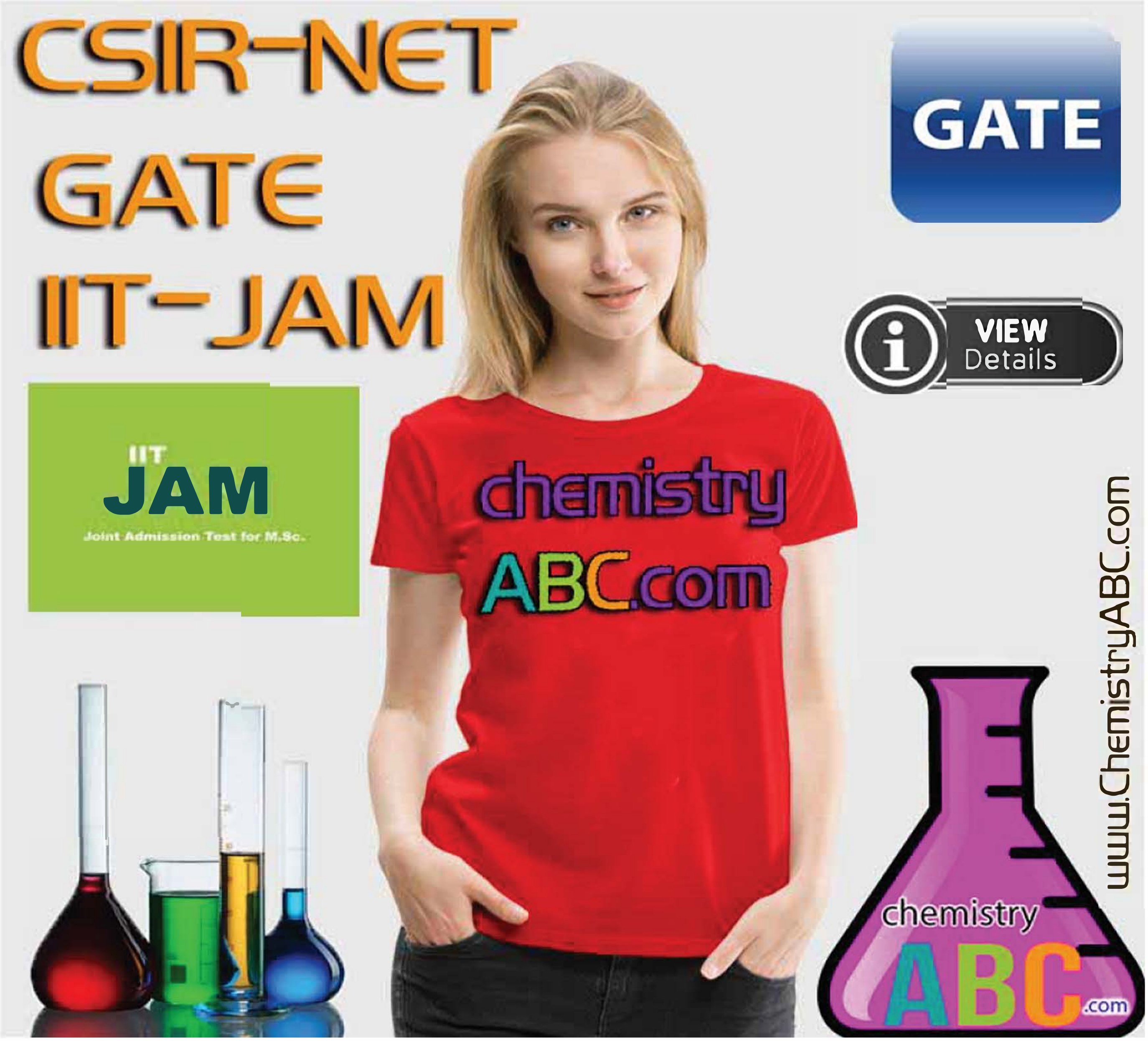
Thermodynamics Class Notes 2015

Handwritten by Aman Sir



www.ChemistryAbc.com free CSIR UGC NOTES

Chemical Sciences Study material is complete Handwritten Class Notes by one of the best coaching for NET CSIR IIT-JAM possesses the following 15 thick booklets

1. Chemical bonding
2. Chemical Kinetics
3. Coordination Chemistry
4. Electrochemistry
5. Group Theory , Solid State , Aromacity
6. Oraganic Synthesis
7. Organometallic Chemistry
8. Pericyclic Reaction
9. Quantum Chemistry
10. Reaction Mechanism
11. Reagents
12. Spectroscopy
13. Spectrochemistry
14. Sterochemistry
15. Thermodynamics

-: Thermodynamics :-

⇐ Thermodynamic property ⇒

Free Energy = → Gibb's free Energy [G]
→ Halmholtz free Energy [A]

Internal Energy or intrinsic Energy
[E or U]

Entalpy (H)

Entropy (S)

work

Heat

State function

Euler's theorem

Joules Thompson Effect

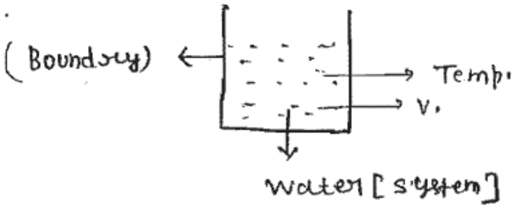
Carnote Engine

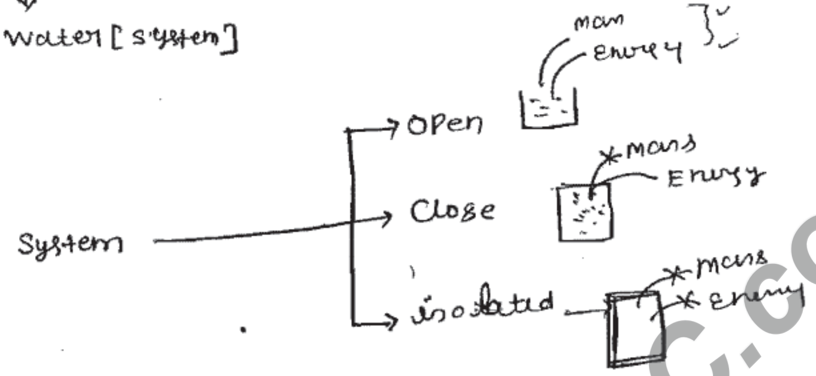
Zeroth, I^{st}, II^{nd} & III^{rd} law of thermo.

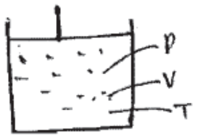
fugacity

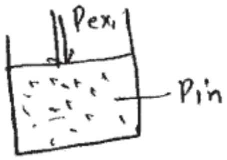
chemical potential

thermochemistry









$P_{ex} > P_{in}$ ⇒ compression

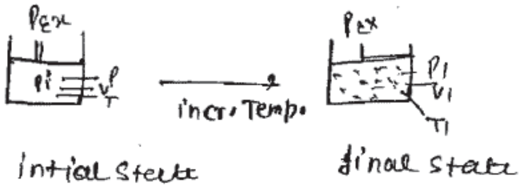
$P_{in} < P_{ex}$ ⇒ expansion

$P_{in} = P_{ex}$ [system as it]

[P, V, + T – fixed]

⇓

(Existance of syst.)



$\Delta V = V_1 - V$

$\Delta T = T_1 - T$

Thermodynamics:-

"It is branched of Science which Study the quantitative relationship b/w heat and another form of energy.

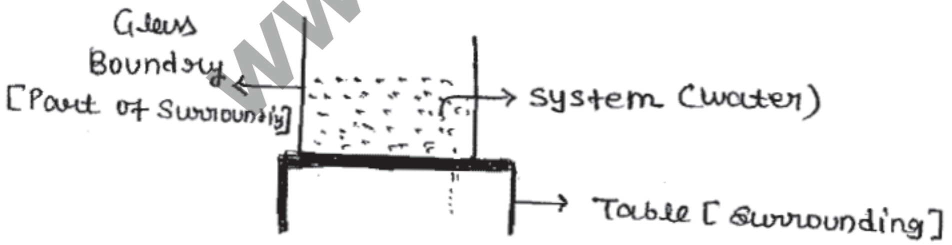
for e.g. ⇒ we Study the energy term like

⇒ Gibb's free energy
⇒ HoltHoltz free energy
⇒ U
⇒ ΔS
⇒ H

there are the two basic concept in the thermodynamics one is <u>System</u> and another is <u>Surrounding</u>.

System:→ It is a part of universe which under investigation experimently or ~~theoretical~~ theoritically

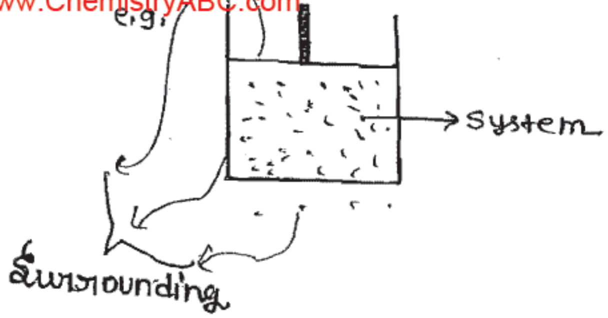
e.g. if we take a Glass of water and if u Study the properties [P, V, & T] of water then water as considered as a System.



Surrounding:⇒

it is a part of universe other then system is called Surrounding. for Practical purpose, Surrounding is the region which is around the System or which is vicinity of the System.

e.g.



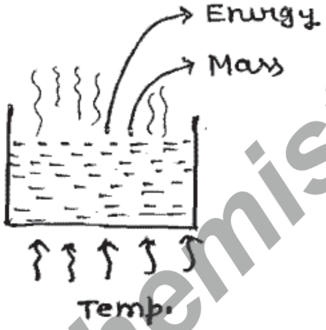
there are three types of System

(I) open System

(ii) close System

(iii) Isolated System

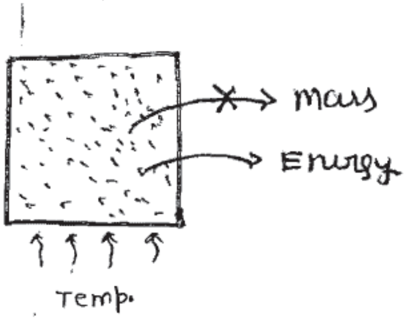
Open System:⇒



the System which exchange mass as well as energy to the surrounding is called open system.

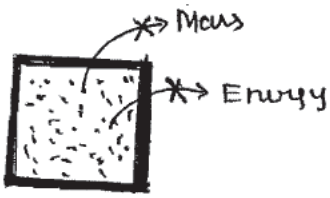
Close System:-

the System which exchange energy not mass to the surrounding is called close system.



the System which Neither Exchange Energy nor mass with the Surrounding that is called Isolated System.

Note ⇨ Practically completely Isolated system is not possible

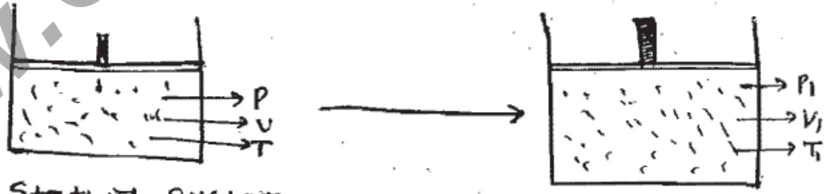


State of the System :⇨

It is the condition of Existence of a particular System when its macroscopic property have a definite value

i.e. Suppose a Gaseous System which having a piston, there pressure, volume, temp. etc. are fixed. this shows fixed properties that system has a particular state of Existence.

e.g. ⇒



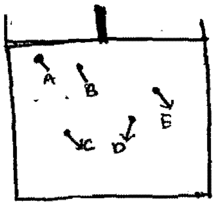
State of System
[Initial State]

[Final State]

Macroscopic properties :⇨

The properties of a System which Contains [atoms/ molecules/ ions], there properties is arise due to [P, V, & T] the collective behaviour of all the molecules, ions, atom, from which the System is made.

e.g. ⇒ Volume is a macroscopic property which arise



$$V = V_A + V_B + V_C + V_D + V_E$$

e.g. ⇒ P, V, T, E, G, S

* EXTENSIVE AND INSTENSIVE PROPERTY *

EXTENSIVE PROPERTY [Depends upon Amount]

⇒ The property of a System which depend upon the quantity of matter contained. or which depends upon Amount.

e.g. ⇒ • Energy [H, G, A, E, S]

- No. of moles
- volume
- Heat capasity [Molar Heat capasity is In. prop.]

[redacted] Molarity [जब Data बहुत होता हो]

Heat capacity
$$\boxed{C = \frac{q}{m.\Delta t}}$$

INTENSIVE PROPERTY:-

⇒ The property of a System which is independent upon the quantity of matter, don't depend upon the amount.

e.g. ⇒

⇒ Temp. ⇒ molarity
⇒ molality
⇒ Molar volume ⇒ Dielectric Const.
⇒ ~~Molarity~~ pressure ⇒ mole fraction
⇒ Density ⇒ conc. [जब Data बहुत बड़ा है]
[uniform distribution]
⇒ pH
⇒ Viscocity ⇒ free Energy per mole
⇒ Refractive Index

Note ⇒ The ratio of two Extensive become Insentive.

e.g. ⇒ $$\underset{[\text{Insentive}]}{\text{Density}} = \frac{\text{Mass [Ext.]}}{\text{Volume [Ext.]}}$$

←: TYPES OF PROCESS :→

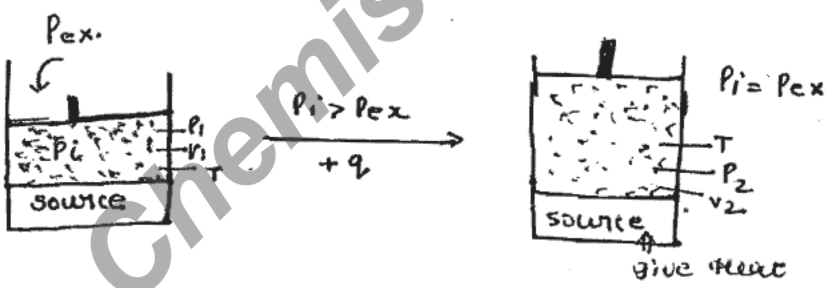
- ⇒ Isobaric process
- ⇒ IsoChoric process
- ⇒ Isothermal process
- ⇒ Adiabatic process
- ⇒ Polytropic process
- ⇒ Reversible process
- ⇒ Irreversible process [spontaneous process]
  ⇓
  [Natural process]
- ⇒ Cyclic process
- ⇒ IsoEntropic Process

Isothermal Process →

When a System change from one State to another State, during this the temp. remain same then the process is called

there is two type of possibility of isothermal process one is isothermal Expension and another is isothermal compression.

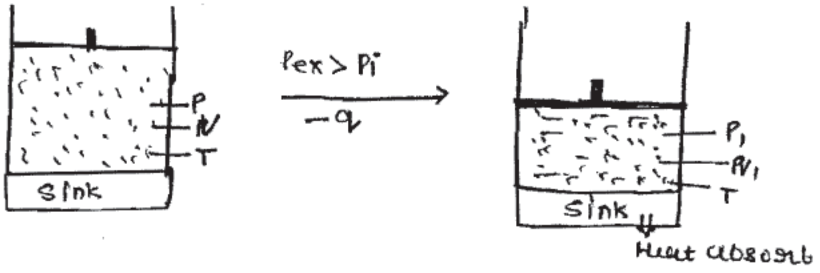
→ Isothermal Expension



in isothermal Expan. work is done by the System during expansion the System absorb heat from the Surrounding.

- in isothermal Ex. temp. only remain same when a System absorb heat from outside but if the System expend among itself then temp. definitely lower at final State.
- we use the Source for Heat absorbance.

Isothermal compression :→



In Isothermal compression work is done on the System by the Surrounding. in this case Heat is rejected to the Surrounding.

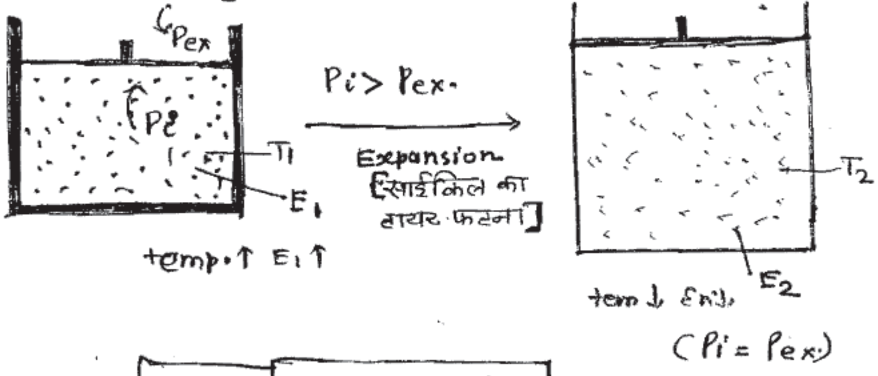
- In Isothermal compression work is done on the system is converted into the heat and ultimately in order to maintain the temp. const. Heat is rejected to the Surrounding.
- In this case work is done by the surrounding on the System.

Adiabatic process :→

[No complete Adiabatic process possible]

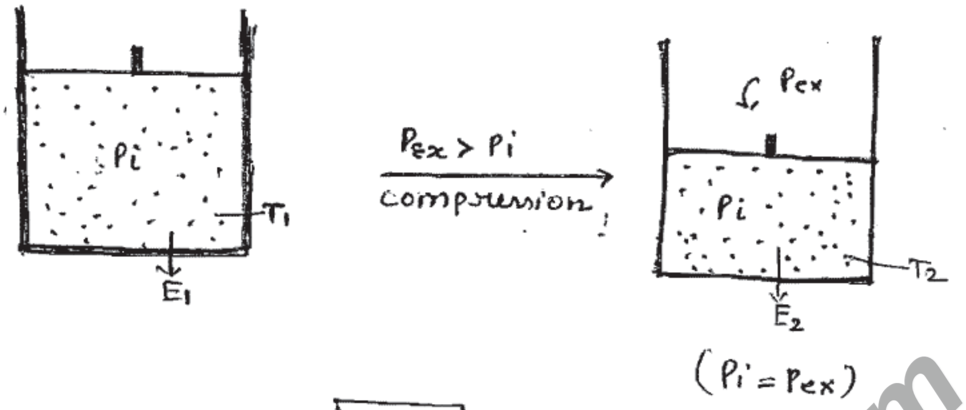
[there is no Exchange of Heat b/w System & Surrounding]

$[q = 0]$



$$\boxed{\Delta E \Rightarrow E_2 - E_1 = -ive}$$

$T_1 > T_2$



$$\boxed{T_2 > T_1}$$

$$\boxed{\Delta E \Rightarrow} \boxed{E_2 - E_1 \Rightarrow +ive}$$

" The System which Neither Exchange Heat with the Surrounding then System is called Adiabatic."

" in adiabatic process there is two possibility-

[1] Adiabatic compression
[2] " Expension

" In Adiabatic Expension System Expend at the Expense of Internal Energy bcoz there is no other possibility of Energy"

- ΔE decreases
- Final temp. lower down

" In adiabatic compression System work is done by the ~~System~~ surrounding.

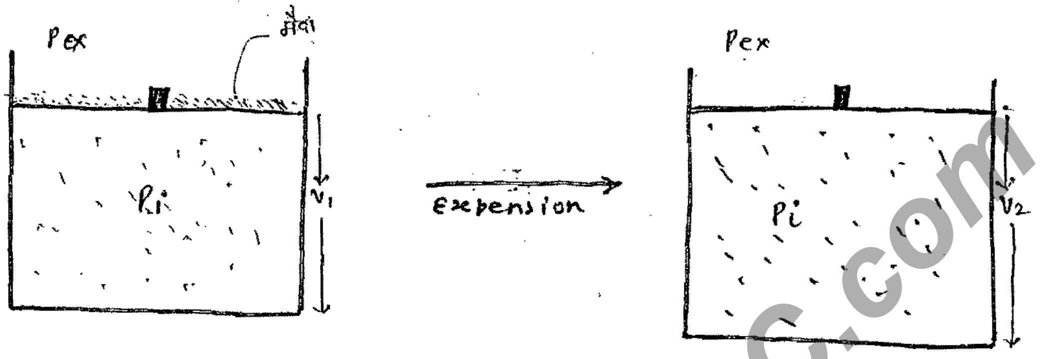
Heat up the molecule of System, there is no possibility of Heat rejection to the given temp.

(10)

One life time possible नहीं

⇑ क्रिया की Imagination (शुरुआत)

⇐ Reversible Process : ⇒ (Ideal, Imagination work)



$P_i = P_{ex} + dP$

$P_{ex} = P_{in}$.

⇒ it is hypothetical and imaginary Process, Practically it is not possible.

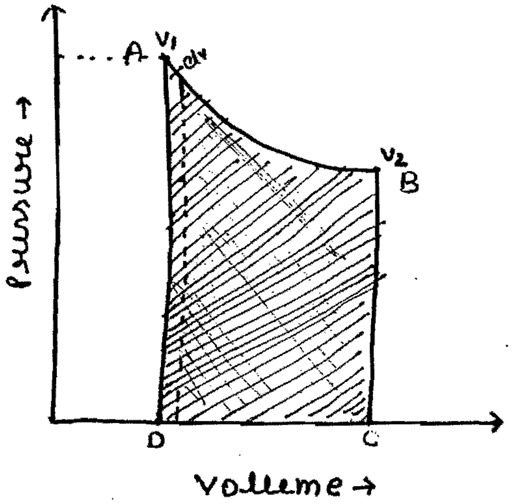
⇒ opposing force and driving force are comparable, so work done is maximum.

⇒ it take infinite time to complete & infinite step to complete,

⇒ it take place ~~step~~ infinite slowly in such a manner the system remaint at Equilibrium at Each & Every Step.

⇒ there is a lot of step of work done take place when you combined all the step then we get total work done.

⇒ It is reverse. at Each & Every Step



Area of ABCD = Total work done in expension from V_1 to V_2

[Graph for work done in Reves. process]

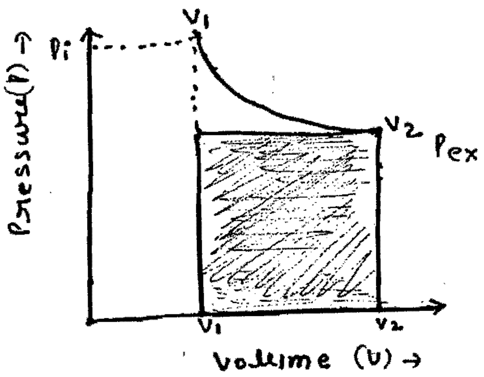
Irreversible Process :→

([illegible]) – due to the Expension
[Internal pressure is very high]

⇒ Irre. process are very rapid process is very rapid.

⇒ there is very large diff. b/w oppos. & Driving force

⇒ Irr. process are also called Natural process and spontenous process ([illegible])



Total work done (w) $= -P_{ex}[V_2 - V_1]$

⇒ It is not reversible, it only reverse when e.g ⇒ combustion of Paper, Gas

⇒ flowing of Heat from High temp. to Low temp.

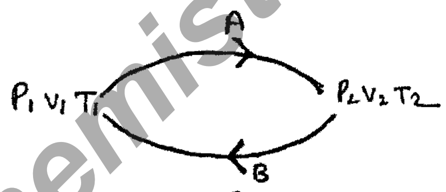
⇒ flow of water from the slope.

⇒ All the natural reaction

⇐: POLYTROPIC PROCESS :⇒

⇒ "The Process in which, when there is no change in heat capasity take place, then this process is called Polytropic process."

⇐ Cyclic Process :⇒ (जहाँ से आये वहीं गिरना)



When a system Follows/ travels many step/state and finally return to the original state then the process is called cyclic process.

[10.10.15]

13

⊛ Isobaric Process:-

→"When there is no change in pressure. then this process is called Isobaric process."

$$(P_1 V_1 T_1) \longrightarrow (P_1 V_2 T_2)$$

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

When a System change from one state to another State during this process pressure is not change then this process is called Isobaric process.

* Isochoric Process:-

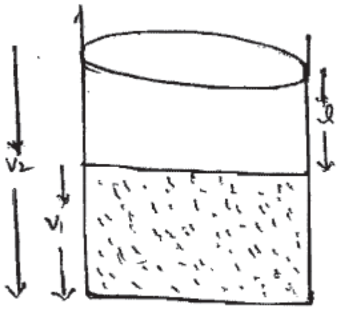
When the System change from one State to another State during this process volume is not change then this process is called Isochoric process.

$$(P_1 V_1 T_1) \longrightarrow (P_2 V_1 T_2)$$

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

* Iso Entropic process:-

When the System Change from one State to another State, when there is no change in Entropy take place ($\Delta S = 0$) is called isoentropic process.



$P = F/a$

$\Delta V = V_2 - V_1$

W = F× displacement

- Work is a organised form of Energy
- It Standard unit is Joule
- It is path dependence function bcoz the value of work is different for differ path so it is not Stable function also
- In General work is done on the System Internal Energy Increases.
- if work is done by the System, internal Energy decreases

Since we know that work (w) = force × displacement

$$w = F \times d$$
$$w = P \times a \times l$$
$$w = P.\underset{\substack{\Downarrow \\ \text{large diff.}}}{\Delta V}$$

($\delta v \Rightarrow$ sm diffi)

10 – 15

$$W = -P(V_2 - V_1)$$

Sign convension for work –

if work is done by the System then we always consider −ive sign, ~~but~~ if work is done on the system then we always consider +ive sign.

Note:➡ we always consider work in the form of $-PdV$.

HEAT :⇒ [absorb(+ive) release (−ive)]

- Heat is a unorganized or Random form of Energy.
- if Heat is absorb by the System then Internal Energy of System Increases.
- if Heat is releases by the System then the Internal Energy of a system is decrease.
- the value of Heat depend upon the path so that that is path dependence function ......

Sign convension for Heat

- If Heat is given out of the System then the sign of Heat is considered negative and if Heat ~~is~~ absorbed by the System then the sign of Heat is considered +ive.

The only two parameter is thermodynamics is a path dependence one is <u>Heat</u> another is <u>work</u>

⇐: EULAR'S THEOREM :⇒

if Z is a function which depend upon x and y –

then,

$$Z = f(x, y)$$

डेपर

$$\partial Z = \left(\frac{\partial Z}{\partial x}\right)_y \partial x + \left(\frac{\partial Z}{\partial y}\right)_x \partial y$$

⇒ Part. diff. at const. x Z changes with changes of y.

Total diff. ↓ (M) (N)

Partial differential ⇓ is at const. y which means that the Z changes with changes x

↓ Which means that the value of Z changes with simultaneously change of x and y

$$\partial Z = M\,dx + N\,\partial y$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)$$

$$\boxed{\frac{\partial^2 z}{\partial x\, \partial y} = \frac{\partial^2 z}{\partial y \cdot \partial x}}$$

⇓

⇒ This conditions shows that Z is a State function.

⇒ This is the conditions of Eular's theorem.

Q. $\partial z = \underset{M}{\underset{\Downarrow}{x\,dy}} + \underset{N}{\underset{\Downarrow}{y\,dx}}$

it must be follow Euler theorem then the function is state function

$$\frac{\partial^2 z}{\partial x\,\partial y} = \frac{\partial^2 z}{\partial y\,\partial x}$$

[By Euler's theorem]

$\underset{\left(\frac{\partial z}{\partial y}\right)_x}{\underset{\Downarrow}{x\,dy}}$ $\quad$ $\underset{\left(\frac{\partial z}{\partial x}\right)_y}{y\,dy}$

$$\frac{\partial}{\partial x}\left[\frac{\partial z}{\partial y}\right] = \frac{\partial}{\partial y}\left[\frac{\partial z}{\partial x}\right]$$

$$\frac{\partial^2 z}{\partial x,\partial x} = \frac{\partial}{\partial x}[x] = \frac{\partial}{\partial y}[y] = \frac{\partial^2 z}{\partial y,\partial x}$$

$1 = 1$

follow Euler's theorem
so that this is state function

Q: $\partial z = \underset{M}{(51x^2y + 47y^4)\,\partial x} + \underset{N}{(17x^3 + 188xy^3)\,dy}$

$$\frac{\partial}{\partial y}[M] = \frac{\partial}{\partial x}[N]$$

$$\frac{\partial}{\partial y}[51x^2y + 47y^4] \pm \frac{\partial}{\partial x}[17x^3 + 188xy^3]$$

$$[51x^2 + 188y^3] = [51x^2 + 188y^3]$$

Q. $\partial z = x^2 \partial y + y^2 \partial x$

$$\frac{\partial}{\partial x}[x^2] = \frac{\partial}{\partial y}[y^2]$$

$$\cancel{2}x = \cancel{2}y$$

$$x = y$$

this is not ~~that~~ Equal

So that doesn't follow Euler theorem

& Not a State function.

Q4. $\partial z = x\,dx + y\,dy$

$$\frac{\partial}{\partial y}[x] + \frac{\partial}{\partial x}[y]$$

$$0 = 0$$

∴ Z follow Euler's theorem

So that is state function.

~~Q. $\partial z = 5t$~~

Net-2014

Qu. the ~~exact~~ diff. ~~of~~

f(x,y) among the following is a State function.

ⓐ $x\,\partial y$ ⓑ $\partial x - \frac{x}{y}\partial y$ ⓒ $y\,dx - x\,\partial y$ ⓓ $\frac{1}{y}\partial x - \frac{x}{y^2}\partial y$

$\Downarrow$ 0 $\quad \Downarrow$ 0 $\quad$ 1 , −1

$-\frac{1}{y^2}$ ~~$= x y^{-2}$~~

$= -$

$\partial z \Rightarrow x\,\partial y +$

$\Rightarrow$ ⓐ $= \underline{0}$

$\frac{\partial}{\partial y}[1] = 0$ $\qquad$ $\frac{\partial}{\partial y}[y] = 1$ $\qquad$ $\frac{\partial}{\partial y}\left[\frac{1}{y}\right] \Rightarrow -\frac{1}{y^2}$

$\frac{\partial}{\partial x}\left[\frac{x}{y}\right] = \frac{1}{y}$ $\qquad$ $\frac{\partial}{\partial x}[x] = -1$ $\qquad$ $\frac{\partial}{\partial x}\left[\frac{x}{y^2}\right] = -\frac{1}{y^2}$

~~[illegible]~~

⇑ [illegible] variable [illegible] constt [illegible]

⬅ CYCLIC RULE :➡ (3 independent variable)

The relation b/w three variables can be represented in well define relation Suppose if z is a function of x and y then-

$$z = f(x, y)$$

$$\partial z = \left(\frac{\partial z}{\partial x}\right)_y \partial x + \left(\frac{\partial z}{\partial y}\right)_x \partial y$$

Suppose z is a constant function

So $dz = 0$

$\therefore dz = 0$

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \partial x + \left(\frac{\partial z}{\partial y}\right)_x \partial y$$

divide both side by dy at a constt. z.

$$\cancel{\left(\frac{\partial 0}{\partial y}\right)_z} \xrightarrow{} 0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \cancel{\left(\frac{\partial y}{\partial y}\right)_z} \xrightarrow{} 1$$

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x$$

$$-\left(\frac{\partial z}{\partial y}\right)_x = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z$$

$$\boxed{\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1}$$

this relation can be represents in terms of P, V & T.

