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4. Thermodynamics.

★ <u>Heat</u> → form of energy
SI unit - Joule   CGS unit - calories
$1 cal = 4.18 J$

★ <u>Temperature</u> → The degree of hotness or coldness
units = $^\circ C, ^\circ F, K$

$$\frac{T_C - 0}{100} = \frac{T_K - 273.15}{100} = \frac{T_F - 32}{180}$$

★ <u>Thermal Equilibrium</u> → Two bodies in thermal contact with each are said to be in thermal equilibrium, if there is no heat exchange between them.

★ <u>Zeroth Law of Temperature</u> → If two bodies are in thermal equilibrium with the third body then those two bodies are in equilibrium with each other.

heat exchange

A   B   C

heat exchange
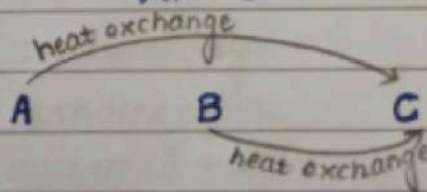
$T_A = T_C$
$T_B = T_C$ $\therefore T_A = T_B$

★ <u>Internal Energy</u> → It is the sum of all kinds of energies i·e kinetic energy, potential energy, rotational energy, vibrational energy etc· due to ordered and disordered motion of molecules.

★ <u>System</u> → An object taken for a thermodynamic study.

★ <u>open system</u> → A system which exchange both energy and matter with surrounding.
eg: Hot tea cup kept in open surrounding.

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* <u>Isolated system</u> → A system which do not exchange both energy and matter with surrounding.
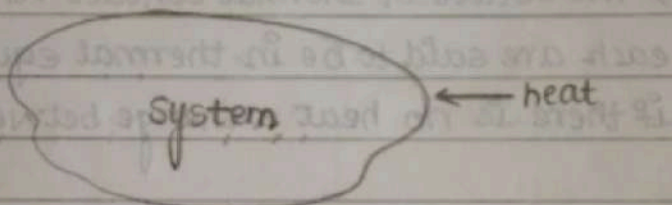
    eg : Thermas.

* <u>Close system</u> → A system which exchange only energy and not matter with surrounding.

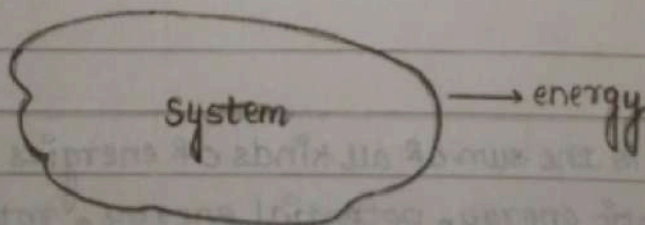   eg: Hot tea cup covered with lid.

* <u>Heat Energy</u> →

(i)

    System   ← heat

T_E = Temperature of environment

T_S = Temperature of system

$T_E > T_S$

heat absorbed by system / heat energy of system increases

Endothermic

Q positive

(ii)

    System   → energy
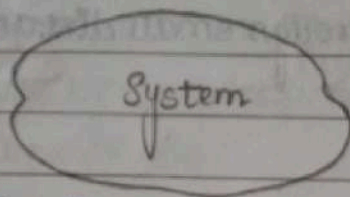
$T_E < T_S$

heat is released / heat energy of system decreases

Exothermic

Q negative

(iii)

System — No heat exchange

$T_E = T_S$

$g = 0$

★ <u>Work :-</u>

P_o

$T\uparrow$

gas ⟶ expands

$T\downarrow$ | compressed

gas
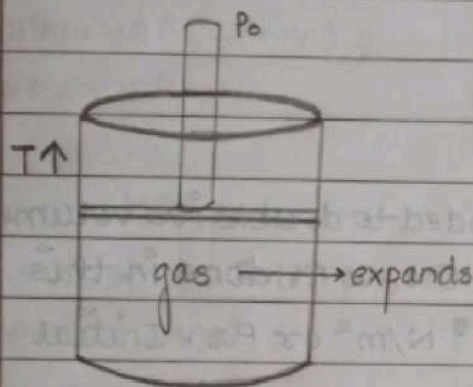
Work done by the gas ⟶ +ve
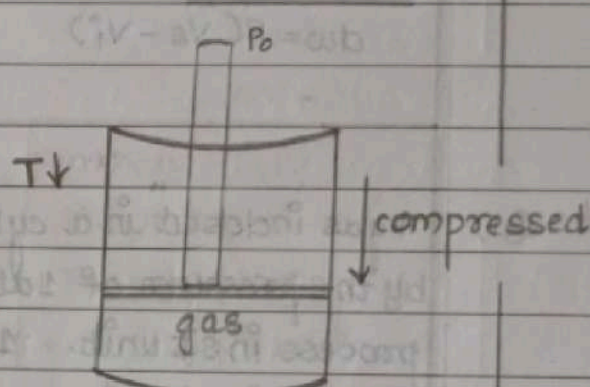
$g = +ve$

