Introduction

Thermodynamics is the study of mutual conversions of heat energy and other forms of energies, its conditions and necessary devices.

12.1 - Concept of thermodynamic system and environment

Thermodynamic system is a part of the universe under thermodynamic study which can be one, two or three dimensional and may consist of one or more objects called components of the system. A system may be made up of radiation or radiation may be one of the components of the system. Remaining part of the universe surrounding the system and interacting with it is known as its environment. The boundary separating the system and its environment is called wall of the system. The type of interactions between the system and its environment depends on the nature of its wall.

The macroscopic description of any system in physics is done in terms of its measurable properties. For example, in kinematics of rotational motion, position and velocity are macroscopic properties which are called mechanical coordinates. Potential and kinetic energy of a rigid body are determined using these mechanical coordinates w. r. t. to some system of coordinate axes. Similarly, in thermodynamics, macroscopic quantities are thermodynamic coordinates which help in determining internal state of the system. Thermodynamic state of a system is determined from values of its mechanical and thermal properties like pressure, volume, temperature, internal energy, etc.

Interaction between a system and its environment is called a thermodynamic process. If no interaction occurs, the system is called an isolated system. Thermal and mechanical properties of an isolated system remain constant and the system is said to be in a definite thermodynamic equilibrium state. During interaction with the environment, thermal and mechanical properties of the system change continuously at the end of which the system attains an equilibrium state. The amount of heat energy exchanged during the interaction, known as heat, is denoted by Q and the mechanical energy exchanged, called work, is denoted by W.

The thermodynamic equilibrium state of a gas is decided by its pressure, volume, temperature and quantity, not all of which are independent. These are called thermodynamic or state variables. The mathematical equation of state gives the relations between these variables, e.g., $PV = \mu RT$ is the equation of state of an ideal gas. Thermodynamic state variables are of two types: (i) extensive variables which depend upon the dimensions of the system, e.g., mass, volume, internal energy, and (ii) intensive variables which are independent of the dimensions of the system, e.g., temperature.

12.2 Thermal equilibrium

When two systems are brought in thermal contact with each other, heat flows from the system at higher temperature to that at lower temperature till both the systems attain the same temperature. Now the heat exchange between the systems stops and they are said to be in thermal equilibrium with each other.

When the system and its environment are separated by a thermal insulator (adiabatic wall), no heat exchange occurs between them. When this wall is a good conductor of heat (diathermic wall), heat exchange occurs between the system and its environment till their temperatures become equal.

When the force acting between a system and its environment is balanced, the system will be in mechanical equilibrium with the environment. When there is no chemical reaction occurring

in a system and no chemical component moves from one part of the system to the other, the system is said to be in chemical equilibrium. A system which is in thermal, mechanical and chemical equilibrium is said to be in thermodynamic equilibrium.

12.3 Zeroth law of thermodynamics
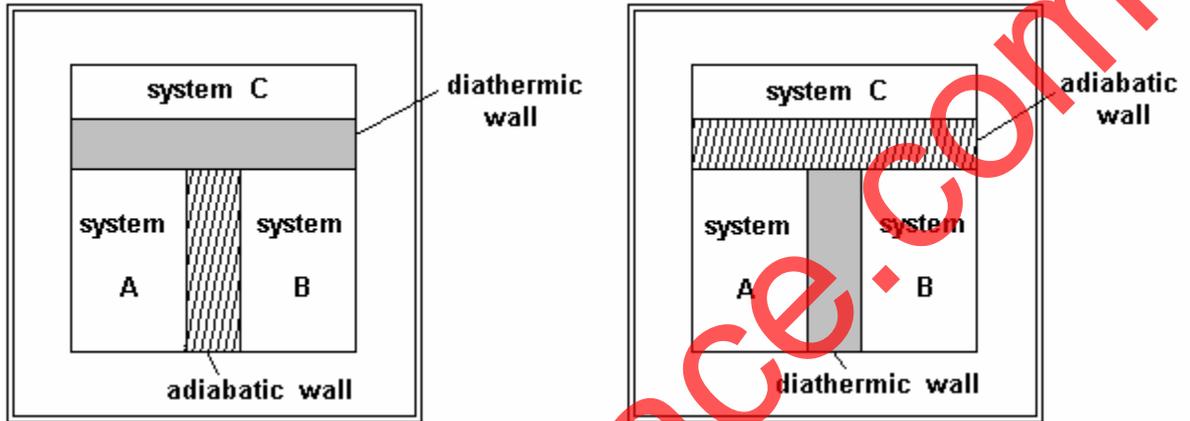
Suppose, as shown in the first figure, systems A and B are separated by an adiabatic wall and both are in contact with system C through a diathermic wall. An insulating wall covers the whole device. It is experimentally observed that after systems A and B have attained thermal equilibrium with C, if the adiabatic wall between the systems A and B is replaced by a diathermic wall, no changes occur in systems A and B indicating that they are in thermal equilibrium with each other.

Thus, if A and B are in thermal equilibrium with a third body (e.g., thermometer), A and B are also in thermal equilibrium with each other. This statement represents the zeroth law of thermodynamics. When bodies in thermal contact with each other attain thermal equilibrium, their temperatures become equal. Thus, zeroth law of thermodynamics indicates that temperature is a property of the system.

