$q_v = \Delta U$

$q_p = \Delta H$

* Thermochemical Reactions :-

If any thermodynamic Quantity is referred against a thermochemical Reaction then it is defined for the amount taken equal to its stichemetric coefficient of Reactant or Product.

$$2A_{(g)} + B_{(s)} \longrightarrow 3D_{(g)} \qquad \Delta H = -20\ KJ/mol.$$

2 mol. 1 mol.

If 2 mol. A, react with one mole $B_{(s)}$ and forms 3 mol $D_{(g)}$ then. change in enthalpy will be equal to -20 KJ.

Que: 5 mol A react with 2 mol. of $B_{(s)}$ then what will be change in ΔH ? 5A + 2B →

Ans: -40 KJ

Que: At 727°C Calculate ΔU For / heat change for a given ~~Container~~ Rx^n in a rigid Container

$q_v = \Delta U$

$$2A_{(g)} + B_{(s)} \longrightarrow 3D_{(g)} \qquad \Delta H = -20\ KJ/mol.$$

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

$$-20 = \Delta U + (1)\left(\frac{8.3}{1000}\right)(1000)$$

R : 8.3 J / cal 2.

$$\Delta U = -28.3\ KJ/mol$$

Thermo 0-1 : 7 to 15.
Chemical Eq 8-1 - 19 to 25

Q.: $3X_{(g)} + 2Y_{(liquid)} \longrightarrow 2Z_{(g)}$ $\Delta U = -20$ kcal/mol.

At a constant Pressure 1 bar and Const. temp 727°C 6 mole of X gas React with 3 mol of Y liquid then Calculate change in heat in given process

(R)

$3X_{(g)} + 2Y_{(liq)} \longrightarrow 2Z_{(g)}$

6 mol. 3 mol.

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

$\Delta H = -20 - 1\left(\frac{2}{1000}\right)(1000)$

$= -22$ kcal/mol

for 2 mol of Y (liq) $= \Delta H = -22$ if 2 mol.

50 for 1 mol. of Y (liquid) : $\Delta H = -11$

3 mol — $\Delta H = -33$

Q.: At a constant pressure 760 torr a system Realease 1 kJ of Heat in this Process Vol. of system reduce from 1100 ml to 10 ml Calculate ΔH and ΔU for given process in System.

$q_p = \Delta H = -1$ kJ

$-1 = \Delta U + 1\left(\frac{100 - 1100}{1000}\right)\left(\frac{101.3}{1000}\right)$

kJ.

* Different process in thermodynamics

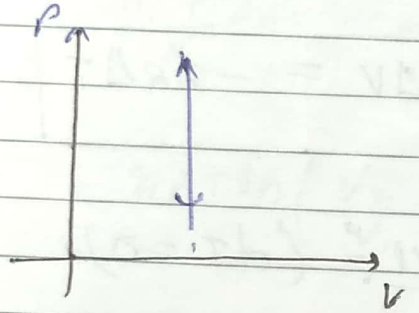
We will studies these Reaction for non-Reaching Ideal gas in a Close system.

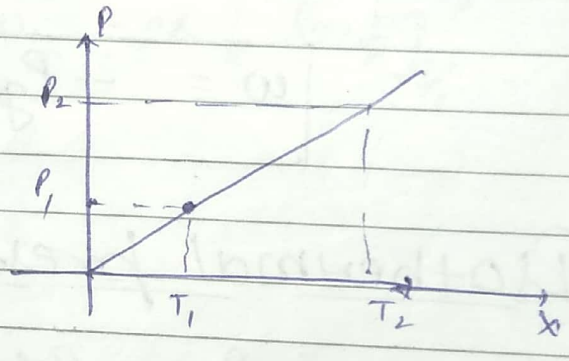
η = constant

$\Delta H = n C_{p,m} \Delta T$

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

(1) Isocheric Process :- ($dV = 0$)





$PV = nRT$

$P = \left(\frac{nR}{V}\right) T$

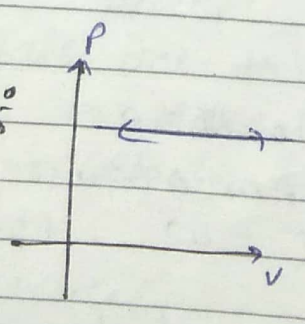
$V = \text{const}^{V} \times$

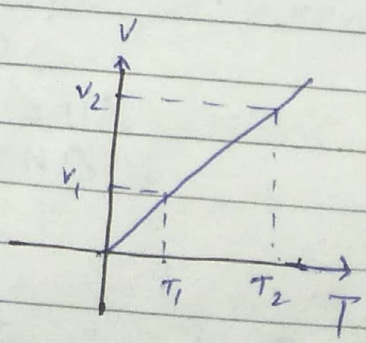
$\frac{P_2}{P_1} = \frac{T_2}{T_1}$

* $W =$
* $\Delta H = n C_{pm} \Delta T$
* $\Delta U = n C_{vm} \Delta T$

$q_v + W = \Delta U$

* Isobaric Process :