$T\uparrow = E\uparrow$

$P_{gas} > P_o$

In chemistry, work done by the system is -ve.

Work done on the gas ⟶ -ve

$g = -ve$

$T\downarrow = E\downarrow$

$P_{gas} < P_o$
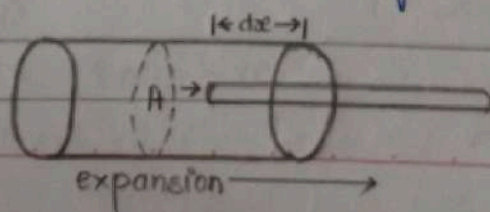
In chemistry, work done on the system is +ve.

★ <u>Expression for work done by the gas :-</u>

consider a gas inclosed in a cylinder of movable, frictionless piston.

Let A be the area of cross section of cylinder.

|← dx →|

(A) →

expansion ⟶

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As gas expands it pushes the piston through small distance dx.
$V_i \longrightarrow$ volume before expansion
$V_f \longrightarrow$ volume after expansion
$dv = V_f - V_i$ — change in volume
Now, work done due to expansion is given by

$$dw = f \times dx$$

but $f = PA$

$$dw = P \times A \times dx$$
$$dw = P \, dv$$
$$dw = P(V_f - V_i)$$

Q1) A gas inclosed in a cylinder is expanded to double its volume, by the pressure of 1 atm. Calculate the work done in this process in SI unit. $1\,atm = 1.01 \times 10^5 \, N/m^2$ or Pa. Initial volume is $1cm^3$.

$\longrightarrow$ Let the volume be 'v'
According to given condition,
volume is doubled

$\therefore V_f = 2V_i$ $P = 1 \times 10^5 \, Pa$
$V_i = 1cm^3 = 10^{-6} m^3$
$V_f = 2V_i = 2 \times 10^{-6} m^3$

$$dw = 1 \times 10^5 (2 \times 10^{-6} - 1 \times 10^{-6})$$
$$dw = 1 \times 10^5 (2-1) 10^{-6}$$
$$dw = 1 \times 10^5 \times 1 \times 10^{-6}$$
$$dw = 10^{-1}$$
$$dw = 0.1$$

Ans: Work done in this process is 0.1 J.

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Q2. A gas does 2·02J work so that its volume is double is initial volume by the pressure of 1 atm. Find value of initial volume of gas.

→

$dw = 2·02 J$

$P = 1 atm = 10^5 Pa$

$V_i = V$

$V_f = 2V$

$dw = P(V_f - V_i)$

$2·02 = 10^5 (2V - V)$

$2·02 = 10^5 \times V$

$V = \dfrac{2·02}{10^5}$

$V = 202 \times 10^{-2} \times 10^{-5}$

$V = 202 \times 10^{-7}$

$V = 2·02 \times 10^{-5}$

Ans: <u>Value of initial volume of the gas is $2·02 \times 10^{-5}$</u>

★ <u>Mathematical expression for first law of Thermodynamics:-</u>

$\Delta U = \text{Q} - W$

ΔU = change in internal energy of the system.

Q = heat

W = work

i) → heat added to the system
→ workdone by the system

$\Delta U = (+\text{Q}) - (+W)$

$\Delta U = \text{Q} - W$ ↑$\Delta U = +ve$

$\Delta U = 200 - 100$
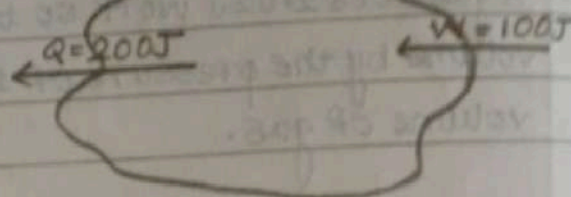
$\Delta U = 100 J$
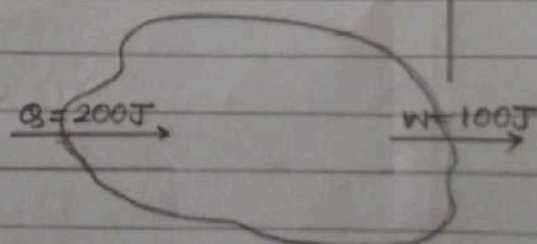
Q = 200J   W = 100J

