# MODULE 1

Thermodynamics can be defined as the science of energy. The name thermodynamics stems from the Greek words therme (heat) and dynamics (power).

## Role of thermodynamics in engineering and science

The principle of thermodynamics plays a vital role to achieve improved design and better performance

1. By increasing output of the system
2. Reducing input of a scarce resource.
3. Reducing total cost
4. Lesser environmental impact

All forms of energy, conventional and nonconventional energy that we harness in our life can be benefitted by knowledge of thermodynamics.

## Applications

a. Automobile engines
b. Turbines,pumps,compressor
c. Fossil and nuclear power station.
d. Heating,ventilating and air conditioning
e. Fuel cell
f. Wind power system
g. Geothermal system
h. Biomedical application
i. Ocean,thermal and tidal power generation system.
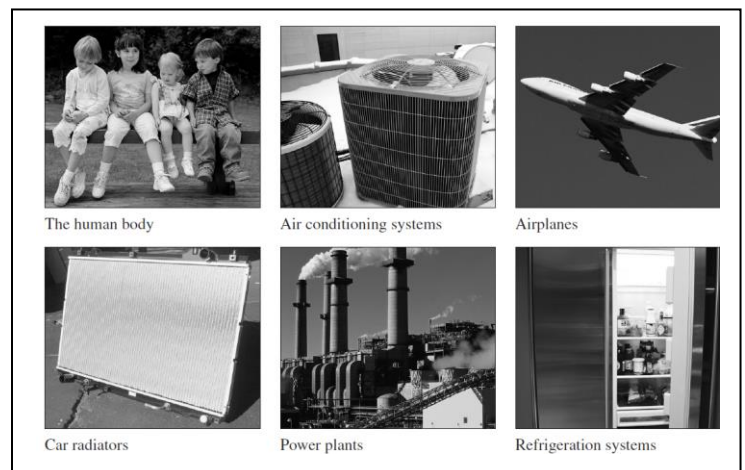
## Macroscopic or classical view (classical thermodynamics)

In microscopic view or approach, attention is focussed on certain quantity of matter without consideration of the events occurring at the molecular level.ie the gross behaviour or the effect of the action of many molecules is considered. These effects can be perceived by our human sense and measured by instruments.

eg :pressure is the average rate of change of momentum due to molecular collisions made on a unit area. The effect of pressure can be felt by human senses and measured quantitatively by pressure gauge.

## Microscopic or statistical view (statistical thermodynamics)

The average behaviour of a large group of individual particles is taken in to account and properties of matter are studied at the molecular level.

## Concept of continuum

Concept of continuum is an idealisation of the continuous description of matter where the properties of matter are considered as the continuous functions of space variable.ie continuum idealisation allow us to treat properties as point functions and can assume properties vary continuously in space from point to point.

From the macroscopic view point, we are always concerned with volumes which are very large compared to molecular dimensions. Even a very small volume of the system is assumed to contain large number of molecules so that statistical averaging is meaningful and a property value can be assigned to it. Disregarding the behaviour of the individual molecules, matter is treated as continuous.

Let us consider the mass $\delta m$ in a volume $\delta V$ surrounding the point P. the ratio $\delta m/\delta V$ is the average mass density of the system within the volume $\delta V$.



Definition of the macroscopic property, density
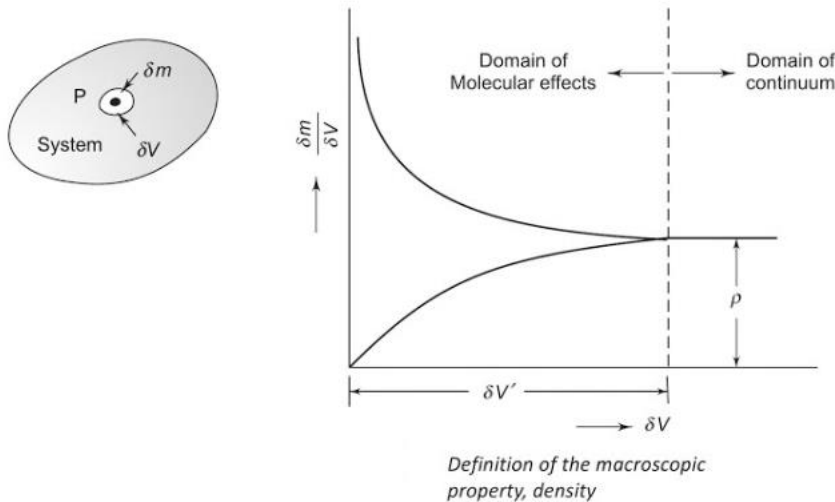
$$\rho = \lim_{\delta V \to \delta V^1} \frac{\delta m}{\delta V}$$

Concept of continuum loses validity when the mean free path of the molecules approaches the order of magnitude of the dimensions of the vessel.

