HEAT AND THERMODYNAMICS

RS 60

HEAT

Heat is defined as the sum of kinetic energy of all the molecules of a substance.

It is the form of energy associated with molecular motion.

UNITS

Classical units of heat are Calorie and British thermal unit (B.T.U) and modern unit is joule (J).

CALORIE

It is the amount of heat needed to raise the temperature of 1g of air free water from 14.5°C to 15.5°C.

BRITISH THERMAL UNIT

It is the amount of heat needed to raise the temperature of $\frac{1}{32}$ slug of air free water from 64°F to 65°F

JOULE

Heat is a form of energy, so also measured in joule (J) in SI system.

RELATION

1 calorie = 4.184 joule

1 B.T.U = 1254.87 joule

1 B.T.U = 251.996 calorie

TEMPERATURE

Temperature is defined as the average kinetic energy of all the molecules of a substance.

It determines the direction of flow of heat from one body to another when they are in thermal contact. Heat flows from a body at higher temperature to a body at lower temperature.

Temperature is measured in °C, °F and K. where °C (degree centigrade), °F (Fahrenheit) and K (Kelvin)

SYSTEM

A system is a collection of matter which has a distinct boundary.

For example, a gas enclosed in a container or cylinder with a frictionless piston.

SURROUNDING

Everything other than system in the universe is termed as surroundings.

CLOSED SYSTEM

The system in which there is no transfer of mass across its boundary.

OPEN SYSTEM

The system in which mass and heat energy may enter or leave the system.

ISOLATED SYSTEM

The system in which mass and energy cannot be transfered across the boundary of the system.

THERMAL EQUILIBRIUM

A system is in thermal equilibrium if temperature of the system is the same as that of the surroundings.

THERMODYNAMIC STATES

Thermodynamic state of a system refers to physical conditions of the system or is usually described in terms of pressure, volume and temperature

When a vessel containing gas reaches thermal equilibrium, the gas has a definite volume, pressure and temperature and this situation is called a state of the system. For an ideal gas, the relation $PV = nRT$ represents thermodynamic state.

STATE VARIABLES

The state of a system is described by certain variables, called "state variables". When these variables are changed, the state of the system is also changed. For a system consisting of a gas, P, V and T are state variables.

INTERNAL ENERGY Is A STATE VARIABLE

When heat is added to or taken out of the system, its internal energy changes and we can find that change. Thus, internal energy is also a state variable.

HEAT IS NOT A STATE VARIABLE

Heat is not a state variable, because there is no way to find how much heat a system contains.

DIATHERMIC WALLS

Walls that allow heat to flow through them are called diathermic walls.

ADIABATIC WALLS

Walls that do not allow heat to flow through them are called adiabatic walls.

THERMODYNAMICS

That branch of Physics which deals with the conversion of heat into mechanical work and vice versa.

Thermodynamics is the name given to the study of the relationship between heat and others forms of energy.

KINETIC THEORY OF GASES

The theory that explains the behaviour of gases in terms of interaction of molecules and their energy is called "kinetic theory of gases".

The proof in favour of the theory is shown in the diffusion of gases and Brownian motion of smoke particles etc.

BASIC POSTULATES OF KINETIC THEORY OF GASES

The following postulates help us to formulate a mathematical model of gases.

(i) A finite volume of gas consists of a very large number of molecules.

(ii) The size of the molecules is much smaller than the separation between molecules.

(iii) The gas molecules are in random motion and may change their direction of motion after every collision.

(iv) Collision between gas molecules themselves with walls of the container are assumed to be perfectly elastic.

(v) Molecules do not exert force on each other except during a collision.

PRESSURE OF A GAS

According to kinetic theory, the pressure exerted by a gas is nearly the momentum transferred to the walls of the container per second

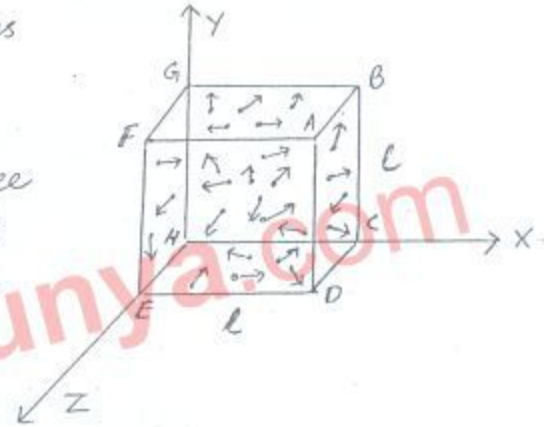
per unit area due to the continuous collisions of molecules of the gas. An expression for the pressure exerted by a gas can be obtained as follows.

Consider a cubical container of side l and having N number of molecules each of mass 'm' of a gas.

The area of each face of the container is $A = l \times l = l^2$

and volume of the container is

$$V = l \times l \times l = l \times A = l^3$$



Anyone of these molecules having velocity v_i in a certain direction can be resolved into three rectangular components v_{ix}, v_{iy} and v_{iz} parallel to three coordinate axis X, Y and Z.

$$\left(\begin{array}{c}\text{Initial momentum of molecule} \\ \text{striking the face ABCDA}\end{array}\right) = P_i = m v_{ix}$$

If the collision is assumed to be perfectly elastic, the molecule will rebound from the face ABCDA with same speed. Thus each collision produces a change in momentum.

Final momentum of the molecule $= P_f = -m v_{ix}$

Change in momentum $= \Delta P = P_f - P_i$

$$= \Delta P = -m v_{ix} - m v_{ix}$$

Change in momentum $= \Delta P = -2 m v_{ix}$ ⟶ (i)

After recoil, the molecule travels to opposite face EFGHE and collides with it,

rebounds and travels back to the face ABCDA after covering a distance $2l$.

The time Δt between two successive collisions with face ABCDA is

$$2l = v_{ix}\,\Delta t$$

$$\Rightarrow \quad \Delta t = \frac{2l}{v_{ix}} \longrightarrow (ii)$$

So, The no. of collisions of molecules in time $\Delta t = \frac{v_{ix}\cdot \Delta t}{2l}$

$$\left(\begin{matrix}\text{The number of collisions per second}\\ \text{that the molecule will make with this face}\end{matrix}\right) = \frac{v_{ix}}{2l}$$

Thus,

$$\left(\begin{matrix}\text{The rate of change of momentum of the molecule}\\ \text{due to the collisions with face ABCDA}\end{matrix}\right)$$

= Change in collision in one momentum × Number of collisions per second with this face

$$= -2mv_{ix}\left(\frac{v_{ix}}{2l}\right) = -\frac{mv_{ix}^2}{l}$$

The rate of change in momentum of the molecule equals the force applied by the wall. According to Newton's third law of motion, force F_{ix} exerted by the molecule on face ABCDA is equal but opposite, so,

$$F_{ix} = -\frac{(-mv_{ix}^2)}{l}$$

$$\text{or} \qquad F_{ix} = \frac{mv_{ix}^2}{l}$$

Similarly the forces due to all other molecules can be found out. Thus the total x-directed force F_x due to N number of molecules of the gas moving with velocities

