Fundamentals of Thermodynamics

- the equation of state for a substance provides the additional information required to calculate the amount of work that the substance does in making a transition from one equilibrium state to another along some specified path.
- The equation of state is expressed as a functional relationship connecting the various parameters needed to specify the state of the system.
- The basic concepts apply to all thermodynamic systems, but here, in order to make the discussion specific, a simple gas inside a cylinder with a movable piston will be considered.
- The equation of state then takes the form of an equation relating *P*, *V*, and *T*, such that if any two are specified, the third is determined.
- In the limit of low pressures and high temperatures, where the molecules of the gas move almost independently of one another, all gases obey an equation of state known as the ideal gas law: $PV = nRT$, where n is the number of moles of the gas and R is the universal gas constant, 8.3145 joules per K.
- In the International System of Units, energy is measured in joules, volume in cubic

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, radiation, and physical properties of matter.

Thermodynamics is the branch of physics that deals with the relationships between heat and other forms of energy.

In particular, it describes how thermal energy is converted to and from other forms of energy and how it affects matter.

Thermo dynamical System

An assembly of an extremely large number of particles whose state can be expressed in terms of pressure, volume and temperature, is called thermodynamic system.

Thermodynamic system is classified into the following three systems

(i) **Open System** It exchange both energy and matter with surrounding.

(ii) **Closed System** It exchanges only energy (not matter) with surroundings.

(iii) **Isolated System** It exchanges neither energy nor matter with the surrounding.

A thermodynamic system is not always in equilibrium. For example, a gas allowed to expand freely against vacuum. Similary, a mixture of petrol vapour and air, when ignited by a spark is not an equilibrium state. Equilibrium is acquired eventually with time.

Concept of Thermodynamic State

- The state of system means the particular condition of a system that described by measured quantities like **pressure,temp,volume and entropy** etc. is called thermodynamic state.
- The state of system described set of variable **pressure ,temp. volume entropy of system**
- Eg. Thermodynamics state of system can be completely described by the set of 3 variables(P, V, T)
- For e.g. Thermodynamics state of system in the form of stretching force, length of the wire and temperature.of wire

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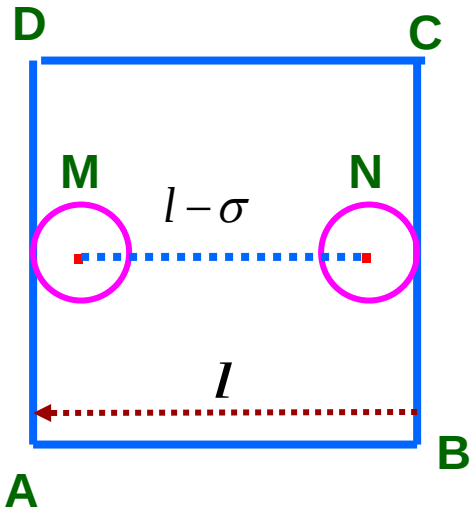
System	Thermodynamics variable
Surface film	1) S.T 2) surface area film 3)Temperature
Reversible cell	1) e.m.f of cell 2) charge 3)Temperature
Paramagnetic sub	1) M.I 2) Magnetization 3)Temperature

Van der Waal's equation of state

- Van der Waals equation was derived by Johannes Diderik van der Waals in the year 1873.
- The equation is basically a modified version of the **Ideal Gas Law** which states that gases consist of point masses that undergo perfectly elastic collisions.
- However, this law fails to explain the behaviour of real gases. Therefore, Van der Waals equation was derived and it helps us define the physical state of a real gas.
- More significantly, the Van der Waals equation takes into consideration the molecular size and molecular interaction forces (attractive and repulsive forces). Sometimes, it is also referred to as Van der Waals equation of state. .
- In the derivation of Prefect gas PV=RT on the basis of K.T there are several assumptions
- Out of 2 assumptions which were not hold good **1 The mole are mere mass point with no volume**
- **2.The mol. exert no force of attraction on each others.**
- 1.2 assumptions are not quite good true at high pressure.

