

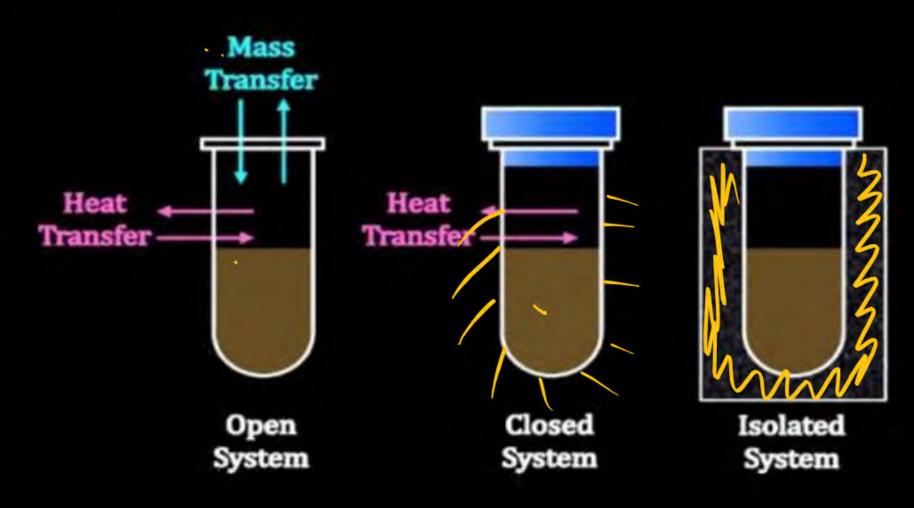
Physical Chemistry Summary Lecture

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Note:-

System + Surrounding = Universe



Function of a System



State:- Depend on initial and final state

$$P_1V_1T_1 \rightarrow P_2V_2T_2$$

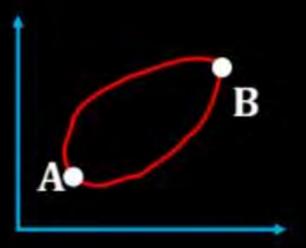
Ex.: U, H, G, S, T, etc



Path:- Depend on path

Ex.: w, q, etc









Intensive (Independent of mass of the system)		Extensive (Depends on mass of the system)	
1.	Pressure	1. Mass	
2.	Temperature	2. Volume	
3.	Density	3. Internal energy	
4.	Concentration	4. Heat capacity	
5.	Melting point	5. Enthalpy	
6.	Boiling point	6. Entropy	
7.	Surface tension	7. Gibbs energy, etc	
8.	Viscosity, etc		

If x & y one two estensive knop.