$v_1, v_2, v_3 \ldots\ldots v_N$ is

$$F_x = F_{1x} + F_{2x} + F_{3x} + \ldots\ldots + F_{Nx}$$

or $$F_x = \frac{mv_{1x}^2}{l} + \frac{mv_{2x}^2}{l} + \frac{mv_{3x}^2}{l} + \ldots\ldots + \frac{mv_{Nx}^2}{l}$$

As pressure is normal force per unit area, hence, pressure P_x on the face perpendicular to x-axis is

$$P_x = \frac{F_x}{A} = \frac{F_x}{l^2}$$

or, $$P_x = \frac{1}{l^2}\left(\frac{mv_{1x}^2}{l} + \frac{mv_{2x}^2}{l} + \frac{mv_{3x}^2}{l} + \ldots\ldots + \frac{mv_{Nx}^2}{l}\right)$$

or, $$P_x = \frac{m}{l^3}\left(v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \ldots\ldots + v_{Nx}^2\right) \longrightarrow (iii)$$

As the mass of single molecule is m, the mass of N molecules will be Nm.

Since Density $= \frac{\text{Mass}}{\text{Volume}}$

or, $$\rho = \frac{mN}{l^3}$$

or, $$\frac{\rho}{N} = \frac{m}{l^3}$$

or $$\frac{m}{l^3} = \frac{\rho}{N}$$

put this value of $\frac{m}{l^3}$ in eq. (iii)

$$P_x = \frac{\rho}{N}\left(v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \ldots + v_{Nx}^2\right)$$

or $$P_x = \rho\left(\frac{v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \ldots\ldots + v_{Nx}^2}{N}\right)$$

where $\left(\frac{v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots + v_{Nx}^2}{N}\right)$ is called the mean of squared velocities of the molecules moving ~~with~~ along x-direction known as mean square velocity represented by $\langle v_x^2 \rangle$ i.e.

$$\langle v_x^2 \rangle = \frac{v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots + v_{Nx}^2}{N}$$

$$\Rightarrow P_x = \rho \langle v_x^2 \rangle \longrightarrow (iv)$$

Similarly, pressure on the faces perpendicular to Y and z-axis will be

$$P_y = \rho \langle v_y^2 \rangle$$

and $$P_z = \rho \langle v_z^2 \rangle$$

As molecules are moving randomly, the mean square of all the components velocities will be equal.

Hence

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

and from vector addition,

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$
$$= \langle v_x^2 \rangle + \langle v_x^2 \rangle + \langle v_x^2 \rangle$$

$$\langle v^2 \rangle = 3 \langle v_x^2 \rangle$$

or $$\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

Put value of $\langle v_x^2 \rangle$ in eq. (iv), we get

$$P_x = \frac{\rho}{3} \langle v^2 \rangle$$

By Pascal's law, the pressure on other sides and everywhere inside the vessel will be the same provided the gas is

of uniform density. So,

$$P_x = P_y = P_z = \frac{\rho}{3} \langle v^2 \rangle$$

Thus in general,

$$P = \frac{1}{3} \rho \langle v^2 \rangle$$

Since $\rho = \frac{mN}{V}$

$$\therefore \quad P = \frac{1}{3} \frac{mN}{V} \langle v^2 \rangle \longrightarrow (v)$$

or $$P = \frac{2}{3} \frac{N}{V} \langle \frac{1}{2} m v^2 \rangle$$

or, $$P = \frac{2}{3} N_0 \langle \frac{1}{2} m v^2 \rangle \longrightarrow (vi)$$

where $N_0 = \frac{N}{V}$ (The number of molecules per unit volume)

In above equation,

$\frac{2}{3} N_0$ = Constant

$$\Rightarrow \quad P = \text{Constant} \langle \frac{1}{2} m v^2 \rangle$$

or $$P = \text{constant} \langle K.E \rangle$$

or $$P \propto \langle K.E \rangle$$

While deriving equation for pressure, we do not consider the rotational and vibrational motion of molecules but only the linear motion is considered.

Hence, the pressure exerted by the gas is directly proportional to the average translational kinetic energy of the gas molecules.

PROVE THAT $T \propto \langle K.E \rangle$

Since the ideal gas law is

$$PV = nRT \longrightarrow (i)$$

where 'n' is the number of moles of the gas contained in volume V at absolute temperature T and R is called universal gas constant. Its value is $8.314\ J\ mol^{-1}\ K^{-1}$

If N_A is the Avogadro's number,

Then $$n = \frac{N}{N_A}$$

Thus eq. (i) can be written as

$$PV = \frac{N}{N_A} RT$$

$$PV = N\left(\frac{R}{N_A}\right) T$$

where $\frac{R}{N_A} = k$ (Boltzman constant)

$$\Rightarrow \quad PV = NkT \longrightarrow (ii)$$

As $$P = \frac{2}{3} \frac{N}{V} \left\langle \frac{1}{2} m v^2 \right\rangle$$

or $$P = \frac{2}{3} N_0 \left\langle \frac{1}{2} m v^2 \right\rangle \longrightarrow (iii)$$

comparing eqs (ii) and (iii), we have

$$NkT = \frac{2}{3} N_0 \left\langle \frac{1}{2} m v^2 \right\rangle$$

or $$T = \frac{2}{3k} \left\langle \frac{1}{2} m v^2 \right\rangle$$

where, $\frac{2}{3k}$ = constant

$$\Rightarrow \quad T = \text{constant } \langle K.E \rangle$$

or $$T \propto \langle K.E \rangle.$$

Thus absolute temperature of an ideal gas is directly proportional to the average translational kinetic energy of gas molecules.

We can also say that average translational kinetic energy of the gas molecules shows itself macroscopically in the form of temperature.

DERIVATION OF GAS LAWS

BOYLE'S LAW

From kinetic theory of gases

$$P = \frac{2}{3}\frac{N}{V}\left\langle \frac{1}{2} m v^2 \right\rangle$$

As $T \propto \langle K.E \rangle$

If we keep the temperature constant, then average K.E i.e $\left\langle \frac{1}{2} m v^2 \right\rangle$ remains constant.

$$\Rightarrow PV = \frac{2}{3} N \left\langle \frac{1}{2} m v^2 \right\rangle$$

or $PV = \text{Constant}$

or $P \propto \frac{1}{V}$

Thus pressure P is inversly proportional to volume V at constant temperature of the gas which is Boyle's Law.

CHARLES' LAW

From kinetic theory of gases,

$$P = \frac{2}{3}\frac{N}{V}\left\langle \frac{1}{2} m v^2 \right\rangle$$

We can write above eq. as

$$V = \frac{2}{3}\frac{N}{P}\left\langle \frac{1}{2} m v^2 \right\rangle$$

If pressure P is kept constant,

Then $V = \text{constant} \left\langle \frac{1}{2} m v^2 \right\rangle$

or $V \propto \left\langle \frac{1}{2} m v^2 \right\rangle$

As $T \propto \left\langle \frac{1}{2} m v^2 \right\rangle$

Hence, $V \propto T$

Thus volume is directly proportional to absolute temperature of the gas provided pressure is kept constant. This is known as Charle's law.