$PV = nRT$

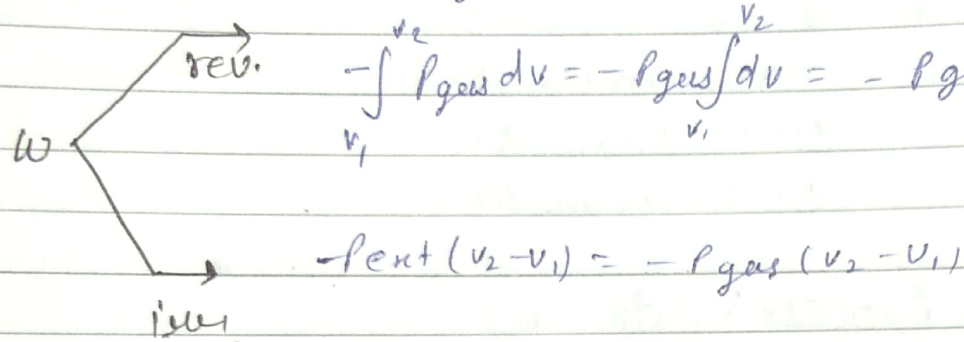
$V = \left(\frac{nR}{P}\right) T$

$V = \text{const} \cdot T$

$y = \text{const} \times$

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

* $\Delta H = n C_{pm} \Delta T$
* $\Delta U = n C_{vm} \Delta T$
* $q = \Delta U - w$ { $q_p = \Delta H$.



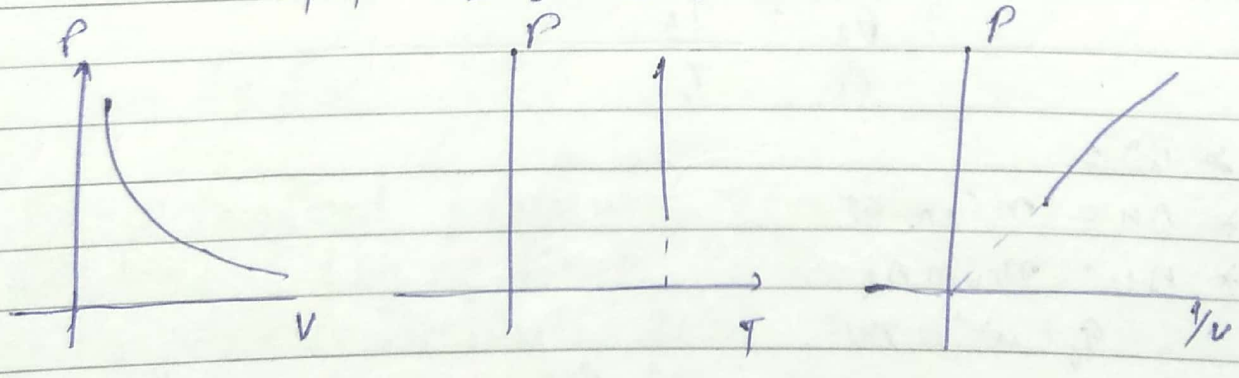
$$\boxed{w = -P_{gas}\, \Delta V = -nR\Delta T}$$

(3) Isothermal process: ($dT = 0$)

$PV = nRT$

$pv = Const \Rightarrow P = \frac{Const}{V}$

$P_1V_1 = P_2V_2 = P_3V_3$



$\Delta U = n C_{vm} \Delta T = 0$

$\Delta H = n C_{pm} \Delta T = 0$

$q = -w$

* Work in Isothermal irreversible Process:

w.

$$\boxed{w = -P_{ext}(\Delta V_2 - V_1)}$$

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

* If P_{ext} is not provided in question then

$$P_2 = P_{ext}$$

* **Work in Reversible Isothermal Process**

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

$$w = \int_{V_1}^{V_2} \frac{nRT}{V}\, dV \Rightarrow w = -nRT\left[\ln \frac{1}{x}\right]_{V_1}^{V_2}$$

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

$$P_1V_1 = P_2V_2 = P_3V_3 = nRT$$

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

$$\boxed{w = -nRT \ln(P_1/P_2)}$$

$$w = -P_1V_1 \ln(P_1/P_2)$$

Que: By a irreversible process a system is taken from State One to two then from State 2 to State 3 then Calculate Work in Complete process in Fig. if State 1, 2, 3 are 1(10 bar, 10 litre)
State-2 (5 bar, V_2 litre
State-3 (1 bar, V_3 litre)

