

Thermodynamics

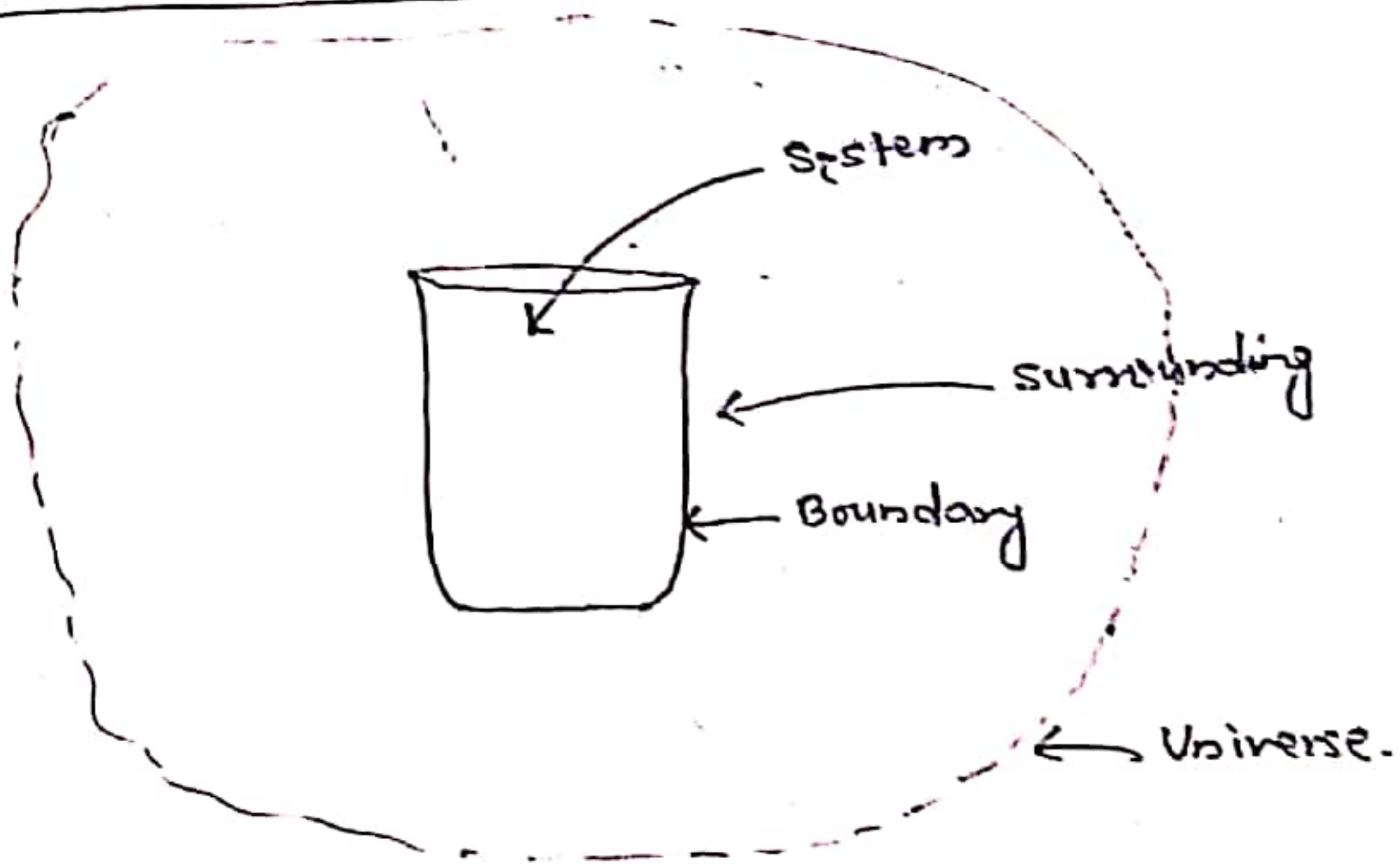
Thermo = heat

dynamics = to flow.

The term 'Thermodynamics' implies flow of heat. It deals with energy changes accompanying all types of physical and chemical processes.

chemical thermodynamics deals with heat changes during chemical reactions.

* Some Basic terms used in Thermodynamics:



* System :- The part of the Universe which is under experimental study and whose properties are being measured is called system.

* Surrounding :- The rest part of the Universe which might be in a position to exchange energy and matter with the system is called the surroundings.

* Universe :- The part of the system + the part of surrounding is called Universe.

Thus, $\text{Universe} = \text{system} + \text{surrounding}$

* Boundary :- It is real or imaginary surface which separates the system from the surroundings.

Types of systems:

* Isolated system - A system which can exchange neither energy nor matter with its surroundings is called an isolated system.

* closed system - A system which can exchange energy but not matter is called a closed system.

* open system - A system which can exchange matter as well as energy with its surrounding is called an open system.

* Thermodynamic processes :-

1). Isothermal process - A process is said to be isothermal if the temperature of the system remains constant during each stage of the process. $\Delta T = 0$ & $\Delta U = 0$.

2). Adiabatic process - A process is said to be adiabatic if no heat enters or leaves the system during any steps of the process. $q = 0$.

3). Isobaric process - A process is said to be isobaric if pressure of the system remains constant.

4). Isochoric process - A process is said to be isochoric if volume of the system remains constant.

5). cyclic process - In this process system comes back to its original state after undergoing a number of changes.

In cyclic process,
 $\Delta U = 0$ & $\Delta H = 0$.

ΔU = change in internal energy.

ΔH = change in enthalpy.

Thermodynamics

(3)

Thermodynamic function:-

Energy :-

* Different way to Express energy change -

1. Pressure - Volume work (mechanical work)

This type of work is associated with increase or decrease of the volume either on expansion or compression of the system.