$\lambda/L < 0.01$ (continuum approximation is valid) where $\lambda$- mean free path –statistical average distance a molecule travel between two successive collisions ,L-characteristic dimension of the physical situation .
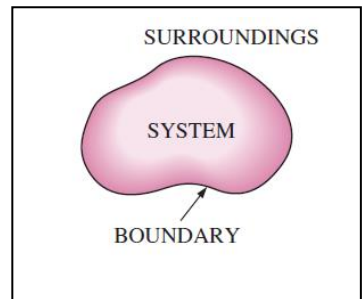
$\lambda/L \rightarrow$knudsen number

**Thermodynamic system:** It is defined as the quantity of matter or region in space bounded by closed surface upon which attention is concentrated in the analysis of problem.

**Surroundings:** everything external to the system.

**Universe**: system +surrounding

## Classification of systems

a. **Closed system (control mass system)**: no mass transfer, but energy transfer across the system boundary.
b. **Open system (control volume system)**: both mass and energy transfer across the system boundary.
c. **Isolated system**: neither mass nor energy crosses system boundary
   eg: universe


A closed system


An open system


An isolated system
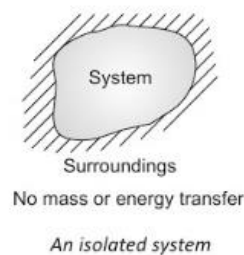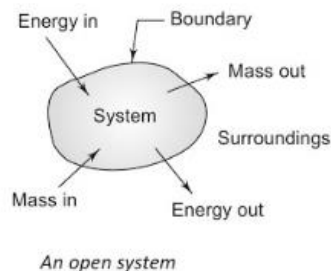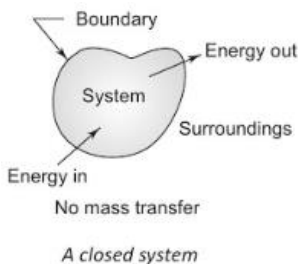
**Boundary**: The surface (real or imaginary) that separates the system from its surroundings.

    i.     Fixed/rigid boundary

    ii.    Movable boundary

   iii.   Diathermal boundary(heat transfer)

   iv.   Adiabatic boundary( no heat transfer)

**Thermodynamic properties**: The observable or measurable characteristics of a system by which its physical conditions may be described are called properties of a system.

**Extensive property**: the properties which are dependent on mass of the system. Its quantitative value is dependent on the size or extent of the system.

eg: mass,volume,internal energy,enthalpy,entropy

**Intensive property**: the properties which are independent of mass of the system.ie its value doesnot depends on the size or extent of the system.

eg: pressure, temperature, specific internal energy, specific enthalpy, specific entropy, specific volume

**Thermodynamic state of a system**: The condition of the physical existence of the system at any instant is called its state. The state of the system can be represented by a point on a diagram whose ordinates are properties like pressure, temperature, volume etc.

**Path**: the succession of state passed through during a change in state or process.

**Thermodynamic process**: the system is said to go through a process if it goes through series of change in state or path which is well defined.

**Thermodynamic cycle**: it is defined as a series of state changes such that the final state is identical with the initial state.

# Thermodynamic equilibrium

**Note**: Classical Thermodynamics places primary emphasis on equilibrium states and changes from one equilibrium state to another. Thus, the concept of equilibrium is fundamental. ie Thermodynamics deals with system when it is in equilibrium.

**A system is said to exist in a state of thermodynamic equilibrium**, when no change in any macroscopic property is registered, if the system is isolated from its surroundings

Thermodynamic equilibrium means no unbalanced potential (driving force )within the system.

A system is said to be in a state of thermodynamic equilibrium if it satisfies the conditions of three types of equilibrium.