12.4 Phase diagram

The phase (solid, liquid, gas) in which matter exists depends on pressure and temperature. Matter can co-exist in more than one phase in equilibrium. The figure shows phase diagram of some substance which shows the phase or phases in equilibrium in which the substance can exist at different temperatures and pressures.
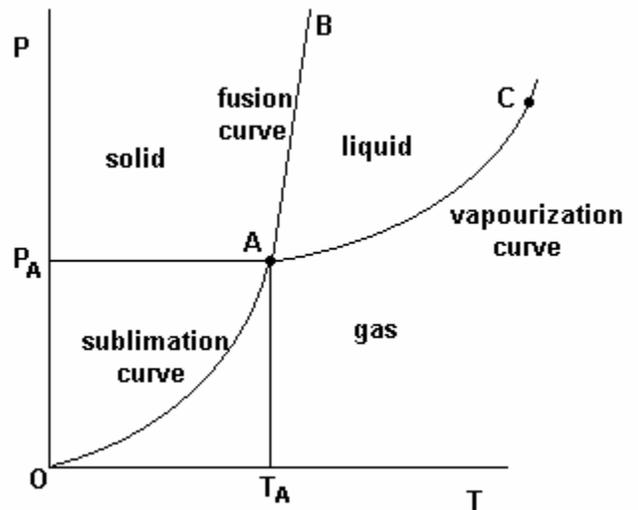
AB is a fusion curve, points on which indicate the pressures and temperatures, at which both solid and liquid phases coexist in equilibrium. OA is a sublimation curve, points on which indicate the pressures and temperatures, at which both solid and gas phases co-exist in equilibrium. Similarly, AC is a vapourization curve, points on which indicate the pressures and temperatures, at which liquid and gas phases co-exist in equilibrium.

At the values of pressure and temperature, corresponding to point A, where the three curves meet, all the three states of matter co-exist in equilibrium. This point is called the triple point of that matter. Triple point of water is obtained at the pressure of 4.58 mm of Hg and 273.16 K temperature. Triple point of water is used to fix the scale of thermometers.

12.5 Measurement of temperature: Thermometry

Unique real numbers can be assigned corresponding to different thermal equilibrium states of the body. Such a real function defined on thermal equilibrium state is called temperature function. The zeroth law of thermodynamics ensures such a function to be one-one. The device used to measure the unique real number which is the temperature of the body at a given thermal equilibrium state is called thermometer.

A thermometer can be prepared using a thermometric substance having the numerical value of its thermal property changing in a definite manner with different thermal equilibrium states. The magnitude of this thermometric property can be related to the numerical value of the temperature, e.g., length of a rod, resistance of a wire, pressure of a gas at constant value or its volume at constant pressure. For this it is necessary to know the type of relationship between the thermosensitive property to be used and temperature and select the most reliable thermal property of a thermometric substance which can form the basis of universal scale of temperature.

12.6 Ideal gas temperature scale

It is experimentally found that the temperature of the substance measured by a constant volume gas thermometer using different gases at very low pressures are almost the same. This means that the pressure of a constant volume gas at low pressure can be considered as a standard thermal property for measuring temperatures and the thermometer so prepared is known as a constant volume gas thermometer. For such a thermometer,

T_p = aP, …   … (1) where, T_p = temperature as a function of gas pressure,
  a = constant and
  P = pressure of gas at constant volume.

From the above equation, it follows that $\dfrac{T(P_1)}{T(P_2)} = \dfrac{P_1}{P_2}$

Taking the temperature 273.16 K, which is the triple point of water, as standard, the value of constant a can be determined. If P_{tr} is the pressure of gas in the bulb of the thermometer when it is kept at 273.16 K, then the value of a is given by

a = $\dfrac{273.16}{P_{tr}}$ Using this value of a in equation (1), we get

$T_p = \dfrac{273.16}{P_{tr}} P$ … (2)

Thus, when the bulb of the thermometer is in thermal equilibrium of the bath, its pressure gives the temperature of the bath from the above equation.

When different gases are filled in the bulb of the thermometer at a given high value of P_{tr}, they all show slightly different values for the boiling point of water at atmospheric pressure as may be seen from the adjoining graph. However, if the different gases are filled in the bulb of the thermometer at very low pressure such that $P_{tr} \rightarrow 0$, then the boiling point of water obtained at atmospheric pressure is the same. The temperature measured in such a condition is independent of the type of the gas used. Therefore, the ideal temperature scale is defined by the equation,
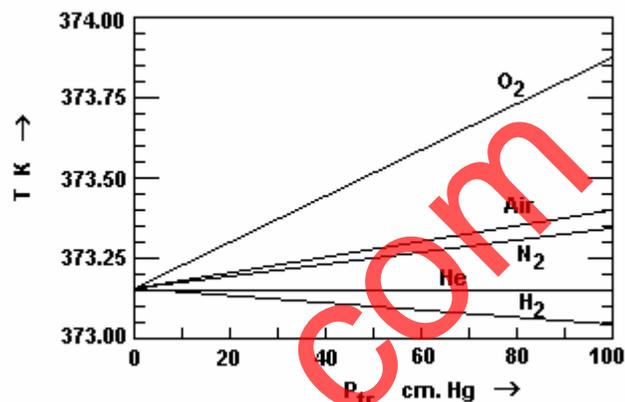
$$T_p = 273.16 \lim_{P_{tr} \rightarrow 0} \frac{P}{P_{tr}} \text{ (at constant volume of gas in the bulb of the thermometer)}$$

When we use a very small amount of any gas in a gas thermometer, the above equation is almost the same as equation (2).

