

THERMAL PROPERTIES OF MATTER

Heat and Temperature

Heat is often confused with temperature, but the two are different concepts.

If a hot body is kept in contact with a cold body, the temperature of cold body increases and that of hot body decreases. Here we can see that 'something' is transferred from hot body to cold body.. *This 'something' that flows from a body at higher temperature to one at a lower temperature is called heat.* This transfer will continue till the temperature of both bodies become the same.

Heat is a form of energy transferred between two (or more) systems or a system and its surroundings by virtue of temperature difference. Temp is a measure of hotness of a body.

. Conventionally, *the heat energy Q supplied to a body is taken to be positive ($+Q$) and the heat energy given out of a body is taken to be negative ($-Q$).*

Heat is a form of energy transferred between two (or more) systems or a system and its surroundings by virtue of temperature difference. Temp is a measure of hotness of a body.

Thermometer: a device which is used to measure the temperature of a body is known as thermometer.

Commonly used thermometer scales are: (i) Celsius scale ($^{\circ}\text{C}$) (ii) Kelvin scale (K) (iii) Fahrenheit scale ($^{\circ}\text{F}$)

Relation between different temperature scales. At standard pressure

Freezing point of water: 0°C 32°F 273.15 K - Lower fixed point

Boiling point of water : 100°C 212°F 373.15 K . - Upper fixed point.

In Celsius scale and Kelvin scale, the temperature difference between freezing point and boiling point of water are the same, but they have different starting points. The size of degree on Celsius scale and Kelvin scale are same.

$\text{K} = ^{\circ}\text{C} + 273.15$. i.e. $0\text{ K} = -273.15^{\circ}\text{C}$. 0K is called **absolute zero**, because below this value we cannot find any temperature in the universe.

Conversion of temperature from one scale to another.

$$\frac{\text{temp on one scale} - \text{lower fixed point}}{\text{upper fixed point} - \text{lower fixed point}} = \frac{\text{temp on another scale} - \text{lower fixed point}}{\text{upper fixed point} - \text{lower fixed point}}$$

$$\text{i.e. } \frac{\text{C} - 0}{100} = \frac{\text{F} - 32}{180} = \frac{\text{K} - 273.15}{100}$$

Thermodynamics

It is a branch of physics which deals with the study of heat, temperature and the interconversion of heat energy into other forms of energy.

The various terms involved in thermodynamics are:-

(i) Thermodynamic System

A thermodynamic system consists of a large number of atoms or molecules at a particular temperature, pressure and volume. The system may exist in solid, liquid and gaseous state.

(ii) Surroundings

Everything outside a thermodynamic system is its surrounding.

(iii) Thermodynamic Variables or Parametres

These are quantities like pressure, volume and temperature which help us to study the behaviour of thermodynamic system.

(iv) Thermodynamic process

It is any process in which there is some change in pressure, volume or temperature of a system.

Isothermal process or Isothermal change

If a thermodynamic system, which is perfectly conducting to the surroundings, undergoes a physical process (say a change in pressure or volume) in which the temperature remains constant throughout, the process is said to be an isothermal process.

In such a process, if heat is developed in the system, it is given out to the surroundings or if heat is lost, it is taken from the surroundings, so that the temperature of the system remains unchanged.

Eg: Melting and Boiling.

Consider some gas contained in a barrel of conducting material, fitted with an airtight piston. As the gas is compressed, heat is liberated. The liberated heat goes out to keep the temp constant. When the gas is expanded, heat is absorbed. This absorption is compensated by the transfer of heat from the surroundings, again keeping the temp constant. Such a change is called isothermal change or process.

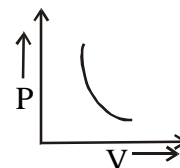
P – V diagram for isothermal change is shown in fig:

The curve AB is called an *isothermal curve or an isothermal*.

Since temp remains constant, Boyle's law can be applied to study this change.

Hence equation of state for isothermal change is given by :

$$P V = \text{constant.} \quad \text{ie } P V = R T = \text{constant.}$$



Adiabatic process or adiabatic change

If a thermodynamic system, which is perfectly insulated from the surroundings, undergoes a physical process in which no exchange of heat takes place between the system and the surroundings, the process is said to be an adiabatic process.

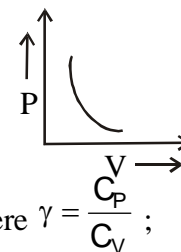
In such a process, no heat is allowed to enter or leave the system.

Consider some gas contained in an insulating barrel fitted with an airtight piston. On compressing the gas, heat is liberated. This liberated heat cannot go out due to the insulation of the barrel, resulting in a rise of temp. On expanding the gas, heat is absorbed.

This result in a fall of temp.

P – V diagram for an adiabatic process is as shown:

The curve AB is called adiabatic curve or adiabatic.



The equation of state for adiabatic change is given by $P V^\gamma = \text{constant} \rightarrow \text{(I)}$; where $\gamma = \frac{C_p}{C_v}$;

where C_p and C_v are the molar specific heats at constant pressure and volume respectively.

Now we know $P V = R T$.

$$\therefore P = \frac{RT}{V} \quad \text{Substituting in (I), } \frac{RT}{V} V^\gamma = \text{constant.}$$

$$\text{Or } T V^{\gamma-1} = \text{Constant} / R \quad \text{ie} \quad T V^{\gamma-1} = \text{Constant} \rightarrow \text{(II)}$$

$$\text{Again } V = \frac{RT}{P} \quad \text{ie} \quad P \left(\frac{RT}{P} \right)^\gamma = \text{constant.}$$

$$\text{i.e. } P^{1-\gamma} R^\gamma T^\gamma = \text{Constant} \quad \text{Or } P^{1-\gamma} T^\gamma = \text{Constant} / R^\gamma$$

$$\text{i.e. } P^{1-\gamma} T^\gamma = \text{Constant} \rightarrow \text{(III)}$$

(I), (II) and (III) are the equations of state for adiabatic change.

Isobaric change: A change in volume and temp of a gas, which takes place at a constant pressure, is called an isobaric change.

Isochoric change: A change in pressure and temp, which takes place at constant volume is called isochoric change.

Cyclic Process: It is a thermodynamic process in which the system returns to its initial state after undergoing a series of changes.

Non cyclic porcess: It is a process in which the system doesnot return to its initial state after a series of changes.