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1}$$

$$PV = RT$$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$$

Qu. Prove that cyclic Rule verify for Ideal Gas–

$$PV = RT$$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V$$

$$PV = RT$$

$$P = \frac{R}{V} T$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \frac{\cancel{\partial T}}{\cancel{\partial T}} = \frac{R}{V}$$

✓ $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$

✓ $\left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{}$

$$PV = RT$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{RT}{P} = \frac{RT \, dP}{P}.$$

$$= -RT \cdot \frac{1}{P^2}$$

$$T = \frac{P}{R} V$$

✓ $\left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{R}\left(\frac{\partial V}{\partial V}\right)$

$$= -\frac{RT}{} \cdot \cancel{P} \cdot \cancel{R}$$

Clausius - Clapeyron Equation

$$\boxed{\ln \frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right]}$$

⇒ Scattering पर ⇒

(Ice)

Press. ↑ करने से Tem ↓ [m.pt. ↓] ⇒ (Variation of temp. with pressure)

⇒ water film बन जाती है।

for an Ideal Gas ⇒

Ques:- $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = ?$ ㉑

(i) $-\frac{R^2}{P^2}$ (ii) -1 (c) $\frac{V}{T}$ ✓~~(d)~~ $-\frac{R^2}{V^2}$

$$PV = RT$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$\left(\frac{\partial P}{\partial V}\right)_T$$

$$PV = RT$$

$$\partial P = + \frac{RT}{V}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = RT\ \partial V \cdot \frac{1}{V}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = RT \cdot \frac{-1}{V^2}$$

$$= \frac{R}{V} \cdot \frac{R}{P} \cdot -\frac{RT}{V^2}$$

$$= \frac{-R^2}{PV \cdot V^2} \cdot RT$$

$$= \frac{-R^2 \cdot \cancel{RT}}{\cancel{RT} \cdot V^2}$$

$$= \frac{-R^2}{V^2}$$

$P(V-b) = RT$

$PV - Pb = RT$

$PV = RT + Pb$

$V = \frac{RT + Pb}{P}$

$dV = \frac{RT}{P} + b$

$\left(\frac{dV}{dT}\right)_P = \frac{R}{P}\frac{\partial T}{\partial T} + 0$

$\left(\frac{dV}{\partial T}\right)_P = \frac{R}{P}$ —①

$P = \frac{RT}{(V-b)}$

$\left(\frac{dP}{\partial T}\right)_V = \frac{R}{(V-b)}\frac{\partial T}{\partial T}$

$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{(V-b)}$ —⑪

$T = \frac{P(V-b)}{R}$

$\left(\frac{dT}{\partial P}\right) = \frac{(V-b)}{R}\frac{\partial P}{\partial P}$

$\left(\frac{dT}{dP}\right)_V = \left(\frac{V-b}{R}\right)$

$PV - Pb = RT$

$P(V-b) = RT$

$P = \frac{RT}{V-b}$

$\left(\frac{dP}{dV}\right)_T = RT \frac{d}{dV}\left(\frac{1}{(V-b)}\right)$

$= RT\left(\frac{-1}{(V-b)^2}\right)$

$\left(\frac{dP}{dV}\right)_T = \frac{-RT}{(V-b)^2}$

$\left(\frac{\partial V}{dT}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T$

$\frac{R}{P} \times \frac{-\cancel{R}T}{(V-b)^{\cancel{2}}} \times \frac{\cancel{(V-b)}}{\cancel{R}}$

$-RT \quad -RT \quad = \quad$ hence proved

[16.10.15]

Net-2010 [Sub.]

Integrating factor

the factor which making the function become exact by simply multiplying with an exact function then that ~~function~~ factor is called Integrating factor.

Let us consider -

$$dz = y\,dx + (-x)\,dy$$

applying Euler's theorem -

$$\frac{\partial^2 z}{\partial x \partial y} \neq \frac{\partial^2 z}{\partial y \partial z}$$

$$1 = -1$$

it doesn't follow Euler's theorem.

Multiplying in Equation by one by x^2 $[1/x^2]$ then the function become -

$$\frac{dz}{x^2} = \frac{y}{x^2}\,dx + \frac{x}{-x^2}\,dy$$

$$\frac{\partial\, dz^2}{\partial x \partial y} = \frac{\partial z^2}{\partial y \partial x} = \frac{1}{x^2}$$

Now the function follow Euler's theorem -

then that this is State function.

Now the function become Exact

So $\frac{1}{x^2}$ is Integration factor.

STATE- FUNCTION :→

- * The value of state function depend upon Initial state and final state.
- * the value of state function path Independent
- * It must be Exact differential.
- * It must follow Euler's theorem.
- * their cyclic Integral is zero.

$Z = T, P, V, G, H, A, E$ Etc.

$Z \neq q, w$ [Path dependent function]

$$\oint dE = 0$$

$$\oint dV = 0$$

but

$$\oint dq \neq 0$$

$$\oint dw \neq 0$$

÷ INTERNAL ENERGY :-

or "Intrinsic Energy" (per mole)

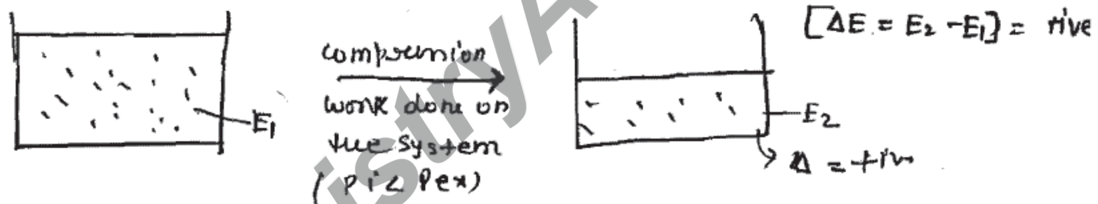
[E or U]

* Internal Energy is State function

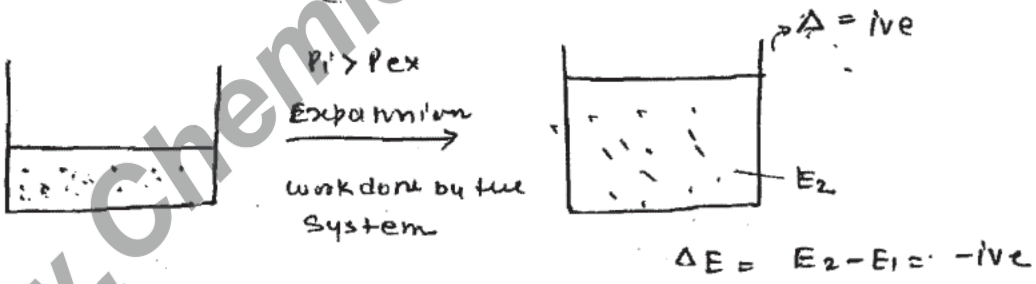
* Int. Engy. is an extensive property.

* The value of Int. Ene. following System depend up chemical nature of the ~~Existance~~ce of a System.

*



*

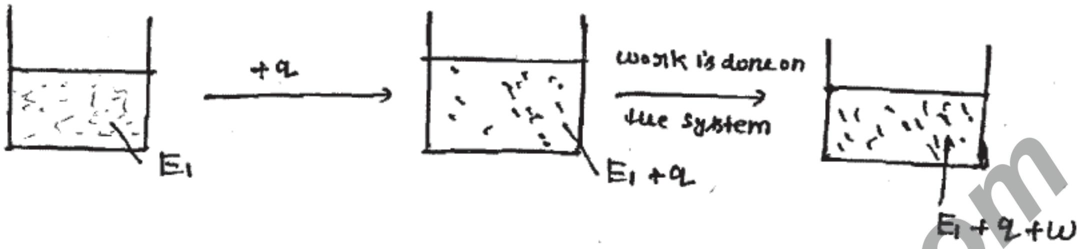


In Gen.

If work is done on the System Internal energy Increases.

If work is done by the System Internal Energy decreases.

FIRST-LAW OF THERMODYNAMICS :



$$E_2 = E_1 + q + w$$

$$E_2 - E_1 = q + w$$

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

Energy can Neither be created Nor be destroyed It can only converted into one Form to another form.

It is not possible to creat Energy.

Energy always be conserved

SIGNIFICANCE OF INTERTAL ENERGY :⇒

or Heat change at constt volume

Heat change at constant volume is called Chang is Internal Energy.

$$\Delta E = q + w$$

$$\Delta E = Z - P.\, d\delta V$$

$$\Delta E = 0$$

at constant volume

$$\Delta E = q - 0$$

$$\Delta E = q_v$$

$$\boxed{\Delta E = q_v}$$

workdone नही हुआ तो जितनी Heat change उतनी Internal Energy

or

$$\boxed{dE = dq_v}$$ – small change

or,

~~that~~ then there is not (PdV) work

(dv=0), then the Heat change is called change is internal Energy.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\Downarrow$$

(Isobaric Expansion cofficient)

$$\beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Isothermal compressibility cofficient

$$\gamma = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$$

Isochoric thermal-Pressure cofficient

Isobaric Expansion Coefficient [α] $\left[\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]$

α - Shows that Increase in temp. take place with increase in volume.

V & T having direct relation

i.e we can say that α is isobaric Expansion coefficient.

- It having a dimension $\underset{\text{(Temp.)}}{T^{-1}}$
- The value of α for an ideal gas $= \frac{1}{T}$

Proof. since we know that

$$PV = RT$$

$$V = \frac{RT}{P}$$

$$\left(\frac{dV}{\partial T}\right)_P = \left[\frac{d}{\partial T}\left(\frac{R}{P}\right)T\right]_P$$

$$\left(\frac{dV}{\partial T}\right)_P = \frac{R}{P}\cdot 1$$

$$\left(\frac{dV}{\partial T}\right)_P = \frac{R}{P}$$

$$\because \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \frac{1}{V}\cdot\frac{R}{P} = \frac{R}{PV} = \frac{\cancel{R}}{\cancel{R}T} = \frac{1}{T}$$

Qu. Calculate the value of α for a gas which Having Equation $P(V-b) = RT$.

$$P(V-b) = RT$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$PV - Pb = RT$$

$$PV = RT + Pb$$

$$V = \frac{RT}{P} + b$$

$$\left(\frac{dv}{\partial T}\right)_P = \left(\frac{d}{\partial T}\left[\frac{R}{P}T + b\right]\right]_P$$

$$\left(\frac{dv}{\partial T}\right)_P = \frac{R}{P}\cdot 1 + 0$$

$$\left(\frac{dv}{\partial T}\right)_P = \frac{R}{P}$$

$$\alpha = \frac{1}{V}\cdot\frac{R}{P} =$$

$$= \frac{R}{PV}$$

Q4. Find out the value of α for vander-wall Equation.

$(P+\frac{a}{V^2})(V-b) = RT$ —① $\because \alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P$

We can find out the value of $\frac{dV}{dT}$ at constant Pressure - by ①

$$\frac{d}{dt}\Big[\underset{I}{(P+\frac{a}{V^2})}\;\underset{II}{(V-b)}\Big]_P = \frac{d}{dt}[RT]_P$$

$$(P+\frac{a}{V^2})\frac{d}{dt}(V-b) + (V-b)\frac{d}{dt}(P+\frac{a}{V^2}) = R$$

$$(P+\frac{a}{V^2})\left(\frac{dv}{dt}\right)_P + (V-b)\left[0 + -\frac{2a}{V^3}\right]\left(\frac{dV}{dt}\right)_P = R$$

$$(P+\frac{a}{V^2})\left(\frac{dv}{dt}\right)_P + (v-b)\left(\frac{-2a}{V^3}\right)\left(\frac{dv}{dt}\right)_P = R$$

$$\left(\frac{dv}{dT}\right)_P\left[(P+\frac{a}{V^2}) - \frac{2a(V-b)}{V^3}\right] = R$$

$$\left(\frac{dV}{dT}\right)_P = \left[\frac{R}{(P+\frac{a}{V^2}) - \frac{2a(V-b)}{V^3}}\right]$$

$$\alpha = \frac{1}{V}\left[\frac{R}{(P+\frac{a}{V^2}) - \frac{2a(V-b)}{V^3}}\right]$$

$$\alpha = \frac{1}{V}\left[\frac{R}{\frac{RT}{(V-b)} - \frac{2a(V-b)}{V^3}}\right]$$

$$\alpha = \cancel{\frac{1}{V}}\left[\frac{R}{\frac{RTV^3 - 2a(V-b)^2}{V^{3\,2}}}\right]$$

$$\alpha = \frac{RV^2}{RTV^3 - 2a(V-b)^2}$$

Isothermal Compressibility Cofficient

$$\beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

- β - Shows that pressure increases with decre. in Volume that's why β has -ive sign
- Dimension P^{-1}
  *pressure.
- the value of β for an ideal gas $\left[\beta = \frac{1}{P}\right]$

Proof:-

$$PV = RT$$

$$V = \frac{RT}{P}$$

$$\left(\frac{dV}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\cdot\frac{RT}{P}\right)_T$$

$$\left(\frac{dV}{\partial P}\right)_T = RT \cdot \frac{-1}{P^2}$$

$$\beta = \frac{-1}{V}\cdot RT \cdot \frac{-1}{P^2}$$

$$= \frac{RT}{PV\cdot P}$$

$$= \frac{\cancel{RT}}{\cancel{RT}\cdot}\frac{1}{P}$$

$$\beta = \frac{1}{P}$$

Isochoric thermal- Pressure Cofficient

$$\gamma = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$$

- γ -Shows that Pressure & Temp. having direct relation.
- It having dimension T^{-1}
- the value of γ for Ideal gas. $\left[\frac{1}{T}\right]$

Proof.

$$PV = RT$$

$$P = \frac{RT}{V}$$

$$\left(\frac{dP}{dT}\right)_V = \left[\frac{d}{dT}\left(\frac{RT}{V}\right)\right]_V$$

$$\left(\frac{dP}{dT}\right)_V = \left(\frac{R}{V}\right)$$

$$\gamma = \frac{1}{P}\cdot\frac{R}{V}$$

$$\gamma = \frac{\cancel{R}}{\cancel{R}T} = \frac{1}{T}$$

$$\boxed{\gamma = \frac{1}{T}}$$

Enthalpy :

- Enthalpy is a State function, it is path Independent
  Enthalpy is a Heat content of a System at a constant pressure and temp. when system is open.

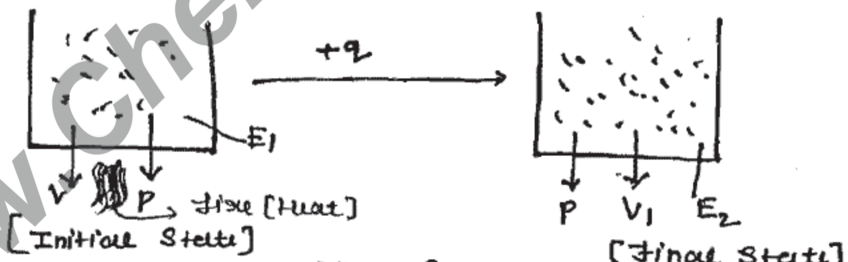
Mathematically, Enthalpy is sum of Internal Energy and PV.

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

we can't measure the Enthalpy, we only measure the change in Enthalpy.

change in Enthalpy at const. temp., pressure is equal to Heat change so,

e.g. in liquid. Having Internal Energy E



Open System

∴ first-law of thermodynamics

$$\Delta E = q - P\Delta V$$

$$E_2 - E_1 = q - P(V_2 - V_1)$$

$$E_2 - E_1 = q - PV_2 + PV_1$$

$$E_2 + PV_2 = q + E_1 + PV_1$$

$(E_2 + PV_2)$ or $(E_1 + PV_1)$ is represented by a term i.e. called Enthalpy (H)

$(E+PV)$ is also called Heat content of the system at constant and pressure.

Now,

$$H_2 = q + H_1$$

$$H_2 - H_1 = q_p.$$

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

Heat Change at a constant Pressure is called Enthalpy change.

Imp.

Max-Well-Equation :→

Max well Equation in term of change in Internal Enrgy.

this Equation Shows that Internal Enrgy changes with Simultenously change of S and V

$$dE = Tds + (-p)\,dv \quad — ①$$

We can also calculate -

[at a constant S]

$$\boxed{\left(\frac{dE}{dv}\right)_S = -P}$$

$$\left(\frac{dE}{\partial v}\right)_S = T\overset{0}{\Uparrow}ds + -(p)\cancel{\left(\frac{dv}{dv}\right)}^{\to 1}$$

or

$$\boxed{-\left(\frac{dE}{dv}\right)_S = P}$$

$$\left(\frac{dE}{\partial v}\right)_S = \boxed{-P}$$

we can also calculate

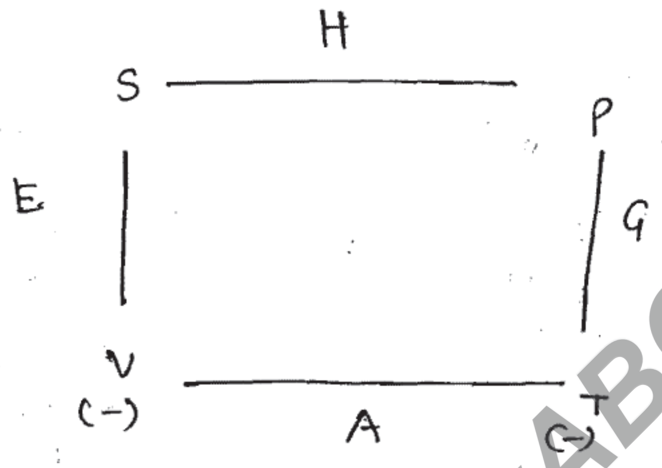
$$\boxed{\left(\frac{dE}{ds}\right)_v = T}$$

Constt → ⓥ

$$dE = Tds + (-p)\underset{\Downarrow 0}{dV}$$

$$\left(\frac{dE}{ds}\right)_v = T\left(\frac{ds}{ds}\right)$$

we can also calculate max-wele relation ⇒



Note ⇒ diagonal multiply में sign

Include नही करना

$$\boxed{dH = TdS + VdP}$$

$$\therefore \quad dE = Tds + (-P)\,dv \quad \text{—(i)}$$

$$E = f(S,V)$$

above Equation shows that E is function of S and V

$$\therefore \quad dE = \left(\frac{dE}{ds}\right)_V ds + \left(\frac{dE}{dV}\right)_S dv \quad \text{(ii)}$$

Compare (i) and (ii)

$$dE = T\,ds + (-P)\,dV$$

$\therefore$ E is state function, so it must follow Euler's theorem, Applying Euler's theorem →

$$\boxed{\left(\frac{dT}{dV}\right)_S = -\left(\frac{dP}{dS}\right)_V}$$

Max-well Eqn in terms of change in Enthalpy →

$$\therefore \quad dH = Vdp + Tds$$

$$\left(\frac{dv}{ds}\right)_P = \left(\frac{dT}{dP}\right)_S$$

Above relation shows that Enthalpy change with Simulteneously change in S an P

$$\left(\frac{dH}{dP}\right)_S = V$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

$$\partial H = V\overset{\overset{0}{\Uparrow}}{dP} + Tds$$

$$\left(dH\right) = T\,ds$$

$$dH = Vdp + T\overset{\overset{0}{\Uparrow}}{ds}$$

$$\left(\frac{dH}{dP}\right)_S = V\frac{dp}{dp}$$

$$\left(\frac{\partial h}{\partial p}\right)_S = V$$

Max-well equation - (Prove by Euler theory

$$\left(\frac{dv}{ds}\right)_P = \left(\frac{dT}{\partial P}\right)_S$$

Prove> :It is

$$\left(\frac{dv}{ds}\right)_P$$

Max well Equation in terms of G. [Gibbs free Energy]

$$dG = VdP - SdT$$

$$\therefore \left(\frac{dG}{dP}\right)_T = V \qquad \left(\frac{dG}{dP}\right)_T = V\cancel{\frac{dP}{dP}} - S\,\overset{0}{\overset{\uparrow}{dT}}$$

$$= V$$

$$\therefore \left(\frac{dG}{dT}\right)_P = -S \qquad \left(\frac{dG}{dT}\right)_P = V\,\overset{0}{\overset{\uparrow}{dP}} - S\left(\cancel{\frac{dT}{dT}}\right) = S$$

max well - Relation

$$\left(\frac{dV}{dT}\right)_P = -\left(\frac{dS}{\partial P}\right)_T$$

Prove>

Max well Equation in terms of Halholtz-free Energy ⇒

$$dA = -Pdv - SdT$$

$$\left(\frac{dA}{dv}\right)_T = -P$$

$$\left(\frac{dA}{\partial T}\right)_V = -S$$

Max well rellation ⇒

$$\boxed{\left(\frac{dP}{dT}\right)_V = \left(\frac{ds}{dv}\right)_T}$$

Proof ⇒

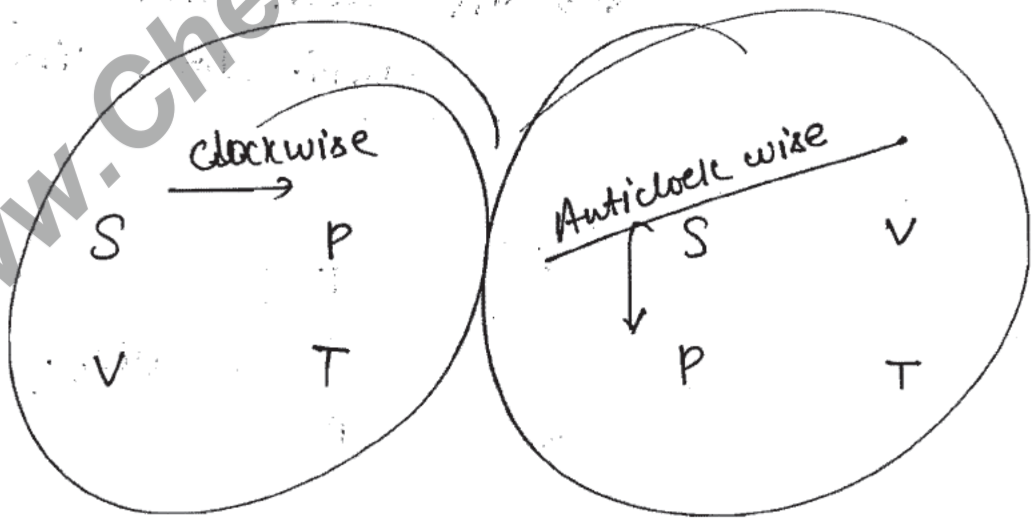
Max well Relation

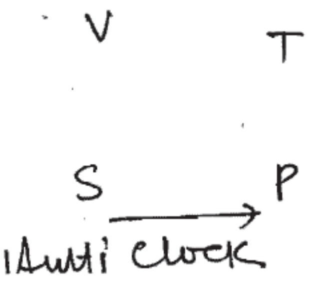
$$-\left(\frac{\partial V}{\partial S}\right)_P \quad \left(\frac{\partial T}{\partial P}\right)_S$$

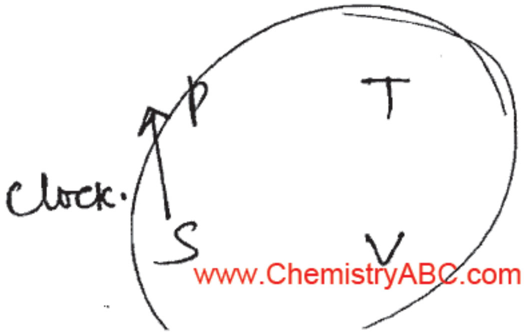
$$\left(\frac{\partial S}{\partial V}\right)_T \quad \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

$$\ominus \left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$







Ques: For a system of constant composition [No. of moles remain same]

the pressure P is given by ⇒

(a) $-\left(\frac{du}{ds}\right)_V$

(b) $-\left(\frac{du}{dV}\right)_S$

(c) $\left(\frac{\partial V}{\partial S}\right)_T$

(d) $\left(\frac{du}{dV}\right)_T$

0 at constt (S)

$$dU = T\boxed{dS} - PdV$$

⇒ क्यों कि P पूछ रहे हैं। और अगर constt. V होता है तो P का zero हो जाएगा

$$-\left(\frac{du}{dV}\right)_S = P$$

2012 June (Net)

Q. Indicate which one of the following relation is Not correct. (सभी संबंधों में correct क्या है)

(a) $-\left(\frac{dT}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$ (Correct)

✓(b) $-\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ [Not Correct]

(c) $+\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V$ (Correct)

(d) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ (Correct)

(2013) Net (June)

Qu. The correct thermodynamics relation among the following is

✓(a) $\left(\frac{dE}{\partial V}\right)_S = -P$

(b) $\left(\frac{dH}{\partial V}\right)_S = -P$

(c) $\left(\frac{\partial G}{\partial V}\right)_S = -P$

(d) $\left(\frac{dA}{dV}\right)_S = -S$

$$dH = TdS + V\overset{\overset{0}{\Uparrow}}{dP}$$

$$\left(\frac{dH}{dS}\right)_P = T$$

2013

Qu. The maxwell relationship derived from the Equation

$$dG = VdP - (S)dT$$

① $\left(\frac{dV}{dT}\right)_P = \left(\frac{\partial S}{dP}\right)_T$

$$\left(\frac{dV}{dT}\right)_P = -\left(\frac{dS}{dP}\right)_T$$

✓(II) $\left(\frac{dV}{dT}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

(III) $\left(\partial P\right. = \left(\partial T\right.$ (IV) $\left(\partial P\right) = -\left(\partial T\right.$

(2014) For a process in a closed System Temp. is Equal to –

ⓐ $\left(\frac{\partial H}{\partial P}\right)_S$

(b) $\left(\frac{dq}{dP}\right)_T$

(c) $-\left(\frac{dA}{dV}\right)_T$

~~(d)~~ $\left(\frac{dH}{\partial S}\right)_P$

$$dH = \overset{\checkmark}{T}\,\overset{\theta}{\underline{dS}} + V\,d\overset{\overset{0}{\Uparrow}}{P}$$

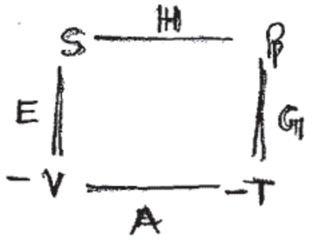
$$\left(\frac{dH}{dS}\right)_P = T \cdot \frac{\cancel{dS}}{\cancel{dS}}$$

$$\boxed{\left(\frac{dH}{dS}\right)_P = T}$$

← First thermodynamic Equation of a State →

we know that from the max well eqⁿ -

$$dE = T\,dS - P\,dV$$



Diff. Both side with respect to V, at Constant temp.

$$dE = T\,ds - P\,dV$$

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\cancel{\partial V}}{\cancel{\partial V}}\right)_T$$

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$\because \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\boxed{\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} \ast$$

$\left(\frac{\partial E}{\partial V}\right)_T \Rightarrow$ Internal Pressure or π [पाई]

$\left(\frac{dE}{\partial V}\right)_T$ at a constt. T is called

change in Internal energy with change in volume at a constt. temp. is called Internal pressure

→ Calculation of Internal pressure for an Ideal Gas →

$$PV = RT \qquad P = \frac{RT}{V}$$

$$\left(\frac{dP}{dT}\right)_V = \frac{R}{V} \times \frac{\cancel{dT}}{\cancel{dT}}$$

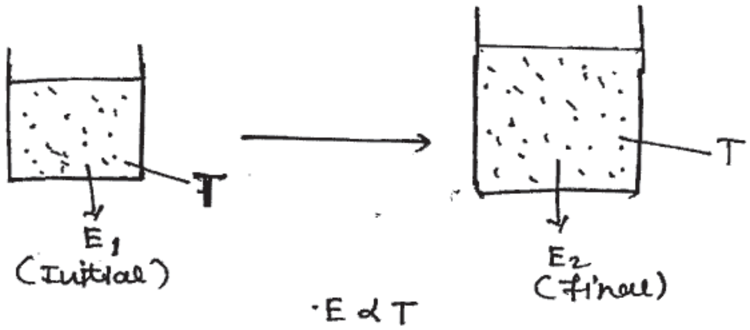
$$\left(\frac{dP}{dT}\right)_V = \frac{R}{V}$$

$$\left(\frac{dE}{dV}\right)_T = T \times \underset{\downarrow\ \frac{R}{V}}{\left(\frac{dP}{dT}\right)_V} - \overset{\frac{RT}{V}\ \uparrow}{P}$$

$$\Rightarrow \frac{\cancel{RT}}{V} - \frac{\cancel{RT}}{V}$$

$$\left(\frac{dE}{\ }\right) = \frac{TR}{\ } - \frac{RT}{\ } = 0$$

⇐ PHYSICAL SIGNIFICANCE OF INTERNAL PRESSURE FOR IN IDEALGAS :⇒



$\cdot E \propto T$

For Ideal gas → $\Delta E = 0$ or $\boxed{dE = 0}$

Since we know that in Ideal Gas there is no interection b/w molecule, so no energy is wasted in order to overcome the interection. in Isothermal expansion for an Ideal gas there is No change in Internal Energy b/w Initial & final State.

So,

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

or

$$\boxed{\partial E = 0}$$

& i.e. the change in internal energy with change in volume at constt. temp. is Equal to zero.

$$\boxed{\left(\frac{\partial E}{\partial V}\right)_T = 0}\ \boxed{\text{Ideal Gas}}$$

→ Internal pressure (π) for an Ideal Gas zero

⇐ Calculation of Internal pressure for an Real gas:⇒

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{—①}$$

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT$$

To find $\left(\frac{dP}{dT}\right)_V$

$$\left[\frac{d}{dT}\left(P+\frac{a}{V^2}\right)(V-b)\right]_V = R\,\frac{dT}{dT}$$

$$\left(P+\frac{a}{V^2}\right)\cancel{\frac{d(V-b)}{dT}}^{\,0} + \left(\frac{dP}{dT}\right)_V (V-b)\times(1) = R$$

$$\left(\frac{dP}{dT}\right)_V = \left(\frac{R}{V-b}\right)$$

put the value in (1) then,

$$\boxed{\left(\frac{dE}{\partial V}\right)_T = \frac{T\times R}{(V-b)} - P}$$

$$= \frac{\left(P+\frac{a}{V^2}\right)\cancel{(V-b)}}{\cancel{(V-b)}} - P$$

$$= \cancel{P} + \frac{a}{V^2} - \cancel{P}$$

$$\boxed{\left(\frac{dE}{\partial T}\right)_T = \frac{a}{V^2}}$$

⇒ bcoz the Interaction b/w molecule in Real gas ~~so that~~

Internal pressure

Internal pressure for a real Gas is $\frac{a}{V^2}$ which significance that [illegible] strong Inte. present in the Real Gas, so when you supply the energy, some of the Energy is wasted in order to overcome the Interaction b/w the Gas molecule.

