

Thermodynamics

Anne Jose M

Department of Physics.

Little Flower College, Guruvayoor

- **Heat** is a form of energy

Unit of heat : Joule (S I system)

Calorie (CGS system)

- **Calorie:**

It is defined as the quantity of heat required to raise the temperature of 1 gram of water through 1°C.

$$1 \text{ calorie} = 4.2 \text{ J}$$

Temperature

- Temperature of a body indicates the degree of hotness of the body. When the two bodies at different temperatures are brought into contact, heat energy will flow from the hot body to the cold body until both attain a common temperature. Thus, temperature is that property of a body which tells us the direction in which heat energy is transmitted when the body is placed in contact with another

Heat capacity of a body

It is the quantity of heat required to raise the temperature of the body by 1 kelvin

Unit: J/ K

Specific heat capacity of a substance(c)

It is the quantity of heat required to raise the temperature of unit mass of the substance through one Kelvin

Unit: $Jkg^{-1}K^{-1}$

Relation between quantity of heat and rise of temperature

Let 'm' be the mass of the body and 'c' its specific heat. When a quantity of heat 'Q' is supplied, let the temperature rise by $\theta^{\circ}\text{C}$.

Then, $Q=mc\theta$

Specific heat of gases

- Specific heat of a gas at constant volume(c_v)

It is the amount of heat required to raise the temperature of unit mass of the gas through one kelvin keeping its volume constant.

- Molar specific heat at constant volume(C_v)

It is the amount of heat required to raise the temperature of one mole of the gas through one Kelvin at constant volume

- The specific heat of a gas at constant pressure(c_p)

It is the amount of heat required to raise the temperature of unit mass of the gas through one kelvin keeping pressure constant

- Molar specific heat at constant pressure(C_p)

It is the amount of heat required to raise the temperature of one mole of the gas through 1 kelvin at constant pressure

Unit of molar specific heat: $Jmol^{-1}K^{-1}$

Why C_p is greater than C_v ?

When unit mass or one mole of a gas is heated at constant volume, the heat supplied is utilised only to increase the internal energy of the gas. When it is heated at constant pressure, the heat supplied is utilised not only to increase the internal energy but also for doing external work during expansion. For the same rise of temperature, the increase in internal energy is the same in both cases. Hence C_p is greater than C_v .

Mayer's relation: $C_p - C_v = R$

Ratio of specific heats(γ)

The ratio of specific heats of a gas is the ratio of its specific heat at constant pressure to the specific heat at the constant volume of the gas.

$$\gamma = \frac{C_p}{C_v}$$

- It is a constant for a gas.
- $\gamma = 1.4$ for diatomic molecule

Monoatomic molecule

The molecule of a monatomic gas has only one atom.

Example: helium, neon

Diatomic molecule

The molecule of a diatomic gas is made up of two atoms joined rigidly through a bond

Example: H_2 , O_2

Triatomic molecule

Example: CO_2 , NO_2

Change of state (Change of phase)

A substance may exist in one of the three states, **solid, liquid or gas**, depending on the temperature.

A change of state can be affected by the addition or subtraction of heat from a substance.

The change from **solid to liquid** is known as **fusion (melting)** and the reverse change from **liquid to solid** is known as **freezing (solidification)**.

The change from **liquid to vapour** is known as **vaporisation** and the reverse change is known as **condensation**.

Laws of fusion

- Every crystalline substance, when heated, melts at a particular temperature called **melting point** of the substance.
- During melting, the temperature remains steady until the whole substance has melted.
- Unit mass of a substance, at its melting point, requires a definite quantity of heat to change it from solid to the liquid state without change of temperature. This quantity of heat is called **specific latent heat of fusion of the substance** (simply Latent heat).
- The volume of a solid changes during melting. Some substance like **ice contracts on melting** while others like **wax expands on melting**
- A **change of pressure changes the melting point**. For substances like ice, an increase of pressure lowers the melting point, where as for substances like wax, an increase of pressure raises the melting point.