1. **Mechanical equilibrium**
2. **Chemical equilibrium**
3. **Thermal equilibrium**

**Mechanical equilibrium**: When there is no unbalanced force within the system itself or between the system and surrounding, the system is said to be in a state of mechanical equilibrium (dP = 0).

**Chemical equilibrium**: If there is no chemical reaction or transfer of matter from one part of the system to another, such as diffusion, the system is said to be in a state of chemical equilibrium.ie the chemical potential dC=0.

**Thermal equilibrium**: When the system is separated from its surrounding by a diathermic wall (allows heat transfer) and if there is no spontaneous change in temperature, property of system; the system is said to exist in a state of thermal equilibrium (dT=0).When this is not satisfied, a system will undergo a change of state till thermal equilibrium is restored.

**Reversible process**: A process which is capable of restoring its original state by reversing the factors responsible for occurrence of process leaving no change in either system or surrounding. Thus upon reversal of a process, there can be no traces of process being occurred.

# QUASI STATIC PROCESS

Note: Consider a system of gas contained in a cylinder .the system is initially at equilibrium state represented by the properties $p_1$, $v_1$ and $t_1$. The weight of the piston just balances the upward force exerted by the gas. If the weight is removed, due to unbalanced force between system and surroundings, piston will move up and comes to final equilibrium state denoted by $p_2$, $v_2$,$t_2$. But the intermediate states passed through by the system are no equilibrium states which cannot be described by thermodynamic coordinates. Therefore the p-v plot should be drawn in dotted line.
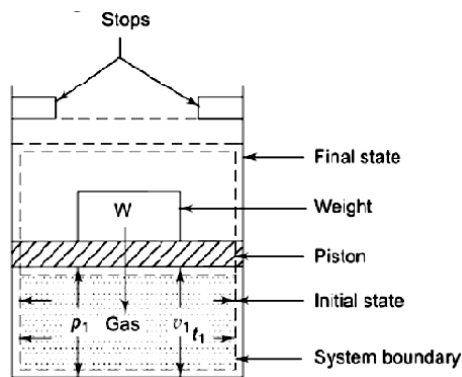


*Transition between two equilibrium states by an unbalanced force*
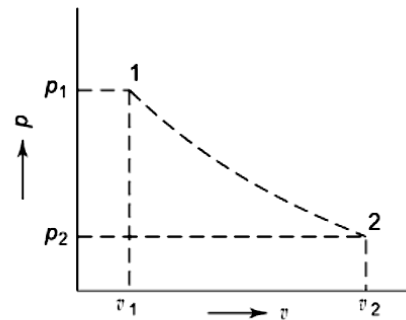
*Plot representing the transition between two equilibrium states*

Quasistatic process: If the single weight on the piston is made up of many very small pieces of weights and these weights are removed one by one very slowly from the top of the piston at any instant of the upward travel of piston. Therefore every state passed through by the system will be an equilibrium state .The process which is the locus of all the equilibrium points passed through by the system is called quasi static process.
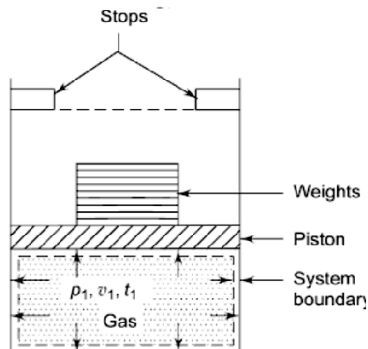


*Infinitely slow transition of a system by infinitesimal force*
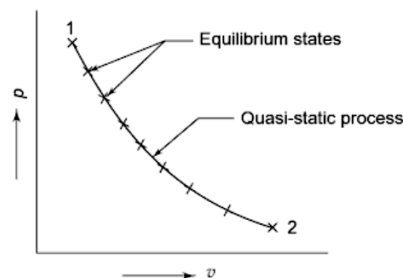
*A quasi-static process*

Important points

1. All states of the system pass through equilibrium states.
2. Deviation from thermodynamic equilibrium is infinitesimal.
3. The process is very slow in nature which allows system to maintain equilibrium all the time.
4. The direction of the process can be reversed by changing the thermodynamic variable infinitesimal.
5. All reversible process is quasistatic, but all quasi static process are not reversible.