So we conclude that due to Interaction b/w the Real Gas molecule Internal pressure can never to zero but it is Equal to a/V^2

Qu. calculate the Internal pressure for a Gas Equation $(\pi$

$$P(V-b) = RT$$

$$PV - Pb = RT$$

$$P = \left(\frac{RT}{V-b}\right)$$

$$\left(\frac{dP}{dT}\right)_V = \left(\frac{R}{(V-b)}\right)_V \times \frac{\cancel{dT}}{\cancel{dT}}$$

$$\left(\frac{dP}{dT}\right)_V = \frac{R}{(V-b)}$$

$$\left(\frac{dE}{dV}\right)_T = \frac{T \times R}{(V-b)} - P$$

$$= \frac{RT}{(V-b)} - P$$

$$= \frac{P\cancel{(V-b)}}{\cancel{(V-b)}} - P$$

$$= \cancel{P} - \cancel{P}$$

$$\left(\frac{dE}{\partial V}\right)_T = 0$$

⬅ Second thermodynamic Equation of State :➡

we know that, from max well Equation ⇒

$$dH = TdS + VdP$$

Diff. w.r. to P at const. temp.

$$\left(\frac{dH}{dP}\right)_T = T\left(\frac{dS}{dP}\right)_T + V\left(\frac{\cancel{\partial P}}{\cancel{\partial P}}\right)_T$$

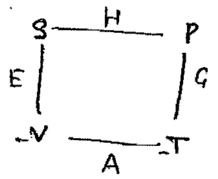
$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\cdot\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$\left[\because \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P\right]$$

$$\therefore \boxed{\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_T + V}$$

Criteria for Spontaneity :→



$$\boxed{(\Delta S)_{U,V} > 0}$$

By Seeing the Sign of change in thermodynamic parameter we can predict the process spontaneous, reversable, or Equilibrium.

Entropy change :→

(+ive)

$$(\Delta S)_{U,V} > 0 \quad \text{[Spontaneous]}$$

$$(\Delta S)_{U,V} = 0 \quad \text{[Reversable or Equilibrium]}$$

Change in Enthalpy

$$(\Delta H)_{S,P} < 0 \quad \text{[Spontaneous]}$$

$$(\Delta H)_{S,P} = 0 \quad \text{[Reversable or Equilibrium]}$$

Change in Gibb's free Energy

$$(\Delta G)_{P,T} < 0 \quad \text{[Spontaneous]}$$

$$(\Delta G)_{P,T} = 0 \quad \text{[Reversable or Equi.]}$$

Change in Halholmotz free Energy

$$(\Delta A)_{V,T} < 0 \quad \text{[Spon.]}$$

$$(\Delta A)_{V,T} = 0 \quad \text{[Rev. + Equi.]}$$

Change in Internal Energy

$$(\Delta E)_{V,S} < 0 \quad \text{[Spon.]}$$

$$(\Delta E)_{V,S} = 0 \quad \text{[Rev. + Equi.]}$$

October, 23 2015

Relation b/w C_p and C_v

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$C_p - C_v = R$ [for an Ideal Gas]

$C_p - C_v = R\left[1 + \frac{2a}{RTV}\right]$ → for an Real gas

$$C_p - C_v = \frac{\alpha^2 . T V}{\beta}$$

$C_p - C_v = R$ → for an Gas whose Eqn is $\boxed{P(V-b) = RT}$

$$C_p - C_v = -T \left(\frac{\partial P}{\partial T}\right)_V^2 \left(\frac{\partial V}{\partial P}\right)_T$$

⊛ $C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P$

Proof ⇒ $S = f(T, V)$

Total differential

$$dS = \left(\frac{dS}{dT}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \partial V$$

Divide both side by ∂T at constant pressure

$$\left(\frac{dS}{\partial T}\right)_P = \left(\frac{dS}{\partial T}\right)_V \cdot 1 + \left(\frac{dS}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Multiply both side by T

$$T\left(\frac{dS}{\partial T}\right)_P = T \cdot \left(\frac{\partial S}{\partial T}\right)_V + T \cdot \left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

∵ $T\,dS = dq$ (we know that from Entropy change)

$$\left(\frac{dq_p}{\partial T}\right)_P = \left(\frac{\partial q_v}{\partial T}\right)_V + \left(\frac{\partial q}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

[∵ ∂q at constt. P $= \partial H$, ∵ ∂q at constt. V $= \partial E$]

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + T \cdot \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

[∵ From maxwell relation -

$$\left[\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V\right]$$

$$C_p = C_v + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$\boxed{C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$$

* $C_p - C_v = R$ [for an Ideal-gas]

Proof :→

$$C_p - C_v = T \cdot \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial V}{\partial T}\right)_P$$

$PV = RT$ [Ideal gas Equation]

$$\because \left(\frac{dP}{dT}\right)_V = \frac{R}{V}$$

$$\because \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Put the values in above eqn-

$$C_p - C_v = T \cdot \frac{R}{V} \cdot \frac{R}{P}$$

$$C_p - C_v = \frac{T \cdot R}{PV} \cdot R$$

$$C_p - C_v = \frac{\cancel{PV}}{\cancel{PV}} \cdot R$$

$$\boxed{C_p - C_v = R}$$

$$C_p - C_v = \frac{\alpha^2 \cdot T \cdot V}{\beta}$$

$$\because \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\because \quad C_p - C_v = T \cdot \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

$$\therefore \quad C_p - C_v = T \cdot \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial T}{\partial P}\right)_V} \qquad -①$$

By cyclic Rule

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

$$-\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial T}{\partial P}\right)_V \qquad -②$$

Put the value from [2] in [1st]

$$C_p - C_v = \frac{T \cdot \left(\frac{\partial V}{\partial T}\right)_P}{-\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T}$$

$$= \frac{T \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial V}{\partial T}\right)_P}{-\left(\frac{\partial V}{\partial P}\right)_T}$$

$$= \frac{T \cdot \alpha^2 \cdot V^{\cancel{2}}}{(-1)(-1)\beta \cdot \cancel{V}}$$

$$\boxed{C_p - C_v = \frac{T \cdot \alpha^2 \cdot V}{\beta}}$$

$$C_p - C_v = -T \left(\frac{\partial P}{\partial T}\right)_V^2 \left(\frac{\partial V}{\partial P}\right)_T$$

from Cyclic Rule

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1 \, .$$

$$\because \; C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -1 \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T$$

$$C_p - C_v = -T \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T$$

$$\boxed{C_p - C_v = -T \left(\frac{\partial P}{\partial T}\right)^2 \left(\frac{\partial V}{\partial P}\right)_T}$$

$$C_p - C_v = R$$

$$P(V-b) = RT$$

$$\because C_p - C_v = T \cdot \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

$$P = \frac{RT}{(V-b)}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{(V-b)} \cdot \frac{\cancel{dT}}{\cancel{\partial T}}$$

$$= \frac{R}{(V-b)}$$

$$\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow$$

~~P~~ $(V-b) = \frac{RT}{P}$

$$V = \frac{RT}{P} + b$$

$$\left(\frac{dV}{\partial T}\right)_P = \frac{R}{P} \cdot \frac{\cancel{dT}}{\cancel{\partial T}} + 0$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$C_p - C_v = T \cdot \frac{R}{(V-b)} \times \frac{R}{P}$$

$$= \frac{\cancel{T} \cdot \cancel{R} \times R}{\cancel{R} \cdot \cancel{T}}$$

$$\boxed{C_p - C_v = R}$$

$C_p - C_v = R\left[1 + \frac{2a}{RTV}\right]$ for real gas-

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \quad -①$$

$$\because \quad C_p - C_v = T \cdot \left(\frac{dP}{dT}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P \quad -⑪$$

By ①

$$\left(\frac{dP}{dT}\right)_V \Rightarrow$$

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

$$\left(P + \frac{a}{V^2}\right) = \frac{RT}{(V-b)}$$

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

$$\left(\frac{dP}{dT}\right)_V = \frac{d}{dT}\left[\frac{RT}{V-b} - \frac{a}{V^2}\right]_V$$

$$\left(\frac{dP}{dT}\right)_V = \frac{R}{(V-b)} \times 1 - 0$$

$$\left(\frac{dP}{dT}\right)_V = \frac{R}{(V-b)} \quad -iii)$$

$$\left(\frac{dV}{dT}\right)_P \Rightarrow$$

$$\left(P + \frac{a}{V^2}\right) = \frac{RT}{(V-b)}$$

$$\left(\frac{d}{dT}\left[P + \frac{a}{}\right]\right) = \frac{d}{} R\left[\frac{T}{}\right]$$

$$0 + \frac{(-2a)}{V^3}\left(\frac{dV}{dT}\right)_p = R \times \frac{d}{dT}\left(\underset{I}{T} \times \cdot \underset{II}{(V-b)^{-1}}\right]$$

$$= R \times \left[1 \cdot (V-b)^{-1} + T \times \left(\frac{-1}{(V-b)}\left(\frac{dV}{dT}\right)_p \right]$$

$$-\frac{2a}{V^3}\left(\frac{dV}{dT}\right)_p = \frac{R}{(V-b)} - \frac{RT}{(V-b)^2}\left(\frac{dV}{dT}\right)_p$$

$$\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right]\left(\frac{dV}{dT}\right)_p = \frac{R}{(V-b)}$$

$$\left[\frac{\cancel{R}T\cancel{(V-b)}}{\cancel{R}(V-b)^{\cancel{2}}} - \frac{2a(V-b)}{R \cdot V^3}\right]\left(\frac{dV}{dT}\right)_p = 1$$

$$\left[\frac{T}{(V-b)} - \frac{2a(V-b)}{R}\right]\left(\frac{dV}{dT}\right)_p = 1$$

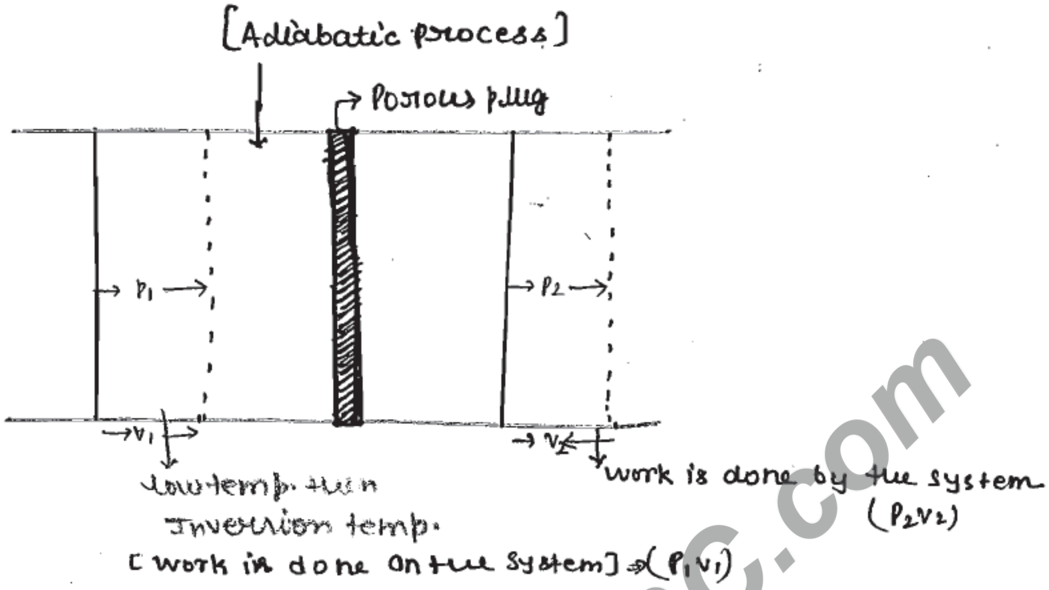
$$\left(\frac{dV}{dT}\right)_p = \frac{1}{\left[\frac{T}{(V-b)} - \frac{2a(V-b)}{V^3 \cdot R}\right]}$$

put these value in Equn → ⑪

$$C_p - C_v = T \times \frac{R}{(V-b)} \times \left[\frac{1}{\frac{T}{(V-b)} - \frac{2a(V-b)}{V^3 \cdot R}}\right]$$

$$C_p - C_v = \frac{T \times R}{(V-b)}\left[\right.$$

Joules- Thomson EFFECT :→



*→ It is a Experimental observation which says that, when a Gas is allowed to Expand adiabatically from High pressure to low pressure the temp. of the Gas in the final State changes.

*→ Joule-Thomson Effect is a iso Enthalpic Process

$$\boxed{\text{Net work done} = P_1V_1 - P_2V_2}$$

Since we know that, from Ist law of thermodynamics -

$$\Delta E = q + w$$

$$q = 0 \text{ [adiabatic process]}$$

$$E_2 - E_1 = P_1V_1 - P_2V_2$$

$$E_2 + P_2V_2 = E_1 + P_1V_1$$

$$\boxed{H_2 = H_1}$$

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

or

$$\boxed{\partial H = 0}$$

Inversion temp. :⇒

→ The temp. below which the Gas become cool down during Expansion, that temp. is called Inversion Temp.

→ All the Gases show cooling Effect Except Hydrogen & Helium bcoz inversion temp. of 'H' and He is so low it can't be achive at R/T.

i.e they show heating Effect

DERIVATION OF ISOENTHALPIE JOULE-THOMSON COFFICIENT :➡

Suppose H is is function of P and T then,

$$H = f(P, T)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \overset{\overset{C_p}{\Downarrow}}{\left(\frac{\partial H}{\partial T}\right)_P} dT$$

diff. both side with respect to dP at constt. H

$$\underset{\underset{0}{\Downarrow}}{dH} = \left(\frac{\partial H}{\partial P}\right)_T \partial P + C_p \cdot dT$$

$$0 = \left(\frac{\partial H}{\partial P}\right)_T \times 1 + C_p \cdot \left(\frac{dT}{dP}\right)_H$$

$$-C_p \left(\frac{dT}{dP}\right)_H = \left(\frac{\partial H}{\partial P}\right)_T$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_H = \mu_{J.T.} = \frac{-1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T}$$

$\mu_{J.T}$ ⇒ Joule-Thomson coefficient

$$\boxed{-\left(\frac{\partial T}{\partial P}\right)_H = \mu_{J.T.}}$$

→ Prove that $\mu_{(J.T.)}$ for an Ideal Gas →

Since we know that -

$$\mu_{J.T.} = -\frac{1}{C_p}\left[\frac{dH}{dP}\right]_T$$

$$\because \; H = E + PV$$

$$= -\frac{1}{C_p}\left[\frac{\partial[E+PV]}{\partial P}\right]_T$$

$$= -\frac{1}{C_p}\left[\left(\frac{\partial E}{\partial P}\right)_T + \left[\frac{\partial(PV)}{\partial P}\right]_T\right]$$

$$= -\frac{1}{C_p}\left[\left(\frac{\partial E}{\partial P}\right)_T + \left(\frac{\partial(RT)}{\partial P}\right)_T\right]$$

$$= -\frac{1}{C_p}\left[\cancelto{0}{\left(\frac{\partial E}{\partial V}\right)_T}\cdot\left(\frac{\partial V}{\partial P}\right)_T + \cancelto{0}{\left(\frac{\partial(RT)}{\partial P}\right)_T}\right] \longrightarrow \text{Both are constant}$$

↳ (Ideal Gas के लिए Internal Energy 0)

$$= -\frac{1}{C_p}\left[0+0\right]$$

$$= -\frac{1}{C_p}\times 0$$

$$\boxed{\mu_{J.T.} = 0}$$

This Results shows that Ideal Gas does not Show Joule-Thomson Effect.

Derivation of Isothermal Joule-Thomson Cofficient:⇒

$$\mu_{J.T.} = \frac{-1}{C_p}\left[\frac{dH}{dP}\right]_T$$

$$\boxed{-C_p \cdot \mu_{J.T} = \left[\frac{\partial H}{\partial P}\right]_T}$$

$\Downarrow$

Isothermal Joule-Thomsom cofficient

DERIVATION OF Joule-Thomson Cofficient [$\mu_{J.T.}$] for A Real Gas:⇒

$$\mu_{J.T.} = -\frac{1}{C_p}\left[\frac{dH}{dP}\right]_T \quad - Ⓐ$$

By second thermodynamic Eqn →

$$V = T\left(\frac{dV}{dT}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T$$

$$V - T\left(\frac{dV}{dT}\right)_P = \left(\frac{\partial H}{\partial P}\right)_T$$

put this value in Ⓐ

$$\mu_{(J.T)} = \frac{-1}{C_p}\left[V - T\left(\frac{dV}{dT}\right)_P\right]$$

$$\mu_{J.T} = \frac{1}{C_p}\left[T\left(\frac{dV}{dT}\right)_P - V\right]$$

$$\because \; -\left(\frac{\partial H}{\partial P}\right)_T = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V \right]$$

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

neglect $-\frac{ab}{V^2}$

$$PV - Pb + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V} + Pb \quad \text{— ([illegible])}$$

$$V = \frac{RT}{P} - \frac{a}{PV} + b \quad \text{— (4)}$$

Diff. Eq^n (4) by T at const. (P)

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\frac{R}{P} \times T\right] - \frac{\partial}{\partial T}\left(\frac{a}{PV}\right) + \left(\frac{\partial P}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} - \frac{\partial}{\partial T}\left(\frac{a}{RT}\right) + \cancel{\left(\frac{\partial P}{\partial T}\right)_P} \to 0$$

[∵ $PV = RT$ assuming]

$$\left(\frac{\partial V}{\partial T}\right)_P = \cancel{V-b}\;\frac{R}{P} + \frac{a}{RT^2} + 0$$

$$\left(\frac{dV}{dT}\right)_P = \frac{R}{P} + \frac{a}{RT^2} \quad \text{— (5)}$$

Put the value of R/p from Eq^n-(4)

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{a}{RT^2} + \frac{a}{RT^2}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{2a}{RT^2} + \frac{(V-b)}{T}$$

Put the value of [6] in Eq^n-[3]

$$\mu_{J.T.} = \frac{1}{C_p}\left[\frac{2a}{RT} + \cancel{V} - b - \cancel{V}\right]$$

$$\boxed{\mu_{J.T.} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]}$$

Conclusion of Joule-Thomson Effect: ⇒

- Ideal Gas doesn't Show Joule Thomson Effect

  $\mu_{J.T.}$ for an Ideal Gas is Equal to zero

  Iso Enthalpic Joule-Thomson coefficient is Equal to $\mu_{J.T.}$

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu_{J.T.} = \frac{-1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T$$

All Gases at R/T shows cooling Effect Except Hydrogen + Helium bcoz their inversion temp. does not $\overset{I.T.}{\text{achivable}}$ at R/T.

In the case of Real Gas the nature of $\mu_{J.T.}$

$$\mu_{J.T.} = +\frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

→ In the case of Real Gas if the nature of $\mu_{J.T.}$ is +ive, it means that cooling takes place.

If the value of $\mu_{J.T.}$ is -ive it means that Heating take place

If the value of $\mu_{J.T.}$ is zero it means that neither Heating nor cooling of Gas takes place

$$\mu_{J.T.} = \left(\frac{\partial T}{\partial P}\right)_H = +ive \quad [\text{cooling}]$$

$$\mu_{J.T.} = \left(\frac{\partial T}{\partial P}\right)_H = -ive \quad [\text{Heating}]$$

A temp. at which Gas shows neither heating nor cooling that temp. is called inversion temp.

$$\mu_{J.T.} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

$$0 = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

$$\frac{2a}{RT_i} = b$$

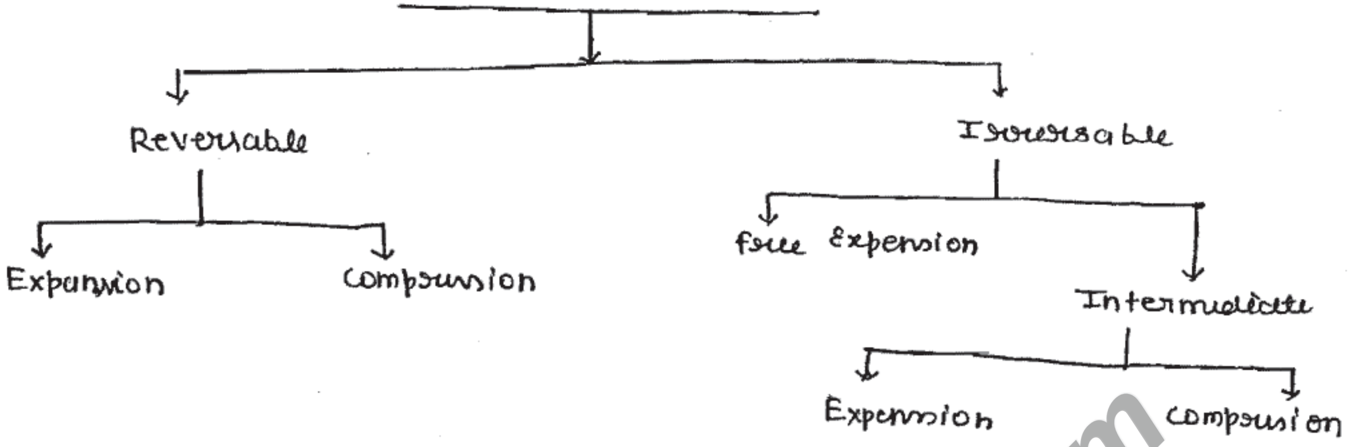
$$\boxed{\frac{2a}{Rb} = T_i}$$

T_i ⇒ Inversion temp.

Above T_i the Gas shows heating Effect and below the inversion temp. Gas shows cooling Effect.

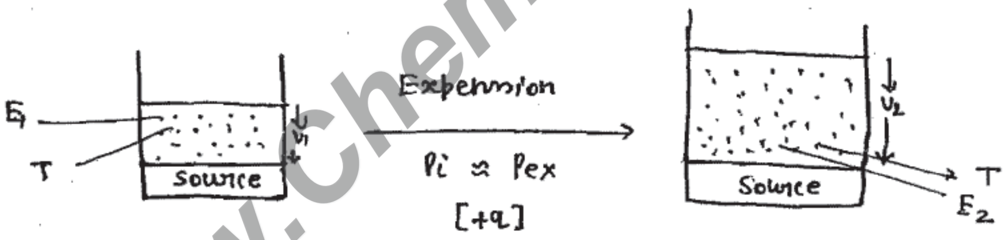
In J-T. Effect, the Gas is adiabatically Expand from high pressure to low pressure, there is a change is occure, the Extent of change depend upon initial Temp., pressure difference, nature of Gas used.

ISOTHERMAL PROCESS



Isothermal Reversable Expension or compression for an Ideal Gas :-

[1] Expension :→ Suppose a System which contain an Ideal Gas Expand isothermally from V_1 to V_2. In this case temp remain same so +q heat must be absorb by the Surrounding.



Calculation of ΔE :⇒

In the case of Ideal Gas, E is a function of temp. As temp. remain same initial state & final state change in internal energy is Equal to zero.

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

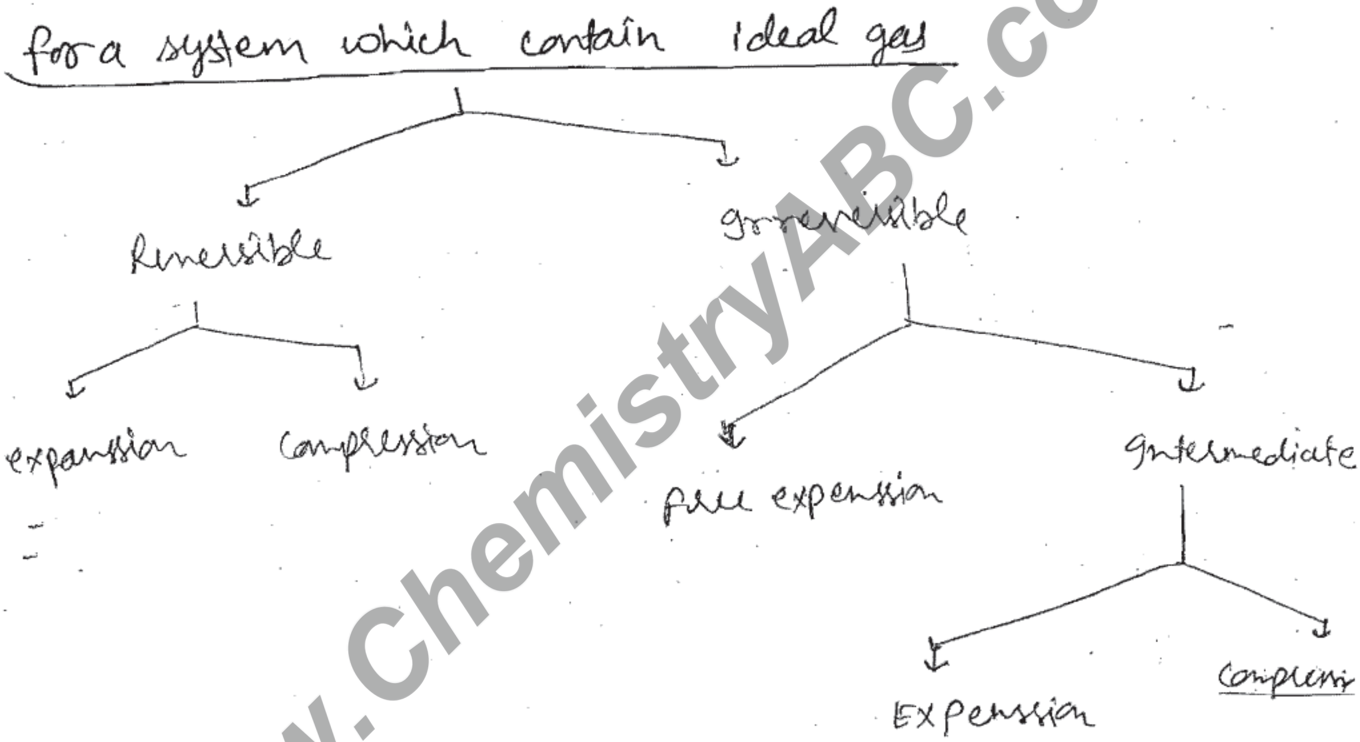
In the adiabatic System.

Temp. is same, then E doesnot change

cooling effect.

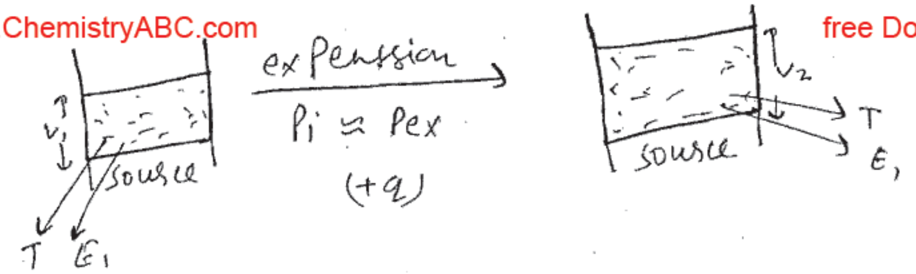
⇒ In J - T effect, the gas is adiabatically expand from high pressure to low pressure, there is a change in occurs. the extent of change depend upon initial Temp. pressure difference, nature of gas used.

Isothermal Process



Isothermal Reversible expansion 'or' compression for an ideal gas

① Expension Suppose a system which contain an ideal gas expand isothermally from V_1 to V_2. In this case Temp. remain same so +q heat must be absorb by the surrounding.



Calulation of ΔE

In the case of ideal gas, E is a funct^n of Temp.

As temp. remains same initial state & final state, change in internal energy is equal to zero $\boxed{\Delta E = 0}$

In the abv. system temp. is same, then internal energy does not change.

$\boxed{E \propto T}$

$\boxed{\Delta E = 0}$

$\boxed{dE = 0}$

Calulation in change of enthalphy

$$\therefore \Delta H = \Delta E + P\Delta V$$

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

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

$$\Delta H = \Delta E + R\Delta T$$

$$\Delta T = 0$$

$$\boxed{\Delta H = \Delta E = 0}$$

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

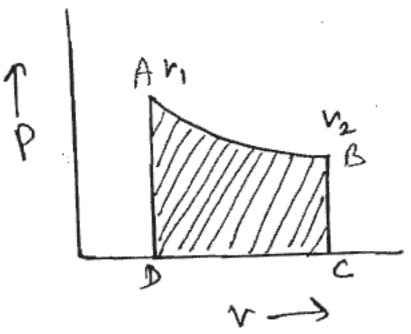
Calaulation of workdone

$$w = -\int_{V_1}^{V_2} P\,dV$$

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

$$\boxed{w = -nRT \ln \frac{V_2}{V_1}}$$

In the reversible case,



work done = area of ABCD

Note: $\boxed{\text{In reversible work done, we always use integration}}$

Calculation of Heat absorb

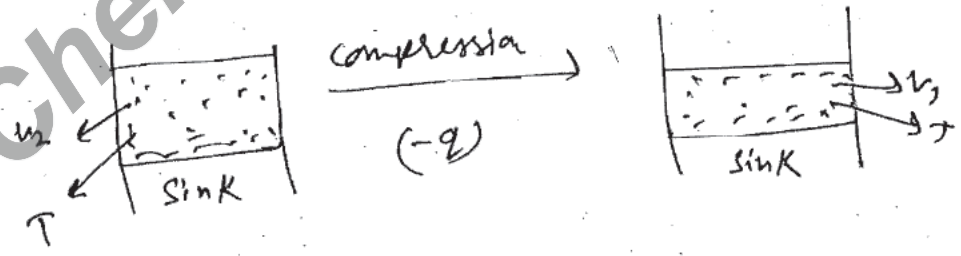
$$\Delta E = q + w$$

$$\Delta E = 0$$

$$+q - PdV = 0$$

$$\boxed{+q = nRT \ln \frac{v_2}{V_1}}$$

For compression



In isothermal compression, work is done on the system, this work may increase the temp. of the system. But in the above case temp. remain same so all the heat rejected to the sink (surrounding)

Calculation of ΔH, ΔE

$$\boxed{\Delta H = \Delta E = 0}$$

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

$$\boxed{dH = 0}$$

$$\boxed{dE = 0}$$

Calculation of workdone

$$w = -\int_{V_2}^{V_1} P\,dV$$

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

$$\boxed{w = -nRT \ln \frac{V_1}{V_2}}$$

Calculation of Heat Rejected

Calculation of

$$\Delta E = q + w$$

$$-q = w$$

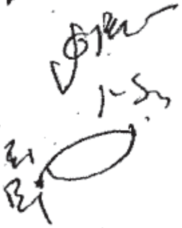
$$\boxed{-q = -nRT \ln \frac{V_1}{V_2}}$$

Calculation of Total workdone in isothermal reversible compression & expansion to the same extent

only consider the magnitude

$$w = nRT \ln \frac{V_2}{V_1} + nRT \ln \frac{V_1}{V_2}$$

$$= nRT \ln \frac{V_2}{V_1} - nRT \ln \frac{V_2}{V_1}$$



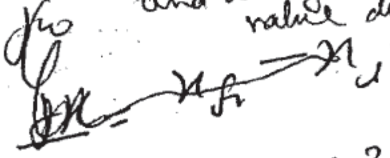
$$\boxed{W_{Total} = 0}$$

$$\boxed{\oint w = 0}$$

But $\boxed{\oint \underline{dw} \neq 0}$

(final − initial)

and always have a value does not zero



Irreversible when driving force & opposing force is comparable.

dw does not zero bcz work is path dependent function.

