

WORK

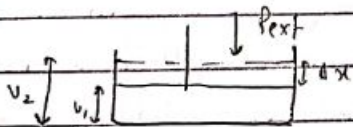
Work $\begin{cases} \rightarrow \text{PV work} \\ \rightarrow \text{non-PV work} \end{cases}$

PV work —
work involving expansion or compression of a system due to pressure.
For solid and liq. PV is (work) almost negligible. Generally
it is applicable for gases.

Non-PV work

Work other than expansion or compression like mechanical /
chemical / muscular work etc.

\rightarrow PV work



$$\begin{aligned} \text{Work} &= \text{force} \times \text{disp.} \\ &= P \cdot A \times \Delta x \\ &= -P_{\text{ext}} \Delta V. \end{aligned}$$

Here, This is irreversible process. So, pressure is constant.

Expansion

$$\Delta V = +ve$$

$$W = -ve$$

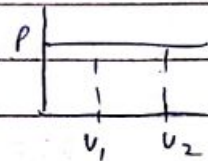
Work done by system

Compression

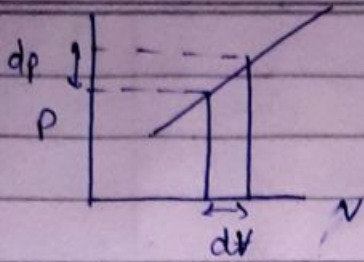
$$\Delta V = -ve$$

$$W = +ve$$

Work done on system



If process is reversible then pressure should be vary, not a constant.



$$W = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$$

Workdone in Isochoric process -

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

$$dV = 0$$

$$W = 0$$

Workdone in isobaric process -

$$W = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$$

$$P = \text{constant}$$

$$W = - P_{\text{ext}} \int_{V_1}^{V_2} dV$$

$$W = - P_{\text{ext}} [V]_{V_1}^{V_2}$$

$$W = - P_{\text{ext}} [V_2 - V_1]$$

$$W = - P_{\text{ext}} \Delta V$$

Workdone in Isothermal process -

a) Isothermal irreversible process -

$$W = - P_{\text{ext}} \Delta V$$

$$P = \text{constant}$$

b) Reversible Isothermal process - $P = \text{variable}$

$$W = - \int_{V_1}^{V_2} P_{\text{ext}} dV$$

$$W = - \int_{V_1}^{V_2} (P_{\text{gas}} + dp) \cdot dV$$

$$W = - \int_{V_1}^{V_2} P_{\text{gas}} \cdot dV$$

for ideal gas $PV = nRT$

$$W = - \int_{V_1}^{V_2} \left(\frac{nRT}{V} \right) dV$$

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

$$W = -nRT \log_e \left(\frac{V_2}{V_1} \right)$$

$$W = -2.303 nRT \log_{10} \left[\frac{V_2}{V_1} \right]$$

$$W = -2.303 nRT \log_{10} \left[\frac{P_1}{P_2} \right]$$

$$W = -2.303 P_1 V_1 \log_{10} \left[\frac{V_2}{V_1} \right]$$

Workdone in adiabatic process

Irreversible process (adiabatic) $P = \text{constant}$

$$W = -P_{\text{ext}} \int_{V_1}^{V_2} dV \Rightarrow -P_{\text{ext}} \Delta V$$

Work done in Adiabatic process -

Irreversible

$$q = 0 \quad \text{or} \quad \Delta q = 0$$
$$\Delta U = q + w \quad (\text{1st law of thermo})$$

$$\Delta U = w$$

internal energy

$$\Delta U = w$$

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

We know that

$$\Delta U = n C_v \Delta T$$
$$\Delta U = n C_v (T_2 - T_1) \quad \text{--- (i)}$$
$$w = n C_v (T_2 - T_1) \quad \text{--- (i)}$$

also we know that $C_p - C_v = R$ (Mayer eqⁿ)
divide the above eq. with C_v (molar h.c. at const V)

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

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

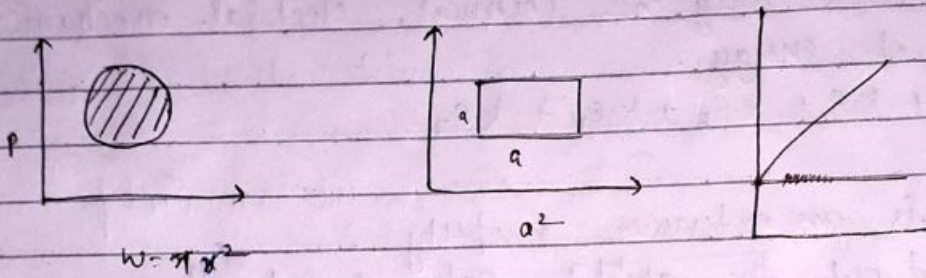
$$C_v = \frac{R}{\gamma - 1} \quad \text{--- (ii)}$$