**Irreversible process**: It is a process which is not capable of retracing the same pat or state upon reversal of process. Such a process will be indicated as dotted lines in p-v diagram

**Causes of irreversibility**

1. Mechanical and fluid friction
2. Unrestricted expansion
3. Heat transfer with finite temperature difference
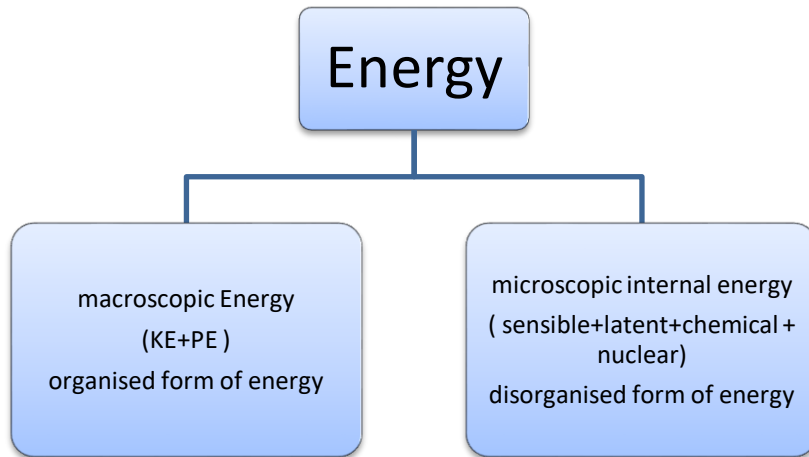4. Mixing
5. Hysteresis

# ENERGY AND ITS VARIOUS FORMS

Energy: the ability to do work.

Energy exists in several forms in nature as kinetic energy, potential energy, thermal energy, mechanical energy chemical, nuclear energy etc.

**Total energy denoted by E(KJ)**

**Specific total energy, e=E/m (KJ/kg)**

**Macroscopic form of energy**: energy possessed by the system with respect to the outside reference frame.

eg: kinetic energy, potential energy, magnetic, electrical, surface tension energy etc.

Note: All materials consists of a large number of particles (molecules, atoms, electrons)

**Microscopic form of energy**: Energy possessed by the system due to molecular structure and degree of molecular activity. It is a disorganised form of energy consisting of sensible, latent, chemical, nuclear energy.

**Sensible energy**: The energy possessed due to translational, rotational and vibrational energy of molecules (kinetic energy at the molecular level).

At low temperature, energy of gas is mostly due to translational and rotational motion. At high temperature vibrational modes contribute more to the energy of the molecules.

**Latent energy**: The internal energy associated with phase change of system.

**Chemical energy**: The energy associated with atomic bonds in a molecule.

**Nuclear energy**: Energy associated with nuclear bond of the atom.

**Internal energy** (U)= Sum of all microscopic form of energy.

The microscopic energy is quite difficult to measure directly.

**Total energy = macroscopic form of energy + microscopic form of energy=KE+PE+U  (KJ)**

**Specific total energy ,e=E/m =ke+pe+u  (KJ/kg)**

Note: The main task of thermodynamics is to devise ways and means to convert internal energy in to useful form of energy, work.

The macroscopic form of energy → organised form of energy is much more useful than disorganised microscopic kinetic energy of molecules.
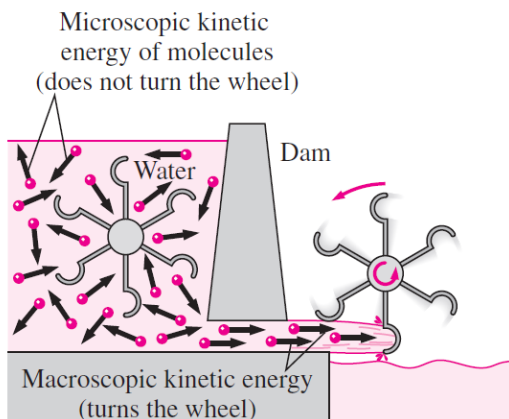