$\underline{dB} = 9.5 - 8.3$

$\underline{\Delta B} = \underline{10 - 5}$

But in case of E, — reversib dE may be to zero.

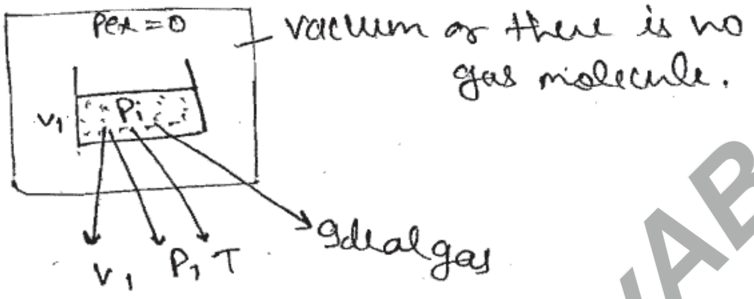
reversible process are those process in which their large diff. in driving force & opposing force.

In Irreversible their is two process passible

free expenssion ② intermediate

Expansion in vaccum or free Expansion

This is a stream case of irreversible bcz opposing rce is equal to zero.



lculation of ΔE, ΔH $\Delta E = 0$, $dE = 0$

$$\Delta H = \Delta E = 0 , \quad dH = 0$$

ulation of workdone $w = -P_{ex}(V_2 - V_1)$

$$= 0(V_2 - V_1)$$

$$\boxed{w = 0}$$

e external pressure zero in a vaccum, ansion take place, their is no work e by the system.

lculation of Heat   Since,

$$\Delta E = q + w$$

$$0 = q + 0$$

$$\boxed{q = 0}$$

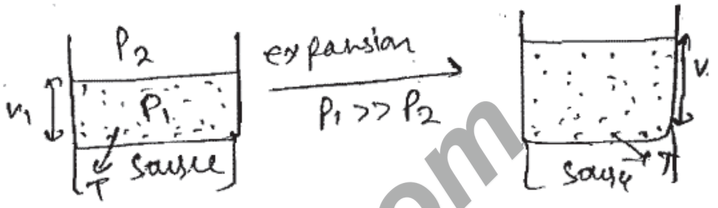
Intermediate

$P_1 > P_2$ (Expansion)

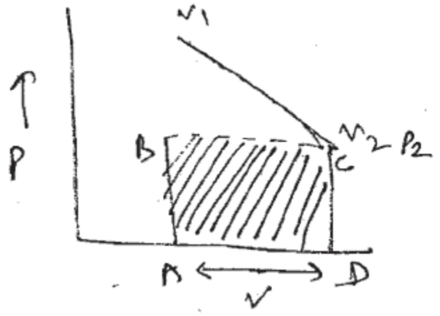
$P_2 >> P_1$ (compression)

Intermediate Expansion

sourse → energyprovide



$$\boxed{\begin{array}{c}\Delta E = 0 \\ \Delta H = 0\end{array}}$$



Calculatⁿ of work done area of ABCD

$$\boxed{w = -P_2(V_2 - V_1)}$$

Calculation of Heat

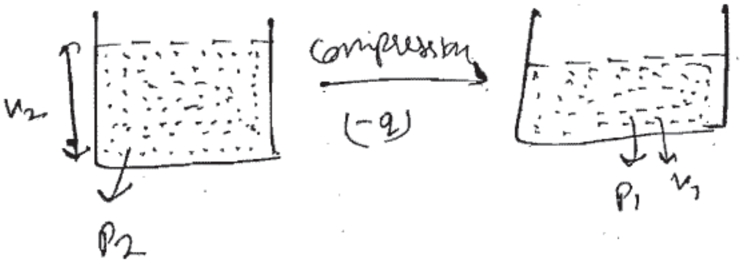
$$\Delta E = q + w$$

$$0 = q + w$$

$$\boxed{+q = P_2(V_2 - V_1)}$$

Intermediate Compression

$$\boxed{\begin{array}{c}\Delta E = 0 \\ \Delta H = 0\end{array}}$$



$$\boxed{w = -P_1(V_1 - V_2)}$$ [Bcz external pressure P_1]

$$\Delta E = q + w$$

$$0 = q + w$$

$$\boxed{q = -w} \quad \boxed{q = P_1(V_1 - V_2)}$$

Total workdone in an intermediate process

$$w = P_2(V_2 - V_1) + P_1(V_1 - V_2)$$

$$w \neq 0$$

$$\boxed{\oint w \neq 0}$$

NOTE ① Reversible workdone or irreversible workdone can be expressed in terms of pressure –

Reversible workdone in terms of P

for expansion $w = -nRT \ln \frac{V_2}{V_1}$

$RT = \therefore P_1V_1 = P_2V_2$ (ideal gas)

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

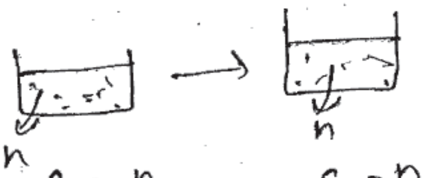
now the (1) equatn

$$\boxed{w = -nRT \ln \frac{P_1}{P_2}}$$

In terms of concn

$$\frac{V_2}{V_1} = \frac{C_1}{C_2}$$

$$\boxed{w = -nRT \ln \frac{C_1}{C_2}}$$



$C_1 = \frac{n}{V_1}$ $C_2 = \frac{n}{V_2}$

Irreversible workdone can also be represent in terms of P & C

$w_{irr} = -P_2[V_2 - V_1]$ —① (expansion)

$P_2V_2 = RT$

$V_2 = \frac{RT}{P_2}$ —②

$V_1 = \frac{RT}{P_1}$ —③

$w_{irr} = -P_2\left[\frac{RT}{\ } - \frac{RT}{\ }\right]$

Q. Calculate ΔE, ΔH, q, w for isothermal expansion of 1 mole of an ideal gas at 27°C from a vol. of 10 dm³ to a 20 decimeter³ (dm³) in reversible expansion.

$\Delta E = 0 \qquad \Delta H = 0$

27+273
300

$$w = -nRT \ln \frac{V_2}{V_1}$$

$$= -8.314 \times 300 \ln \frac{20}{10}$$

$$= -8.314 \times 300 \times 2.303 \times 0.3010$$

$$w = -1728.99\ J$$

$$q = +1728.99\ J$$

unit

Joule × $JK^{-1}mol^{-1} \times K$

J

$$\boxed{\begin{aligned} R &= 0.082\ dm^3\,atm\,mol^{-1}K^{-1} \\ &= 8.314\ JK^{-1}mol^{-1} \\ &= 1.98\ cal\ K^{-1}mol^{-1} \end{aligned}}$$

Q. Calculate q, w, ΔH, ΔV for 1 mole of ideal gas which expand reversibly from 10 atm to 2atm at 300 K.

$\Delta E = 0$, $\Delta H = 0$

$$w = -nRT \ln \frac{P_1}{P_2}$$

$$= 1 \times \ \times 300 \times 2.303 \times \log \frac{10}{2}$$

$$= 1 \times 8.314 \times 300 \times 2.3030 \log 5$$

$$= 1 \times 8.314 \times 300 \times 2.303 \times 0.698$$

$$= -3993.62$$

$$\boxed{q = +3993.62}$$

4015.15

Q. 6 mole of an ideal gas expand against a constant external pressure of 1 atm from a vol. of 10 dm^3 to a vol. of 20 dm^3 calculate ΔH, ΔV, q,

at 300 K
Irreversibly

$\Delta H = 0$

$\Delta V = 0$

$w = -P_1(V_2 - V_1)$

$= -1(20-10)\ dm^3 atm$

$\boxed{w = -10} \times 101.39\ J$

$\boxed{w = -1013.9\ J}$

$\boxed{q = 10}$

$\boxed{q = 1013.9\ J}$

$0.082\ dm^3 atm\ mol^{-1} K^{-1}$

$8.314\ J K^{-1} mol^{-1}$

$1\ dm^3 atm = \frac{8.314}{0.082}\ J$

$\boxed{1\ dm^3 atm = 101.39\ J}$

Comparision b/w work of Reversible expansion and work of irreversible expansion

W_{rev} (expansion) $= nRT \ln \frac{P_1}{P_2}$

$= nRT \ln\left(1 - 1 + \frac{P_1}{P_2}\right)$

$= nRT \ln\left[1 - \left(1 - \frac{P_1}{P_2}\right)\right]$

$\because \ln(1-x) \simeq -x$

~~$= nRT \ln\left[1 - \left(1 + \frac{P_1}{P_2}\right)\right]$~~

~~$= nRT \ln [1 + P_1]$~~

$$\Rightarrow nRT\left(1-\frac{P_1}{P_2}\right) \text{ —— } ①$$

$PV = nRT$

W_{irr} (expansion) $= P_2(V_2 - V_1)$

$$= P_2\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$$= nRT\left[1-\frac{P_2}{P_1}\right] \text{ — } ②$$

substract ① — ②

$$W_{rev} - W_{irr} = -nRT\left(1-\frac{P_1}{P_2}\right) - nRT\left(1-\frac{P_2}{P_1}\right)$$

$$= nRT\left(\frac{P_1}{P_2} - 1\right) + nRT\left[\frac{P_2}{P_1} - 1\right]$$

$$= nRT\left[\frac{P_1 - P_2}{P_2}\right] + nRT\left[\frac{P_2 - P_1}{P_1}\right]$$

$$= nRT\left[\frac{P_1}{P_2} - 1 + \frac{P_2}{P_1} - 1\right]$$

$$= nRT\left[\frac{P_1}{P_2} + \frac{P_2}{P_1} - 2\right]$$

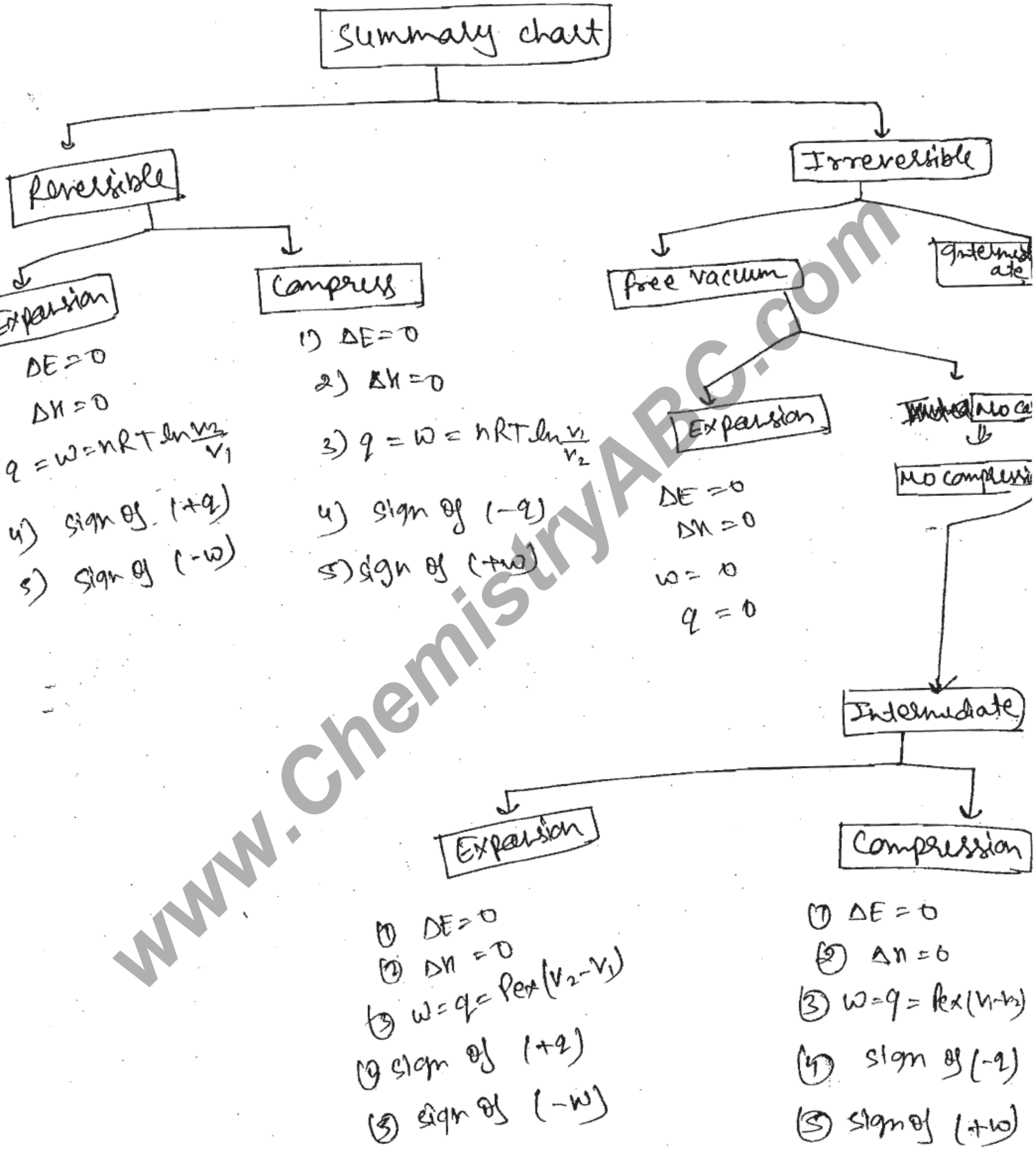
$$= \frac{nRT}{P_1 P_2}\left[P_1^2 + P_2^2 - 2P_1P_2\right]$$

$$= \frac{nRT}{P_1 P_2}(P_1 - P_2)^2$$

$$\boxed{\therefore\ W_{rev} > W_{irr}}$$

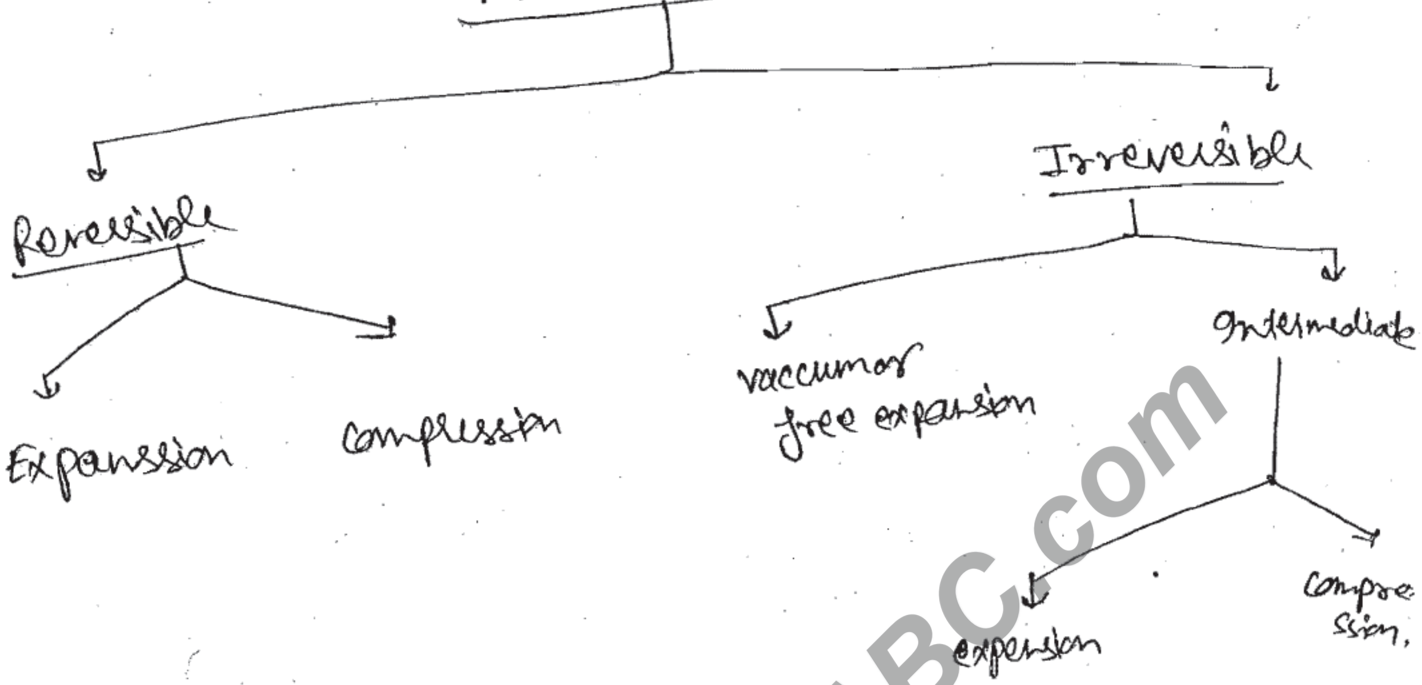
$$\boxed{W_{rev} - W_{irr} = +ve}$$

You get the square of the name, which shows that work of reversible expansion is always greater than work of irreversible expansion.



26 Oct

Adiabatic Process for an ideal gas

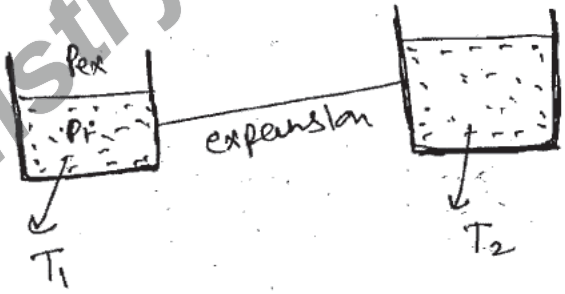


Adiabatic Reversible expansion / or compression for an ideal gas

Expansion

$\Delta E = q + w \quad q = 0$

$\boxed{\Delta E = w}$



C_v is fixed at particular system, at particular Temp.

$\boxed{T_2 < T_1}$

$\left(\frac{\partial E}{\partial T}\right)_V = nC_v \quad n = \text{no. of mole}$

Since, we know that an adiabatic process system expand and compress, there is internal energy change is and temp. also change.

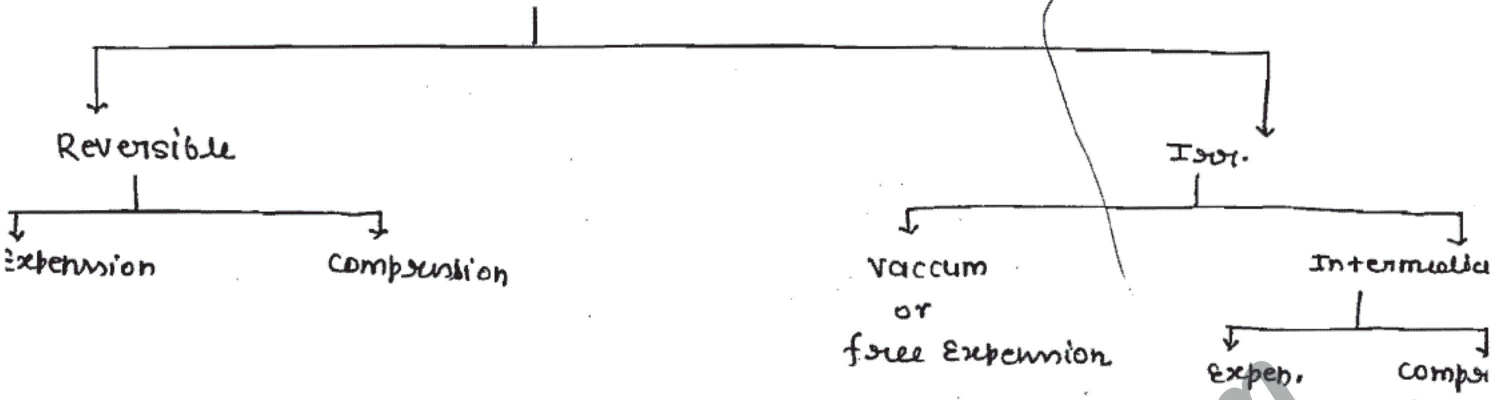
$\frac{\Delta E}{\Delta T} = nC_v$

$\boxed{\Delta E = nC_v(T_2 - T_1)}$

$\boxed{\Delta E = w}$

[26, October, 2015]

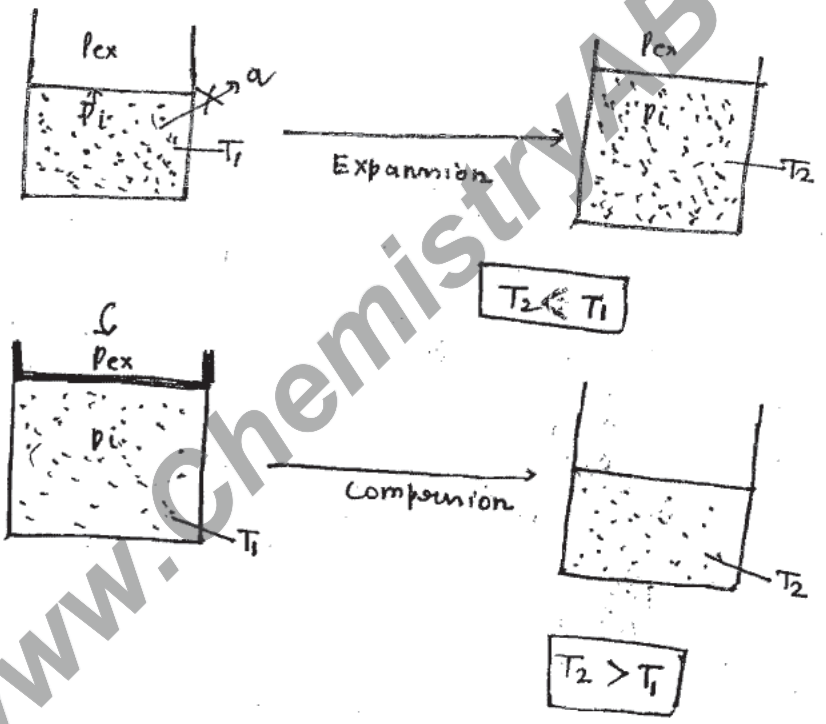
-: Adiabatic Process for an Ideal Gas :-



Adiab. I

✱ Adiabatic Reversible Exp. or comp. for an Ideal gas

- calculation of ΔE



Since we know that in adiabatic process the System expend ~~or~~ compressed there is ΔE take place and temp. also changes

So $\boxed{\Delta E = nC_v(T_2 - T_1)}$

⇒ In Exp. ⇒ $T_2 < T_1$, where in comp. ⇒ $T_2 > T_1$

Calculation of Change in Enthalpy (ΔH)

Enthalpy changes during the process bcoz Enthalpy term include internal Energy so it also changes -

$$\boxed{\Delta H = nC_p(T_2 - T_1)}$$

So, in Expansion $T_2 < T_1$

in compression, $T_2 > T_1$

Calculation of work done :→

in adiabatic process we represent a equation - [The Gas Eqⁿ]

Since $PV^{\gamma} = K =$ constant

$\gamma \Rightarrow$ Atomocity of gas

and System goes from initial state to final state

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$$

Since we know that for the calculation of rever. work done -

$$w = -\int_{V_1}^{V_2} P\,dV$$

$$= -\int_{V_1}^{V_2} \frac{K}{V^{\gamma}}\cdot dV$$

$$= -K\int_{V_1}^{V_2} V^{-\gamma}\,dV$$

$$= \frac{-K}{(-\gamma+1)}\left[V^{-\gamma+1}\right]_{V_1}^{V_2}$$

$$= \frac{-K}{[-\gamma+1]}\left[V_2^{-\gamma+1} - V_1^{-\gamma+1}\right]$$

$$= \frac{-1}{[-\gamma+1]}[P_2V_2 - P_1V_1]$$

$$= \frac{-1}{[-\gamma+1]}[nRT_2 - nRT_1]$$

$$\boxed{w = \frac{nR}{[\gamma-1]}[T_2 - T_1]}$$

for Expan. → $T_1 > T_2$

for Comp. → $T_2 > T_1$

work can also be calculated ~~dia~~ adiabatic rev. work done can also be calculated in terms of Change in Internal Energy.

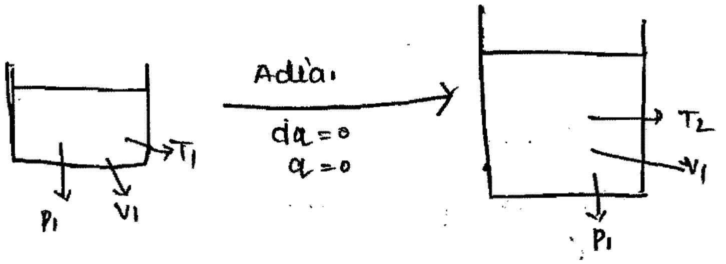
from First law of thermodynamics–

$$\Delta E = \overset{0\ [\text{Adia. Process}]}{\cancel{q}} + w$$

$$\boxed{\Delta E = w}$$

$$\boxed{nC_V(T_2 - T_1) = w}$$

⇐: Relation b/w Temp. & Volume in the case of Adiabatic reversible process :⇒



Since we know that from Ist law of thermodynamics

$$du = dq - Pdv$$

$$du = 0 - Pdv$$

$$\underline{C_v \cdot dT} = -\frac{RT}{V}dv$$ [for one mole of Ideal gas]

Inte. both side

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R\int_{V_1}^{V_2} \frac{dv}{V}$$

$$C_v \cdot \ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1}$$

$$\ln\frac{T_2}{T_1} = \frac{-(C_p - C_v)}{C_v}\ln\frac{V_2}{V_1} \qquad \left(\because \frac{C_p}{C_v} = \gamma\right)$$

$$\ln\frac{T_1}{T_2} = (\gamma - 1)\ln\frac{V_2}{V_1}$$

$$\ln\frac{T_1}{T_2} = \ln\left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

taking antilog on both side

Imp

$$\boxed{\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}}$$

[illegible]r

T_1 is a initial Temp. & V_1 is a initial volume

& T_2 is a final Temp. & V_2 is a final Volume

⇒ and this Eqn - can use for Expansion and compression

⇐ Relation b/w temp. and pressure ⇒

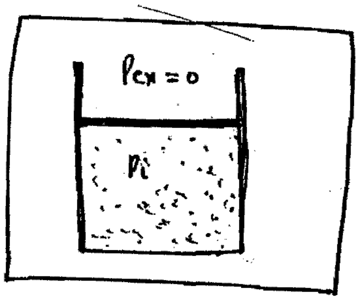
$$\because \quad P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$$

$$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$$

$$\boxed{T_1^{\gamma} \cdot P_1^{1-\gamma} = T_2^{\gamma} \cdot P_2^{1-\gamma}}$$

Proof ⇒

Irreversible
↓
Vaccum or free Expansion



$W = P_{ex}.\,dv$

$T_1 = T_2$

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

$\boxed{\Delta E = 0}$

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

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

$\Delta H = \Delta E + R\Delta T$ [Here No work No change in temp. so $\Delta T = 0$]

$\Delta H = \Delta E + 0$

$\boxed{\Delta H = \Delta E = 0}$

Calculation of thermodynamic parameter in the case of Adiabatic free Expansion or Expansion in vaccum →

(i) calculation of (ΔE) ⇒ we know that in vaccum pressure is zero, so there is no change in Internal Energy during expansion and that is Equal to ($\Delta E = 0$)

(ii) Calculation of ΔH ⇒ Internal Energy is a part of Enthalpy, so H is also not changes during Expan. in vaccum.

So, $\boxed{\Delta H = 0}$

(iii) calculation of work done: → In vaccum expansion outer pressure is zero or the pressure which is against to the system is zero, so finally there is no work done in vaccum expansion.

mathematically, $W = -P_{ex}.\,dv$

$P_{ex.} = 0$ [vaccum]

Irreversible process
↓
Intermediate process
↓
Expansion   Compression

$$\Delta E = nC_v(T_2 - T_1)$$

$$\Delta H = nC_p(T_2 - T_1)$$

$$W = -P_{ex}(V_2 - V_1)$$

$$= -P_{ex}\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]$$

$$\boxed{W = -P_2\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]}$$

$T_2 < T_1$ → for Expansion

$T_2 > T_1$ → for compresn.

(i) calculation of ΔE ⇒

$$\boxed{\Delta E = nC_v(T_2 - T_1)}$$

In exp. $T_2 < T_1$

In com. $T_2 > T_1$

(ii) Calculation of ΔH ⇒

$$\boxed{\Delta H = nC_p(T_2 - T_1)}$$

(iii) calculation of work done ⇒

$$\boxed{W = -P_2\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]}$$

∵ In case of Expanssion,-

$P_2 < P_1$

∴ In case of compression

Ans:⇒ One mole of an Ideal Monoatomic gas at 27°c expanpends rever. & Adiabitically from a volume 10 dcm³ to 20 dcm³, calculate, q, Δu, ΔH, w and assume that $\left[C_V = \frac{3}{2}R\right]$

$$\because \; C_p - C_v = R$$

$$C_p - \frac{3}{2}R = R$$

$$C_p = \frac{5}{2}R$$

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

$$\Delta E = n\,C_v\,(T_2 - T_1)$$

$$\Delta E = 1 \cdot C_v\,(T_2 - 300\,K)$$

$$\Delta E = C_v\,(T_2 - 300)$$

$$\because \; \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\frac{T_1}{T_2} = \left(\frac{20}{10}\right)^{\gamma-1}$$

$$\frac{T_1}{T_2} = (2)^{\gamma-1}$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.6$$

$$\gamma = (2)^{1.6-1}$$

$$\gamma = (2)^{0.6}$$

$$\because \; [2]^{0.6} = 1.515$$

$$\frac{300}{T_2} = (2)^{0.6}, \qquad T_2 = \frac{300}{1.515} = 188.9 \cong 189\,K$$

$$\ln 300 - \ln T_2 = 0.6 \ln 2$$

$\Delta E = \frac{3}{2}R(189-300)$

$\Delta E = \frac{3}{2} \times 8.314\,[-111]$

~~$= 55.5 \times 8.314 \times 5$~~

~~$= 277.5$~~

$= -12.195 \times (111)$

$= -1384\ J$

$\Delta E = q + W$

$\Delta E = 0 + W$ (Expansion)

$(W = -1384$ Joule$)$

$\Delta H = n.C_p\,(T_2 - T_1)$

$= 1 \times \frac{5}{2} \times 8.314\,(189-300)$

$= -\frac{5}{2} \times 8.314 \times 111$

$= -\frac{4614.27}{2}$

$\Delta H = 2307.135\ J$

Qu. one mole of an Ideal Gas at 27°c Expen. adiabatically against a constt. External pressure at 1 atm. From volume of 10 dcm^3 to 20 dcm^3 Calculate, q, w, ΔU, ΔH.