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(iii) $\Delta U = (-Q) - (-W)$

$\Delta U = -Q + W$

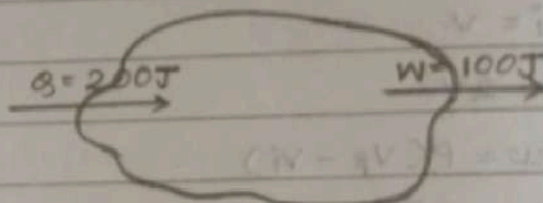$\Delta U = -200 + 100$ $\downarrow \Delta U = -ve$

$\Delta U = -100 J$

$Q = 200J \leftarrow$ $\leftarrow W = 100J$

(iii) $Q = 200 J$

$W = 200 J$

$\Delta U = Q - W$

$\Delta U = 200 - 200$

$\Delta U = -0$

$Q = 200J \rightarrow$ $W = 100J \rightarrow$

TB Q5. A system releases 125 KJ of heat while 104 KJ of work is done on the system. Calculate the change in internal energy.

$\longrightarrow$ $Q = 125 KJ$

$W = 104 KJ$

$\Delta U = Q - W$

$\Delta U = 125 + 104$

$\Delta U = -21 KJ$

Ans: The change in internal energy is -21 KJ.

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3) Calculate the change in internal energy of a system if it absorbs 25 KJ of heat and does 15 KJ of work.

→ $Q = +25$ KJ

$W = + 15$ KJ

$\Delta U = Q - W$

$\Delta U = 25 - 15$

$\Delta U = 10$ KJ

Ans: Change in internal energy is 10 KJ.

4) Calculate the change in internal energy if 15 KJ work is done on the system and 25 KJ of heat is given out.

→ $W = -15$ KJ

$Q = -25$ KJ

$\Delta U = Q - W$

$\Delta U = -25 - (-15)$

$\Delta U = -25 + 15$

$\Delta U = -10$ KJ

Ans: Change in internal energy is - 10 KJ.

★ Thermodynamic Process:-

system changes from initial state to final state.

P_1, V_1, T_1 = Initial state variables

P_2, V_2, T_2 = Final state variables

(i) Isothermal Process

→ constant temperature

→ $\Delta T = 0$

→ $\Delta V = 0$

→ $PV = constant$

Boyle's law (T constant) = $P \propto 1/V$

$$P_1 V_1 = P_2 V_2$$

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

★ **Expression for work done in Isothermal expansion:-**

Consider an isothermal expansion of ideal gas. Let V_i and V_f be initial and final value respectively.
Then work done due to expansion is-

$$dw = Pdv$$

But, $P = \dfrac{nRT}{V}$

$$dw = \frac{nRT}{V} dv$$

Total work done from initial volume (V_i) to final volume (V_f) is given by -

$$W = \int_{V_i}^{V_f} dw$$

$$W = \int_{V_i}^{V_f} \frac{nRT}{V} dv$$

$$W = nRT \int_{V_i}^{V_f} \frac{1}{V} dv$$

$$W = nRT [\ln V]_{V_i}^{V_f}$$

$$W = nRT [\ln V_f - \ln V_i]$$

$$W = nRT \ln \left(\frac{V_f}{V_i}\right)$$
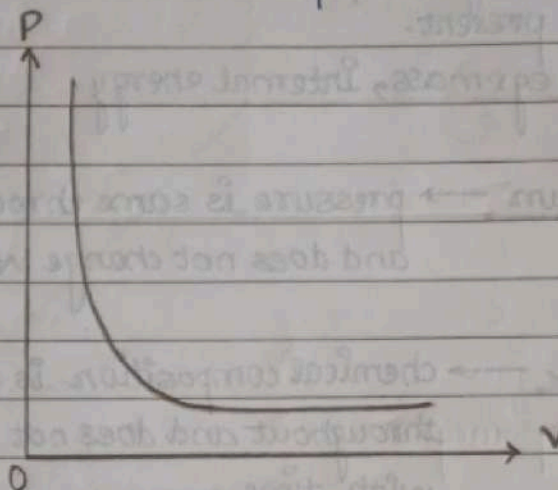
$$W = 2.303 \, nRT \log_{10} (V_f/V_i)$$

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$$\because \frac{Pi}{Pf} = \frac{Vf}{Vi} \quad\text{---} [\therefore PV \cdot constant]$$

$$\therefore W = 2.303 \, nRT \, \log_{10}\left(Pi/Pf\right)$$

* **P-V graph for isothermal process:-**

TB.Q4. A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400J of thermal energy from its surroundings. Determine the change in internal energy of system.