on dx = Intensive

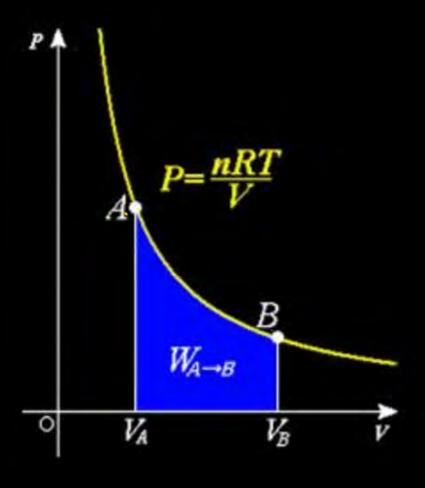




► Iso-thermal Process:-

 $T \rightarrow Constant$

$$\Delta T = 0$$



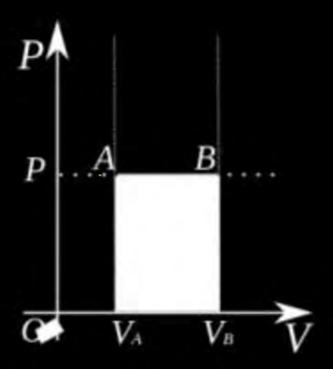




Iso-baric Process

 $P \rightarrow Constant$

$$\Delta P = 0$$



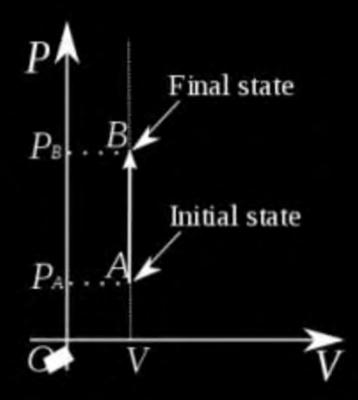




Iso-choric Process

 $V \rightarrow Constant$

$$\Delta V = 0$$







Adiabatic Process:-

Transfer of heat is 0

i.e.,
$$q = 0$$







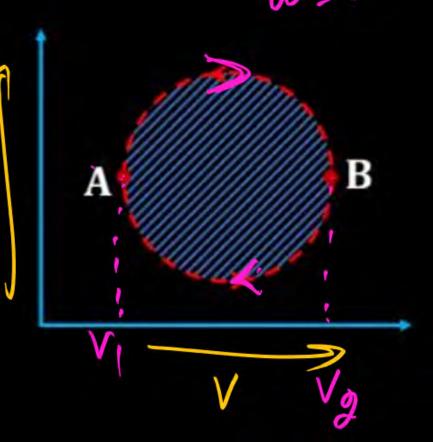
AJB AV = (+) Ve

Cyclic Process:

Process in which initial and final point is same

i.e., for cyclic process

$$\Delta P = 0$$
, $\Delta V = 0$, $\Delta U = 0$, $\Delta S = 0$, $\Delta H = 0$



Note:- Clockwise $\Rightarrow \Delta V = +ve \Rightarrow W = -ve$ process Anticlock process $\Rightarrow \Delta V = -ve \Rightarrow W = +ve$





> Sum of all the components of energy due to internal factor of the system,

i.e.,
$$U = K.E. + P.E. +$$





- Mode of transfer of energy between system and surrounding.
- Mathematical expression: (If P_{ext} = Constant)

$$W = -P_{\text{ext}} (V_2 - V_1)$$

Note: Work done in any process is equal to area under PV diagram.



Note:-

SIGN CONVENTION

For expansion $\Rightarrow \Delta V = +ve$

W = -ve

{Work is done by the system}

For compression $\Rightarrow \Delta V = -ve$

W = +ve

{Work is done on the system}

Heat
$$(9)$$
 \div

$$9 = (m - \Delta)$$

$$= C \Delta T$$





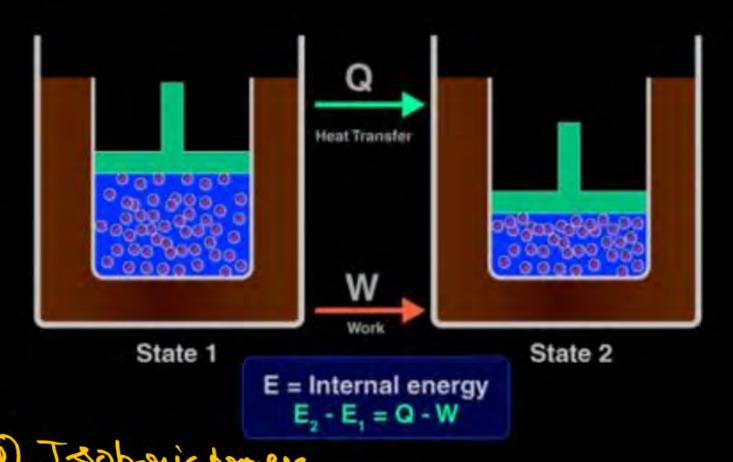


- Based on 'Conservation of Energy' principle.
- Mathematical expression:

$$\Delta U = q + w$$

O Zeothermal proces = AT=0=1 AU=0 Cyclic process: q=-w

(2) Adiabatic proon = 9=0 DU=W



Work Done for Different Processes



- \triangleright Iso-choric \Rightarrow W = 0
- > Iso-baric ⇒ $W = -P_{ext} (V_2 V_1)$
- ► Iso-thermal \Rightarrow W_{rev} = -2.303 nRT $\log \frac{V_2}{V_1} = -2.3 \text{ 3.3 nRT } \log \frac{\rho_1}{\rho_2} = -0.87 \ln \frac{\rho_2}{\rho_3}$

$$W_{irr} = -P_{ext} \left\{ \frac{nRT}{P_2} - \frac{nRT}{P_1} \right\} \quad \left(P_{ext} = P_2 \right)$$