(Irrev.)

⇒ $q = 0$, adia. , $C_v = \frac{3}{2}R$, $T_1 = 27°c$

$V_1 = 10\ dcm^3$, $V_2 = 20\ dcm^3$

$\Delta E = n.C_v\,(T_2 - T_1)$

$\Delta E = 1 \times \frac{3}{2} \times R(T_2 - 300)$

$\Delta E =$

$\Delta E = \overset{0}{\cancel{q}} + W$

$\Delta E = W$

$W = -P_{ex.}\,[V_2 - V_1]$

$W = -1[\,20 - 10\,]$

$W = -10$ atm. dcm^3

$W = \dfrac{-10 \times 8.314}{0.082}$

$W = -1012.6$ Joule

∵ process is isoth.

$\Delta E = W = -1012.6$

$\Delta E = C_V\,(T_2 - T_1) = -1012.6$

$\frac{3}{2} R\,(T_2 - 300\,K) = -1012.6$

$\underset{\substack{\Downarrow \\ 12.471}}{\frac{3}{2} \times 8.314}\,[\,T_2 - 300\,] = -1012.6$

$T_2 - 300 = \dfrac{-1012.6 \times 2}{8.314 \times 3}$

$T_2 - 300 = \dfrac{-1012.6 \times 2}{\text{[illegible]}} = -81.196$

$T_2 = 218.7\ K$

$\Delta H = n\,c_p\,(T_2 - T_1)$

$= \cancel{n}\ \frac{5}{2} \times 8.314\,[\,218.7 - 300\,]$

$= 2.5 \times 8.314\,[$

$= -1351.8564$ Joule.

Ques:- One mole of an Ideal Gas Expanded rev. & adiabatically from 1 dcm³ to 10 dcm³, if initial temp. is 750 K

$C_p = 29.334$ Joule K^{-1} mol^{-1}

C_V

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\frac{750}{T_2} = \left(\frac{10}{1}\right)^{\gamma-1}$$

$$\frac{750}{T_2} = (10)^{\gamma-1}$$

$$\frac{750}{T_2} = (10)^{1.3-1}$$

$$T_2 = \frac{750}{(10)^{0.3}}$$

$$T_2 = \frac{750}{1.995}$$

$$T_2 = 376\,K \cong \underline{300\,K}$$

$C_p - C_v = R$

$29.234 - 8.314 = C_v$

$C_v = 20.92$

$$\frac{C_p}{C_V} = \gamma$$

$$\frac{29.234}{20.92} = \gamma$$

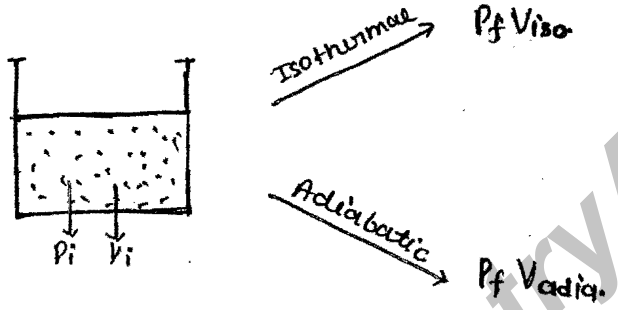
$\gamma = 1.3$

27, October, 2015

Comparison b/w Isothermal and adiabatic Process :→

[Comparison of Iso. + adia. Expansion]

Case-I → when a System Started [Pressure (P_i) and Volume (V_i)] is two different situation. one is adiabatic and another is Isothermal, during both Expansion final pressure P_f is same in both the situation.



For isothermal Expansion →

$$nRT = P_iV_i = P_fV_{iso.} \quad -①$$

Because temp. is same for adiabatic process

$$P_iV_i^{\gamma} = P_fV_{adia}^{\gamma} \quad -(II)$$

from (i) →

$$\frac{P_i}{P_f} = \left(\frac{V_{iso}}{V_i}\right)^{\gamma} \quad — (III)$$

from - (II)

$$\frac{P_i}{P_f} = \left(\frac{V_{adiabatic}}{V_i}\right)^{\gamma} \quad -(IV)$$

from [III] and [IV]

$$\left(\frac{V_{adia}}{V_i}\right)^{\gamma} = \frac{V_{iso}}{V_i}$$

taking log on both side

$$\gamma \ln \frac{V_{adia}}{V_i} = \ln \frac{V_{iso}}{V_i}$$

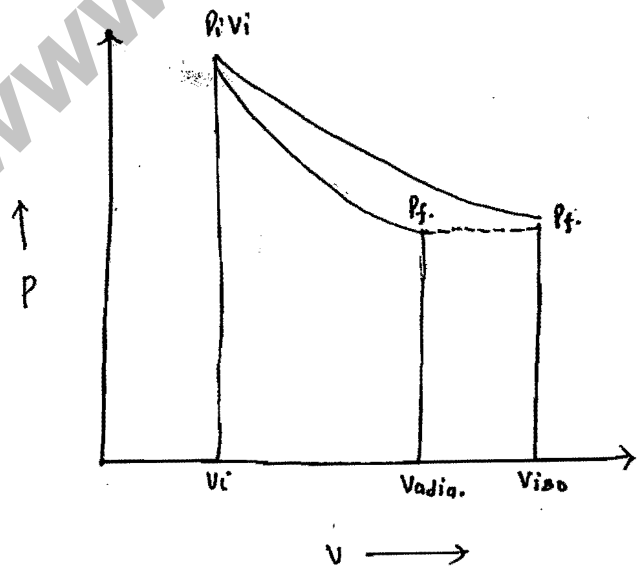
∵ γ is greater then (1)

∴ we can conclude →

$$\frac{V_{iso}}{\cancel{V_i}} > \frac{V_{adia}}{\cancel{V_i}}$$

$$\boxed{V_{iso} > V_{adia}}$$

Graph for Viso & Vadia



The above result shows that the final volume in the case of Isothermal expansion [$V_{iso.}$] is greater than final volume ~~of~~ the case of adiabatic. this also prove that work done in the case of Isothermal Expansion is greater than work done in the case of Adiabatic Expansion.

Case - II

When final volume in both the cases of (adia. & Isoth.) are Same (V_f).

for Isothermal process

$$P_i V_i \longrightarrow P_{iso.} V_f \quad -①$$

for Adia. process.

$$P_i V_i^{\gamma} \longrightarrow P_{adia.} V_f^{\gamma} \quad -Ⓘ$$

from (I)

$$\frac{P_i}{P_{iso}} = \left(\frac{V_f}{V_i}\right) \quad - (III)$$

from (II)

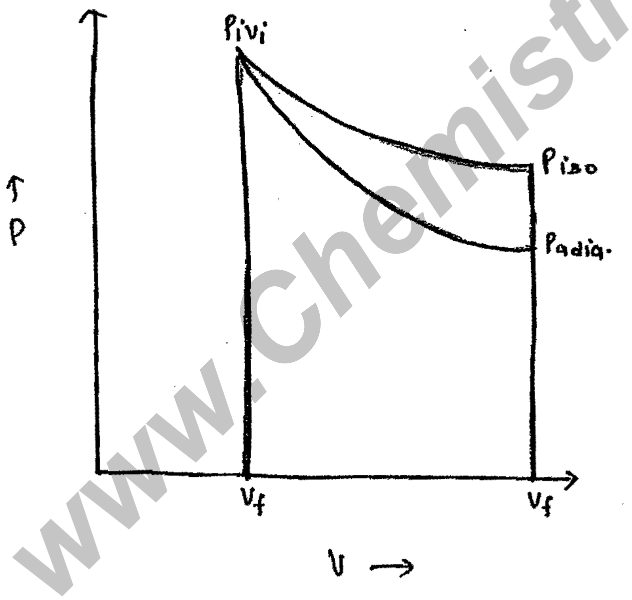
$$\frac{P_i}{P_{adia.}} = \left(\frac{V_f}{V_i}\right)^{\gamma} \quad -(IV)$$

from [3] and [4]

$$\left(\frac{V_f}{V_i}\right)^{\gamma} > \left(\frac{V_f}{V_i}\right)$$

$$\frac{\cancel{P_i}}{P_{adia.}} > \frac{\cancel{P_i}}{P_{iso}}$$

$$\boxed{P_{iso.} > P_{adia.}}$$



the above results shows that the final pressure in the case of Isothermal expansion is greater than final pressure in the case of adiabatic Expansion

- Summary -

$V_{isothermal} > V_{adiabatic}$

$\Delta V_{iso.} > \Delta V_{adia.}$

$P_{iso.} > P_{adia.}$

$\Delta P_{iso.} > \Delta P_{adia.}$

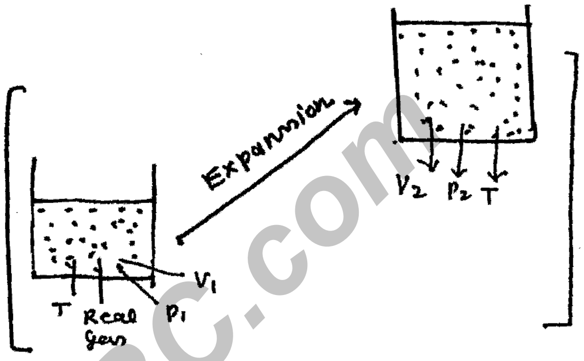
$W_{iso} > W_{adia.}$

#-: CALCULATION OF THERMODYNAMIC PARAMETER IN CASE OF ISOTHERMAL REVERSIBLE PROCESS FOR AN REAL GAS :-

[i] Calculation of work done -

we know that-

for n mole →



$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

$$\because \quad W = -\int_{V_1}^{V_2} P \cdot dV$$

$$W = -\int_{V} \left[\frac{nRT}{(V - nb)} - \frac{an^2}{V^2}\right] dV$$

$$W = -\left[nRT \int_{V_1}^{V_2} \frac{dV}{(V - nb)} - an^2 \int_{V_1}^{V_2} \frac{dV}{V^2} \right]$$

$$W = -\left[nRT \ln\frac{(V_2 - nb)}{(V_1 - nb)} + an^2 \left(\frac{1}{V_2} - \frac{1}{V_1}\right) \right]$$

Calculation of Change in Internal Energy

We know that Internal Pressure for an real gas -

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{an^2}{V^2}$$

real Gas Expend reversibally

$$V_1 \longrightarrow V_2$$

$$dE = \frac{an^2}{V^2} . dV$$

Inte. both Side

$$\int dE = an^2 \int_{V_1}^{V_2} \frac{dV}{V^2}$$

$$\Delta E = -an^2 . \left[\frac{1}{V}\right]_{V_1}^{V_2}$$

$$\boxed{\Delta E = -an^2 \left[\frac{1}{V_2} - \frac{1}{V_1}\right]}$$

Calculation of ΔH

Since we know that

∴ During initial State

$$H_1 = E_1 + P_1V_1 \quad \text{—①}$$

Final State-

$$H_2 = E_2 + P_2V_2 \quad \text{—⑪}$$

$$(II) - (I)$$

$$H_2 - H_1 = E_2 - E_1 + P_2V_2 - P_1V_1$$

$$\Delta H = \Delta E + P_2V_2 - P_1V_1$$

$$\because P = \frac{nRT}{(V-nb)} - \frac{an^2}{V^2}$$

$$\because P_1 = \frac{nRT}{(V_1-nb)} - \frac{an^2}{V_1^2}$$

$$\therefore P_2 = \frac{nRT}{(V_2-nb)} - \frac{an^2}{V_2^2}$$

then

$$\boxed{\Delta H = \Delta E + \left[\frac{nRT}{(V_2-nb)} - \frac{an^2}{V_2^2}\right]V_2 - \left[\frac{nRT}{(V_1-nb)} - \frac{an^2}{V_1^2}\right]V_1}$$

Note⇒ {compression मे V_2 less हो जाते जायेगा।।}

Calculation of q :→

By first law of thermodynamics

$$\Delta E = q + w$$

$$\Delta E = q - nRT \ln \frac{V_2 - nb}{V_1 - nb} + an^2 \left[\frac{1}{V_2} - \frac{1}{V_1} \right]$$

$$\cancel{an^2 \left[\frac{1}{V_2} - \frac{1}{V_1} \right]} = q - nRT \ln \frac{V_2 - nb}{V_1 - nb} + \cancel{an^2 \left[\frac{1}{V_2} - \frac{1}{V_1} \right]}$$

$$\boxed{q = nRT \ln \frac{V_2 - nb}{V_1 - nb}}$$

comparision btw work done in the case of reversible process for an Ideal gas and Real Gas:- [Isothermal process]

∵ we know that in a real Gas-

$$\underset{[Rev.]}{W_{Real}} = nRT \ln \frac{V_2 - nb}{V_1 - nb} + an^2 \left[\frac{1}{V_2} - \frac{1}{V_1}\right] \quad \text{— [I]}$$

& work done in Ideal Gas →

$$\underset{[Rev.]}{W_{Ideal}} = nRT \ln \frac{V_2}{V_1} \quad \text{—[ii]}$$

[∵ in Expanssion $V_2 > V_1$]

then (II) - (I)

nb → neglect

$$W_{Ideal} - W_{real} = nRT \ln \frac{V_2}{V_1} - nRT \frac{V_2 - nb}{V_1 - nb} - an^2 \left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

[bcoz this is constt. & very small]

$$W_{Ideal} - W_{real} = nR\cancel{T} \frac{V_2}{V_1} - nR\cancel{T} \frac{V_2}{V_1} - an^2 \left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

$$W_{Ideal} - W_{real} = - an^2 \left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

$$W_{Ideal} - W_{real} = an^2 \left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

[∵ in Expansion V_2 is always Greater Than V_1]

∴ ($W_{Ideal} - W_{Real}$) comes +ive

and we also Intercept in terms of intercept

⇒ In Case of Ideal Gas whole Energy is converted into work done.

⇒ In the case of real Gas some part of Energy is wasted in terms of overcome the interaction

CARNOT-CYCLE

[Ideal of Human being]
⇓
(maxi. Heat into work)
(Not Total Heat into work)

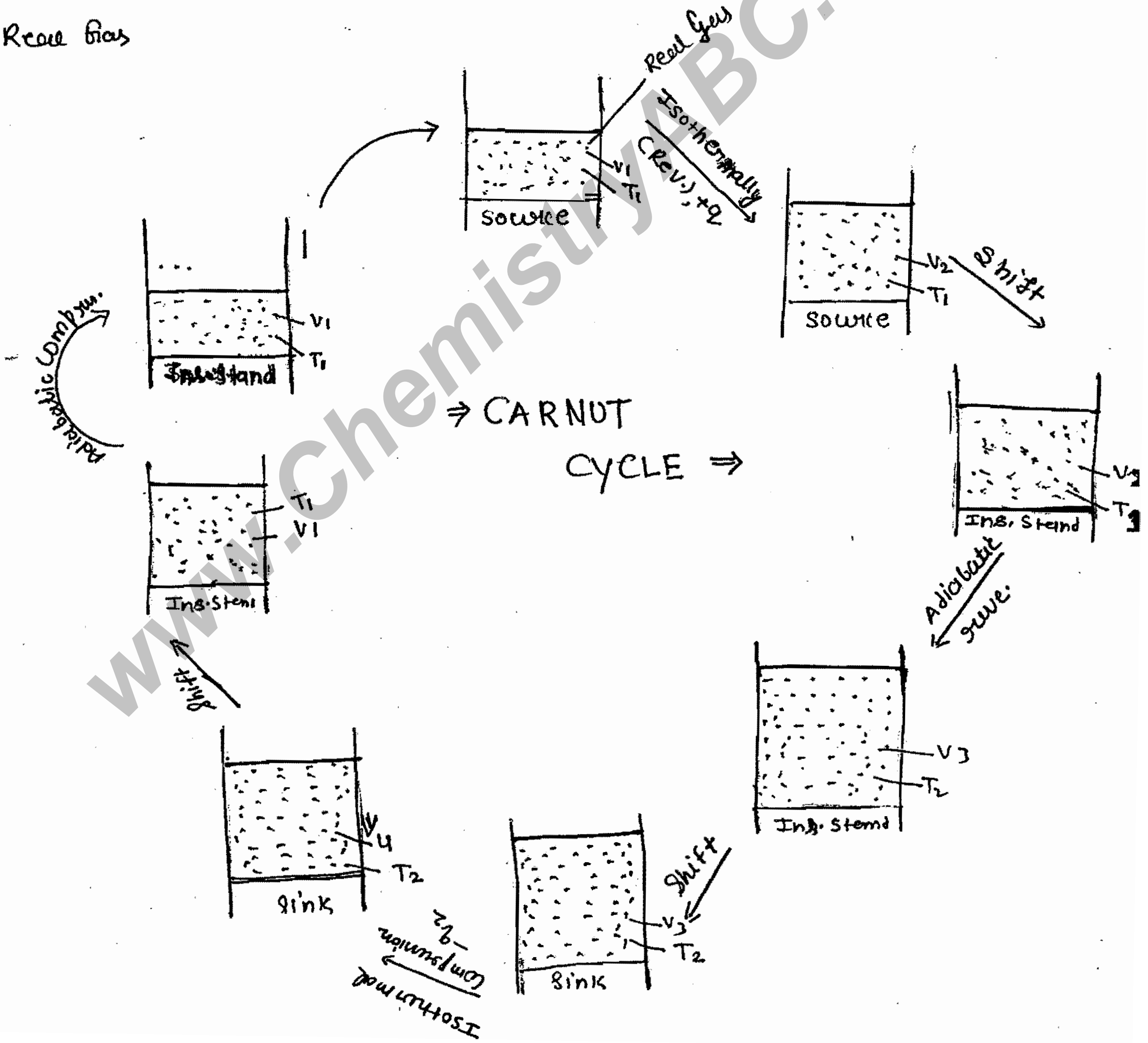
Source (T_1)

Sink (T_2)

Insulating Stand

Chamber

Real Gas



$$\eta = \frac{q_1 - q_2}{q_1}$$

$$\eta = -1 - \frac{q_2}{q_1}$$

$\therefore \frac{q_2}{q_1}$ is alwalys less tuen 1

[28.10.2015]

Total work $\boxed{w = \left[R \ln\left(\frac{V_2}{V_1}\right)\right](T_2 - T_1)}$

It is a Imaganary, Ideal, Hypothetical Engine which are going to demostrate maximum convertibility heat into work.

Inorder to showing maximum work, Heat taking all the process reversible and considering Ideal Gas as a working substance.

Carnot reversible Engine operating through four process

All the four process are reversible

The Efficiency of carnot Engine only depend upon operating temp.

In a carnot Rev. Engine inspite of ~~taking~~ all the process are reversible taking Ideal Gas as working Substance but we get Efficiency 100%.

Some amount of Heat $(-q_2)$ is rejected to the Surrounding

Efficiency of C.E. Independent of working Substance but only depend upon operating temp.

⇒ Source:-

which is maintained at high temp. T_1 and which also provide Energy during Isothermal Expansion

⇒ Sink:-

which is maintained at lower temp. T_2 which act as obserber as heat $(-q_2)$. that is part of surrounding

⇒ Insulating stand:-

It is used during adiabatic Expansion or compression.

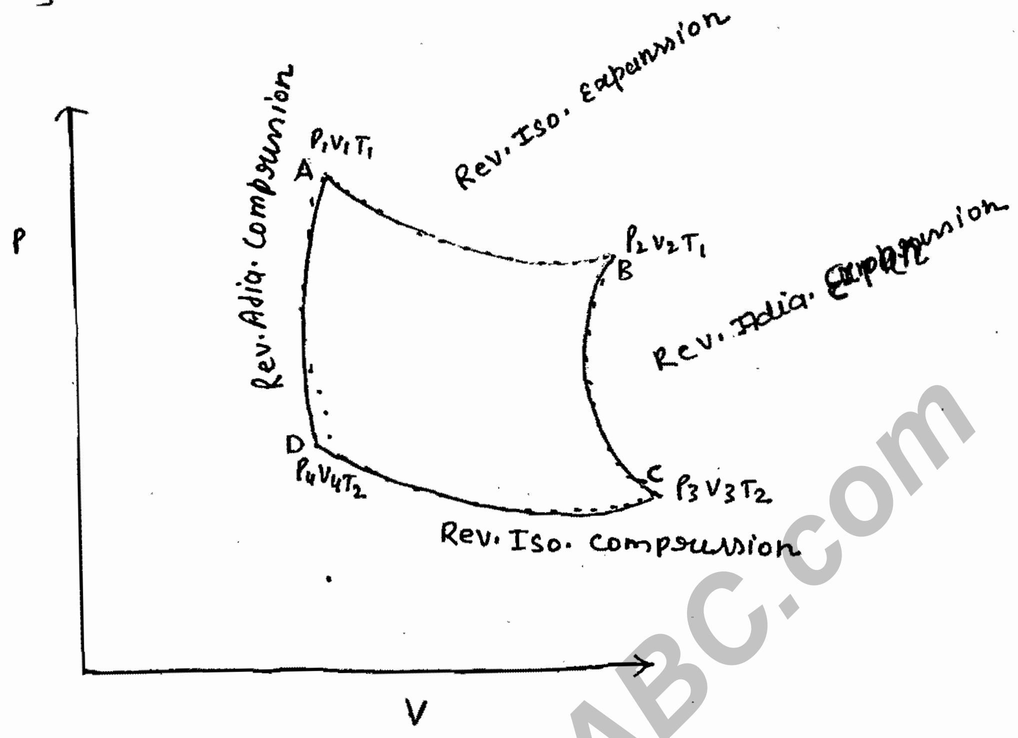
⇒ working Substances

(i) Ideal Gas:- we taking Ideal Gas as a working Substance bcoz there is no Interection b/w Gas molecule so there is not wasting of Energy take place during Expansion or compression of Ideal Gas.

⇒ calculation of thermodynamic parameter during various process of Carnot Engine.

[1] Reversible Isothermal Expansion:⇒

{28.october.2015}



[1] Isothermal Expansion

$$\underset{A}{P_1V_1T_1} \xrightarrow[\Downarrow]{\text{Iso. Expan}} \underset{B}{P_2V_2T_1}$$

$\Delta V > 0$

$\Delta E = 0 \quad \because \Delta E = q_1 + W$

$\Delta H = 0$

$q_1 = W = nRT_1 \ln \frac{V_2}{V_1}$ (n=1 mole)

$\Delta T = 0$

[2] Adiabatic Expansion

$$\underset{B}{P_2V_2T_1} \xrightarrow[\Downarrow]{\text{Adia. Expan.}} \underset{C}{P_3V_3T_2}$$

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

$\Delta V > 0$

$\Delta E = C_v(T_2 - T_1) = w$

$\Delta T < 0$

$\Delta H = C_p(T_2 - T_1)$

[3] Isothermal compression

$$\underset{C}{(P_3V_3T_2)} \xrightarrow[-q_2]{\text{Iso. compre.}} \underset{D}{(P_4V_4T_2)}$$

$\Delta E = 0 \quad \Delta V < 0$

$\Delta H = 0$

$\Delta T = 0$

$\Delta E = q_2 + w$

[4] Adiabatic compression

$$\overset{P_4V_4T_2}{D} \xrightarrow{\text{Adia. compr.}} \overset{P_1V_1T_1}{A}$$

$$\Delta E = C_v(T_1 - T_2)$$

$$\Delta H = C_p(T_2 - T_1)$$

$$\Delta V < 0$$

$$\Delta T > 0$$

⇒ Total work done in Reve. Carnot Engine

$$W_{Total} = W_{\substack{\text{Isotherm.}\\ \text{Expan.}}} + W_{\substack{\text{adia.}\\ \text{Expan.}}} + W_{\substack{\text{iso.}\\ \text{comp.}}} + W_{\text{adia. com.}}$$

$$W = RT_1 \ln \frac{V_2}{V_1} + \cancel{C_v(T_2 - T_1)} + \cancel{C_v(T_1 - T_2)} + RT_2 \ln \frac{V_4}{V_3}$$

$$W = RT_1 \ln \frac{V_2}{V_1} + RT_2 \ln \frac{V_4}{V_3}$$

$$T_1 . V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad [B \rightarrow C]$$

$$\frac{T_1}{T_2} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$$

$$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1} \quad [D \rightarrow A]$$

$$\frac{T_1}{T_2} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\frac{V_1}{V_2} = \frac{V_4}{V_3}$$

$$W = RT_1 \ln \frac{V_2}{V_1} + RT_2 \ln \frac{V_1}{V_2}$$

$$W = RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_2}{V_1}$$

$$\boxed{W_{(Total)} = R(T_2 - T_1)\ln\frac{V_2}{V_1}}$$

Calculation of Efficiency of Carnot Engine :→

$$\eta_{(Efficiency)} = \frac{W_{Total}}{q_1} = \frac{q_1 - q_2}{q_1} = \frac{\cancel{R}\,\cancel{\left(\ln\frac{V_2}{V_1}\right)}(T_1 - T_2)}{\cancel{R}\,T_1\,\cancel{\left(\ln\frac{V_2}{V_1}\right)}}$$

$$\boxed{\eta = \frac{W_{Total}}{q_1} = \frac{q_1 - q_2}{q_1} = \frac{T_1 - T_2}{T_1}}$$

Cofficient of Performance of Carnot heat Engine :-

Reciprocal of Efficiency is called Cofficient of performance —

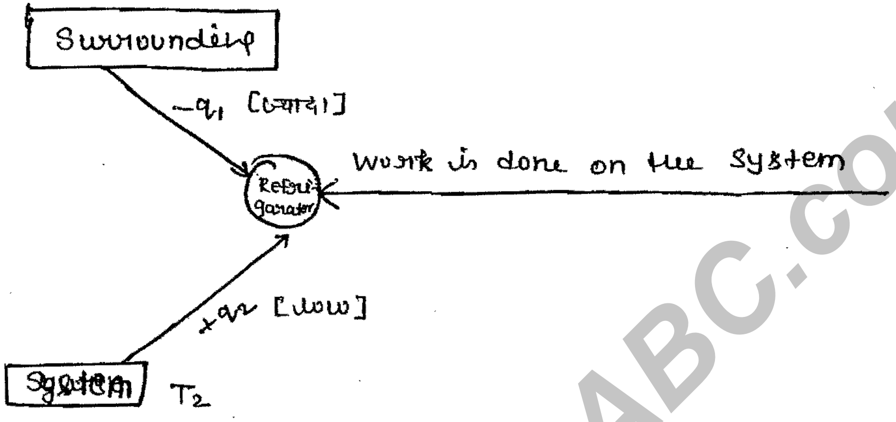
$$\boxed{COP = \frac{1}{\eta} = \frac{1}{\frac{T_2 - T_1}{T_1}} = \frac{T_1}{T_2 - T_1} = \frac{q_1}{q_1 - q_2} = \frac{\text{Heat absorb.}}{\text{Total work done}}}$$

Efficiency of Carnot Refrigerator

$$\boxed{\eta = \frac{T_1 - T_2}{T_2} = \frac{q_1 - q_2}{q_2}}$$

$$\boxed{COP = \frac{T_2}{T_1 - T_2} = \frac{q_2}{q_1 - q_2}}$$

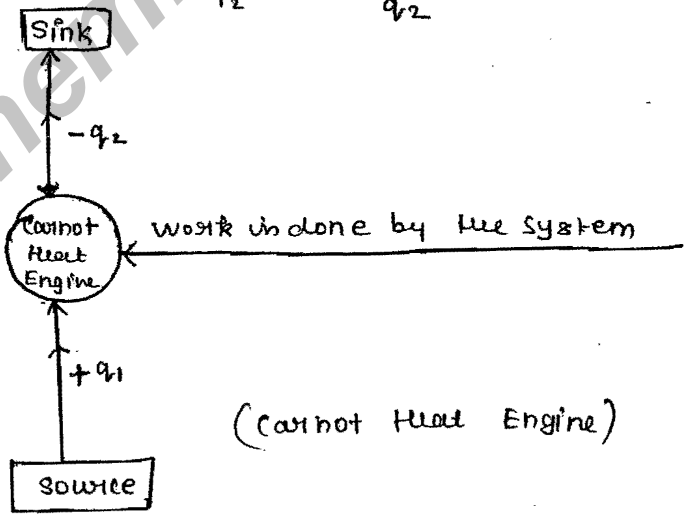
→ Pictorial Representation of Carnot Heat Engine and Carnot Refrigerator ⇒



Carnot-Refrigerator

[low temp. ⟷ High temp.]

$$\text{efficiency} = \frac{T_1 - T_2}{T_2} = \frac{q_1 - q_2}{q_2}$$



(Carnot Heat Engine)

$$\boxed{\eta = \frac{T_1 - T_2}{T_1} = \frac{q_1 - q_2}{q_1}}$$

Note:⇒

CARNOT - THEOREM

"All Periodic machine working reversibally b/w the same two temp. have same Efficiency."

Conclusion:⇒

- Efficiency can never be Equal to 100%
- Carnot cycle work both as a heat Engine and refrigarator.
- All the process of Carnot is reversible, so work done is maximum but never be 100%.
- Carnot cycle is a Hypothetical cycle bcoz it is perfectly reversible process.
- Efficiency of Carnot Engine is never be 100% this means that complete convertivility of Heat into work is impossible.