It is a process in which a thermodynamic system proceeds extremely slowly such that at every instant of time, the temperature and pressure are the same in all parts of the system.

Isolated system

It is the system which is completely separated from its surroundings.

Thermal equilibrium and temperature

If a hot body be brought in contact with a cold body, heat energy will be transferred from hot body to cold body until their temperatures become the same. Thereafter no exchange of heat takes place between them. At this stage, the two bodies will be at the same temperature and they are said to be in **thermal equilibrium** with each other.

Two bodies are said to be in thermal equilibrium with each other, if no exchange of heat takes place when they are kept in contact with each other.

Zerth law of thermodynamics

The zeroth law of thermodynamics states that “ *If two systems A and B are separately in thermal equilibrium with a third system C, then A and B are also in thermal equilibrium with one another*”.

Consider three systems A, B and C. A and B are separated by an insulating wall, while there is a conducting wall which separates C from A and B. Exchange of heat takes place between A and C and B and C, till thermal equilibrium is reached.

Now change the positions of the walls. Bring conducting wall in between A and B, while the insulating wall separates C from A and B. then we can see that no exchange of heat takes place between A and B indicating that they are in thermal equilibrium.

i.e. If $T_A = T_C$ and $T_B = T_C$, then $T_A = T_B$.

From zeroth law of thermodynamics, the temp can be defined as follows:

There exist a quantity called temperature, which is the property of all thermodynamic systems in equilibrium state, such that temp equality is the necessary and sufficient condition for thermal equilibrium.



Heat, Work and Internal Energy

Heat is that part of internal energy which is transferred from one body to another on account of the temperature difference.

When a system gets displaced from one position to other as a result of some force, **work** is said to be done. It is observed that the amount of heat produced is proportional to the amount of mechanical work done.

Work and heat are two equivalent forms of energy but work is the transfer of mechanical energy irrespective of temperature difference whereas heat is the transfer of thermal energy because of temp difference only.

Internal energy is the sum of kinetic and potential energies of the molecules of the system. This energy is possessed by a system due to its molecular motion and molecular configuration.

Thus, internal energy $U = K.E + P.E$.

First law of Thermodynamics

Let an amount of heat ΔQ be supplied to a system. This heat will be utilized for two purposes

- (i) To change the thermal state of the system; and
- (ii) To change the mechanical state of the system, i.e. to increase the volume.

(1) When the system receives heat, the molecules of the system move more vigorously. As a result, the internal energy of the system increases. Let ΔU be the increase in internal energy.

(2) When heat is supplied, volume of system may increase. If pressure P of the system is constant and the volume increases by ΔV , the work done by the gas against pressure P is given by $\Delta W = P \Delta V$.

$$\Delta Q = \Delta U + \Delta W. \text{ OR } \Delta Q = \Delta U + P \Delta V.$$

This is called **first law of thermodynamics**.

Hence the first law of thermodynamics can be stated as follows: “*The amount of heat given to a system is equal to the sum of the increase in the internal energy of the system and the external work done*”.

Specific heat of a substance

Specific heat of a substance is the quantity of heat required to raise the temperature of unit mass of the substance through one kelvin.

If ΔQ is the amount of heat absorbed by a substance of mass m and ΔT is the change in temperature,

then specific heat capacity, $s = \frac{1}{m} \frac{\Delta Q}{\Delta T}$. Unit: J/kg/K. ($\text{J kg}^{-1} \text{K}^{-1}$)

Molar Specific Heat (C)

It is the amount of heat energy required to raise the temperature of one mole of a substance through one degree celsius or one kelvin.

$$C = \frac{1}{\mu} \frac{\Delta Q}{\Delta T}; \text{ where } \mu = \text{number of moles, } \Delta Q = \text{Heat absorbed to raise the temp by an amount } \Delta T.$$

Unit: J/mol/K. ($\text{J mol}^{-1} \text{K}^{-1}$)

Molar Specific Heat of solids - Dulong and Petits law

In 1819, Dulong and Petit put forward a law based on their investigations on the specific heat of solids. This law states

“*the product of atomic weight and specific heat of is constant for elements in the solid state*”.

** *Product of atomic weight and specific heat is called atomic heat.*

Near room temp, the value of atomic heat of almost all solids is nearly $3R$, where R is the universal gas constant.

Thus the heat required to rise the temp of a sample of metal depends only on how many molecules the sample contains and not on the mass of an individual molecule. Energy of a molecular oscillator in one dimension = $K_B T$, K_B = Boltzmann constant. In three dimension, the average energy is $3K_B T$. For one mole of a solid, the total energy is $U = 3 K_B T \times N_A = 3 R T$, Where N_A = Avagadro number. $K_B \times N_A = R$, universal gas constant.

At constant Pressure, $\Delta Q = \Delta U + P \Delta V \approx \Delta U$

$$\text{So } C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} \text{ But } U = 3 RT, \Delta U = 3R \Delta T, \frac{\Delta U}{\Delta T} = 3R = 3 \times 8.314 = 25 \text{ J / mol/}^\circ\text{C}$$

Molar Specific Heat of gas.

There are two specific heats for gases (i) Specific heat at constant volume C_v (ii) Specific heat at constant pressure C_p .

Molar specific heat at constant volume (C_v)

Molar specific heat of a gas at constant volume is the amount of heat required to raise the temperature of one mole of the gas through 1K when its volume is kept constant

Molar Specific heat at constant pressure (C_p)

Molar specific heat of the gas at constant pressure is defined as the amount of heat required to raise the temperature of one mole of the gas through 1K, when its pressure is kept constant.

Relation between C_p and C_v . [Mayer's relation]

If molar specific heat capacity of constant pressure is C_p and that at constant volume is C_v then

$C_p - C_v = R$, for an ideal gas.

Proof

According to 1st law of thermodynamics $\Delta Q = \Delta U + P \Delta V$.

If ΔQ heat is absorbed at constant volume ($\Delta V = 0$).

$$C_v = \left[\frac{\Delta Q}{\Delta T} \right]_v = \left[\frac{\Delta U}{\Delta T} \right]_v = \frac{\Delta U}{\Delta T} \dots\dots\dots(1)$$

[The subscript V is dropped because internal energy of ideal gas depends only on temperature]

Similarly we get,

$$C_p = \left[\frac{\Delta Q}{\Delta T} \right]_p = \left[\frac{\Delta U}{\Delta T} \right]_p + P \left[\frac{\Delta V}{\Delta T} \right]_p \dots\dots\dots(2)$$

From ideal gas equation for one mole $PV = RT$.