Van der Waal's equation of state

- Van der Waals modified the perfect gas eq. PV=RT for real gas taking into account
- i.e we consider finite size of mol. And inter-molecular attraction.
- 1**) Correction in Volume of gas molecules** :- suppose mol are like hard El. Spheres of Dia.(σ) ABCD rep. container of volume V containing gas.

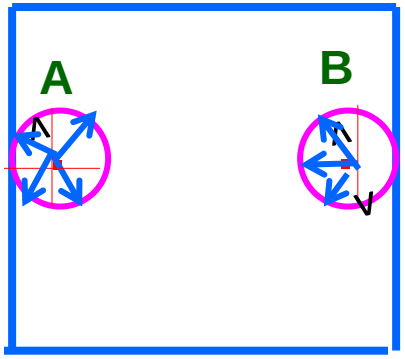


- We know that mol. are mere mass point and travelled distance AD to BC and back it will 2l.
- If mol. has finite volume it has some diameter σ
- Therefore it has travel a distance $2(l-\sigma)$ instead of $2l$
- by considering the motion of all the mol.

- The effective volume in which the mol. can move Is less than that of total volume V of the container.
- The corrected volume is taken as $(V-b)$ Where b is called co-volume.
- 4 times actual volume of the molecules of the gas.

Van der Waal's equation of state

- 2) **Correction in Pressure (inter-molecular attraction)** :- consider a mol. **A** well within gas. It is surrounding on all sides by other similar molecules
- Due to the similar force acting upon it symmetrically .from all sides so net intermol. Force acting on it is 0



- Consider mol. **B** near the wall of container. This mol. will experience pull due to the cohesive force between the gas mol. (same molecules)
- Due this it will experience the inward pull so velo. decrease therefore the momentum will be imparted to the wall and hence pressure exerted on the wall of container gets reduced.
- Thus actual pressure exerted is less than true pressure of gas.
- Decrease in pressure is (p)is proportional to squre of density

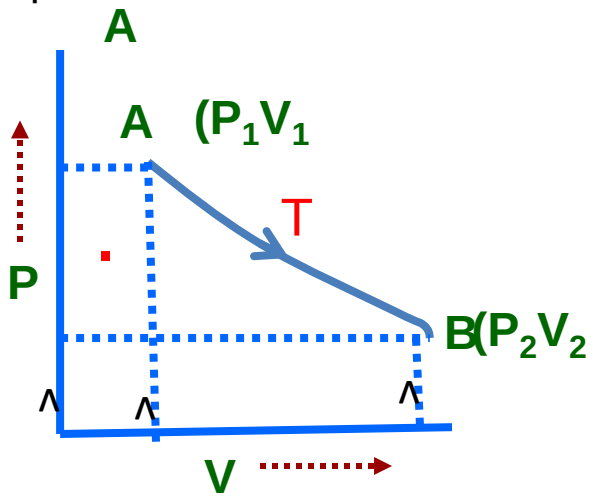
$$p \propto \frac{1}{V^2} \therefore p = \frac{a}{V^2} ..whera..is..cons\tan t..V..is..volume..of..gas$$