Specific latent heat of fusion of a solid(L)

It is the quantity of heat required to convert unit mass of the solid at its melting point into liquid at the same temperature.

Unit: J/kg

Quantity of heat required to convert a solid of mass m and specific latent heat L into liquid without any change of temperature is $Q=mL$.

Specific latent heat of fusion of ice

Specific latent heat of fusion of ice is the quantity of heat required to convert unit mass of ice at 0°C to water at the same temperature.

Specific latent heat of ice, $L=336000\text{J/kg}$

Laws of boiling

- Every liquid boils at a particular temperature called boiling point of the liquid.
- During boiling, temperature remains steady until the whole liquid has vapourized.
- Unit mass of liquid, at its boiling point, requires a definite quantity of heat for its conversion into vapour state. This is known as latent heat of vaporization.
- An increase of pressure raises the boiling point of the liquid

Specific latent heat of vaporisation of a liquid (L)

It is the quantity of heat required to convert unit mass of liquid at its boiling point into vapour at the same temperature.

Unit: J/kg

Quantity of heat required to convert a liquid of mass m and specific latent heat L into vapour without any change of temperature, $Q=mL$

Specific latent heat of steam

Specific latent heat of steam is the quantity of heat required to convert unit mass of water at 100°C to steam at the same temperature.

Latent heat of steam = 2268000J/kg

Thermodynamics

Thermodynamics is the branch of physics that deals with the concepts of heat and the exchange of heat energy. That is, interconversion of heat and other forms of energy.

System: When we study thermodynamics, we focus our attention on a particular region of space or a finite portion of matter. This is called thermodynamics system

Thermodynamics system: A system which can be described in terms of thermodynamics coordinates is called thermodynamics system.

Thermodynamic variables or coordinates : The variables which define the thermodynamical state of a system are called thermodynamic variables or coordinates. Thermodynamic coordinates are pressure, volume, temperature and entropy.

Examples of the thermodynamics systems : Steam vapour, gas..

Surrounding: Anything outside the system which has got some bearing on the behaviour of the system is called the surrounding.

Universe : The combination of a system and its surroundings is called universe.

Microscopic and macroscopic approach

Microscopic approach

In microscopic approach we go into the details of the internal structure of the system.

Macroscopic approach

In macroscopic approach, we take into account only the properties of the system as a whole without reference to internal structure.

Example: volume, pressure, temperature, entropy

Thermal equilibrium

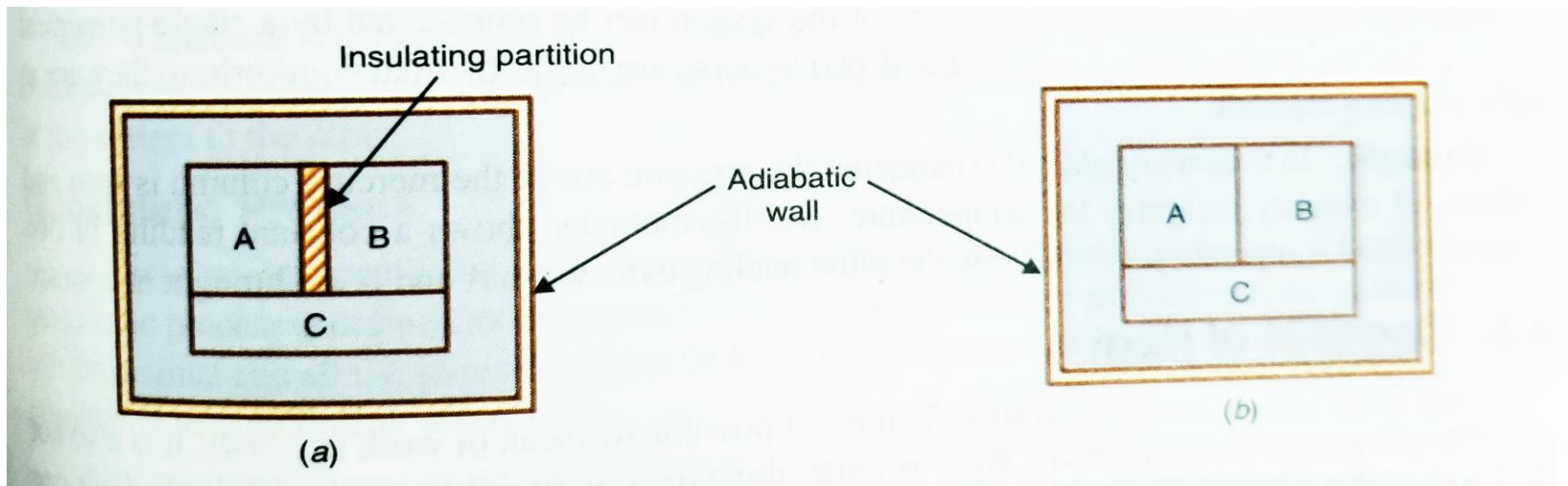
For a system to be in thermal equilibrium, there should be no temperature difference between the parts of the system or between the system and the surroundings.