Differentiating w.r.t. temperature (at constant pressure)

$$P \left[\frac{\Delta V}{\Delta T} \right]_p = R \dots\dots\dots(3)$$

Substituting in (2) $C_p = \frac{\Delta U}{\Delta T} + R \dots\dots\dots (4)$

(4) - (1), we get

$C_p - C_v = R$ This is called **Mayer's relation**.

C_p is greater than C_v . Why?

When one mole of the gas is heated at constant volume, the heat is used only to increase the internal energy of the gas. But when the gas is heated at constant pressure, the heat is used not only for increasing the internal energy but also for doing external work during expansion. For same rise of temp, the increase in internal energy is same in both cases. Hence C_p is greater than C_v .

Work done by an ideal gas during isothermal expansion

Let the volume of a gas having pressure P change by dV. Then work done, $dW = P dV$.

Now, during expansion, let the volume change from V_1 to V_2 .

Then work done, $W = \int_{V_1}^{V_2} P dV$. But $PV = RT$. Or $P = \frac{RT}{V}$

$$\therefore W = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \left[\log_e V \right]_{V_1}^{V_2} \text{ ie}$$

$$W = RT \log_e \left[\frac{V_2}{V_1} \right]$$

Or work done, $W = 2.303 RT \log_{10} \left[\frac{V_2}{V_1} \right]$

But $P_1 V_1 = P_2 V_2$.

Or $\frac{V_2}{V_1} = \frac{P_1}{P_2}$

$$\therefore W = 2.303 RT \log_{10} \left[\frac{P_1}{P_2} \right]$$

Work done in an adiabatic process

Let an ideal gas undergoes adiabatic charge from (P_1, V_1, T_1) to (P_2, V_2, T_2) .

The equation for adiabatic charge is $PV^\gamma = \text{constant} = k$.

ie; $P_1V_1^\gamma = P_2V_2^\gamma = k \dots\dots\dots (a)$.

The work done

$$W = \int_{V_1}^{V_2} P dV$$

$$W = k \int_{V_1}^{V_2} \frac{dV}{V^\gamma} \quad (\text{since } P = \frac{k}{V^\gamma})$$

$$W = k \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2} = \frac{k}{1-\gamma} \left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right] = \frac{1}{1-\gamma} \left[\frac{k}{V_2^{\gamma-1}} - \frac{k}{V_1^{\gamma-1}} \right] = \frac{1}{1-\gamma} \left[\frac{P_2V_2^\gamma}{V_2^{\gamma-1}} - \frac{P_1V_1^\gamma}{V_1^{\gamma-1}} \right]$$

from equation (a)

$$W = \frac{1}{1-\gamma} [P_2V_2 - P_1V_1]$$

$$W = \frac{1}{1-\gamma} [P_2V_2 - P_1V_1] = \frac{R}{1-\gamma} (T_2 - T_1)$$

Substituting ideal gas equation.

$$W = \frac{1}{\gamma-1} [P_1V_1 - P_2V_2] \quad \text{or} \quad W = \frac{R}{\gamma-1} [T_1 - T_2]$$

Workdone in isochoric process.

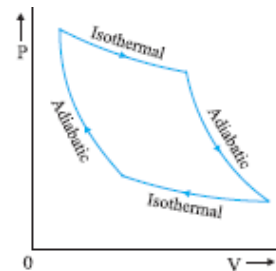
Here $V = \text{constant}$, Small workdone, $dW = PdV$. Here $dV = 0$, therefore, $W = 0$.

Work done in an isobaric process

Here $P = \text{constant}$. $dW = PdV$. The total workdone to change the volume from V_1 to V_2 , $W = P(V_2 - V_1)$

Cyclic process

In cyclic process, the system returns to its initial state such that charge internal energy is zero. The $P - V$ diagram for cyclic process will be closed loop and area of this loop gives work done or heat absorbed by system.



Heat Engines

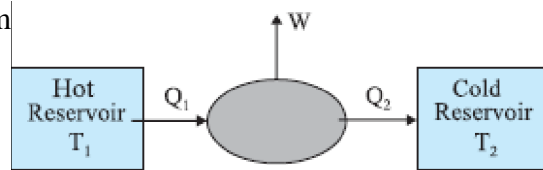
Heat engines converts heat energy into mechanical energy.

Heat engine is a device by which a system is made to undergo a cyclic process that results in conversion of heat to work.

Heat engines consists of : (1) Working substance (the system which undergoes cyclic process) eg: mixture of fuel vapour and air in diesel engine, steam in steam engine.

(2) An external reservoir at a high temperature (T_1) - it is the source of heat.

(3) An external reservoir at low temperature (T_2) or sink



Working

The working substances absorbs an energy Q_1 from source reservoir at a temperature T_1 . It undergoes cyclic process and releases heat Q_2 to cold reservoir. The change in heat ($Q_1 - Q_2$) is converted in to work (mechanical energy)

Efficiency of heat engine (η)

The efficiency of heat engine is the ratio of work done to input heat.

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Note :

(1) $Q_2 = 0$, $\eta = 1$. When entire heat input is converted into work heat engine is 100% efficient. But practically 100% efficiency cannot be achieved. It is limited by second law of thermodynamics.

(2) Heat engine can be external combustion engine or internal combustion engine.

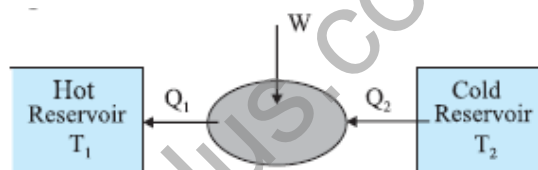
In external combustion engine, the fuel (system) is heated by external furnace. Eg.: Steam engine.

In internal combustion engine, fuel is heated internally by exothermic chemical reactions. Eg: Diesel engine, Petrol engine.

Refrigerators and Heat pumps

Refrigerator is reverse of heat engine, the device used to cool a portion of space (inside a chamber) is refrigerator. The device used to pump heat into a portion of space (to warm-up room) is called heat pump.

In both devices, the working substance absorbs heat Q_2 from cold reservoir at temperature T_2 . Some external work (by compression of gas by electric means) is done on it and heat Q_1 is supplied to hot reservoir at T_1 .