$$corrected...pressure = P + p = (P + \frac{a}{V^2})$$

$$appling..both..of..theses..corrections..in..a.gas..eq..PV = RT$$

$$(P + \frac{a}{V^2})(V - b) = RT...this..is..van.der..waals..eqution$$

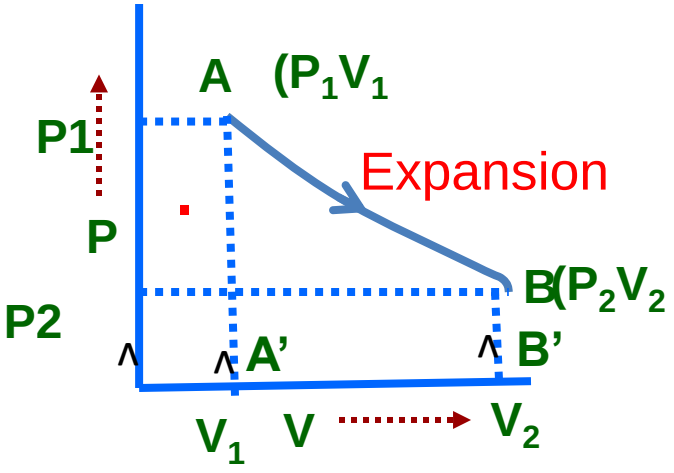
- When thermodynamic system under goes a change in its state without any exchange of heat between it and its surrounding. the change is said to be adiabatic .condition dQ=0
- When a cycle tube bursts the air in it rushes out suddenly and undergoes adiabatic expansion.

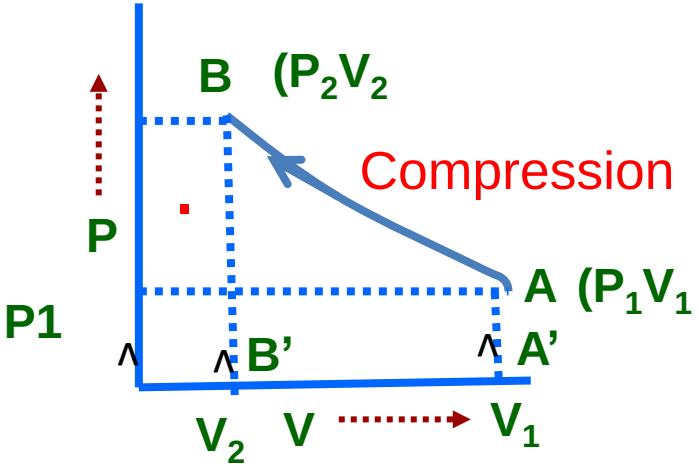


Isothermal Change

- Water is converted into its vapour at a constant temperature (boiling point) undergoes an isothermal expansion
- During isothermal process the temp. of working substance remains constant. It can be absorb heat or given heat to the surrounding PV=RT for n mole PV=nRT
- Q=w heat supplied to an ideal gas is equal to the work done by the gas

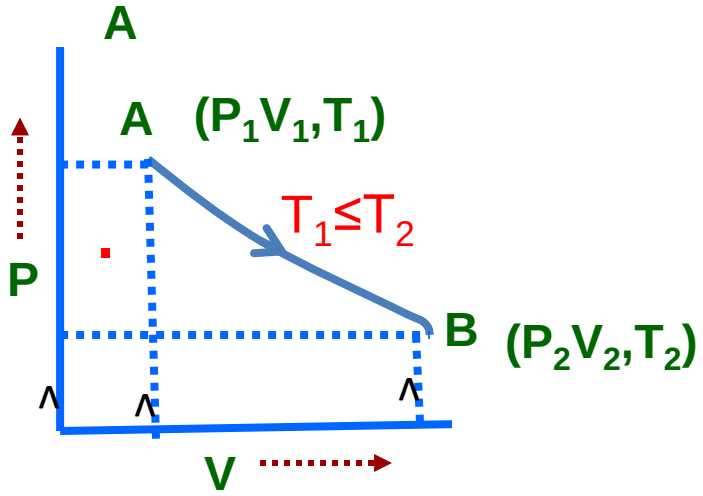
Isothermal Change





Adiabatic Change

- When thermodynamic system under goes a change in its state at a constant temperature the change is said to be isothermal .condition dT=0
- Ice is converted into water at a constant temperature (melting point) undergoes an isothermal compression



- Water is converted into its vapour at a constant temperature (boiling point) undergoes an isothermal expansion
- During isothermal process the temp. of working substance remains constant. It can be absorb heat or given heat to the surrounding PV=RT for n mole PV=nRT
- Q=w heat supplied to an ideal gas is equal to the work done by the gas

- When an object or a body is brought in contact with another body with different temperatures, then the heat gets transferred from high temperature to low temperature, till both the bodies attain thermal equilibrium.