INTERNAL ENERGY

Thus sum of all forms of molecular energies (kinetic and potential) of a substance is termed as its internal energy.

It is denoted by U.

EXPLANATION

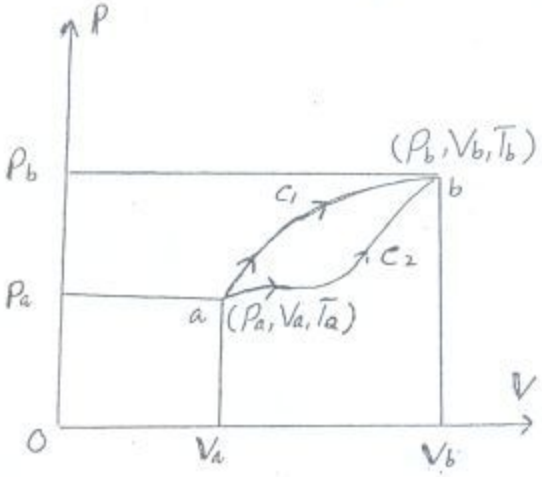
In case of ideal gas the molecules have no interaction between them so their P.E is zero. In this case internal energy of a gas is equal to total translational K.E of all the molecules of a gas. Hence, for an ideal gas system, the value of internal energy depends upon its Kelvin's temperature. Because in case of an ideal gas the total translational K.E is directly proportional to its kelvin temperature.

When a thermodynamic system is heated, then energy of the gas molecules is increased. The internal energy of a system also changed due to work done on or by the system. This work may be due to rubbing or sliding one body over the other.

The internal energy of a system is the function of its state. Its value depends upon its initial and final states only and is independent of the way this change of state is made.

INTERNAL ENERGY IS INDEPENDENT OF PATH

Consider a system whose state is changed from a to b as shown in figure.



The value of pressure and volume of the system at its initial and final states are denoted by P_a, V_a and P_b, V_b respectively. By experiment, it has been seen that the change in internal energy is always the same and it is independent of the paths C_1 and C_2 as shown. In calculations of thermodynamics, the change in internal energy is important but not its absolute value.

WORK AND HEAT

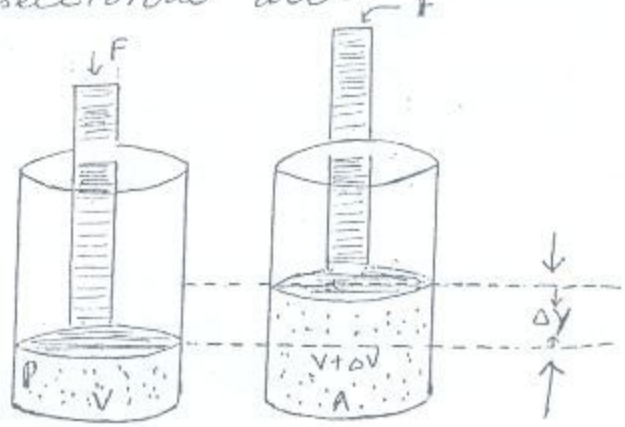
Heat and work are interconvertable i.e heat can be converted into work and work can be converted into heat. The amount of heat given to the system is called 'input' and is written with positive sign. The part of heat which is converted into mechanical work is called 'output'. It is also written with the positive sign.

It is a convension that work done by a system on its surrounding is taken as positive, while work done by the surroundings on a system is taken as negative.

If an amount of heat Q enters the system then its internal energy increases which may further be used as to do work.

The value of work done by a system or on a system can be expressed in terms

of directly measureable variables. For example, we consider a definite volume of a gas inside a cylinder with a moveable, friction-less piston of cross-sectional area. A. When the system is in equilibrium, then the values of pressure and volume are represented by P and V. If the gas is allowed to expand slowly so that it remains in equilibrium and to have a change in its volume equal to ΔV. As the piston moves up through a small distance ΔY, the work done by the gas is



$$\text{Work} = (\text{Force})(\text{Displacement})$$

$$\Rightarrow W = F\Delta Y$$

As $P = F/A$

or $F = PA$

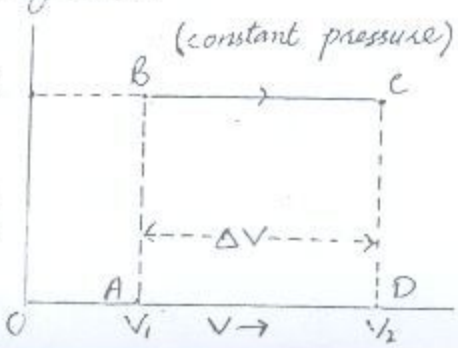
$$\Rightarrow W = PA\Delta Y$$

Since $A\Delta Y = \Delta V$ (Change in volume)

$$\Rightarrow W = P\Delta V$$

This work done can also be calculated by graphical method on P–V diagram.

PV-DIAGRAM: On the graph, between pressure P and volume V, the area under the graph between points B to C is equal to $P\Delta V$, which is the value of work done.



Fsc Part 1 Chapter 11

The general principles which deal with heat energy and its conversion into mechanical energy are known as 'Laws of thermodynamics'.

The laws of thermodynamics are named as

1. Zeroth law of thermodynamics
2. First law of Thermodynamics
3. Second law of Thermodynamics
4. Third law of Thermodynamics

IDEAL GAS

The gas which obeys gas laws under all conditions of temperature and pressure is called an ideal gas.

CHARACTERISTICS

Molecules of an ideal gas exert no force on each other. They exert force only they collide physically.

The molecules of an ideal gas have only kinetic energy but no potential energy.

The molecules behave as hard impenetrable sphere.

Most of gases with low densities and well above the liquification temperature behave as an ideal gas.

If P.E of a real gas becomes zero then it will behave as an ideal gas.

BOLTSMAN CONSTANT

It is the gas constant per molecule.

$$k = \frac{R}{N_A}$$

Its numerical value is

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

FIRST LAW OF THERMODYNAMICS

In any thermodynamic process, when heat Q is added to a system, this energy appears as an increase in the internal energy ΔU stored in the system plus the work W done by the system on its surroundings.

Mathematically,

$$Q = \Delta U + W$$

or $$Q = (U_2 - U_1) + W$$

EXPLANATION

Consider a Thermodynamic system. Let Q be the amount of heat added to the system. It changes the internal energy from U_1 to U_2 due to rise of temperature. The system expands and does work W on its surroundings.