Using He^3 gas at very low pressure, the temperature upto 0.5 K can be measured with the help of such a thermometer.

Celsius scale:

Temperature, t_C, in Celcius scale is given by $t_C = T - 273.15$, where T is temperature in Kelvin scale. Temperature of triple point of water on Celsius scale is $t = 273.16 - 273.15 = 0.01° C$.

Fahrenheit scale:

Temperature, t_F, in Fahrenheit scale is given by $t_F = 32 + 1.8 \, t_C$.

12.7 Thermal expansion

Most substances expand with increase in temperature and contract with decrease in temperature. Such expansion is called thermal expansion.

When the distance between constituent particles of solids is more than some definite distance, r_0, the force between them is attractive in nature which becomes repulsive when the distance is less than r_0. There is no net force when the distance is r_0. Thus at a definite temperature, the molecules oscillate about their mean position between r_{min} ($< r_0$) to r_{max} ($> r_0$) such that $r_0 - r_{min} < r_{max} - r_0$. As a result potential energy of the oscillating molecule is less at a distance r_{min} than when it is at a distance r_{max}. This asymmetry (also called anharmonicity) of intermolecular potential energy versus intermolecular distance is responsible for thermal expansion which results in the average intermolecular distance between molecules, $r = \dfrac{r_{min} + r_{max}}{2}$ increasing with temperature.

Linear expansion

For small changes in temperature, the increase in length, Δl, of a body is directly proportional to its original length, l, and increase in its temperature, ΔT.

$\therefore$ $\Delta l \propto l$ and $\Delta l \propto \Delta T$.

$\therefore$ $\Delta l = \alpha l \Delta T$, where α is a constant called co-efficient of linear expansion. Its value depends on the material of the body and its temperature. For small changes of temperature, its variation with temperature is negligible.

$\therefore$ $\alpha = \dfrac{\Delta l}{l\,\Delta T}$ The unit of α is $(°C)^{-1}$ or K^{-1}.

Some solids expand uniformly in all directions. Such substances are called isotropic substances. For isotropic solids,

increase in area, $\Delta A = 2\,\alpha\,A\,\Delta T$ and increase in volume, $\Delta V = 3\,\alpha\,V\,\Delta T$.

Increase in volume is more in liquids than in solids and is maximum in gases.

Change in volume of water with temperature is anomalous. Water contracts when its temperature is reduced upto 4° C, but when its temperature is decreased from 4° C to 0° C, it expands. As a result, the density of water is maximum at 4° C. The anomalous expansion of water has a favourable effect for animals living in water. As the density of water is maximum at 4° C, even in severe winter when the water on the surface of the lake freezes, water at its bottom remain at 4° C, which allow marine animals to remain alive and move near the bottom.

12.8 Heat, heat energy and internal energy

- The molecules of a substance possess momentum and kinetic energy due to their random motion. Due to randomness of motion, probability of motion in all directions is the same. Hence, the total momentum associated with all the molecules of the substance, $\vec{p}_{int}$, is zero, but the total kinetic energy, $\vec{K}_{int}$, is not zero. The total kinetic energy associated with random motion of molecules of a substance (i.e., energy associated with zero momentum state) is called heat (or thermal) energy possessed by the substance.

- Besides this, the molecules also possess potential energy, $\vec{U}_{int}$, due to mutual interactions. The sum of these two energies, i.e., $\vec{K}_{int} + \vec{U}_{int}$, is called the internal energy of the substance.

- Moreover, when a body as a whole is moving in the gravitational field, it also possesses gravitational potential energy, $\vec{U}_{ext}$ due to its position and kinetic energy, $\vec{K}_{ext}$, due to its motion. The sum of these two energies, i.e., $\vec{K}_{ext} + \vec{U}_{ext}$, is called the mechanical energy of the substance.

- When two bodies at different temperatures are brought in thermal contact with each other, the exchange of heat energy that takes place between them is called heat.

12.9 Work in thermodynamics

The amount of mechanical energy exchanged between two bodies during mechanical interaction is called work. A body can possess mechanical energy but not work. Mechanical energy of the body is its capacity to do work. When a body A does work on body B, the body A loses mechanical energy and the body B gains it. Similarly, transfer of internal energy from one body to the other is called heat. When heat is transferred from body A to body B, the body A loses internal energy and the body B gains it. In thermodynamics, work done by the system is considered positive and on the system as negative.