For example, when a hot cup of tea is kept under room temperature, then the heat gets transferred to the atmosphere with respect to time, till the temperature of tea and atmosphere is equal.

THERMAL EQUILIBRIUM - DEFINITION

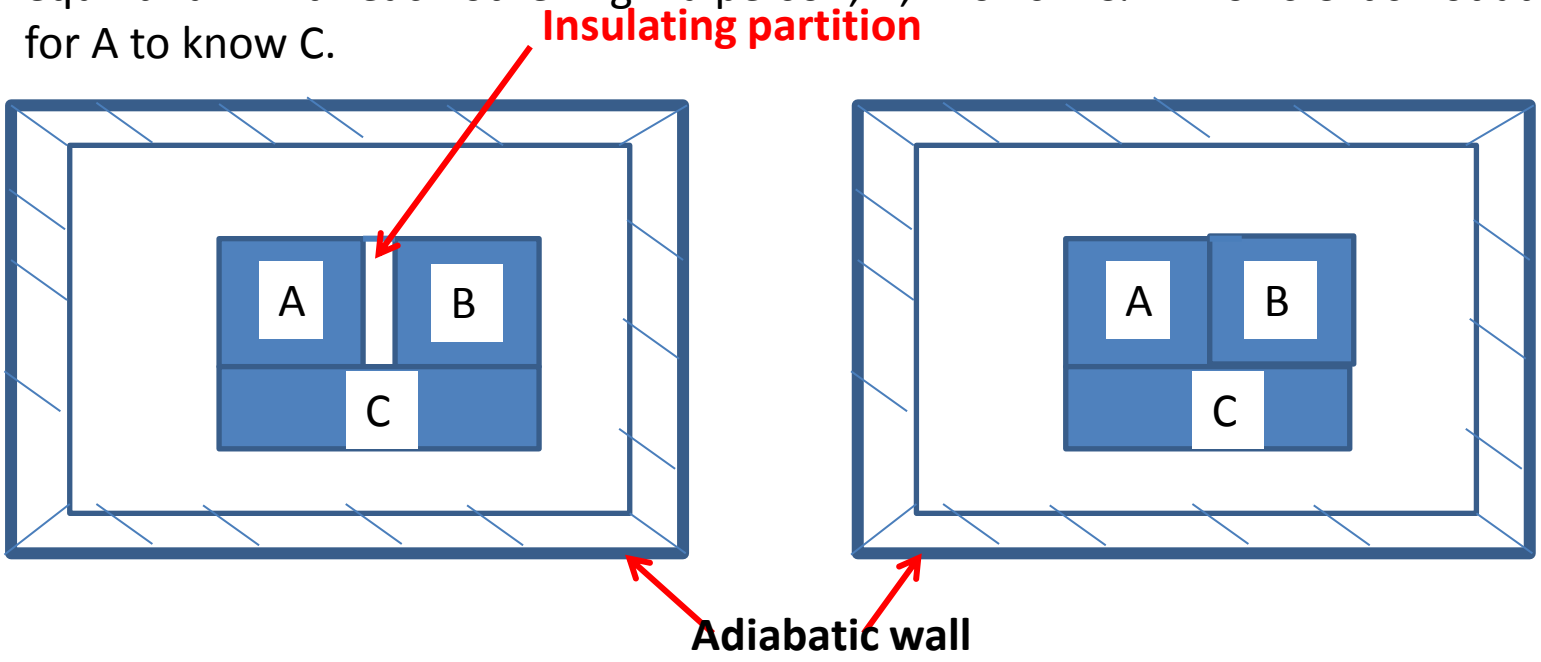
Two physical systems are in thermal equilibrium if no heat flows between them when they are connected by a path permeable to heat. Thermal equilibrium obeys the zeroth law of thermodynamics. Cooling a hot object. The cooling of a hot object, say in a container of water, is an example of an approach to thermal equilibrium.

Two systems are said to be in thermal contact if they can exchange energy through the process of heat transfer.

Two systems are in thermal equilibrium if there is no transfer of heat between them and both have the same temperature i.e. in accordance with the zeroth law of thermodynamics.

