.$$

for rx^n to be at eq., find temp.

A) $$(\Delta S)_{rxn} = \sum p_i (\Delta S)_{Prod.} - \sum r_i (\Delta S)_{React.}$$

$$= 50 - 60/2 - 3\cdot 40/2 \Rightarrow (\Delta S)_{rxn} = (-40)\ J/K$$

Now, $(\Delta G)_{rxn} = (\Delta H)_{rx^n} - T(\Delta S)_{surr}$

for eq., $\Delta G = 0 \Rightarrow T = \left(\frac{\Delta H_{rxn}}{\Delta S_{rxn}}\right) = \left(\frac{-30}{-40}\right)\frac{kJ}{J/K}$

$$\Rightarrow \boxed{T = 750\,K}$$

Q) For rxⁿ at 300K; $A(g) + B(g) \longrightarrow C(g)$

$\Delta U = (-3)\ kcal/mol \qquad \Delta S = (-10)\ cal/K$

$\Delta G = ?$

A)

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

$$\Rightarrow \Delta H = \left[(-3) + 2 \cdot 300 \cdot (-1) \times 10^{-3}\right] kcal/mol$$

$$\Rightarrow \Delta H = (-3.6)\ kcal/mol$$

Now,

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

$$= \left[(-3.6) - 300 \cdot (-10) \times 10^{-3}\right] kcal$$

$$\Rightarrow \boxed{\Delta G = (-0.6)\ kcal}$$

Q) What is ΔG for synthesis of NH_3 at 298 K at following set of partial pressures?

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \ ; \quad \Delta G^\circ = (-33)\ kJ/mol$$

~~Gas~~

Gas	N_2	H_2	NH_3
Prsre (atm)	1	3	0.02

A) $\boxed{Q} = \left(\frac{P^2_{NH_3}}{P_{N_2} \cdot P^3_{H_2}}\right) = \frac{4 \times 10^{-4}}{1 \cdot 27} = \boxed{\frac{4 \times 10^{-4}}{27}}$

Now, $\Delta G = \Delta G^\circ + RT \ln(Q)$

$$= \left((-33) + \underset{\uparrow\,(25/3)}{\cancel{2}} \cdot 300 \cdot \ln\left(\frac{4 \times 10^{-4}}{27}\right) \times 10^{-3}\right) \frac{kJ}{mol}$$

$$= \left[(-33) + (2.5)\left[2\ln(2) - 3\ln(3) - 4\right]\right] kJ/mol$$

$\Rightarrow$ $\boxed{\Delta G = (-60.5)\ kJ/mol}$

Q) What is ΔG when 1 mol water at 100°C and 1 atm P is converted into steam at 100°C & 2 atm P ?

A) $(\Delta G)_{\substack{water \rightarrow steam \\ at\ 1atm \quad at\ 1atm}} = 0$ $\{$as both ΔT & $\Delta P = 0\}$

Now, $(\Delta G)_{\substack{Steam\ at\ 1\ atm \rightarrow Steam\ at\ 2\ atm}} = nRT \ln\left(\frac{P_2}{P_1}\right)$

$$= \left[1 \cdot 2 \cdot 273 \ln\left(\frac{2}{1}\right)\right] \cancel{k}\ cal$$

$\Rightarrow$ $\boxed{\Delta G = 517.13\ cal}$

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Thermochem Rx^n

Incomplete : $A + B \rightarrow C + D$

Complete : $\underset{\text{(allotrope)}}{aA(s)} + bB(g) \rightarrow cC(g) + dD(l);\ \Delta H^\circ = (\ldots$

To completely represent rx^n, specify —
Stoich coeff, phy. states of react. & prod, allotrope of solid, $\underset{\text{(Enthalpy of } Rx^n)}{\Delta H^\circ}$, ...
└ taken

Types of Enthalpy of Rx^n

1) Formation
2) Combustion
3) Neutralisation
4) Hydration
5) Sol^n
6) Phase Change
7) Dimerisation
8) Atomisation
9) Hydrogenation

⋮

Enthalpy of Formation (ΔH_f)

Amt. of heat involved when 1 mol comp. is formed from its pure stable & elemental constituents.