$(10-5)$
$w =$

$$w = w_1 + w_2$$

$$w = -5(V_2 - 10) - 1(V_3 - V_2)$$

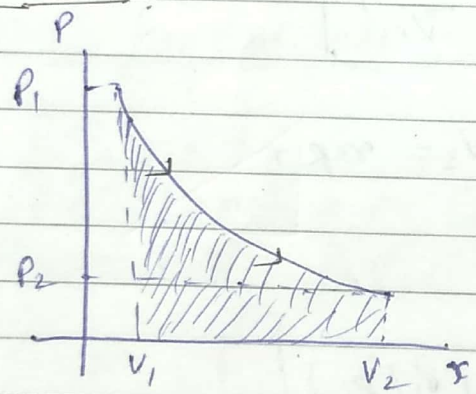
$$P_1 V_1 = P_2 V_2 = P_3 V_3$$

$$100 = 5 V_2 = 1(V_3)$$

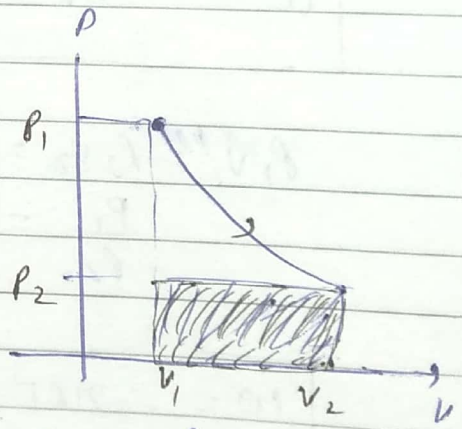
* Comparison for Work in Reversible and Irreversible Isothermal process:

(1) Comparision in Expension:

i) rev. expansion:

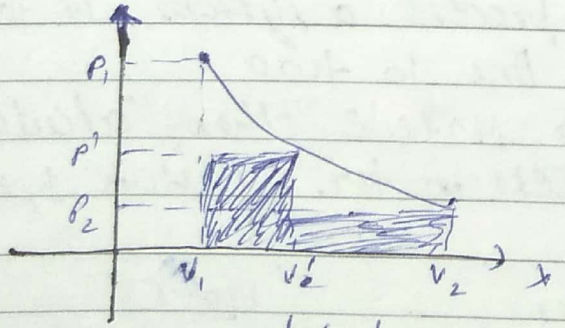


2) Irr single step Expansion



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

(3) irr double expension:



$$w = -P'(V' - V_1) - P_2(V_2 - V')$$

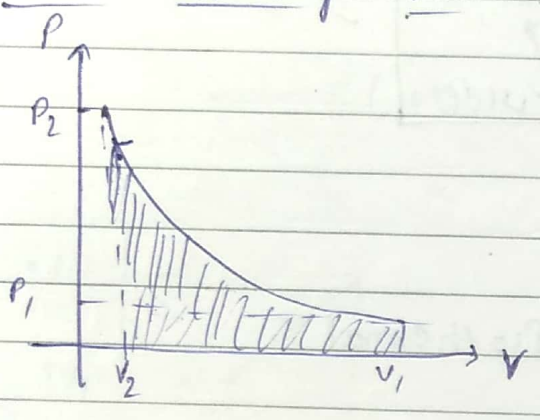
In Expension :- single
|W| step < |W| double step - - -

- - - - - - < |W| rev.

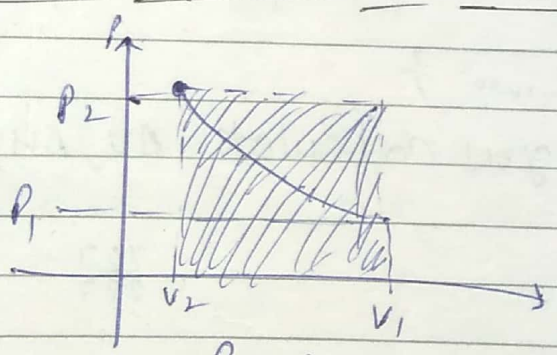
W single step > W double step - - - -> W rev.

In Compression :-

(1.) Reversible Compression :-



(2) Irr. Compression :- in single step :-

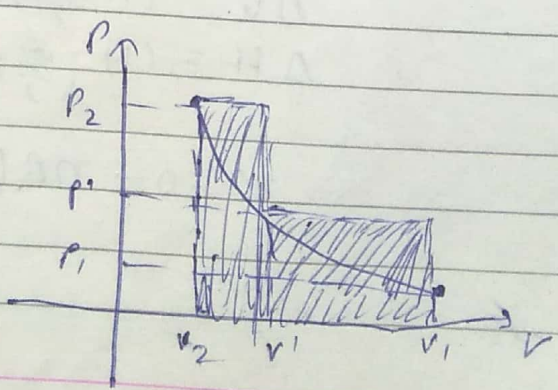


$$w = -P_{ext} + (V_2 - V_1)$$

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

3) Irr. double step :-

$$w = -P'(V' - V_1) - P_2(V_2 - V').$$



Final Result:- In any process

$$W_{irr} > W_{rev.}$$

learn

Expansion:

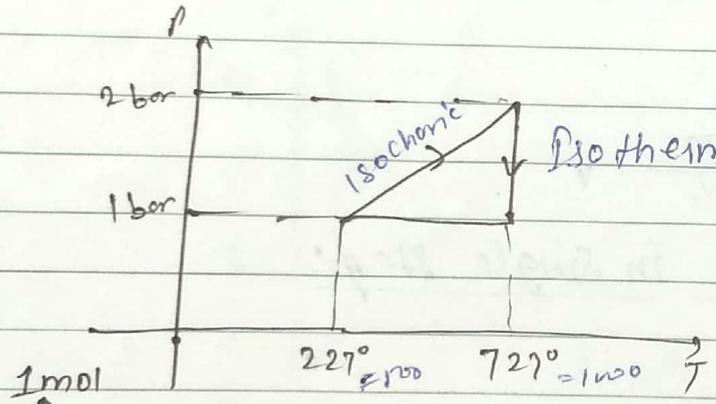
$$|W_{irr}| < |W_{rev}|$$

Remember

Compression: $|W_{irr}| > |W_{rev}|$

$$q_{irr} < q_{rev}$$

Qu:-



For a monoatomic Ideal gas calculate $\Delta U, \Delta H, q, w$ in given process

$$\eta_{CVm} * \Delta t$$

$727 - 227$

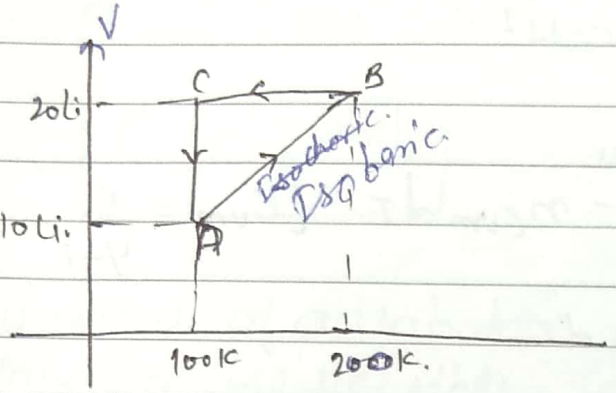
$$\Delta U = (1)\left[\frac{3}{2}R\right] * (500)$$

$$\Delta H = (1)\left(\frac{5}{2}R\right)(500)$$

$$w = 0 - nR(1000)\ln\left(\frac{2}{1}\right)$$

J main (1, 2, 4, 5, 6, 7, 8, 10, 11)

(ii) For a 1 mol of Ideal gas Processed acc. to given Curve Calculate q, w, ΔH, ΔU in complete process



$\gamma = \frac{5}{3}$

$\Delta H = 0$

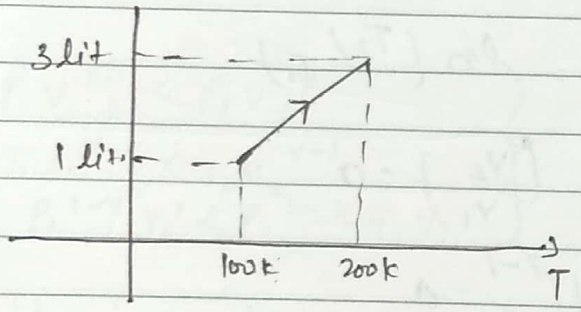
$\Delta U = 0$

$q = -w$

$w = w_{AB} + 0 - nR(100)\ln\left(\frac{10}{20}\right)$

$= -R(100) - 100R\ln\left(\frac{1}{2}\right)$

Que!



$\frac{V_2}{V_1} \neq \frac{T_2}{T_1}$

for 1 mole of that mono atomic Ideal gas Calculate q, w, ΔH, ΔU

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

$$w = -\int_1^3 P\,dV$$

$$V - 1 = \frac{2}{100}(T - 100)$$

$$50V - 50 = T - 100$$

$$50V + 50 = T$$

$$50V + 50 = \frac{PV}{nR}$$

$$P = 50R + \frac{50R}{V}$$

* Adiabatic Process :- ($dq = 0$)

