

(B) $\Delta H = nC_p \Delta T = 0$

(C) $\Delta H > 0$

(D) $\Delta U > 0$

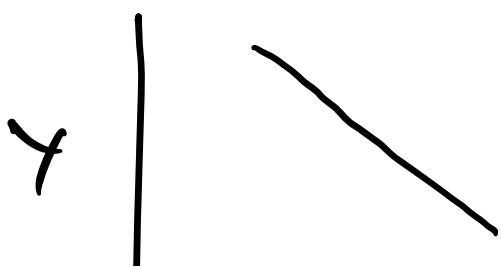
"A Process is carried out at constant external pressure"

This means process will be reversible.

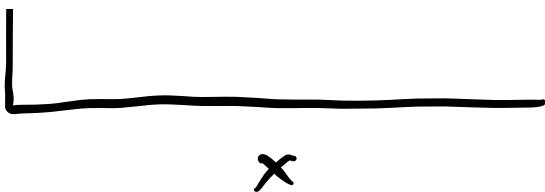
** Reversible processes can be plotted graphically.

Work done Calculation :-

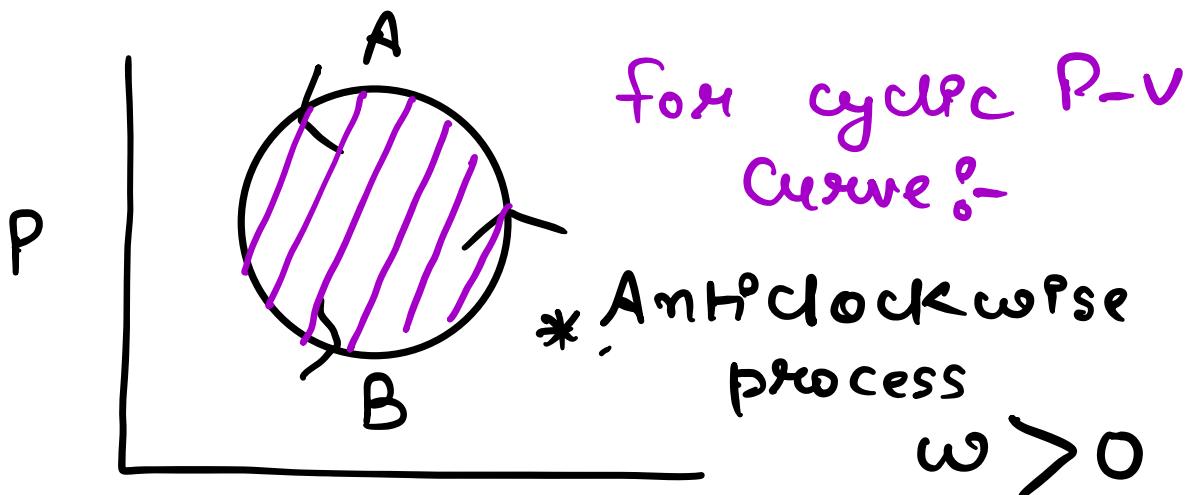
If $w = - \int P_{\text{ext}} dV$



$\int Y dx = \text{Area under the curve } Y - x.$



$w = - \int P dV = \text{Area under the } P-V \text{ curve.}$



✓

* Clockwise
cyclic process
 $w < 0$

* * for cyclic V-P curve

Anticlockwise work $\rightarrow w < 0$

Clockwise " $\rightarrow w > 0$

1.) Work done for isochoric process :-

$$V = \text{Constant}$$
$$w = - \int P_{\text{ext}} dv = 0$$

from f.L.O.T

$$\Delta U = q + w$$

$$\Delta U = q$$

for ideal gas

$$\Delta U = n C_V \Delta T$$

If $T \uparrow \Rightarrow U \uparrow$
 $T \downarrow \Rightarrow U \downarrow$

2.) for isobaric process :-

$$P = \text{constant.}$$

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

$$w = -P(v_2 - v_1)$$



$$w = -[Pv_2 - Pv_1]$$

$$= -[mRT_2 - mRT_1]$$

$$w = -mR[T_2 - T_1]$$

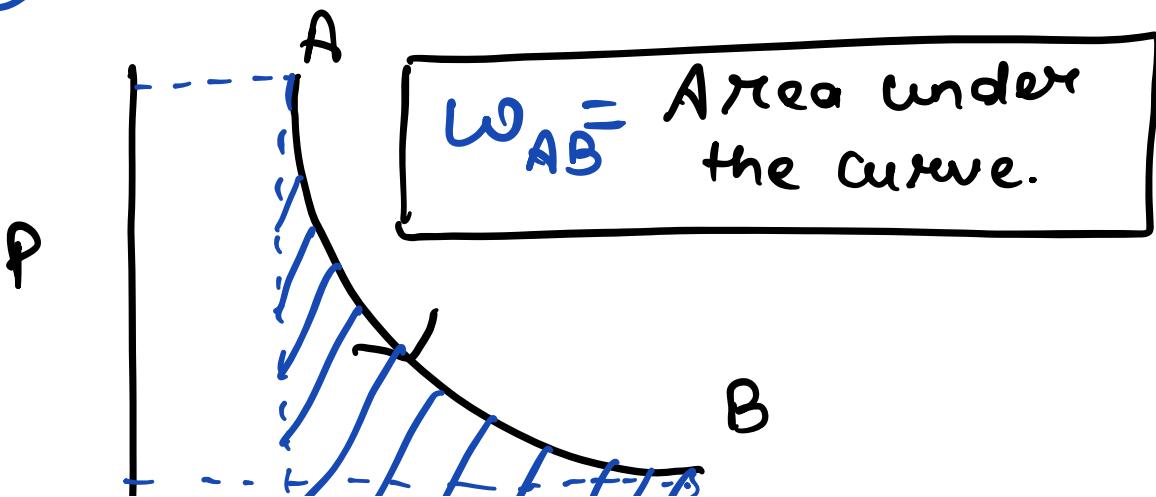
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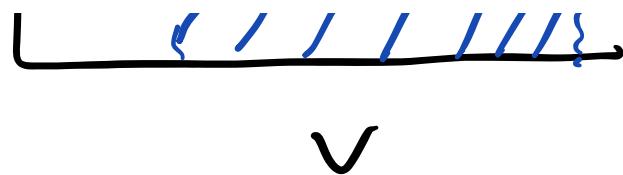
Only for ideal gas.

3) Isothermal process $\frac{P}{T} = \text{constant}$

$T = \text{Constant}$

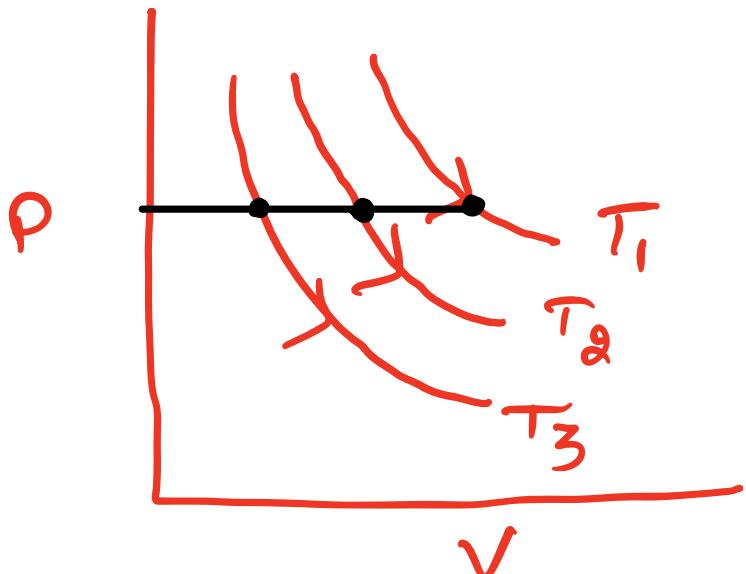
a) Reversible Isothermal process $\frac{P}{T} = \text{constant}$





Ques

Compare T_1 , T_2 & T_3 .



Soln

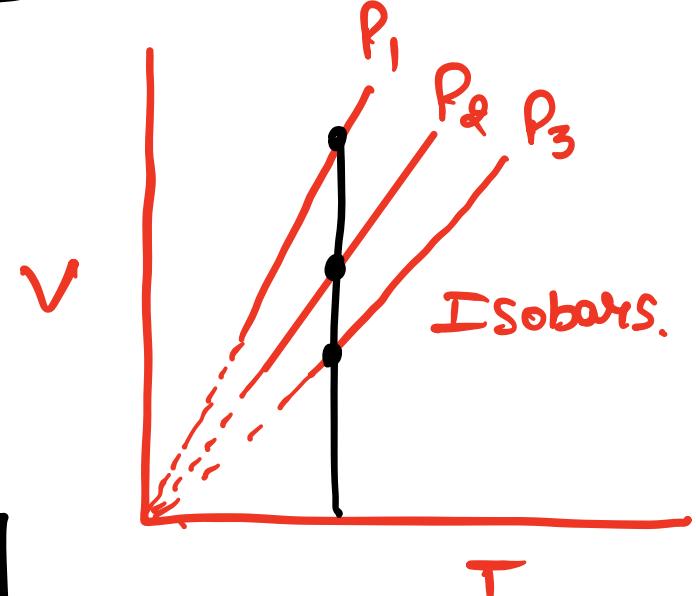
$$P = \text{Constant}$$

$$V \propto T$$

$$T_1 > T_2 > T_3$$

Ques

Compare
 P_1 , P_2 & P_3



Soln

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

$$\boxed{P_3 > P_2 > P_1}$$

$$W_{\text{reversible}} = - \int P_{\text{ext}} \cdot dV$$

$$= - \int P_{\text{gas}} dV.$$

$$= - \int \frac{nRT}{V} dV$$

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

$$\boxed{W_{\text{rever}} = -nRT \ln \frac{V_2}{V_1}}$$

Or

$$\boxed{W_{\text{revers.}} = -2.303 nRT \log \frac{V_2}{V_1}}$$

On

$$W_{\text{rever}} = -nRT \ln \frac{P_1}{P_2}$$

⑤ Isothermal irreversible process :-

$$W_{\text{irr}} = - \int P_{\text{ext}} \cdot dv$$

For irreversible process $\Rightarrow P_{\text{ext}} = \text{const.}$

$$W_{\text{irr}} = -P_{\text{ext}} \int_{v_1}^{v_2} dv$$

$$W_{\text{irr}} = -P_{\text{ext}} (v_2 - v_1)$$

$$W_{\text{irr}} = -P_{\text{ext}} \left[\frac{nRT}{P_2} - \frac{nRT}{P_1} \right]$$

$$W_{\text{irr}} = -P_{\text{ext}} \cdot nRT \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$$

** In case of expansion lower pressure will be the external pressure.

** In case of compression higher pressure will be the external pressure.

Ques:- 2 moles of ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm determine the work done under the following conditions.

i.) Reversible expansion.

ii.) Irreversible expansion.

$$\text{Sol:- } @ \quad W_{\text{rever.}} = -nRT \ln \frac{V_2}{V_1}$$

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

$$= -2 \times R \times 300 \cdot \ln \frac{10}{1}$$

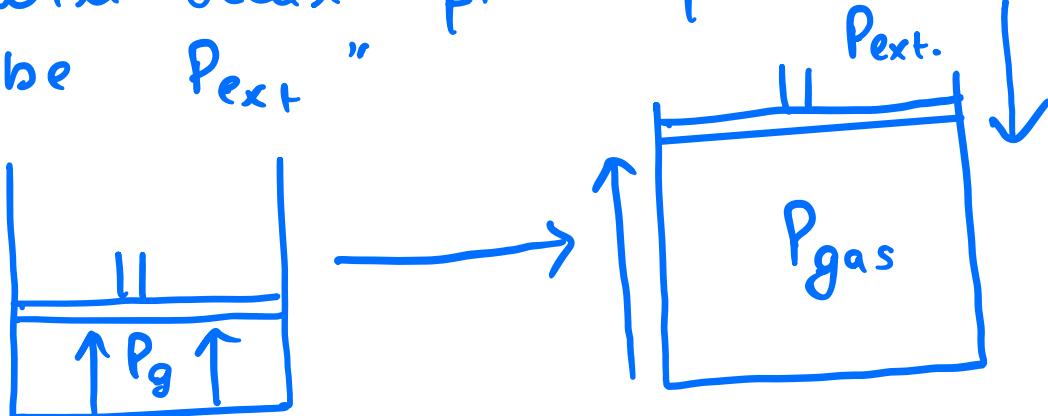
$$\omega_{\text{rever.}} = -600 R \ln 10$$

(b) $\omega_{\text{Pxx.}} = -P_{\text{ext.}} (V_2 - V_1)$

$$= -P_{\text{ext.}} nR + \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$$

$$= -1 \times 2 \times R \times 300 \left[1 - \frac{1}{10} \right]$$

"Generally whenever expansion will occur final pressure will be $P_{\text{ext.}}$ "



$$\omega_{\text{Pxx.}} = -540 R.$$

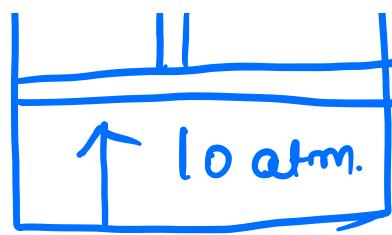
Special Case.

Iron nail.

$P_{\text{ext.}} = 1 \text{ atm.}$



$$P_{\text{gas}} = 10 \text{ atm}$$



when P_{piston} has reached upto P_{gas}
i.e. 10 atm.

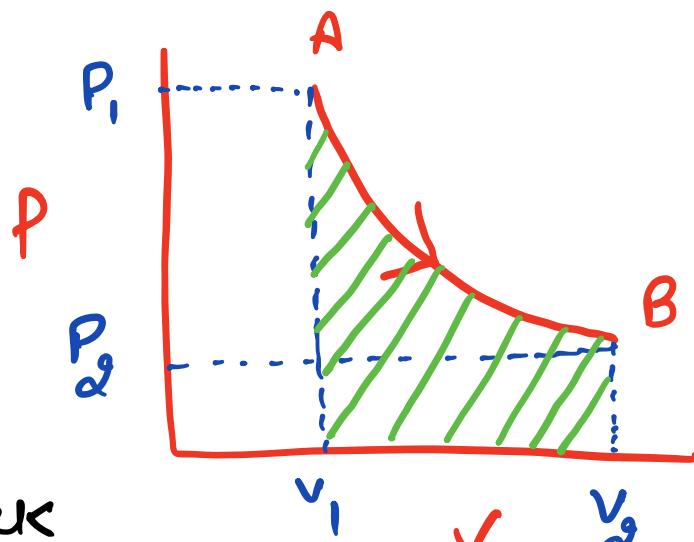
let $P_{\text{gas}} = 8 \text{ atm}$

* In this Case all pressure values p.e. initial, final and external are different.

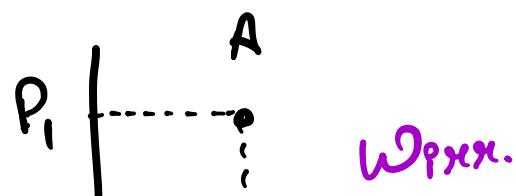
Ques :-

Sol :-

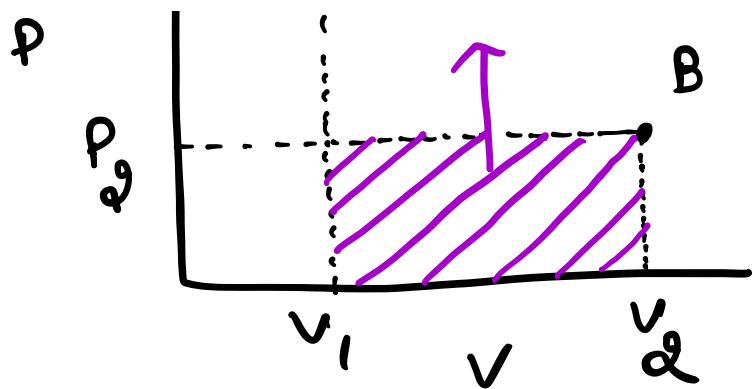
Area under the curve will represent work done by the system.



$$W_{\text{rev}} = \text{Area under the curve AB}$$



from A \rightarrow B
work of expansion.

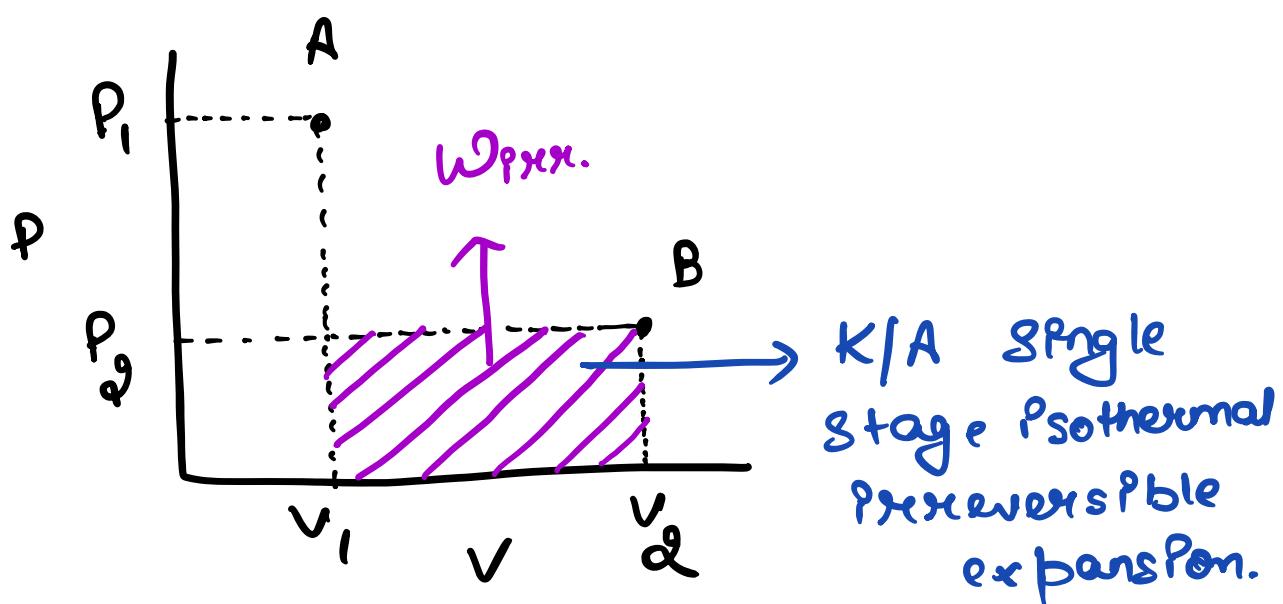


$$W_{p\text{reversible}} = -P_{\text{ext}} (v_2 - v_1)$$

$$W_{p\text{exx.}} = -P_2 (v_2 - v_1)$$

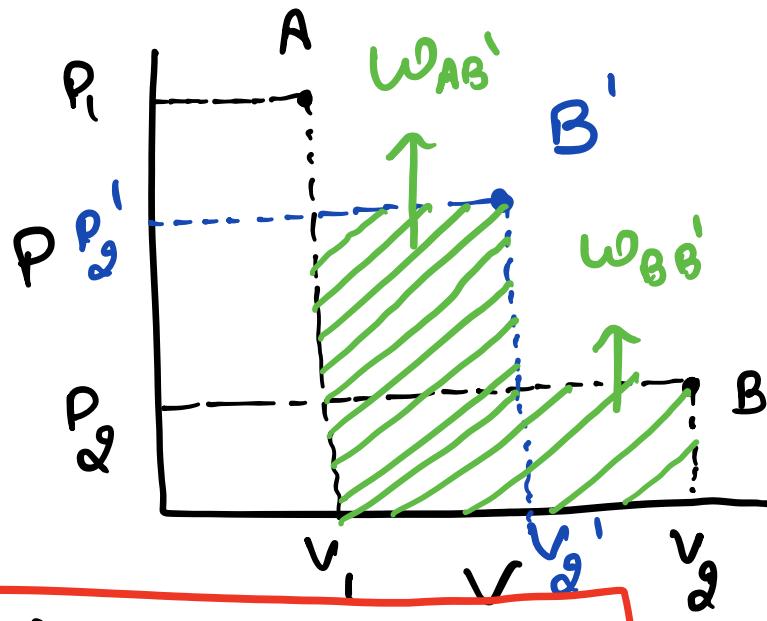
\Rightarrow for expansion :-

$$|W_{\text{rev}}| > |W_{\text{pexx.}}|$$



Special Case :-

$$\omega_{AB} = \omega_{AB'} + \omega_{B'B}$$

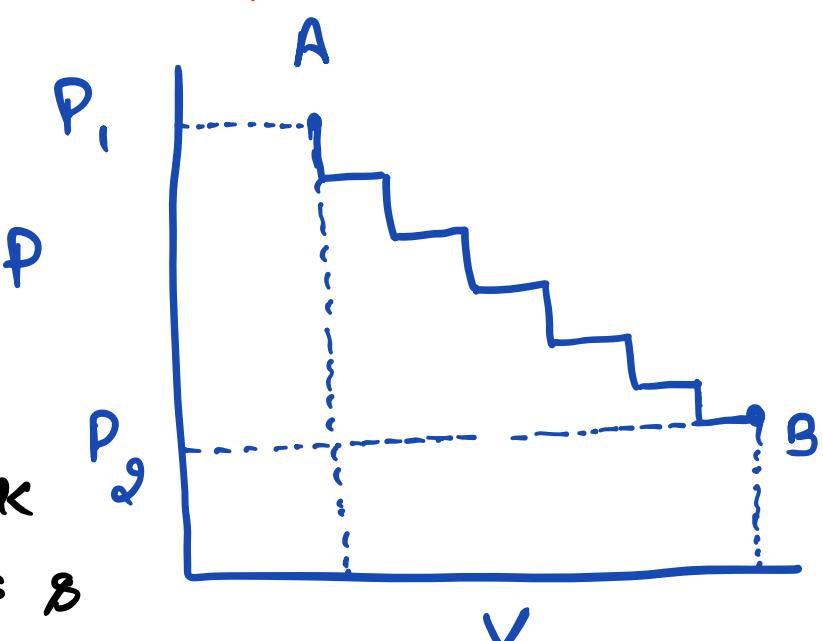


$$\boxed{\omega_{AB} = -P_2'(V_2' - V_1) - P_2(V_2 - V_2')}.$$

↓

Work for two stage Isothermal
Reversible expansion.