Eg : $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; ΔH°_{rxn}

$$\boxed{\Delta H^\circ_{rxn} = \Delta H^\circ_f(H_2O(l))}$$

Eg : $2\underset{\text{(graphite)}}{C(s)} + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$; ΔH°_{rxn}

$$\boxed{\Delta H^\circ_{rxn} = \Delta H^\circ_f(C_2H_5OH(l))}$$

Eg : $2\underset{\text{(graphite)}}{C(s)} + 2H_2(g) + O_2(g) \rightarrow CH_3COOH(l)$; ΔH°_{rxn}

$$\boxed{\Delta H^\circ_{rxn} = \Delta H^\circ_f(CH_3COOH(l))}$$

☆ For pure stable elemental molecules, we assume their std^n H_f is <u>zero</u>.

i.e.

$$\boxed{\Delta H^\circ_f\left(\begin{array}{c}\text{Pure elemental Stable}\\ \text{molecule}\end{array}\right) = 0}$$

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for Carbon we assume, $\boxed{\Delta H_f^\circ(\text{Graphite}) = 0}$

When ∃ multiple allotropes for solid comp., we assume ΔH_f° of a particular allotrope to be zero.

☆ for ANY rx^n,

$$\boxed{\Delta H^\circ_{rx^n} = \left[\sum\left(\underset{\text{Stoic. coeff. of prod.}}{p_i} \cdot \Delta H_f^\circ(\text{Prod.})\right) - \sum\left(\underset{\text{Stoich. coeff. of react.}}{r_i} \cdot \Delta H_f^\circ(\text{React.})\right)\right]}$$

Stoic. coeff. of prod.

Stoich. coeff. of ~~prod~~ react.

Enthalpy of Combustion

Amt. of heat released when 1 mol of comp. is completely burnt into ~~th~~ its proper oxide.

Element :	C	H	N	S	Na
Proper Oxide :	CO_2 (g)	H_2O (l)	NO_2 (g)	SO_2 (g)	Na_2O (s)

Eg: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$; ΔH°_{rxn}

$$\boxed{\Delta H^\circ_{rxn} = \Delta H^\circ_r\left(C_2H_5OH(l)\right)}$$

Eg: $C_{(graphite)}(s) + O_2(g) \longrightarrow CO_2(g)$; ΔH°_{rxn}

$$\boxed{\Delta H^\circ_{rxn} = \Delta H^\circ_r\left(C_{(graphite)}(s)\right) = \Delta H^\circ_f\left(CO_2(g)\right)}$$

Eg: $C_{(diamond)}(s) + O_2(g) \longrightarrow CO_2(g)$; ΔH°_{rxn}

$$\boxed{\Delta H^\circ_{rxn} = \Delta H^\circ_r\left(C_{(diamond)}(s)\right) \neq \Delta H^\circ_f\left(CO_2(g)\right)}$$

Hess's Law

On adding 2 therm. rxns, their ΔH is also added.

On multiplying rxn by a const., ΔH gets multiplied by the same const.

A rxn be carried out by any path, finally ΔH will be same.

Eg: Assuming all these rxn are at same temp.

$$C_{(graphite)} + \frac{1}{2}O_2(g) \rightarrow CO(g) \; ; \; \Delta H = \Delta H_1$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \; ; \; \Delta H = \Delta H_2$$

$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g) \; ; \; \Delta H = (\Delta H_1 + \Delta H_2)$$

Q) At 300 K, ΔH_f° of $C_6H_5COOH(s)$, $CO_2(g)$ & $H_2O(l)$ are a, b, c, $\frac{kJ}{mol}$ resp.

Calc. heat of combustion of benzoic acid at const. vol.