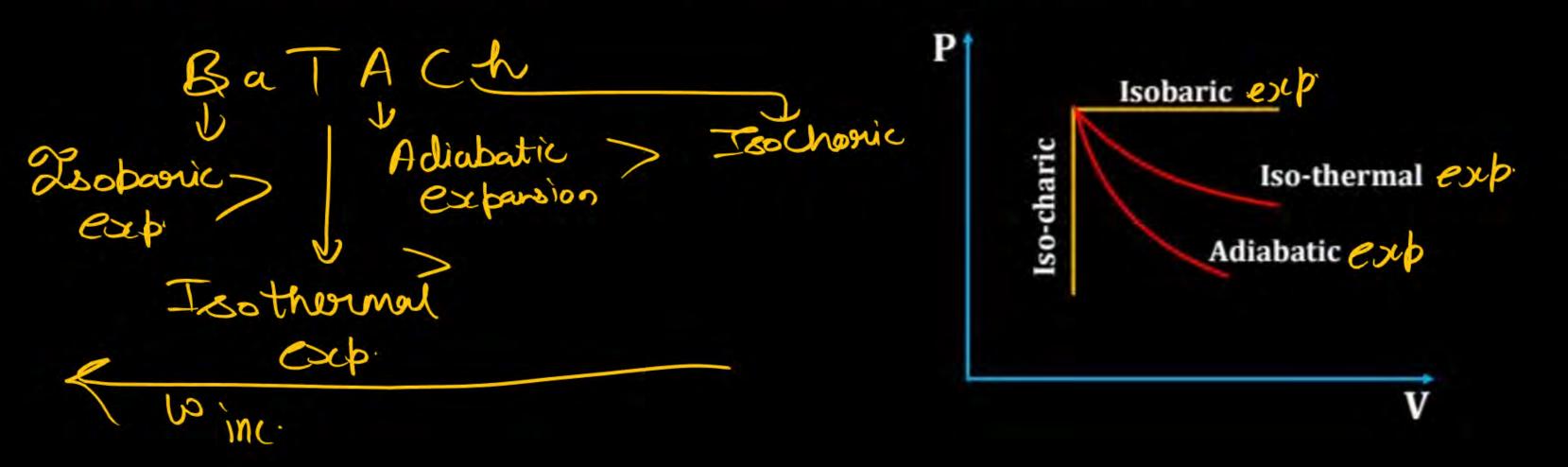
Adiabatic
$$\Rightarrow W_{rev} = \frac{R}{R} = \frac{$$

$$Adi esid. = \frac{P_{ext} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right) - \frac{nR}{N-1}}{P_1} - \frac{nR}{N-1} - \frac{nGv_1 mA}{N-1}$$



Work Done in Various Processes (Graph)









- It represents the net heat content of the system.
- Mathematical expression:

$$H = U + PV$$

Ex.: for a reaction,
$$aA + bB \longrightarrow cC + dD$$

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

Where
$$\Delta n_g = (c + d) - (\underline{a + b})$$

$$\operatorname{Pr}(g) \quad \operatorname{Nor}(g)$$



Endothermic & Exothermic Process



	Exothermic Process		Endothermic Process
1	$\Delta H < 0$	1	$\Delta H > 0$
1	$\Delta H = -ve$	1	$\Delta H = +ve$
1	Energy of released	1	Energy is absorbed





- ➤ It is the amount of heat required to raise the temperature of a system by 1° C.
- Mathematical Expression:

$$C = \frac{q}{\Lambda T} \qquad q = (\Delta T)$$
; Units = J/°C or J/K

Extensive property



Type of Heat Capacity



Specific Heat Capacity (&)

✓ Raise temperature of 1 kg of substance by 1°C.

$$\checkmark S = \frac{q}{m\Delta T}$$

✓ Intensive property

Molar Heat Capacity (Cm)

✓ Raise temperature of 1 mole of substance by 1°C.

$$\checkmark C_{\rm m} = \frac{q}{n\Delta T}$$

✓ Intensive property



Molar Heat Capacity (C_m)

► At constant volume (C_v)

$$q_v = \Delta U = nC_v \Delta T$$

At constant pressure (C_p)

$$q_p = \Delta H = nC_p \Delta T$$

Jan Toriatomic an Polyatomic
Cym=3R
Cpm=4R
N=1.33

fen Diatomic good Cr,m==気R Cp,m=えR



Relation Between C_p & C_v



$$ightharpoonup C_{p,m} - C_{v,m} = R$$

(Gas constant)