**Thermodynamic concept of energy**
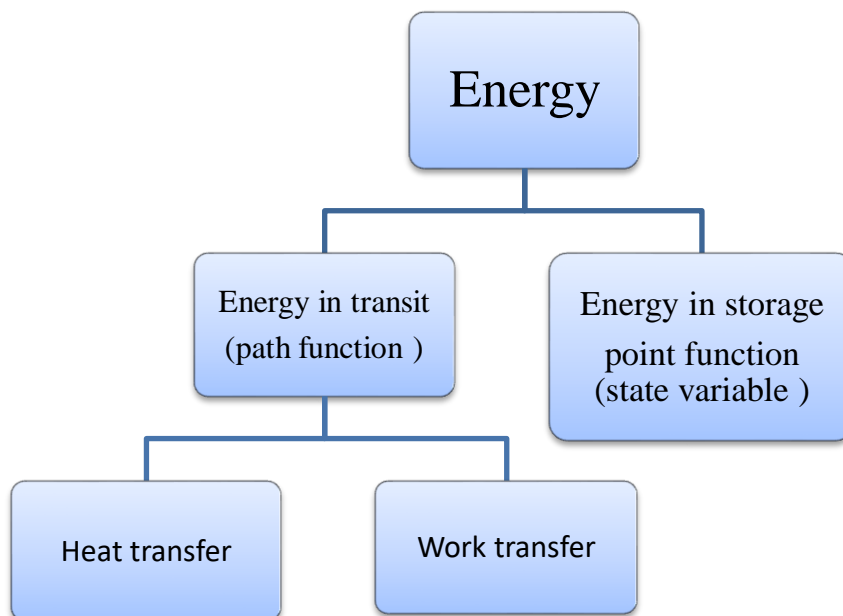
# ENERGY AND ITS INTERACTIONS

A system interacts with its surroundings in two different ways.

1. Work transfer     2. Heat transfer

## Work transfer

It is the energy transfer associated with force acting through a distance.

## Thermodynamic definition of work

Work is done by a system on its surroundings if the sole effect on everything external to the system can be reduced to the raising of weight.

Note: Thermodynamic work involves both system and surrounding. It does not state that the mass is actually raised by application of force. But it only states that the sole effect external to the system is to raise mass through a distance against gravitational pull.

## Important conclusions

1.  Work done by the system is a path function and not point function.
2.  It is not a property of the system.
3.  Work is energy in transit and can be identified only when system undergoes a process.
4.  Energy is stored in a system, but not work.

## Requirement of work between system and surrounding

1.  There must be force acting on the boundary.
2.  The boundary must move.
3.  The presence of force on the boundary without any displacement does no work.
4.  Displacement of boundary without any force to oppose does no work.

    eg: expansion of gas in to an evacuated space does no work.

**Mechanical work transfer** can occur between system and surroundings in following different modes.

1. **displacement or pdv work**
2. **paddle wheel work**
3. **flow work**
4. **shaft work**

**pdV work or Displacement work**

Let the gas in the cylinder be the system .Initially the system

is at equilibrium state denoted by thermodynamic coordinates

$P_1, V_1$. Let the system moves to new final equilibrium state

denoted by thermodynamic coordinates $P_2, V_2$ as shown in

figure. If the process is quasi static, each state passed through

by the system will be equibrium state and displacement work

$$W_{1-2} = \int_{V_1}^{V_2} PdV$$

❖ **PdV work in various quasi static processes**

**Isochoric,isobaric,isothermal,adiabatic,polytropic process →refer note**

**Paddle wheel work**

As the weight is lowered, and the paddle wheel turns, there is work transfer in to the fluid system which gets stirred. Since the volume of the system remains constant, $\int pdV$ =0.If m is the mass of the weight lowered through a distance dz and T is the torque transmitted by the shaft in rotating through an angle dθ, differential work transfer to the fluid is given by
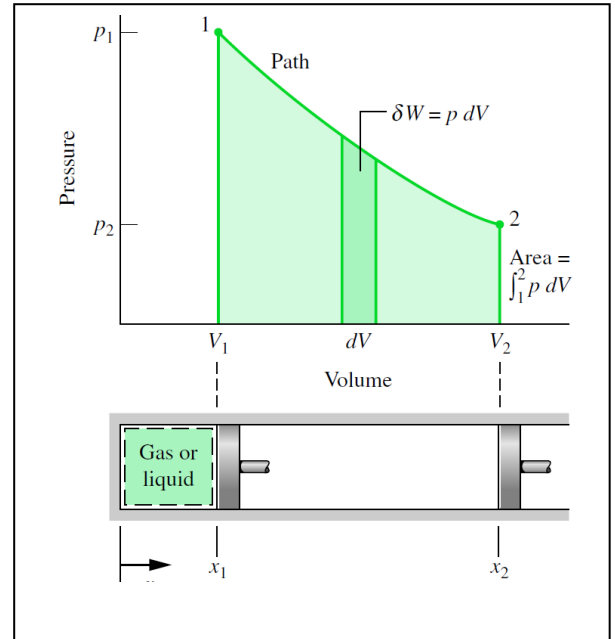
A decrease in potential energy of mass =work done on the system; dw= mgdz=Td$\theta$