The working cycle of refrigerator

In refrigerator the working substance is gas (freon)

Step 1 : The gaseous working substance is converted into vapour - liquid mixture at lower temperature (T_2)

Step 2 : The cold fluid absorbs heat from region to be cooled (cold reservoir) and convert it into vapour.

Step 3 : The vapour is heated by external work.

Step 4 : The vapour release heat to surroundings and then comes to initial temperature T_2 .

The coefficient of performance (α)

The coefficient of performance of refrigerator is defined as $\alpha = \frac{Q_2}{W}$; where Q_2 is heat extracted from cold reservoir and W is work done on system.

Note : (1) The working substance in refrigerator is termed as refrigerant.

(2) For heat engine η can not exceed 1. But α can be greater than one.

Second law of Thermo dynamics

Kelvin - Plank statement

No process is possible whose sole result is the absorption of heat from a reservoir and complete conversion of heat into work.

Clausius statement

No process is possible whose sole result is the transfer of heat from a colder object to hotter object.

Reversible and Irreversible process

A reversible process is one, which can be retraced in the reverse order an in the opposite sense, so that it passes exactly through the same state as in the direct process.

Thus during the direct process, if heat is absorbed, during the reverse process, the same amount of heat is liberated.

Condition for a process to be reversible:

- (a) All steps of the process must be infinitely slow. (b). Loss of heat due to friction, viscosity, resistance etc should be completely absent. (c). The temp and pressure of the system must not change considerably from the surrounding at any stage.

Actually, no process is perfectly reversible.

Eg- (1) Slow evaporation of substance in an insulated container. (2) The slow compression of a spring. (3) Melting and boiling. (4) Ideal case of adiabatic and isothermal process.

Any process, which cannot be retraced in the opposite direction by reversing, controlling factors, is called an irreversible process.

Eg: (1) Almost all process in nature are irreversible. (2) Rusting of iron, dissolving of soap in water etc.

Carnot's Engine and Carnot's cycle

Saelli Carnot developed an ideal heat engine free from all the defects of practical engines. The essential parts of Carnot's engine are:

- 1) *Working Substance*: It is an ideal gas taken in a cylinder with perfectly insulating walls and a perfectly conducting base. Cylinder is provided with a tight, smooth and perfectly insulated piston.
- 2) *Source*: It is a body of infinite heat capacity kept at a constant high temperature T_1 K.
- 3) *Sink*: It is a body of infinite heat capacity, kept at a lower temperature T_2 K.
- 4) *A perfectly insulating stand*: The cylinder may be placed on the source, sink or the stand and may be moved from one to the other without doing work.

The working substance is subjected to a cycle of changes consisting of two isothermal operations and two adiabatic operations. Such a cycle is known as Carnot's cycle.

Carnot's cycle:

(1) Isothermal expansion:

The cylinder is placed on the source. The gas is allowed to expand isothermally. Hence the working substance takes necessary heat for expansion from the source by conduction. Thus the gas expands isothermally at the constant temp T_1 K of the source. This is represented by the isothermal AB in the diagram. Here the pressure and volume of gas changes from P_1 and V_1 to P_2 and V_2 respectively. Let Q_1 be the quantity of heat absorbed by the gas in this process.

The work done by the gas during isothermal expansion is given by area $ABB'A'A$.

The work done, $W_1 = R T_1 \log_e \left(\frac{V_2}{V_1} \right)$

(2) Adiabatic expansion:

The cylinder is now removed from the source and placed on the insulating stand. The gas is allowed to expand adiabatically by raising the piston. Since no heat is supplied to the gas, its temp falls. The expansion is continued till the temp falls to T_2 , the temp of sink. The adiabatic expansion is represented by adiabatic BC, P_3 and V_3 are pressure and volume of gas after this expansion. The work done by the gas during this process

is given by area $BCC'B'B$. Work done, $W_2 = \frac{R}{\gamma - 1} (T_1 - T_2)$

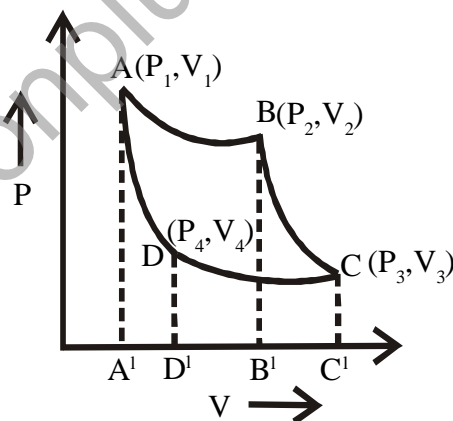
(3) Isothermal compression:

Now the cylinder is placed on the sink and the gas is subjected to isothermal compression. The heat developed during compression is rejected to the sink so that the temp remains constant at T_2 . This compression is represented by curve CD. The final pressure and volume are P_4 and V_4 . Let Q_2 be the heat rejected to the

sink. The work done is given by area $CDD'C'C$. Work done, $W_3 = -R T_2 \log \left(\frac{V_4}{V_3} \right) = R T_2 \log \left(\frac{V_3}{V_4} \right)$

4) Adiabatic compression:

The cylinder is again placed on the insulating stand. The gas is subjected to adiabatic compression. No heat will enter or leave the working substance. The gas is compressed till its temp rises to T_1 K and



returns to its initial condition with pressure P_1 and volume V_1 . This is represented by curve DA. The work

done is represented by area DAA'D'D. Work done, $W_4 = -\frac{R}{\gamma-1}(T_2 - T_1) = \frac{R}{\gamma-1}(T_1 - T_2)$

Thus the working substance is subjected to complete cycle of operations. This is called **Carnot's cycle**.

The working substance absorbs an amount of heat Q_1 from source and rejects an amount of heat Q_2 to the sink. Hence $(Q_1 - Q_2)$ amount of heat is converted into useful work. The area of indicator diagram ABCDA gives the total work done by the working substance during one cycle.

Now the total work done, $W = W_1 + W_2 - W_3 - W_4$. i.e. $W = R T_1 \log_e \left(\frac{V_2}{V_1} \right) - R T_2 \log_e \left(\frac{V_3}{V_4} \right)$

Efficiency of heat engine.

Efficiency is the ratio of the amount of heat converted into useful work to the amount of heat absorbed from the source.