(Poisson's ratio)

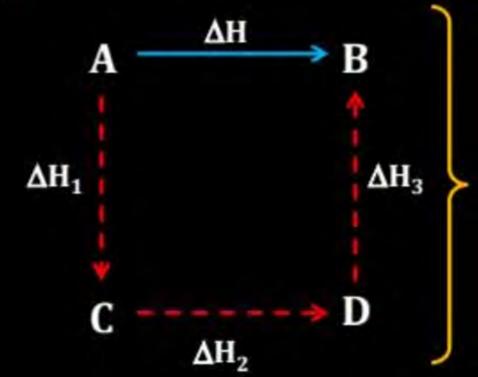
- ❖ For monoatomic ⇒ γ = 1.66
- ❖ For diatomic ⇒ $\gamma = 1.4$
- ♦ For triatomic $\Rightarrow \gamma = 1.33$





The overall enthalpy change of a chemical process is independent of

the path taken



$$A \rightarrow C$$

$$C \rightarrow D$$

$$A + C + D \rightarrow G + D + B$$

$$C \rightarrow D$$

$$A \rightarrow B$$

$$A \rightarrow B$$

$$A \rightarrow B$$

$$A \rightarrow B$$



Different Type of Enthalpies





Enthalpy of formation (ΔH_f): When one mole of compound is formed from its elements in elementary state. \(\frac{1}{2}\lambda(g) + \frac{1}{2}\lambda(g) -> \(\text{IHU(g)} \) \(\text{AH} = \text{AH}_C \)

$$\Delta H = \Sigma \Delta H_{f (products)}^{o} - \Sigma \Delta H_{f (reactants)}^{o}$$

Enthalpy of combustion (ΔH_c): When one mole compound undergoes of combustion. | C(graphite) + 100(9) -> 100(9) AH = AH combing = AH fundamental ((graphit) al costs)

$$\Delta H = \Sigma \Delta H_{c \, (reactants)}^{o} - \Sigma \Delta H_{c \, (products)}^{o}$$



Enthalpy of Hydrogenation:- When one mole of unsaturated compound converts into saturated compound.

Enthalpy of Hydration: When one mole of anhydrous salt converts into hydrated salts.

(uSou(s) + Ho O - CuSou 5 Moo(s)

White

Bond Dissociation Enthalpy: Energy needed to break one mole of the

bond to give separated atoms

1 (g) - 2 (g) AH-B.E. xalq)

1 (la 19) - 2 (lq) AM-B.E (la 19)

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1 (la 19) - 2 (lq) AM-



Calculation of Enthalpy

$$\Delta H = \Sigma \Delta H_{(product)} - \Sigma \Delta H_{(reactant)}$$

Always use this formula, except

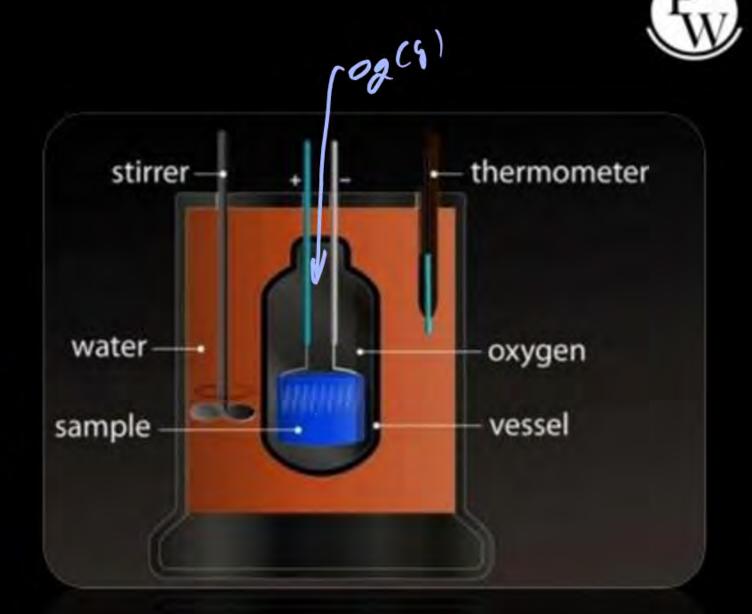




Bomb Calorimeter

In Bomb Calorimeter, we measure $q_v = \Delta U$

 $q_V = \Delta U =$ (Heat absorbed by Bomb Calorimeter + Heat absorbed by Water)