Total work transfer, W $=\int_1^2 mgdz=\int_1^2 Td\theta$

Here friction is the agent for the work to be transfer

to the system. Paddle wheel work is a dissipative work

.ie it is an irreversible process.
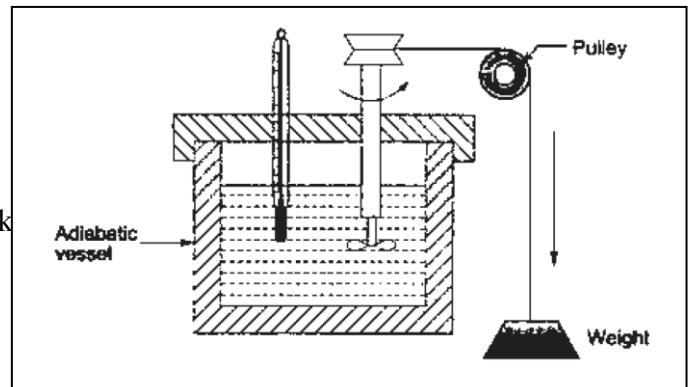


## Flow work

It represents the workdone in pushing a fluid mass across any section of fluid passage by the application of pressure.ie it represents the work required to maintain flow.

It is significant only in a flow process or an open system.

Note:It represents the energy transferred across the system boundary as a result of the energy imparted to the fluid by a pump blower or compressor to make the fluid flow across the control volume .

### Shaft work

When a shaft taken as a system,is rotated by a motor ,there is work transfer in to the system. This is because ,the shaft can rotate a pulley which can raise a weight .if T is the torque applied to the shaft and d$\theta$ is the angular displacement of the shaft ,shaft work is W=$\int_1^2 Td\theta$

Shaft power =T$\omega$, where $\omega$is the angular velocity of the shaft
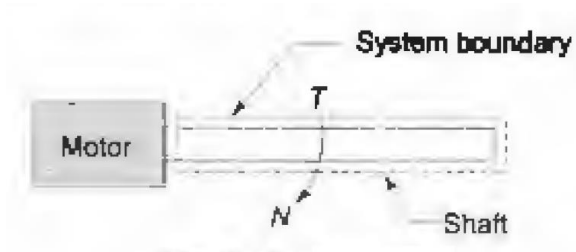
**Spring work**

Work done by the spring when the length of the spring changes by a differential amount dx under the action of force F;

$$\delta W_{spring} = F\,dx$$

Also the functional relationship between force and displacement is $F = kx$, where k is spring constant (N/m).

Total work done, $W = \int_{x_1}^{x_2} F\,dx = \int_{x_1}^{x_2} kx\,dx = 1/2\ K\ (x_2{}^2 - x_1{}^2)$

**Work done in changing the area of a surface film**

A film on the surface of a liquid has a surface tension, which is a property of the liquid and the surroundings .the surface tension acts to make the surface area of the liquid a minimum. It has the unit of force per unit length. The work done on a homogeneous liquid film in changing its surface area by an infinitesimal amount dA is $dW = -\sigma dA$, where $\sigma$ is surface tension (N/m)

$W = -\int_1^2 \sigma dA$

# Non mechanical forms of work

## a)Electrical work

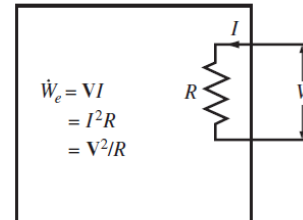In general, both **V** and $I$ vary with time, and the electrical work done during a time interval $\Delta t$ is expressed as

$$W_e = \int_1^2 VI\, dt \qquad (kJ)$$

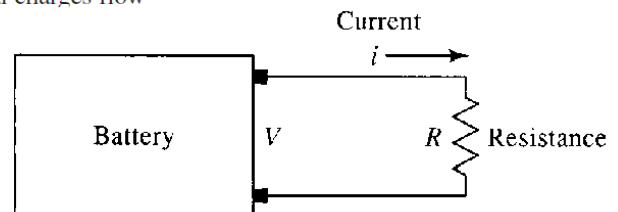When both **V** and $I$ remain constant during the time interval $\Delta t$, it reduces to