The change of internal energy $(U_2 - U_1) = \Delta U$ and work done (W) both are the results of addition of heat (Q). Considering no loss we can use the law of conservation of energy to get equation of first law of Thermodynamics.

$$Q = (U_2 - U_1) + W$$

or $$Q = \Delta U + W$$

i.e. Heat supplied = Change in internal energy + Work done

From above equation,

$$\Delta U = Q - W$$

i.e. Change in internal energy = Heat supplied − Work done

Mathematical form of the law shows that when heat Q is converted into internal energy ΔU and work done W,

the total amount of energy remains constant. Thus first law of thermodynamics is actually the law of conservation of energy.

If the system undergoes a cyclic process, then

$$U_1 = U_2$$

$$\Rightarrow \quad \Delta U = U_2 - U_1 = 0$$

Thus according to first law of thermodynamics,

$$Q = \Delta U + W$$

Hence $$Q = 0 + W$$

or $$Q = W$$

Thus the work done is equal to the heat absorbed when there is no change in internal energy. This is the maximum work that a system can do. It shows that it is impossible to construct a machine which performs more work than the energy absorbed by it in the form of heat. Such a machine is called perpetual motion machine of first kind.

First Law Of Thermodynamics can also be defined as

"A perpetual motion machine of first kind is impossible."

EXAMPLES OF THE LAW

1. HEAT ENGINE

First law of thermodynamics is well-observed in heat engines.

2. BICYCLE PUMP

A bicycle pump is a good example of first law of thermodynamics. When we pump on the handle, it becomes hot due to mechanical work done on

The air increasing thereby its internal energy. The arrangement consists of a bicycle pump with a blocked outlet. A thermocouple connected to the blocked outlet allows the air temperature to be seen. When piston is pushed quickly, thermometer shows a temperature rise due to the increase of internal energy of the air. The push force does work on the air, thereby increasing its internal energy which is shown by the increase in temperature of the air.

3. HUMAN METABOLISM

Human metabolism is an other example of energy conservation. Human beings and other animals do work when they walk, run or move heavy objects. Work requires energy. Energy is also needed for growth to make new cells and to replace old cells that have died.

"So energy transforming processes that occur within an organism are named as metabolism."

We can apply first law of thermodynamics $\Delta U = Q - W$ to an organism of human body. Work done (W) will result in the decrease in internal energy of the body. Hence temperature or internal energy is maintained by food.

APPLICATIONS

ISOTHERMAL PROCESS

A process in which temperature of the system remains

constant is known as isothermal process.

To keep temperature constant, the system is placed on a heat reservoir (A body at higher temperature).

EXPLANATION

In the case of a gas system the condition of Boyle's law is fulfilled for isothermal process. When gas expands or compresses at constant temperature, the product of its volume and pressure during the process remains constant. i.e.

$$PV = \text{Constant}$$

If P_1 and V_1 are initial pressure and volume whereas P_2 and V_2 are pressure and volume after the isothermal change Then,

$$P_1 V_1 = \text{Constant}$$

and $$P_2 V_2 = \text{Constant}$$

$$\Rightarrow P_1 V_1 = P_2 V_2$$

In case of an ideal gas, the P.E associated with the molecules is zero, hence, the internal energy of an ideal gas depends only on its temperature which in this case remains constant.

$$\Rightarrow U = \text{Constant}$$

and change of internal energy is zero - i.e.

$$\Delta U = 0$$

According to first law of thermodynamics

$$Q = \Delta U + W$$

$$\Rightarrow Q = 0 + W$$

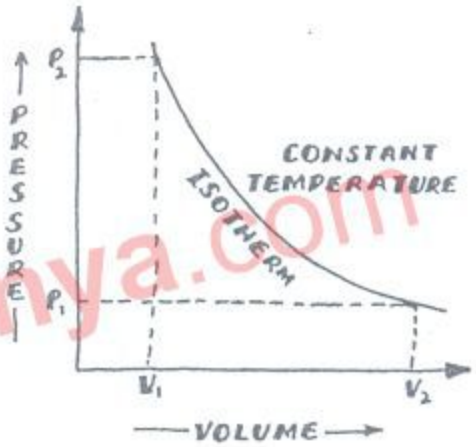
or $$Q = W$$

This shows that if gas expands and does external work W, an amount of heat Q must be supplied to the gas to keep temperature constant during the process. As transfer of heat from one place to another needs time, hence, to keep the temperature constant, the expansion or compression must take place slowly.

P-V DIAGRAM

A graph between pressure P and volume V at constant temperature is a curve called an "isotherm". This isothermal curve or isotherm obey's Boyles law.

i.e. PV = Constant



ADIABATIC PROCESS

A process in which no heat enter or leave the system is called an adiabatic process.

i.e. $\Delta Q = 0$

CONDITION

To stop the heat flow, the system is surrounded by a thick layer of heat insulating material such as cork, asbestass etc. or by performing an expansion or compression process quickly.

EXPLANATION

In an adiabatic process,

Q = constant

and $\Delta Q = 0$

Using first law of thermodynamics,

$$\Delta Q = \Delta U + \phi W$$

$$\Rightarrow \quad 0 = \Delta U + W$$

$$\text{or} \quad W = -\Delta U$$

This shows that work done by a gas is equal to decrease of its internal energy and, therefore, temperature of the gas decreases i.e. work is done at the expense of internal energy.

We can write above equation as

$$\Delta U = -W$$

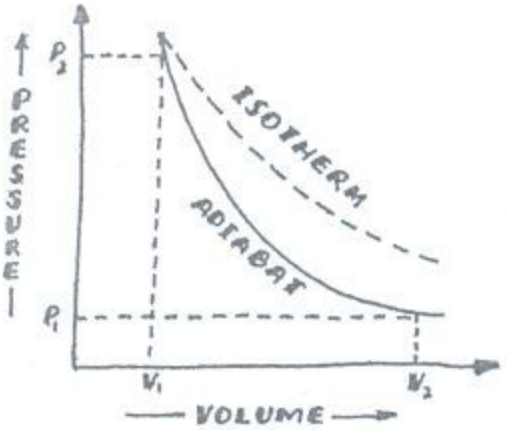
This shows that work is done on the gas and compression increases the temperature of the gas.

Hence, we can say,

"Adiabatic expansion of a gas decreases its temperature and adiabatic compression of the gas increases its temperature."

P-V DIAGRAM

A graph between pressure P and volume V is a curve giving graphical representation of an adiabatic process. Such a curve representing an adiabatic process is called an adiabat. The curve is obtained by using the relation,



$$PV^{\gamma} = \text{constant}$$

where γ is the ratio of the molar specific heat of the gas at constant pressure to the molar specific heat

at constant volume. i.e. $\gamma = C_p/C_v$

EXAMPLES OF ADIABATIC PROCESS

(i) The rapid escape of air from a burst tyre.
(ii) The rapid expansion and compression of air through which a sound wave is passing.
(iii) Cloud formation in the atmosphere.

MOLAR SPECIFIC HEAT

The molar specific heat of a substance is defined as the heat required to raise the temperature of one mole of a substance through 1K.

