CHEMISTRY CLASS -XI

UNIT -6
THERMODYNAMICS

MODULE -2/5

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OUTLINE

- Work

- Heat

- Zeroth Law of thermodynamics

- First law of thermodynamics

- Calculation of work for various process

WORK

- Energy that is transmitted from one system to another in such a way that difference of temperature is not directly involved. This definition is consistent with our understanding of work as dw=Fdx. The force F can arise from electrical ,magnetic ,gravitational and other sources. It is a path function. It is a mechanical way of transfer of energy.

- Various types of work-

- Electrical Work = q x v

- Gravitational work=mgh

- Pressure volume work=f x dx.

- We shall discuss about pressure volume work in this chapter

- For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. *If* external pressure is pex which is greater than *p, piston* is moved inward till the pressure inside becomes equal to *pex*. Let this change be achieved in a single step and the final volume be V_f. During this compression,

  suppose piston moves a distance, *l and is* cross-sectional area of the piston is A

- then, volume change = $l \times A = \Delta V = (V_f - V_i)$
- We also know, pressure= Force/area
- Therefore, force on the piston = *pex . A*
- If w is the work done on the system by
- movement of the piston then w = force × distance = *pex . A .l*

  = *pex . (–ΔV) = – pex ΔV = – pex $(V_f - V_i)$*

- The negative sign of this expression is required to obtain conventional sign for W , which will be positive. It indicates that in case of compression work is done on the system.Here $(Vf - Vi)$ will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive.

- If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\Sigma p \blacktriangle V$

- Litre atmosphere term is unit of energy . It is useful to remember the conversion.

- **1 litre atmosphere=101.3joules**

  =24.206 cal
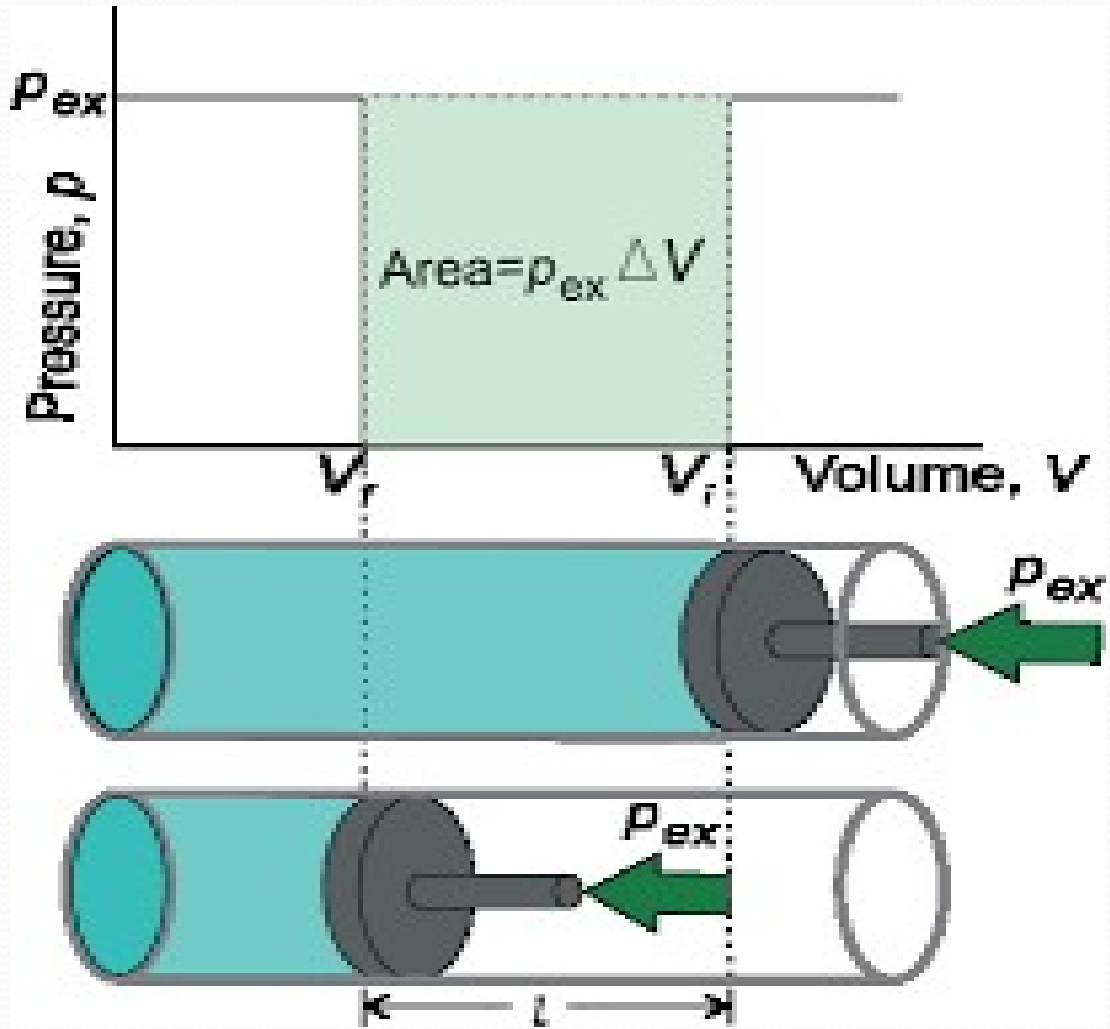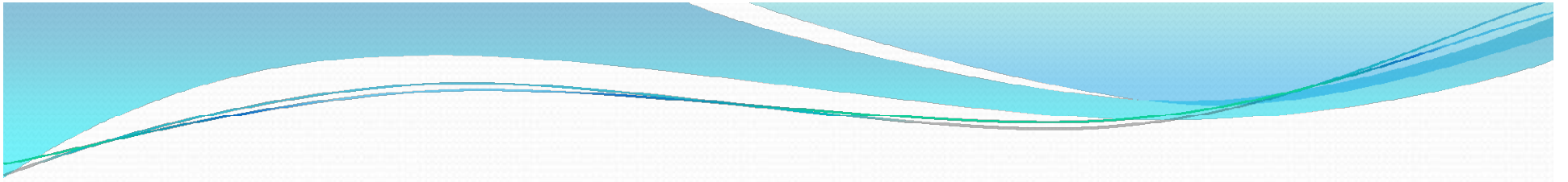
Question-Find the work done in each case-