Equation of adiabatic Process :

$$dq + w = du$$

$$-Pdv = n C_{vm} dT \quad \left[C_{vm} = \frac{R}{\gamma - 1}\right.$$

$$-\frac{nRT}{V} dV = \frac{nR}{\gamma - 1} dT$$

$$-(\gamma - 1) \cdot \frac{dV}{V} = \frac{dT}{T}$$

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

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

$$\ln\left(\frac{T_2}{T_1}\right) + (\gamma - 1) \ln\left(\frac{V_2}{V_1}\right) = 0$$

$$\ln\left(\frac{T_2}{T_1}\right) + \ln\left(\frac{V_2}{V_1}\right)^{\gamma - 1} = 0$$

$$\ln \frac{T_2 V_2^{\gamma - 1}}{T_1 V_1^{\gamma - 1}} = 0$$

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

$$\boxed{T V^{\gamma - 1} = \text{const.}}$$

$$\frac{RT}{nR} V^{(\gamma - 1)} = \text{const.}$$

$$\boxed{P V^{\gamma} = \text{Const}}$$

$$P\left(\frac{mRT}{P}\right)^{\gamma} = \text{const.}$$

$$P^{1-\gamma} T^{\gamma} (mR)^{\gamma} = \text{const}$$

$$\boxed{P^{1-\gamma} T^{\gamma} = \text{const.}}$$

Note:

1) Equations of adiabatic process are Applicable only for reversible for adiabatic process.

$$\left.\begin{aligned} P_1 V_1^{\gamma} &= P_2 V_2^{\gamma} \\ T_1 V_1^{\gamma-1} &= T_2 V_2^{\gamma-1} \\ P_1^{1-\gamma} T_1^{\gamma} &= P_2^{1-\gamma} T_2^{\gamma} \end{aligned}\right\} \text{Reversible adiabatic process}$$

$$\left.\begin{aligned} P_1 V_1^{\gamma} &< P_2 V_2^{\gamma} \\ T_1 V_1^{\gamma-1} &< T_2 V_2^{\gamma-1} \\ P_1^{1-\gamma} T_1^{\gamma} &< P_2^{1-\gamma} T_2^{\gamma} \end{aligned}\right\} \text{irreversible adiabatic}$$

(2) if a gas is processed from same initial state then final temp will be greater/more in irreversible process as compare to reversible adiabatic process.

$$q + w = \Delta U = n C_{v,m} \Delta T$$

$$w_{irr} > w_{rev}$$

$$n C_{v,m} (T_{2(irr)} - T_1) > n C_{v,m} (T_{2(rev)} - T_1)$$

$$T_{2(irr)} - T_1 > T_{(rev)} - T_1$$

$$T_{2(irr)} > T_{2(rev)}.$$

Heating of Ideal gas occur in adiabatic compression and cooling of Ideal gas occur in adiabatic expension.

$$W = \Delta U = n C_v \Delta T$$

Expension	& Compression.
$W < 0$	$V > 0$
$\Delta U < 0$	$\Delta U > 0$
$\Delta T < 0$	$\Delta T > 0$
$T_2 < T_1$	$T_2 > T_1$

V.V Imp.

An Ideal gas prossesed from same initial state in a reversible and irreversible adiabatic process the Select the correct option.

(i) If V_2 Ps same then $T_{2(irr)} > T_{2(rev)}$.

(ii) If V_2 is same then $P_{2(irr)} > P_{2(rev)}$.

(iii) if T_2 is same then $P_{2(irr)} > P_{2(rev)}$.

(iv) If V_2 is same $\Delta T_{(irr)} > \Delta T_{(rev)}$.

(v) if V_2 is same $|\Delta T_{(irr)}| > |\Delta T_{(rev)}|$ in Expansion.

$$T_{2(rev)} V_{2(rev)}^{\gamma} < T_{2(irr)} V_{2(irr)}^{\gamma}$$

$$P_{2(rev)} V_{2(rev)}^{\gamma} < P_{2(irr)} V_{2(irr)}^{\gamma}$$

$$P_{2(rev)}^{1-\gamma} T_{2(rev)}^{\gamma} < P_{2(irr)}^{1-\gamma} T_{2(irr)}^{\gamma}$$

$P_{2(rev)} < P_{2(irr)}$ $\quad W_{rev} < W_{irr}$

$P_{2(rev)} > P_{2(irr)}$.

Expansion.

$|W_{rev}| > |W_{irr}|$

$|n C_{vm} \Delta T_{rev}| > |n C_{vm} \Delta T_{irr}|$

$|\Delta T_{rev}| > |\Delta T_{irr}|$.

* $q = 0$

$\Delta H = n C_{pm} \Delta T$

$\Delta U = n C_{vm} \Delta T$

$$\boxed{W = \Delta U = n C_{vm} \Delta T}$$

$$W = \frac{nR\Delta T}{\gamma - 1}$$

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

Important

* Calculation of final temp. in adiabatic Process

(i) in reversible adiabatic

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

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

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

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

In irreversible adiabatic

$w(irr) = n C_{vm} (T_2 - T_1)$

$- P_{ext}(V_2 - V_1) = n C_{vm} (T_2 - T_1)$

$- P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right) = n C_{vm} (T_2 - T_1)$

against a → irr

(In irr)

If P_{ext} is not given in the Que. then $P_{ext} = P_2$

Que: 1 mol of an ideal monoatomic gas Initially one/ 100K and 1 atm Pressure. Is compressed adiabatically against a constant P_{ext} Pressure of 32 atm then calculate q, W, ΔH, ΔU for gas.