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

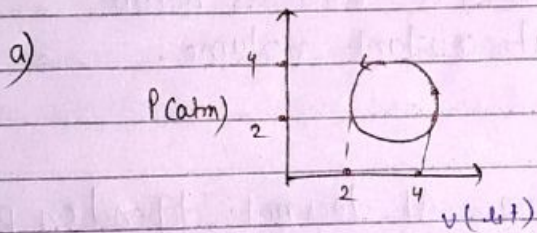
$$w = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

Workdone in cyclic process -

In cyclic process workdone should be equal to curve area.
 If curve is clockwise it means workdone by stem (-ve) sign
 Anticlockwise - workdone on system (+ve)



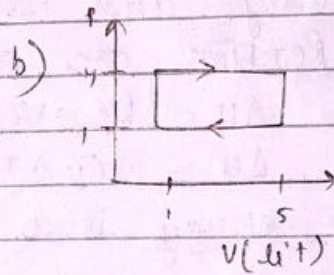
Qn Calculate the workdone in following -



$$W = \pi r^2 = 3.14 \times 1 \text{ atm lit}$$

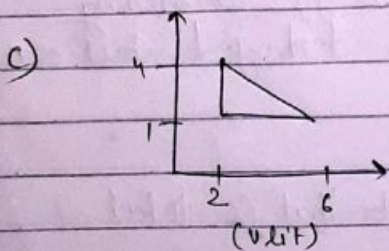
$$1 \text{ atm lit} = 101.3 \text{ J}$$

$$W = 3.14 \times 101.3 \text{ Joule}$$

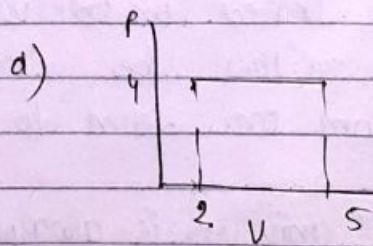


$$W = -12 \times 101.3 \text{ Joule}$$

$$W = -1215.6 \text{ Joule}$$



$$W = \frac{1}{2} \times 3 \times 3 \times 101.3$$



$$W = 12 \times 101.3 \text{ Joule}$$

Internal Energy (U) :-

Internal energy of a system is defined as the sum of diff energy associate with its atom and molecules like potential energy. kinetic energy (due to rotatory, vibratory and transitory motion). It may be chemical, electrical, mechanical or another type of energy.

$$I.E = P.E + K.E + K.E_r + K.E_v + K.E_T$$

$$I.E \propto T$$

→ Internal energy is an extensive property. विस्तार के साथ change होता है।

We can never find out the absolute value of internal energy of a system.

• We can calculate the change in internal energy of the system (u) by using an instrument which is known as bomb calorimeter. Reaction are carried out at constant volume.

$$\Delta u = U_f - U_i$$

$$\Delta u = n C_v \Delta T$$

→ Internal energy is a state function. It does not depend on path.

Note — for Ideal gases, $I.E \propto \text{Temp.}$

First Law of Thermodynamics —

This law is based on conservation of energy according to it energy can neither be created nor destroyed but can be transferred from one form to another.

The total energy of universe is always constant that is total energy at an isolated system conserved.

→ Mathematically it can be represented as —

$$\Delta u = q + w \quad \text{--- (i)}$$

Here, $\Delta u =$ change in internal energy.

q = Heat absorb by the system
 w = Workdone on the system

Here ΔU is state function and q and w are path function.

Note - Put the value to q and w with proper sign.

Conclusion - from the 1st law of thermo.

1) During isothermal process of an ideal gas,

$$\Delta T = 0, \quad \Delta U = 0 = nC_V \Delta T$$

$$q = -w$$

$$\text{or } -q = w$$

In isothermal process, heat absorbed by the system is equal to workdone by system or heat evolve by the system is equal to workdone on the system.

2) During isochoric process of an ideal gas,

$$\Delta V = 0, \quad w = 0$$

$$\Delta U = q_v \quad (q \text{ at constant vol.})$$

$$\text{or } -\Delta U = -q_v$$

absorb = take

During isochoric process, heat absorbed by the system is equal to increase in internal energy of the system

$$\Delta U = q_v$$

In isochoric process or heat is a state function.

or at constant vol, use (evolve) of heat is equal to use in internal energy of system

$$-\Delta U = -q_v$$

3) During adiabatic process of an ideal gas —

$$\Delta U = q + w$$

$$q = 0$$

$$\Delta U = w \text{ or } -\Delta U = -w$$

In ~~an~~ adiabatic process, work done on the system is equal to \uparrow se in internal energy of the system that is when a gas compressed adiabatically its internal energy \uparrow se

or

Work done by the system is equal to \downarrow se in internal energy of the system that is when a gas expanded adiabatically its internal energy \downarrow ses.