Mathematically,

$$C_m = \frac{Q}{n\Delta T}$$

and is measured in J/mol.K or $Jmol^{-1}K^{-1}$

MOLAR SPESIFIC HEATS OF A GAS

In case of solids and liquids, the change of volume and the work done against the external pressure during a change of temperature is very small. But the same is not in the case of gases. Thus to study the effect of heating the gases, either pressure or volume is kept constant. The amount of heat per mole necessary to raise unit temperature is different in each case.

MOLAR SPECIFIC HEAT AT CONSTANT VOLUME: C_v

It is defined as the amount of heat transfer required to raise the temperature of one mole of the gas through 1K at constant volume.

It is denoted by C_v

MATHEMATICALLY

If 1 mole of an ideal gas is heated at constant volume so that its temperature rises by ΔT, the heat transferred Q_v is

$$Q_v = C_v \Delta T$$

According to first law of thermodynamics,

$$Q_v = \Delta U + W$$

Since

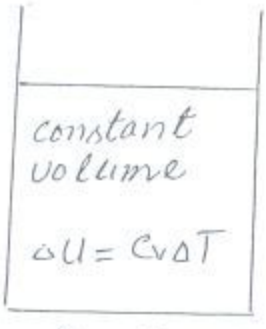
V = constant, $\Rightarrow \Delta V = 0$ i.e. no work is done as $W = P\Delta V = 0$

$$\Rightarrow Q_v = \Delta U + 0$$

$$\text{or } Q_v = \Delta U$$

$$\text{or } C_v \Delta T = \Delta U$$

$$\text{or } \Delta U = C_v \Delta T$$



$Q = C_v \Delta T$

It is measured in $J\ mole^{-1}\ K^{-1}$.

MOLAR SPECIFIC HEAT AT CONSTANT PRESSURE: C_p

It is defined as the amount of heat transfer required to

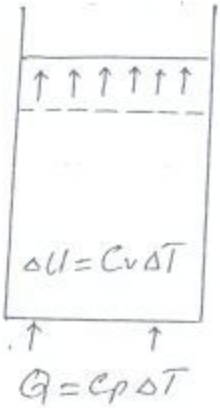
raise the temperature of one mole of the gas through 1K at constant pressure. It is denoted by C_p.

MATHEMATICALLY

To raise the temperature of one mole of the gas by ΔT at constant pressure, the heat transfer Q_p is

$$Q_p = C_p \Delta T$$

It is measured in $J\ mol^{-1} K^{-1}$.



PROVE THAT

$$C_p - C_v = R$$

AND $C_p > C_v$

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PROOF

When one mole of a gas is heated at constant pressure, the internal energy increases by the same amount as at constant volume for the same rise in temperature ΔT. Thus

$$\Delta U = C_v \Delta T$$

Since the gas expands to keep the pressure constant, so, it does work $W = P\Delta V$, where ΔV is the increase in volume.

Using first law of thermodynamics, we have

$$Q = \Delta U + W$$

$$C_p \Delta T = C_v \Delta T + P \Delta V \longrightarrow (i)$$

As ideal gas law is

$$PV = nRT$$

And for one mole of an ideal gas,

$$PV = RT$$

For initial value of volume V_1 and temperature T_1, the above equation is

$$PV_1 = RT_1 \quad \text{(at constant pressure)}$$

and for final value of volume V_2 and temperature T_2

$$PV_2 = RT_2$$

and $$PV_2 - PV_1 = RT_2 - RT_1$$

$$P(V_2 - V_1) = R(T_2 - T_1)$$

or $$P\Delta V = R\Delta T \longrightarrow (ii)$$

where $P\Delta V$ is the amount of work done at constant pressure P by one mole of a gas due to expansion ΔV by the rise in temperature ΔT.

Putting value of $P\Delta V$ in eq.(i)

$$C_p \Delta T = C_v \Delta T + R\Delta T$$

or $$C_p = C_v + R$$

$$C_p - C_v = R$$

Also, we have

$$C_p > C_v$$

i.e. C_p is greater than C_v by an amount equal to R.

REVERSIBL PROCESS

"A reversible process is one which can be retraced in exactly reverse order without producing any change in the surroundings."

EXPLANATION

In the reverse process, the working substance passes through the same stages as in the direct process but thermal and mechanical effects at each stage are exactly reversed.

If heat is absorbed in the direct process, it will be given out in the reverse process. If work is done by the substance in the direct process, it will be done on the substance in the reverse process. Hence the working substance is restored to its original state.

EXAMPLES

As no actual change is completely reversible but the processes of liquification and evaporation of a substance performed slowly are practically reversible.

The slow compression of a gas in a cylinder is a reversible process as the compression can be changed to expansion by slowly decreasing the pressure on the piston to reverse the operation.

IRREVERSIBLE PROCESS

If a process can not be retraced in the backward direction by reversing the controlling factors is called an irreversible process.

All changes which occur suddenly or which involve friction or dissipation of energy through conduction, convection or radiation are irreversible.

EXAMPLE

(i) An explosion is the example of highly irreversible process.

(ii) Work done against friction.
(iii) All engines of practical life are reversible.

CYCLE

A succession of events which bring the system back to its initial state is called a cycle.

REVERSIBLE CYCLE

A reversible cycle is one in which all changes are reversible.

LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

First law of thermodynamics fails to tell us
(i) How heat is converted into work.
(ii) How much heat is converted into work.

HEAT ENGINE

It is a device which converts heat energy into mechanical energy (work).

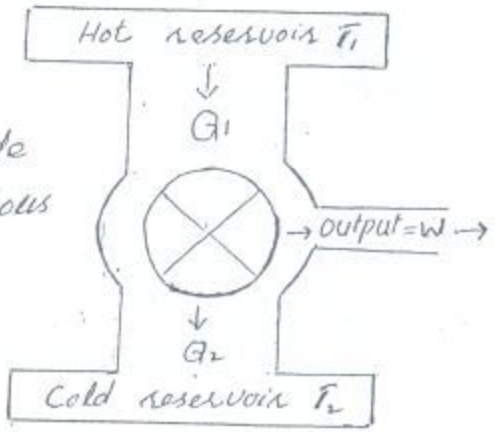
CONSTRUCTION

A heat engine consists of a high temperature source of heat called hot body or high temperature reservoir (HTR), a low temperature reservoir called cold body or heat sink and a mechanical operator called the central part or working substance which converts some amount of heat energy into mechanical work.

WORKING

Heat engine absorbs heat Q from heat source or hot reservoir, converts a part of heat energy into mechanical energy (work) and rejects the remaining heat Q_2 to the cold reservoir or sink. The working substance converts some of

heat into work W by its expansion thereby causing drop in its temperature. So a heat engine is made cyclic to provide a continuous supply of work.