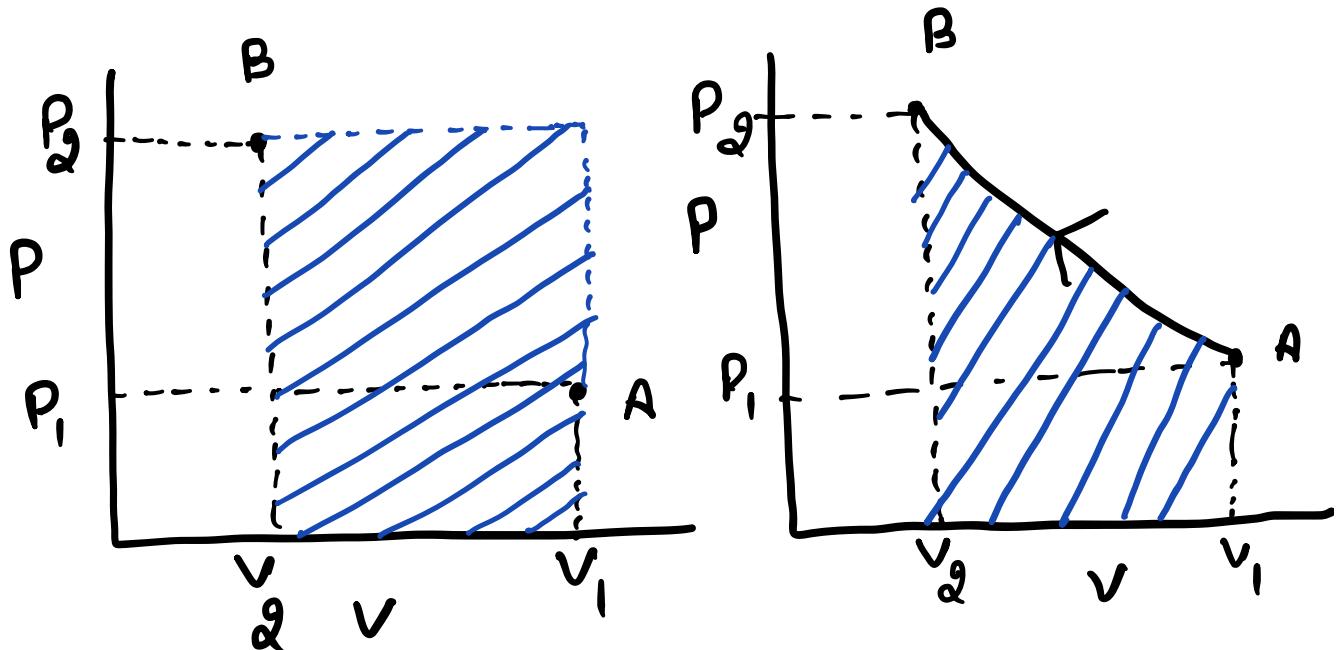
* In case of Isothermal reversible expansion as the no. of stages increases work done increases w.r.t. the no. of stages



tends to finite then

$$W_{\text{irr.}} = W_{\text{rever.}}$$

Isothermal Reversible Compression:-



$$W_{AB(\text{irr.})} = -P_{\text{ext.}}(V_2 - V_1)$$

$$= -P_2(V_2 - V_1)$$

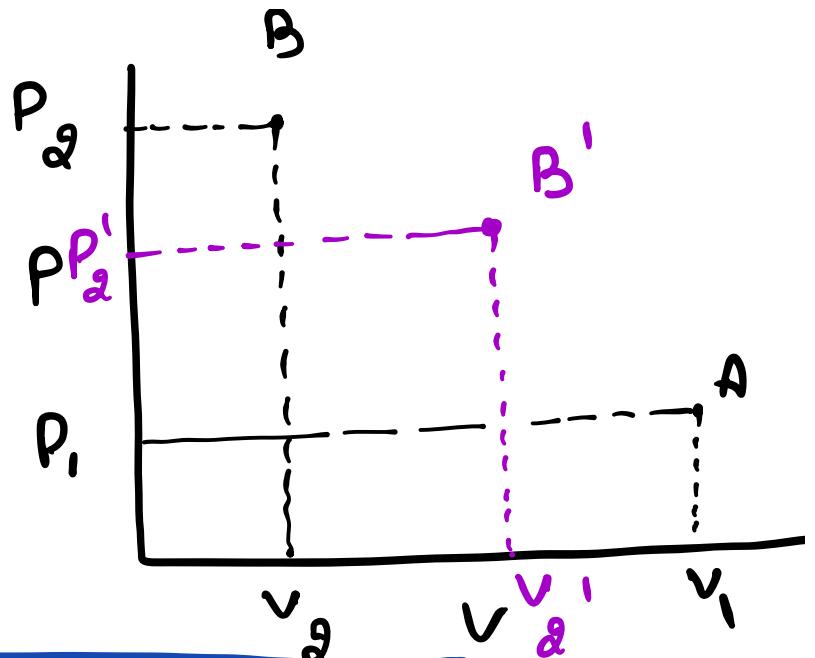
↓
Reversible Isothermal
Compression.

Single stage compression.

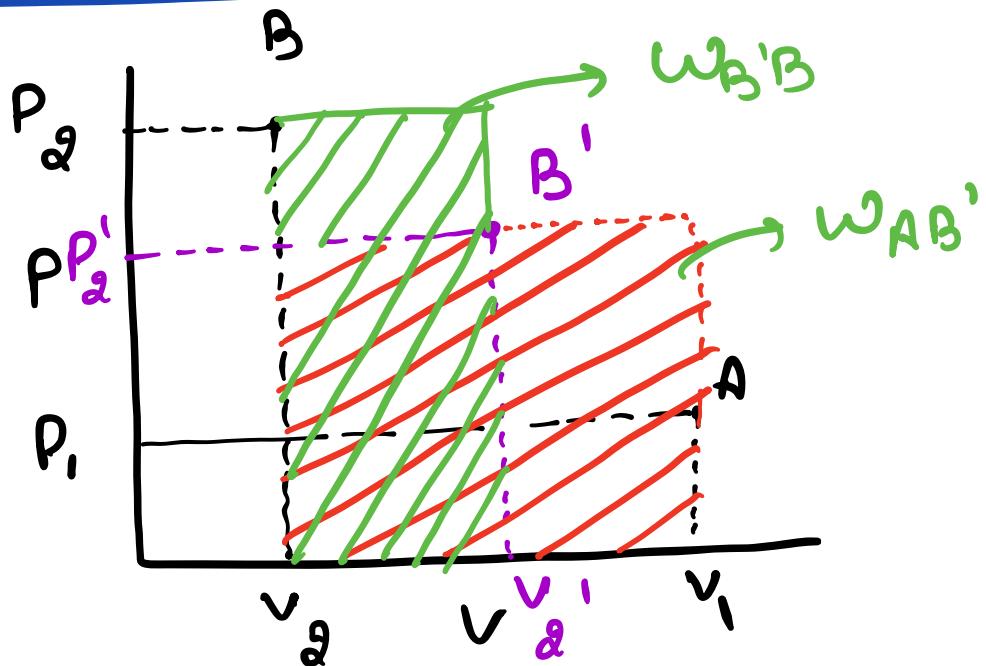
$$W_{\text{irr.}} > W_{\text{rever.}}$$

$$\omega_{AB} = \omega_{AB'} + \omega_{B'B}$$

$$= -P_g'(v_g' - v_i) + (-P_g(v_g - v_g'))$$



$$= -P_g'(v_g' - v_i) - P_g(v_g - v_g')$$



In Case of Isothermal Pre-reversible Compression as the no. of stages increases work done decreases

8 If no. of stages tends to infinite then

$$\omega_{\text{per stage}} = \omega_{\text{rever.}}$$

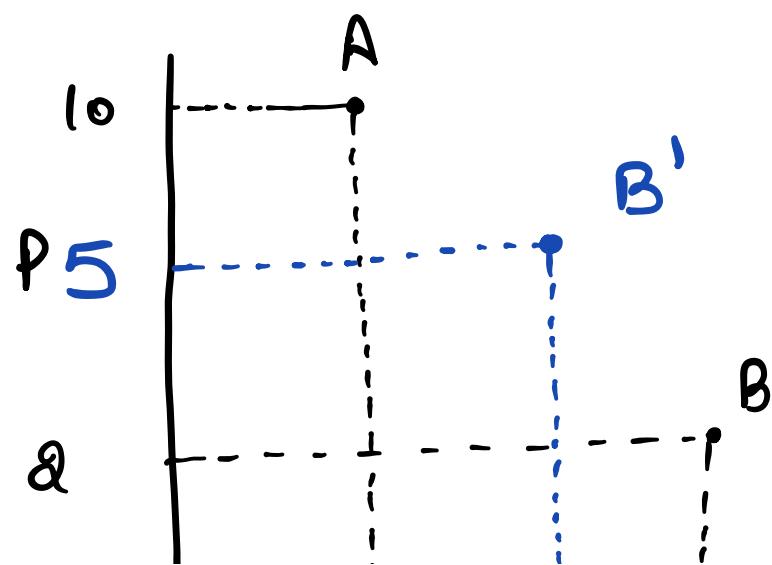
Ques. One mole of an ideal gas is expanded isothermally from (10 atm, 10 lit) to (2 atm, 50 lit.) first with external pressure of 5 atm then 2 atm. Determine the work done in each step & compare it with single stage expansion with external pressure 2 atm.

Soln.

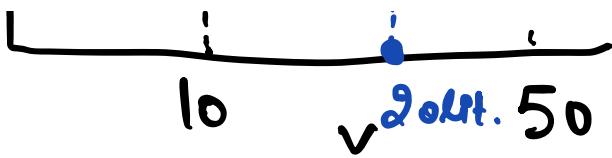
$$n = 1$$

$$P_1 V_1 = P_2 V_2$$

$$10 \times 10 = 5 \times V_2$$



$$V_2 = 20 \text{ lit}$$



$$\omega_{AB} = \omega_{AB'} + \omega_{B'B}$$

$$= -P_{ext}(V_2 - V_1) - P_{ext}(V_2 - V_1)$$

$$= -5(20 - 10) - 2(50 - 20)$$

$$\omega_{AB} = -110 \text{ lit. atm.}$$



two stage work.

for single stage

$$\omega_{AB} = -2(50 - 10)$$

$$\omega_{AB} = -80 \text{ lit. atm}$$

Imp.

~~# Adiabatic process :-~~

for adiabatic process

$$dq = 0$$

$$du = dq + dw$$

$$du = dw$$

for ideal gas $du = nC_V dT$

We know $dw = -P dv$

$$\Rightarrow nC_V dT = -P dv$$

We know that $C_P - C_V = R$

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

$$\Rightarrow n \frac{R}{\gamma-1} dT = - \frac{\gamma RT}{V} dv$$

$$\int_{T_1}^{T_2} \frac{dT}{T} = -(\gamma-1) \int_{V_1}^{V_2} \frac{dv}{v}$$

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

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

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

$PV^\gamma = \text{Const}$

$$T_2 \cdot V_2^{\gamma-1} = T_1 \cdot V_1^{\gamma-1}$$

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



valid for ideal gas
↔ reversible process

* work done for an adiabatic process

$$dq = 0 \quad \text{or} \quad q = 0$$

$$\Delta U = q + w$$

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

for ideal gas

$$w_{\text{rev}} = n c_v \Delta T$$

$$\boxed{= n c_v (T_2 - T_1)}$$

Here T_g is calculated with
the help of $P V^\gamma = \text{constant}$.

$$= n \cdot \frac{R}{\gamma-1} (T_2 - T_1)$$

$$= \frac{n R T_2 - n R T_1}{\gamma-1}$$

$$\boxed{w_{\text{rev}} = \frac{P_2 V_2 - P_1 V_1}{\gamma-1}}$$

\Rightarrow Irreversible adiabatic process :-

$$q_v = 0$$

$$\Delta U = \omega$$

for ideal gas

$$nC_V(T_g' - T_i) = \omega$$

\Rightarrow Calculation of T_g' :-

$$nC_V(T_g' - T_i) = \omega_{\text{ext}} = -P_{\text{ext}}(V_2 - V_1)$$

$$n \cdot \frac{R}{\gamma-1} (T_g' - T_i) = -P_{\text{ext}} \left[nR \frac{T_g'}{P_2} - nR \frac{T_i}{P_1} \right]$$

$$\frac{T_g' - T_i}{\gamma-1} = -P_{\text{ext}} \left[\frac{T_g'}{P_2} - \frac{T_i}{P_1} \right]$$

* T_g' is the final temp. of irreversible adiabatic process for both expansion and compression.

\Rightarrow for adiabatic expansion or

$$W_{\text{rev}} = n C_V (T_2 - T_1)$$

for expansion $W_{\text{rev}} < 0$

$$(T_2 - T_1) < 0$$

$$\boxed{T_2 < T_1}$$

* In case of adiabatic expansion temp. decreases

$$W_{\text{PXR.}} = n C_V (T_g' - T_1) < 0$$

$$T_2' - T_1 < 0$$

$$\boxed{T_2' < T_1}$$

* In case of adiabatic expansion temp. decreases.

* x for adiabatic compression o-

$$\omega = nC_V(T_2 - T_1) > 0$$

$$\boxed{T_2 > T_1}$$

In case of adiabatic compression temp. increases.

Note If it is written that a process is suddenly expanded then it means we are talking about an adiabatic process.

~~# Relation b/w T_2 & T_2' :-~~

$T_2 \rightarrow$ final temp. of reversible adiabatic process

$T_2' \rightarrow$ final temp. of irreversible adiabatic process.

for expansion :-

$$|\omega_{\text{irrev.}}| > |\omega_{\text{rev.}}|$$

$$|nC_v(T_2 - T_1)| > |nC_v(T_2' - T_1)|$$

$$T_1 - T_2 > T_1 - T_2'$$

$$\boxed{T_2' > T_2}$$

* final temp. of irreversible adiabatic expansion is greater than the final temp. of

reversible adiabatic expansion.

* for compression :-

$$\omega_{\text{reh.}} > \omega_{\text{rev.}}$$

$$n C_v (T_g' - T_1) > n C_v (T_2 - T_1)$$

$$\boxed{T_g' > T_g}$$

IIT

Ques:- 1 mole of monoatomic ideal gas is expanded adiabatically at T_K from 1 lit. to 2 lit. against constant external pressure 1 atm. Determine the final temp.

Soln :-

$$\omega = n C_v (T_g' - T_1) = - P_{\text{ext.}} (V_2 - V_1)$$

$$1 \times \frac{3}{2} [T_g' - T_1] = -1 (2-1)$$

$$T_2' - T_1 = -\frac{2}{3} R$$

$$T_2' = T_1 - \frac{2}{3} R$$

Ques - 1 mole of a mono linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm. Calculate the work done under the following conditions

- 1.) free expansion. ($P_{ext} = 0$)
- 2.) Reversible expansion.
- 3.) Irreversible expansion.

Soln - 1.) free expansion

$$P_{ext} = 0 \Rightarrow W = 0$$

2.) Reversible expansion

$$W_{\text{rever.}} = n C_V (T_2 - T_1)$$

$$P \cdot T^\gamma = \text{constant.}$$

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

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

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

$$P_1 = 16, \quad P_2 = 1 \quad \gamma = \frac{4}{3}$$

$$\boxed{\gamma = \frac{f}{2R}}$$

$$T_2 = \left(\frac{16}{1}\right)^{\frac{1-4/3}{4/3}} \times 300$$

$$T_2 = 150$$

$$w_{rev.} = nC_V (T_2 - T_1)$$

$$= 1 \times 3R (150 - 300)$$

$$w_{rev} = -450 R$$

3) Irreversible expansion :-

$$w_{irr.} = nC_V (T_2' - T_1)$$

$$w_{irr.} = nC_V (T_2' - T_1) = -P_{ext} (V_2 - V_1)$$

$$3R (T_2' - 300) = -P_{ext} nR \left[\frac{T_2'}{P_2} - \frac{T_1}{P_1} \right]$$

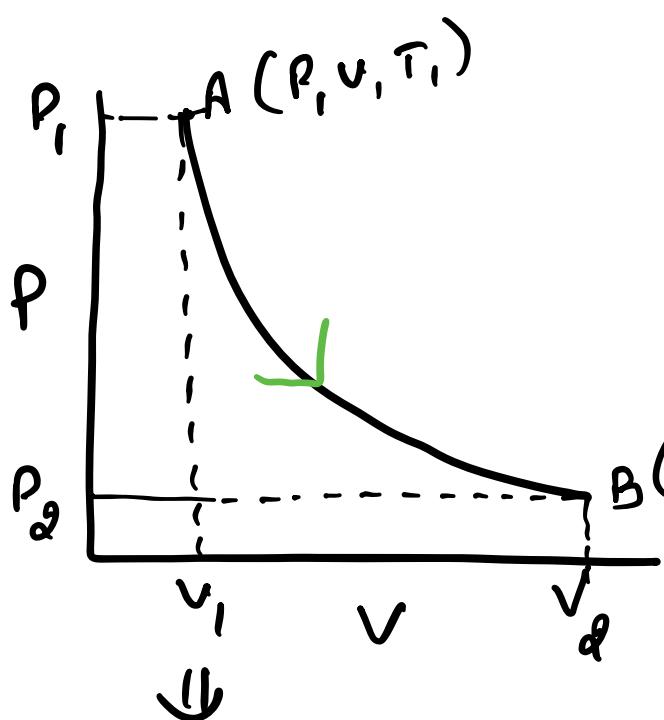
$$P_{ext} = 1 \text{ atm.}$$

$$3T_2' - 900 = -1 \left[\frac{T_2'}{1} - \frac{300}{16} \right]$$

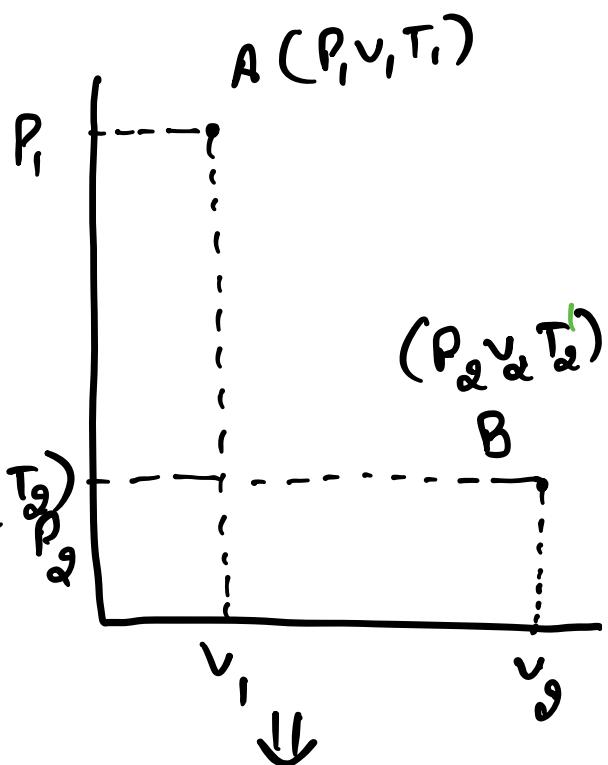
$$4T_2' = 900 + \frac{300}{16}$$

$$T_2' = 230 \text{ K}$$

** Graphs :-



Reversible
adiabatic
expansion.