Zeroth law of thermodynamics

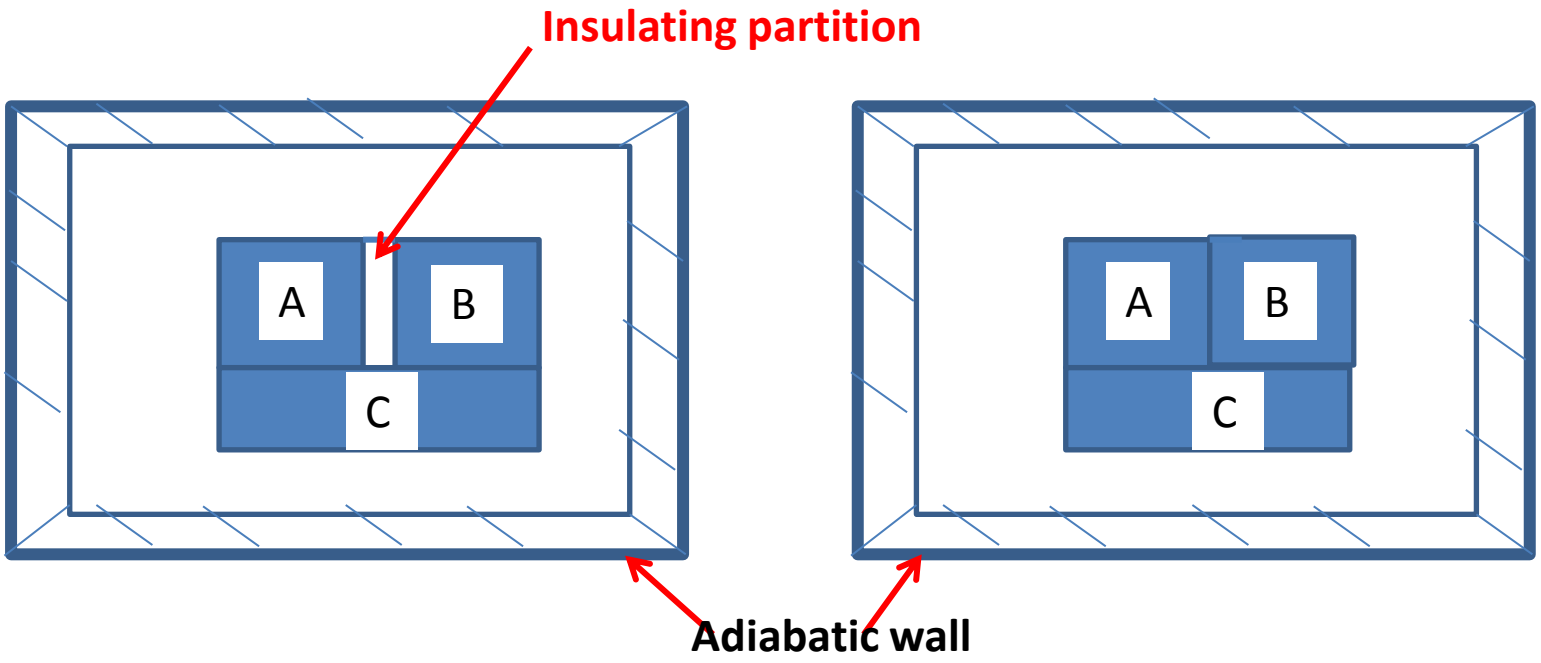
- **Zeroth law of thermodynamics** tells us the concept of temperature. This **law** states that if two bodies are each in thermal equilibrium with a **third** one, then they are in thermal equilibrium with each other. Eg if a person, A, knows B & B knows C it's not at all necessary for A to know C.