Qu. 25 Gate→

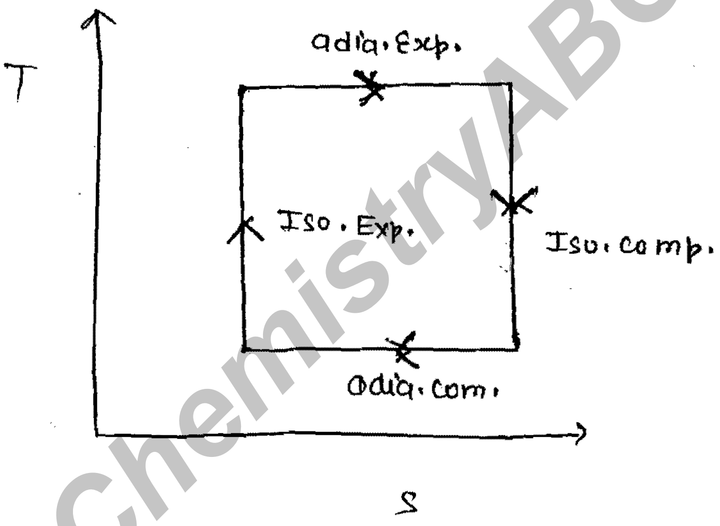
$$\Delta S = \frac{q}{T} = 0/T = 0$$

A → B [ΔS = +ive] → Iso. फैल जाता (ज्यादा से कम दाब पर +ive)

B → C [$\Delta S = 0$] adiabatic

C → D [ΔS = −ive] → disorder घट जाता है। Iso.

D → A [$\Delta S = 0$] → (adia. batic)



{T-S- diagram of Carnot Engine}

(Tephigram)

(S-T- graph)

Qu.28

$T_1 - T_2 = 200\,K$, $T_1 = 200 + T_2$

$w = 400 J$

$\therefore q_2 = \frac{q_1}{3}$

$$\frac{T_1 - T_2}{200 + T_2} = \frac{w}{q_1}$$

$$\frac{q_1 - q_2}{q_1} \qquad \frac{q_1 - \frac{q_1}{3}}{q_1}$$

$$\frac{2\cancel{q_1}}{3\cancel{q_1}} = \frac{400}{q_1}$$

$$q_1 = \frac{1200}{2} = 600 J$$

$$\boxed{q_1 = 600 J}$$

$$\frac{200}{T_2 + 200} = \frac{24\cancel{0}\cancel{0}}{36\cancel{0}\cancel{0}}$$

$200 \times 3 = 2T_2 + 400$

$600 - 200 = 2T_2$

$200 = 2T_2$

$\boxed{T_2 = 100}$

$$\frac{600 - q_2}{\cancel{600}} = \frac{400}{\cancel{600}}$$

$600 - q_2 = 400$

$\boxed{q_2 = 200}$

$T_1 - T_2 = 200$

$T_1 - 100 = 200$

$\boxed{T_1 = 300}$

Entropy :→

* It is a State function.

* It is a Extensive property.

* It's unit is Joule/Kelvin.

* If a System undergoing change, then the Surrounding must be affacted by this . .Change. .

So, While calc. ΔS_{Total}, we always calculate $\Delta S_{sys.} + \Delta S_{surr.}$

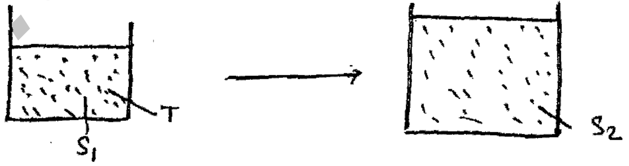
* mathematically ~~Suppose~~ we can derive Entropy change which is equal to –

$$\boxed{\Delta S = \frac{q}{T}}$$

q ⇒ Heat absorb

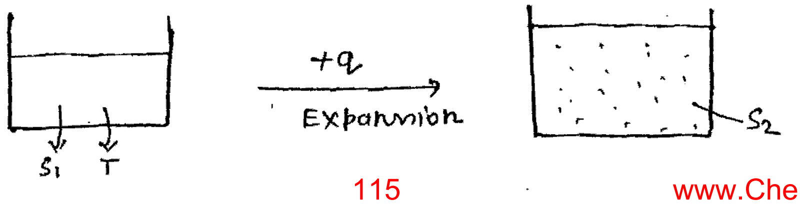
e.g. Suppose a system which having temp. T if they absorb heat (q) from the surrounding

then $\Delta S\,(\text{System}) = +\frac{q_{rev.}}{T}$



$$\boxed{S_2 - S_1 = \Delta S_{sys} = \frac{q_{rev.}}{T}}$$

Calculation of Total Entropy change for Rev. Process→

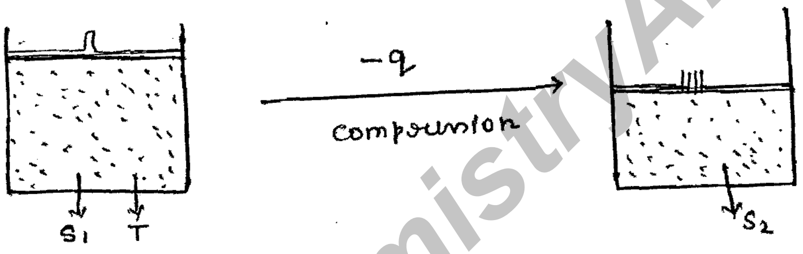


$$S_2 - S_1 = \Delta S_{sys.} = +\frac{q}{T}$$

$$\Delta S_{surr.} = -\frac{q}{T}$$

$$\boxed{\Delta S_{universe} = \Delta S_{total} = 0}$$

for compression →



$$S_2 - S_1 = \Delta S_{sys.} = -\frac{q}{T}$$

$$\Delta S_{surr.} = +\frac{q}{T}$$

$$\boxed{\Delta S_{Total} = \Delta S_{uni.} = 0}$$

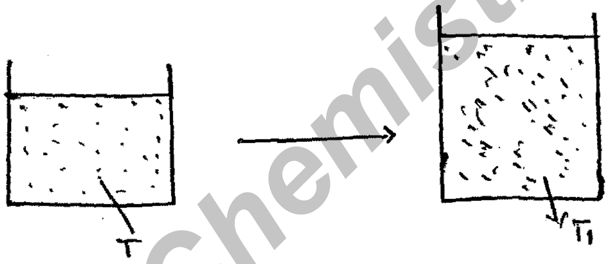
$$\Delta S_{surr.} = \frac{q}{T} = 0$$

$$\boxed{\Delta S_{Total} = \Delta S_{sys.} + \Delta S_{surr.}}$$

Since there is no Heat Exchange b/w system and surrounding so that $q = 0$. [$\Delta S_{surr.}$]

$$\boxed{\Delta S_{Total} = 0}$$

Adiabatic Irreversible Process :⇒



$$\boxed{\Delta S_{sys.} = +ive}$$

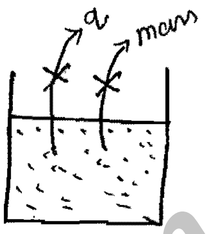
The Extent of this order is not compensated by ordered arrangement. disorder is take place due to expansion and order is take place due to lowering in temp.

$$\Delta S_{surr.} = 0/T = 0$$

$$\boxed{\Delta S_{Total} > 0}$$

Calculation of ΔS_{Total} for Isolated Process :→

Reversible ⇒



[No contact with Surrounding]
⇓
Isolated

$\Delta S_{syst.} = 0$

$\Delta S_{surro.} = 0$

$\boxed{\Delta S_{Total} = 0}$

Irreversible :⇒

$\Delta S_{sys.} = 0$

$\Delta S_{surr.} = +ive$ ⇒ (can't predict) so that +ive

$\Delta S_{Total} = +ive$ or >0

$\boxed{\Delta S_{Total} > 0}$

Calculation of Entropy Change of a System where temp. and volume undergo Simultaneous Change: ⇒

for an Ideal gas ⇒

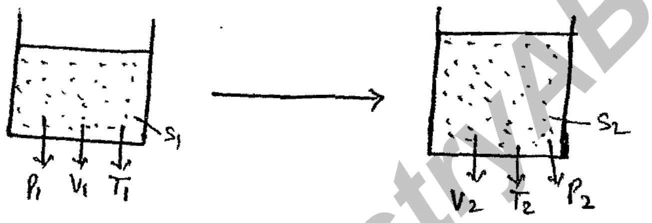
$dE = dq - Pdv$ [From Ist Law of thermodynamics]

$\because ds = \frac{dq}{T}$

$dq = Tds$

$\because PV = nRT$

$\therefore P = \frac{nRT}{V}$



$$nC_v dT = Tds - \frac{nRT}{V} dV$$

$$nC_v \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dv}{V} = \int_{S_1}^{S_2} dS$$

$$\boxed{nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = \Delta S}$$

Volume change with constant temp. [isothermal]

$dT = 0$

$$\boxed{\Delta S_{isothermal} = nR \ln \frac{V_2}{V_1}}$$

For iso-Choric process [dV = 0] , then,

Imp

$$\boxed{\Delta S_{isochoric} = n C_V \ln \frac{T_2}{T_1}}$$

Calculation of ΔS of a System when temp and pressure undergo simulteneous change

$$\because \quad nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = \Delta S$$

[from above relation]

we know that , from Ideal Gas →

$$\frac{PV}{T} \cancel{\propto} \text{ constant}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_1}\right)$$

$$nC_V \ln \frac{T_2}{T_1} + nR \ln \left(\frac{T_2}{T_1}\right) \times \left(\frac{P_1}{P_2}\right) = \Delta S$$

$$nC_V \ln \frac{T_2}{T_1} + nR \ln \left(\frac{T_2}{T_1}\right) + nR \ln \frac{P_1}{P_2} = \Delta S$$

$$(nC_V + nR) \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = \Delta S$$

$$\because \quad nC_P - nC_V = nR$$

$$nC_P = nR + nC_V$$

$$\boxed{nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = \Delta S}$$

at constt Pressure →

For Isoboric process → [$dp = 0$]

$$\boxed{\Delta S_{Isoboric} = n c_p \ln \frac{T_2}{T_1}}$$

at constt. temp. [Isothermal process]

$$\boxed{\Delta S_{isothermal} = n R \ln \frac{P_1}{P_2}}$$

Entropy change during Phase transformation

during Phase transformation temp., pressure, conc. etc. remain constt.,

e.g. • Solid changes into liquid

• liquid changes " gas

• Solid " " Gas

eg [Dry CO_2 → as a Refrigerant] etc.
$\downarrow$ (Gas)

[चूंकि Heat Syst. से निकल रही है अतः -ive sign]

$\left[\Delta S = \frac{\Delta H}{T_{m}}\right]$ Solid (fusion) $\rightleftharpoons$ liquid $\longrightarrow \left[\Delta S = -\frac{\Delta H}{T_m}\right]$

$\left[\Delta S = \frac{\Delta H}{T_{Vap}}\right]$ Liquid (Vapori.) $\rightleftharpoons$ Gas $\longrightarrow \left[\Delta S = -\frac{\Delta H}{T_b}\right]$

$\left[\Delta S = \frac{\Delta H}{T_{sub}}\right]$ Solid (sub.) $\rightleftharpoons$ Gas $\longrightarrow \left[\Delta S = -\frac{\Delta H}{T_{sub}}\right]$

e.g.

Que. Calculate the Total Entropy change when -10°c of water at Perticular amount is changes to -10°c of ice at Perticular amount.

Solⁿ⇒

$$-10^\circ c\ [\text{Super cooled water}] \longrightarrow [-10^\circ c]\ \text{ice}$$

$$\Delta S = ?$$

$$-10^\circ C\ \text{water} \xrightarrow[\Downarrow\ \Delta S_1]{} 0^\circ c(\text{water}) \underset{\Downarrow\ \Delta S_2}{\rightleftharpoons} 0^\circ c(\text{ice}) \xrightarrow[\Downarrow\ \Delta S_3]{} -10^\circ c(\text{ice})$$

$$\Delta S_1 = n\overset{\overset{(\text{Water})}{\Uparrow}}{c_p} \ln \frac{273}{263}$$

$$\Delta S_2 = -\frac{\Delta H}{273}$$

$$\Delta S_3 = n\underset{\underset{(\text{ice})}{\Downarrow}}{c_p} \ln \frac{263}{273}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

e.g.

Qu. 1 mol. of Solid I_2 [360 K] ⟶ liquid I_2

$$\underset{360}{\text{Solid}(I_2)} \xrightarrow[\Downarrow\ \Delta S_1]{} \underset{387\text{ K}}{\text{Solid}(I_2)} \underset{\Downarrow\ \Delta S_2}{\rightleftharpoons} \underset{387\text{ K}}{\text{liquid}(I_2)} \xrightarrow[\Downarrow\ \Delta S_3]{} \underset{410\text{ K}}{\text{liquid}(I_2)}$$

$T_m = 387$

(Solid I_2) $C_p = 54.44\ k^{-1}\ mol^{-1}$

(liqid I_2) $C_p = 80.67\ k^{-1}\ mol^{-1}$

$$\Delta S_1 = 1 \times \overset{\overset{55.44}{\Uparrow}}{C_p} \times \ln \frac{387}{360}$$

$$\Delta S_2 = 7.87 = 7870\ J\ mol^{-1}$$

$$\Delta S_{Total} = 54.44 \times \ln\frac{387}{360} + \frac{7870}{387} + 80.67 \ln\frac{410}{387}$$

$$= 54.44 \times 0.072 + 20.33 + 80.67 \times 0.057$$

$$= 28.84\ J\ K^{-1} mol^{-1}$$

$$= 28.9\ J\ K^{-1} mol^{-1} \quad [b]$$

Entropy change during a reaction

$$\begin{tikzcd} 3A \arrow[d] & + & 4B \arrow[d] \arrow[rr] & & 5C \arrow[d] \\ S_A & & S_B & & S_C \end{tikzcd}$$

$$\Delta S = 5S_C - (4S_B + 3S_A)$$

S_A = absolute Entropy at temp. aboven then 0K

$S_A = 0$ at 0°K ⇒ (this is convension)

e.g. Gold - Particle -
1 mol (Au)
$S_A = 0$ at 0K
Absolute Entropy at 0K any Element is zero [convension] -(No disorder)

$$A(\text{Solid}) \rightleftharpoons B(\text{Gas})$$

S_A S_B

$$\boxed{\Delta S = +ive}$$

$$A(g) \rightleftharpoons B(g)$$

we can't say

$$AB_2(s) + B(s) \rightleftharpoons C(g)$$

$(\Delta S = +ive)$

$$A(g) \rightleftharpoons B(g) + C(g)$$

$\Delta S = +ive$

* According to convension the Entropy of any Element at absolute 0 K is zero.

* The Entropy appears in the Element above then zero kelvin is called absolute Entropy of any Element at any perticular temp.

29, october, 2015

Residual ENTROPY

According to the third law " THE ENTROPY OF PERFECTLY CYSTTILINE SUBSTANCE AT ABSOLUTE OK is zero"

But this law has a Exception also.

e.g. ⇒ Co crystalline Structure at absolute 0 K is not zero. bcoz co molecule have two different orientation.

CO	CO	CO	CO
O≡C	C≡O	CO	CO
CO	CO	OC	CO
CO	CO	OC	CO

mathematical formula of Residual Entropy

$$\boxed{S = R\ln W}$$

R ⇒ Gas constt

W ⇒ orientation

e.g. ⇒ CO molecule, NO, N_2O, H_2O etc. they all have two orientation at absolute 0 K.

ENTROPY CHANGES WITH SIMULTENIOUS CHANGE OF TEMP. AND VOLUME IN CASE OF IDEAL GAS! ⇒

$$\boxed{dS = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2-nb}{V_1-nb}}$$

$$\because \; E = f(T,V)$$

$$dE = \left(\frac{dE}{dT}\right)_V dT + \left(\frac{dE}{dV}\right)_T dV$$

$$dE = \underset{\substack{\Downarrow \\ C_V}}{\left(\frac{dE}{dT}\right)_V} dT + \left(\frac{dE}{\partial V}\right)_T dV$$

$$dE = C_V\, dT + \left(\frac{dE}{dV}\right)_T dV$$

$$\frac{dq}{T} - \frac{P\,dV}{T} = C_V\frac{dT}{T} + \left(\frac{dE}{dV}\right)_T \frac{dV}{T} \quad \because \; \frac{dq}{T} = dS$$

$dS -$

$$\because \; P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

$$\because \; \left(\frac{dE}{dV}\right)_T = \frac{a}{V^2}$$

(Gate 2010)

Qu. The Molar Entropy of a Crystalline CO at absolute 0 K.

(i) R ln 2   (ii) −R ln 2   (iii) 2 ln R²   (iii) −2

Qu. Standard Entropy of Cryst. CO at 0 K

(i) R ln 2

R x

(i) 0.03 J/mole kelvin
(ii) 2.5 J/mole kelvin
(iii) zero
(iv) 5.76 J/mole kelvin

(Gate-2003)

Qu.12

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$= 2 \times (192.3) - 3 \times (130.6) - 191.5$

$= 2 \times 192.3 - 3 \times 130.6 - 191.5$

$= -198.7$ J/K mol

(−ive sign indicates that there is a decrease in the Gaseous species during the reaction.

[Syst. की Entropy घट जा रही है But Surro. की Entropy जुड़ते ही +ive हो जाएगी]

Qu.14

$$2Cl(g) \longrightarrow Cl_2(g)$$

[spontaneous process]

ΔG = −ive
ΔH = −ive
ΔS = −ive

Qu.17

One mole of Ideal Gas $\xrightarrow{\text{compressed}}$ $\frac{V_1}{4}$

V_1 $\qquad$ T_1 $\qquad$ $2T_1$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR.\ln \frac{V_2}{V_1}$$

$$\Delta S = 1\times C_v \ln \frac{2T_1}{T_1} + 1\times R.\ln \frac{\left(\frac{V_1}{4}\right)}{V_1}$$

$$\Delta S = C_v \ln \frac{2\cancel{T_1}}{\cancel{T_1}} + R \ln \frac{1}{4}$$

$$\Delta S = C_v.\ln 2 + R \ln \frac{1}{4}$$

$$\Delta S = C_v.\ln 2 + R \ln (2)^{-2}$$

$$\Delta S = C_v.\ln 2 - 2R \ln 2$$

$$\boxed{\Delta S = \ln 2\,(C_v - 2R)}$$

Qu.41 2 mole of Argon Gas

$T_1 = 300\,K$

$T_2 = 500\,K$

$$\Delta S = n\,C_v \ln \frac{T_2}{T_1}$$

$$\Delta S = 2\times C_v\times \ln \frac{5\cancel{0}\cancel{0}}{3\cancel{0}\cancel{0}}$$

$$\Delta S = \cancel{2}\times \frac{3}{\cancel{2}}\times R\times \ln \frac{5}{3}$$

$$\Delta S = 3\times 8.314\times \ln \frac{5}{3}$$

(2 mole) $\Delta S = 24.942 \ln \frac{5}{3}$

(1 mole) $\Delta S = \dfrac{24.942 \ln \frac{5}{3}}{2} = 6.37\ JK^{-1}\,mol^{-1}$

$N_2 + 3H_2 \longrightarrow 2NH_3$

$T = 298K$

$\Delta S^\circ_{sys.} = -197\ J\ K^{-1}$

$\Delta H^\circ_{sys.} = -91.8\ KJ = -91.8 \times 10^3 J$

cons. Temp. & pressure

[जितनी Heat System से गयी अतः Surro. में जायेगी तो +ive होगी]

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

$$= -197\ JK^{-1} + \frac{(+91.8 \times 10^3)}{298}$$

$$= -197\ JK^{-1} + \frac{91.8 \times 10^3}{298}$$

$$= -197\ J\ K^{+1} + 308{,}05$$

$$= 111{,}05\ J\ K^{-1}$$

Qu1 → $T_1 = 300K$

$T_2 = 400K$

$C_p = (5 + 0.1T)$

$\Delta S = ?$

$$\Delta S = n\, C_p \frac{dT}{T}$$

$$\Delta S = 1 \times \int_{300}^{400} (5 + 0.1T) \frac{dT}{T}$$

~~$\Delta S = 5(T) + 0.1\left(\frac{T^2}{2}\right)_{300}^{400}$~~

~~$\Delta S = 5(400-300) + \frac{0.1}{20} \times \left[(400)^2 - (300)^2\right]$~~

~~$\Delta S = 500 + \frac{1}{20}\left[160000 - 90000\right]$~~

$$\Delta S = \int_{300}^{400} \frac{5}{T}\,dT + \int_{300}^{400} 0.1\,dT$$

$$= 5\left[\ln T\right]_{300}^{400} + \left[0.1\,T\right]_{300}^{400}$$

$$= 5\left[\ln 400 - \ln 300\right] + 0.1\left[400-300\right]$$

$$= 5\left[\ln(20)^{2} - \ln 300\right] + 0.1\times 100$$

$$= 5\left[5.99 - 5.70\right] + 10$$

$$= 5\left[0.28\right] + 10$$

$$= 1.45 + 10$$

$$= 11.45\ J\,K^{-1}\,mol^{-1}$$

[Que. 11] ⇒ $T = 100°C + 273 = 373\ K$

$\Delta H_{vap.} \approx 41\ kJ\ mol^{-1} = 41\times10^{3}\ J\ mol^{-1} \Rightarrow 41000\ J\ mol^{-1}$

$P = 1\ atm$

$$L \rightleftharpoons V$$

$$(1\ mole)\ H_2O \longrightarrow H_2O\ (vapour)$$

$$\Delta S = \frac{\Delta H}{T} = \frac{41000}{373}$$

$$= 110\ J\,K^{-1}\,mol^{-1}$$

Qu. 17

$n = 10$ mole

$C_p = 300\ JK^{-1}$

$C_v = ?$

$$nC_p - nC_v = nR$$

$$10 \times 300 - 10 \times C_v = 8.314 \times 10$$

$$300 - C_v = 8.314 \times 10$$

$$300 - 8.314 \times 10 = C_v$$

$$300 - 83.14 = C_v$$

$$C_v = 300 - 83.14$$

$$C_v = 216.86\ JK^{-1}$$

$$C_v \cong 217\ JK^{-1} \quad [b]$$

Ass. 2nd

Qu. 25 Gate-2011

$$1\ Ar\ (300K, 1\ bar) \longrightarrow 1\ Ar\ (200K, 10\ bar)$$

$$\Delta S = n C_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$= 1 \times \frac{5}{2} \times R \times \ln \frac{200}{300} + 1 \times 8.314 \times \ln \frac{1}{10}$$

$$= \frac{5}{2} \times 8.314 \times \ln \frac{2}{3} - 8.314 \times [2.302]$$

$$= \frac{41.57}{2} \times \ln\left(\frac{2}{3}\right) - 19.143692$$

$$= \frac{41.57}{2} \times \ln\left(\frac{2}{3}\right) - 19.143692$$

$$= -\frac{41.57}{2} \times 0.405 - 19.143692$$

Q4. Calculate ΔS, if →

costt. temp.

$$\underset{[10\,dcm^3}{V_1} \longrightarrow \underset{20\,dcm^3]}{V_2}$$

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$$\Delta S = 1 \times 8.314 \times \ln \frac{2\cancel{0}}{1\cancel{0}}$$

$$\Delta S = 8.314 \times \ln 2$$

~~ΔS = 8.314 × 2.303~~

~~ΔS = 19.147~~

$$\Delta S = 8.314 \times 0.6931$$

$$\Delta S = 5.7616\ JK^{-1}mol^{-1}$$

Q4. Calculate the ΔS, when a System ~~Expend Isotherm~~ containing an Ideal Gas expend isothermally from a pressure of 10atm to pressure of one 1atm.

$$\Delta S = nR \ln \frac{P_1}{P_2}$$

$$\Delta S = 1 \times 8.314 \times \ln \frac{10}{1}$$

$$\Delta S = 8.314 \times 2.303$$

$$\Delta S = 19.147\ JK^{-1}\ mol^{-1}$$

GIBB'S FREE ENERGY

↓ Const (T, P)

- It is a Extentive property.
- It is a State function.
- It is a form of Energy which can be used in any useful work
- ↓ in free Energy is use as a non-mechanical work
- It's unit is Joule
- mathematical it can be written as

$$G = H - TS$$

where H is a total energy of a system

where TS is unavailable Energy.

[or U can say that disorder can't never be use as a work, bcoz u used this energy the substance change their Phase]

- Derivation of Maxwell Equation in term of G.

$$G = H - TS$$

$$G = U + PV - TS \qquad [\because H = E + PV]$$

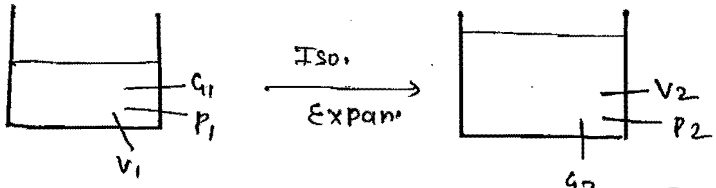
Diff. both side

$$dG = dE + Pdv - T\,ds - S\,dT + V\,dP$$

$$\because dE = dq - Pdv$$

$$dE = Tds - Pdv$$

→ Calculation of Change in free Energy for an Isothermal process in the Case of Ideal Gas →



we know that -

from. maxwell Eqn

$$\left(\frac{dG}{dP}\right)_T = V$$

$$dG = V\,dP \qquad [\because PV = RT]$$

$$V = \frac{RT}{P}$$

$$\Delta G = RT \int_{P_1}^{P_2} \frac{dP}{d}$$

$$\boxed{\Delta G = RT \ln \frac{P_2}{P_1}}$$

(Gate-2009)
Ans. ①
Qu.32

ΔG

$n = 1$

$P_1 = 1$ atm

$P_2 = 2$ atm

$$\Delta G = RT \ln \frac{2}{1}$$

$$\Delta G = RT \ln 2$$

⇒ calculation of ΔG for a reaction.

Impt

$$\boxed{\Delta G = \Sigma G_{PRODUCT} - \Sigma G_{REACTANT}}$$

e.g. $3A + 4B \longrightarrow 5C$

A $G_1 \Rightarrow$ J/ mole

B $G_2 \Rightarrow$ J/ mole

C $G_3 \Rightarrow$ J/ mole

$$\boxed{\Delta G = 5G_3 - 4G_2 - 3G_1}$$

⇒ For Spontaneous process ΔG always be -ive -

⇓

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

∵ ΔS always be positive

& ΔH ~~always~~ may be positive or negative

∴ $\Delta G \rightarrow$ {always Negative}

[ΔG को -iv लाने के लिये
ΔH की value TdS से
छोटी होनी चाहिए
H

✱ Prove that for Sponteneous process ΔG is less then zero (Irrev. proc.)

we know that the Heat change in a reversible process is more than the Heat change in a Irreversible process.

$$dq_{rev.} > dq_{irr.}$$

$$T\,ds > dq_{irr} \qquad \because \left(\Delta S = \frac{q_{rev}}{T}\right)$$

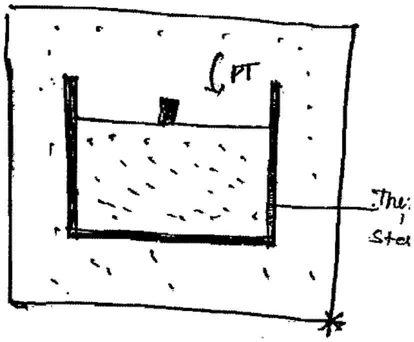
$$0 > dq_{irr.} - Tds \quad — ①$$

$$(dq_{irr.})_P = dH \quad — ②$$

put the value of (2) in ①

$$0 > dH - Tds$$

$$0 > (dG)_{T,P}$$



Gibbs Helmholtz- Equation

we know that

$$G = H - TS$$

For initial →

$$G_1 = H_1 - TS_1 \quad — ①$$

for final, $G_2 = H_2 - TS_2$ —(ii)

at constant temp. &

$$\Delta G = \Delta H - T\Delta S \quad — ③$$

$$dG = V\,dp - S\,dT$$

$$\left(\frac{dG}{dT}\right)_P = -S$$

for initial

$$\left(\frac{dG_1}{dT}\right)_P = -S_1 \quad — ④$$

for final

$$\left(\frac{dG_2}{dT}\right)_P = -S_2 \quad — ⑤$$

Substrate → ⑤ − ④

$$\left(\frac{d(\Delta G)}{dT}\right)_P = -\Delta S \quad — ⑥$$

Put the value of (3) in (6)

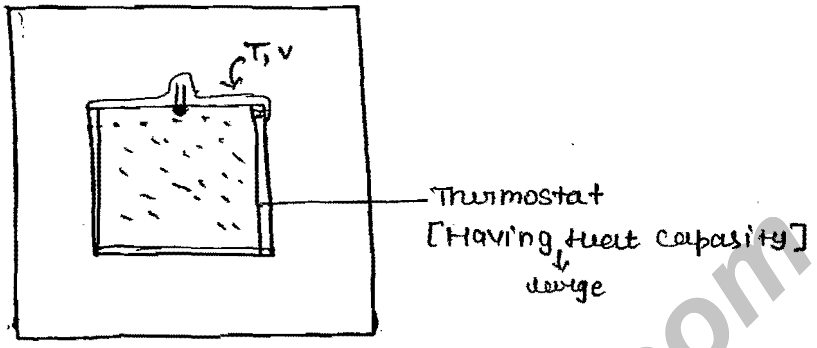
$$\left(\frac{d(\Delta G)}{dT}\right)_P = \frac{\Delta G - \Delta H}{T}$$

$$\boxed{T \cdot \left(\frac{d(\Delta G)}{dT}\right)_P + \Delta H = \Delta G}$$

⇓

⇐ Gibb's Halmhotz Equation ⇒

Halmholtz Function



for -(T,V)

Work- function
or
Helmholtz Function or 'A'

$$A = \underbrace{E}_{\text{Energy}} - \underbrace{TS}_{\text{disorder}}$$

⇒ It is a Energy function

⇒ It is also Extensive property

⇒ It Unit Expresses in Joule

⇒ It is also called work function and represented by 'A'

⇒ when a system undergoing change at a constt. volume then their Energy expression term in internal Energy & when you substract disorder from total Energy, we get Helmholtz free Energy or work function.