Irreversible
adiabatic
expansion.

for Reversible adiabatic \rightarrow

$$P_2 V_2 = n R T_2$$

for reversible adiabatic \rightarrow

$$P_2 V_2 = n R T_2'$$

\Rightarrow

$$\boxed{T_2' > T_2}$$



As $P_2 V_2 = n R T_2'$ it means whether $P_2 = P_2'$ or $V_2 = V_2'$

such that

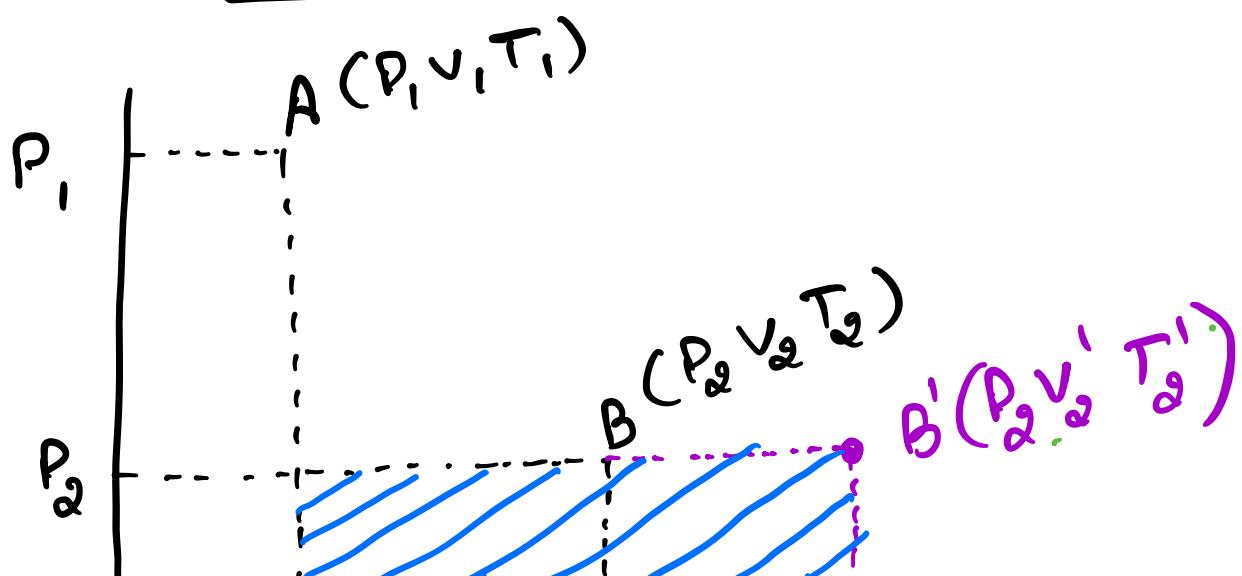
$$\boxed{P_2' > P_2}$$

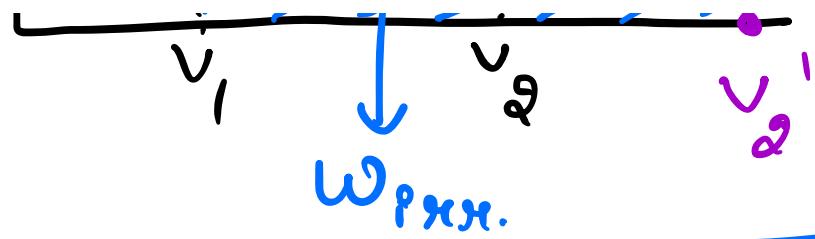
and

$$\boxed{V_2' > V_2}$$

let

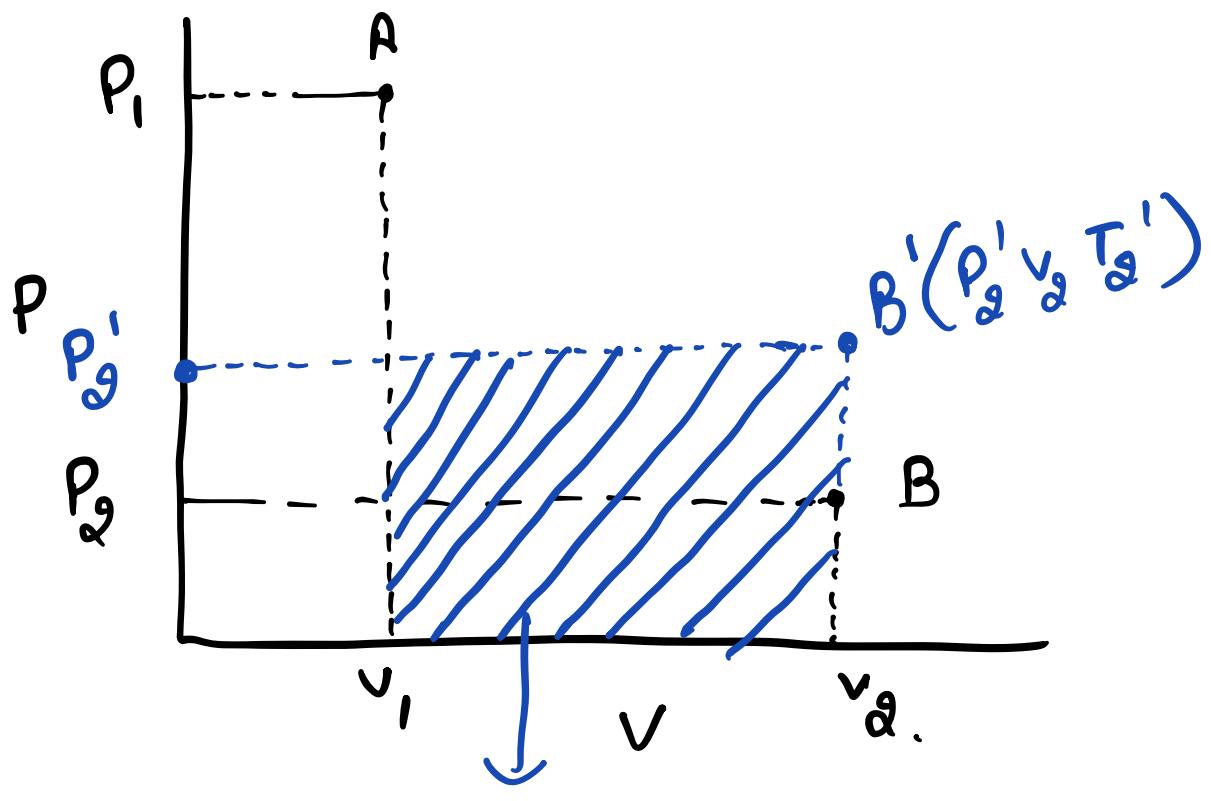
$$\boxed{P_2 V_2' = n R T_2'}$$





$$w_{pxx} = -P_g(v_2' - v_1)$$

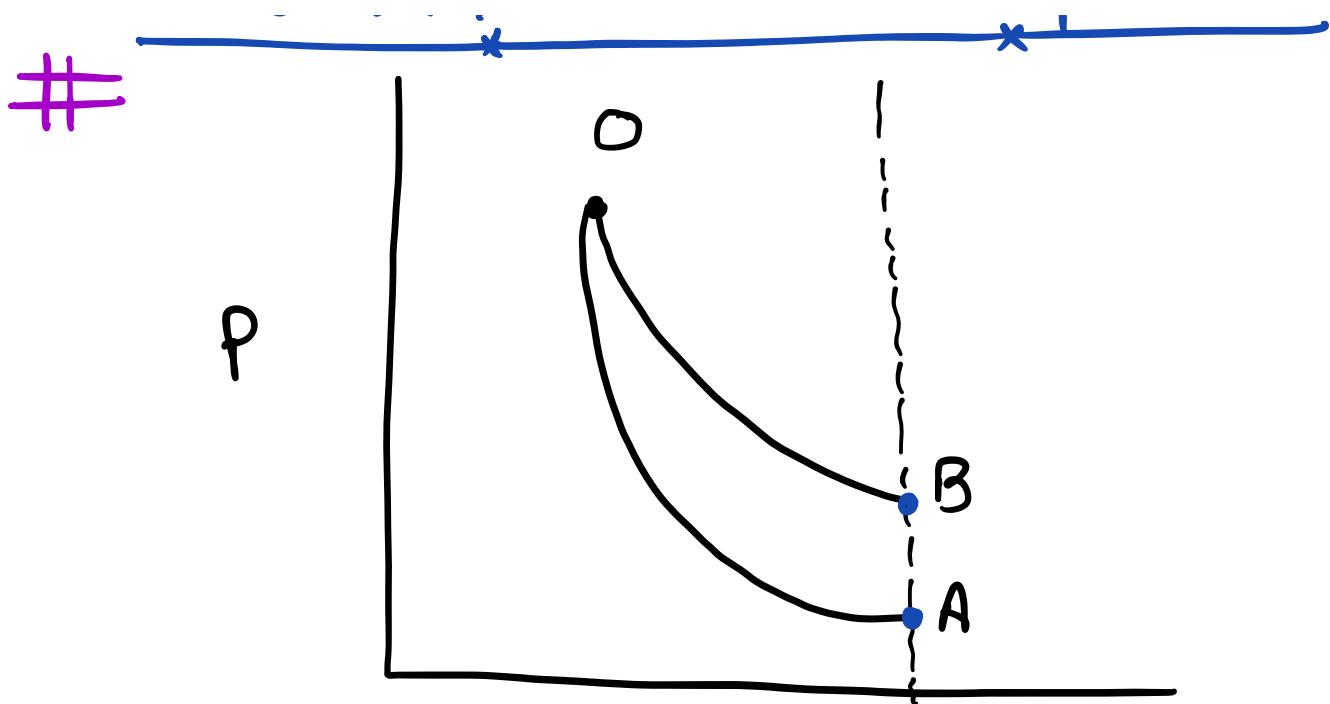
If $P_g'v_2 = mRT_g'$



w_{pxx} .

$$w_{pxx} = -P_g'(v_g - v_1)$$

Isothermal & Adiabatic expansion :-



At Const. volⁿ



$$P \propto T$$

It means that final temp. of process OB is greater.

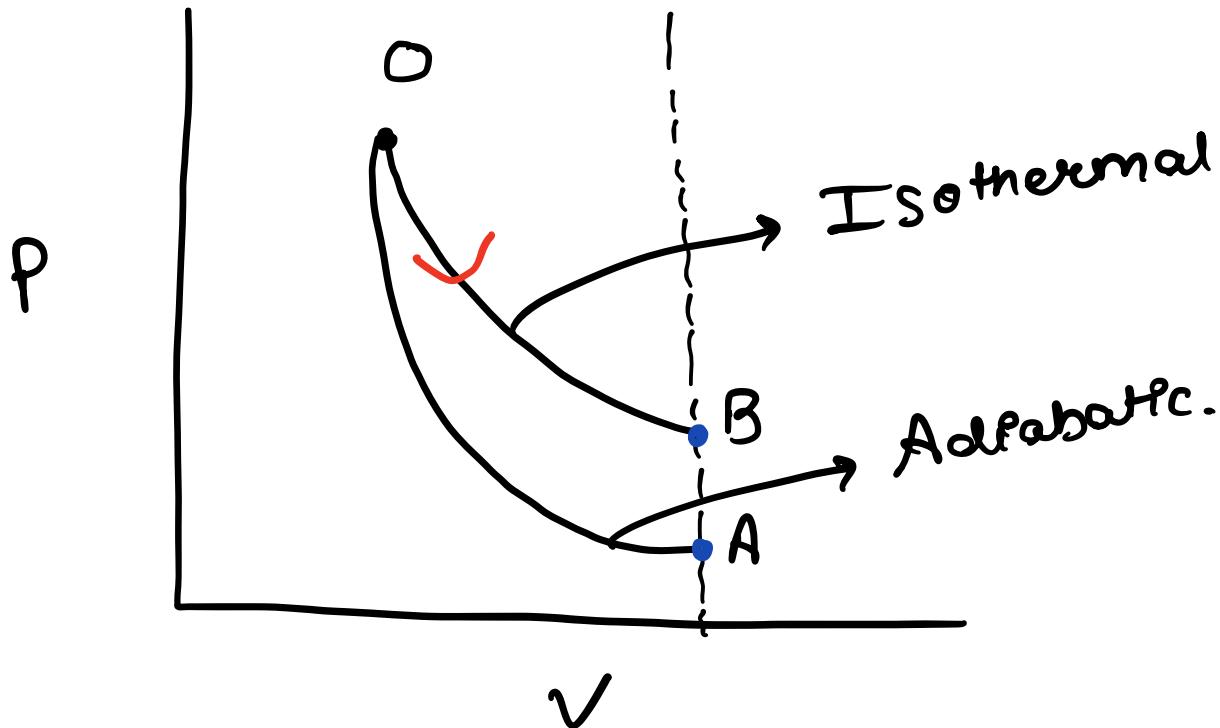
* Out of OA & OB which is isothermal & which is adiabatic?

We know that for an isothermal process

$$\Delta T = 0$$

$$\Delta T = 0$$

* For adiabatic expansion
final temp. decreases.

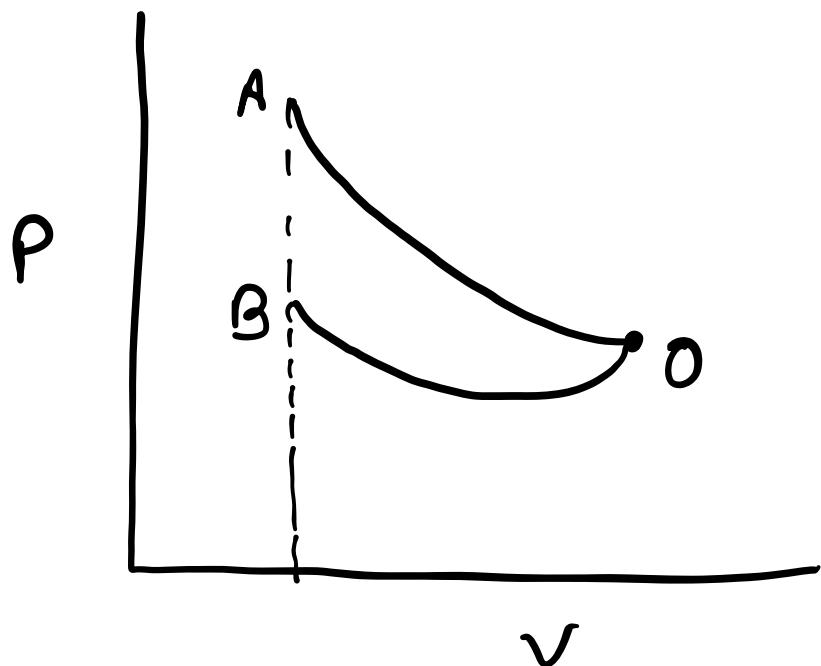


In case of isothermal expansion
temp. remains constant. But
in case of adiabatic expansion
temp. decreases therefore the
final temp. of isothermal
process is greater than
adiabatic expansion.

⇒ Isothermal & adiabatic compressions :-

At const.
vol^m

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



* We know that final temp. of adiabatic compression is greater than the final temp. of Isothermal Compressio.

O A → Adiabatic

O B → Isothermal.

Polytropic process :-

General formula for polytropic process

$$PV^\gamma = \text{Constant}$$

γ = Polytropic index.

If $\gamma=0 \Rightarrow$ Process will be isobaric.

$$P = \text{Constant}$$

If $\gamma=1 \Rightarrow$ Process will be isothermal.

$$PV = \text{Constant}$$

If $\gamma=\gamma \Rightarrow$ Process will be adiabatic.

$$PV^\gamma = \text{Constant}$$

$$\Rightarrow P^{\frac{1}{\gamma}} \cdot V = \text{Constant}$$

$$\text{If } \gamma=\infty \Rightarrow V = \text{Constant}$$

ISOCHORIC process

Work done of a polytropic process :-

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

Replace γ with α .

such that $\alpha \neq 1$

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

for ideal gas.

$$W = \frac{n R \Delta T}{\alpha - 1}$$

$$\alpha \neq 1$$

Molar heat capacity for polytropic process :-

* If C_m is the molar heat capacity of any process then

$$\boxed{q = n C_m \Delta T}$$

from f.L.O.T :-

$$\Delta U = q + w$$

for ideal gas.

$$\text{If } \Delta U = q + w$$

$$\Rightarrow n C_v \Delta T = n C_m \Delta T + \frac{n R \Delta T}{x-1}$$

$$C_v = C_m + \frac{R}{x-1}$$

* * *

$$\boxed{C_m = C_v + \frac{R}{1-x}}$$

Ques for diatomic ideal gas

$P^2 \propto T^3$ find C_m &
polytropic index.

Soln :- for polytropic process

$$PV^\gamma = \text{constant}$$

$$P^2 \propto T^3$$

$$\Rightarrow P^2 \cdot T^{-3} = \text{constant.}$$

$$PV = nRT$$

$$T = \frac{PV}{nR}$$

$$\Rightarrow P^2 \left[\frac{PV}{nR} \right]^{-3} = \text{constant}$$

$$P^2 (PV)^{-3} = \text{constant.}$$

$$P^{-1} \cdot V^{-3} = \text{constant.}$$

$$P V^3 = \text{Constant}$$

$$\boxed{\gamma = 3} \rightarrow \text{Polytropic Index.}$$

We know that

$$C_m = C_v + \frac{R}{1-\gamma}$$

$$C_v \text{ for diatomic gas} = \frac{5}{2} R.$$

$$C_m = \frac{5}{2} R + \frac{R}{1-3} \quad \left\{ C_v = \frac{5}{2} R \right\}$$

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

$$\boxed{C_m = 2 R.}$$

* If $C_m > 0 \Rightarrow \text{if } q > 0 \Rightarrow T \uparrow$

* If $C_m < 0 \Rightarrow \text{If } \gamma > 0 \Rightarrow T \downarrow$

If $1 < x < \gamma$

Then $C_m < 0$

$$C_m = C_v + \frac{R}{1-x}$$

Or

$$C_m = \frac{R}{\gamma - 1} - \frac{R}{x - 1}$$

\Rightarrow

$C_m < 0$

Que e $PV^{\frac{6}{5}} = \text{const.}$ for monat.
gas.

Soln $PV^{\frac{6}{5}} = \text{const.}$

$$\boxed{x = 1 \cdot 2}$$

$$C_m = \frac{3}{2} R + \frac{R}{1 - 1 \cdot 2}$$

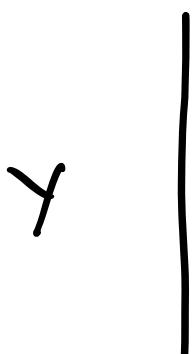
$$C_m = 1.5 R - 5R.$$

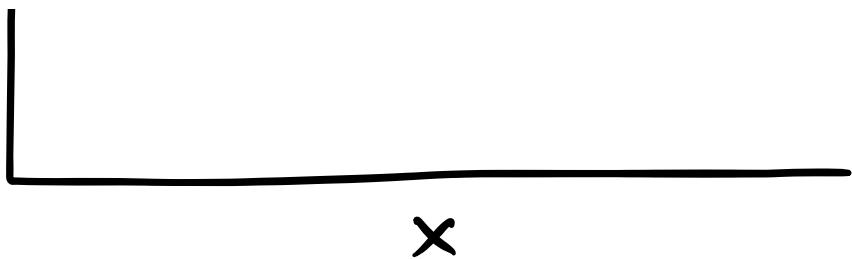
$$\boxed{C_m = -3.5 R}$$

Comparison b/w adiabatic & isothermal process :-

I.) Comparison of slope :-

let $\boxed{\gamma^m \cdot x^m = \text{Constant}}$





Slope $\Rightarrow \frac{dy}{dx}$

value of $\frac{dy}{dx}$ in terms of m
 n are.

$$\boxed{\frac{dy}{dx} = -\frac{n}{m} \cdot \frac{y}{x}}$$

* $y^m \cdot x^n \Rightarrow$ Curve



$$\boxed{\text{Slope} = -\frac{n}{m} \cdot \frac{y}{x}.}$$

* for PSO thermal process

$$PV = \text{Constant}$$



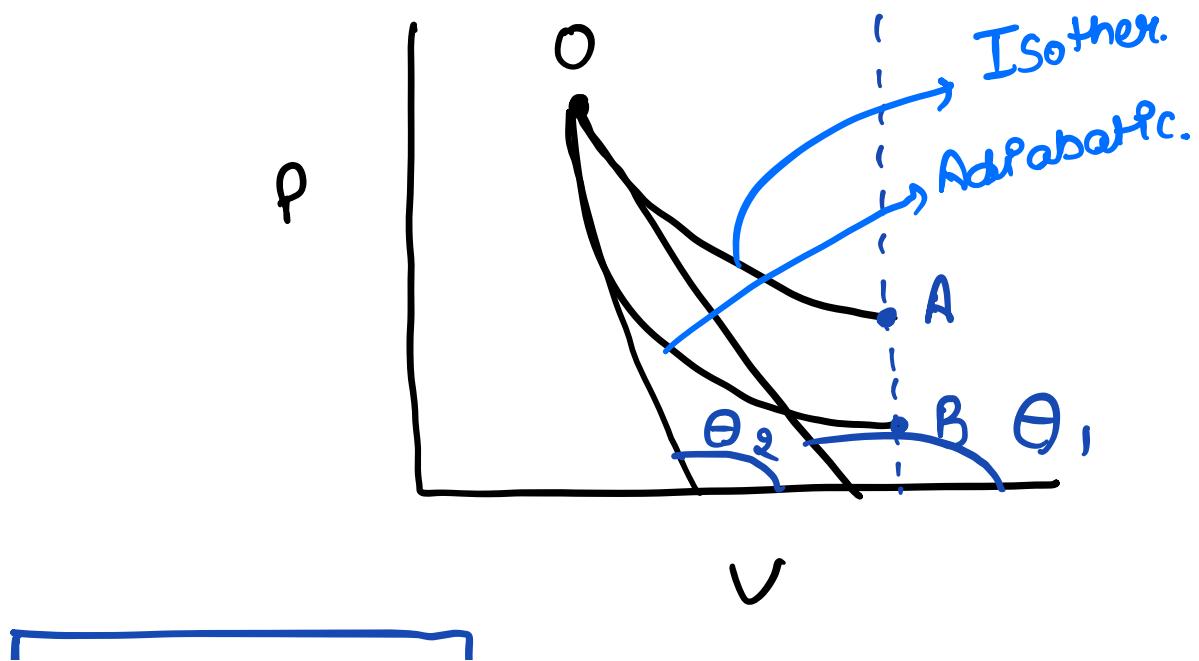
$$\boxed{\text{Slope} = - \frac{P}{V} = \frac{dP}{dV}}$$

* for adiabatic process.

$$PV^\gamma = \text{Const.}$$

$$\boxed{\text{Slope} = -\gamma \cdot \frac{P}{V}}$$

** for comparison of slope for adiabatic & isothermal process value of P & V should be same.



$$\boxed{\theta_1 > \theta_2}$$

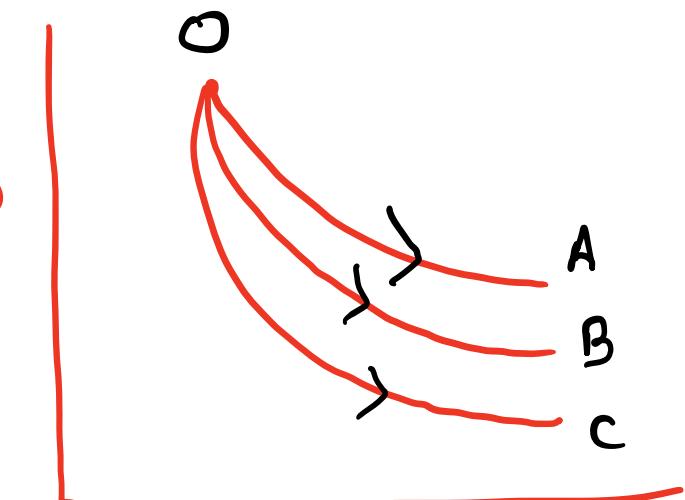
$$\boxed{\tan \theta_1 > \tan \theta_2}$$

* We know that $\tan \theta$ is an increasing function from 0 to 180°

Slope of Isothermal $>$ Slope of adiabatic.

Ques :-

for He, O₂ & O₃ three adiabates are drawn.