→ ~~If rev~~

$W_{irr} = n C_{vm} (T_2 - T_1)$

$= -P_{ext} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right) = n C_{vm} (T_2 - T_1)$

$-32 \left(\frac{nRT_2}{32} - \frac{nR(100)}{1} \right) = n \left(\frac{3}{2} R \right) (T_2 - 100)$

$-32 \left(\frac{T_2}{32} - 100 \right) = \frac{3}{2} (T_2 - 100)$

$T_2 = 1340$ kelvin.

$\Delta H = (1) \left(\frac{5}{2} R \right) (1340 - 100)$

$W = \Delta U = (1) \left(\frac{3}{2} R \right) (1340 - 100)$

[m at. → $\frac{3}{2}R$; rd. : $\frac{5}{2}R$; irr.]

$= 1 \times \frac{3}{2} \times (T_2 - T_1)$

$1 \times \frac{3}{2} \times 32 = 48$

(2) Calculate value of q, W, ΔH, ΔU in above process if process is considered Reversible adiabatic process upto final pressure of 32 atm. from same initial state.

Ans: $T_2 = 100 \left(\frac{1}{32} \right)^{\frac{1-5/3}{5/3}}$

$T_2 = 100 \left(\frac{1}{32} \right)^{-2/5}$

$T_2 = 400$ K.

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

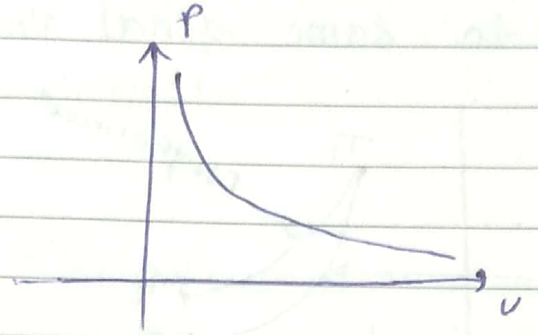
$T_2 = 1340$

graph of Adiabatic process

* P v/s V

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

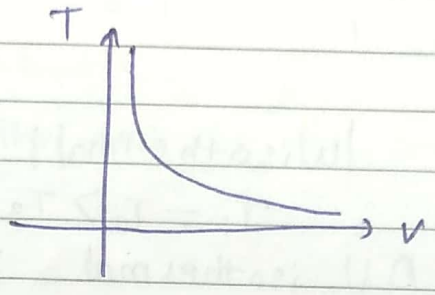
$P = \frac{\text{const.}}{V^{\gamma}}$



* T v/s V

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

$T = \frac{\text{const}}{V^{\gamma-1}}$



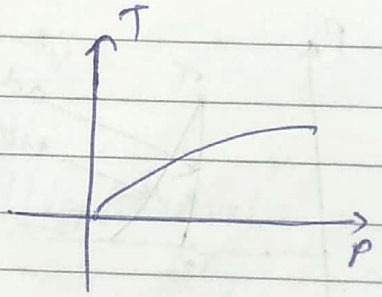
* T v/s P

$P^{1-\gamma} T^{\gamma} = \text{const}$

$T^{\gamma} = \text{const} \cdot P^{\gamma-1}$

$T = \text{const} \cdot P^{\gamma-1/\gamma}$

$\gamma = n^{4} \quad n < 1$



* Comparision b/w reversible Isothermal and reversible adiabatic process:

rev. adiabatic process

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

$V^{\gamma} \frac{dP}{dV} + P\gamma V^{\gamma-1} = 0$

$\left(\frac{dP}{dV}\right) = -\frac{P\gamma V^{\gamma-1}}{V^{\gamma}}$

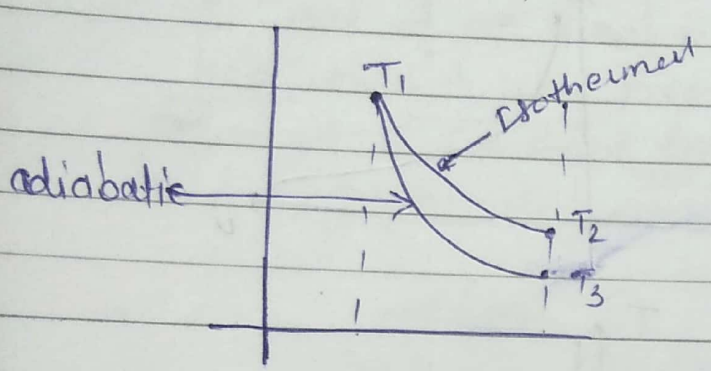
$\left(\frac{dP}{dV}\right)_{\text{adiabatic}} = -\gamma\left(\frac{P}{V}\right)$

Isothermal process: $PV = \text{const.}$

$\left(\frac{dP}{dV}\right)_{\text{isothermal}} = -\left(\frac{P}{V}\right)$

Expansion : from same initial state.