- a)When one mole of ideal gas in 10 litre container at 1atm,is allowed to enter a vaccuated bulb of capacity 100 litre.

- b)When one mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

- Answer-

$W = - P \triangle V$

But since gas enter the vacuum bulb and pressure in vacuum is zero. This type of expansion is called free expansion and work done is zero

b) W=-P V =-1(5-1)=-4 litre atmosphere

- **REVERSIBLE ISOTHRERMAL WORK**

- If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work

  done on the gas by the relation.

  dW= -pex ∫ dv

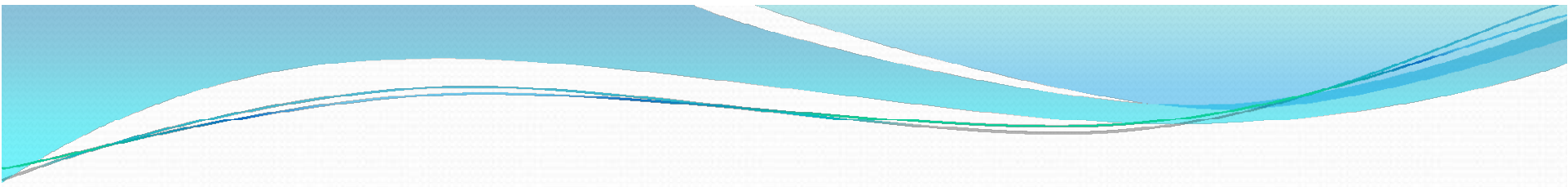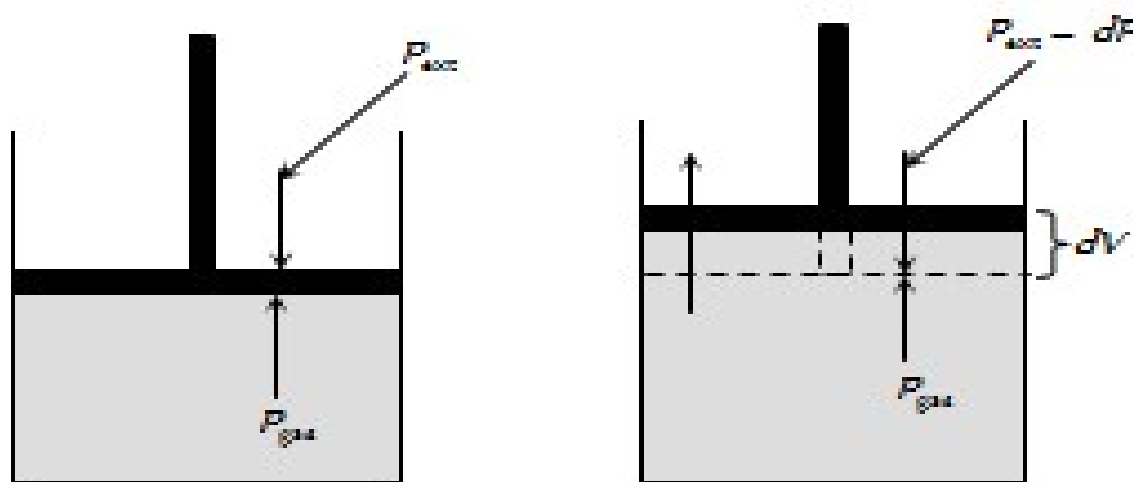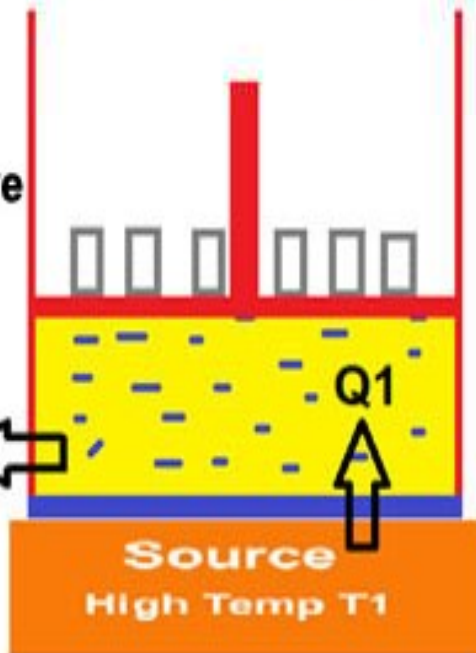Fig. 10.1