Predict that
which adiabate represents
which gas.

Solⁿ for an adiabatic process

$$Pv^{\gamma} = \text{constant}$$

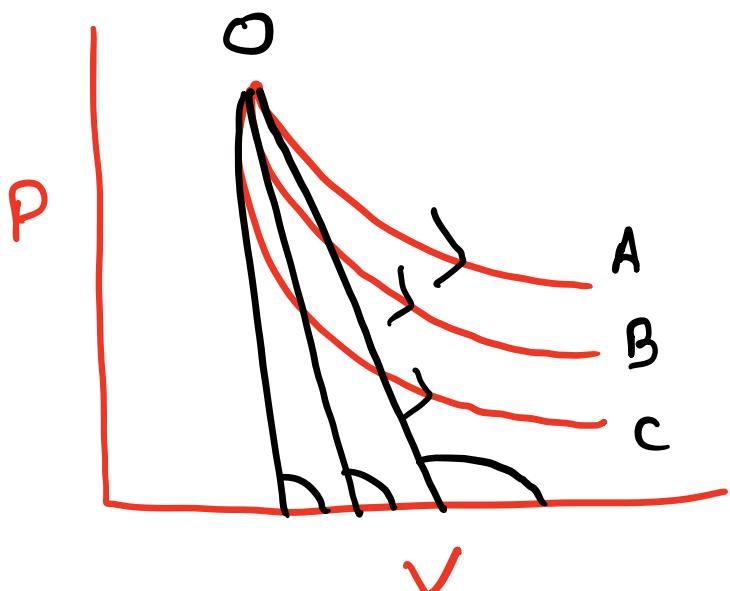
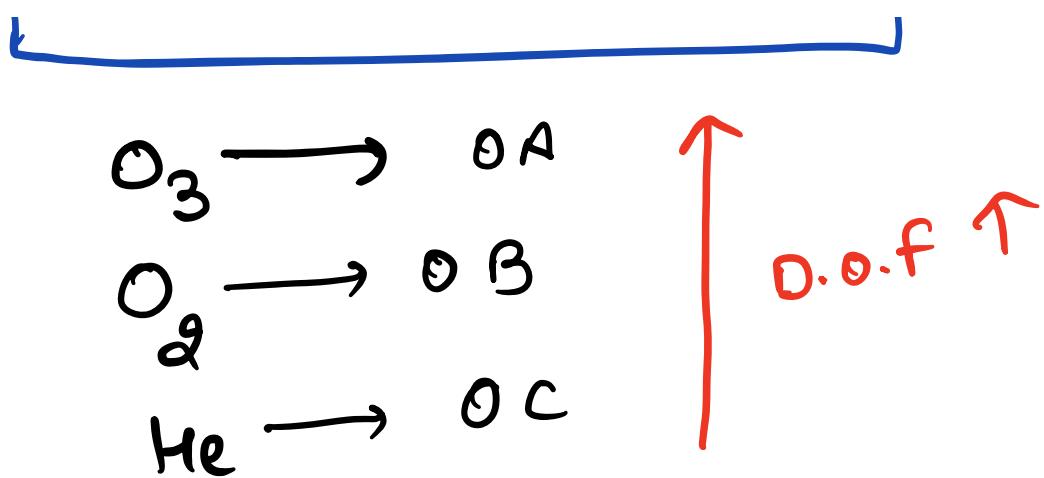
Slope = $-\gamma \cdot \frac{P}{v}$

$$\text{Slope} \propto \frac{1}{\gamma}$$

$$\gamma = 1 + \frac{\alpha}{f}$$

* * *
only translational
not rotational
D.O.F.

$$\text{Slope} \propto \frac{1}{\gamma} \propto f$$

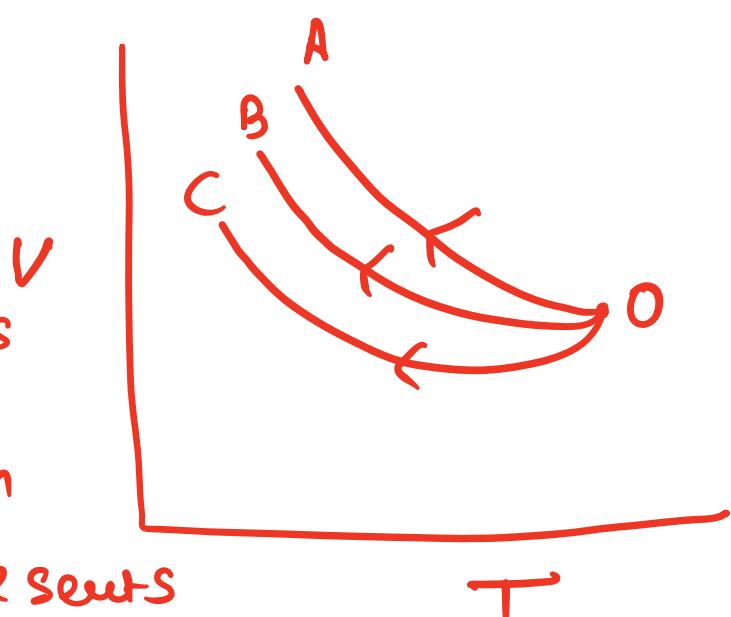


One σ

for He, O_2

& O_3 adiabates

are drawn
predict which
adiabate represents



which gas ?

Eqn for v-T diagram.

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

or

$$V^{\gamma-1} : T = \text{constant.}$$

$$y^m \cdot x^n = \text{constant}$$

$$\text{Slope} = -\frac{n}{m} \cdot \frac{y}{x}.$$

$$\text{Slope} = -\frac{1}{\gamma-1} \cdot \frac{V}{T}$$

$$\text{Slope} \propto T \propto \frac{1}{f}$$

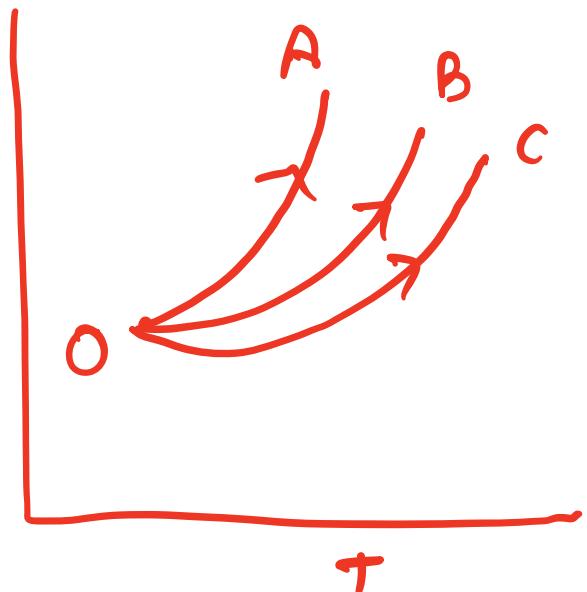
$OC \rightarrow$ He gas.

$OB \rightarrow O_2$ gas

$OA \rightarrow O_3$ gas.

Ques :-

Adiabates for
 O_3 , O_2 & He
are given, compare
which adiabate
will represent
which gas.



Soln :- $P^{1-\gamma} \cdot T^\gamma = \text{Constant}$.

$$Y^m \cdot X^n = \text{Constant}$$

$$\text{slope} = -\frac{n}{m} \cdot \frac{Y}{X}$$

$$\Rightarrow \text{slope} = -\frac{\gamma}{1-\gamma} \cdot \frac{P}{T}$$

$$\text{slope} = \frac{\gamma}{\gamma-1} \cdot \frac{P}{T}$$

$\text{slope} = \frac{1}{1 - \frac{1}{\gamma}} \cdot \frac{P}{T}$

$\text{slope} \propto \frac{1}{\gamma} \propto f.$

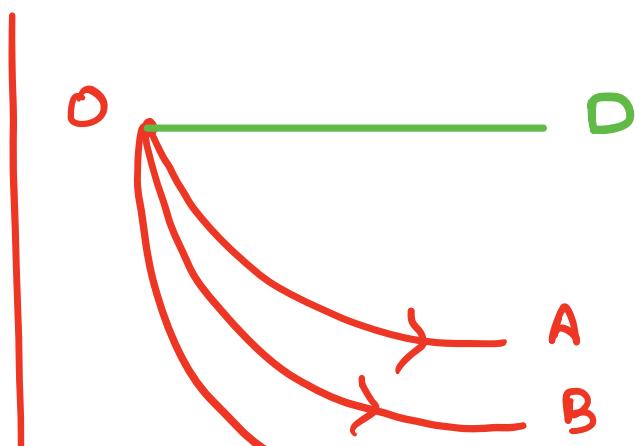
O A → O₃ gas.

O B → O₂ gas

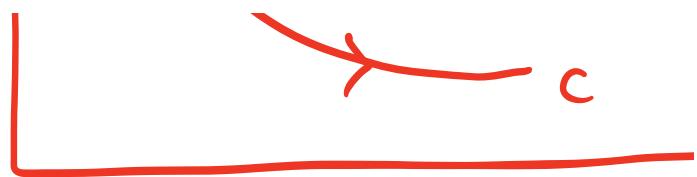
O C → He gas.

Trick

on the given
curve draw
a horizontal
line or a



vertical line
w.r.t. point O



And now keeping OD as
a base line, check the
curve which is nearest to
OD.

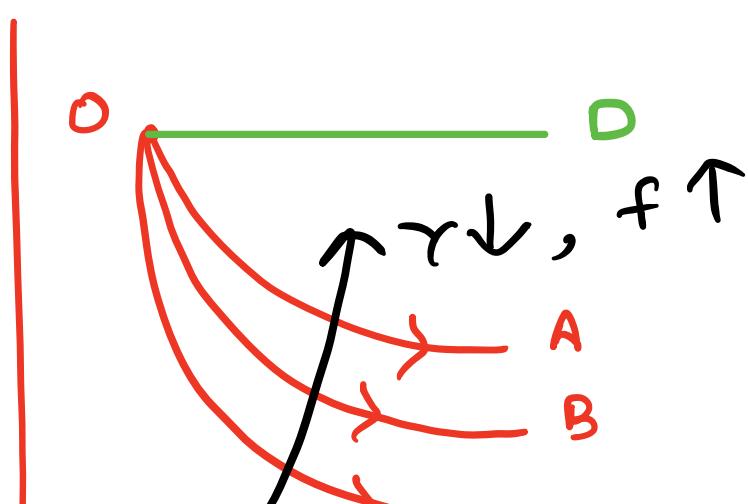
The curve which will be
nearest will have minimum
value of γ .

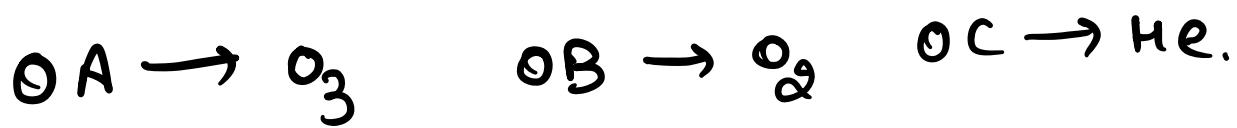
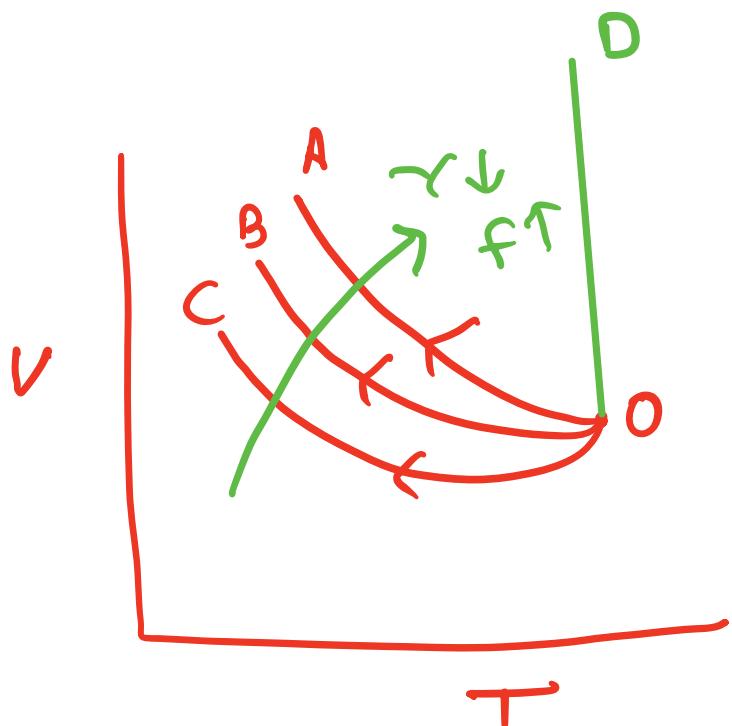
& we know that

$$r \propto \frac{1}{f}$$

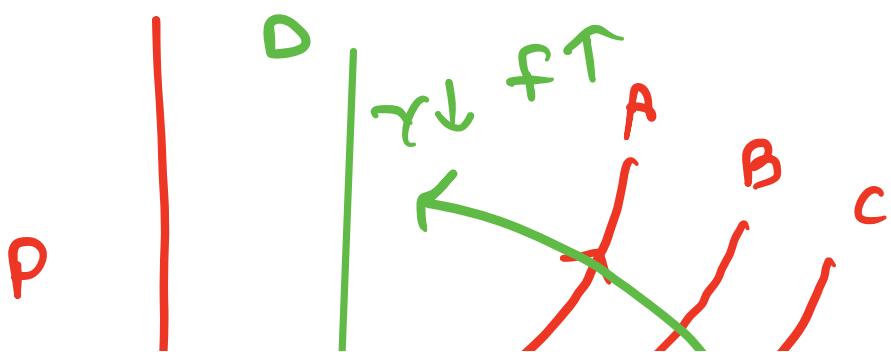
Hence minimum value

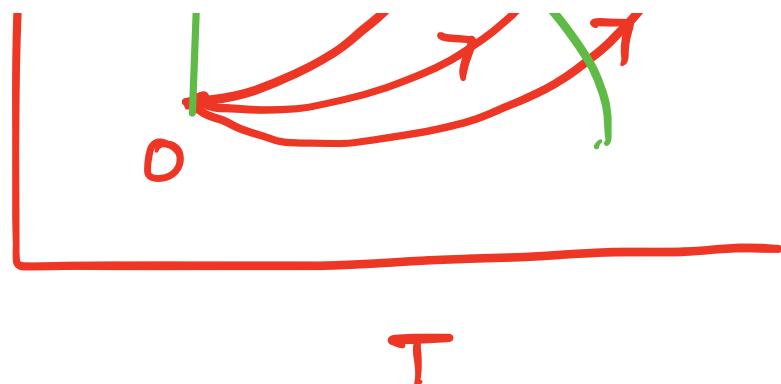
of γ means maxⁿ value of
f. i.e. Degree of freedom.





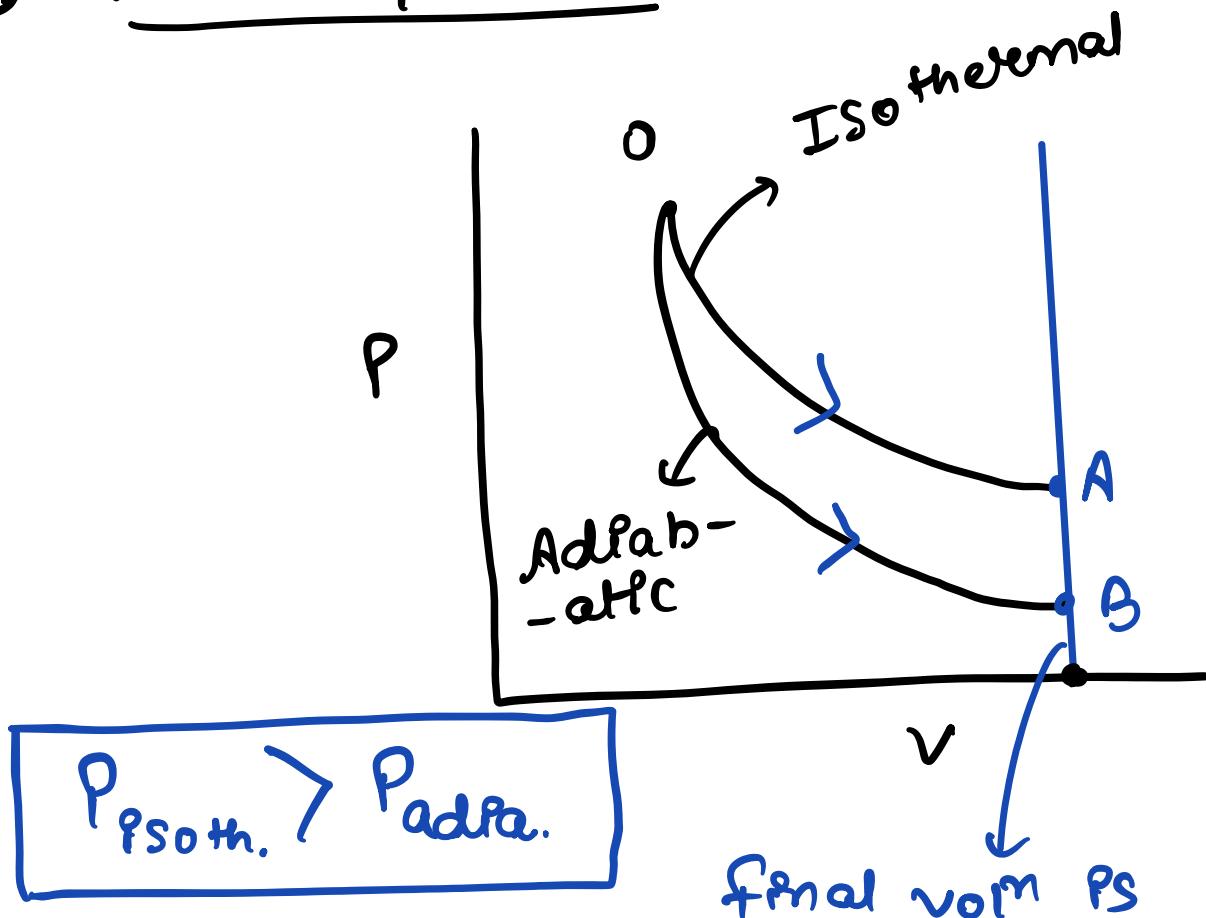
Que θ^-





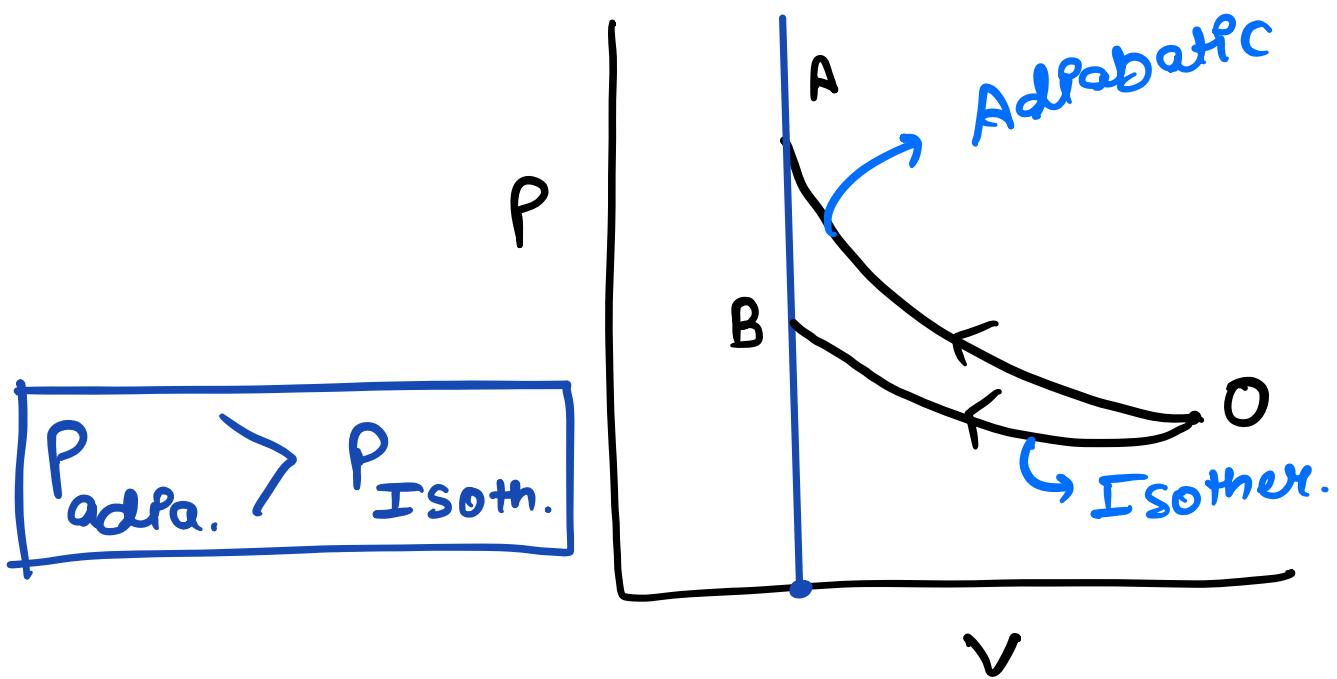
Q.) Comparison of final pressure if final vol^m PS same :-

@ for expansion :-



Same for
a diabatic &
isothermal
process.