Formula for work:

The figure shows a cylinder containing a gas with an air-tight piston moving without friction. The conducting bottom of the cylinder is kept on an arrangement to maintain desired temperature of the gas. The graph of pressure P versus volume V is plotted by measuring values of volume corresponding to different pressures.
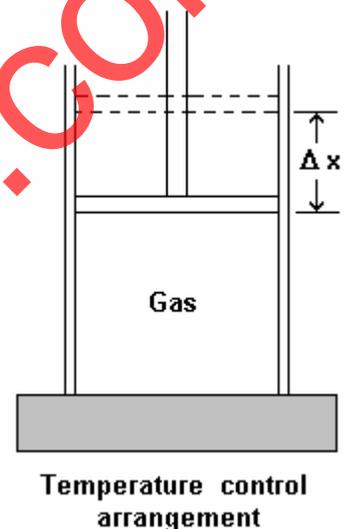
Suppose P_i and V_i are the initial pressure and volume of the gas respectively as shown by point i on the graph and

P_f and V_f are the final pressure and volume of the gas respectively as shown by point f on the graph after the expansion of the gas and sliding of the piston upwards.

P and V are the intermediate values of pressure and volume respectively of the gas. Now if the piston moves slightly outwards by Δx and volume of the gas increases by so small an amount ΔV that the pressure does not change appreciably, then work done by the gas,

$$ΔW = F Δx = PA Δx = P ΔV$$

If the volume of the gas increases from V_i to V_f through such small changes, the total work done,

$$W = \sum ΔW = \sum_{V_i}^{V_f} P ΔV$$

$$= \int_{V_i}^{V_f} P \, dV \qquad \left[\text{taking } \lim_{ΔV \to 0} \right]$$
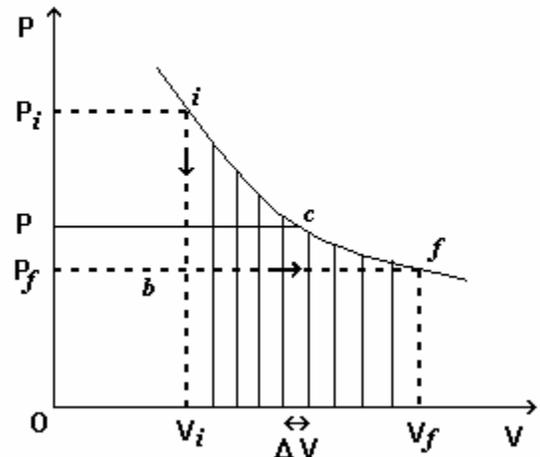
The work done by the gas is the area enclosed by P → V curve as shown in the figure. Work is an extensive variable as it is the product of one extensive variable (V) and other intensive variable (P).

12.10 First law of thermodynamics

Suppose, a system absorbs heat, Q and does work, W and changes from initial

thermodynamic state i to a final state f. The system can undergo this change through several different paths, e.g., processes iaf, ibf and icf as shown in the figure. Although the values of Q and W for all these processes are different, it is found experimentally that the value of Q - W is the same. Thus the value of Q - W does not depend on the path but depends only on the initial and final states of the system.
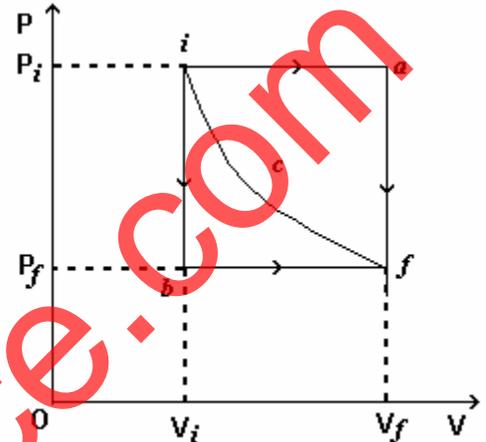
Hence, it is concluded that a thermodynamic state function can be defined such that the difference in its values for the initial and final states is equal to Q - W.

Such a function is called internal energy U of the system. The system absorbs energy Q in the form of heat, spends energy W to do work and the balance Q - W increases its internal energy.

If U_i and U_f are the initial and final values of the internal energy, then

$$U_f - U_i = \Delta U = Q - W$$

$$\therefore \quad Q = W + (U_f - U_i)$$

This equation is called the first law of thermodynamics. This law is just another form of the law of conservation of energy as applied in thermodynamics.

12.11 Heat capacity and specific heat

The ratio of heat supplied, ΔQ, to a body to the change in its temperature, ΔT, is called heat capacity, H_C, of the body. Thus,

$$H_C = \frac{\Delta Q}{\Delta T}.$$ The unit of H_C is cal / °C.

The heat capacity of a body depends on the material of the body as well as its mass.

The quantity of heat required per unit mass for unit change in the temperature of a body is called specific heat of the material of the body. Its unit is $calorie (g)^{-1} (°C)^{-1}$. It is the heat capacity of the body per unit mass and its value depends only on the material of the body and not on its mass.

Specific heat, $C = \dfrac{\text{heat capacity}}{\text{mass}} = \dfrac{\Delta Q}{m \, \Delta T}$ $\therefore \quad \Delta Q = m \, C \, \Delta T$

The values of heat capacity and specific heat also depend upon the temperature at which the temperature interval ΔT is considered.

Specific heats of gases

In the case of gases, specific heat is defined per mole of a gas instead of unit mass and is called molar specific heat.