→ $dw = P(Vf - Vi)$

$dw = 1.01 \times 10^5 (10-5) \times 10^{-3} m^3$

$dw = 1.01 \times 10^5 \times 5 \times 10^{-3}$

$dw = 5.05 \times 10^2$

$dw = 505J$

$\Delta U = q - \omega$

$\Delta U = 400 - 505$

$\Delta U = -105J$

-ve sign indicates decrease in ΔU.

Ans: Change in internal energy of the system is -105 J.

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* <u>Intensive Variables</u> → do not depend on amount of matter present.

  eg: pressure, temperature

* <u>Extensive Variables</u> → they do depend on amount of matter present.

  eg: mass, Internal energy

* <u>Mechanical Equilibrium</u> ⟶ pressure is same throughout and does not change with time.

* <u>Chemical Equilibrium</u> ⟶ chemical composition is same throughout and does not change with time.

* <u>Thermal Equilibrium</u> → temperature is uniform throughout and does not change with time.

* <u>Degree of freedom</u> ⟶ No. of independent translational, rotational, vibrational motion a molecule or molecules can have.

  $$dof = 3N - R$$

(I) <u>Monoatomic gas</u> → He, Ne, Ar etc.

Translational motion
dof = 3

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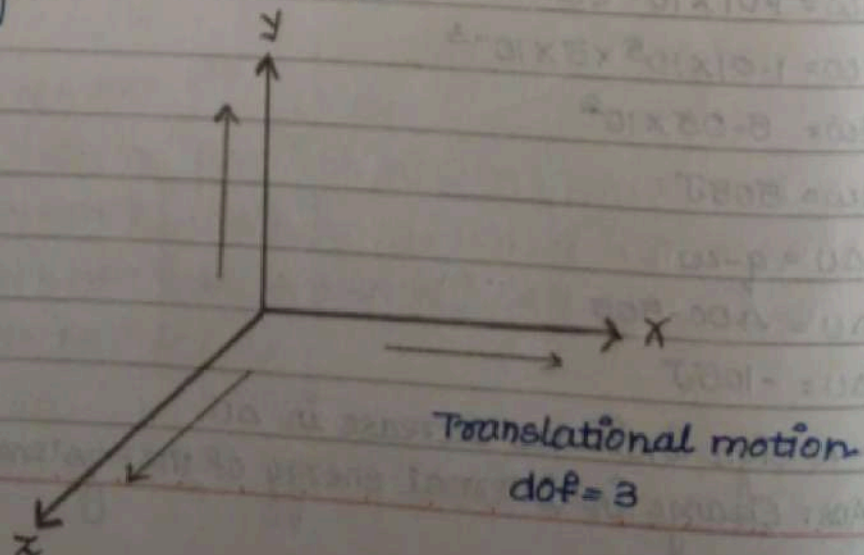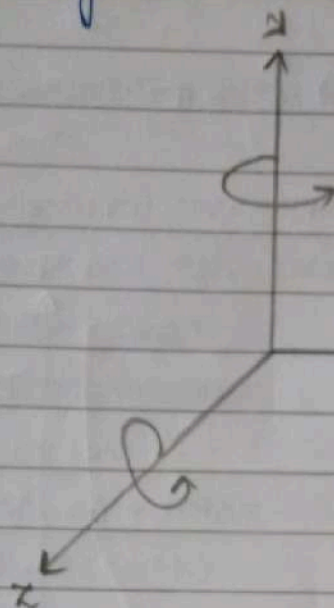
(II) Diatomic gas →