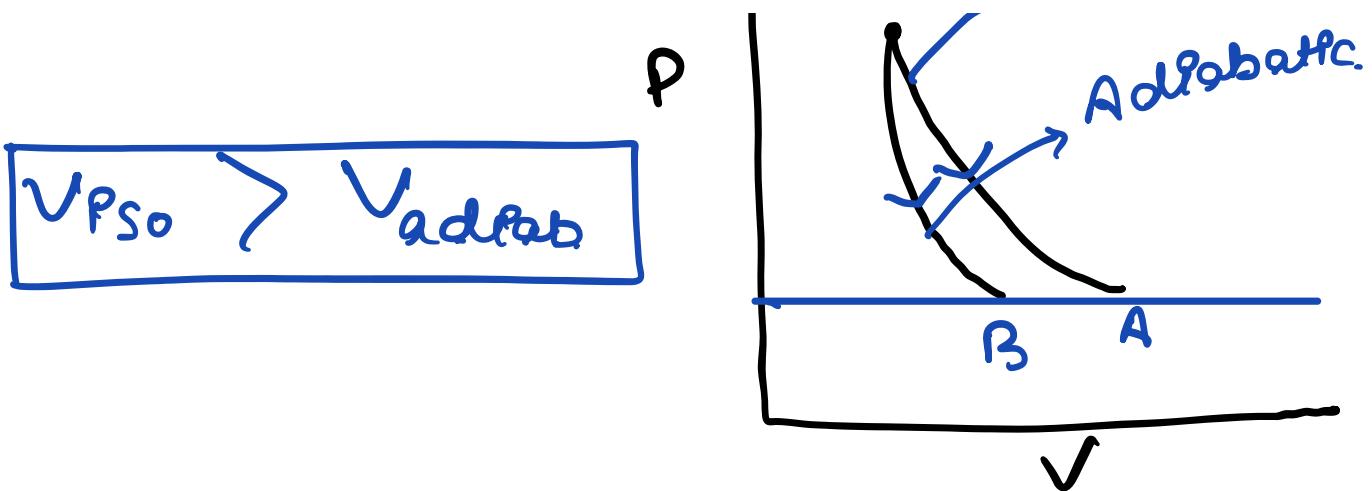
⑤ Compression :-



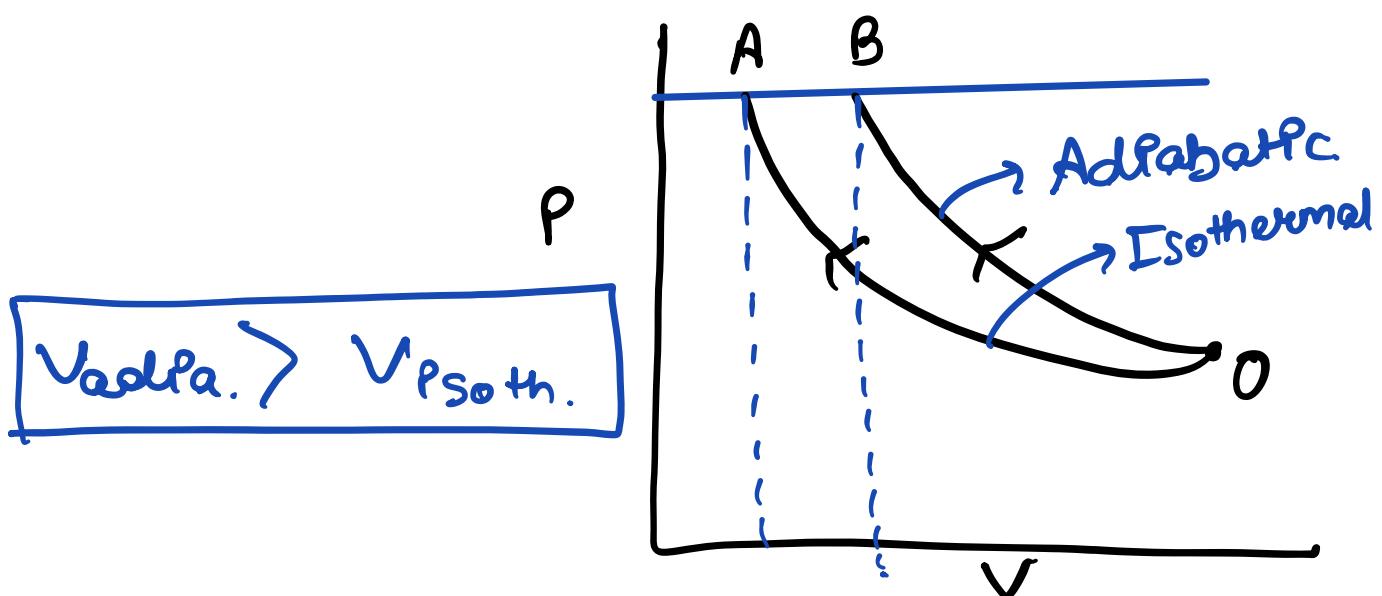
3.) Comparison of final volⁿ if
final pressure is same

⑥ Expansion :-





(b) Compression :-



Limitations of 1st law of thermodynamics :-

- i.) From 1st law of thermodynamics we cannot predict the feasibility of the process.

2) From 1st law of thermodynamics we cannot predict the information about the equilibrium.

3) From 1st law of thermodynamics we cannot predict the efficiency of the process.

Heat engine & heat pump :-

* Heat engine is a device which converts heat into work.

e.g. → electric motor

** Reservoir

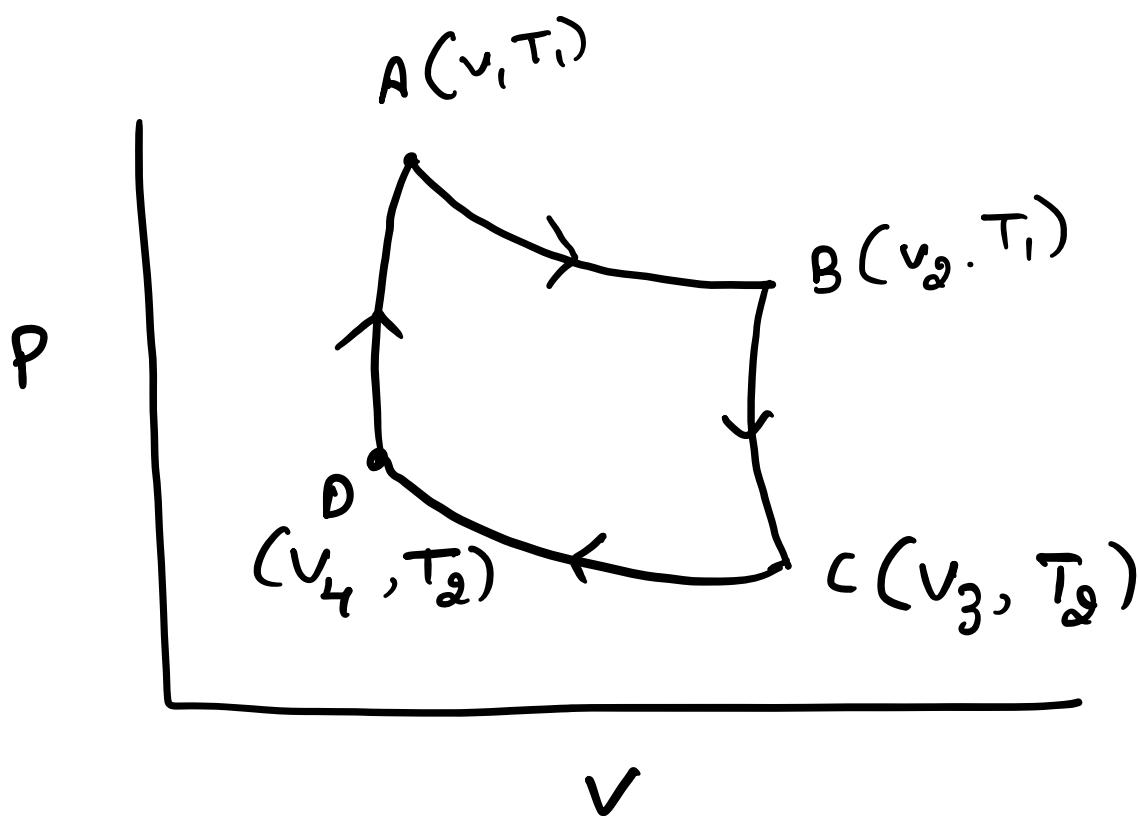
Reservoir is an infinite source of energy.

e.g. → Electric switch.

* * Heat pump is a device which converts work into heat.

e x → Refrigerator

Carnot Engine :-



$AB \rightarrow$ Reversible Isothermal expansion

$BC \rightarrow$ Adiabatic expansion.

CD → Isothermal compression.

DA → Adiabatic compression.

"In case of adiabatic expansion temp. decreases"

$$T_1 > T_2$$

for process AB :-

$$\Delta U = 0 \quad q_v = -w.$$

$$w_{AB} = -nR T_1 \ln \frac{V_2}{V_1}$$

$$q_{AB} = q_v = -w_{AB}.$$

$$q_v = nR T_1 \ln \frac{V_2}{V_1}$$

If q_v is +ve hence w

process AB system absorbs heat.

for process BC :-

$$q_{VBC} = 0 \quad \{ \text{Adiabatic} \}$$

$$\Delta U_{BC} = w_{BC}$$

$$w_{BC} = n C_V (T_2 - T_1)$$

for process CD :-

$$\Delta U = 0 \quad q_{VCD} = -w_{CD}.$$

$$w_{CD} = -n R T_2 \ln \frac{V_4}{V_3}$$

$$q_{VCD} + w_{CD} = 0$$

$$q_{VCD} = q_{V2}$$

$$q_{V2} = -n R T_2 \ln \frac{V_4}{V_3}$$

work
+
compression

- * For compression $w = +ve.$
- * As $q_{cd} = -ve$ it means in process CD heat is lost.

for process DA :-

$$q_{DA} = 0 \quad \{ \text{Adiabatic} \}.$$

$$\Delta U_{DA} = w_{DA}.$$

$$w_{DA} = n C_V (T_1 - T_2)$$

$$w_{\text{Total}} = w_{AB} + w_{BC} + w_{CD} + w_{DA}$$

$$= n R T_1 \ln \frac{V_2}{V_1} + n C_V (T_2 - T_1)$$

$$- n R T_2 \ln \frac{V_3}{V_4} + n C_V (T_1 - T_2)$$

$$w = -n R T_1 \ln \underline{\underline{V_2}} + n R T_2 \ln \underline{\underline{V_4}}$$

Total

v_1

v_3

* for BC & DA both are adiabatic.

$$\text{for } BC \rightarrow T_1 v_2^{\gamma-1} = T_2 v_3^{\gamma-1}$$

$$\text{for } DA \rightarrow T_1 v_1^{\gamma-1} = T_2 v_4^{\gamma-1}$$

On div? deng.

$$\boxed{\frac{v_2}{v_1} = \frac{v_3}{v_4}}$$

$$\Rightarrow \omega_{\text{Total}} = nR T_1 \ln \frac{v_2}{v_1} + nR T_2 \ln \frac{v_3}{v_4}$$

$$\boxed{\omega_{\text{Total}} = -nR (T_1 - T_2) \ln \frac{v_2}{v_1}}$$

$$\boxed{|\omega_{\text{Total}}| = nR (T_1 - T_2) \ln \frac{v_2}{v_1}}$$

Efficiency of Carnot engine
is independent of working substance

Efficiency (η) :-

It is the %age conversion of heat into work.

$$\eta = \frac{|\text{Work}_{\text{total}}|}{\text{Heat taken from Reservoir}} \times 100$$

$$= \frac{nR(T_1 - T_2) \ln \frac{V_2}{V_1}}{nR T_1 \ln \frac{V_2}{V_1}} \times 100$$

The diagram illustrates a Carnot cycle. A rectangular box labeled "Source" contains the temperature T_1 . An arrow labeled Q_1 points from this box down to a circle labeled "H.E." (Heat Engine). From the "H.E." circle, an arrow labeled Q_2 points down to a rectangular box labeled "Sink" containing the temperature T_2 . A curved arrow labeled "Reservoir" points from the "Sink" box back up to the "Source" box.

$$\eta = \left(1 - \frac{T_2}{T_1} \right) \times 100$$

* valid only for ideal gas and for reversible Carnot engine.

$$w = q_1 + q_2$$

Because q_2 is the heat released by the system.

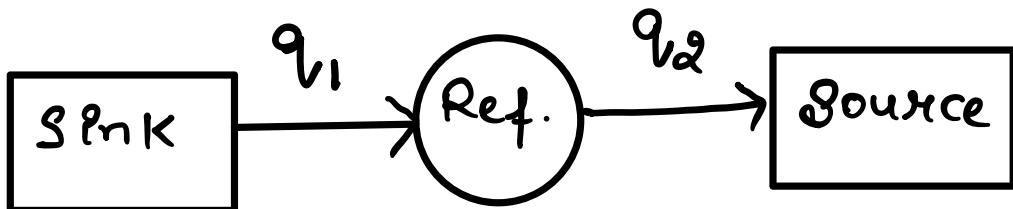
$$w = q_1 - q_2$$

$$\begin{aligned}\eta &= \frac{q_1 + q_2}{q_1} \times 100 \\ &= \left(1 + \frac{q_2}{q_1} \right) \times 100\end{aligned}$$

$$\eta = \left(1 - \frac{|q_2|}{q_1} \right) \times 100$$

valid for all.

Coefficient of performance
of a refrigerator :-



$q_{l1} \rightarrow q_{l_n} \rightarrow$ High temp.

$q_{l2} \rightarrow q_{l_c} \rightarrow$ Low temp.

$$\text{C.O.P} = \frac{q_{l_c}}{|w|}$$

$$\frac{q_{l_c}}{|w|} = \frac{q_{l_c}}{|q_{l_n} - q_{l_c}|}$$

Acc. to Carnot's cycle efficiency
can be

$$\eta = 1 - \left| \frac{q_{l_c}}{q_{l_n}} \right|$$

$$\Rightarrow \left| \frac{q_{lc}}{q_h} \right| = 1 - \eta$$

$$C.O.P = \frac{q_c}{q_h(1 - \frac{q_c}{q_h})}$$

$$C.O.P = \beta = \frac{1 - \eta}{\eta}$$

\Rightarrow Significance of C.O.P :-

* If the C.O.P of the refrigerator is 3 then means motor of 1 watt of refrigerator will produce 3 watt cooling.

2nd law of thermodynamics

1.) Kelvin Plank statement :-

It is impossible for a heat engine operating on a cyclic process, connected with a single reservoir to produce work done.

Single reservoir → Temp. of both source and sink is same.

2.) Clausius statement :-

It is impossible for a heat engine operating on a cyclic process to produce work done without simultaneous transfer of heat from higher temp. to lower temp.

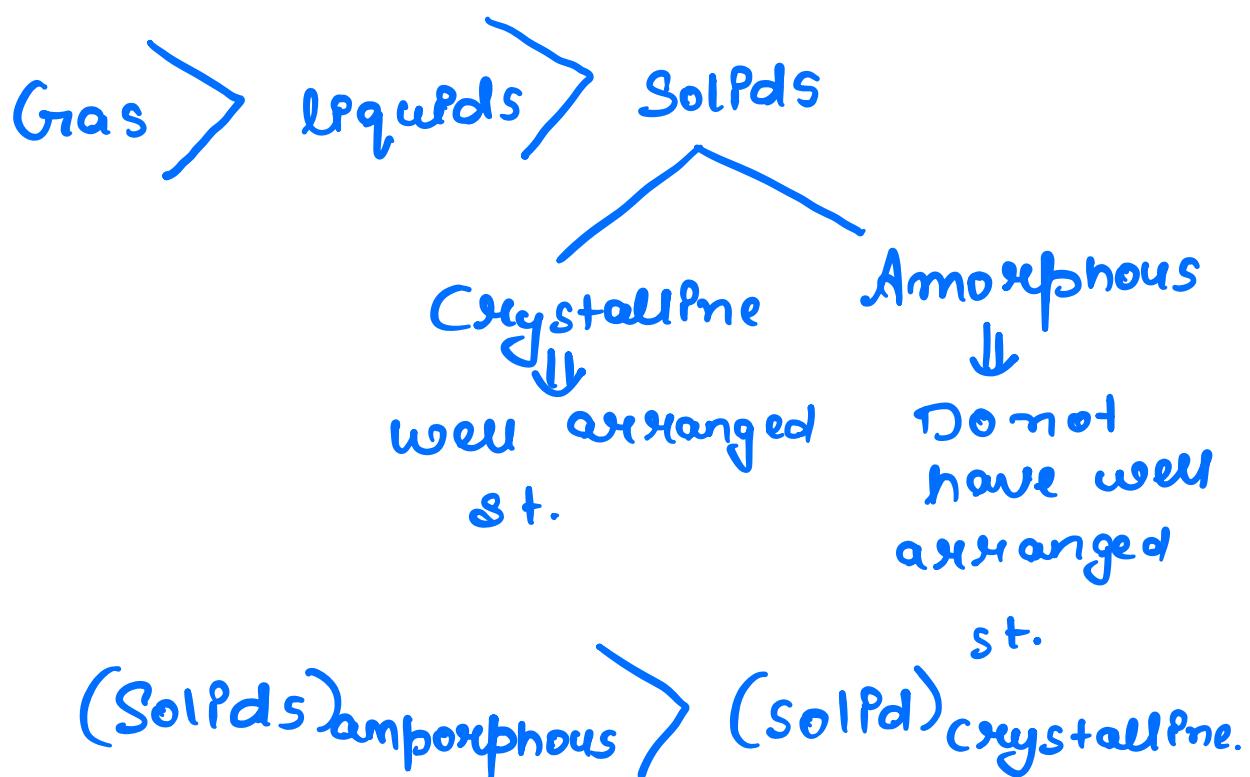
Conclusion

It is impossible for a heat engine to convert heat into work with 100% efficiency.

This means there is no engine in this world which has 100% efficiency.

~~Imp.~~ Concept of entropy (S) :-

* Entropy is a direct measurement of randomness or disorderness.



\Rightarrow for reversible Carnot eng fine :-

$$\eta = 1 - \frac{T_2}{T_1} = 1 + \frac{q_2}{q_1}$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

$$\boxed{\sum \frac{q_p}{T_p} = 0} \Rightarrow \text{for cyclic process.}$$

$$\oint d\left(\frac{q}{T}\right) = 0$$

$$\oint d\left(\frac{q_{\text{reversible}}}{T}\right) = 0$$



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



for a cyclic process

$$dS = 0$$

$\Rightarrow S$ is a state function.

$$dS = \frac{dq_{\text{reversible}}}{T}$$



- * mathematical definition of entropy.

- * Valid only for reversible process

- * If $dq_{\text{reversible}} = \text{Constant}$.

$$\int_{S_1}^{S_2} dS = \int \frac{dq_{\text{rever.}}}{T}$$

$$\Delta S = \frac{q_{\text{reversible}}}{T}$$



- * When q is not a

function ^{Irrever.} of temperature.

- * If $q_{\text{irreversible}}$ is the function of temp.

$$d q_{\text{irreversible}} = n C dT$$

$$\Rightarrow \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} nC \frac{dT}{T}$$

$$\boxed{\Delta S = n C \ln \frac{T_2}{T_1}} \quad * * *$$

** Entropy always increases
in %

1.) Boiling.



2.) Sublimation.

Solid \rightleftharpoons Gas.

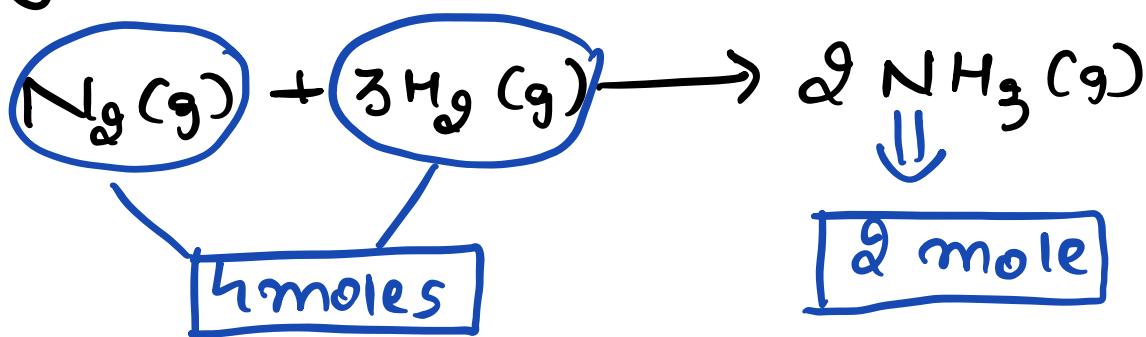
- 3.) The chemical rxns for which Δn_g is greater than zero.



$$\boxed{\Delta n_g = 1} \Rightarrow \boxed{\Delta S > 0}$$

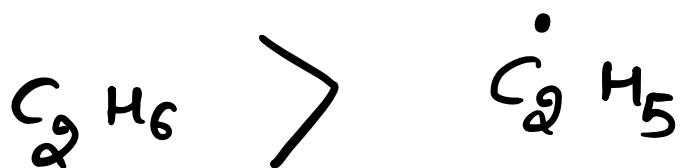
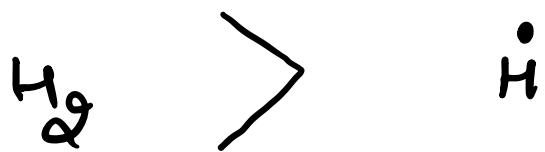
- 4.) Isothermal expansion of gas.

- 5.) Mixing of non reacting gases.



- 6.) On heating entropy increases.
(condition is $C > 0$)

** Entropy also depends upon the complexity of the molecule.



* Dominating factor for entropy is no. of moles of gas.



