Heat and Thermodynamics

Thermodynamics is a branch of physics concerned with heat and temperature and their relation to energy and work.

Heat and Thermal Energy

When scientists originally studied thermodynamics, they were really studying heat and thermal energy. Heat can do anything: move from one area to another, get atoms excited, and even increase energy.

Did we say energy (Heat)?

That's what heat is. When you increase the heat in a system, you are really increasing the amount of energy in the system.

Now that you understand that fact, you can see that the study of thermodynamics is the study of the amount of energy moving in and out of systems.

Heat of Atoms

Now all of this energy is moving around the world. You need to remember that it all happens on a really small scale. Energy that is transferred is at an atomic level. Atoms and molecules are transmitting these tiny amounts of energy. When heat moves from one area to another, it's because millions of atoms and molecules are working together. Those millions of pieces become the energy flow throughout the entire planet.

Heat Movement

Heat moves from one system to another because of differences in the temperatures of the systems. If you have two identical systems with equal temperatures, there will be no flow of energy. When you have two systems with different temperatures, the energy will start to flow. Air   mass   of   high   pressure   forces   large   numbers   of   molecules   into

areas of low pressure. Areas of high temperature give off energy to areas with lower temperature. There is a constant flow of energy throughout the universe. Heat is only one type of that energy.
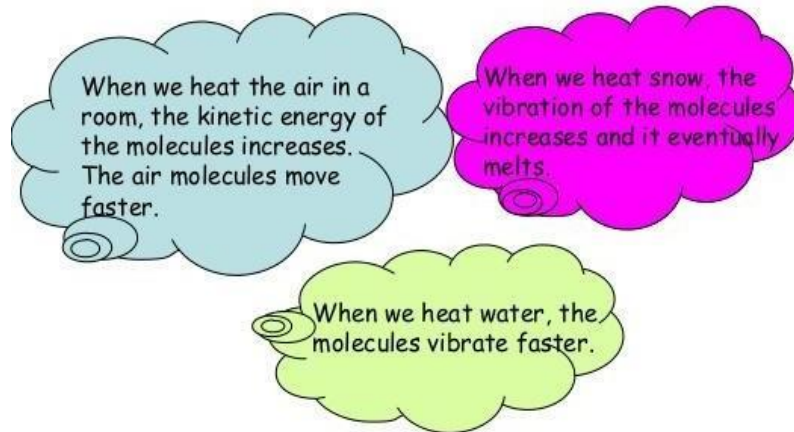
Heat

Heat is a form of energy whose absorption makes a body hot and rejection makes a body cold. Heat is a form of energy which produces the sensation of hotness or coldness of a body.

Heat is a form of energy which flows from higher temperature to lower temperature by conduction, convection and radiation processes.

Temperature

When we touch a piece of ice, we feel cold but if we touch a boiling kettle we feel hot. The amount of hotness or coldness of a body is measured by a quantity called temperature. Apparently, the degree of hotness is expressed by temperature. Alternatively, the temperature of a body is the property that determines whether or not the body is in thermal equilibrium with another body.

<u>Distinction between heat and temperature</u> Though closely related, heat and temperature do not bear same meaning' There is a great difference between them. The differences are stated below:

1. Heat is a form of energy but temperature represents a thermal condition of the body.

2. Heat is the cause and temperature is the effect.

3. The instrument for measuring heat is called calorimeter and the instrument for measuring temperature is called thermometer.

4. The unit of heat is Joule and the unit of temperature is oC or K or oF.

5. Heat is energy and temperature is the demonstration of energy.

6. Heat flows from a body of higher temperature to a body of lower temperature.

7. Heat is proportional to the total energy of the molecules in the body; but temperature is proportional to the average kinetic energy of a molecule of the body.

8. The branch of physics which measures heat is called calorimetry and the branch which measures temperature is called thermometry.