dw = -(p – dp)dv

= -pdv +dpdv

= -pdv ....(due to negligible value of dp.dv, the product can be neglected)

$\therefore$ dw =- pdv

Integrating the above equation between the **limits of initial volume V1 and final volume V2**

∫dw = -∫ pdv

$= -p \int dv_{V_1}{}^{V_2}$

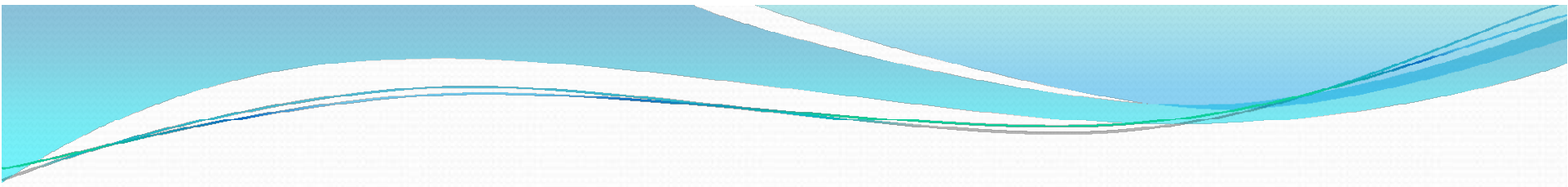$= -nRT/V \int dv$ ....PV=nRT acc. to ideal gas equation

$$= -nRT \int dv / V$$

$$= -nRT [\ln V]_{V1}^{V2}$$

$$= -nRT [\ln V_2 - \ln V_1]$$

$$= -nRT \ln V_2 / V_1$$

$$= -2.303\ nRT \log_{10} V2/V1$$

- When Work is done by the system on the surrounding
- (expansion) the expression is given as……

$$W_{max} = -\ 2.303\ nRT\ \log_{10} V_2/V_1$$

- When work is done by the surrounding on the system (compression) $\log(V_2 -/V_1)$ will be negative , the expression becomes……..

$$W_{max} = +\ 2.303\ nRT\ \log_{10} V_2/V_1$$

- For isothermal reversible work,
- According to Boyel's law $P_1V_1=P_2V_2$
- therforefore$V_2/V_1 = P_1/P_2$
- Therefore work maximum in terms of pressure is-
- Expansion work

$$W_{max} = -\ 2.303\ nRT\ \log_{10} P_1/P_2$$

- Work done on the system-

$$W_{max} = +\ 2.303\ nRT\ \log_{10} P_1/P_2$$

Work done in reversible isothermal process is possible only when the difference between the opposing force and driving force is infinitesimally small

Heat(q)

- It occurs when there is a difference of temperature between system and surroundings.

- It is a random form of energy and **path dependent**. Its units are joule or calorie.