Translational and
Rotational motion
dof = 5

(III) Triatomic gas → CO_2, SO_2

(a) Linear

$$O \text{———} C \text{———} O$$
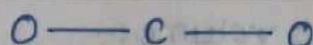
dof = 7

dof = 3N − R

Entrance
Restrictions

no. of molecules

(b) Non-linear

$$S$$
$$O \text{———} O$$
dof = 6

---
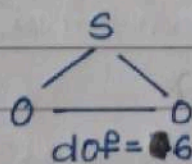
* ## Specific heat capacity :-

$$\Delta Q = mc\Delta t$$

specific heat
capacity

mass
(principle)

$$\therefore C = \dfrac{\Delta Q}{m\Delta T}$$

★ **Molar and Principle specific heat :-**

$$\Delta Q = nC\Delta t$$
$$\uparrow \text{molar}$$

But $n = \dfrac{m}{M}$

$$\therefore \Delta Q = \dfrac{m}{M} c\Delta t$$

$$\therefore c = \dfrac{\Delta Q M}{\Delta t m}$$

but, $\dfrac{\Delta Q}{\Delta t m} = c$

$$\boxed{\therefore C = Mc} \text{ — principle}$$
$$\text{molar}$$

★ **Specific heat at constant volume :-**

$$\Delta Q = nC_v \Delta$$
$$\downarrow$$

$$\therefore \Delta Q = U + W$$

$W = 0$ (constant volume)

$$\Delta Q = U = nC_v \Delta T$$
Specific heat

★ **Specific heat at constant pressure :-**

$$\Delta Q = nC_p \Delta T$$
$$\Delta Q = U + W$$
$$\boxed{C_p - C_v = R}$$

★ Expression for Isobaric Process :-

It is a constant pressure process. $\Delta P = 0$

$W = P\Delta V$ and $PV = nRT$

$\therefore W = nR\Delta T$ and $P\Delta V = nR\Delta T$
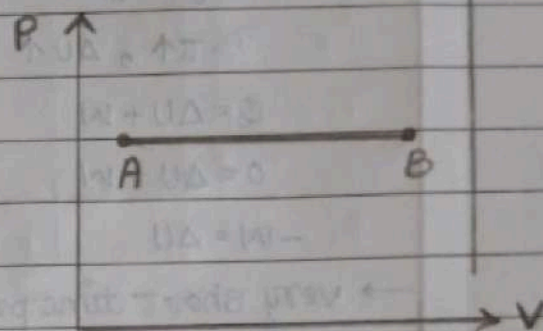
also $\Delta U = Q = nC_v\Delta T$

for isobaric process

$Q_p = \Delta U + W$

$Q_p = nC_v\Delta T + nR\Delta T$

$Q_p = n\Delta T(C_v + R)$

$Q_p = n\Delta T C_p$

$Q_p = nC_p(T_f - T_i)$

P-v diagram

★ Expression for Isochoric Process :-

It is a constant volume process. $\Delta V = 0$

$\Delta U = 0$

$\Delta V = 0$

$\Delta U = Q$

$W = 0$

$\Delta T \neq 0$

$W = P\Delta V$ but $\Delta V = 0$

$\therefore W = 0$

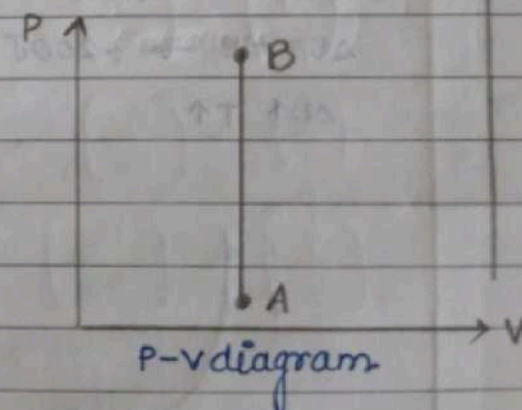from first law of thermodynamics.

$Q = \Delta U + W$

$\therefore Q = \Delta U \underline{\quad} \{W = 0\}$

also, $\Delta U = nC_v\Delta T$

$\therefore \boxed{Q = \Delta U = nC_v\Delta T}$

P-v diagram

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* **Adiabatic Process :-**

No exchange of heat energy from or into system.