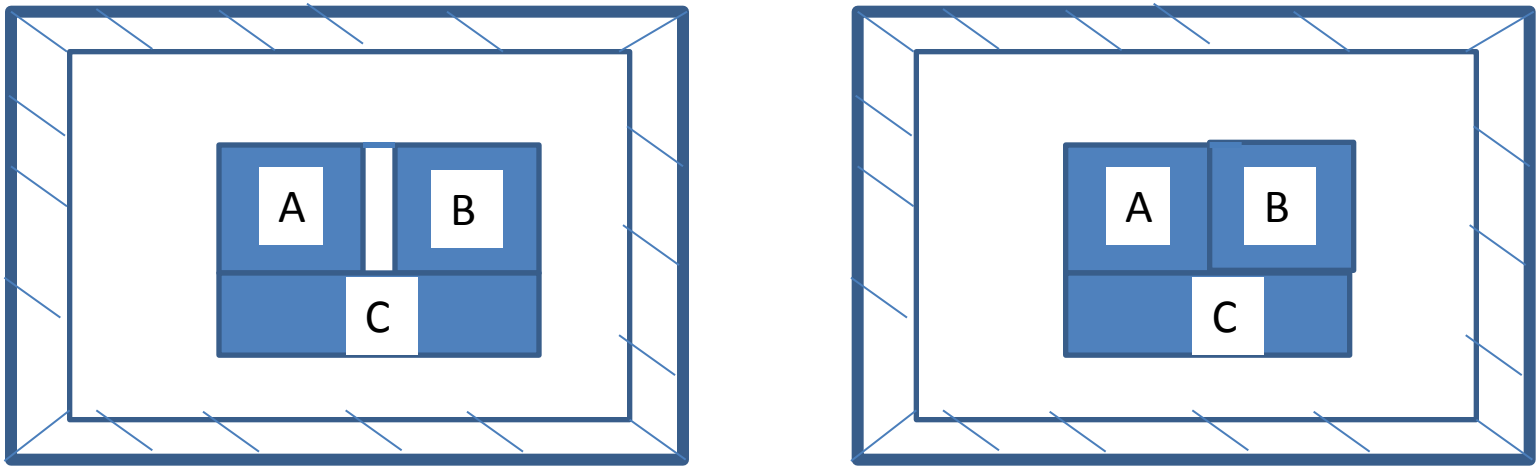
- When hot body **A** is brought in thermal contact with a cold body **B heat flow from A to B after some time flow stops body is said to be** thermal equilibrium with each other
- **Zeroth law of thermodynamics** states that if 2 bodies **A** and **B** are separated from each other in thermal equilibrium with3 body **C** then **A** and **B** are also in thermal equilibrium with each other.