- According to IUPAC convention heat given by system is expressed with –ve sign and heat given to system is expressed with positive sign
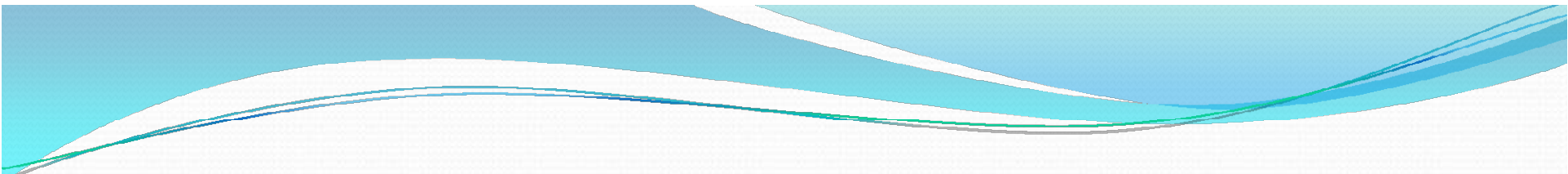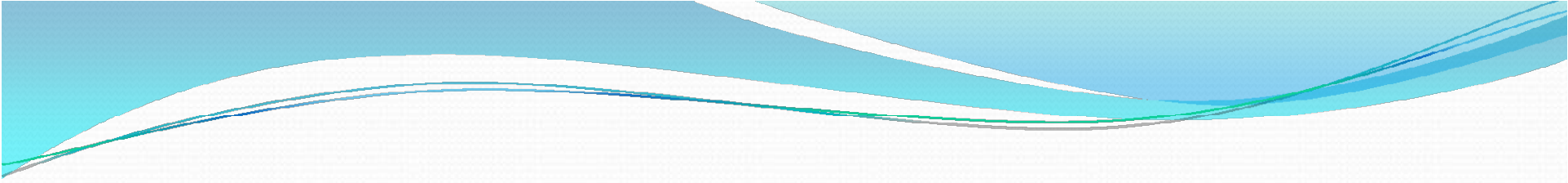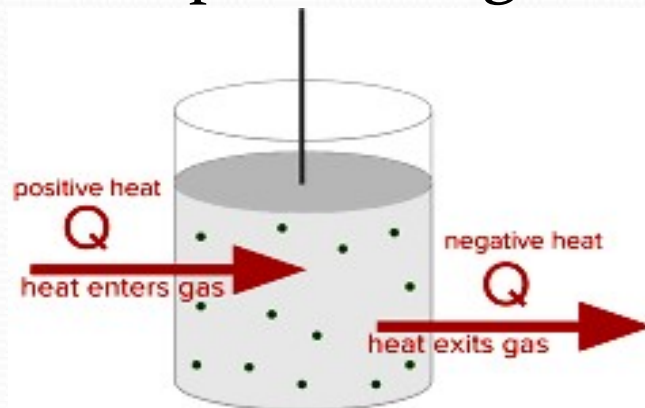
- **Sign conventions Heat and Work**
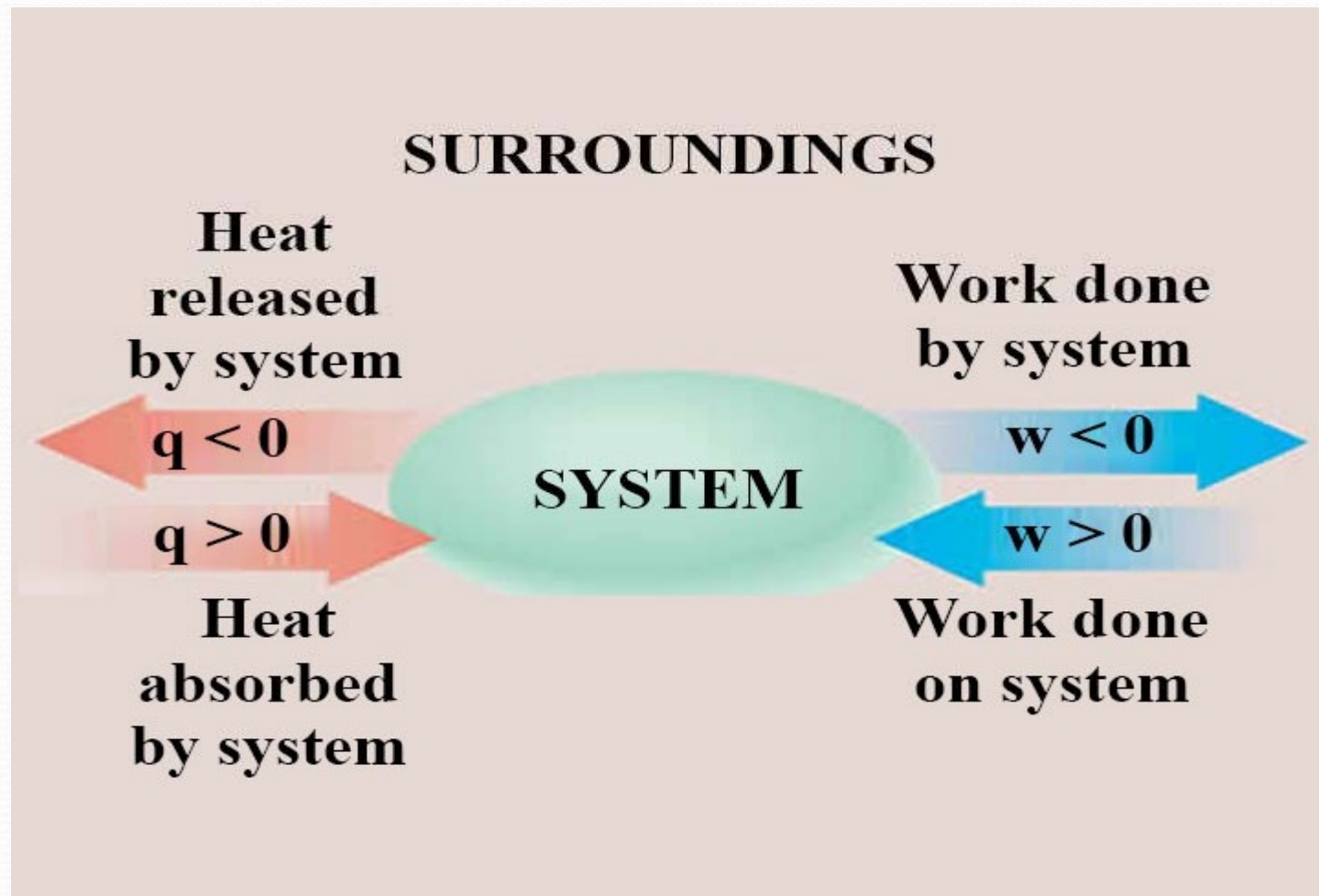
Numerical