If Q_1 is the heat taken from source and Q_2 is, heat rejected to sink, then

$$\text{Efficiency, } \eta = \frac{\text{Heat converted into work}}{\text{Heat absorbed from source}} \quad \text{i.e. } \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{R T_2 \log_e \left(\frac{V_3}{V_4} \right)}{R T_1 \log_e \left(\frac{V_2}{V_1} \right)} = 1 - \frac{T_2 \log_e \left(\frac{V_3}{V_4} \right)}{T_1 \log_e \left(\frac{V_2}{V_1} \right)}$$

Here B and C are on the same adiabatics, so $T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$

The points A and D are on the same adiabatics, so $T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$

$$\text{Dividing } \frac{T_1 V_2^{\gamma-1}}{T_1 V_1^{\gamma-1}} = \frac{T_2 V_3^{\gamma-1}}{T_2 V_4^{\gamma-1}}$$

$$\text{i.e. } \left(\frac{V_2}{V_1} \right)^{\gamma-1} = \left(\frac{V_3}{V_4} \right)^{\gamma-1} \quad \text{i.e. } \frac{V_2}{V_1} = \frac{V_3}{V_4} \quad \text{i.e. } \log_e \left(\frac{V_2}{V_1} \right) = \log_e \left(\frac{V_3}{V_4} \right)$$

$$\therefore \text{ efficiency, } \eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$$

We know, $T_1 > (T_1 - T_2)$ Therefore, η will be always less than unity or less than 100%.

Carnot's Theorem

Carnot showed that no engine can be more efficient than the perfectly reversible engine. No heat engine working between given temperatures can have efficiency greater than that of a reversible engine working between the same temperatures.

Kinetic theory of gases.

A gas is that type of matter, which has neither fixed shape nor fixed volume. Kinetic theory of gases is a theory, which is based on the concept of molecular motion as is able to explain the behavior of gases. The theory is based on some basic postulates or assumptions given below:

Postulates:

1. The molecules of a gas are hard, smooth and perfectly elastic spheres.
2. The molecules are supposed to be point masses, the size of a molecule being negligible compared to the distance between them.

3. There is no force of attraction or repulsion between molecules.
4. The molecules are in a state of random motion, moving with all possible velocities in all possible directions.
5. During their motion, they collide with one another and also with the walls of the container. These collisions are elastic.
6. Between successive collisions, the molecules move in straight lines with uniform velocity. The distance travelled between two successive collisions is called free path. Average distance between the successive collisions is called mean free path
7. Time for a collision is negligibly small compared to the time taken to traverse mean free path.
8. The mean KE of the molecule is a constant at a given temperature and is proportional to absolute temperature. ie $KE \propto T$.

Concept of Pressure.

According to kinetic theory, the gas molecules collide each other and with the walls of the container during their random motion. When they collide with the walls of the container, they exert force and hence pressure.

Thus pressure exerted by a gas may be defined as the total momentum imparted to unit area of the walls of the container per second due to molecular impacts (collisions).

Root mean square (rms) velocity of gas molecules.

According to kinetic theory of gases, the gas molecules are in random motion. So average velocity of a molecule is zero. So we have to find rms velocity of a molecule.

rms velocity of gas molecules is the square root of the mean of the squares of individual velocities of the molecules.

If $c_1, c_2, c_3, \dots, c_n$ are the velocities of a gas molecules, then mean square velocity,

$$\overline{c^2} = \frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n} \quad \text{Hence root mean square velocity, } c_{\text{rms}} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}}$$

Expression for pressure exerted by a gas.

Consider a gas in a cubical vessel of unit side. Let m be the mass of one molecule and n be the total number of molecules. Let W_1 and W_2 be two opposite walls perpendicular to X axis.

Consider a molecule moving towards the wall W_1 with a velocity v . This molecule will collide with wall W_1 and bounce back with same velocity.

Hence momentum of the molecule before collision = $m v$.

Momentum of the molecule after collision = $- m v$.

\therefore change in momentum of the molecule due to a single collision of the wall $W_1 = - m v - m v = - 2m v$.

\therefore change in momentum of the wall W_1 due to a single collision of the molecule = $2m v$.

Now as the distance between the walls W_1 and W_2 is unity, the molecule will travel v times between the walls in one second.

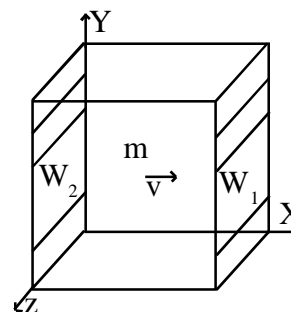
\therefore Number of collisions of the molecule with wall W_1 per second = $v/2$.

Hence rate of change of momentum of wall W_1 ie the force exerted by molecule on wall W_1 = change in

$$\text{momentum} \times \text{number of collisions} = 2m v \cdot \frac{v}{2} = m v^2$$

Now since the vessel contains n molecules, we can assume that at least $\frac{1}{3} n$ molecules will be moving in X direction.

$$\therefore \text{Force exerted by the gas on wall } W_1 = \frac{1}{3} m n v^2.$$



Since area of wall is unity, pressure exerted on wall W_1 , $P = \frac{1}{3} m n v^2$. This is true for all sides of the vessel.

Hence pressure exerted by the gas on the walls of the vessel, $P = \frac{1}{3} m n v^2$.

Now, since different molecules are moving with different velocities, it will be convenient to consider rms velocity.

$$P = \frac{1}{3} m n v_{rms}^2 \quad \text{ie} \quad P = \frac{1}{3} m n \overline{c^2} \quad ; \quad \text{where } \overline{c^2} \text{ is mean square velocity.}$$

Now mn = total mass of the gas. Since volume is unity, mn = density of the gas, ρ .

$$\therefore \text{Pressure, } P = \frac{1}{3} \rho \overline{c^2}$$

Kinetic Energy of gases.

Consider one mole of a gas of mass m and volume V .

$$\text{Then, pressure } P = \frac{1}{3} \rho \overline{c^2} = \frac{1}{3} \frac{M}{V} \overline{c^2}.$$

$$\text{ie } PV = \frac{1}{3} M \overline{c^2} \quad \text{ie } PV = \frac{2}{3} \frac{1}{2} M \overline{c^2}$$

But $PV = RT$ and $\frac{1}{2} M \overline{c^2}$ is the average KE of one mole of gas.

$$\therefore RT = \frac{2}{3} \text{ average KE of one mole of gas.}$$

$$\therefore \overline{\text{KE}} \text{ of one mole of gas} = \frac{3}{2} RT; R = \text{universal gas constant.}$$

$$\text{KE of one molecule of gas} = \frac{3}{2} \frac{R}{N} T; N = \text{Avagadro number. Here } \frac{R}{N} = k \text{ (Boltzmann's constant)}$$

$$\therefore \text{Average KE of one molecule of gas} = \frac{3}{2} k T.$$

$$\therefore \overline{\text{KE}} \propto T.$$

\therefore **Average KE of gas molecules is directly proportional to absolute temperature.**

Mean, rms and most probable speeds.