9. Temperature does not have dimension but dimension of heat is the dimension of energy [ML2T-2].
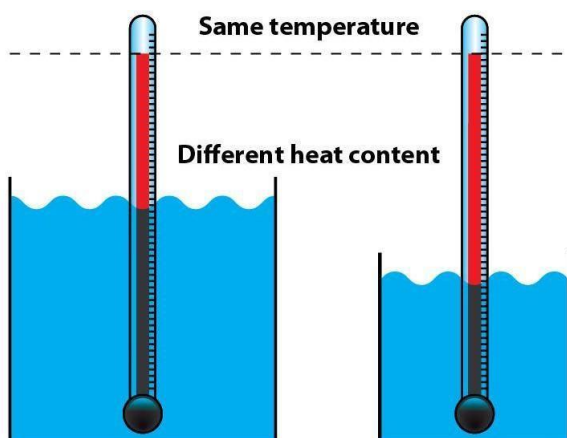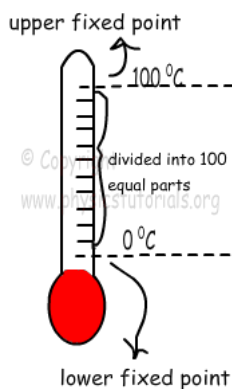
Thermometer

The name of the thermometers depends on which property or thermal properties used to measure temperature. Like

| Name	Thermal Property	Example
Liquid Thermometer	Liquid	Mercury thermometer
Constant volume gas thermometer	Pressure of gases	Constant volume H2 gas thermometer
Resistance Thermometer	Resistance of the material	Platinum resistance thermometer
Thermo – electric Thermometer	EMF/Current	Platinum-Rhodium thermometer
Radiation thermometer	Radiated heat	Pyrometer

Temperature Scale

There are four types of temperature scales. The temperature scales are Celsius, Kelvin, Fahrenheit and Romer / Rankine scale.
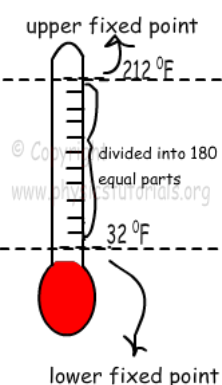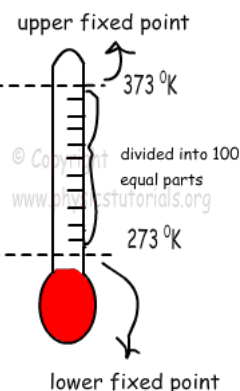

The relation of the temperature scales are based on the relation in

Temperature scale – ice point / steam point – ice point

$$\frac{C-0}{100-0} = \frac{F-32}{212-32} = \frac{K-273}{373-273} = \frac{R-492}{672-492}$$

$$\frac{C}{100} = \frac{F-32}{180} = \frac{R-492}{180} = \frac{T-273}{100}$$

$$\text{Or, } \frac{C}{5} = \frac{F-32}{9} = \frac{R-492}{9} = \frac{T-273}{5}$$

Exercise

Find the temperature in the Fahrenheit scale corresponding to absolute zero.

Solution: Absolute Zero, $C = -273^0 C$

$$\text{We know, } \frac{C}{5} = \frac{F-32}{9}$$

$$\text{Or, } \frac{-273}{5} = \frac{F-32}{9}$$

By solving, We get, $F = -459.4^0 F$

Exercise: Find the temperature for which Farenheit reading is three times the Centigrade reading.

Solution: Let x be the Centigrade reading. Then $F = 3x$

$$\text{We have, } \frac{C}{5} = \frac{F-32}{9}$$

$$\text{Or, } \frac{x}{5} = \frac{3x-32}{9} \quad \text{By solving } x = 26.66^0 C$$

The required Fahrenheit reading is, $F = 3 \times 26.66 = 79.99^0 F$

Platinum Resistance Thermometer

The platinum resistance thermometer is based on the principle that the electrical resistance of metallic wire is found to increase uniformly with temperature. The device in which temperature can be found out by measuring the resistance is called a resistance thermometer. Platinum is extensively used as resistance thermometer. Platinum is very rigid metal and dependable. Its characteristics are not changed by repeated use.
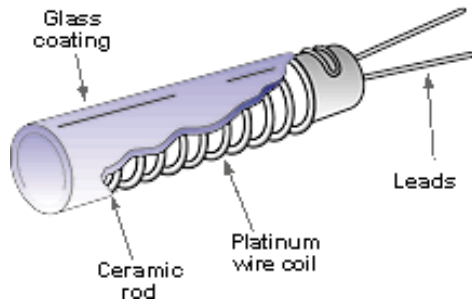
Advantages of platinum resistance thermometer:-

a)   it use is easier than that of a gas thermometer .