The amount of heat required to change the temperature of one mole of a gas by 1 K (or 1° C) is called molar specific of that gas. The value of molar specific heat of a gas depends upon the method of heating the gas and is defined for two important processes of heating the gas as under.

(1) Molar specific heat at constant volume C_V :

The amount of heat required to raise the temperature of 1 mole of gas at constant volume is defined as its molar specific heat at constant volume.

(2) Molar specific heat at constant pressure C_P :

The amount of heat required to raise the temperature of 1 mole of gas at constant pressure is defined as its molar specific heat at constant pressure.

Relation between two specific heats (for an ideal gas)

According to the first law of thermodynamics, for infinitesimally small changes,

$$dQ = dU + dW = dU + PdV \quad \ldots \quad (1)$$

$$\therefore \ C_V = \left(\frac{dQ}{dT} \right)_V = \left(\frac{dU}{dT} \right) \ \ldots \ \ldots \ (2) \qquad \left[\because \ \frac{dV}{dT} = 0 \text{ at constant volume} \right] \text{ and}$$

$$C_P = \left(\frac{dQ}{dT} \right)_P = \left(\frac{dU}{dT} \right) + P \left(\frac{dV}{dT} \right)$$

But for one mole of ideal gas, PV = RT. $\qquad \therefore \ P \left(\frac{dV}{dT} \right) + V \left(\frac{dP}{dT} \right) = R$

$$\therefore \ P \left(\frac{dV}{dT} \right) = R \text{ at constant pressure} \qquad \left[\because \ \frac{dP}{dT} = 0 \text{ at constant pressure} \right]$$

$$\therefore \ C_P = \left(\frac{dU}{dT} \right) + R \quad \ldots \ \ldots \ \ldots \ (3)$$

$$\therefore \ C_P - C_V = R \quad \ldots \ \ldots \ \ldots \ \ldots \ (4) \qquad [\text{ from equations (2) and (3)}]$$

If the degrees of freedom of constituent particles (molecules) of a gas are i, then the energy of one mole of gas is $U = i \frac{RT}{2}$

$$\therefore \ C_V = \left(\frac{dU}{dT} \right) = \frac{i R}{2} \quad \text{and} \quad C_P = \frac{i R}{2} + R$$

The values of C_V, C_P and $\gamma = \dfrac{C_P}{C_V}$ for monoatomic and diatomic molecules are calculated using the appropriate values of degrees of freedom, i, in the following table.

Type of molecule	Degrees of freedom, i	C_V	C_P	$\gamma = \dfrac{C_P}{C_V}$
Momoatomic	3	$\dfrac{3R}{2}$	$\dfrac{5R}{2}$	$\dfrac{5}{3}$ = 1.67
Diatomic (rigid rotor)	5	$\dfrac{5R}{2}$	$\dfrac{7R}{2}$	$\dfrac{7}{5}$ = 1.41
Diatomic (with vibrations)	7	$\dfrac{7R}{2}$	$\dfrac{9R}{2}$	$\dfrac{9}{7}$ = 1.29

Specific heat increases with increase in number of atoms in a molecule of a gas. This is so because molecules of diatomic and polyatomic gases possess kinetic energy due to rotational and vibrational motion besides translational motion.

Dulong and Petit's Law

'For many substances (except some very light substances), the product of their atomic mass number and specific heat is almost constant.' This is called Dulong-Petit's law. Regnault showed experimentally that this product is equal to 6.38 calorie / (mole - °C).

One mole of a substance has Avogadro number (N_A) of molecules. From Dulong-Petit's law it follows that the amount of heat required to raise the temperature of a substance depends on the number of its constituent particles and not on the mass of individual particles. Specific heat decreases with temperature and becomes zero at absolute zero temperature.

12.12 Some thermodynamic processes

A gas may be taken from one thermodynamic state to the other through many different processes. Some of the commonly encountered processes during the study of thermodynamics are discussed below.

<u>Isobaric process:</u> "The process during which pressure of the system remains constant is called isobaric process." The thermodynamic equilibrium state of a system keeps changing during such a process and its $P \rightarrow V$ graph is a straight line parallel to the V-axis. Work done by the gas in such a process is given by

$$W = \int_{V_i}^{V_f} P\,dV = P \int_{V_i}^{V_f} dV = P(V_f - V_i) \qquad [\because \text{ P is constant }]$$

Isochoric process: Volume of a system remains constant during this process. As $\Delta V = 0$, work, $W = P \Delta V = 0$. Since no work is done, $Q = \Delta U$ from the first law of thermodynamics..

Adiabatic process:

No heat exchange occurs between a system and its environment in this process. This happens when either the system is thermally insulated or is very rapid. As $\Delta Q = 0$ in the adiabatic process, $\Delta U = - W$ from the first law of thermodynamics. For the adiabatic process,

$$PV^{\gamma} = \text{constant}, \quad \text{where} \quad \gamma = \frac{C_P}{C_V}.$$

Isothermal process: "A thermodynamic process during which temperature of a system remains constant is called an isothermal process."