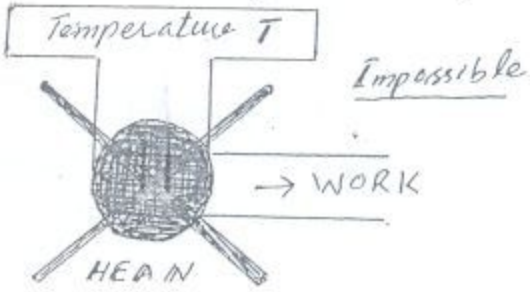
SECOND LAW OF THERMODYNAMICS

KELVIN'S STATEMENT

It is impossible to device a process which may convert heat, extracted from a single reservoir, entirely into work without leaving any change in the working system.

EXPLANATION

This means that a single heat reservoir cannot be made to perform any work. According to second law of thermodynamics, two bodies at different temperatures are necessary for the conversion of heat into work. Hence, for the working of heat engine there must be a source of heat at a high temperature and a sink at low temperature. The work performed will be less than the heat absorbed.



Q: Why heat contents of oceans and atmosphere are not converted into mechanical work?

Ans: According to second law of thermodynamics, a single heat reservoir, no matter

how much energy it contains, cannot be made to perfoam any useful mechanical work. This is true for oceans and our atmosphere which contain a large amount of heat energy but cannot be converted into useful mechanical work. A high temperature reservoir and low temperature reservoir are necessary for the conversion of heat into work. So we cannot use the heat contents of oceans and atmosphere as there is no reservoir at a temperature lower than any one of the two.

CARNOT ENGINE

In 1824, a French scientist Sadi Carnot proposed an ideal heat engine which is free from friction and heat losses and could have maximum possible efficiency (but not 100%)

PRINCIPLE

It works on the same principle as that of any heat engine operating in a cycle between the two given reservoires.

CONSTRUCTION

Carnot engine consists of a cylinder with non-conducting walls and a conducting base. Ideal gas is enclosed in the cylinder by a frictionless and non-conducting piston. Two heat reservoirs at temperatures T_1 and T_2 serve as source and sink respectively.

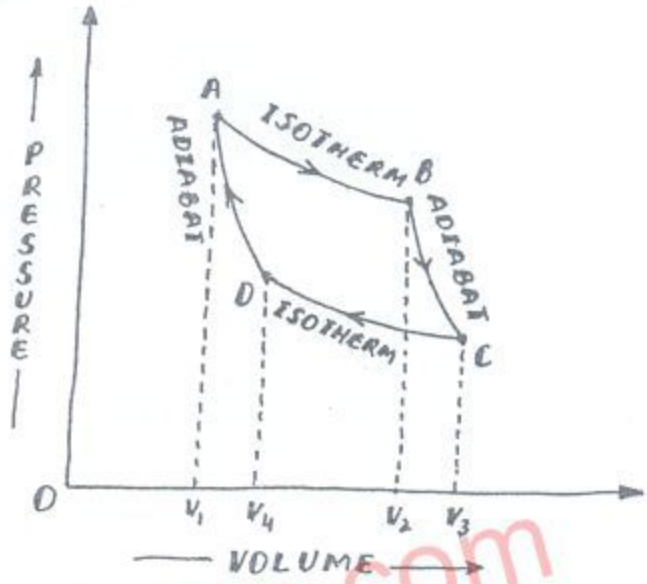
CARNOT CYCLE

The working cycle of Carnot engine is called Carnot cycle. It is a reversible cycle completes in four steps using isothermal and adiabatic processes.

A Carnot cycle using an ideal gas as the working substance is shown on PV-diagram. It consists of following four steps.

(i) ISOTHERMAL EXPANSION

The gas is allowed to expand isothermally at temperature T_1 by absorbing heat Q_1 from the hot reservoir. The process is represented by curve AB.



(ii) ADIABATIC Expansion

The gas is allowed to expand adiabatically till its temperature drops to T_2. The process is represented by the curve BC.

(iii) ISOTHERMAL COMPRESSION

The gas at this stage is compressed isothermally at temperature T_2 rejecting heat Q_2 to the cold reservoir. The process is represented by the curve CD.

(iv) ADIABATIC COMPRESSION

Finally the gas is compressed adiabatically to restore its initial state at temperature T_1. The process is represented by the curve DA.

Since the working cycle of Carnot engine is perfectly reversible, the working substance returns to its initial state. There is no change in its internal energy. i.e

$$U_1 = U_2$$

$$\Rightarrow \Delta U = 0$$

The total work done during one cycle equals

to the area enclosed by the path ABCDA of the P-V diagram. It can also be estimated from total heat ΔQ absorbed in one cycle.

i.e. $$\Delta Q = Q_1 - Q_2$$

From first law of thermodynamics,

$$\Delta Q = \Delta U + \Delta W$$

$$\Rightarrow Q_1 - Q_2 = 0 + \Delta W$$

or $$\Delta W = Q_1 - Q_2$$

EFFICIENCY OF HEAT ENGINE

The efficiency of heat engine is defined as the ratio of output to input.

It is denoted by η (eta).

Thus $$\eta = \frac{\text{Output}}{\text{Input}}$$

Here Output = Work Done

and input = Heat energy supplied

$$\therefore \eta = \frac{\text{Work Done}}{\text{Heat energy supplied}}$$

or $$\eta = \frac{\Delta W}{Q_1}$$

Thus $$\eta = \frac{Q_1 - Q_2}{Q_1}$$

The energy transfer in an isothermal expansion or compression turns out to be proportional to kelvin temperature. So, Q_1 and Q_2 are proportional to kelvin temperatures T_1 and T_2 respectively.

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

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

The efficiency is usually known taken in percentage.

Thus

$$\eta = \text{Percentage efficiency} = \left(1 - \frac{T_2}{T_1}\right) \times 100$$

The efficiency of Carnot engine depends upon the temperature of hot and cold reservoirs. It is independent of the nature of working substance. Larger the temperature difference of two reservoirs, the greater is the efficiency i.e the efficiency increases as T_2 decreases and becomes equal to 1 or 100% as T_2 equal to zero. Since such reservoir is not available which have absolute zero temperature ($T_2 \neq 0$) hence efficiency must be less than 100%. But Carnot engine has maximum efficiency than practical heat engines.

CARNOT'S THEOREM

"All Carnot engines operating between the same two temperatures have the same efficiency irrespective of the working substance and no heat engine can be more efficient than a Carnot engine operating between the same two temperatures."

In most practical cases, the cold reservoir is near room temperature. So the efficiency can be only increased by raising the temperature of hot reservoir All real heat engines are less efficient than Carnot engine due to friction and other heat losses.

THERMODYNAMIC SCALE OF TEMPERATURE

that scale of temperature which is independent of nature of the working substance. This scale of temperature was defined on the base provided by Carnot's theorem. The efficiency of Carnot engine is also independent of the nature of working substance, hence it is used to define thermodynamic scale.

FIXED POINTS

Thermodynamic scale of temperature is defined by choosing one fixed point as 273.16 K as the absolute temperature of the tripple point of pure water and the other fixed point on this scale of temperature is taken as absolute zero.