- Calculate the work obtained in a process when 1 mole of an ideal gas is compressed isothermally and reversibly from 2.02×10^5 Pa to 20.2×10^5 at 300K ($R = 8.314$ jK^{-1} mol^{-1})

- Answer-n=1mol

- $R = 8.314$ jK^{-1} mol^{-1}

- $P_1 = 2.02 \times 10^5$ Pa

- $P_2 = 20.2 \times 10^5$ Pa

- For isothermal reversible compression work done is given as-

- $W_{max} = -2.303$ $nRT log_{10} P_1/P_2$

    $= -2.303 \times 8.314 \times 300 \times log_{10}$ 2.02×10^5 / 20.2×10^5

- Work max=-2.303 x 8.314 x 300 x log 0.1

$$= -2\ 2.303 \times 8.314 \times 300 \times \log 10^{-1}$$

$$= -2.303 \times 8.314 \times 300 \times (-1 \log 10)$$

$$= -2.303 \times 8.314 \times 300 \times -1$$

$$= +5.744.14\ J$$

Internal Energy(UorE)

- It is the total energy within the substance. It is the sum of many types of energies like

- vibrational energy, translational energy. etc. It is a extensive property and state function.

- U=Ukinetic + U potential + Unuclear + ...

- Its absolute value cannot be determined but experimentally change in internal energy (Δ) can be determined by

- $\Delta U = U_2 - U_1$ or $\Sigma U_p - \Sigma U_R$

- For exothermic process, ΔU = -ve, whereas for endothermic process ΔU = +ve

- U depends on temperature, pressure, volume and quantity of matter.

- It is heat change at constant value since all the heat supplied goes to increase the internal energy of the gas.

- $\Delta U = q_v$

- For an ideal gas change in internal energy with change in volume at constant temperature is zero.

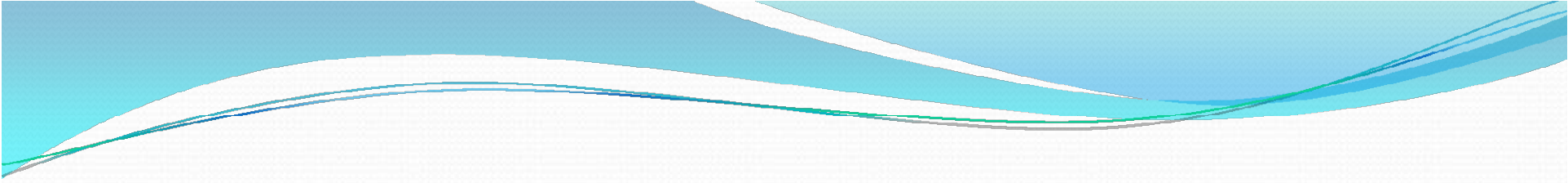- We know Q is not a state function, but .....

- Qv=?

First law of thermodynamics

- Energy can neither be created nor destroyed although it can be converted from one form to the other.
- Mathematically, $\Delta U = q + W$
- where, ΔU = internal energy change
- q = heat added to system
- W = work added to system
- **Sign convention**
- (i) q is + ve = heat is supplied to the system
- (ii) q is – ve = heat is lost by the system
- (iii) Wis + ve = work done on the system
- (iv) Wis – ve =work done by the system