Work of expansion is an isothermal reversible process:-

Let us consider a cylinder containing 1-mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_1 and pressure of the gas is P . Let External pressure is P_{ext} . Its final volume is V_2 . The gas is compressed and piston moves a distance l . The cross-sectional area of the piston is A .

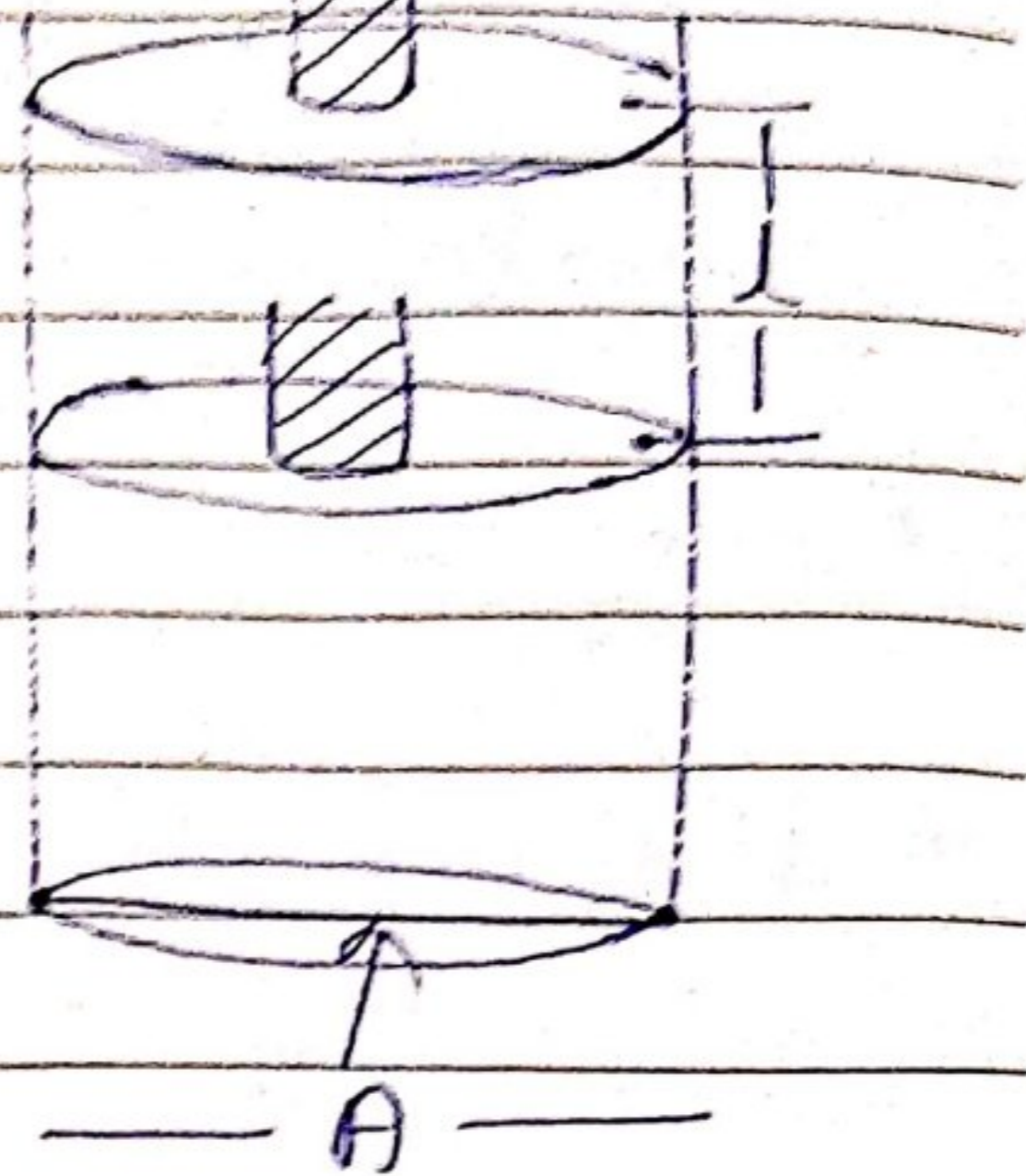


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change in volume -

$$-\Delta V = l \times A = (V_2 - V_1)$$

But pressure = $\frac{\text{force}}{\text{Area}}$

$$P_{\text{ex}} = \frac{\text{force}}{A}$$

$$\text{force on the piston} = P_{\text{ex}} \times A.$$

$$\text{work} = \text{force} \times \text{distance}$$

$$W = P_{\text{ex}} \times A \times l.$$

$$\therefore W = P_{\text{ex}} \times -\Delta V$$

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$$dW = -P_{\text{ex}} \cdot dV$$

Since, work is done in a reversible isothermal process. —

$$W_{rev} = - \int_{V_1}^{V_2} P_{ex} dv = - \int_{V_1}^{V_2} (P_{in} \pm dp) dv$$

Since, $dp \times dv$ is very small quantity so, it may be neglected.

$$\therefore W_{rev} = - \int_{V_1}^{V_2} P_{in} \cdot dv$$

$$\text{Ans} \quad W_{rev} = - \int_{V_1}^{V_2} P \cdot dv$$

Since, for n -mole of an ideal gas —

$$PV = nRT$$

$$\text{or} \quad P = \frac{nRT}{V}$$

$$\therefore W_{rev} = - \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dv$$

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

$$W_{rev} = -2.303 nRT \log \frac{V_2}{V_1}$$



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At constant temperature -

$$P_1 V_1 = P_2 V_2$$

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

$$\Delta \text{Intrev} = -2.303 nRT \log \frac{P_1}{P_2}$$