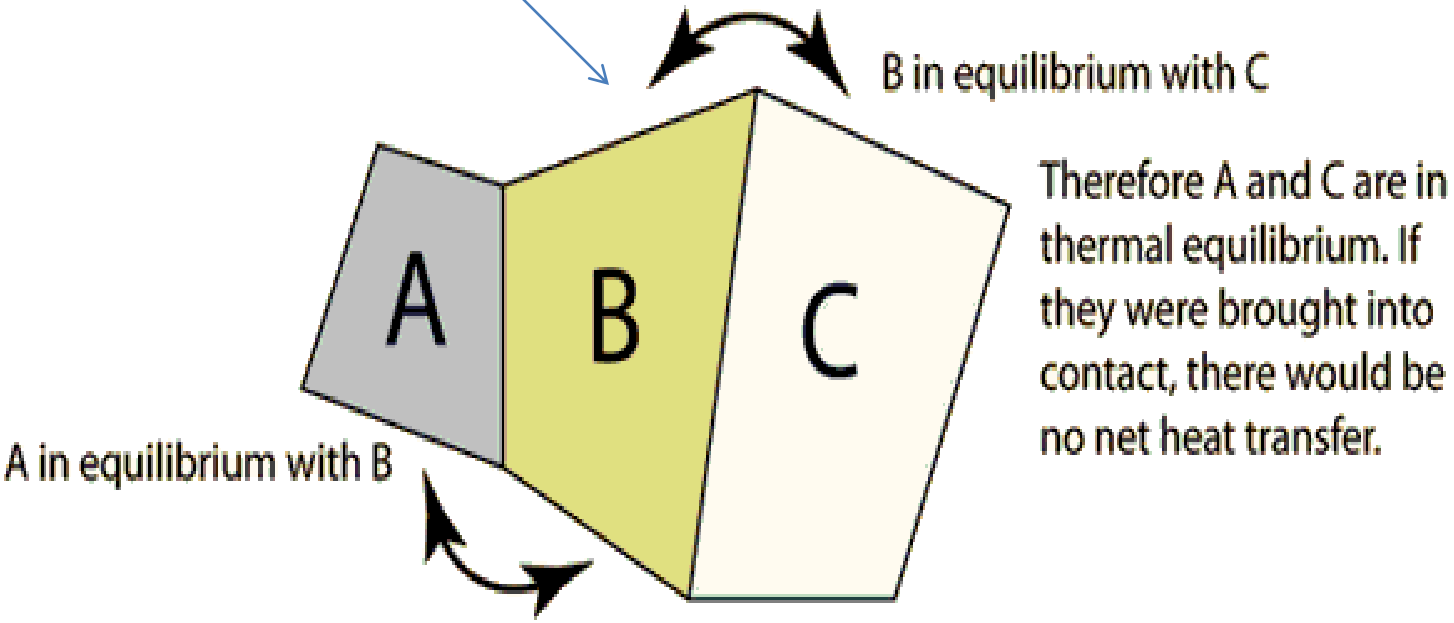
Zeroth law of thermodynamics

- We consider 2 system A and B insulating from each others but good thermal contact in common system C



- When hot body **A** is brought in thermal contact with a cold body **B heat flow from A to B after some time flow stops body is said to be** thermal equilibrium with each other
- **Zeroth law of thermodynamics** states that if 2 bodies **A** and **B** are separated from each other in thermal equilibrium with3 body **C** then **A** and **B** are also in thermal equilibrium with each other.



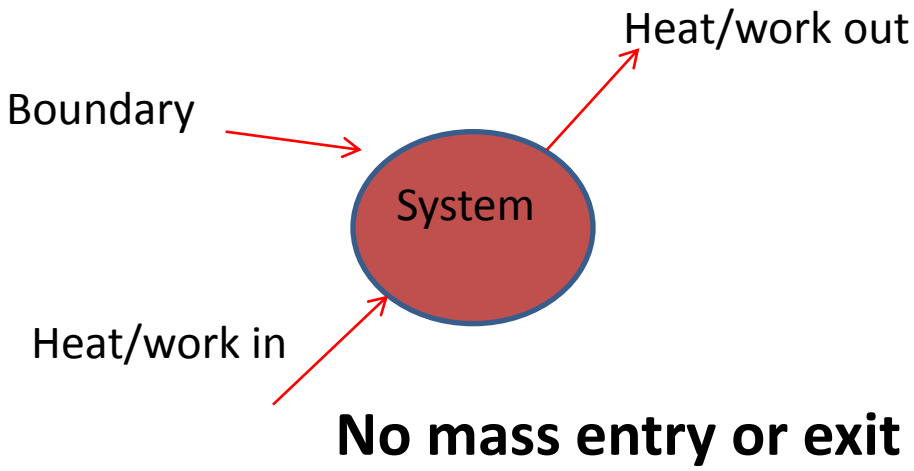


Therefore A and C are in thermal equilibrium. If they were brought into contact, there would be no net heat transfer.