[$S \propto$ molecular weight]

Change in entropy for a chemical rxn. :-

* for any chemical rxn

$$\Delta_H S = \Delta S(\text{Products}) - \Delta S(\text{Reactants})$$



$$\Delta_H S = 2 \cdot \Delta S(NH_3) - \Delta S(N_2) - 3 \Delta S(H_2)$$

Entropy change for ideal gas:-

$$dU = dq + dw$$

$dS = \frac{dq_{rev}}{T}$

$$nC_v dT = T \cdot ds - Pdv$$

$$nC_v dT + Pdv = T \cdot ds.$$

$$nC_v \frac{dT}{T} + \left(\frac{P}{T} \right) dv = ds$$

$$nC_v \frac{dT}{T} + \frac{nR}{V} dv = ds.$$

$$S_{2r} \quad \int_{T_1}^{T_2} \quad V_{2r}$$

$$\int_{S_1} dS = \int_{T_1} n C_V \frac{dT}{T} + \int_{V_1} n R \cdot \frac{dV}{V}$$

$$\Delta S = n C_V \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1}$$

* * * =

* for ideal gas $P_1 V_1 = n R T_1$
 $P_2 V_2 = n R T_2$

$$\Rightarrow \Delta S = n C_V \ln \frac{T_2}{T_1} + n R \ln \frac{P_1 T_2}{P_2 \cdot T_1}$$

$$= n C_V \ln \frac{T_2}{T_1} + n R \ln \frac{T_2}{T_1} + n R \ln \frac{P_1}{P_2}$$

$$= n (C_V + R) \ln \frac{T_2}{T_1} + n R \ln \frac{P_1}{P_2}$$

* * *

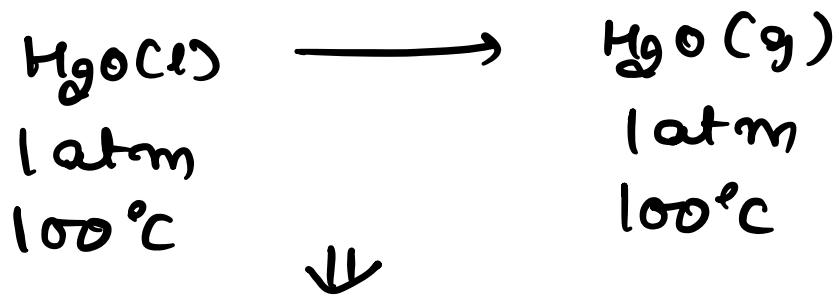
$$\boxed{\Delta S = n C_P \ln \frac{T_2}{T_1} + n R \ln \frac{P_1}{P_2}}$$

T_1

T_2 .

Entropy change for reversible phase transition :-

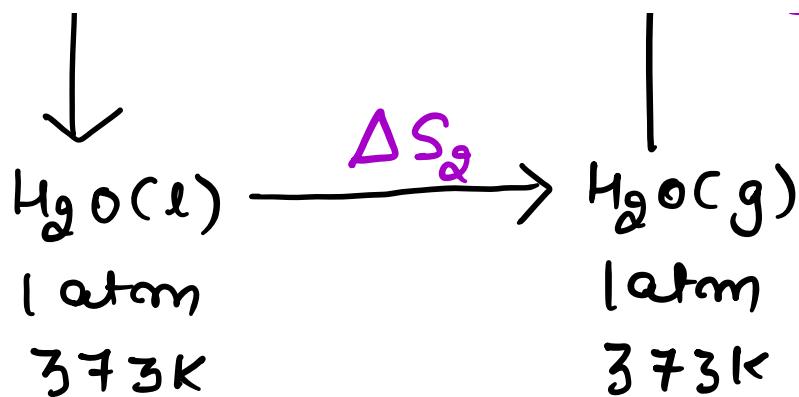
* Every state transition is a phase transition but reverse is not always true.



$$\Delta H = \Delta H_{\text{vapourisation}}$$

$$dS = \frac{dq_{\text{reversible}}}{T}$$

$$\boxed{\Delta S = \frac{\Delta H_{\text{vapourisation}}}{373}}$$



$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

* In order to determine the entropy change for irreversible process break the irreversible process into some equivalent reversible processes. Because entropy is a state function therefore entropy change for equivalent reversible process is equal to the entropy change for irreversible process.

$$\Delta S_1 = n C_p (\text{H}_2\text{O(l)}) \ln \frac{T_2}{T_1}$$

$$\Delta S_1 = C_p \ln \frac{373}{273}$$

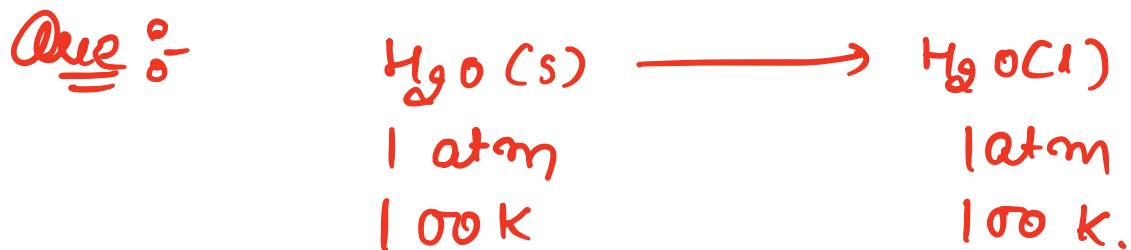
500

$$\Delta S_g = \frac{\Delta H_{\text{vapourisation}}}{373}$$

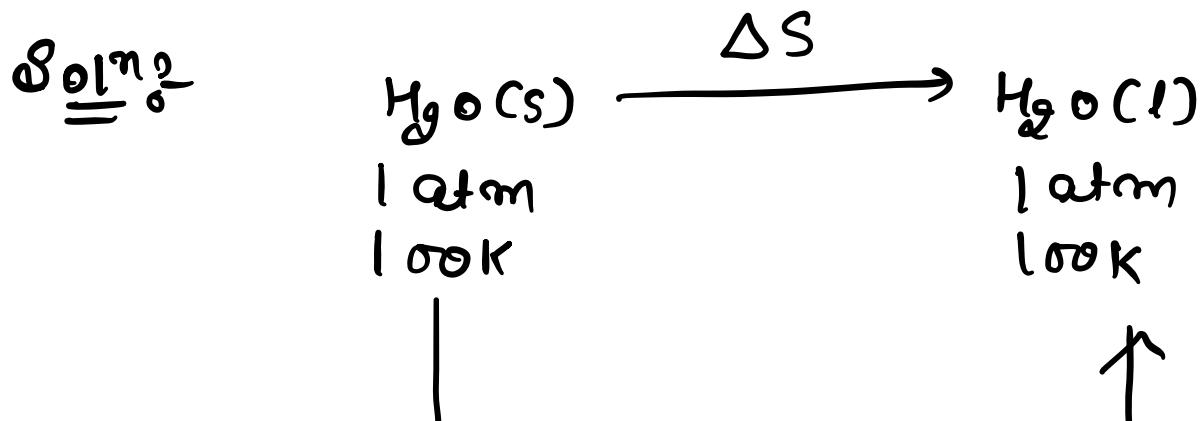
$$\Delta S_3 = n C_p \ln \frac{T_2}{T_1}$$

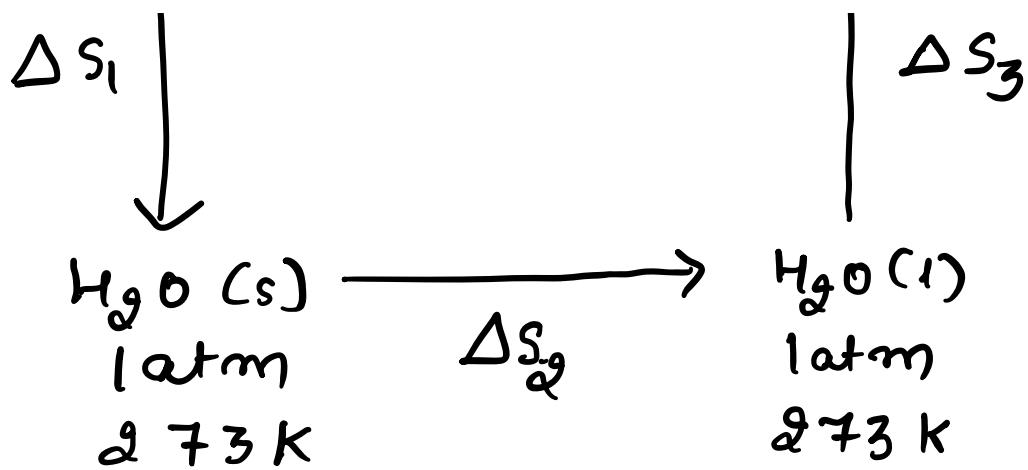
$$\Delta S_3 = C_p \ln \frac{300}{373}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$



Find ΔS for the process.





$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_1 = n C_p_{\text{H}_2\text{O (s)}} \ln \frac{T_2}{T_1}$$

$$\Delta S_1 = C_p \ln \frac{273}{100}$$

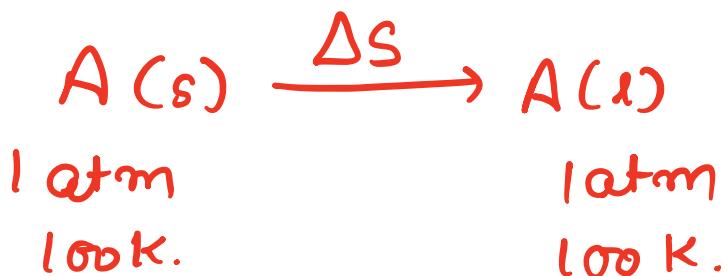
$$\Delta S_2 = \frac{\Delta H_{\text{fusion}}}{273}$$

"for solid or liquid values of C_p and C_v are same".

$$\Delta S_3 = n C_p \ln \frac{T_2}{T_1}$$

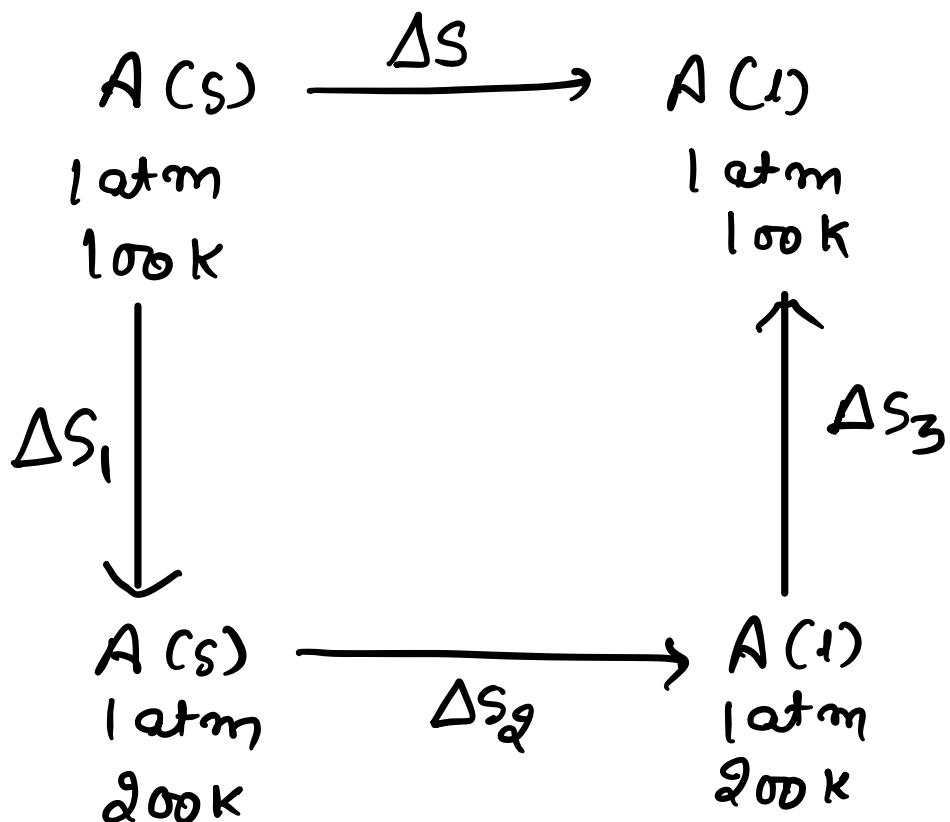
$$\Delta S_3 = C_p \ln \frac{100}{273}$$

Ques :-



melting point of $A(s)$ is 200 K
find ΔS .

Ques :-



$$\Delta S = \Delta S_1 + \Delta S_g + \Delta S_3$$

Spontaneous and non spontaneous process :-

- * The process which can takes place without any external agent then process is k/A spontaneous process.
- * The process which occurs with the help of external agent is k/A non spontaneous process.

Conditions for a spontaneous & a non spontaneous process :-

$$\Delta S_{\text{System}} =$$

$$\frac{q_{\text{reversible}}}{T}$$

only for reversible process.

$$\Delta S_{\text{Surroundings}} = - \frac{q_{\text{System}}}{T}$$

All types of process e.g.
for reversible as well as irreversible.

Universe = System + Surroundings

$$\Delta S_{\text{Universe}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$$



At Constant Temp. & Pressure.

$$\Delta S_{\text{Universe}} = \Delta S_{\text{System}} - \frac{q_{\text{System}}}{T}$$

At Constant Pressure

$$q_{\text{system}} = \Delta H_{\text{system}}$$

$$\Rightarrow \Delta S_{\text{universe}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

$$\Delta S_{\text{universe}} = - \frac{[\Delta H - T \Delta S]}{T}$$

$$G = H - TS$$

OR

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

$$\Rightarrow \Delta S_{\text{universe}} = - \frac{\Delta G}{T}$$

$\Delta G < 0$ for spontaneous process :-

$$\Delta G < 0$$

$$\Delta S_{\text{universe}} > 0$$

"Spontaneity of a process depends only upon $\Delta S_{\text{universe}}$ "

* for non spontaneous process :-

$$\Delta G > 0$$

$$\Delta S_{\text{universe}} < 0$$

** At equilibrium

$$\Delta G = 0 \quad \Delta S_{\text{universe}} = 0$$

Entropy change for different thermodynamic process :-

for an ideal gas :-

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

1. > Isochoric process :-

$$\Delta S_{\text{System}} = n C_v \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{Surround.}} = - \frac{q_{\text{System}}}{T_{\text{Surround.}}}$$

for Isochoric process

$$\Delta S_{\text{Surround.}} = - \frac{q_{\text{lv}}}{T}$$

$$q_{\text{lv}} = n C_v \Delta T \quad \text{Temp. of system.}$$

$$\Rightarrow \Delta S_{\text{Surround.}} = - \frac{C_v (T_2 - T_1)}{T_{\text{Surround.}}}$$

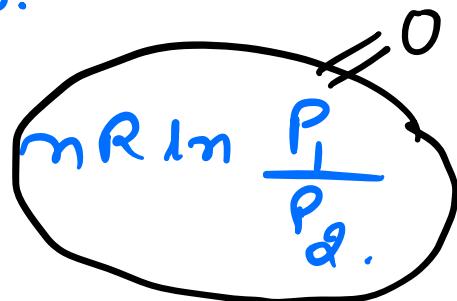
$$\Delta S_{\text{Universe}} = n C_v \ln \frac{T_2}{T_1} - n \frac{C_v (T_2 - T_1)}{T_{\text{Surround.}}}$$

2) Isobaric process :-

$$\Delta S_{\text{system}} = nC_p \ln \frac{T_2}{T_1}$$

for an ideal gas.

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



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

At Constant pressure.

$$q = q_{\text{p}} = nC_p \Delta T$$

$$\Rightarrow \Delta S_{\text{surr.}} = -\frac{nC_p(T_2 - T_1)}{T_{\text{surr.}}}$$

3) Isothermal process :-

Q) free expansion :-

for free expansion $P_{ext} = 0$

* free expansion is an irreversible process.

$$\Delta S_{\text{System}} = - \frac{\cancel{q_{\text{irreversible}}}}{T}$$

We know that for an ideal gas

$$\Delta S = nC \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{System}} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{Surx}} = - \frac{\underline{q_{\text{System}}}}{\underline{T}_{\text{Surx}}} = 0$$

∴ for free expansion of an ideal gas $q_r = 0$
 $\omega = 0$, $\Delta U = 0$

$$\Delta S_{\text{universe}} = nR \ln \frac{V_2}{V_1} > 0$$

P.I.) Reversible expansion :-

$$\Delta S_{\text{System}} = \frac{Q_{\text{rever}}}{T}$$

$$\Delta S_{\text{System}} = -\frac{\omega_{\text{rever.}}}{T}$$

[for psothermal process $\Delta U = 0$]
 $q_r = -\omega$

$$\Rightarrow \omega_{\text{rever.}} = -nRT \ln \frac{V_2}{V_1}$$

$$\Rightarrow \Delta S_{\text{system}} = \frac{n R T \ln \frac{V_2}{V_1}}{T}$$

$$\Delta S_{\text{system}} = n R \ln \frac{V_2}{V_1}$$

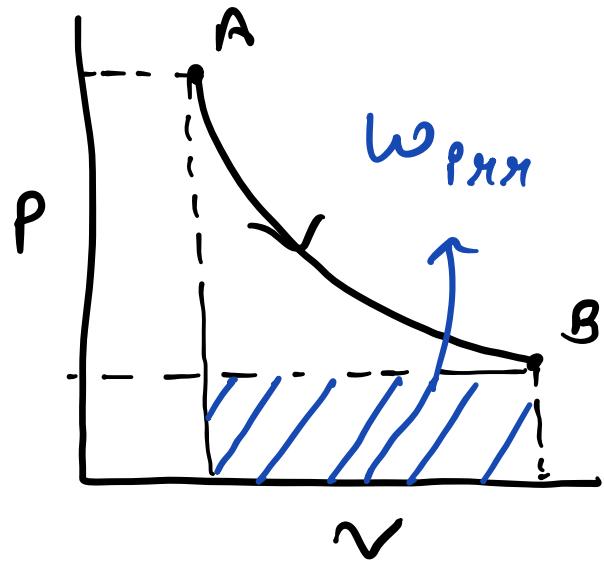
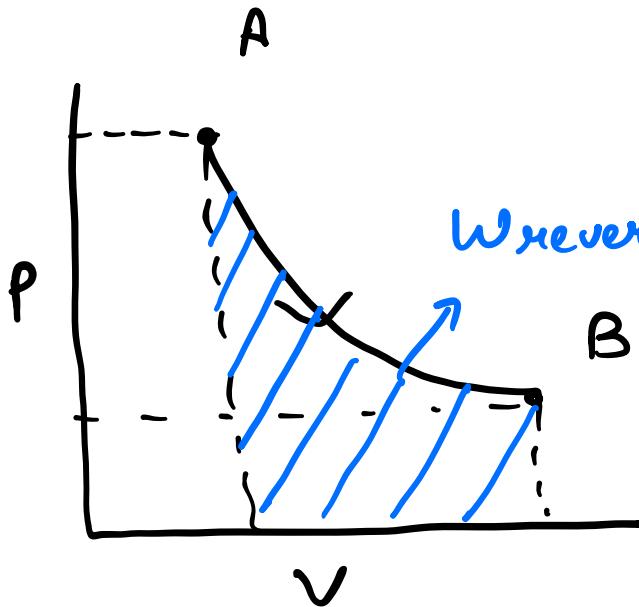
$$\Delta S_{\text{surx}} = -\frac{q_{\text{rev}}}{T}$$

$$\Delta S_{\text{surx}} = -n R \ln \frac{V_2}{V_1}$$

$$\Rightarrow \Delta S_{\text{universe}} = 0$$

Irreversible Isothermal process

$$\Delta S_{\text{system}} = \frac{q_{\text{rever.}}}{T}$$



We can write.

$$\Delta S_{\text{System (Rev.)}} = n R \ln \frac{V_2}{V_1} = - \frac{W_{\text{rev}}}{T}$$

As entropy is a state function

$$\Delta S_{\text{reversible}} = \Delta S_{\text{Irreversible}}$$

$$\Delta S_{\text{Surround}} = - \frac{q_{\text{system}}}{T} = - \frac{q_{\text{irr.}}}{T}$$

for isothermal process

$$q + w = 0$$

$$q_r = -w \cdot$$

$$\Rightarrow \Delta S_{\text{surh}} = \frac{w_{\text{per.}}}{T} = - \frac{P_{\text{ext}}(V_2 - V_1)}{T}$$

$$V_2 = n \frac{RT}{P_2} \quad V_1 = n \frac{RT}{P_1}$$

$$\Rightarrow \Delta S_{\text{surh}} = -P_{\text{ext}} \cdot \frac{nRT}{T} \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$$

$$\Delta S_{\text{surh}} = -P_{\text{ext}} \cdot nR \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$$

$$\Rightarrow \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surh.}}$$

$$\Delta S_{\text{universe}} = - \underline{w_{\text{rever.}}} + \underline{w_{\text{per.}}}$$

T

T

* for expansion :-

$$|w_{\text{rev}}| > |w_{\text{irrev.}}|$$

$$w_{\text{rev}} = -7$$

$$w_{\text{irr}} = -5$$

$$|w_{\text{rev}}| > |w_{\text{irrev.}}|$$

$$\Delta S_{\text{universe}} = -\frac{w_{\text{rev}}}{T} + \frac{w_{\text{irr}}}{T} > 0$$

"for all irreversible process

$\Delta S_{\text{universe}}$ is always greater than zero."