AH = AU + Ang RT

$$1CH_{N}(9) + 29(9) \rightarrow 1CO_{R}(9) + 2H_{R}(9)$$

$$\Delta n_{g} = 1 - (1+2) = -2$$





- No information about direction in which flow of energy takes place
- It does not differentiate between spontaneous and nonspontaneous process



Spontaneous and Non-spontaneous Process



Factors affecting spontaniety

- 1) Tendency for minimum energy: DH = t Ive
- Dendency from maximum transformers.

 AS = (+)ve.





measurement of disorder or randomness.

$$zR \longrightarrow P$$

$$\Delta S = \sum S_{\text{(product)}} - \sum S_{\text{(rectant)}}$$

Mathematical Expression:

$$\Delta S = \frac{q_{rev}}{T}$$
; Unit = J/K

- **Extensive property**
- State function



Important Points:-

S ∝ Temperature,

But

$$\Delta S \propto \frac{1}{Temperature}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$



2nd Law of Thermodynamics



For a spontaneous change:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

In a reversible process the entropy of the Universe remains constant,

i.e.,
$$\Delta S_{\text{total}} = 0$$

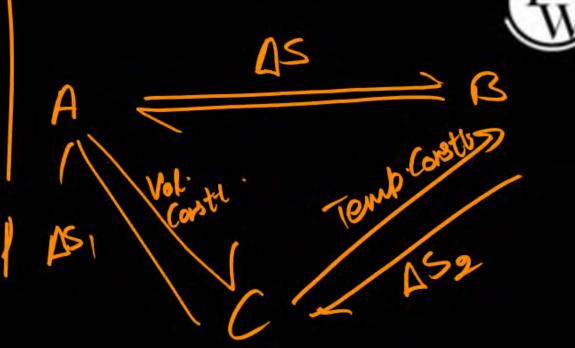


Entropy Change for an Ideal Gas



$$= nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

- Iso-thermal process: $\Delta S_{system} = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$
- So-baric process: $\Delta S_{system} = n C_{Pm} \left(\frac{T_2}{T_1}\right)$
- Iso-choric process: $\Delta S_{system} = n C_v \ln \left(\frac{T_2}{T_1}\right)$





Entropy Change in Various Physical Process



During phase transformation

$$\Rightarrow \Delta S_{Fusion} = \frac{\Delta H_{Fusion}}{T_m}$$

$$\Rightarrow \Delta S_{Vapourisation} = \frac{\Delta H_{Vapourisation}}{T_{Q}}$$

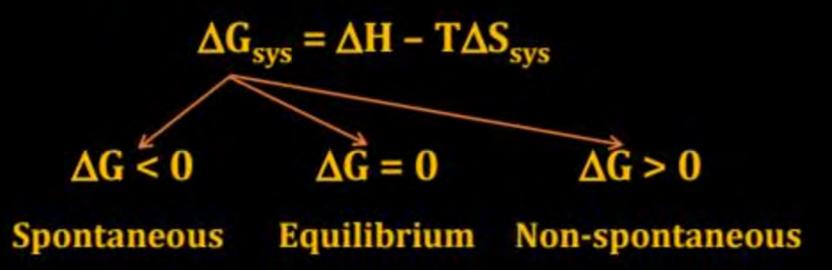
$$\Rightarrow \Delta S_{Sublimation} = \frac{\Delta H_{Sublimation}}{T_S}$$

ASVap. = 88 J K' molt except por H-Bond Liquid on metallic Bond.





At constant temperature:



- * Unit ⇒ Joule
- * State function
- Extensive property



1	H	4	0
	•	-	

0< HA

DS 20

spontaneous at all temp

AGICO

Spon at shigh T = 16000

Spon at low T AGREO Non-spon at all temp



3rd Law of Thermodynamics



For a perfectly crystalline solid, entropy is 0 at 0 K (absolute zero)

Mathematically,

$$\lim_{T\to 0K} S = 0$$



Curve Between Entropy v/s Temperature



$$\Delta S_{\alpha} = \frac{\Delta H fwsion}{T_{\alpha}}$$