$$W_e = VI\, \Delta t \qquad (kJ)$$

$$\dot{W}_e = VI \qquad (W)$$

where $\dot{W}_e$ is the **electrical power** and $I$ is the number of electrical charges flowing per unit time, that is, the *current*

$$\dot{W}_e = VI$$
$$= I^2 R$$
$$= V^2/R$$

Electrical power in terms of resistance $R$, current $I$, and potential difference **V**.

Battery  $V$   $R$ Resistance
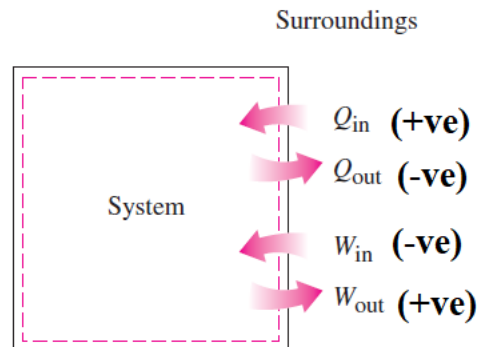
Current $i \longrightarrow$

## b)Magnetic work

Net work done by a system

$$W_{total} = W_{displacement} + W_{stirring} + W_{flow} + W_{shaft} + W_{electrical} + \text{etc}$$
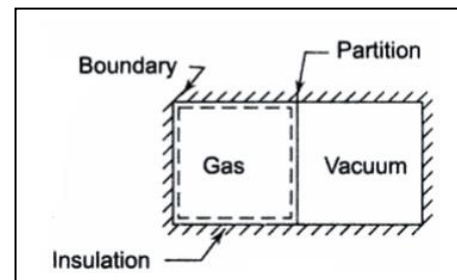
# Sign Convention and Notation

Surroundings

$Q_{in}$ **(+ve)**

$Q_{out}$ **(-ve)**

System

$W_{in}$ **(-ve)**

$W_{out}$ **(+ve)**

Work done by the system is taken as +ve

Work done on the system is taken as -ve

## Free expansion with zero work transfer.

Fig shows a gas is separated from vacuum by a partition.

The expansion of gas against vacuum when the partition is

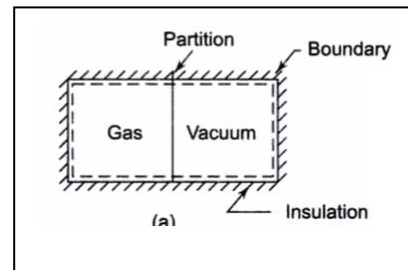removed is called **free expansion.**

**Note:**

Case 1: considering gas and vacuum together as system

Here no work crosses the system boundary ,hence $\int_1^2 dW = 0$,
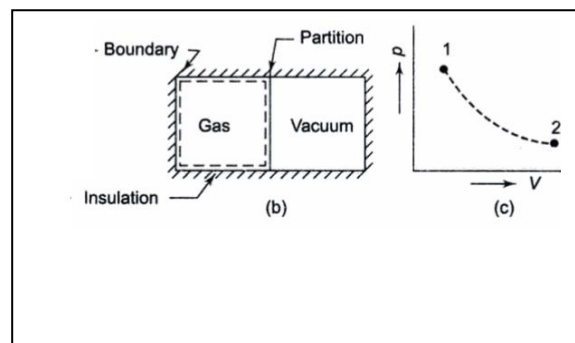
Although $\int_1^2 pdV \neq 0$

Case 2: considering gas only as system

When partition is removed,,there is a change in

Volume of gas.but $\int_1^2 pdV$ cannot be calculated in

this case because this process is not quasistatic,

although the initial and final states are in equilibrium.

The PV diagram should be represented by a dotted line (irreversible process).