Mean speed (\overline{v}): It is the arithmetic mean of the speeds of gas molecules at a given temperature.

$$\overline{v} = \sqrt{\frac{k T}{\pi M}} = \sqrt{\frac{8 R T}{\pi M}}; M = \text{mass of one mole of gas.}$$

rms speed (c_{rms} or \overline{c}) $\overline{c} = \sqrt{\frac{3 k T}{m}} = \sqrt{\frac{3 R T}{M}}$ (M is the mass of one mole of gas, m = mass of one molecule of gas.)

Most probable speed (v_p): The most probable speed is the speed at which the maximum number of molecules moves in a given gas at a given temperature.

Mean free path.

Mean free path of a molecule in a gas is the average distance travelled by the molecule between two successive collisions.

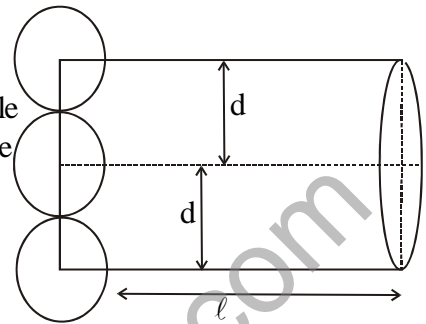
Molecules of a gas have finite size and behave like rigid spheres. The molecular motion is random and hence they collide against one another frequently. Between two successive collisions, a molecule moves along a straight path with uniform velocity. This path is known as free path.

Let $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n$ are the free paths travelled by the molecules in n successive collisions, then

$$\text{mean free path} = \frac{\text{total distance travelled}}{\text{total no. of collisions}} \quad \text{i.e. } \lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n}{n}$$

Derivation of expression for mean free path.

Assume that only one molecule is in motion and all other molecules are at rest. Let d be the diameter of each molecule. The moving molecule will collide against all those molecules whose centres lie within a distance d from the centre of the moving molecule. Suppose ℓ is the distance travelled by the moving molecule. The moving molecule will make a collision with all those molecules whose centres lie inside



a volume $\pi d^2 \ell$

Suppose n is the no. of molecules per unit volume in the gas, then no. of collisions = no. of molecules in

the volume $\pi d^2 \ell \cdot n = n \pi d^2 \ell$. Now $\lambda = \frac{\text{distance travelled}}{\text{no. of collisions}} = \frac{\ell}{n \pi d^2 \ell} = \frac{1}{n \pi d^2}$.

In the above derivation, we have assumed that all the molecules are stationary. But this is not correct. So the chances of collision by a molecule is greater. Taking this into account, the mean free path can be shown to

be $\sqrt{2}$ times less than that shown above. i.e. $\lambda = \frac{1}{\sqrt{2} n \pi d^2}$ i.e. $\lambda = \frac{m}{\sqrt{2} \pi d^2 n m}$

Here $n m = \frac{\text{total no. of molecules}}{\text{volume}} \times \text{mass of one molecule} = \frac{m}{V} = \rho$, density of gas

$$\therefore \lambda = \frac{m}{\sqrt{2} \pi d^2 \rho}$$

- * The smaller the no. of molecules per unit volume of the gas, larger is the mean free path.
- * Smaller the diameter, larger is the mean free path.
- * Smaller the density, larger is the mean free path.

Degrees of freedom and law of equipartition of energy.

We know that the KE of a single molecule is $E_t = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$. For a gas in thermal

equilibrium at a temperature T , the average KE/molecule is $\frac{3}{2} K_B T$.

$$\text{i.e. } \langle E_t \rangle = \left\langle \frac{1}{2} m v_x^2 \right\rangle + \left\langle \frac{1}{2} m v_y^2 \right\rangle + \left\langle \frac{1}{2} m v_z^2 \right\rangle = \frac{3}{2} K_B T$$

A molecule free to move in space needs three co-ordinates to specify its location. If it is constrained to move in a plane, it needs two and if constrained to move along a line, it needs only one co-ordinate to locate it.

So a molecule has only one degree of freedom for motion in a line, two for motion in a plane and three for motion in space.

The total number of co-ordinates or independent quantities required to completely specify the position and configuration of a system is called the degrees of freedom of that system.

So for a mono atomic molecule free to move in space has three translational degrees of freedom.

Certain molecules (O_2, N_2) shows rotational motion also in addition to translational motion. a diatomic

molecule can't rotate about the axis connecting the two atoms. Thus the molecule has two rotational degrees of freedom also. So the total energy of such a molecule is

$$E_t + E_r = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 = \frac{5}{2}K_B T ; \text{ where } \omega_1 \text{ and } \omega_2 \text{ are}$$

the angular speeds and I_1 and I_2 are the corresponding moment of inertia.

Some molecules like Co has another mode of vibration also and contribute a vibrational energy term to the total energy.

$$E_t + E_r + E_p = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}m\left(\frac{dy}{dt}\right)^2 + \frac{1}{2}ky^2 = \frac{7}{2}K_B T$$

where k is the force constant of the oscillator and y the vibrational co-ordinate.

Each term involving the square of a variable of motion occurring in the expression for energy is a mode of absorption of energy by the molecule.

According to Maxwell, "in equilibrium, the total energy is equally distributed in all possible energy

modes with each mode having an average energy = $\frac{1}{2}K_B T$ ". This is known as law of equipartition of energy.