The necessary and sufficient condition for thermal equilibrium between two systems is that they have the same temperature.

Zeroth law of thermodynamics

The Zeroth law of thermodynamics states that two systems, in thermal equilibrium with a third, are in thermal equilibrium with each other.

Consider three systems A, B and C. Let A and B are separately in thermal equilibrium with C. Then A and B are also in thermal equilibrium with each other.



Thermodynamic equilibrium

Any state of homogeneous system in which any two of the three variables P, V and T remain constant, as long as the external conditions remain unchanged is said to be in thermodynamics equilibrium.

A system is said to be in thermodynamics equilibrium if it is in mechanical, chemical and thermal equilibrium.

Extensive and Intensive variables

The **extensive variable** depends upon the mass or size of the substance present in the system.

Example: mass, volume, internal energy, entropy, length, area, heat capacity

Intensive variable is independent of mass or size of the system.

Example: pressure, temperature, viscosity, refractive index, density, specific volume, surface tension

Thermodynamic process

Any change which causes the thermodynamic variables to a new set of values is called thermodynamic process.

Different types of thermodynamics processes:

1. Isothermal process
2. Isobaric process
3. Isochoric process
4. Adiabatic process

Isothermal process

In the isothermal process the **temperature of the system remains constant.**

Consider an ideal gas is enclosed in a cylinder of perfectly conducting walls and is fitted with a smooth frictionless Piston. If the gas is slowly compressed, the heat newly generated in the gas will be rejected to the surrounding to keep its temperature constant. Similarly when the gas is slowly expanded, it absorbs heat from the surrounding to keep the temperature constant. For an isothermal process, temperature difference of the system **$\Delta T = 0$.**

Since internal energy of the gas is a function of temperature, during isothermal process change in internal energy **$\Delta U = 0$.**

Example:

Slow melting of ice into water at 0°C is an isothermal process

Slow vaporization of water at 100°C is an isothermal process

For an ideal gas of pressure P and volume V , **isothermal equation** becomes

$$PV = \text{constant.}$$

But if the gas initially at the state (P_1, V_1) undergone isothermal change to the state (P_2, V_2) , the equation becomes $P_1V_1 = P_2V_2$

An ideal gas at one atmosphere is slowly compressed to 1/8 of its original volume. Find the resulting pressure.

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2} = 1\text{atm} \times 8 = 8\text{ atm}$$

Isobaric process

In the isobaric process, the **pressure of system remains constant.**

Consider an ideal gas enclosed in a cylinder by a smooth frictionless Piston and piston is moved up or down to maintain a constant pressure. In this case, some amount of work is done by the gas or on the gas to keep its pressure constant. Since pressure is constant, volume of the gas V is directly proportional to the absolute temperature T .

$$V \propto T$$
$$\frac{V}{T} = \text{constant}$$

For an ideal gas undergoing isobaric change from the state (V_1, T_1) to the state (V_2, T_2) the equation becomes,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Ideal gas at STP is isobarically compressed to 1/4 of its original volume. find the resultant temperature.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_2 = V_2 \frac{T_1}{V_1} = T_1 \frac{V_2}{V_1} = 273 \left(\frac{1}{4} \right) = 68.25\text{K}$$

$$V_2 = \frac{V_1}{4}$$

$$\frac{V_2}{V_1} = \frac{1}{4}$$

Isochoric Process

In isochoric process, the volume of the system is kept constant. The process is also called isometric process.