"One degree or unit of thermodynamic scale is equal to $\frac{1}{273.16}$ of the thermodynamic temperature of the tripple point of water."

Tripple point of water represents a state at which ice, water and vapours exist in equilibrium with each other.

READING

The readings of temperature on the thermodynamic scale of temperature are calculated by using the formula derived as

If Q be the amount of heat absorbed or rejected by a system during a part of Carnot cycle at temperature T (Kelvin) and Q_3 be the amount of heat absorbed or rejected by the same system when it is at a temperature of tripple point of water, then value of T in Kelvin is given by

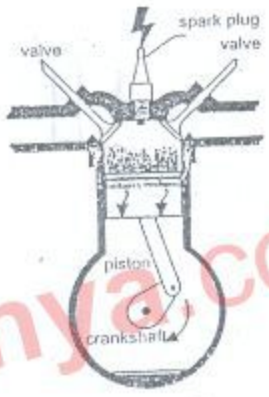
$$\frac{T}{273.16} = \frac{Q}{Q_3}$$

or $T = 273.16 \frac{Q}{Q_3}$

This formula is written by using the property of thermodynamic scale that ratio of two different temperatures on this scale is equal to the ratio of amounts of heats transferred at these temperatures i.e.

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1}$$

PETROL ENGINE



The construction technology of different types of engines may be different but the working principle of all these is the same as that of Carnot engine.

A typical four stroke petrol engine perform four successive processes to complete its cycle just as completed by Carnot engine.

1. CHARGING STROKE

At the start of the cycle, the piston moves out to draw a mixture of air and petrol through inlet valve into the cylinder from the carburator at atmospheric pressure.

2. COMPRESSION STROKE

On the compression stroke, the inlet valve is closed and the mixture is compressed adiabatically by inward movement of the piston.

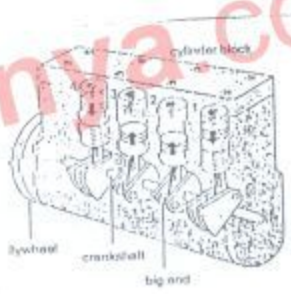
3. POWER STROKE

spark fires the mixture causing a rapid increase in pressure and temperature. The burning mixture expands adiabatically and forces the piston to move outward. This is the stroke which gives the power to crank shaft to drive the flywheels..

4. EXHAUST STROKE

On the exhaust stroke the outlet valves open. The gases formed due to the burning of petrol are taken out of cylinder and piston moves inward.

Most motorbikes have one cylinder engine but cars have usually four cylinders on the some crank shaft. The cylinders are timed to fire turn by turn in succession for a smooth running of the car.

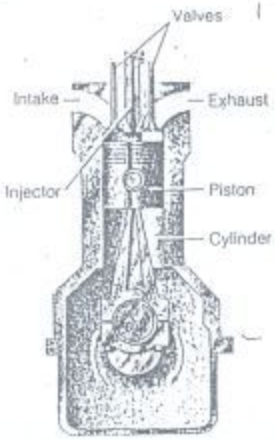


EFFICIENCY OF PETROLE ENGINE

The actual efficiency of petrol engine is usually not more than 25 – 30% because of friction and other heat losses.

DIESEL ENGINE

No spark plug is needed in the diesel engine. The air is compressed adiabatically to a very high pressure so that its



temperature rises to high value. Diesel is sprayed into the cylinder at high compression and at very high temperature so that it takes fire and burns to produce gases of large volume. This makes the piston to move outward.

EFFICIENCY

The efficiency of diesel engine is greater than the efficiency of a petrol engine. The efficiency of diesel engine is about 35 – 40%.

IMPORTANCE OF SECOND LAW OF THERMODYNAMICS

First law of thermodynamics tells us that heat energy can be converted into mechanical work but it is silent about the conditions under which this conversion takes place. The second law of thermodynamics tells about the conditions in which heat can be converted into work and direction of flow of heat.

ENTROPY

Entropy is that physical quantity which describes the unavailability of energy of the system.

It is the measure of disorder of a system.

The concept of entropy was introduced into the study of thermodynamics by Rudolph Clausius in 1856. Entropy of a system is represented by symbol 'S'.

FORMULA FOR CHANGE In Entropy

The change in entropy is denoted by ΔS. During a reversible process at temperature of T, the heat absorbed by a system is denoted by ΔQ. Then the increase in entropy ΔS is defined by the relation

$$\Delta S = \frac{\Delta Q}{\Delta T}$$

The change of entropy is measured in $J\,K^{-1}$

The change of entropy of a system is more important than its absolute value.

SIGN CONVENTION

The change of entropy ΔS is positive when heat is added to a system and ΔS is negative when heat is taken out of the system.

Positive change of entropy means the increase of entropy and negative change of entropy means the decrease of entropy.

Consider there are two reservoirs which are at two different temperatures T_1 and T_2. The heat Q flows from a reservoir at higher temperature T_1 to another at lower temperature T_2 through a conducting rod.

If $T_1 > T_2$ then change of entropy of reservoir at higher temperature T_1 which losses heat is negative and is equal to $-Q/T_1$ and the change of entropy of the other reservoir which absorbs heat is positive and is equal to $+Q/T_2$.

Hence, total change of entropy of the system is

$$\Delta S = \frac{Q}{T_2} - \frac{Q}{T_1}$$

As $T_1 > T_2$ so, $\frac{Q}{T_1} < \frac{Q}{T_2}$

Thus ΔS is written with the positive sign or entropy of the system is increased.

It follows that in all natural processes where heat flows from system to another, there is always a net increase in

ENTROPY AND SECOND LAW OF THERMODYNAMICS

Second law of thermodynamics in terms of entropy can be stated as,

"If a system undergoes a natural process, it will go in the direction that causes the entropy of the system plus the environment to increase."

There is a relation between molecular disorder and entropy. As there is increase of disorder of molecules due to every real or natural process. For example, when heat flows from hot to cold a substance then due to this flow both substances come equilibrium. Thus molecules move with random motion. Hence addition of heat to a system increases its disorder because of increase in average molecular speeds.

Similarly expansion of a gas also increase disorder because their random motion is increased in expansion.

Principle Of Increase Of Entropy

This states that "either entropy of the universe increases or it remains constant after every process."

DEGRADATION OF ENERGY

Consider an example of two tanks of water. One tank contains hot water while the other contains cold water. These two tanks can be taken as source and sink of a heat engine to get some useful mechanical work.

When hot and cold waters are mixed to get one particular temperature of mixture, then disorder increased as the mixture cannot be separated into a hot layer and cold layer of water. There is no loss of energy but some of energy is not available for conversion into work. So we can say that entropy is increased due to increase of disorder. Therefore, increase in enthopy means degradation of energy.

ENTROPY IS A STATE VARIABLE

Clausius proved that a system has the same entropy under same conditions. Thus entropy is also a state variable like pressure, volume, temperature and internal energy and measures disorder.