A)
$$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l)$$

$$\Delta H_r = (3c + 7b - a) \; kJ/mol$$

Now,
$$\Delta U_r = \Delta H_r - RT(\Delta n_g)$$

$$\Rightarrow q_v = (3c+7b-a) - (300)\left(\frac{25\times10^{-3}}{3}\right)\left(\frac{-1}{2}\right)$$

$$\Rightarrow \boxed{q_v = (3c+7b-a+1.25) \; \frac{kJ}{mol}}$$

Q) Given — ΔH_f° of $H_2O(l) = a$ kcal/mol

$\Delta H^\circ_{comb.}$ of $C_2H_2 = b$ kcal/mol

$\Delta H^\circ_{comb.}$ of $C_2H_4 = c$ kcal/mol

find ΔH for $C_2H_2 + H_2 \rightarrow C_2H_4$.

A) $$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \; ; \; \Delta H = a$$

$$C_2H_2 + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l) \; ; \; \Delta H = b$$

$$C_2H_4 + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \; ; \; \Delta H = c.$$

Req : ① + ② − ③ $\Rightarrow$ $\boxed{\Delta H_r = (a+b-c) \text{ kcal/mol}}$

Kirchoff's Eqn

for rxns,

$$\left(\Delta_r H_{T_2} - \Delta H_{r,T_1}\right) = \Delta_r C_p \left(T_2 - T_1\right)$$

$$\left(\Delta_r U_{T_2} - \Delta_r U_{T_1}\right) = \Delta_r C_V \left(T_2 - T_1\right)$$

$$\left(\Delta_r S_{T_2} - \Delta_r S_{T_1}\right) = \Delta_r C_{p,m} \ln\left(\frac{T_2}{T_1}\right)$$

Enthalpy of Neutralisation —

Energy released when 1 gm eq. of acid & 1 gm eq. of base undergo neutralisation in aq. solⁿ.

OR

Energy released when 1 mol H^+, coming from acid, & 1 mol OH^-, coming from base, react to form 1 mol $H_2O(l)$.

$$\boxed{\Delta H^\circ_{neu} = \Delta H^\circ_{ion(acid)} + \Delta H^\circ_{ion(base)} + \Delta H^\circ_{w}}$$

ΔH°_{ion} is energy needed to completely ionise the acid or base. For strong acids & strong bases, $\Delta H^\circ_{ion} = 0$.

Also, $H^+ + OH^- \rightarrow H_2O$, $\Delta H = \Delta H_w$

$$\boxed{\Delta H_w = (-57.1)\ kJ/mol = (-13.7)\ k\text{-}cal/mol}$$

Eg: $\underset{(aq.)}{NaOH} + \underset{(aq.)}{HCl} \longrightarrow \boxed{\underset{(aq.)}{NaCl}} + \underset{(l)}{H_2O}$

Observe (aq.) & NOT (s).

Q) ΔH_{neu} (Oxalic Acid) = ~~10.6~~ (-106.7) kJ/mol using NaOH.

Find ΔH of, $H_2C_2O_4 \rightarrow C_2O_4^{2-} + 2H^+$

A) $\Delta H_{neu} = \Delta H_{ion} + \underset{\uparrow \text{ as } 2H^+ \text{ available}}{2\Delta H_w} = \Delta H_{ion} - 2(57.1) = (-106.7)$