⇒ for Spontenious $\boxed{(dA)_{T,V} < 0}$

➾ Comparison b/w Helmholtz free Energy and Gibb's free Energy

✱ For an Isothermal process, for an Ideal Gas $(\Delta G = \Delta A)$

$$G = H - TS$$

$$G = E + PV - TS$$

$$dG = dE + Pdv + Vdp - Tds - S\cancel{dT} \quad [\because dT = 0]$$

$$dG = dA + \cancel{Tds} + \cancel{SdT} + Pdv - VdT - \cancel{Tds} - \cancel{SdT} \quad \because A = E - TS$$

$$\therefore dA = dE - Tds - SdT$$

$$dG = dA + \partial(PV)$$

$$[\because PV = RT]$$

$$\partial G = dA + \partial(RT)$$

$$\partial G = dA + R\,\partial T \quad [\because \partial T = 0]$$

$$\boxed{dG = dA}$$

To proof ⇒

$$\boxed{\Delta A = \Delta E + T\left(\frac{\partial(\Delta A)}{dT}\right)_V}$$ ✱

Partial Molar Property :⇒

Suppose z- is a function of →

$$z = f(T, P, n_1, n_2, n_3 \ldots\ldots n_i)$$

= where system having different mole of gases $(n_1, n_2, n_3, \ldots\ldots n_i)$

⇒ The Total diff. of this ⇒

$$dz = \left(\frac{dz}{dT}\right)_{P, n_1, n_2, n_3, \ldots n_i} dT + \left(\frac{\partial z}{\partial P}\right)_{T, n_1, n_2, n_2, n_3 \ldots n_i} \partial P$$

$$+ \left(\frac{dz}{\partial n_1}\right)_{P, T, n_2 \ldots n_i} \partial n_1 + \left(\frac{dz}{\partial n_2}\right)_{T, P, n_1, n_3 \ldots n_i} \partial n_2$$

at const. T, & P

$$dz = \left(\frac{dz}{\partial n_1}\right)_{T, P, n_2, n_3 \ldots n_i} \partial n_1 + \left(\frac{\partial z}{\partial n_2}\right)_{T, P, n_1, n_3, \ldots n_i} \partial n_2 + \left(\frac{\partial z}{\partial n_3}\right)_{T, P, n_1, n_2, n_4 \ldots n_i} \partial n_3$$

$$\boxed{dz = \left(\frac{\partial z}{\partial n_i}\right)_{T, P, n_1, n_2, \ldots (n_i - 1)}}$$

⇓

Partial molar property

this is called P.M.P. bcoz Δz [G, E, A] ↑ (with change in ith) component of the System where all other component are constant.

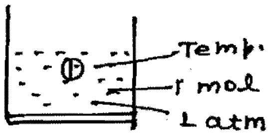
Note:⇒ [1] The properties which is occur in the pure state of the System is different for the impure system

(Pure state)
e.g. When we adding one mole of water 100 cm³ of pure water When we get $\Delta V = 18\ cm^3$. bcoz (one mole of water = 18 cm³)

but in the impure state when we adding a 1 mole of H_2O in

2[c] the change in property in impure state is arises due to bcoz of different interaction take place.

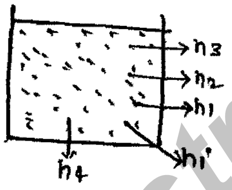
CHEMICAL POTENTIAL



$\mu_i^\circ = \frac{G}{n}$

$\mu_i^\circ \Rightarrow$ (temp. dependent)

$Z = G$



$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2, \dots (n_i - 1)}$$

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, \dots n_i}$$

$$\mu_2 = \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1, n_3 - \dots n_i}$$

$$\mu_3 = \left(\frac{\partial G}{\partial n_3}\right)_{T, P, n_1, n_2, \dots n_i}$$

$\vdots$

⇒ change in free Energy with change in particular component in a system which containing diff. no. of moles where all other moles are constant

➡ Gibb's free Energy changes with the change in particular component as constant T & P where all other component are constant that is represented by chemical potential.

➡ for a pure state free Energy per mole is called chemical potential. Standard chemical potential can be defined for a pure state of a compound, amount 1 mole, 1 atm. pressure at any temp. then it is called standard chemical potential.

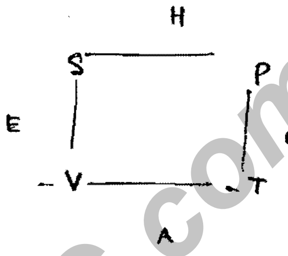
$[\mu^\circ] = G/n$

⇒ Standard chemical potential only depends upon temp. where chemical potential of a particular component is a impure state depends upon T & P both.

$$\boxed{\mu = \mu^\circ + RT \ln P_i} \Rightarrow \text{interm of partial pressure}$$

$$\boxed{\mu = \mu^\circ + RT \ln X_i} \Rightarrow \text{in terms of mole fraction}$$

Chemical potential can also be represented in diff thermodynamically.



$$\left(\frac{dA}{\partial n_i}\right)_{V,T} = \mu_i$$

$$\left(\frac{dH}{\partial n_i}\right)_{S,P} = \mu_i$$

$$\left(\frac{dG}{\partial n_i}\right)_{P,T} = \mu_i$$

$$\left(\frac{\partial E}{\partial n_i}\right)_{S,V} = \mu_i$$

⇒ Variation of chemical potential with temprature

{∵ G decreases with temp.  }

तो μ also be ↓ with temp.

⇒ [जहाँ phase transfer वहाँ μ_i same रहेगा]

we know that ⇒

$$\left(\frac{dG}{\partial n_i}\right)_{T,P} = \mu_i$$

$$\frac{d}{\partial T}\left(\frac{\partial G}{\partial n_i}\right) = \frac{\partial \mu_i}{\partial T}$$

$$\frac{\partial^2 G}{\partial T\, \partial n_i} = \frac{\partial \mu_i}{\partial T} \quad -①$$

$\because \quad dG = VdP - SdT$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

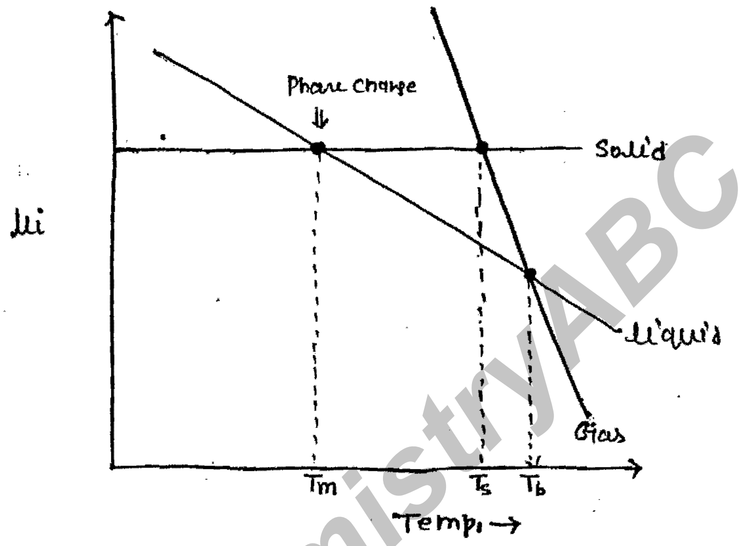
$$\frac{\partial^2 G}{\partial n_i \cdot \partial T} = -\left(\frac{\partial S}{\partial n_i}\right)$$

$$\frac{\partial^2 G}{\partial n_i \cdot \partial T} = -\bar{S_i} \quad \text{—(II)}$$

by (I) and (II)

$$\boxed{\left(\frac{\partial \mu_i}{\partial T}\right)_P = -\bar{S_i}}$$

Gate-2010



Ts = Sublimation temp.

Tb = Boiling temp.

Tm = melting temp.

Graph:⇒ variation of chemical potential with change in temp.

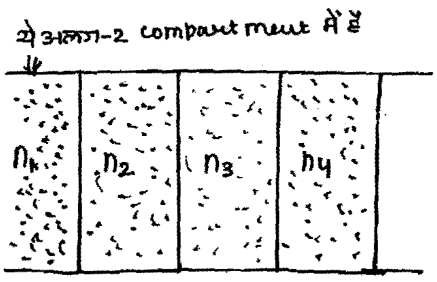
⇒ during phase transform^n chemical potential remain^{in} same for both the phases.
[where T, V, & all other component are constant],

⇒ Since we know that G is state function so it must follow Euler's theorem.

$$\boxed{\left(\frac{\partial (\mu_i)}{\partial T}\right)_P = -\bar{S_i}}$$

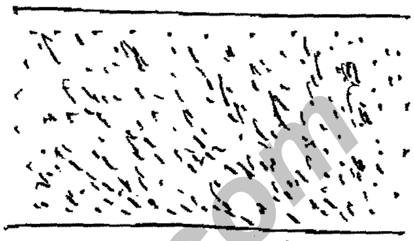
V.Imp

Calculation of thermodynamic parameter [$\Delta H^{mixing}, \Delta V^{mixing}, \Delta S^{mixing}, \Delta A^{mixing}$] in the case of Ideal Gases



(Before mixing)

(After removing compartment) →
[सारे compartment को open कर दिया जाएगा]



(After mixing)

n_1 [Pure State] *

$$\mu_1^\circ = \frac{G_1}{n_1}$$

n_2, $\mu_2^\circ = \frac{G_2}{n_2}$

n_3, $\mu_3^\circ = \frac{G_3}{n_3}$

n_4, $\mu_4^\circ = \frac{G_4}{n_4}$

$G_{Total} = n_1\mu_1^\circ + n_2\mu_2^\circ + n_3\mu_3^\circ + n_4\mu_4^\circ$
[Before mixing]

$\mu_1 = \mu_1^\circ + RT\ln x_1$
$\mu_2 = \mu_2^\circ + RT\ln x_2$
$\mu_3 = \mu_3^\circ + RT\ln x_3$
$\mu_4 = \mu_4^\circ + RT\ln x_4$

$G_{Total} = n_1\mu_1 + n_2\mu_2 + n_3\mu_3 + n_4\mu_4$
[After mixing]

$$\Delta G_{mixing} = \underset{\text{(After mixing)}}{G_{Total}} - \underset{\text{(Before mixing)}}{G_{Total}}$$

$$= (n_1\mu_1 + n_2\mu_2 + n_3\mu_3 + \cdots) - (n_1\mu_1^\circ + n_2\mu_2^\circ + n_3\mu_3^\circ + \cdots$$

$$= n_1(\mu_1^\circ + RT\ln x_1) + n_2(\mu_2^\circ + RT\ln x_2) + n_3(\mu_3^\circ + RT\ln$$
$$+ \cdots\cdots - (n_1\mu_1^\circ + n_2\mu_2^\circ + \cdots)$$

$$= n_1RT\ln x_1 + n_2RT\ln x_2 + \cdots\cdots$$

$$\Delta G_{mix.} = RT \sum n_i \ln x_i$$

$$\frac{\Delta G_{mix.}}{T} = R \sum n_i \ln x_i$$

$$\frac{\partial}{\partial T}\left[\frac{\Delta G_{mix.}}{T}\right]_P = \frac{R\partial}{\partial T}\sum\left(n_i \ln x_i\right)_P$$

$$-\frac{\Delta G_{mix.}}{T^2} + \frac{1}{T}\left(\frac{\partial(\Delta G_{mix.})}{\partial T}\right)_P = 0 \quad -①$$

$$\because \Delta G_{mix.} = \Delta H_{mix.} + T\left(\frac{\partial(\Delta G_{mix.})}{\partial T}\right)_P$$

Divide both side by T^2 then,

$$\frac{\Delta G_{mix.}}{T^2} = \frac{\Delta H_{mix.}}{T^2} + \frac{1}{T}\left(\frac{\partial(\Delta G_{mix.})}{\partial T}\right)_P$$

$$-\frac{\Delta H_{mix.}}{T^2} = -\frac{\Delta G_{mix.}}{T^2} + \frac{1}{T}\left(\frac{\partial(\Delta G_{mix.})}{\partial T}\right)_P \quad -②$$

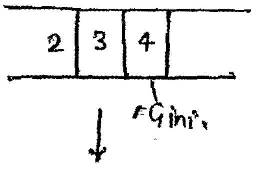
By Eqn- ① + (ii)

$$-\frac{\Delta H_{mix.}}{T^2} = 0$$

$$\boxed{\Delta H_{mixi.} = 0}$$

04, Nov. 2015

e.g. 2 mol O_2, 3 mol N_2, 4 mol H_2



$n_{Total} = 9$

G_f.

$\Delta G = G_f - G_i$

$$\underset{(\text{Per mole})}{\Delta G_{mix.}} = \frac{RT\left(2\ln\frac{2}{9} + 3\ln\frac{3}{9} + 4\ln\frac{4}{9}\right)}{9}$$

$$= RT\left[\left(\frac{2}{9}\right)\ln\left(\frac{2}{9}\right) + \frac{3}{9}\ln\left(\frac{3}{9}\right) + \frac{4}{9}\ln\left(\frac{4}{9}\right)\right]$$

(Rxn से Kinetic Energy बढ़ेगी) → ↑ temp. ↑ K.E., P.E. ⇒

$$\Delta G_{mix.} = \frac{RT\sum n_i \ln x_i}{n_{Total}}$$

$$\boxed{\underset{(\text{Per mole})}{\Delta G_{mix.}} = RT\sum x_i \ln x_i}$$

Qu.8

2 mole of N_2

3 mole of H_2

2 mole of NH_3

$$\Delta S_{mixing} = 8.314 \times \left[\frac{2}{\ } \ln\left(\frac{2}{7}\right) + \left(\frac{3}{\ }\right) \ln\left(\frac{3}{7}\right) + \left(\frac{2}{\ }\right) \ln\left(\frac{2}{7}\right)\right]$$

$$= 8.314 \times 2.303 \left[2 \log\frac{2}{7} + 3 \log\frac{3}{7} + 2 \log\left(\frac{2}{7}\right)\right]$$

$$= 8.314 \times 2.303 \times \left[4 \log\frac{2}{7} + 3 \log\frac{3}{7}\right]$$

$$= -8.314 \times 2.303 \times [-2.1764 + (-0.36 \times 3)]$$

$$= -8.314 \times 2.303 [-2.1762 - 1.1039]$$

$$= -8.314 \times 2.303 \times (-3.280)$$

$$= 62.80 \text{ J K}^{-1}$$

Qu.9

⇒ loose Energy very much

$$\text{monatomic} \xrightarrow[\text{Expan.}]{\text{adia.}} \text{ज्यादा ठंडा}$$

$$\text{diatomic} \xrightarrow[\text{Expan.}]{\text{adia}} \text{कम ठंडा}$$

⇓

$\boxed{\text{No. of atom} \propto \text{Rotation}, \propto \text{Vibration}}$

No. of atom ∝ Heat capacity

✓ $T_m < T_D < T_T$

monoatomic ⇒ Temp. independent.

$$\Delta G_{mixing} = \overset{0}{\cancel{\Delta H_{mixing}}} - T.\,\Delta S_{mixing}$$

$$\Delta G_{mixing} = -T.\,\Delta S_{mixing}$$

$$\Delta S_{mixing} = -\frac{\Delta G_{mixi}}{T}$$

$$\Delta S_{mixing} = -R\sum n_i \ln x_i$$

$$\boxed{\Delta S_{mixing,\,per\,mole} = -R\sum x_i \ln x_i}$$

$$\boxed{\Delta G_{mixing} = \Delta A_{mixing}}$$

[bcoz isothermal] ⇒ Ideal working substance

⇒ When a Ideal Gases mixing with Each other since their is no Interaction b/w the molecule so their is no absorption or rejection of Heat take place so that $\boxed{\Delta H = 0}$

$$\boxed{\Delta H_{mixing} = 0}$$

(ऊर्जा का आना जाना नहीं
No Interaction
No waste Energy)

Qu' One mole of CO_2, one mole of NO_2 & two mole of O_2 when mixed at 300 K calculate the Entropy of mixi, ΔH mixing ΔVmixi., ΔAmixi. Δ

1 mole of CO_2
1 mole of NO_2
2 mole of O_2

$$\Delta G = RT\left[1\cdot\ln\frac{1}{4} + 1\ln\frac{1}{4} + 2\ln\frac{2}{4}\right]$$

$$\Delta G = RT\left[2\ln\frac{1}{4} + 2\ln\frac{1}{2}\right]$$

$$\Delta G = RT \times 2.303\left[2\log\frac{1}{4} + 2\log\frac{1}{2}\right]$$

$$\Delta G = 8.314 \times 300 \times 2.303 \times [-2\times(0.60) - 2\times(0.30)]$$

$$= 8.314 \times 300 \times 2.303 \times [-1.2 - 0.6]$$

$$= 8.314 \times 300 \times 2.303 \times [-1.8]$$

$$= -10{,}374$$

$$\boxed{\Delta H_{mix.} = 0}$$

$$\Delta G = \Delta A = -10{,}374$$

$$= -10.374\ KJ$$

$$\Delta S = -\frac{\Delta G}{T} = +34.58\ J$$

$$\boxed{\Delta V_{mixing} = 0}$$

or

$$\Delta S = 6R\ln 2$$

Qu.7

$$\boxed{\ln \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2-T_1}{T_1 \cdot T_2}\right]}$$ — Arrhenius Eqⁿ [in term of rate constant]

$$\boxed{\ln \frac{Kp_1}{Kp_2} = \frac{\Delta H^\circ}{R}\left[\frac{T_2-T_1}{T_1 \cdot T_2}\right]}$$ in term of Kp [Equi. constt]

Vant-Hoff Relation

$$\boxed{\ln \frac{Kc_1}{Kc_2} = \frac{\Delta E^\circ}{R}\left[\frac{T_2-T_1}{T_1 \cdot T_2}\right]}$$ [in terms of Kc]

⇒ For chemical Equilibrium first conditions system must be close. [It is Dynamic in Nature]

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

K ⇒

Kx ⇒

Kp ⇒

Kc ⇒

(Kp & Kc ⇒ (may or may not unitless) mean depends upon stoichiometry)

$$a = \frac{5M}{1M} = 5$$

5M ↑ 4M ↑

$$3A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 4B$$

unitless (mole fraction) (always)

$$K_x = \frac{[X_B]^4}{[X_A]^3}$$

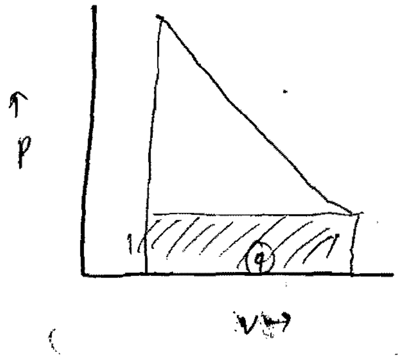
$$\frac{K_1}{K_2} = K_c = \frac{[C_B]^4}{[C_A]^3}$$

K = thermodynamic equi. (in term of activity) = (unitless) always

$$K_p = \frac{[P_B]^4}{[P_A]^3}$$ (gas in mixture)

Irrev.

Q4.21



Rev. $= \frac{1}{\cancel{2}} \times \overset{2}{\cancel{4}} \times 4 + 4 \times 1$

$8 + 4 = 12$ [X]

Irrev $= 1 \times 4 = 4$ L.atm

[05.01.2015]

$$\boxed{\frac{\partial}{\partial T}(\ln k_p) = \frac{\Delta H^\circ}{RT^2}}$$

$$\boxed{\frac{\partial}{\partial T}(\ln k_c) = \frac{\Delta E^\circ}{RT^2}}$$

–: CLASIEUS – CLAYPERON RELATION

$\because \Delta G = 0$ [at Equilibrium]

[Phase-transformation]

chemical potential $= 0$ & $\Delta G = 0$] (bcoz at Equi.)

Clasiecus Clayperon Equation is applying for any phase transformation a phase transformation which is a imidiate process, during this the temp., pressure, Equilibrium conc., free Energy of two different phases Etc. are Equal.

For e.g. ⇒ There is a lot of phase transfer

(i) $A_{(Solid)} \rightleftharpoons A_{(Liquid)}$

(ii) $A_{(Liquid)} \rightleftharpoons A_{(Gas)}$

(iii) $A_{(Solid)} \rightleftharpoons A_{(Gas)}$

(iv) $S_R \rightleftharpoons S_M$

Rhombic Monoclinic

for Solid ⇌ liquid Equi.

$$A_{[Solid]} \rightleftharpoons A_{[Liquid]}$$

~~for~~ Solid changes into liquid at their melting point during this they absorb heat at a constt. pressure from the surrounding. during this phase transformation the sign of Heat absorb is +ive.

[अगर liquid से solid जाता तो −ive]

$$A_{(s)} \rightleftharpoons A_{[l]}$$

$$\because \quad G_{(s)} \rightleftharpoons G_{(l)} \quad [\text{at constt. } T \,\&\, \text{pressure}] \quad -①$$

At a slight Increases of temp. (T+dT, P+dP)

$$G_{(s)} + dG_{(s)} \rightleftharpoons G_{(l)} + dG_{(l)} \quad -⑪$$

from ① & ⑪

$$dG_{(s)} \rightleftharpoons dG_{(l)}$$

applying maxwell Equation →

~~dG(s)~~)

$$V_{(s)}dP - S_{(s)}dT = V_{(l)}dP - S_{(l)}dT$$

$$\frac{dP}{dT} = \frac{\Delta S}{V_{(l)} - V_{(s)}} \quad -(III)$$

$$\because \quad \Delta S = \frac{\Delta H}{T} \quad -(IV)$$

Here Integrated form not possible bcoz we neglect V(s) &

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T}}$$ Differential form of

$A_{(l)} \rightleftharpoons A_{(g)}$

∵ $G_{(l)} \rightleftharpoons G_{(g)}$ [at const. T, P] —①

when you slight increases the $(T+\partial T,\ P+\partial P)$ then,

$G_{(l)} + \partial G_{(l)} \rightleftharpoons G_{(g)} + \partial G_{(g)}$ —②

from Ist & IInd-

$$\partial G_{(l)} \rightleftharpoons \partial G_{(g)}$$

∵ $\partial G = Vdp - SdT$ [maxwell Equation]

$$V_{(l)}dp - S_{(l)}dT = V_{(g)}dp - S_{(g)}dT$$

$$\frac{dP}{dT} = \frac{\Delta S}{V_{(g)} - V_{(l)}}$$

∴ $\Delta S = \frac{\Delta H}{T}$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T}(V_{(g)} - V_{(g)})}$$

⇓

Diff. form of Claus-clayperon Eq^n

∵ $V_g \gg\gg\gg \gg V_{(l)}$

$$\frac{dP}{dT} = \frac{\Delta H}{T \times V_{(g)}}$$

$$\frac{\partial P}{\partial T} = \frac{\Delta H \times P}{T \times RT} \quad [\because PV = RT],\ V = \frac{RT}{P}$$

$$\frac{\partial P}{\partial T} = \frac{\Delta H \cdot P}{RT^2}$$

Integrated on both side

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\boxed{\ln \frac{P_2}{P_1} = \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right]}$$

~~Que.~~

⇐: FUGACITY :⇒

(Latin) many words ⇒ (figure)

⇓ (Corrected pressure for a real Gas) = (f) (fugacity)

⇓ [Scaping tendency]

Ank

- ✱ It is a Corrected Pressure which is used for real Gas
- ✱ Fugacity of a real gas contain all the Interection which is take place in real gas.
- ✱ It can also be understand as a scaping tendency of a real gas.
- ✱ This News terms is given by "G.N. Lewis"
- ✱ at low pressure when pressure tending toward zero then the real gas behave as a Ideal gas.

We know that f is a fugacity & P is pressure.

$$\therefore f/P = \gamma \quad [\text{fugacity cofficient}]$$

$$\lim_{P \to 0} f/P = 1 \qquad [\because \gamma = 1$$

$$\boxed{f = P}$$

The gas behaving as a Ideal gas.

Mathematical Calculation of fugacity ⇒

We know that,

free Energy for an ideal gas at a Perticular temp. can be written as -

$$G = G^\circ + RT \ln P \quad -①$$

this Expression can be used for real Gas also By introducity a new term 'f'

$$G = G^\circ + RT \ln f \quad -(II)$$

free Energy for an real Gas at Perticular temp. can be written above →

Eq^n (ii) differentiate both side w.r.to P at constant temp.

$$\left(\frac{dG}{dP}\right)_T = 0 + RT\left[\frac{d(\ln f)}{dP}\right]_P \quad -$$

$$\left(\frac{dG}{dP}\right)_T = RT\left[\frac{d}{dP}(\ln f)\right]_T \quad -(III)$$

$$\because \; dG = Vdp - \cancel{SdT}^{\,0} \quad [\text{at const- T, } dT = 0$$

$$\left(\frac{dG}{dP}\right)_T = V_m\,(\text{real})$$

Put the value of $\left(\frac{dG}{dP}\right)_T$ in (III)

$$V_{real} = RT \left(\frac{\partial \ln f}{dP} \right)_T$$

$$V_{real} \cdot dP = RT \; (d \ln f) \quad - (\text{IV})$$

$$\therefore \quad \alpha = V_{m(Ideal)} - V_{m(real)}$$

Multiply dp both side by dp

$$\alpha \cdot dp = V_{m(Ideal)} \, dp - V_{m(real)} \, dp$$

$$\alpha \cdot dp = \frac{RT}{P} dp - RT \, d(\ln f)$$

$\therefore$ Inte. both side →

$$\int_0^P \alpha \cdot dp = RT \int \frac{dp}{P} - RT \int d(\ln f)$$

$$\int_0^P \alpha \cdot dp = + RT \ln P - RT \ln f$$

$$\int_0^P \alpha \cdot dp = - RT \left[\ln f/_p \right]$$

$$\boxed{-\frac{1}{RT} \int_0^P \alpha \cdot dp = \ln f/_p}$$

$$\ln f/p = -\frac{1}{RT}\int_0^P \alpha . dP$$

$$f/p = e^{-\frac{1}{RT}\int_0^P \alpha . dP}$$

$$\boxed{f = P . e^{-\frac{1}{RT}\int_0^P \alpha . dP}}$$

$$\boxed{\gamma = f/p = e^{-\frac{1}{RT}\int_0^P \alpha . dP}}$$

$\gamma \Rightarrow$ fugacity cofficient

Fugacity can also be terms of Compressibility factor -

$$Z = \frac{P(V_{real})}{RT}$$

$[1 < Z > 1]$ - real Gas

for an Ideal Gas $[Z = 1]$

$$\ln f/p = \frac{-1}{RT}\int_0^P \left[V_{m(Ideal)} - V_{m(real)}\right] dP$$

$$\ln f/p = \frac{-1}{RT}\int_0^P \left[\frac{RT}{P} - \frac{ZRT}{P}\right] dP$$

$$\ln f/p = -\frac{1}{RT}\int_0^P \alpha . dP$$

$$f/p = e^{-\frac{1}{RT}\int_0^P \alpha . dP}$$

$$\boxed{f = P . e^{-\frac{1}{RT}\int_0^P \alpha . dP}}$$

$$\boxed{\gamma = f/p = e^{-\frac{1}{RT}\int_0^P \alpha . dP}}$$

$\gamma \Rightarrow$ fugacity cofficient

fugacity can also be terms of compressibility factor -

$$Z = \frac{P(V_{real})}{RT}$$

$[1 < Z > 1]$ - real gas

for an Ideal gas $[Z = 1]$

$$\ln f/p = \frac{-1}{RT}\int_0^P [V_{m(Ideal)} - V_{m(real)}]dP$$

$$\ln f/p = \frac{-1}{RT}\int_0^P \left[\frac{RT}{P} - \frac{ZRT}{P}\right] dP$$

$$\ln f/p = \int_0^P \frac{1}{P}(Z-1)\,dP$$

$$\boxed{\ln \gamma = \int_0^P \frac{(Z-1)\,dP}{P}}$$

fugacity at low pressure ⇒

$$\ln f/p = \frac{-1}{RT}\int_0^P \alpha \cdot dP$$

[bcoz No change
in pressure
∴ Initial = final

$$\ln f/p = -\frac{\alpha P}{RT}$$

$\because$ $\ln x = x - 1$ [Strilling formula]

$$\therefore \ln f/p = f/p - 1$$

from (i)

$$-\frac{\alpha P}{RT} = f/p - 1$$

$$1 - \frac{\alpha P}{RT} = f/p$$

$$1 - \frac{\left[\frac{RT}{P} - V_{real}\right]P}{RT} = f/p$$

$$\ln f/P = \int_0^P \frac{1}{P}(Z-1)\,dP$$

$$\boxed{\ln \gamma = \int_0^P \frac{(Z-1)\,dP}{P}}$$

fugacity at low pressure ⇒

$$\ln f/P = \frac{-1}{RT}\int_0^P \alpha \cdot dP$$

[bcoz No change in pressure

∴ Initial = final

$$\ln f/P = -\frac{\alpha P}{RT}$$

∵ $\ln x = x - 1$ [Stirlling formula]

∴ $\ln f/P = f/P - 1$

from (i)

$$-\frac{\alpha P}{RT} = f/P - 1$$

$$1 - \frac{\alpha P}{RT} = f/P$$

$$1 - \frac{\left[\frac{RT}{P} - V_{real}\right]P}{RT} = f/P$$

$$1 - \frac{[RT - PV_{real}]}{RT} = f/p$$

$$\frac{\cancel{RT} - \cancel{RT} + PV_{real}}{RT} = f/p$$

$$\frac{PV_{real}}{RT} = f/p$$

$$\boxed{f = \frac{P^2 V_{real}}{RT}}$$

$\Downarrow$

This is fugacity at low pressure

[16·11·15]

$$P(V_m - b) = RT$$

$$PV - Pb = RT$$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$\ln f/p = \int_0^P \frac{\left(\cancel{1} + \frac{Pb}{RT} \cancel{-1}\right)}{P} dp$$

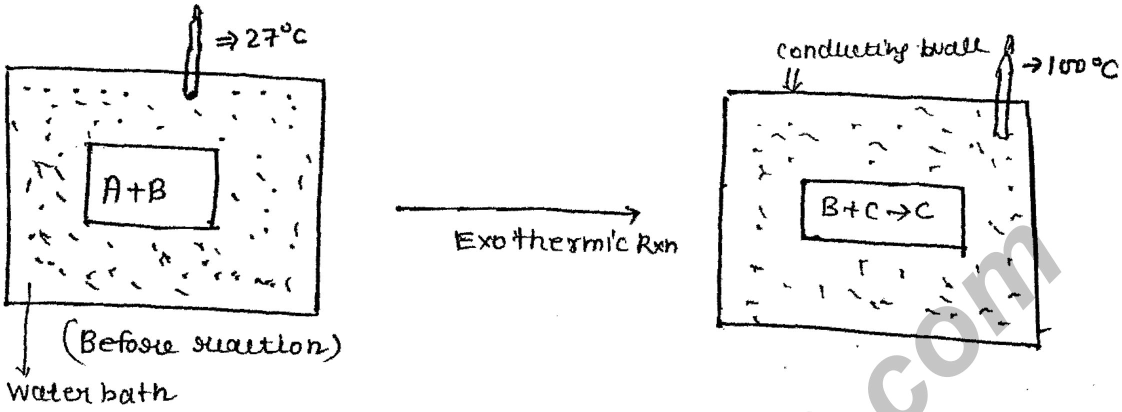
$$= \int_0^P \frac{\cancel{P} b}{RT \cancel{P}} dP$$

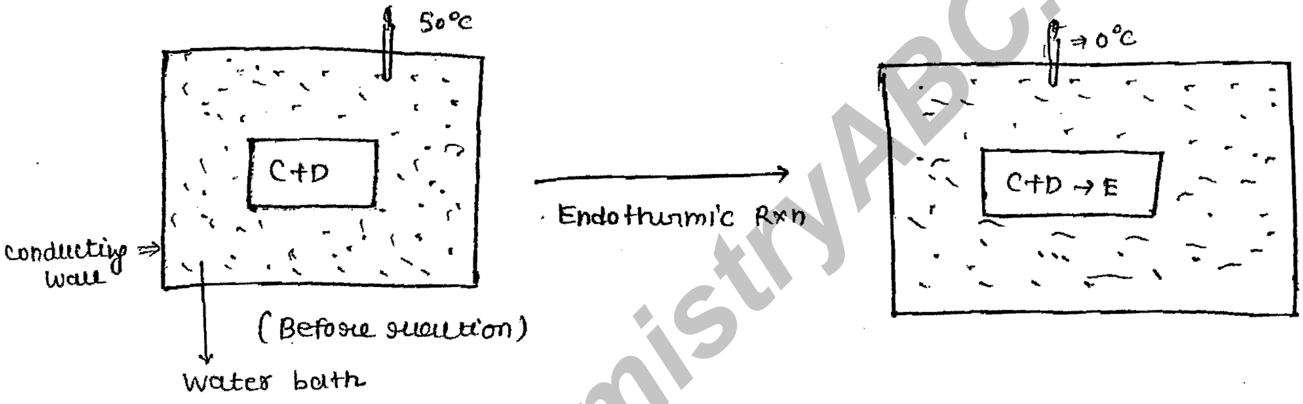
$$= \int_0^P \frac{b}{RT} dP$$

$$\ln f/p = \left(\frac{bP}{RT}\right)$$

$$f/p = e^{bP/RT}$$

$$\boxed{f = Pe^{bP/RT}}$$



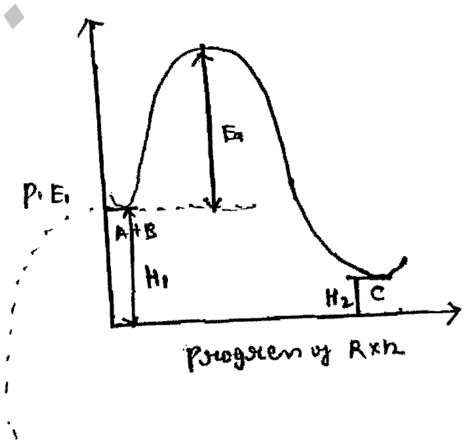


(A mole) → 1 mole

⇓

$A + B \longrightarrow C, \quad \Delta H = -ive \quad [-x\ kJ\,mol^{-1}]$

$C \longrightarrow A + B, \quad \Delta H = +ive \quad [+x\ kJ\,mol^{-1}]$



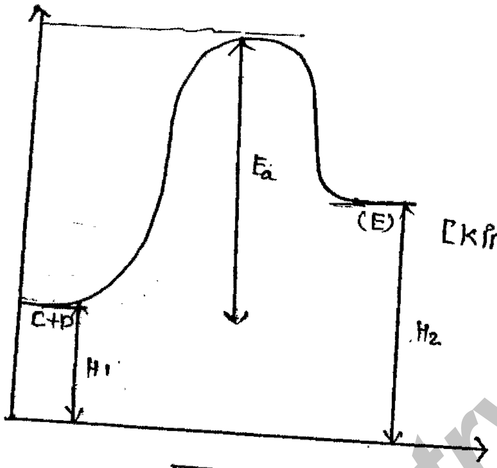
[Threshold Energy − average P.E.] = Activation E

→ Average Potential Energy of Reactant.