**Free expansion** →Case 3: however if the vacuum space is

divided in to a large number of small volumes by partitions

and partitions are removed one by one slowly ,then every

state passed through by the system is in equlilibrium state

and work done can be estimated from relation $\int_1^2 pdV$.
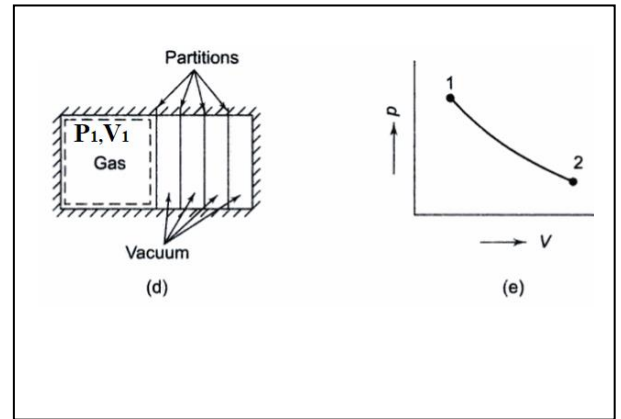
But in free expansion of a gas, there is no resistance to the fluid at the system boundary. Work is done by a system to overcome some resistance. Since vacuum does not offer any resistance, there is no work transfer involved in free expansion.ie displacement of of boundary without any force to oppose does no work.
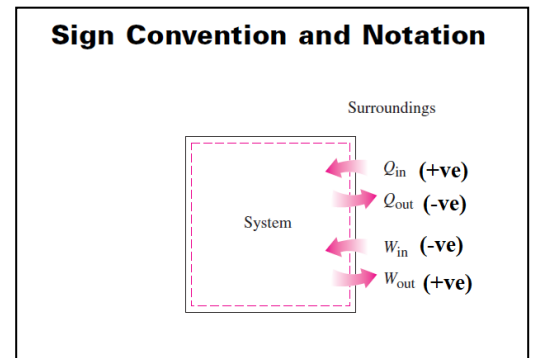
W free expansion =0

# Heat transfer

Heat transfer is defined as the form of energy that is transferred across the boundary by virtue of temperature difference

Major points

1. Heat can be manifested only when system undergoes a change of state.
2. Systems never possess heat.
3. Heat is energy in transit.
4. Heat is a path function. It is not a property of system.

Note: Heat transfer in to the system is taken as +ve, where as heat transfer out of the system is taken as -ve.

**Modes of heat transfer**

1. Conduction
2. Convection
3. Radiation

**Conduction heat transfer**: it is the transfer of energy from the more energetic particles of a substance to adjacent particles that are less energetic due to interactions between particles. Or transfer of heat between two bodies in direct contact.

The conduction heat transfer is quantified macroscopically by *Fourier's law.*

$$\dot{Q}_x = -\kappa A \frac{dT}{dx}$$

Where K is thermal conductivity of the medium, A is the area of heat transfer ,dT/dx is temperature gradient across the medium.

**Convection heat transfer**: It is the energy transfer between a solid surface at a temperature $T_b$ and an adjacent moving gas or liquid at another temperature $T_f$ known as convection.

The rate of energy transfer from the surface to the air can be quantified by the following empirical expression (Newtons law of cooling) as

$$\dot{Q}_c = hA(T_b - T_f)$$

Where h is the convection heat transfer coefficient $(W/m^2 K)$

**Radiation heat transfer**: **Radiation** is the transfer of energy due to the emission of electromagnetic waves (or photons). Unlike conduction, thermal radiation requires no intervening medium to propagate and can even take place in a vacuum.

The rate at which energy is emitted, from a surface of area A is quantified macroscopically by a modified form of the **Stefan–Boltzmann law.**

$$\dot{Q}_e = \varepsilon \sigma A T_b^4$$

Where $\varepsilon$ is the emissivity of the surface ,$\sigma$ - stefans constant,A – area of surface

Adiabatic process: A process in which no heat crosses the boundary of the system ie only work interaction.

Note: the wall that is impermeable to the flow of heat- adiabatic wall

The wall that is permeable to the flow of heat –diathermic wall

Unit of heat –joule

Rate of heat transfer-KWor W

## COMPARISON BETWEEN HEAT AND WORK TRANSFER

1. Both are energy interactions .thermodynamics studies how these interactions bring about property changes in system.
2. They are boundary phenomenon. They both represent energy crossing the boundaries of system.
3. Both heat and work are energy in transit.
4. Heat transfer is the energy interaction due to temperature difference only. All other energy interactions may be termed as work transfer.
5. Both heat and work are path functions and inexact differentials.