$$S = 0$$

$$T\uparrow, \Delta U \uparrow$$

$$S = \Delta U + W$$

$$0 = \Delta U + W$$

$$-W = \Delta U$$

→ very short time process

→ gas expands, volume ↑

    work done by the gas — W +ve

but $\Delta U = -W$

eg: $W = +200J$

$\Delta U = -200J$

ΔU −ve

$\Delta U \downarrow \ T \downarrow$

→ gas compressed, work done on the gas

     W −ve

∴ $\Delta U = -W$ if $W = -200J$

$\Delta U = +ve \longrightarrow +200J$

$\Delta U \uparrow \ T \uparrow$

P-V diagram
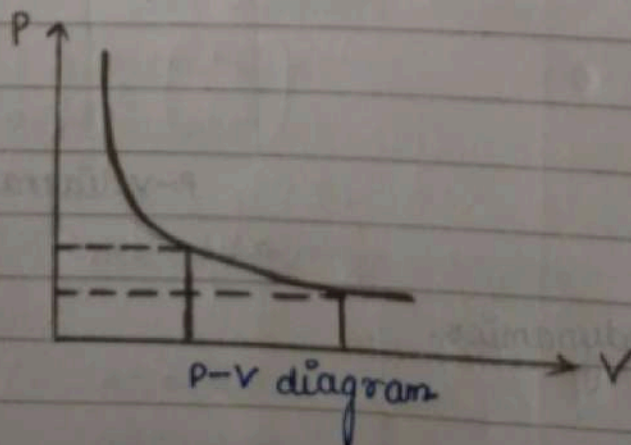
★ <u>Expression for adiabatic process :-</u>

$PV^r = $ constant

$r \longrightarrow$ adiabatic constant

$r = \dfrac{C_p}{C_v}$

→ for Monoatomic

$C_v = \dfrac{3}{2}R \;,\; C_p = C_v + R = \dfrac{3}{2}R + R = \dfrac{5}{2}R$

$r = \dfrac{C_p}{C_v} = \dfrac{5/2\,R}{3/2\,R} = \dfrac{5}{3} = 1.67$

$\longrightarrow \quad PV^r = C$

$P = \dfrac{C}{V^r}$

$\longrightarrow \quad W = \displaystyle\int_{V_i}^{V_f} P\,dv$

$W = \displaystyle\int_{V_i}^{V_f} \dfrac{C}{V^r}\,dv$

$W = C\displaystyle\int_{V_i}^{V_f} \dfrac{1}{V^r}\,dv$

$W = C\displaystyle\int_{V_i}^{V_f} V^{-r}\,dv$

$W = C\displaystyle\int_{V_i}^{V_f} \left[\dfrac{V^{-r+1}}{-r+1}\right]_{V_i}^{V_f}$

$W = C\left[\dfrac{V^{1-r}}{1-r}\right]_{V_i}^{V_f}$

$W = \dfrac{C}{1-r}\left[V_f^{1-r} - V_i^{1-r}\right]$

$W = \dfrac{C}{1-r}\left[\dfrac{1}{V_f^{r-1}} - \dfrac{1}{V_i^{r-1}}\right]$

Now,

$PV^r = $ constant $= C$

$\rightarrow P_i V_i^r = P_f V_f^r = C$

$W = \dfrac{1}{1-r}\left[\dfrac{C}{V_f^{r-1}} - \dfrac{C}{V_i^{r-1}}\right]$

$W = \dfrac{1}{1-r}\left[\dfrac{P_f V_f^r}{V_f^{r-1}} - \dfrac{P_i V_i^r}{V_i^{r-1}}\right]$

$W = \dfrac{1}{1-r}\left[P_f V_f^r \cdot V_f \cdot V_f^{-r} - P_i V_i^r \cdot V_i \cdot V_i^{-r}\right]$

$W = \dfrac{1}{1-r}\left[P_f V_f - P_i V_i\right]$

But, $P_f V_f = nRT_f$ and $P_i V_i = nRT_i$

$P_f V_f - P_i V_i = nR(T_f - T_i)$

$W = \dfrac{1}{1-r}\,nR\left[T_f - T_i\right]$

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TB. 89. An ideal monoatomic gas is adiabatically compressed so that its final temperature is twice its initial temperature. What is the ratio of final temper pressure to its initial pressure?