Work done during isothermal process of an ideal gas

For an isothermal process, $\Delta U = \mu C_V \Delta T = 0$. Hence, $W = Q$ from the first law of thermodynamics. The total work done when volume of μ mole of ideal gas changes from V_1 to V_2 with temperature remaining constant throughout the process is

$$W = Q = \int_{V_1}^{V_2} P \, dV = \int_{V_1}^{V_2} \frac{\mu RT}{V} dV \qquad [\because PV = \mu RT \text{ for an ideal gas }]$$

$$= \mu RT \int_{V_1}^{V_2} \frac{1}{V} dV \qquad [\because T \text{ is constant for an isothermal process }]$$

$$= \mu RT \ln\left(\frac{V_2}{V_1}\right) = 2.303 \ \mu RT \log\left(\frac{V_2}{V_1}\right)$$

Cyclic process: "A thermodynamic process in which system undergoes a series of processes starting from some thermodynamic equilibrium state and finally returns to the original thermodynamic state is called a cyclic process."

In a cyclic process, there is no change in the internal energy of the system (i.e., $\Delta U = 0$) as the initial and final states are the same. Hence, $Q = W$ from the first law of thermodynamics. Thus, the net amount of heat absorbed by the system is equal to the net amount of work done by the system at the end of the cyclic process.

## Reversible and irreversible processes

If a gas in the cylinder in equilibrium with the environment at temperature T is quickly compressed to half its volume and then allowed to come in equilibrium with the environment back to temperature T, it passes through many inequilibrium states in the process. If it is now allowed to return quickly to its original volume, and allowed to return to the thermal equilibrium with the environment, it would not pass through the same intermediate states as

earlier. Such processes are irreversible processes, e.g., rusting of iron, erosion of rocks, growing of a man, etc. are irreversible processes.

Now, consider another type of process. The volume of the gas is made half by several differential decreases of volume made very slowly. Differential decrease in volume results in differential increase of temperature, but the process being slow, the system has sufficient time to give up the excess heat to the environment regaining its temperature and returning to the equilibrium state. Thus, in this process, the system passes through the equilibrium states and the temperature remains constant. Such a process can be reversed by differential increase in volume on the same path of equilibrium states. This is the example of a reversible isothermal process. Here, piston was assumed to be frictionless. A reversible process is one that, by a differential change in the environment, can be made to retrace its path.

12.13 Heat engine and its efficiency

A device that converts heat energy into mechanical energy is known as heat engine. A simple heat engine is shown in the figure. The gas enclosed in a cylinder with a piston receives heat from a burner, expands, pushes the piston upwards and rotates the wheel. To continue the rotations of the wheel, an arrangement is needed in the heat engine which can move the piston up and down periodically.
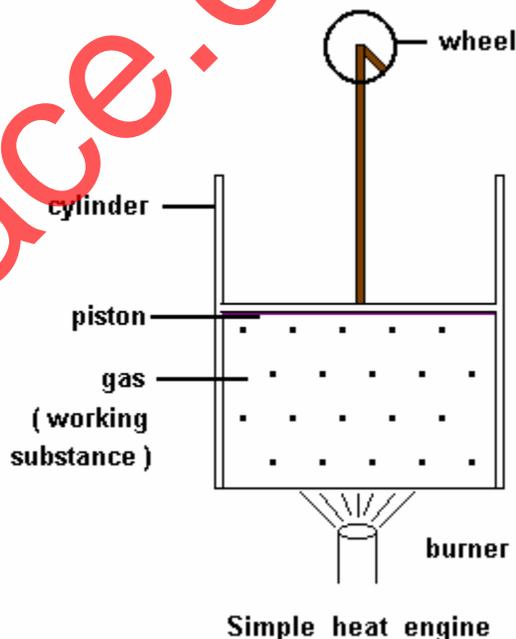
Here, gas is the working substance, burner is the heat source and the arrangement to release the gas and heat after expansion is the heat sink. The working of the engine is explained in the following schematic diagram.
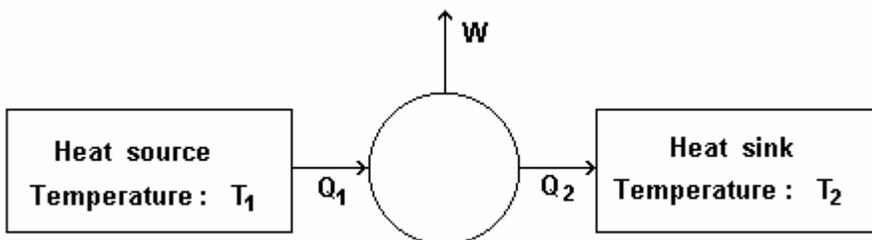
In a heat engine, the working substance undergoes a cyclic process, absorbs heat, Q_1, from the heat source at higher temperature, converts a part of it into mechanical energy and releases the remaining energy, Q_2, into the heat sink.

Simple heat engine

The net amount of heat, $Q = Q_1 - Q_2$ is converted into work W.