Mathematical derivation of first law of thermodynamics
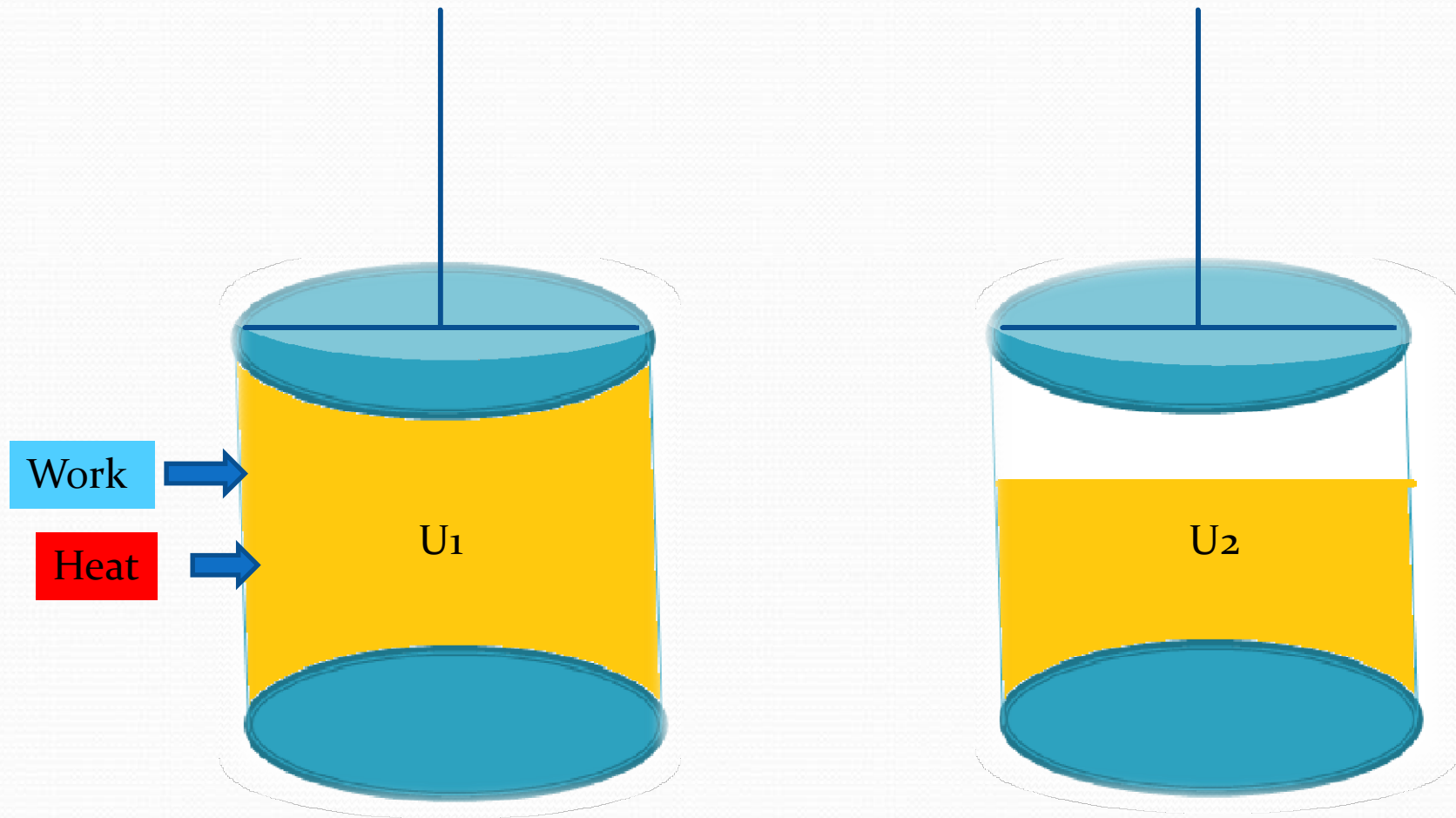
- If Q heat is absorbed by a sytem which has U1 internal enrgy. Internal energy increases from U1 to U1+Q
- Further if work is done on the system the internal energy futher increases and it becomes U1 + Q + W
- U1 + Q + W=U2
- $U_2 - U_1 = Q + W$
- $\therefore \Delta U = Q + W$
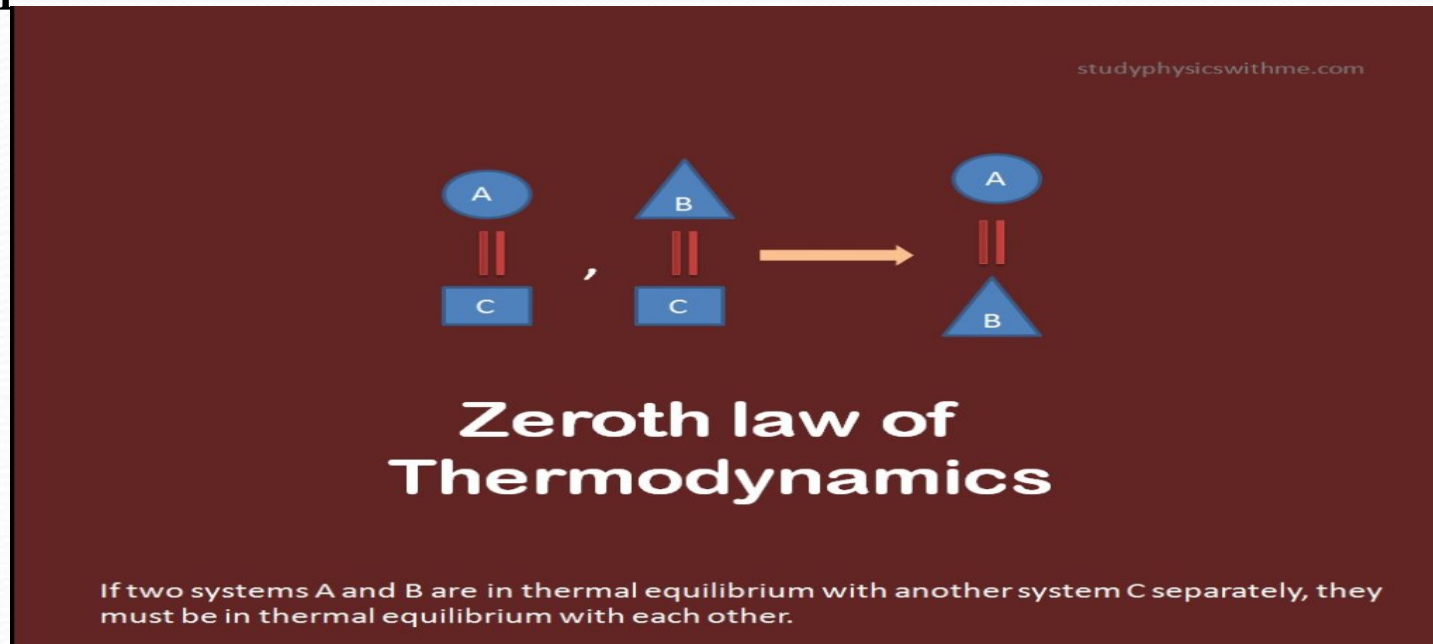- for infinitesimal changes we can write …
- dU = dQ + dW