→ Monoatomic gas

$\therefore \gamma = 5/3$

$T_f = 2T_i$

$\dfrac{P_f}{P_i} = ?$

Note: PV^γ = constant [Adiabatic process]

But $PV = nRT$

$\therefore V = \dfrac{nRT}{P}$

$\therefore P\left[\dfrac{nRT}{P}\right]^\gamma = $ constant

$\therefore P[nR]^\gamma . \dfrac{T^\gamma}{P^\gamma} = $ constant

$\therefore P^{1-\gamma} . T^\gamma = $ constant

$P_i^{1-\gamma} . T_i^\gamma = P_f^{1-\gamma} . T_f^\gamma$

$\left(\dfrac{T_i}{T_f}\right)^\gamma = \left(\dfrac{P_f}{P_i}\right)^{1-\gamma}$

$\left(\dfrac{1}{2}\right)^{5/3} = \left(\dfrac{P_f}{P_i}\right)^{1-5/3}$

$\left(\dfrac{1}{2}\right)^{5/3} = \left(\dfrac{P_f}{P_i}\right)^{-2/3}$

$2^{-5/3} = \left(\dfrac{P_f}{P_i}\right)^{-2/3}$

But, $x^{-x} = y^{-y}$

$1/x^x = 1/y^y$

$\therefore y^y = x^x$

$2^{5/3} = \left(\dfrac{P_f}{P_i}\right)^{2/3}$

On cubing both sides,

$2^5 = \left(\dfrac{P_f}{P_i}\right)^2$

$32 = \left(\dfrac{P_f}{P_i}\right)^2$

Taking square root

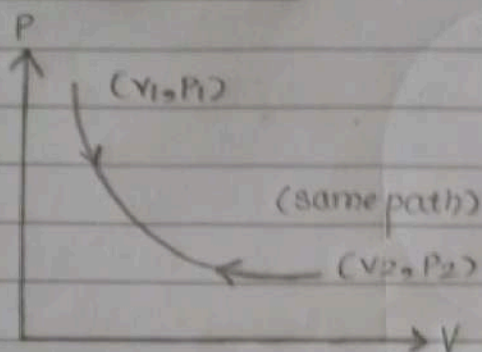$\sqrt{32} = \dfrac{P_f}{P_i}$

$4\sqrt{2} = \dfrac{P_f}{P_i}$

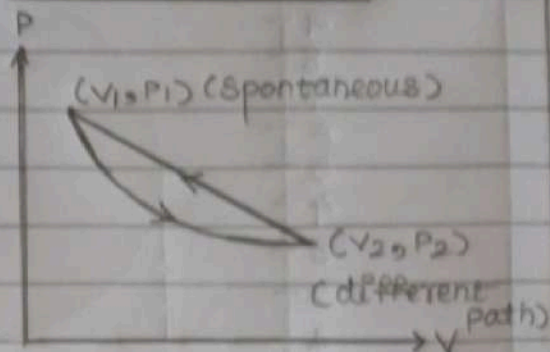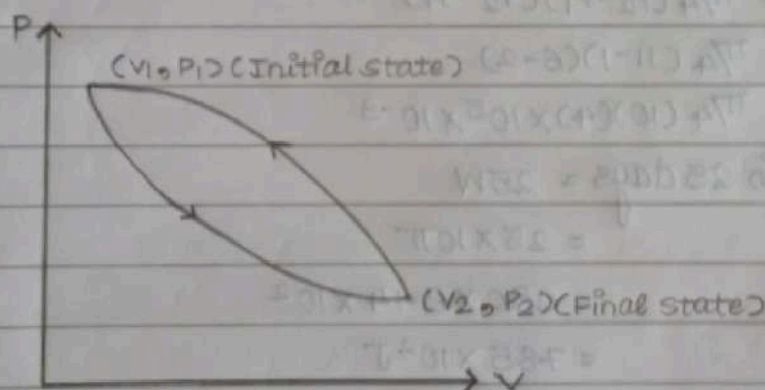$4 \times 1.41 = \dfrac{P_f}{P_i}$