4) During Isobaric process —

$$\Delta U = q + w$$

$$P_{\text{ext}} = \text{constant}$$

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

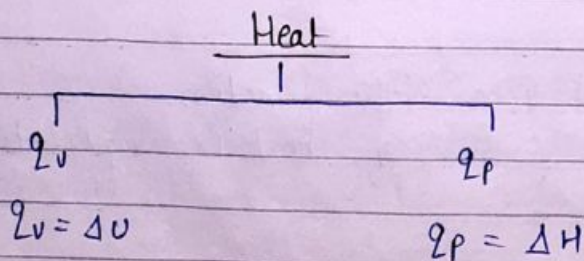
$$q_p = \Delta U + P\Delta V$$

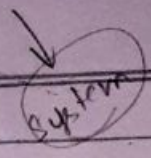
$$q_p = (U_2 - U_1) + P(V_2 - V_1) \quad (H = U + PV)$$

$$q_p = (U_2 + PV_2) - (U_1 + PV_1)$$

$$q_p = H_2 - H_1$$

$$q_p = \Delta H$$





$$q_p = \Delta H$$

→ In isobaric process, heat absorbed by the system is equal to the enthalpy of the system or $-q_p = -\Delta H$ or

→ In isobaric system, heat evolved by the system is equal to the change in enthalpy of system.

→ Enthalpy is a state function or at constant pressure, heat is a state function.

5) During cyclic process, $\Delta U = q + w$
 $\Delta U = 0$
 $q = -w$
or $-q = w$

Enthalpy (H)

It is heat contained in the system measured at constant pressure. The sum of internal energy and pressure vol. is known as enthalpy.

$$H = U + PV$$

here, H, U, P and V are state function

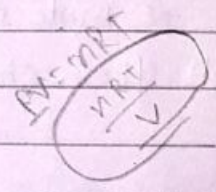
So, we can say: write change in enthalpy as

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

At const. temp. for any ideal gas it can be written as

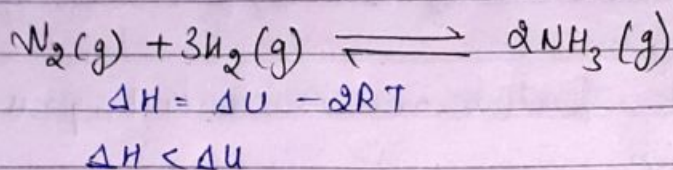
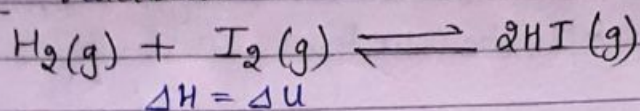
$$\Delta H = \Delta U + \Delta n_g RT$$

$\Delta n_g =$ no. of mole of gaseous product - no. of mole of gaseous reactant.

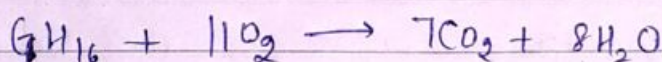


$$\Delta H = \Delta U + n_g RT$$

Ques Write down the relation between ΔH and ΔU for following reactions -



Ques Find out the diff. between ΔH and ΔU when the combustion of heptane (C_7H_{16}) is carried out at temp T .



$$\Delta n_g = 15 - 12 = 3$$
$$\Delta H - \Delta U = 3RT$$

Ques 2 mole of He is heated at const. P from 0°C to 50°C . Find out the change in enthalpy in Joule.

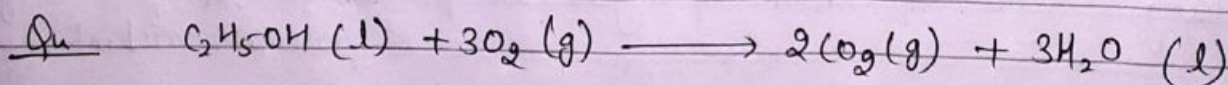
$$\Delta H = n_c P \Delta T$$

$$\Delta H = 2 \times 50 \times C_p$$

$$C_p = \frac{5}{2} \times R = \frac{5}{2} \times 8.31$$

$$C_p = 20.775$$

$$\Delta H = 2077.5 \text{ J/mol.}$$



$$\Delta U = ? \text{ at } 27^\circ\text{C} \quad \Delta H = -1366.5 \text{ kJ/mol.}$$