$\therefore Q = Q_1 - Q_2 = W$

Now, only the heat Q_1 absorbed by the working substance is of economic importance as the heat

Explanation of heat engine by a line diagram

Q_2 rejected to the environment is a loss. Therefore, efficiency of an engine based on the cyclic process can be defined as
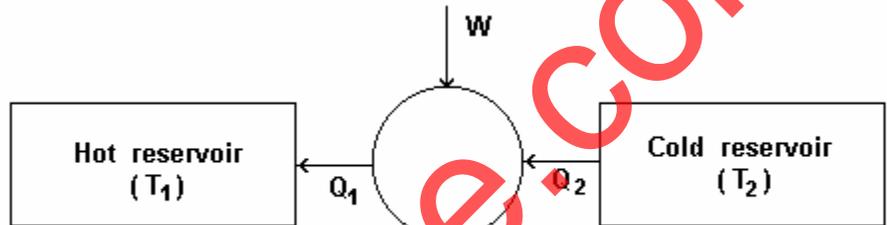
$$\text{Efficiency, } \eta = \frac{\text{net work done}}{\text{heat absorbed}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

η **= 1 if** Q_2 **= 0 which is not possible. The heat engines are of two types:**

(1) External combustion engines such as steam engine and
(2) Internal combustion engines such as diesel and petrol engines.

12.14 Heat pump / refrigerator and co-efficient of performance

If the cyclic process of a heat engine is reversed, it acts as a refrigerator or a heat pump. The schematic diagram of a heat pump / refrigerator is shown in the figure.

Working substance in a heat pump / refrigerator, called refrigerant, draws heat Q_2 **from a cold reservoir at lower temperature** T_2**, external work W is done on the working substance and heat** $Q_1 = Q_2 + W$ **is released into the hot reservoir at higher temperature** T_1**. The co-efficient of performance of a heat engine / refrigerator is defined as**

$$\alpha = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

Here, α **is generally more than 1 (about 4 to 5)**

$$(\because Q_2 > Q_1 - Q_2).$$

Schematic representation of a heat pump / refrigerator

12.15 Carnot cycle and Carnot engine

A Carnot engine converts heat energy into mechanical energy using a cyclic process consisting of two isothermal and two adiabatic reversible processes.

The parts of the Carnot engine are:

(i) a cylinder with insulated sides and a conducting bottom fitted with a frictionless piston,

(ii) ideal gas as working substance,

(iii) Heat source at temperature T_1 **and heat sink at temperature** T_2 **(** $T_1 > T_2$ **) both having very large heat capacity.**
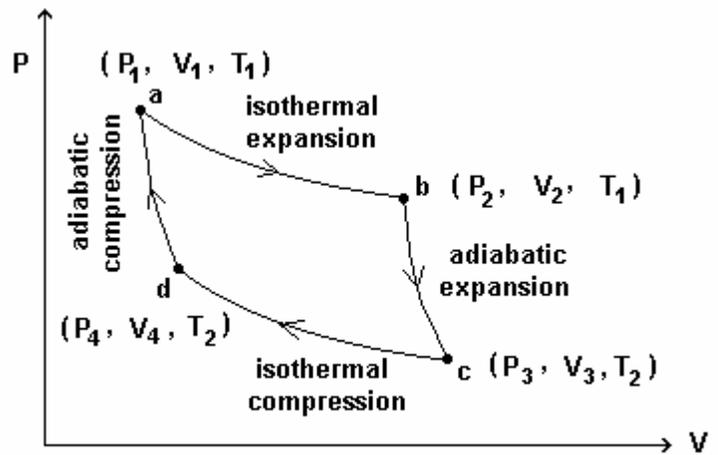
Carnot cycle

The cyclic process, shown by the P $\rightarrow$ **V graph as above is completed in four stages. A Carnot engine and its four different stages are shown in the figure on the next page. The four stages of the Carnot cycle are described as under.**

(i) First Stage - Isothermal expansion:

Initially, the working substance is in the equilibrium state a (P_1, V_1, T_1). Now, the conducting bottom of the cylinder is placed on the heat source at temperature T_1 and the gas is allowed to expand isothermally and reversibly to state b (P_2, V_2, T_1). If Q_1 is the heat absorbed by the gas and W_1 is the work done by the gas in this process, then

$$W_1 \ = \ Q_1 \ = \ \mu\,RT_1 \ln \left(\frac{V_2}{V_1} \right) \ = \ 2.303 \ \mu\,RT \log \left(\frac{V_2}{V_1} \right) \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