↳ Adiabatic process :-

↳ Free expansion :-

for an ideal gas

$$\Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surround.}} = 0 \quad [q_{\text{system}} = 0]$$

$$\boxed{\Delta S_{\text{universe}} > 0}$$

Q) Reversible adiabatic process :-

$$\Delta S_{\text{system}} = \frac{q_{\text{rever.}}}{T} = 0$$

$$\Delta S_{\text{surround.}} = -\frac{q_{\text{system}}}{T} = 0$$

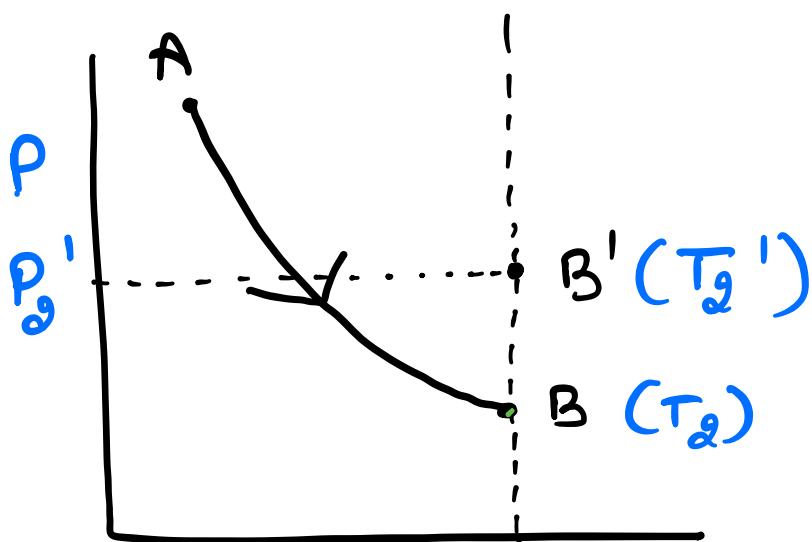
$$\boxed{\Delta S_{\text{universe}} = 0}$$

3.) Irreversible adiabatic process :-

$$\Delta S_{\text{system}} = n C_V \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1}$$

for an adiabatic process T_2 will be replaced by T_2'

$$\Rightarrow \Delta S_{\text{system}} = n C_V \ln \frac{T_2'}{T_1} + n R \ln \frac{V_2}{V_1}$$



\checkmark

$$\Delta S_{AB'} = \Delta S_{AB} + \Delta S_{BB'}$$

$$\Delta S_{AB'} = 0 + n C_V \ln \frac{T_g'}{T_g}$$

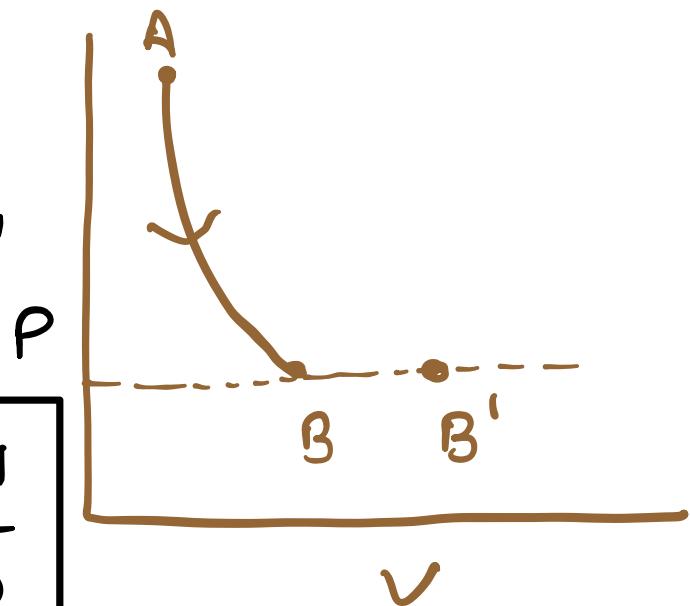
"As value of T_g' is always greater than T_g "

Therefore

$$\Delta S_{AB'} > 0$$

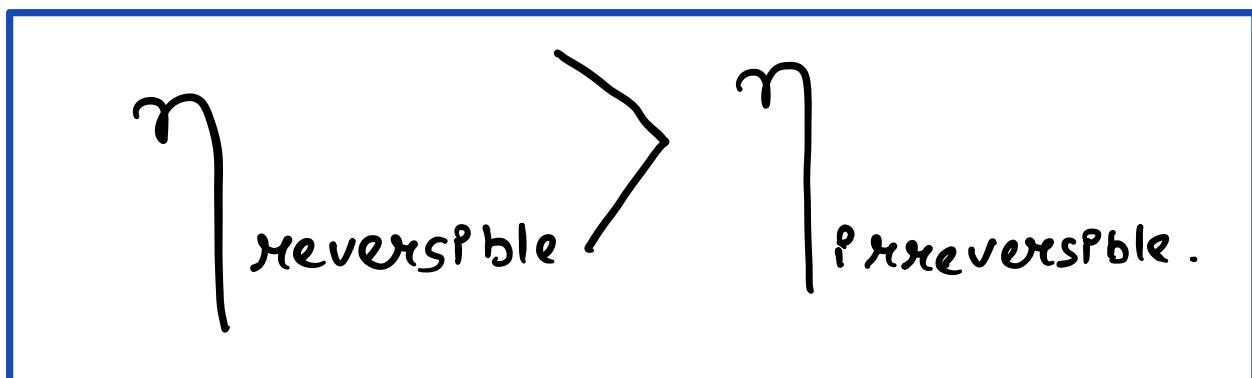
$$\Delta S_{AB'} = n C_V \ln \frac{T_g'}{T_g} > 0$$

$$\Delta S_{AB'} = \Delta S_{AB} + \Delta S_{BB'}$$



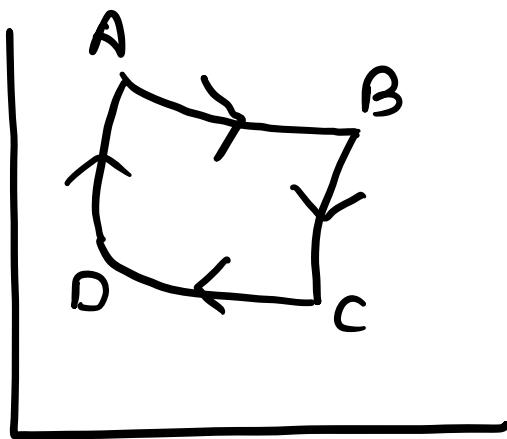
$$\Delta S_{AB'} = 0 + n C_P \ln \frac{T_g'}{T_g}$$

Comparison of efficiency of reversible and irreversible Carnot engine :-

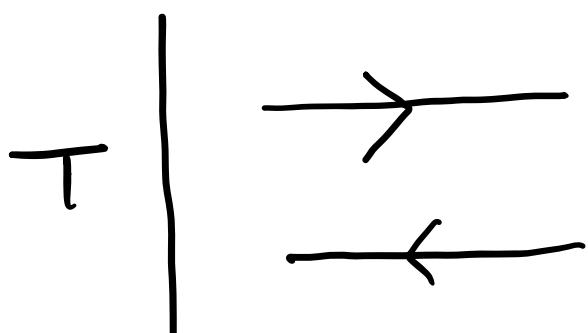


T-S diagram for Carnot engine :-

* for process AB :-

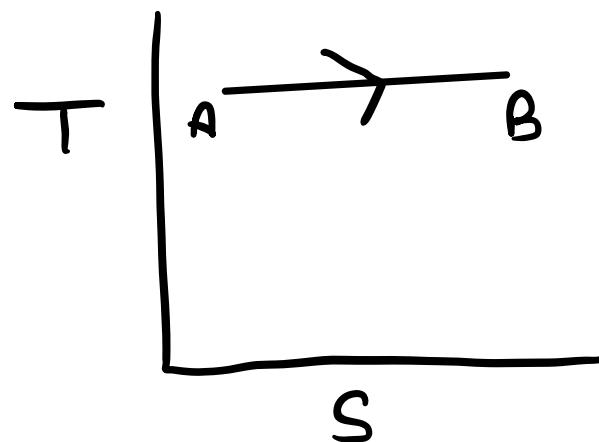


* Isothermal expansion :-

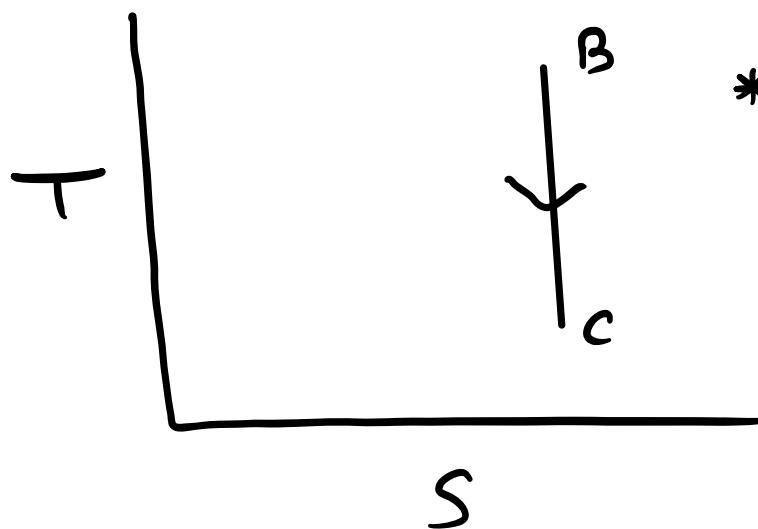




"Entropy always increases for
Isothermal expansion"



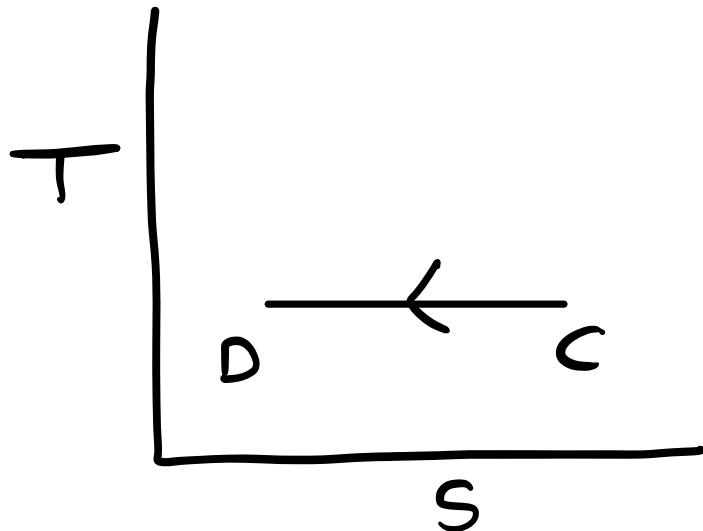
* for B.C process :-



* for reversible
adiabatic
expansion
 $\Delta S = 0$

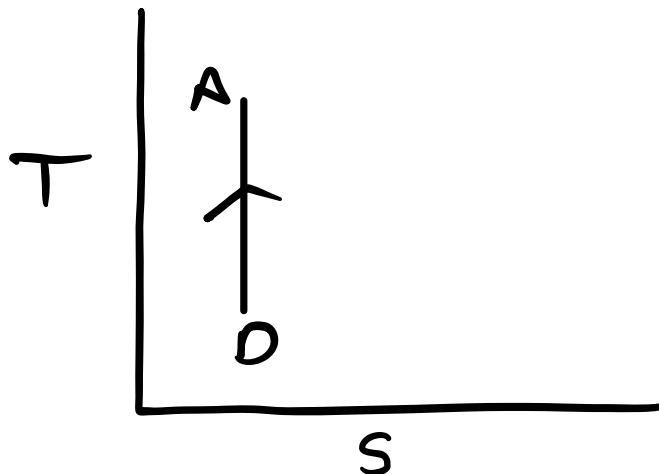
* for C.D Process :-

* C D is isothermal compression.



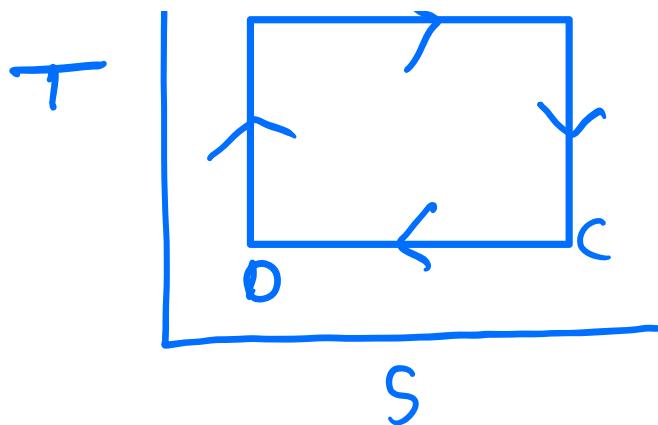
* for DA process :-

DA is adiabatic compression.



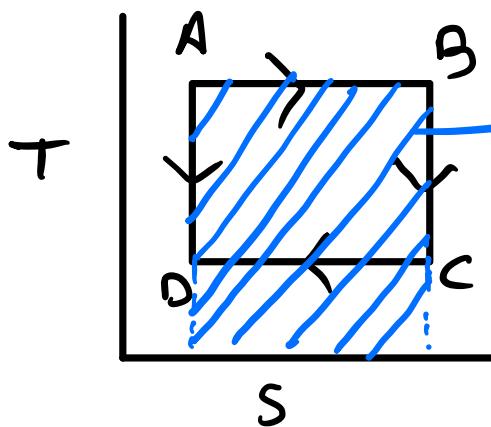
"final T-S diagram for
Carnot engine"

| A - B

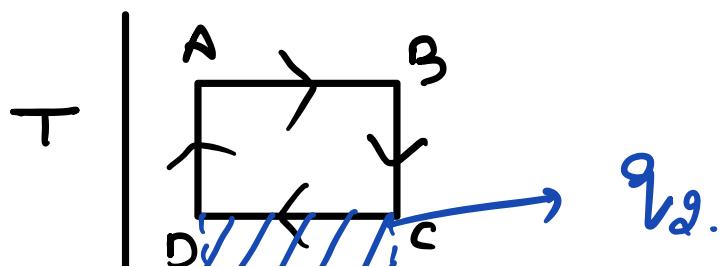


* Area under T-S diagram = Heat.

"Area under = q_{VAB} = q_1 = Heat absorbed from source.



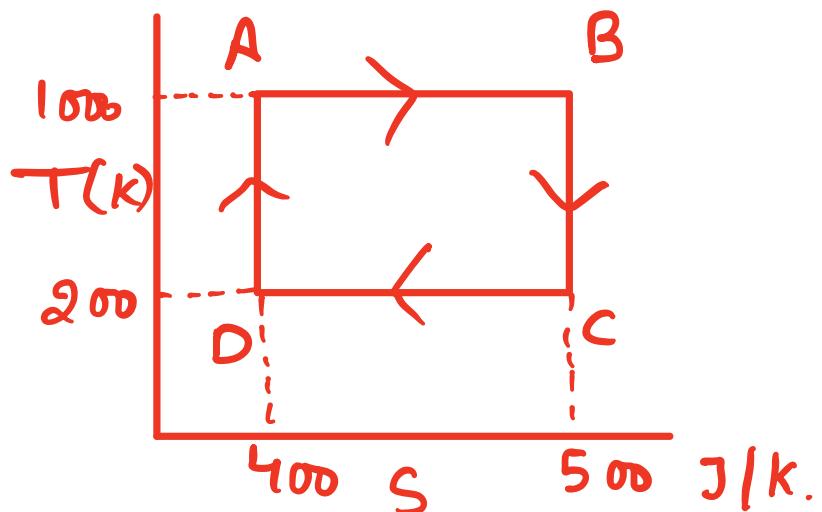
"Area under = q_{VCD} = q_2 = Heat lost to the sink.



V/V/V/V

S

Ques:- from the following T-S diagram for Carnot engine Calculate.



- ① Efficiency.
- ② Heat taken from the source and rejected to sink.
- ③ Work done per cycle.
- ④ In order to illuminate 10000 bulbs 40 watt each how many cycles are required.

① AB = Temp. of source = 1000 K

CD = " " 800 K = 200 K.

$$\eta = \left(1 - \frac{T_2}{T_1}\right) \times 100$$

$$= \left(1 - \frac{200}{1000}\right) \times 100$$

$$\boxed{\eta = 80\%}$$

⑥

$$Q_{AB} = q_i = 100 \text{ KJ}$$

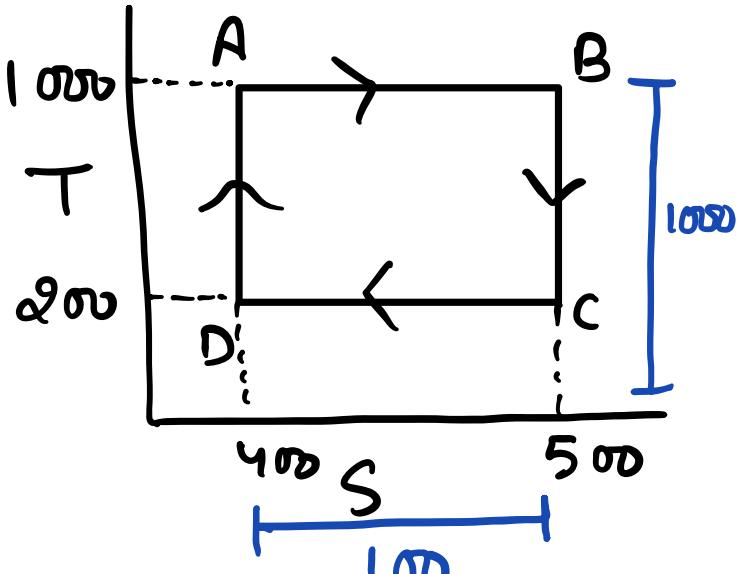
Area under AB

$$= 1000 \times 100$$

$$= 10^5 \text{ Joules}$$

or

$$\boxed{= 100 \text{ KJ}}$$



$$q_{v_0} = q_{v_2} \boxed{= 20 \text{ KJ}}$$

c) Work done per cycle = $q_1 - q_2$

$$w = 100 - 20$$

$$\boxed{w = 80 \text{ KJ}}$$

d) Power = $\frac{w}{t}$ → Let $t = 1 \text{ sec.}$

To illuminate 1 bulb, amount of work done = 40 Joules.

To illuminate 10000 bulbs the amount of work done

$$\boxed{= 10000 \times 40}$$

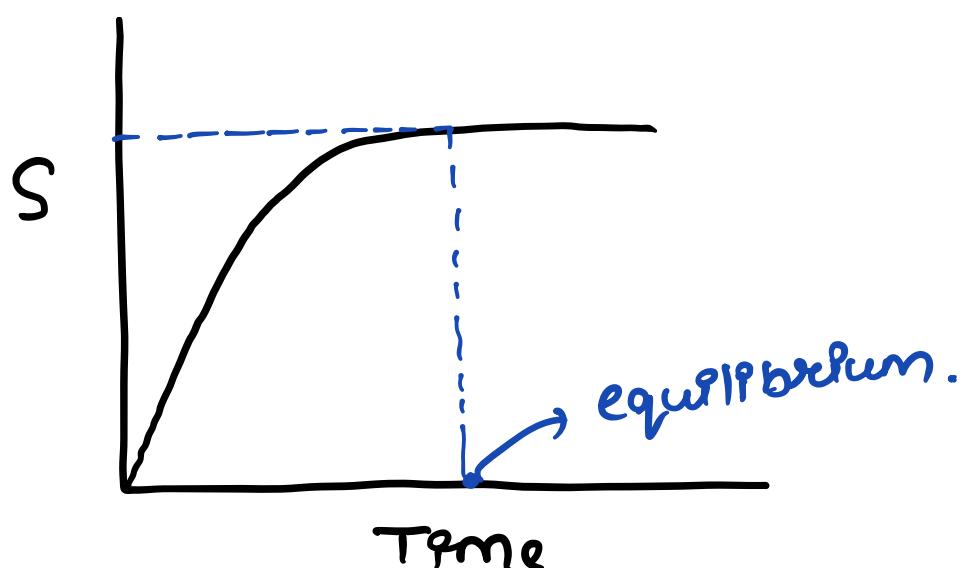
"Work obtained from 1 cycle = 80 KJ.

let no. of cycles done to
do 1000×40 J of work = n .

$$\Rightarrow n \times 80 \times 10^3 \text{ J} = 1000 \times 40$$

$$n = 5$$

"Universe is Considered to be
an Isolated System whose
entropy is always increasing
and it will maximize at
equilibrium!"



Gibbs free energy or (Gibbs function)

* * Gibbs free energy is a non-PV work done at constant temp. & pressure that can be used for useful work.