Specific heat capacity

1. Mono atomic gas

The molecule of a monoatomic gas has three translational degrees of freedom. The average energy of a molecule at temperature T is $\frac{3}{2}K_B T$. The total internal energy of one mole of such a gas is

$$U = \frac{3}{2}K_B T \times N_A = \frac{3}{2}RT$$

$$\Delta U = \frac{3}{2}R\Delta T$$

$$C_V = \frac{\Delta U}{\Delta T} = \frac{3}{2}R \quad \text{But } C_P - C_V = R \quad \text{So } C_P = C_V + R. \quad C_P = \frac{3}{2}R + R = \frac{5}{2}R$$

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

2. Diatomic gas.

They have three translational and two rotational degrees of freedom. So the internal energy of a mole of such

a gas is $U = \frac{5}{2}RT$ Therefore, $\Delta U = \frac{5}{2}R\Delta T$ But $C_V = \frac{\Delta U}{\Delta T} = \frac{5}{2}R$

$$C_P = C_V + R = \frac{5}{2}R + R = \frac{7}{2}R \quad \text{Therefore, } \gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5}$$

If a diatomic molecule has in addition a vibrational mode also, then total internal energy $U = \frac{7}{2}RT$;

$$\Delta U = \frac{7}{2}R\Delta T \quad C_P = \frac{\Delta U}{\Delta T} = \frac{7}{2}R \quad \text{But } C_P = C_V + R = \frac{7}{2}R + R = \frac{9}{2}R$$

$$\text{Therefore, } \gamma = \frac{C_P}{C_V} = \frac{\frac{9}{2}R}{\frac{7}{2}R} = \frac{9}{7}$$

***Specific heat capacity of solids**

Solid atoms are vibration about its mean position. An oscillator in one dimension has an average energy of

$$\frac{1}{2} K_B T \times 2 = K_B T . \text{ In three dimension, average energy} = 3 K_B T. \text{ So the total energy/mole of a solid is ,}$$

$$U = 3 K_B T \times N A = 3 R T. \text{ So } \frac{\Delta U}{\Delta T} = C_v = 3 R$$

***Specific heat capacity of water.**

We treat water like a solid. For each atom, the average energy is $3 K_B T$. Water molecule has three atoms. So total internal energy for one mole of water = $3 \times 3 K_B T \times N A = 3 \times 3 R T = 9 R T$.

Therefore, $\frac{\Delta U}{\Delta T} = C_v = 9 R .$

Thermal Expansion

The change in temperature of a body may change its length, area or volume. The fractional change in dimension [ratio of change in dimension to original dimension] is proportional to change in temperature. The corresponding proportionally constant is called **co-efficient of thermal expansion or thermal expansivity**. *Thermal expansion can be defined as ratio of increase in dimension of body to increase in temperature.* There are different three types of thermal expansion. Which are shown in the table given below

Type of thermal expansion	Linear expansion	Area expansion	Volume expansion
The dimension that changes	length	Area	Volume
Coefficient of	$\alpha_l = \frac{\Delta l}{l \Delta T}$	$\alpha_a = \frac{\Delta A}{A \Delta T}$	$\alpha_v = \frac{\Delta V}{V \Delta T}$
thermal expansion (α)	linear expansivity or co-efficient of linear expansion	Area expansivity or co-efficient of area expansion	Volume expansivity or coefficient of volume expansion
Relation		$\alpha_a = 2\alpha_l$	$\alpha_v = 3\alpha_l$

Note : (1) Show that the coefficient of volume expansion for ideal gas is reciprocal of temperature ($\alpha_v = 1/T$)

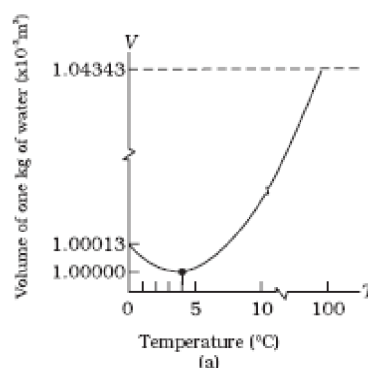
Proof : Ideal Gas Equation is

$$PV = \mu RT \dots\dots\dots (1)$$

At constant pressure $P \Delta V = \mu R \Delta T \dots\dots\dots (2)$. Dividing we get

$$\frac{\Delta V}{V} = \frac{\Delta T}{T}$$

$$\frac{\Delta V}{V \Delta T} = \frac{1}{T} = \alpha_v$$



Anomalous behaviour of water

Generally volume of liquid increases with temperature .When water is heated, its volume starts to decrease from 0°C and reaches minimum at 4°C. Hence density of water is maximum at 4°C.

$$(i) \alpha_a = 2\alpha_\ell \quad (ii) \alpha_v = 3\alpha_\ell.$$

Consider a cube of length ' ℓ '. Due to the increase in temperature ' ΔT ', length of cube increases by $\Delta \ell$ in all directions.

$$\text{Coefficient of linear expansion, } \alpha_\ell = \frac{\Delta \ell}{\ell \Delta T}.$$

$$(i) \text{Increase in area of cube } \Delta A = \text{Final area} - \text{initial area} = (\ell + \Delta \ell)^2 - \ell^2 = 2 \times \ell \times \Delta \ell \quad [\text{Neglecting } \Delta \ell^2]$$

Area expansivity

$$\alpha_a = \frac{\Delta A}{A \Delta T}$$

$$= \frac{2\ell \times \Delta \ell}{\ell^2 \Delta T}$$

$$= \frac{2 \cdot \Delta \ell}{\ell \cdot \Delta T}$$

$$= 2 \cdot \alpha_\ell$$

$$\text{Therefore, } \alpha_a = 2 \cdot \alpha_\ell$$

$$(ii) \text{ Due to } \Delta T \text{ the increase in volume of cube, } \Delta V = (\ell + \Delta \ell)^3 - \ell^3$$

$$= 3\ell^2 \Delta \ell$$

[Neglecting $\Delta \ell^2$ & $\Delta \ell^3$]

$$\alpha_v = \frac{\Delta V}{V \cdot \Delta T}$$

$$= \frac{3\ell^2 \cdot \Delta \ell}{\ell^3 \times \Delta T}$$

$$= 3 \times \alpha_\ell$$

$$\text{Therefore, } \alpha_v = 3\alpha_\ell$$

Change of state

A transition from one state (solid, liquid or gas) to another state is called change of state. There are four such transitions of state.

Change of state	Name of transition
Solid \rightarrow Liquid	Melting
Liquid \rightarrow gas	Vapourisation
Liquid \rightarrow solid	Fusion
Solid \rightarrow gas (without forming liquid)	Sublimation

During change of state, the two different state coexist in thermal equilibrium and temperature remains constant until the completion of change of state.

Melting point :

The temperature at which solid and liquid coexist in thermal equilibrium with each other is called melting point. The melting point decreases with pressure

Boiling point.