(i) up to same final volume.

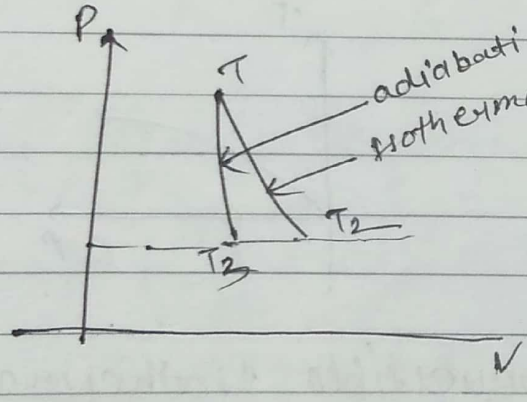


$|W_{isothermal}| > |W_{adiabatic}|$

$T_1 = T_2 > T_3$

$\Delta U_{isothermal} > \Delta U_{adiabatic}$

(ii)



$|W_{adiabatic}| < |W_{isothermal}|$

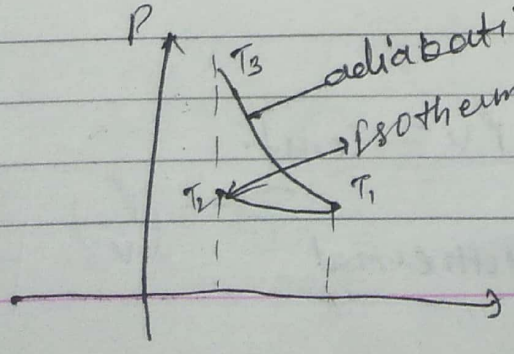
$W_{adiabatic} > W_{isothermal}$

$T_1 = T_2 > T_3$

$\Delta U_{adiabatic} < \Delta U_{isothermal}$

* Compression : from same initial state.

(i) upto same final volume.



H.W :- S-1 ⇒ 15 to 22 Thermo.
J.M :- Complete.

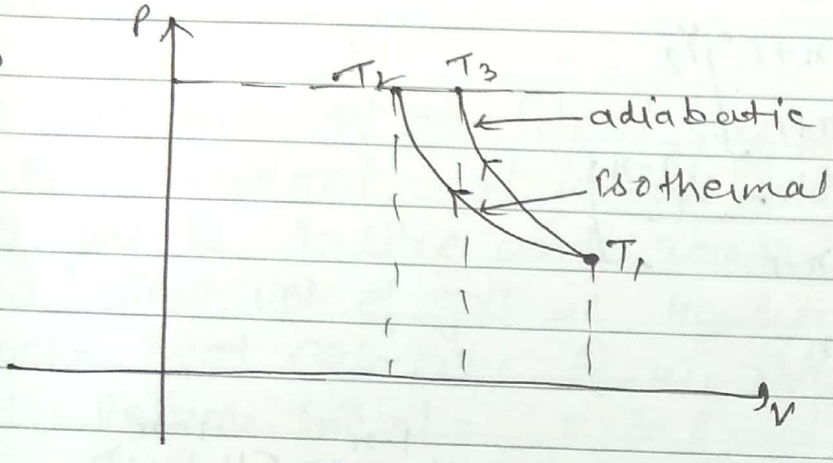
$|W_{adiabatic}| > |W_{isothermal}|$

$W_{adiabatic} > W_{isothermal}$

$T_1 = T_2 < T_3$

$\Delta V_{adiabatic} > \Delta V_{isothermal}$

(ii)



$T_1 = T_2 < T_3$

$\Delta V_{adiabatic} > \Delta V_{isothermal}$

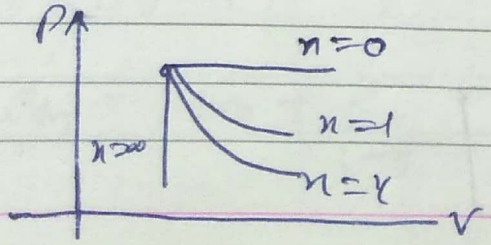
* Comparision of work can not be done without numerical values. because Area Under Isothermal curve is not a subset of Area Under Adiabatic curve.

* Polytropic Process :-

$PV^n = \text{constant}$ $\quad n \in (-\infty, \infty)$

Here n is called Polytropic Index.

$n = 0$	$n = 1$	$n = \gamma$	$n = \infty$
$P = C$	$PV = C$	$PV^\gamma = C$	$PV^\infty = C$
isobaric	Isothermal	adiabatic	$P^{1/n} V = C^{1/n}$
			$V = 1$
			isochoric.