First law of thermodynamics - interpretations

1. Energy can neither be created nor be destroyed but can be converted from one form to another
2. Whenever one form of energy disappears, equivalent amount of another kind of energy appears
3. Total energy of the universe always remains constant
4. Total energy of an isolated system always remains constant

Zeroth law of thermodynamics

- The law states that if the two systems are in thermal equilibrium with a third system then they are also in thermal equilibrium with each other. Temperature is used here to know, the system is in thermal equilibrium or not


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Zeroth law of Thermodynamics

If two systems A and B are in thermal equilibrium with another system C separately, they must be in thermal equilibrium with each other.

ZEROTH LAW-REAL LIFE EXAMPLE

Calculation of work done in various process

- **Isothermal Process**-Work done Can be calculated as-
- $W = -\int PdV$
- Since dT=0 so dU=0
- From first law q=-w
- If process is reversible-
- Wmax = - 2.303 nRT $\log_{10}$ V2/V1
- **Irreversible isothermal expansion** –If external pressure over the piston is abruptly changed from the equilibrium value, the mechanical equilibrium is disturbed and piston rushes out. This type of p,v work irreversible p,v work. To calculate irreversible p,v work. Law of conservation of energy is used. W= -Pext ▲V
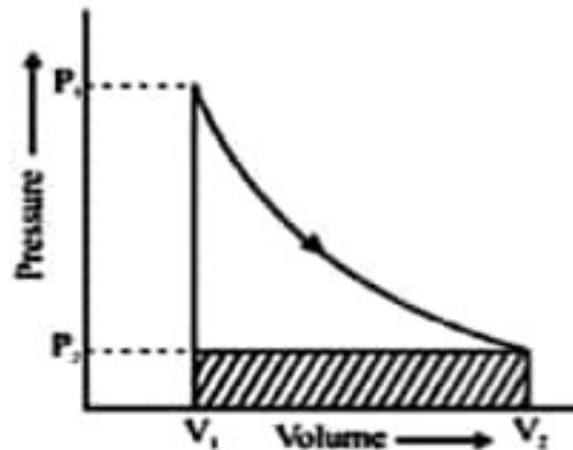
- **P₁rreversible isothermal expansion and compression (many steps)**
- Consider an irreversible expansion of an ideal gas from initial pressure P1 to final Pressure P4 in four steps. The gas is allowed to expand against constant external pressure of P1 P2 P3 P4.Hence system passes through 4 equilibrium states. The work done in the process is shown graphically. The area under the isotherm is the magnitude of reversible work .clearly the magnitude of reversible work is greater than irreversible work. As the number of intermediate steps in irreversible expansion is increased, the magnitude of work increases and as the number of steps tend to infinity Wirr tend to Wrev.
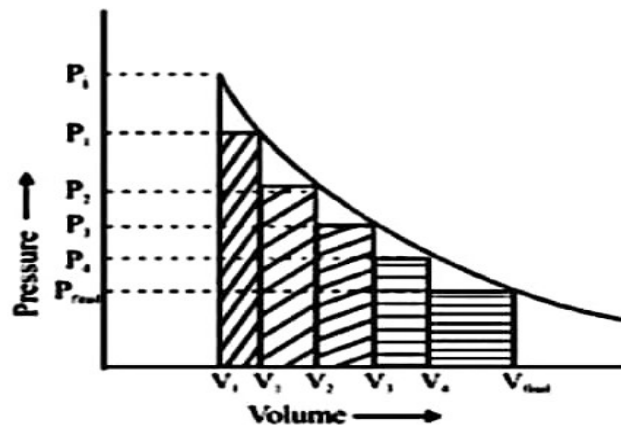
- **Free expansion of ideal gas** –When ideal gas is allowed to expand against zero external pressure, the process is called free expansion. W=0 for free expansion, During the free expansion, the ideal gas do not lose any energy, and hence temperature of ideal gas remains constant. Hence free expansion of ideal gas is an example of isothermal, adiabatic irreversible process.