⇒ $\boxed{\text{Activation Energy = Threshold Energy − Average P.E. of Reactant}}$

⇒ The product form in Exothermic Rxn is thermodynamically stable

⇒ Temp only change when Heat is Evolved or absorb



[Kinetically control Product]

⇓

form very Easily and unstable bcoz it change into reactant bcoz Ea of Product is very less.

[most of the Rxn perform in const. so that change in ΔH]

$\boxed{\Delta H = H_2 - H_1 = +ive}$

Relation b/w ΔH and ΔE in the case of <u>Ideal Gas</u> ⇒

$$n_A A_{(g)} \xrightarrow{\text{Const.} \to \text{'P,T'}} n_B B_{(g)}$$

$PV_A = n_A RT$ [Reactant] —①

$PV_B = n_B RT$ [Product] —⑪

(II)−(I)

$P(V_B - V_A) = (n_B - n_A) RT$

$P\,\Delta V = \Delta n_g RT$ —③

most of the Rxn which is happend in the nature in const. temp. & pressure.

$H = E + PV$

$\partial H = \partial E + d(PV)$

$\partial H = \partial E + P dV + V \cancel{dP}^{0}$ → from [3]

$A_{(s)} \longrightarrow B_{(s)}$, $\Rightarrow$ $(\Delta H = \Delta E)$

$C_{(l)} \longrightarrow D_{(l)}$ $\Rightarrow$ $(\Delta H = \Delta E)$

$C_{(g)} \longrightarrow B_{(g)}$ $\Rightarrow$ $(\Delta H = \Delta E)$

$2F_{(g)} \longrightarrow 2G_{(g)}$ $\Rightarrow$ $(\Delta H = \Delta E)$

$A_{(g)} \longrightarrow 3B_{(g)}$ $\Rightarrow$ $\Delta H = \Delta E + 2RT$

$A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$ $\Delta H = \Delta E + RT$.

$A_{(s)}$ ~~$+ B_{(g)}$~~ $\longrightarrow C_{(g)} + D_{(s)}$, $\Delta H = \Delta E$

Heat Change in constt- volume (ΔE)

$$\Uparrow$$

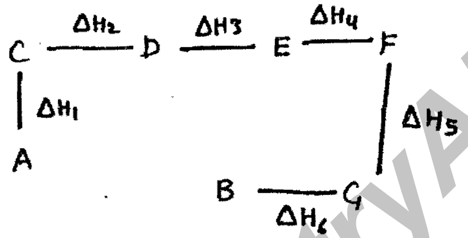
$$\boxed{q_p = q_v + \Delta n_g RT}$$

$$\Downarrow$$

Heat Change in constt-pressure (ΔH)

⇚ Hess's Law :⇛

$A \longrightarrow B \qquad \Delta H$



$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$$

$\boxed{\text{Conservation of Energy}}$

Heat may be absorb or Evolved

Accor^n to Hess's law ⇒ "the Enthalpy change during the reaction is same whether reaction complete one step or several step."

Numerical Question on Hess's law:⇒

Que:- Compute the Standard Heat of formation of methane

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

$\Delta H^\circ(298\,K) = -890.35$ kJ

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

$\Delta H^\circ(298\,K) = -285.84$ kJ

$$C(graphite) + O_2(g) \longrightarrow CO_2(g)$$

$\Delta H^\circ(298\,K) = -373.51$ kJ

$$C(graphite) + 2H_2(g) \longrightarrow CH_4(g)$$

$\Delta H^\circ(298\,K) = ?$

⇒ Calculate the Enthalpy Change for above reaction.

By ①

$\cancel{CO_2(g)} + \cancel{2H_2O(l)} \longrightarrow CH_4(g) + \cancel{2O_2(g)}$, $\Delta H^\circ = +890.35$ kJ

$2H_2 + \cancel{O_2(g)} \longrightarrow \cancel{2H_2O(l)}$, $\Delta H^\circ = -285.84$ kJ ×2

$C(gra.) + \cancel{O_2(g)} \longrightarrow \cancel{CO_2(g)}$, $\Delta H^\circ = -373.51$ kJ

$C(graphite) + 2H_2(g) \longrightarrow CH_4(g)$ $\Delta H^\circ = (890.35 - \overset{\times 2}{285.84} - 373.51)$

= ~~[illegible] 659.35) – 285.84~~

= ~~131.00 – 285.~~84

= –

= 890.35 – 2×285.84 – 373.51

= 890.35 – 571.68 – 373.51

= 890.35 – 945.19

= – 54.84 kJ

Standard- State

Solid State (Pure Crystalline)

Substance at 1 atm or 1 bar at particular temp.

Liquid-State (Pure / molar)

1 atm pressure or 1 bar at particular temp.

$P_{white} > P_{black}$ [Phosphorus]

$S_R > S_m$ [Sulphur]

$\Downarrow$ Rhombic $\Downarrow$ (monoclinic)

$C_{Graphite} > C_{Diamond}$ [Carbon]

Gas ⇒ 1 bar, Pure
or 1 atm

$\boxed{\Delta H^0}$ ⇒ Standard Enthalpy change

Enthalpy of formation for an Element

⇒ The standard Enthalpy of formation for any element in it's stable state of aggregation (इकट्ठा) at 1 bar pressure and specified temp. is assigned as zero

← $O_{2(g)}$ →

$\Delta H_f^\circ [O_{2(g)}] = 0$

$\Delta H_f^\circ [C_{graphite}] = 0$ [Stable]

But $\Delta H_f^\circ [C_{Diamon}] \neq 0$ [Diamond is not stable state]

$\Delta H_f^\circ [Br_2, 1atm] = 0$

$\Delta H_f^\circ [S_{rhombic}] = 0$ [$S_{rhombic}$ is stable state]

$\Delta H_f^\circ [S_{monoclinic}] \neq 0$

$\Delta H_f^\circ [P_{white}] = 0$

$\Delta H_f^\circ [P_{Black}] \neq 0$

⇐ Born - Hyber Cycle :⇒

Born-Hyber cycle is used to calculate lattice energy. Lattice Energy can't be calculate Experimently but with the application of B.H. Cycle we are able to calculate lattice energy.

⇓

"Lattic Energy is defined as the energy required to separate one mole of solid ionic compound into gaseous ion."

Formation of NaCl Crystal from Na(s) + $Cl_2(g)$

(Vaporization) $Na(s) \longrightarrow \cancel{Na(g)}, \quad \Delta H_1$

(Ionization) $\cancel{Na(g)} \longrightarrow \cancel{Na^+_{(g)}} + (\bar{e}), \quad \Delta H_2$

(Dissociation) $\frac{1}{2}Cl_2(g) \longrightarrow \cancel{Cl(g)} + \quad \Delta H_3$

(formaⁿ of Cl⁻) $\cancel{Cl(g) + \bar{e}} \longrightarrow \cancel{Cl^-_{(g)}}, \quad \Delta H_4$

(combination ~~of~~ Na⁺ & Cl⁻) $\cancel{Na^+(g)} + \cancel{Cl^-(g)} \longrightarrow NaCl(s), \quad \Delta H_5$ ⇒ this can't be calculate directly [Practically Impossible]

$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s), \quad \Delta H_6$

from Hess's law -

$$\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

We know, $\Delta H_1, \Delta H_2, \Delta H_3, \Delta H_4, \Delta H_6$ then,

By the applⁿ of Hess's law & Born's Hyber's Cycle ⇒

$$\boxed{\Delta H_5 = \Delta H_6 - (\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4)}$$

⇓

(Lettic Energy)

⇒ $\Delta H^\circ_f (NaCl) = -410.87\ kJ\ mol^{-1}$

⇐: Kirchoff's - Equation :⇒

(variation of temp., ΔH)

કોઈ-પણ Rxn ના ΔH બદલાય છે diff. temp.પર

⇓

Kirchoff Eqⁿ -

at T_1 $A + B \longrightarrow C$, ΔH_1

at T_2 $A + B \longrightarrow C$ ΔH_2

$$\Delta H = H_2 - H_1$$

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left(\frac{\partial(H_2)}{\partial T}\right)_P - \left(\frac{\partial(H_1)}{\partial T}\right)_P$$

$$= (C_P)_{Prod} - (C_P)_{Rct}$$

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \Delta C_P$$

$$\partial(\Delta H) = \Delta C_P \cdot \partial T$$

Inte. both side

$$\int_{H_1}^{H_2} \partial(\Delta H) = \Delta C_P \int_{T_1}^{T_2} \partial T$$

$$\boxed{\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)}$$

Variation of heat of reaction with temp.
mathematical form of this statement is
kirchoff Eqⁿ.

Kirchoff Eqⁿ can be exprⁿᵈ Either in terms of ΔH or ΔE

Kirchoff's Equation in term of ΔE.

$$\because \quad \Delta E = E_2 - E_1$$

$$\left(\frac{\partial(\Delta E)}{\partial T}\right)_V = \left(\frac{\partial E_2}{\partial T}\right)_V - \left(\frac{\partial E_1}{\partial T}\right)_V$$

$$\left(\frac{\partial(\Delta E)}{\partial T}\right)_V = (C_v)_{PRT} - (C_v)_{RCT}$$

$$\left[\frac{\partial(\Delta E)}{\partial T}\right]_V = \Delta C_v$$

$$\partial(\Delta E) = \Delta C_v \cdot \partial T$$

Int on both Side

$$\int_{\Delta E_1}^{\Delta E_2} \partial(\Delta E) = \Delta C_v \int_{T_1}^{T_2} \partial T$$

$$\boxed{\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)}$$

Numerical ⇒

$A + B \longrightarrow C$ $\Delta H_1 = 37\,KJ$ at 298 K

$A + B \longrightarrow C$ $\Delta H_2 = ?$ at 500 K

where C_p of ($C \Rightarrow$ product) ⇒ 5

$(C_p)_B = 3$

$(C_p)_A = 1$

$\Delta H_2 - 37 = (5-3-1)(500-298)$

$\Delta H_2 - 37 = 1 \times (202)$

$\Delta H_2 = 202 + 37$

$\Delta H_2 = 239\ kJ$

$= 23900\ kJ$

⇒ $3A + 5B \longrightarrow 6C$ $\Delta H_1 = 37\ KJ$

$3A + 5B \longrightarrow 6C$ $\Delta H_2 = ?$

$(C_p)_A = 3$

$(C_p)_B = 5$

$(C_p)_C =$ [illegible]

$\Delta H_2 - \Delta H_1 = [3 \times 6 - 3 \times$ [illegible] $- 5 \times 5]\ [500 - 298]$

$\Delta H_2 - 37\,000 = [18 - 28] \times 202$

$\Delta H_2 - 37000 = -2020$

$\Delta H_2 = 37000 - 2020$

$\Delta H_2 = 34980\ J$

(Rxn Higher temp ue ~~un~~ Endothermic)

Qu.6

$\Delta H_1 = -92.2\,KJ$

$\Delta H_2 = ?$

$T_2 = 373$

$T_1 = 298$

$$\begin{array}{r} 106.7 \\ 70.2 \\ \hline 36.5 \end{array}$$

$\Delta H_2 - \Delta H_1 = (2 \times 35.1 - 3 \times 28.8 - 1 \times 29.1)\,(373 - 298)$

$\Delta H_2 + 92.2 = (70.2 - 77.6 - 29.1)\,(75)$

$\Delta H_2 + 92.2 = (70.2 - 106.7)\,75$

$\Delta H_2 + 92.2^{\times 1000} = -45.3 \times 75$

$\Delta H_2 = -45.3 \times 75 - 92.2 \times 1000$

[illegible]

[illegible]

$\Delta H_2 = -45.3 \times 75 - 92200$

$\Delta H_2 > \Delta H_1$

More exothermic

Adiabatic flame temp.

and

Adiabatic - Explossion temp.

(पेट्रोल)
complete
Combustion
↓
$CO_2(g) + H_2O(l)$
(Only product)
(No Rct)

Ist step

$$\underset{(T_0)}{R} \longrightarrow \underset{(T_0)}{P} \quad -\Delta H_0$$

IInd step

$$\underset{(T_0)}{P} \xrightarrow[\Delta H_1]{\text{absorb heat}} \underset{(T_{final})}{P}$$

at a constt. pressure ⇒ Adiabatic-flame
at a constt. volume ⇒ " → explosi

$$-\Delta H_0 = \Delta H_1$$

Ist step. मे Product बनेगा वह Product final temp. achive करेगा वह temp वह Ist step मे $-\Delta H_0$ release हुआ इससे heat होगा अगर यह complete combustion अगर constt. pressure पर होगा तो adiabatic flame temp. अगर constt. volume पर होगा तो adiabatic Explosion temp.

$$-\Delta H_0 = \Sigma n C_p \int_{T_0}^{T_f} dT$$

$$-\Delta H_0 = \Sigma n C_p (T_f - T_0)$$

$$\boxed{\frac{-\Delta H_0}{\underset{(\text{product})}{\Sigma n c_p}} + T_0 = T_f}$$

$$\boxed{-\frac{\Delta E^{\circ}}{\underset{(\text{Product})}{\Delta C_v}} + T_0 = T_f}$$

$\Downarrow$ at Constt volume

Adiabatic flame temp.

⇒ When a complete Combustion of a Substance take place, the final temp. which is achived by product at constt. pressure condition is called A.F.T.

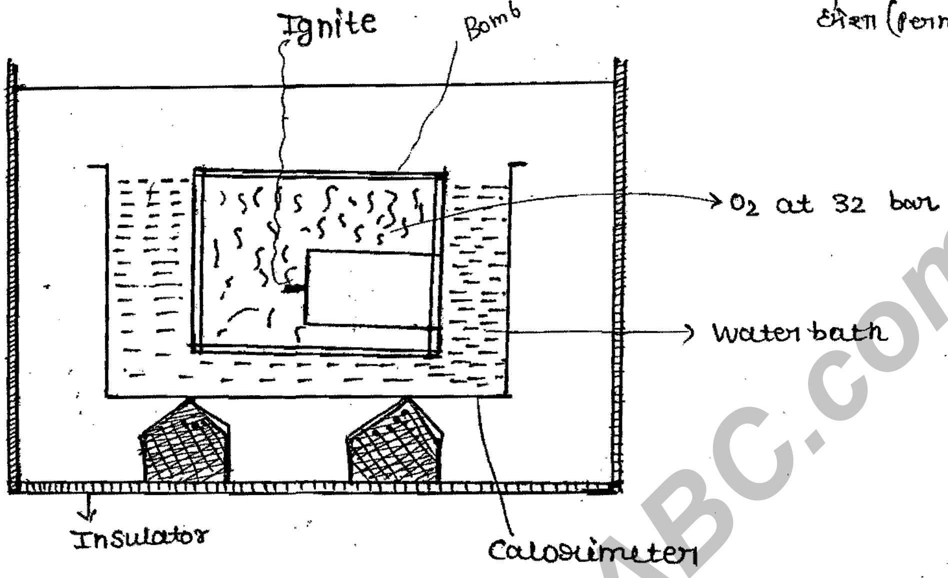
Adiabatic explosion temp.

⇒ When a complete combustion of a substance take place the final temp. which is achived by product at constt. Volume condition is called. A.E.T. [Close]

BOMB- CALORIMETER

*(Heat of Combustion of substance)

ऊष्मा (for mole के लिये)



$$q_{water} = m\, C_{water}\, \Delta T$$

$$q_{Bomb} = m \times C_{bomb}\, \Delta T$$

$$q_{combustion} = q_{water} + q_{Bomb}$$

⇒ Tortoun's Rule :⇒ (failed) [which under go association or dissociation]

$$\Delta S = \frac{\Delta H_{vap.}}{T_b}$$

$$\text{Liq.(Benzene)} \xrightleftharpoons{\text{const. "P"}} \text{vapour}$$

⇒ "For Moll of the liquid at a respective b.pt., molar Entropy of vapourization are fixed. which is 88 $JK^{-1}mol^{-1}$ or 21 cal $K^{-1}mol^{-1}$."

[Statement of tortoun's Rule]

88 $JK^{-1}mol^{-1}$

or

21 cal $K^{-1}mol^{-1}$

this law is failed which liquid is association or dissociation. [like- CH_3COOH]

this law is also failed which having very High + very low b.pt.

Gibb's- dheem Equation :-

$$G = f(T, P, n_1, n_2, n_3, \dots n_i)$$

$$\underline{dG} = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, n_3, \dots n_i} \partial T + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots} \partial P + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2} \partial n_1 + \dots$$

at constt- T, P

$$dG = dn_1\mu_1 + dn_2\mu_2 + dn_3\mu_3 + dn_4\mu_4 + \dots$$

Integrate both side

$$G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \dots \quad - ②$$

Differentiate both side

$$dG = n_1 \partial\mu_1 + \mu_1 \partial n_1 + dn_2 \cdot \mu_2 + n_2 d\mu_2 + \dots \quad - ③$$

Substrate ③ − (2)

$$0 = n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + n_4 d\mu_4 + \dots$$

$$\boxed{\Sigma n_i \, d\mu_i = 0}$$

$\downarrow$

Gibb's Dhuem Equation

TIFR Assignment

Qu. 1 $Mg(s) + \frac{1}{2} O_2(g) \longrightarrow MgO(s)$

$\Delta H^\circ_{rxn} = -602 \text{ kJ/mol}$

$\Delta S^\circ_{rxn} = -108 \text{ kJ/mol}$

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$$

$$= -602 \text{ kJ/mol} - 273 \times (-108)$$

$$= -602 \text{ kJ/mol} + 29484 \text{ kJ/mol}$$

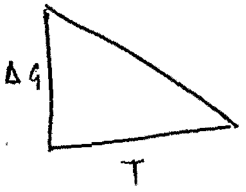
$$= 28882$$

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

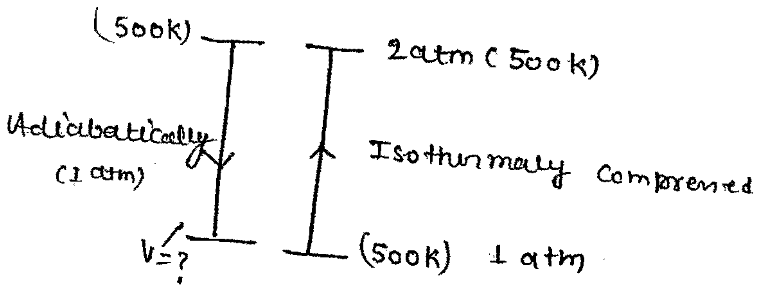
$y = c + mx$

Qu. 3 Slope $\left\{ \tan\theta = \frac{\perp}{\text{Base}} \right] = \frac{3000 \text{ J (P)}}{40 \text{ (B)}}$

$\Rightarrow 75 \text{ J mol}^{-1} \text{ K}^{-1}$



Q.20



[∵ Ideal gas]

$PV = nRT$

$\overset{atm}{2} \times V = \overset{mol}{1} \times \overset{dm^3\,atm\,K^{-1}mol^{-1}}{0.082} \times \overset{K}{500}$

$V = \frac{0.082 \times 500}{2}$

$= 20.5\ dm^3$

$V_1 = 20.5\ dm^3$

$T_1 = 500\ k, \quad T_2 = ?$

$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$

$\left(\frac{500}{T_2}\right)^{1.66} = \left(\frac{1}{2}\right)^{(1-1.66)}$

$\left(\frac{500}{T_2}\right)^{1.66} = \left(\frac{1}{2}\right)^{-0.66}$

$\left(\frac{500}{T_2}\right)^{1.66} = 1.58$

$\frac{500}{T_2} = (1.58)^{1/1.66}$

$\frac{500}{T_2} = 1.33$

$T_2 = \frac{500}{1.33} = 375.9$

$(PV)^{\gamma} = \text{constant}$

$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$\left(\frac{V_1}{V_2}\right)^{\gamma} = \frac{P_2}{P_1}$

$\cancel{\left(\frac{20.5}{V_2}\right)^{\gamma} = \frac{2}{1}}$

$\cancel{\left(\frac{20.5}{V_2}\right)^{1.66} = 2}$

$\cancel{\frac{20.5}{V_2} = 1.5}$

$C_V = 1.5R$

$C_P - C_V = R$

$C_P - 1.5R = R$

$C_P = 2.5R$

$\frac{C_P}{C_V} = \gamma$

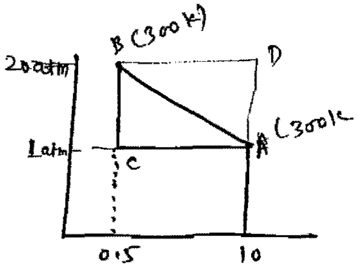
$\frac{2.5}{1.5} = \gamma$

$\gamma = \frac{5}{3} = 1.66$

$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma - 1}$

$\frac{500}{375.9} = \frac{V_2}{}$

㉗



$V_1 = 10\,L$

$V_2 = 0.5\,L$

Expansion

Isothermal (rev. work done)

$PV = nRT$

$\frac{1 \times 10}{300} = nR$

$W = -nRT \ln \frac{V_2}{V_1}$

$= -nR\,300 \times \ln \frac{0.5}{10}$

$= -\frac{10}{\cancel{300}} \times \cancel{300} \ln \frac{0.5}{100}$

$= -10 \ln \frac{5}{100}$ $= (-) -10 \ln \frac{100}{5}$

$=$ ~~-10×(-2.99~~) $= 10 \ln 20$

Q4.30⇒

$T_1 = 15°C$

$T_2 = 75°C$

C_p of water $= 75\ J K^{-1} mol^{-1}$

$\frac{\Delta H}{\Delta T} = nC_p$

$n = \frac{w}{m} = \frac{\cancel{54}}{\cancel{18}} = 3$ mol

$\frac{\Delta H}{\text{~~(75-15)~~}3} = 3 \times 75$

$\frac{\Delta H}{348 - 288} = 3 \times 75$

$\frac{\Delta H}{+60} = 3 \times 75$

$\Delta H = 13.5\ kJ$

(52)

$$\text{ice} \xrightarrow{\uparrow \Delta H} \text{vap.}$$

$$\text{ice} \xrightarrow[6000\,J]{} \text{Liq.} \xrightarrow[44830]{} \text{Va.}$$

(56)

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 \cdot T_2}\right)$$

variation of temp. with pressure

→ Clausius - Clapeyron Eq^n^

$P_1 = 2.02 \times 10^3\ N\,m^{-2}$

$P_2 = 1\ atm = 1 \times 10^5\ N\,m^{-2}$

$\boxed{T_2}$

$\boxed{1364}$

$\Delta H = 41\ kJ\,mol^{-1}$

solve yourself

$$\ln \frac{1 \times 10^{5}}{2.02 \times 10^{3}} = \frac{41000}{8.314}\left(\frac{T_2 - 293}{293\,T_1}\right)$$

$$\ln\left(\frac{100}{2.02}\right) =$$

$$\ln 49.50 = 4931.44\left(\frac{T_2 - 293}{293\,T_1}\right)$$

$$3.902 = 4931.44\left(\frac{T_1 - 293}{293\,T_1}\right)$$

$$\frac{3.902 \times 273}{4931.44} = \frac{(T_1 - 293)}{T_1}$$

$$0.20 = 1 - \frac{293}{T_1}$$

$$1 - 0.20 = \frac{293}{T_1}$$

$$T_1 = \frac{293}{0.9}$$

$= 384\ K$

Qu.57 $U = 3.5\,PV + K$

$V_1 = 0.25\,m^3$

$V_2 = 0.86\,m^3$

$P_1 = 5\,Nm^{-2}$

$PV^{1.3} = \text{constant}$

where $\boxed{\gamma = 1.3}$

$$\underline{5} = \left(\frac{0/86}{0/25}\right)$$

Note⇒

(Water), ΔH_{fusion} = 324 KJ/Kg or J/~~k~~g

$\Delta H_{vaporization}$ = 2264.76 KJ/kg

Cp = Specific heat of water = 4.18 J/g

Cp = specific heat of ice = 2.023 J/g

(Net-Previous)

Q.12 ②

$$\Rightarrow PV^{a} = \text{constant}$$

$$T_1 V_1^{a-1} = T_2 V_2^{a-1} = k$$

$$\therefore \quad T_2 > T_1$$

$$\frac{T_1 V_1^{a-1}}{V_2^{a-1}} = T_2$$

$$\frac{\cancel{T_1} V_1^{a-1}}{V_2^{a-1}} > \cancel{T_1}$$

$$\left(\frac{V_1}{V_2}\right)^{a-1} > 1$$

$$\left(\frac{V_1}{V_2}\right)^{a-1} > \left(\frac{V_1}{V_2}\right)^{0}$$

$$a-1 \leq 0$$

$$\boxed{a \leq 1}$$

Q.128

$$q = -(q_{water} + q_{Cu})$$

$$q = -2500 \text{ J K}^{-1} \times 4$$

$$q = -2500 \times (\Delta T)$$

$$q = -2500 \times 4$$

$$q_{com.} = -10000$$

$$n = \frac{0.5 g}{\cancel{50}} = \frac{1}{100} = 0.01$$

$$q_{com.}/mole = \frac{-10000.00}{0.01}$$

$$= -1000000$$

$$q_{combun.} \text{ per mol} = -1000 \text{ kJ}$$

Q.46

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_{vap.} - V_L)}$$

Degree of Freedom

Tr, Rot, Vib

Linear
⇓
Tr = 3
Rot = 2

CO, O_2, N_2
↓

Non linear
T = 3
R = 3
(NH_3, SO_3
(3N−6)

~~Tr~~ =

$T + R + V = 3N \Rightarrow$ (No. of atom)

$V = 3N - 5$

$V = 3 \times 2 - 5$

$= 6 - 5$

$= 1$

(Contribution)
⇓

$C_v \Rightarrow$ Ⓣ $R/2$

$C_v \Rightarrow$ Ⓡ $\rightarrow R/2$

$C_v \Rightarrow$ Ⓥ $\rightarrow$ R at High

0.2R at R/T

0 at low temp.

Monoatomic
⇓

He, Ne, Ar, Kr, Xe, ~~Rn~~

T = 3
Rotational = 0
Vibrational = 0

(T) $C_v = 3R/2$
Rota = 0
Vibra = 0

Total $C_v = 3R/2 + 0 + 0$

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

$C_p = C_v + R$

$$\boxed{C_p = \frac{5}{2}R}$$

$$\boxed{\frac{C_p}{C_v}} = \frac{5}{3} = 1.66$$

(Monoatomic)

The ratio of $\frac{C_p}{C_V}$ for diatomic gas ⇒

[O_2]

Trans. = 3
Rotat. = 2

$V = 3N - 5$ ⇒ [
$= 3 \times 2 - 5$ ⇒
$= 1$

at High temp.,

Total $C_V = 3 \times R/2 + \cancel{2} \times R/\cancel{2} + 1 \times R$

$= 1.5R + R + R$

$= 3.5R$

$= \frac{7R}{2}$

$C_p = C_V + R$ ⇒ $\frac{7}{2}R + R = \frac{9R}{2}$

$\frac{C_p'}{C_V} = \frac{9}{7} = 1.28$

(29) $C_V = 20\,J\,K^{-1}\,mol^{-1}$

Const. volume, $T_1 = 2T_1$

$\underline{W \neq q}$

$\Delta E = q + w$

$\Delta E = q + 0$

$C_V(T_2 - T_1) = q$

$20(2 \times 298 - 298) = q$

$q = 20 \times 298$

$q = 5960\,J$

$\boxed{q = 5.96\,J}$