$$\Downarrow$$

$$\boxed{\Delta H_{ion} = 7.5 \text{ kJ/mol}}$$

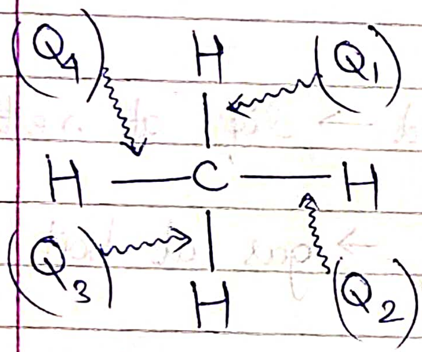
Enthalpy of	Def^n
1) Fusion	1 mol solid → liq. at melt. pt.
2) Vaporisation	1 mol liq. → gas at boil pt.
3) Sublimation	1 mol solid → gas directly, below melt pt.
4) Hydration	1 mol anhyd. sub. → specific hydrate (Eg: $CuSO_4(s) + H_2O(l) \rightarrow CuSO_4 \cdot 5H_2O(s)$)
5) Solution	1 mol sub. dissolved in specific amt of solvent (Eg: $NaCl(s) \rightarrow NaCl(aq)$)
6) Hydrogenation	1 mol Unsaturated comp. $\xrightarrow{\text{excess } H_2}$ Fully saturated comp.
7) Atomisation	1 mol comp. completely diss. into gaseous atoms (Eg: $C_2H_6(g) \rightarrow 2C(g) + \underline{6H(g)}$) NOT $3H_2$
8) Dimerisation	2 mol of sub. → 1 mol of Specific sub. (Eg: $2NO_{2(g)} \rightarrow N_2O_{4(g)}$)

Bond Enthalpy

Avg. amt. of energy req. to break 1 mol of a bond of particular type b/w atoms within a molecule in gaseous state. ~~understand~~

Eg : $H_2(g) \rightarrow 2H(g)$; $\Delta H = BE_{H-H}$

Eg : $CH_4(g) \rightarrow C(g) + 4H(g)$; $\Delta H = \sum Q_i$

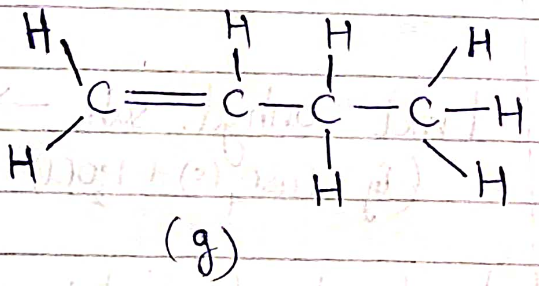


$\{Q_i \neq Q_j\}$

$BE_{C-H} = \left(\frac{\sum Q_i}{4}\right)$

(avg. energy to break C-H bond)

Eg :



$\rightarrow 4C_{(g)} + 8H_{(g)}$

$$\Delta H = 8\,BE_{H-H} + 2\,BE_{C-C} + BE_{C=C}$$

where $:C{=}C:_{(g)} \rightarrow 2C_{(g)}$; $\Delta H = BE_{C=C}$

Q) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$. Calc. ΔH.

BE (kJ/mol)	a	b	c
Bond	H—H	Cl—Cl	H—Cl

A) $\Delta H = 2H_f(HCl) - H_f(H_2) - H_f(Cl_2)$ ✗ use

$= BE_{H-H} + BE_{Cl-Cl} - 2BE_{H-Cl}$ ✓ use

$= \boxed{a + b - 2c}$

(as BE given & H_f NOT given)

To apply this, EVERYTHING should be in gaseous state!

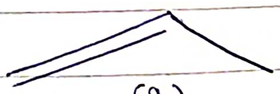
★

$$\Delta H_r^\circ = \left[\sum\left(\overset{r_i}{\cancel{p_{react}}} \cdot BE_{react.}\right) - \sum\left(p_i \cdot BE_{prod.}\right)\right]$$

(stoich. coeff. of reactants) (stoich. coeff. of product.)

Q) Find enthalpy of combustion of propene. $\Delta H^\circ_{vap}(H_2O) = t$.

BE	x	y	z	a	b	c
Bond	C-H	C=C	C-C	O=O	C=O	O-H

A)  (g) $+ \frac{9}{2} O_2 (g) \rightarrow 3CO_2 (g) + 3H_2O (l)$; $\Delta H = \Delta H_{comb.}$

Now, $\Delta H^\circ_{comb.} + 3(\Delta H^\circ_{vap.}) = \left[(6x + y + z) + 9a/2 - 6b - 6c\right]$

$\rightarrow \boxed{\Delta H^\circ_{comb.} = \left(6x + y + z + \frac{9a}{2} - 6b - 6c - 3t\right)}$