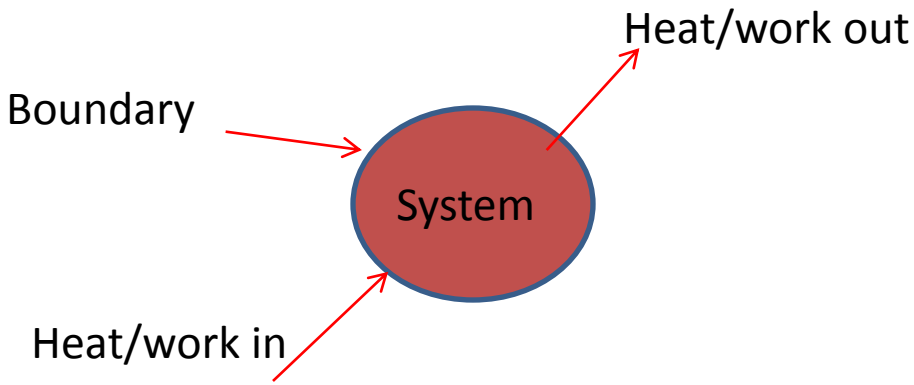
system –Any portion of universe or any portion of matter that chosen for thermodynamic consideration is called system.

- If we like to Rise the temperature of water in kettle
- Burn some fuel in the combustion chamber of an aero engine to propel an aircraft.
- Cool our room on a hot humid day.
- Heat up our room on a cold winter night.
- Have our beer cool. What is the smallest amount of electricity/fuel

- **Closed system -** in which no mass is permitted to cross the system boundary i.e. we would always consider a system of constant mass. Surronding out side the system which has direct.



- **Open system-** in which we permit mass to cross the system boundary in either direction (from the system to surroundings or vice versa). In analysing open systems, we typically look at a specified region of space, and observe what happens at the boundaries of that region. Most of the engineering devices are open system.



No mass entry or exit

Reversible process

A **reversible process** is a process in which the system and environment can be restored to exactly the same initial states that they were in before the process occurred, if we go backward along the path of the process. Note that it is quite easy to restore a system to its original state; the hard part is to have its environment restored to its original state at the same time.

For example, in the example of an ideal gas expanding into vacuum to twice its original volume, we can easily push it back with a piston and restore its temperature and pressure by removing some heat from the gas. The problem is that we cannot do it without changing something in its surroundings, such as dumping some heat there.

A reversible process is truly an ideal process that rarely happens. We can make certain processes close to reversible and therefore use the consequences of the corresponding reversible processes as a starting point or reference. In a reversible process things happen very slowly, without any resisting force, without any space limitation → everything happens in a highly organized way (it is not physically possible - it is an idealization). Examples: Some examples of nearly reversible processes are: (i) Frictionless relative motion. (ii)

Reversible process

.An **irreversible process** is what we encounter in reality almost all the time. The system and its environment cannot be restored to their original states at the same time. Because this is what happens in nature, it is also called a natural process. The sign of an irreversible process comes from the finite gradient between the states occurring in the actual process. For example, when heat flows from one object to another, there is a finite temperature difference (gradient) between the two objects. More importantly, at any given moment of the process, the system most likely is not at equilibrium or in a well-defined state. This phenomenon is called **irreversibility**.In reality, almost all processes are irreversible, and some properties of the environment are altered when the properties of the system are restored., that is, not in an equilibrium state at any moment of the expansion.From the microscopic particles or molecules, where numerous collisions between these molecules tend to erase any trace of memory of the initial trajectory of each of the particles. For example, we can actually estimate the chance for

Reversible process

Examples of irreversible process. (i) Relative motion with friction (ii) Combustion (iii) Diffusion (iv

Free expansion (v) Throttling (vi) Electricity flow through a resistance (vii) Heat transfer (viii

Plastic deformation. In summer we make water to get freezed into ice cubes . Upon use of these

ice cubes they again get converted into water .One which can be considered is Nitrogen taken

from soil by plants is again returned to the soil during decomposition of plants when it is dead .

Reversible process

The first **law of thermodynamics**, also known as **Law** of Conservation of Energy, states that energy can neither be created nor destroyed; energy can only be transferred or changed from **one** form to another. ... In other words, energy cannot be created or destroyed. First Law of Thermodynamics: Energy can be changed from one form to another, but it cannot be created or destroyed. The total amount of energy and matter in the Universe remains constant, merely changing from one form to another. The First Law of Thermodynamics (Conservation) states that energy is always conserved, it cannot be created or destroyed. In essence, energy can be converted from one form into another.