- However if a real gas is allowed to expand in vacuum, the gas may be cooled or heated up depending upon temperature of the real gas .The temperature above which a gas gets heated upon expansion is called inversion temperature.
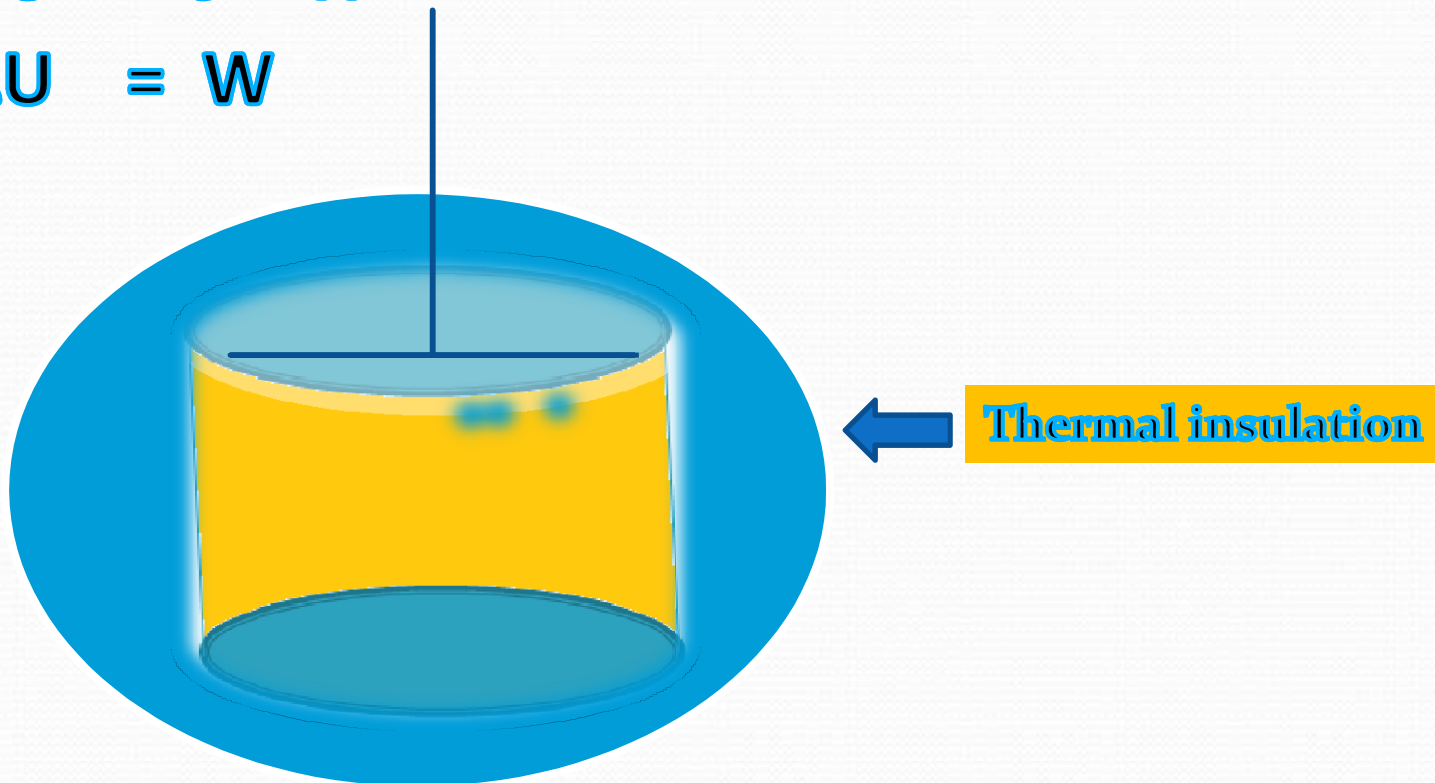
Adiabatic process

As there is no exchange of heat Q = 0

According to first law of thermodynamics..

$\Delta U = Q + W$

$\therefore \Delta U = 0 + W$

$\therefore \Delta U = W$

Thermal insulation

Isochoric process

ΔV = 0 as volume remains constant

∴ W= P ΔV = P X (0) = 0

According to first law of thermodynamics

$$\Delta U = Q + W$$

$$= Q + 0$$

∴ Δ U = Q

∵ change in internal energy of the system = heat transfer at constant volume

∴ Δ U = Q$_v$ .... the subscript ' v' indicates heat is supplied at constant volume

Isobaric process

Reactions carried out at constant pressure ….

all the chemical reactions are generally carried out <u>at atmospheric pressure</u> which is constant

$\Delta U = Q + W$ ... first law of thermodynamics

$\Delta U = Q + (-P \, \Delta V)$ ……… $W = -P \, \Delta V$

since heat is supplied at constant external pressure (P_{ext}) let $Q = Qp$

$\Delta U = Qp + (-P_{ext} \, \Delta V)$

∴ $Qp = \Delta U + P_{ext} \, \Delta V$

THANK YOU