Q. ΔU = ?

* Work in Polytropic Process :

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

$$w = \int_{V_1}^{V_2} \frac{C}{V^n}\, dV$$

$$w = -C\left[\frac{V^{-n+1}}{-n+1}\right]_{V_1}^{V_2}$$

$$w = C\left[\frac{V_2^{1-n} - V_1^{1-n}}{n-1}\right]$$

$$P_1 V_1^{\,n} = P_2 V_2^{\,n} = C$$

$$PV^n = C$$

$$P = \frac{C}{V^n}$$

$$w = \frac{C \cdot V_2^{1-n} - C V_1^{1-n}}{n-1}$$

$$w = \frac{P_2 V_2^{\,n} V_2^{1-n} - P_1 V_1^{\,n} V_1^{1-n}}{n-1}$$

$$\boxed{w = \frac{P_2 V_2 - P_1 V_1}{n-1}}$$

$$\boxed{w = \frac{n R \Delta T}{n-1}}$$

* molar heat capacity in Poly tropic process

$$n C_m \Delta T = n C_{vm} \Delta T - \frac{n R \Delta T}{n-1}$$

$$C_m = C_{vm} - \frac{R}{n-1}$$

$$\boxed{C_m = C_{v.m} + \frac{R}{1-n}}$$

$w = nRT$

" $q = \Delta U - w$, $q = nc_m\Delta T$

$\Rightarrow PV^n = C$

$\frac{T}{V}V^n = C$

$\Rightarrow TV^{n-1} = C$

$P\left(\frac{T}{P}\right)^n = C$ [nR is constant.]

$\Rightarrow P^{1-n}T^n = C$

Que: One mol. of an ideal gas follow they equation $PV^2 = \text{constant}$. if initial volume and temp. of gas is 20 litre and 200 K. respectively and final vol. of gas is 40 litre. then calculate molar heat capacity Q, w, ΔH, Δw in Process.

Ans: Volume initial = = 20 l. [Monoatomic $\gamma = \frac{5}{3}$]

Final volume = 40 l

Initial Temp: 200 k

final Temp. = ?

$PV^2 = \text{Const.}$

$\frac{T}{V}V^2 = C$, $TV = \text{Const.}$

$T_1V_1 = T_2V_2$

$T_2 = T_1\left(\frac{V_1}{V_2}\right) = 200\left(\frac{20}{40}\right) = 100$ kelvin

$w = \frac{(1)(R)(100-200)}{1}$, $\Delta H = (1)\left(\frac{5}{2}R\right)(100-200)$

$\Delta U = (1)\left(\frac{3}{2}R\right)(100-200)$

$q = \Delta U - w$ / $q = nc_m\Delta_T$

$c_m = c_{vm} + \frac{R}{1-n}$ $c_m = \frac{3}{2}R - \frac{R}{1} = \frac{R}{2}$

Qu: Calculate Value of polytropic index in given Process

1. $\frac{P}{r^2} = 1$ $\quad n = -2.$

(2) $T = kv^3$

$Tv^{-3} = k$

$PvV^{-3} = k$

$Pv^{-2} = k$ $\quad n = -2$

(3) $P^2T = \text{Constant}$

M-1:

$P^2 Pv = \text{Const}$

$P^3v = \text{Const}$

$Pv^{1/3} = \text{Const}$

$n = \frac{1}{3}$

* Free expansion of Ideal gas:

Free expansion of gas is always an irreversible Process with $P_{ext} = 0$

$P_{ext} = 0$

$w = -P_{ext}\,\Delta V$

$w = 0$

$K.E. = \text{constant}$

$T = \text{constant}$

$\Delta V = 0$

$q + w^0 = \Delta U^0$

$q = 0$

* Free expansion of Ideal gas is symmetrical is a irreversible isothermal and irreversible adiabatic process

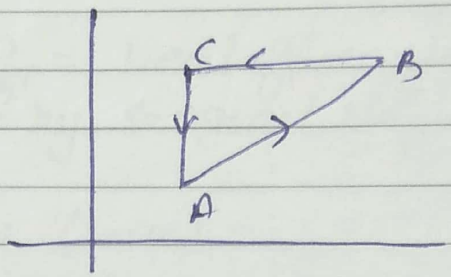
* Cyclic Process:

$\Delta H = 0$

$\Delta U = 0$

$q = -w$

$w = w_{AB} + w_{BC} + w_{CA}$.



Although in overall cyclic process ΔH & ΔU will be equals to zero. but during the cycle value of U and H will change and summation all the change will be equals to zero.

* Work In Reaction :-

$P = C, T = C$

$w = -P\Delta V$

$= -\Delta n_g RT$

$V = C, T = C$

$w = 0$