HEAT DEATH

As universe is going from more orderly form to a less orderly form after every real process, so thermal energy is becoming unavailable for conversion into mechanical work. It is expected that there will be no way to convert heat energy into

useful work. This is so called heat death of the universe.

ENTROPY AS TIME'S ARROW

Since the entropy of the system increases day by day, it can tell us in which direction the time is running. Increase in entropy hints at further events and decrease in entropy hints at past events.

For example, a solid cup is in the state of order. If it is broken after falling the broken pieces of the cup are in disorder and cannot bring themselves to initial state. Thus normal direction of events is an increase of disorder. That's why entropy is called the time's arrow.

ENVIRONMENTAL CRISES AS ENTROPY CRISES

The effort of human being is to order the nature occuring to his own needs and comforts. But according to physical view point disorder is being produced because the original order of nature is disturbed after every real process. Therefore, we can say that entropy crises are being produced. It shows that due to disorder overall life activities are being affected.

In every energy process, a part of it is being lost in the form of heat in the environment that is according to second law of thermodynamics which cannot stopped. Hence, thermal pollution is being produced.

Even due to small change in temperature of environment due to thermal pollution a large effect is produced on metabolic rates and in plants and animals. This can cause serious problems in ecological balance.

In addition to thermal pollution, the heat engines cause air pollution also. Hence all forms of energy production have undesirable effects which are called "Environmental Crises" due to which serious degradation of life is produced on our Earth.

11.1 Why is the average velocity of the molecules in a gas is zero but the average of the square of the velocities is not zero?

Ans. The number of molecules in a gas is large and their motion is random. Statistically, the number of molecules moving in any direction with certain velocity is equal to the number of molecules moving in the opposite direction with the same velocity. Their vector sum is zero. The average velocity of the molecules is, therefore, zero. But as the square of a negative velocity is also a positive number, hence, average of the square of velocities will not be zero.

11.2 Why does the pressure of a gas in a car tyre increase when it is driven through some distance?

Ans. When a car is driven on the road through some distance, its tyre has to overcome the frictional force of the road. The work done against the friction heats up the tyre and hence, the gas in the tyre. This result in the increase in molecular velocities of the air contained in the tyre. The increase in molecular velocities increases the rate of molecular collisions against the wall of the tyre and subsequently increases the pressure of air in it.

11.3 A system undergoes from state P_1V_1 to state P_2V_2 as shown in Fig. 11.13. What will be the change in internal energy?

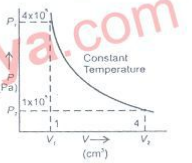


Fig. 11.13

Ans. The temperature of a gas is directly proportional to the average K.E. of its molecules, which is the internal energy of the system (gas). As temperature remains constant, internal energy remains the same; hence there is no change in the internal energy of the system.

10.4 Variation of volume by pressure is given in Fig.11.14. A gas is taken along the paths ABCDA, ABCA and A to A. What will be the change in internal energy?

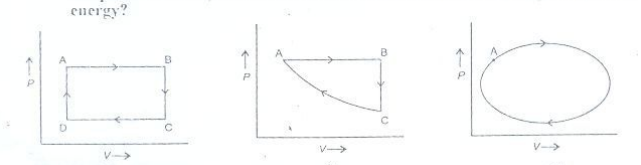


Fig. 11.14

Ans. In all the three cases, the system returns to the initial state, hence, there is no change in internal energy.

11.5 Specific heat of a gas at constant pressure is greater than specific heat at constant volume. Why?

Ans. When heating a gas at constant pressure, heat is required not only to increase the internal energy and temperature, but also to do work as gas expands against constant pressure. In the case of a gas where volume is kept constant, no work is done to expand the gas. The entire heat supplied is utilized in raising the internal energy or temperature. This shows that more heat is required to heat a gas at constant pressure than at constant volume for the same rise of temperature. Hence, specific heat of a gas at constant pressure is greater than the specific heat at constant volume.

11.6 Give an example of a process in which no heat is transferred to or from the system but the temperature of the system changes.

Ans. In an adiabatic expansion of a gas, the temperature deceases as the work in expanding the gas is done at the cost of internal energy of the gas. Conversely, in an adiabatic compression, the work done on the gas increases the temperature of the gas.

11.7 Is it possible to convert internal energy into mechanical energy? Explain with an example.

Ans. Yes, it is possible to convert internal energy into mechanical energy or work by expanding a gas under adiabatic condition.

11.8 Is it possible to construct a heat engine that will not expel heat into the atmosphere?

Ans. No, it is not possible to construct a heat engine that will not expel heat into the atmosphere. A heat engine works only when some of the total heat absorbed from the source is expelled to a sink or atmosphere.

11.9 A thermos flask containing milk as a system is shaken rapidly. Does the temperature of milk rise?

Ans. When milk is shaken rapidly in a thermos flask, its temperature, although very small, should rise as work is done on it.

11.10 What happens to the temperature of the room, when a air conditioner is left running on a table in the middle of the room?

Ans. The temperature of the room will not reduce rather it will rise as the heat absorbed from the room is expelled in the same room plus the work done by the compressor is changed into heat and expelled in the same room.

11.11 Can the mechanical energy be converted completely into heat energy? If so give an example.

Ans. Yes, mechanical energy can be completely converted into heat energy. When work (mechanical energy) is done in compressing the gas by adiabatic process, the increase in the internal energy of the gas is equal to the work done on it.

11.12 Does entropy of a system increases or decreases due to friction?

Ans. The entropy of a system increases due to friction as the work done against friction is changed into heat and heat added to a system increases its entropy.

11.13 Give an example of a natural process that involves an increase in entropy.

Ans. When ice melts due to high temperature of its surroundings, the heat ΔQ transferred to ice from the surroundings at absolute temperature T is positive and is given by the equation

$$\Delta S = \frac{\Delta Q}{T}$$

Hence, entropy of melted ice i.e. water increases.

11.14 An adiabatic change is the one in which

(a) No heat is added to or taken out of a system
(b) No change of temperature takes place
(c) Boyle's law is applicable
(d) Pressure and volume remains constant

Ans. An adiabatic change is the one in which no heat transfer from or to the system takes place. Hence correct statement is (a).

11.15 Which one of he following process is irreversible?

(a) Slow compressions of an elastic spring
(b) Slow evaporation of a substance in an isolated vessel
(c) Slow compression of a gas
(d) A chemical explosion

Ans. A process performed slowly is usually reversible process and hence, (a), (b) and (c) are reversible processes. A chemical expansion is a rapid process. Hence, correct answer of irreversible process is (d).

11.16 An ideal reversible heat engine has

(a) 100% efficiency
(b) Highest efficiency
(c) An efficiency, which depends on the nature of working substance
(d) None of these

Ans. From 2nd law of thermodynamics the efficiency of a heat engine cannot be 100%. Hence an ideal heat engine has highest efficiency but not equal to 100%. Thus correct answer is (b).