$5.64 = \dfrac{P_f}{P_i}$

★ Reversible Process:-

eq: Melting of ice, Boiling of water (Bidirectional)
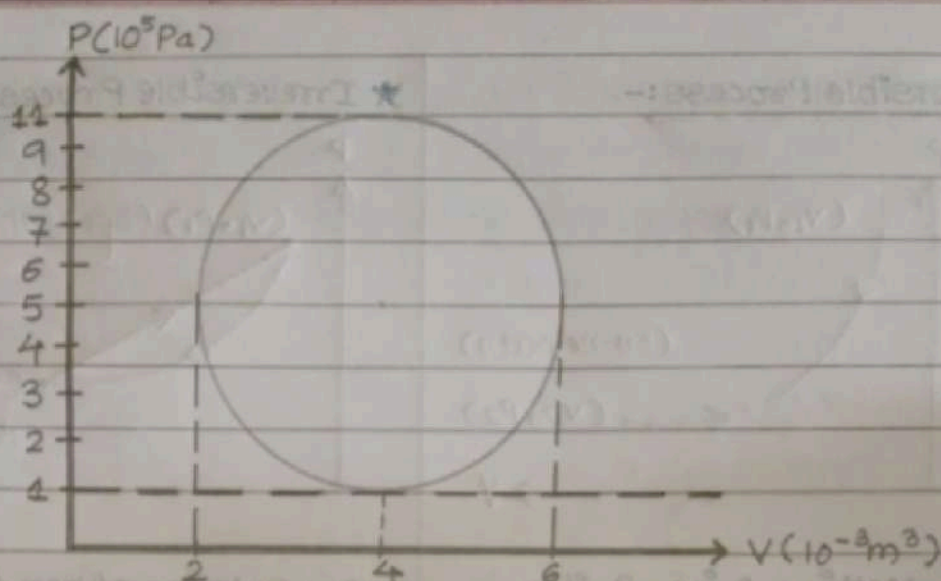
★ Irreversible Process:-

eq: Rubbing of hand, puncturing of tyre.

★ Cyclic Process:-

$\Delta U = 0$, T is constant.

It depends only upon initial and final states of the system.
Does not depend on the path followed.

TB. Q10. A hypothetical thermodynamic process is shown as below, calculate the work done in 25 cycles.

$P(10^5 Pa)$

11
9
8
7
6
5
4
3
2
4

$\rightarrow V(10^{-3}m^3)$

2   4   6

Area of circle = πr^2

$r = D/2$

$A = \pi/4\, D^2$

Work done = $\pi/4\,(P_2-P_1)(V_2-V_1)$

$= \pi/4\,(11-1)(6-2)$

$= \pi/4\,(10)(4)\times 10^5 \times 10^{-3}$

Work done in 25 days = 25W

$= 25\times 10\pi$

$= 250\times 3.14\times 10^2$

$= 785\times 10^2\,J$

$= 78500\,J$

---

extras. A hypothetical thermodynamic process is taken from initial to final state as shown in figure. Calculate work done in each case

$N/m^2 (10^5)\,P$

10 ┼ A ──────────→ B

2 ┼ D   C

$\rightarrow V(L)$

2   4   6
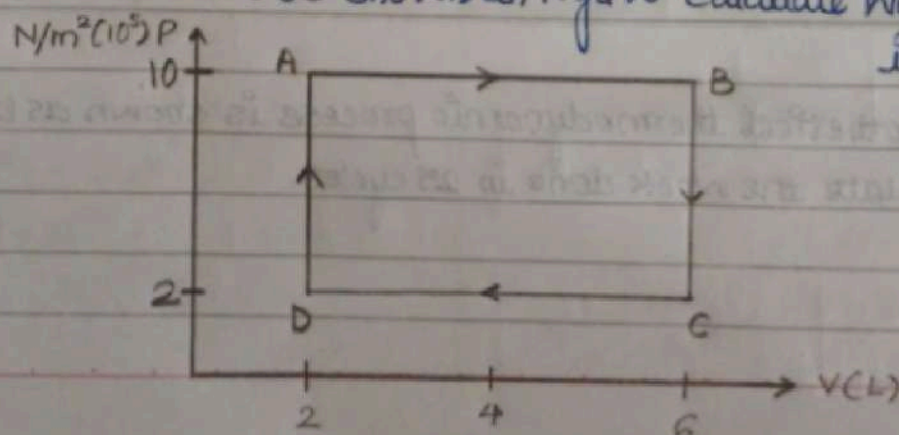
(i) Side BC

workdone in BC as $\Delta V = 0$ (Isochoric)

$$W_{BC} = P\Delta V$$

$$W_{BC} = P(0)$$

$$\therefore W_{BC} = 0$$

(ii) Side DA

$$W_{DA} = 0 \quad\text{——}\quad (\Delta V = 0)$$

(iii) Side AB

$$W_{AB} = P\Delta V$$

$$= P(V_2 - V_1)$$

$$= 10 \times (6-2) \times 10^{-3} \times 10^5$$

$$= 10 \times 4 \times 10^2$$

$$= 4000 J$$

(iv) Side CD

$$W_{CD} = P\Delta V$$

$$= P(V_2 - V_1)$$

$$= P(2-6)$$

$$= 10 \times -4 \times 10^{-3} \times 10^5$$

$$= 10 \times -4 \times 10^2$$

$$= -4000 J$$