Consider an ideal gas enclosed in a cylinder by a rigid Piston. When heat is given to the gas, the entire heat is used up in increasing its internal energy hence the temperature of the gas will increase. Since there is no change in volume of gas, the external work done by the gas is zero. At a constant volume, pressure of given mass of gas P is directly proportional to the absolute temperature T .

$$P \propto T$$
$$\frac{P}{T} = \text{constant}$$

For an ideal gas undergoes going isochoric change from state (P_1, T_1) to the state (P_2, T_2) , the equation becomes

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Ideal gas at STP is isochorically heated to double its temperature. What will be the final pressure?

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$T_2 = 2T_1$$

$$\frac{T_2}{T_1} = 2$$

$$P_2 = P_1 \frac{T_2}{T_1} = 2 P_1 = 2 \text{ atm since } P_1 = 1 \text{ atm}$$

Note:

- In isobaric process, pressure remains constant and work done by the system $W = PdV$
- In isochoric process, volume remains constant. Hence work done by the system $W = 0$.

Adiabatic process or Isoentropic process

In adiabatic process, the system is not allowed to exchange heat with surroundings. Hence entropy of the system remains constant.

Example: Sudden bursting of cycle tyre

Consider an ideal gas enclosed in a cylinder whose walls are adiabatic.

If the heat is compressed or expanded, change in heat $dQ=0$, because there will be no transfer of heat from the gas to the surrounding or from the surrounding to the gas.

The ideal gas equation for 1 mole of gas is $PV=RT$.

On differentiating,

$$PdV+VdP=RdT$$

$$\Rightarrow dT = \frac{PdV + VdP}{R}$$

$$\text{But, } dQ=dU+dW=0 \text{ -----(1)}$$

Here, $dU=C_v dT$, where C_v is the Molar heat capacity at constant volume.

$$\therefore dU = \frac{C_v}{R} [PdV + VdP]$$

Also, $dW=PdV$

Therefore equation (1) becomes

$$\frac{C_v}{R} [PdV + VdP] + PdV=0$$

$$\Rightarrow C_v [PdV + VdP] + RPdV = 0$$

$$\Rightarrow C_v PdV + C_v VdP + R PdV = 0$$

$$\Rightarrow C_v PdV + C_v VdP + (C_p - C_v)PdV = 0 \quad \text{Since } R = C_p - C_v$$

$$\Rightarrow C_v PdV + C_v VdP + C_p PdV - C_v PdV = 0$$

$$\Rightarrow C_v VdP + C_p PdV = 0$$

$$\Rightarrow C_v VdP = - C_p PdV$$

$$\Rightarrow \frac{dP}{P} = - \frac{C_p}{C_v} \frac{dV}{V}$$

On integrating we get, $\ln P = -\frac{C_p}{C_v} \ln V + \text{constant}$

$$\Rightarrow \ln P + \frac{C_p}{C_v} \ln V = \text{constant}$$

$$\Rightarrow \ln P + \gamma \ln V = \text{Constant} \quad \text{since } \gamma = \frac{C_p}{C_v}$$

$$\Rightarrow \ln P + \ln(V^\gamma) = \text{Constant}$$

$$\Rightarrow \ln(PV^\gamma) = \text{Constant}$$

$$\Rightarrow PV^\gamma = \text{constant} \quad (\text{This equation is also called Poisson's equation}).$$

For ideal gas undergoing adiabatic change from the state (P_1, V_1) to the state (P_2, V_2) , the equation becomes $P_1 V_1^\gamma = P_2 V_2^\gamma$