We know that

$$dU = dq + dw$$

At Constant Temp. & pressure

$$dU = dq + dw_{PV} + dw_{non\ PV}$$

$$dU = Tds - Pdv + dw_{non\ PV}$$

$$dU + Pdv = Tds + dw_{non\ PV}$$

$$d(U + Pv) = Tds + dw_{non\ PV}$$

$$dH - TdS = d\omega_{\text{non PV}}$$

$$dG_r = d\omega_{\text{non PV}}$$

$$\Delta G_r = \Delta \omega_{\text{non PV}}$$

→ Only at
Constant
temp.
& pressure.

$$G_r = H - TS$$



"If temp. & Pressure are not
constant then G_r is simply
Gibb's function"

$$G_r = H - TS$$

$$dG_r = dH - TdS - SdT$$

$$= d(U + PV) - TdS - SdT$$

$$= dU + PdV + VdP - TdS - SdT$$

$$= da + d\omega + PdV + VdP - TdS - SdT$$

$$= T \cancel{ds} - P \cancel{dv} + P \cancel{dv} + v dP - T ds - S dT$$

$$dG = v dP - S dT$$

① If temp. = Constant.

$$dG = v dP$$

for solids & liquids $v = \text{Constant}$.

$$\int_{G_1}^{G_2} dG = v \int_{P_1}^{P_2} dP$$

$$\Delta G = v(P_2 - P_1) \Rightarrow \begin{array}{l} \text{for solids} \\ \text{& liquids.} \end{array}$$

* * for ideal gas :-

$$dG = v dP$$

$$G_2 (dG = nRT \int \frac{dP}{P})$$

$\int G_1$

$\int P_1$

$$\Delta G_r = nRT \ln \frac{P_2}{P_1}$$

② If $P = \text{constant}$.

$$dG_r = -S dT$$

$$\Rightarrow d(\Delta G_r) = -\Delta S dT$$

||

Valid for a chemical rxn.

$$\int_{\Delta G_{r1}}^{\Delta G_{r2}} d(\Delta G_r) = -\Delta S \int_{T_1}^{T_2} dT$$

$$\Delta G_{r2} - \Delta G_{r1} = -\Delta S (T_2 - T_1)$$

"At equilibrium $\Delta G_r = 0$ "

$$G_r = H - TS$$

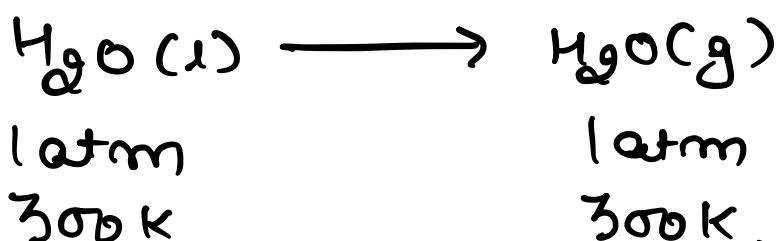
$$\Delta G_r = \Delta H - T \Delta S$$

at equilibrium $\Delta G_r = 0$

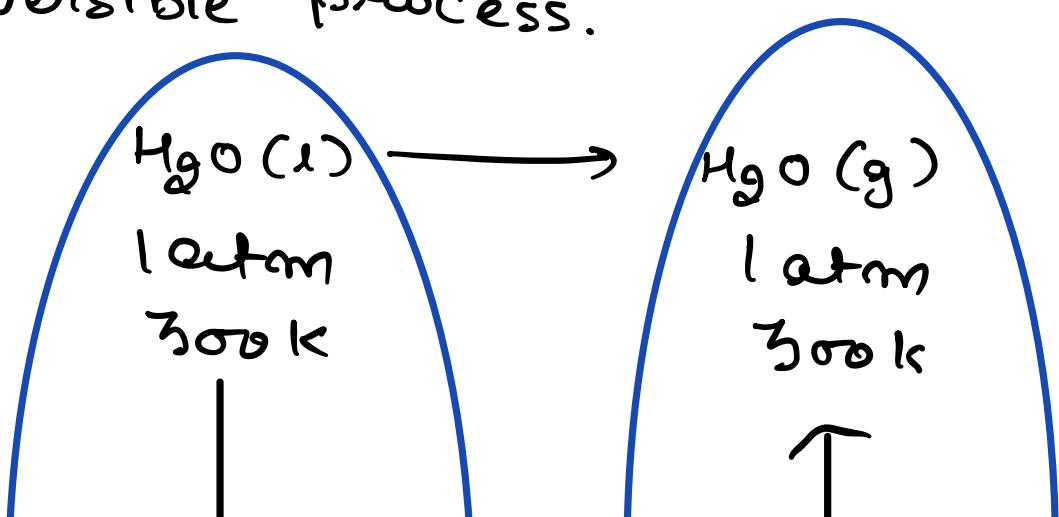
$$\Delta H = T \Delta S$$

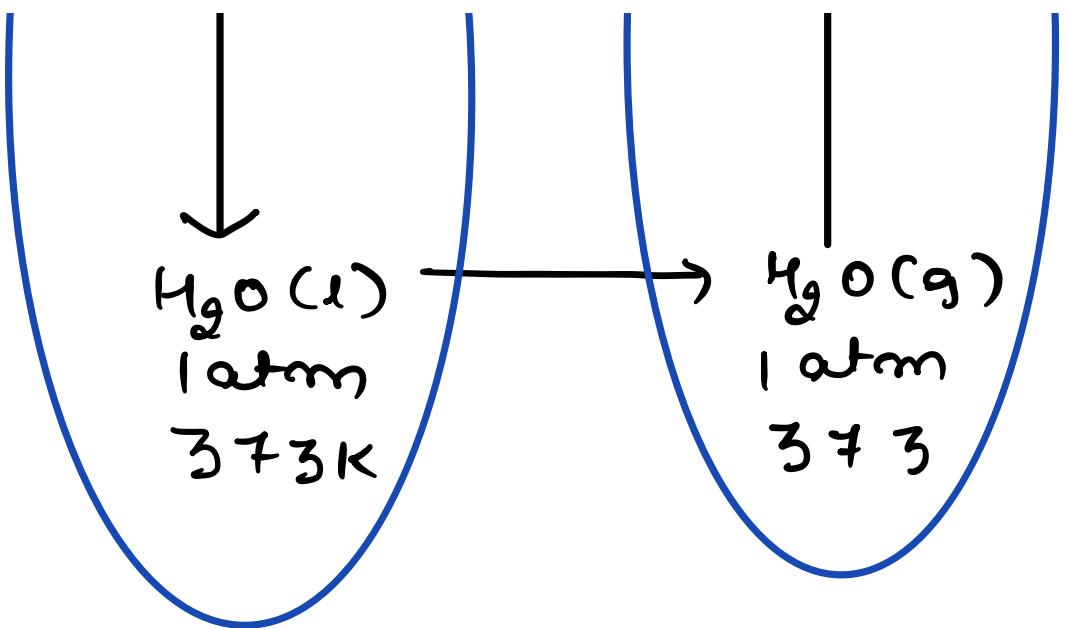
$$\Delta S = \frac{\Delta H}{T}$$

Gibbs free energy for irreversible phase transition :-



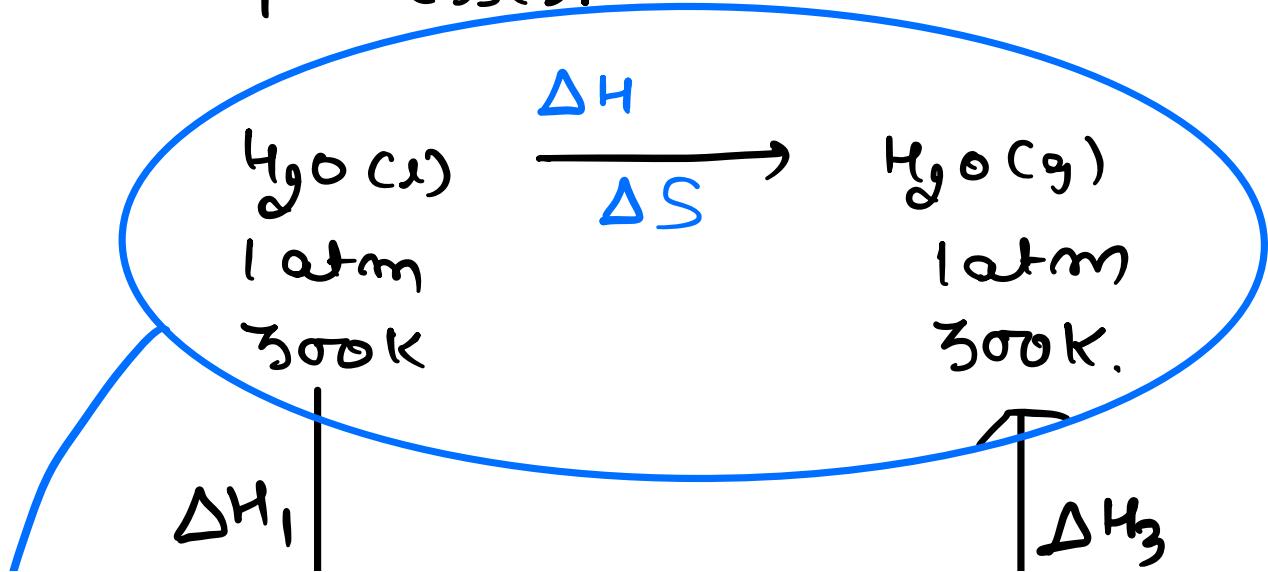
* Break irreversible process into reversible process.

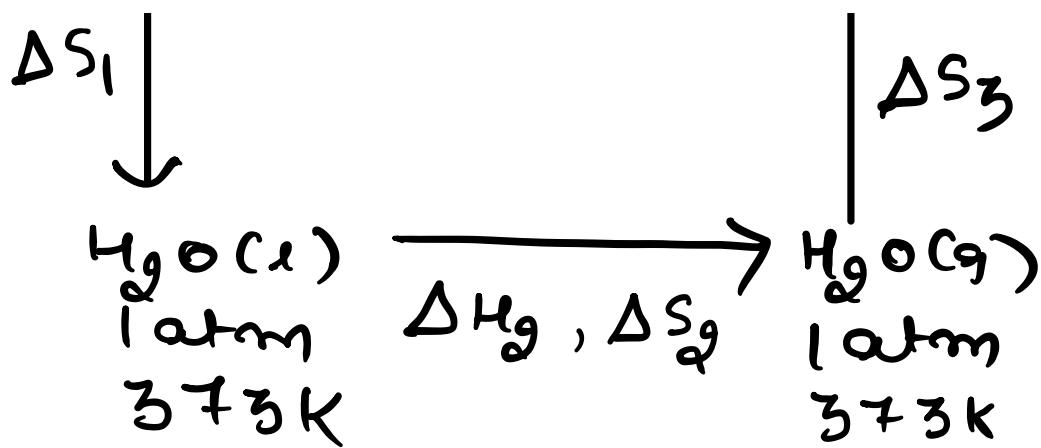




Q) If equilibrium pressure P_s given :-

* If equilibrium pressure is given then instead of calculating ΔG , calculate ΔH & ΔS for the processes.





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

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\boxed{\Delta G = \Delta H - 300 \Delta S}$$

* At Constant P.

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

$$\Rightarrow \Delta H_1 = C_{P\ H_2O(l)} \cdot (373 - 300)$$

$$\Delta S_1 = C_{P\ H_2O(l)} \text{ in } \frac{373}{300}$$

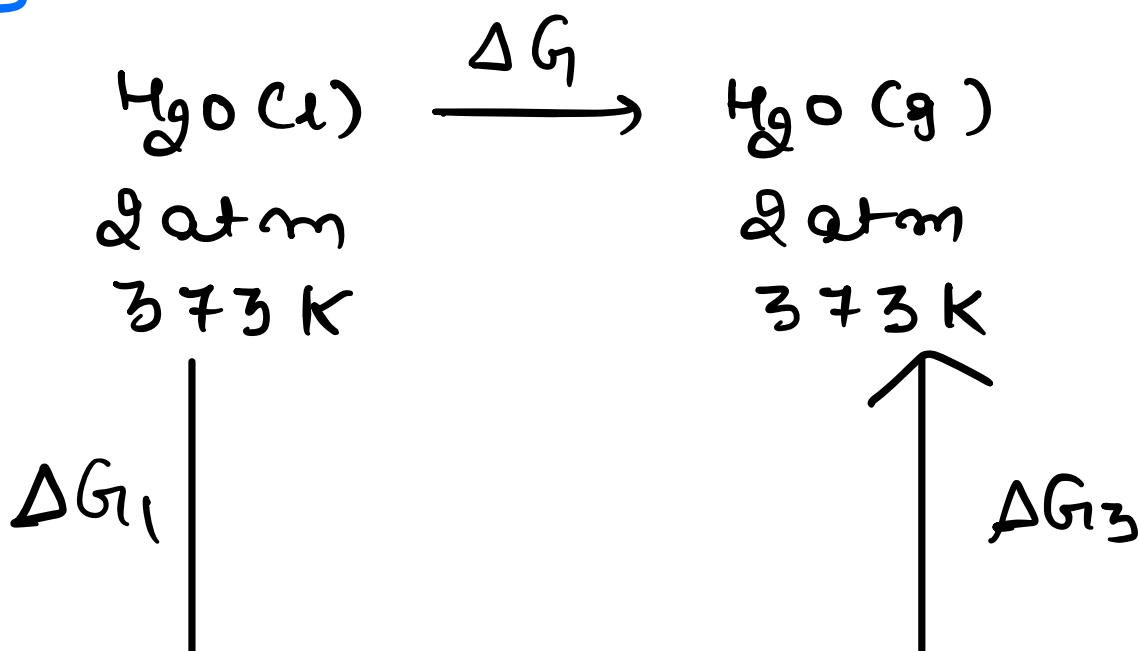
$$\Delta H_2 = \Delta H_{\text{vapourisation}}$$

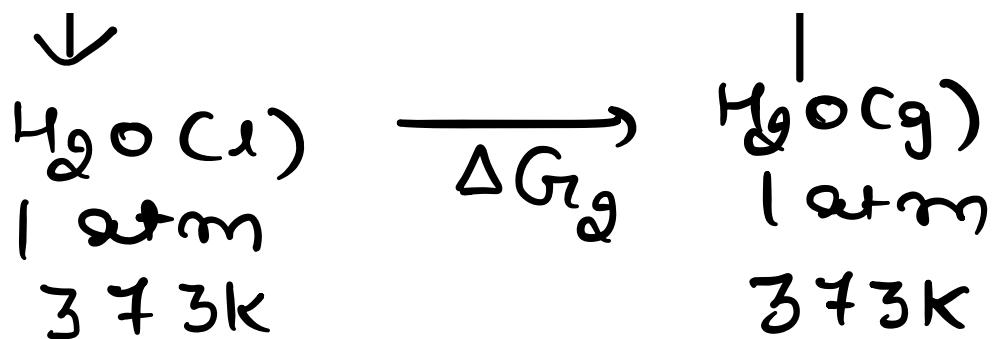
$$\Delta S_2 = \frac{\Delta H_{\text{vapour}}}{373}$$

$$\Delta H_3 = C_{P_{H_2O(g)}} (300 - 373)$$

$$\Delta S_3 = C_{P_{H_2O(g)}} \ln \frac{300}{373}$$

Q) If equilibrium temp. is given :-





* If equilibrium temp. P_S given then we can calculate ΔG_r directly.

$$\Delta G_r = \Delta G_{r1} + \Delta G_{r2} + \Delta G_{r3}$$

for solids and liquids if temp. P_S constant

$$\Delta G_r = \checkmark \Delta P$$



$$\text{Density} = \text{lgm}/\text{ml}$$

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

$$\Rightarrow \boxed{V \text{ vol}'' = \text{mass}}$$

* mass of 1 mole $H_2O = 18$
 $\Rightarrow \text{vol}^m = 18$

$$\Delta G_1 = 18(1-\alpha)$$

$$\Delta G_1 = -18 \times 10^{-3} \text{ Jt atm}$$

$$\Delta G_1 = -1.8 \text{ Joules.}$$

* $\Delta G_{1g} = 0$

{Because process is reversible}

* $\Delta G_3 = mRT \ln \frac{P_\alpha}{P_1}$

$$\Delta G_3 = 1 \times 8.31 \times 373 \times \ln 2.$$

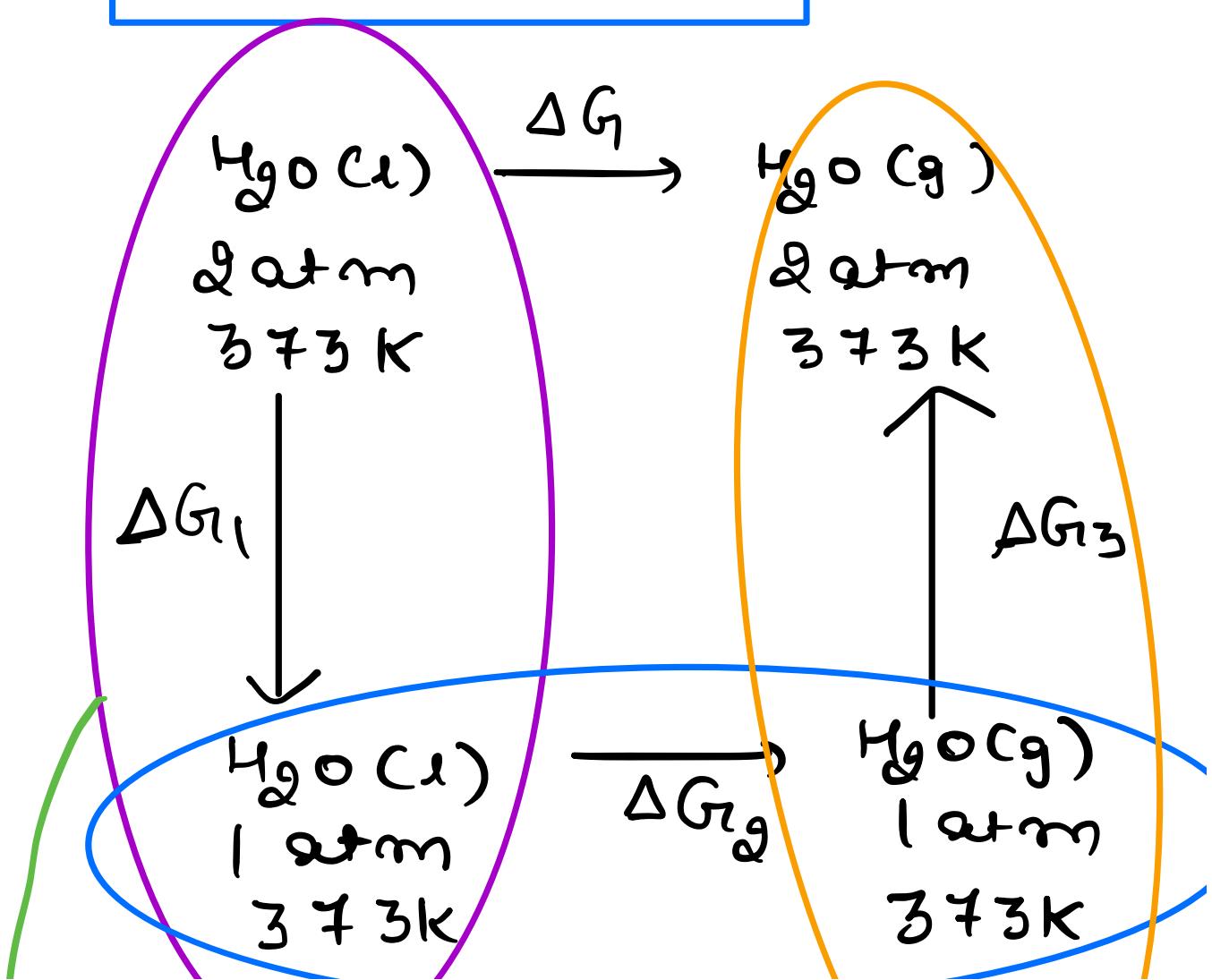
$$\Delta G_3 = 8.31 \times 373 \times 0.693$$

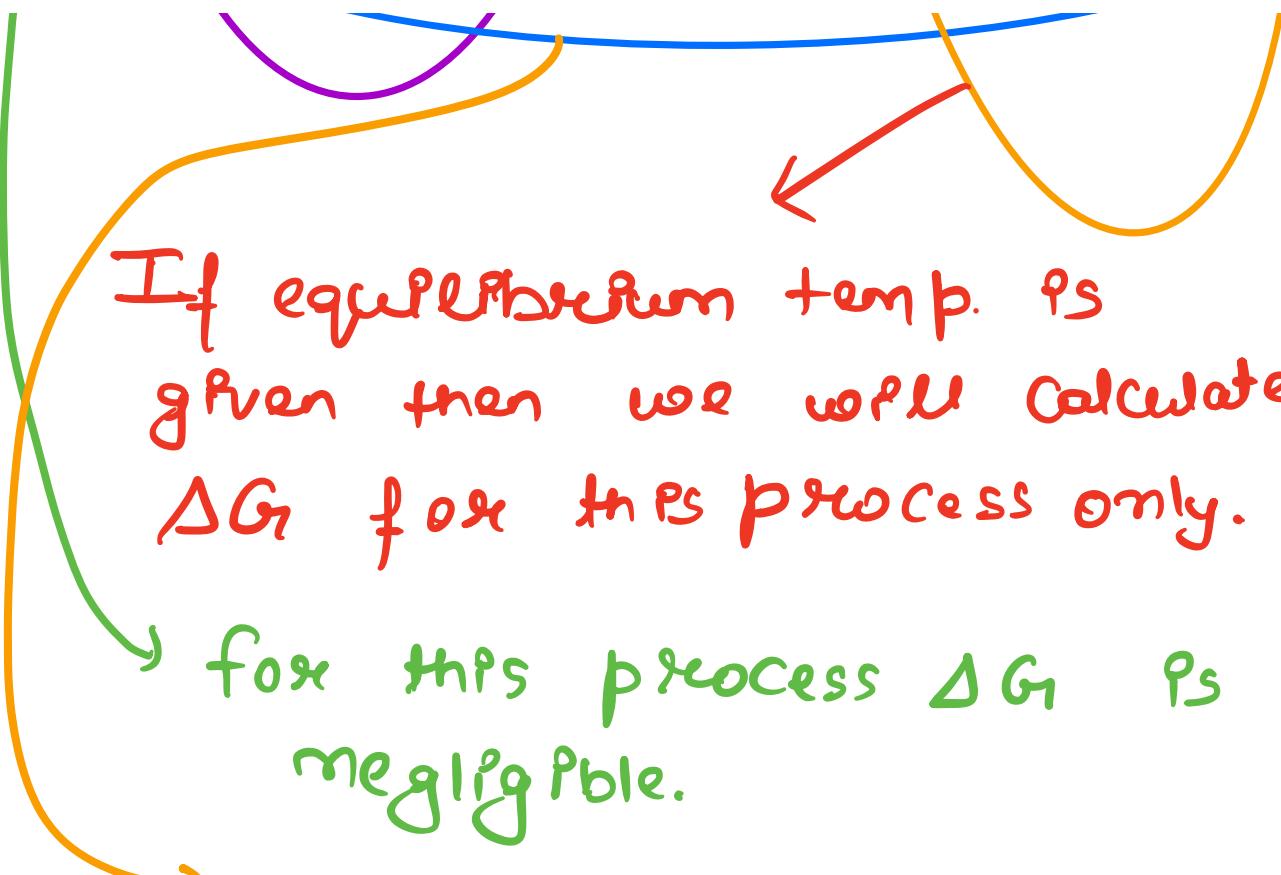
$$\Delta G_r^{\circ} = -148 \text{ Joules}$$

$$\Rightarrow \Delta G_r = -1.8 + 148$$

↓
negligible

$$\Delta G_r \approx 148 \text{ J}$$





Process P_S Reversible
hence $\Delta G_I = 0$

Third law of thermodynamics:

* from 3rd law of thermodynamics we can calculate the absolute entropy at a particular temp.

** Acc. to 3rd law of

thermodynamics of temp.
 of perfectly crystalline
 solid approaches to 0 K.
 then entropy of perfectly
 crystalline solid also approaches
 to zero

$$\int_{S_{T_1}}^{S_{T_2}} dS = \int_{T_1}^{T_2} \frac{dq}{T}$$

If $T_1 \rightarrow 0K$

$$\Rightarrow \int_0^{S_{T_2}} dS = \int_0^{T_2} \frac{dq}{T}$$

$$S_{T_2} - 0 = \int_0^{T_2} \underline{dq}$$

$$S_{T_2} = \int_0^{T_2} \frac{dq}{T}$$

$S \rightarrow S \rightarrow l \rightarrow l \rightarrow \text{Gas}$
 0 K m.p. m.p. B.P B.P.