Also, for this isothermal process, $P_1 V_1 = P_2 V_2$ ... ... (2)
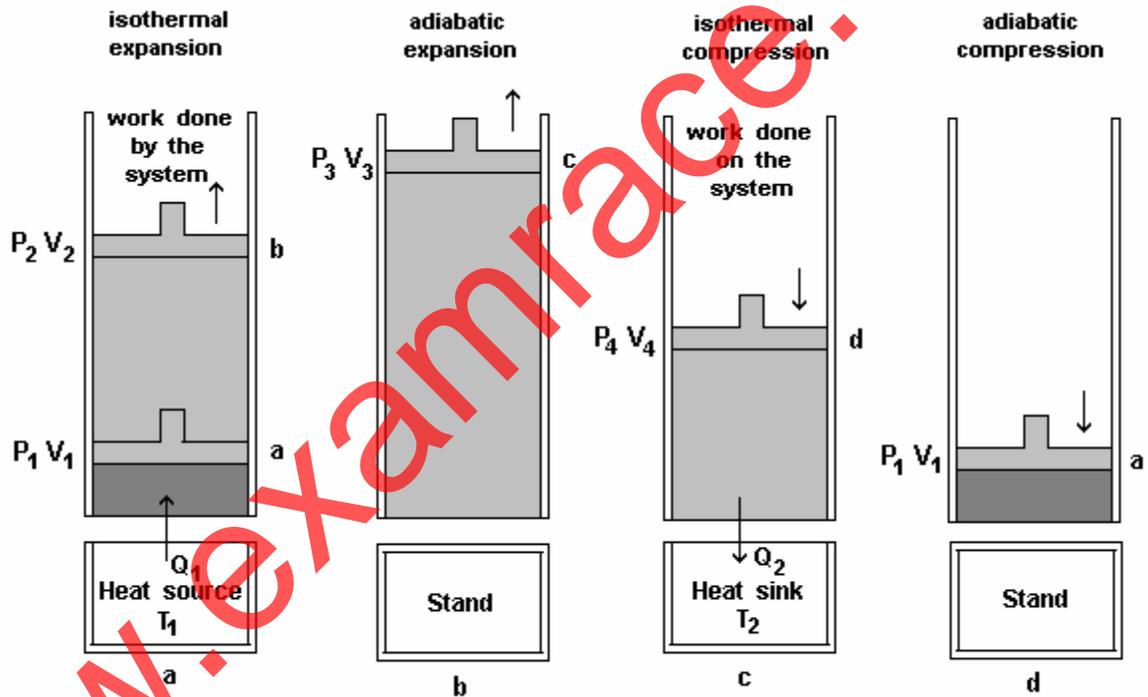
A Carnot engine with its four different stages

(ii) Second Stage - Adiabatic expansion:

Now, the cylinder is placed on a thermally insulated stand and the gas is allowed to expand adiabatically and reversibly to attain the state c (P_3, V_3, T_2). The gas does not absorb heat but does the work and its temperature reduces.

For this adiabatic process, $P_2 V_2^{\gamma} = P_3 V_3^{\gamma}$ ... ... (3)

(iii) Third Stage - Isothermal compression:

Now, the bottom of the cylinder is placed on the cooling device at temperature T_2 and the gas is compressed isothermally and reversibly to attain the state d (P_4, V_4, T_2). If Q_2 is the heat rejected by the gas and W_2 is the work done on the gas in this process, then

$$W_2 \ = \ Q_2 \ = \ \mu\, RT_2 \ln \left(\frac{V_3}{V_4} \right) \ = \ 2.303 \ \mu\, RT \log \left(\frac{V_3}{V_4} \right) \quad \dots \quad \dots \quad \dots \quad (\,4\,)$$

Also, for this isothermal process, $P_3\, V_3 \ = \ P_4\, V_4 \quad \dots \quad \dots \quad \dots \quad \dots \quad (\,5\,)$

(iv) Fourth Stage - Adiabatic compression:

Now, the cylinder is placed on a thermally insulated stand and the gas is compressed by a reversible adiabatic process and taken to its original thermodynamic equilibrium state a (P_1, V_1, T_1). As the process is adiabatic, no heat exchange occurs with the environment, but the work is done on the gas and its temperature rises from T_2 to T_1.

For this adiabatic process, $P_4\, V_4{}^{\gamma} \ = \ P_1\, V_1{}^{\gamma} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (\,6\,)$

The efficiency of the cycle is $\quad \eta \ = \ 1 - \dfrac{Q_2}{Q_1} \ = \ \dfrac{T_2 \ln \left(\dfrac{V_3}{V_4} \right)}{T_1 \ln \left(\dfrac{V_2}{V_1} \right)} \quad$ [from equations (4) and (1)]

Multiplying equations (2), (3), (5) and (6),

$$P_1\, V_1\, P_2\, V_2{}^{\gamma}\, P_3\, V_3\, P_4\, V_4{}^{\gamma} \ = \ P_2\, V_2\, P_3\, V_3{}^{\gamma}\, P_4\, V_4\, P_1\, V_1{}^{\gamma}$$

$$\therefore \quad (\, V_2\, V_4\,)^{\,\gamma\,-\,1} \ = \ (\, V_3\, V_1\,)^{\,\gamma\,-\,1} \qquad \therefore \quad \frac{V_2}{V_1} \ = \ \frac{V_3}{V_4}$$

Putting this result in the equation for efficiency, we get

$$\eta \ = \ 1 - \frac{T_2}{T_1}$$

This equation shows that the efficiency of the Carnot cycle depends only on the temperatures of the source and the sink and does not depend on the working substance. The efficiency is 100 % only if the temperature of the source (T_1) is infinite or the temperature of the sink (T_2) is absolute zero which is impossible.

12.16 Second law of thermodynamics

Different scientists have given the statements of the second law of thermodynamics which explain the impossibility of the Carnot cycle efficiency to be 100 %, two of which are as under.

Statement of Max Plank: " It is impossible to construct a heat engine based on a cyclic process, which by absorbing heat from one body only and without producing any change in the working substance, can convert the heat completely into mechanical energy."

Statement of Kelvin: " It is impossible to have any process in which as a final result, the heat absorbed from a body at a given temperature is completely converted into mechanical work."