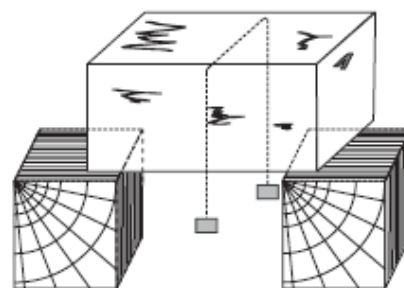
The temperature at which liquid and vapour state of substance coexist in thermal equilibrium with each

other is called boiling point.

The boiling point increases with increase in pressure and it decreases with decrease in pressure.

Regelation

Take an ice block. Put a metal wire over the ice block and attach 5 kg. blocks at the two ends of wire as shown. Then we can see that the metal wire passes through the iceblock to the other side without splitting it.



Explanation : The melting point of ice just below the wire decreases due to increase in pressure. As ice melts wire passes and refreeze (due to decrease in pressure). This process is called regelation.

Q: Cooking is difficult at high attitude. Why ?

At high altitude, pressure is low. Boiling point decreases with decrease in pressure.

Q: For cooking rice pressure cooker is preferred. Why ?

In pressure cooker, boiling point of water is increased by increasing pressure. Thus rice can be cooked at high temperature.

Q: You might have observed the bubbles of steam coming from bottom of vessel when water is heated. These bubbles disappear as it reaches top of liquid just before boiling and they reach the surface at the time of boiling. Explain the reason ?

Just before boiling, the bottom of liquid will be warm and at the top, liquid will be cool. So the bubbles of steam formed at bottom rises to cooler water and condense, hence they disappear. At the time of boiling, temperature of entire mass of water will be 100°C. Now the bubbles reaches top and then escape.

Latent Heat

The amount of heat per unit mass transferred during change of state of substance is called latent heat of substance for the process. Eg: Latent heat of vapourisation (L_v), Latent heat of fusion (L_f).

If 'm' is quantity of substance which undergoes change of state and Q is amount of heat required, then latent heat

$$L = \frac{Q}{m} . \text{ Latent heat is characteristic of substance and it depends on pressure. Its unit is } \text{JKg}^{-1}.$$

Q: Draw the temperature versus heat diagram for water. Mark the three phases of water (including its change of state).

Give reasons for the following

- The slope of phase line during change of state is zero.
- The slope of phase line for the three phases are different.

Q: Burns from steam are usually more serious than boiling water. Why ?

Latent heat of vapourisation for water is $22.6 \times 10^5 \text{J Kg}^{-1}$ (ie; $22.6 \times 10^5 \text{J}$ heat is required to convert 1 kg of water into steam at 100°C). So at 100°C, steam carries $22.6 \times 10^5 \text{J}$. (more heat than water).

Heat transfer

Heat transfer occurs due to temperature difference. The three modes of heat transfer are (1) conduction, (2) convection (3) radiation.

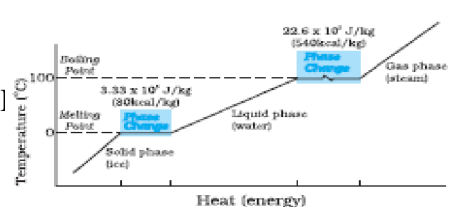
Conduction

In conduction, heat transfers between two adjacent parts of a body due to temperature difference. Heat conduction can be considered as time rate of heat flow (heat current). At steady state the time rate of

heat flow (H) is proportional to temperature difference ΔT , area of cross section (A) and inversely proportional to length of conductor (L).

$$H \propto \frac{A\Delta T}{L} \quad H = \frac{KA\Delta T}{L}$$

K is called thermal conductivity. Its unit is $\text{JS}^{-1}\text{m}^{-1}\text{K}^{-1}$ or Wm^{-1}



Q: Some cooking pots have copper coating on its bottom. Why ?

Because of high thermal conductivity of copper, it distributes heat over the bottom of pot very rasty and promotes uniform cooking.

Note: In the house with concrete roof, a layer of earth or foam insulation is made on the ceiling to prevent heat transfer and hence to keep the room cooler.

Convection

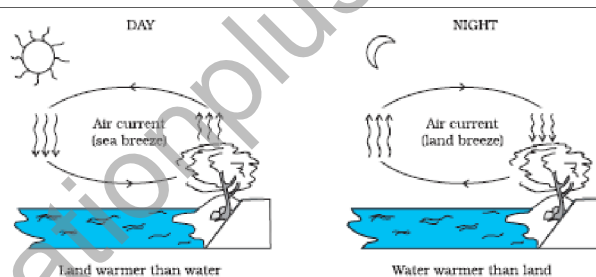
In convection, different parts of fluid moves from one point to other.

Convection can be natural or forced.

In natural convection when fluid is heated, it expands and becomes less dense. It then rises up and colder part replaces it. This process goes on as a cycle.

Q: Explain the reason for sea breeze

During the day, land heats up more quickly than water in lake (due to high specific heat capacity of water). The air on the surface of earth gets heated, expands, becomes less dense and rises up. The colder air (wind) replaces the space created by hot air. It creates a sea breeze. At night the land loses its heat very quickly than water. So water remains more warmer at night.



Note:

In forced convection, material is forced to move by pump or by other physical means. Some examples are cooling system of automobile engines, heart that circulate blood throughout our body.

Radiation

In radiation, energy is transferred in the form of electromagnetic radiation called heat radiation.

It requires no medium for heat transfer. Earth receives energy from sun by means of radiation.

Thermal radiation : *The electromagnetic radiation emitted by a body by virtue of its temperature is called thermal radiation.*

Q: The utensils for cooking purpose are blackened at the bottom. Why ?

This is to absorb maximum heat from fire and hence to fast up cooking.

Newtons laws of cooling

According to Newton's law of cooling the rate of loss of heat is directly proportional to difference of temperature between the body and its surroundings.

$$\frac{dQ}{dT} = K(T_2 - T_1) \quad T_1 \text{ is temperature of surrounding medium and } T_2 \text{ is temperature of body. } K \text{ is constant that depends on nature of surface and area of exposed surface.}$$

constant that depends on nature of surface and area of exposed surface.

Note: (1) The law is applicable for small temperature difference.

(2) For small temperature difference, cooling occurs due to a combination of

conduction, convection and radiation.

(3) The graph between difference in temperature and time is as shown in figure.