b) it gives a precise measurement of a temperature because the resistance of the wire can be measured with high accuracy.

c) it has a wide range from – 200 to 1200 degrees Celsius

d) it is quite sensitive . Its sensitivity is .01 degree up to 600 degree.

e) it is free from change of zero as pure and annealed platinum wire has always the   same resistance at the same temperature.

The relation between temperature and resistance is given below

$$R_\theta = R_0(1 + \alpha\theta).. (1)$$

So, $\theta = \dfrac{R_\theta - R_0}{R_0\alpha}...(2)$

Where R_θ represents the resistance of the platinum wire at R_0 is the resistance of platinum wire at temperature 0^0, and α is a constant.

Let R_0 and R_{100} be the resistance of platinum resistance thermometer at 0^0C and 100^0C respectively.

Now from Eq. (1) we get,
$$R_{100} = R_0(1 + \alpha.100)$$

=> $\alpha = \dfrac{R_{100} - R_0}{100R_0}........................... (3)$

By using Eqs. (2) and (3) we can write,
$$\frac{R_{100} - R_0}{100\alpha} = \frac{R_\theta - R_0}{\theta\alpha}$$

$$\Rightarrow \theta = \frac{R_\theta - R_0}{R_{100} - R_0} \times 100... (4)$$

Eq. (4) represents the temperature measuring equation for platinum resistance thermometer.

Exercise-1

The resistance of the platinum wire of a platinum resistance thermometer at the ice point is 5Ω and at the steam point 5.93 Ω. The pressure exerted by the gas in a constant volume gas thermometer is 100 cm of Hg at ice point, 136.6 cm of Hg at steam point. When both the thermometer are inserted in a hot bath the resistance of the platinum wire is 5.795 Ω and the pressure of the gas is 131.11 cm of Hg. Calculate Celsius temperature of the both
(i)   on   platinum   scale   and   (ii)   on   the   gas   scale.

Solution:

(i)   On the platinum scale:
$R_0 = 5\Omega$, $R_{100} = 5.23\Omega$ and $R_t = 5.795\ \Omega$

We know, $t = (\dfrac{R_t - R_0}{R_{100} - R_0}) \times 100$

$= (\dfrac{5.795 - 5}{5.93 - 5}) \times 100 = 85.48^\circ C$

(ii)   On the gas scale:
$P_0 = 100$ cm of Hg, $P_{100} = 136.6$ cm of Hg and $P_t = 131.11$ cm of Hg

We know, $t = (\dfrac{P_t - P_0}{P_{100} - P_0}) \times 100$

$= (\dfrac{131.11 - 100}{136.6 - 100}) \times 100 = 85^\circ C$

Seebeck effect

When two dissimilar metals makes two junctions and one of them being heated while the other junction is kept cold, without using any cell or battery in the circuit, current flow is the Seebeck effect.

Figure 1: Seebeck effect
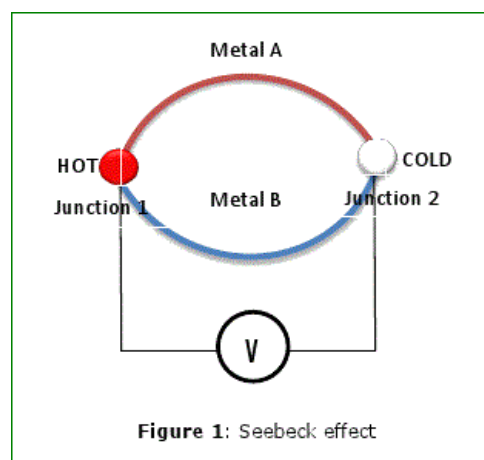
Peltier effect

When two dissimilar metals makes two junctions and by using cell or battery current flows into the circuit, then one of the junction will be heated while other will be cold is called Peltier effect.
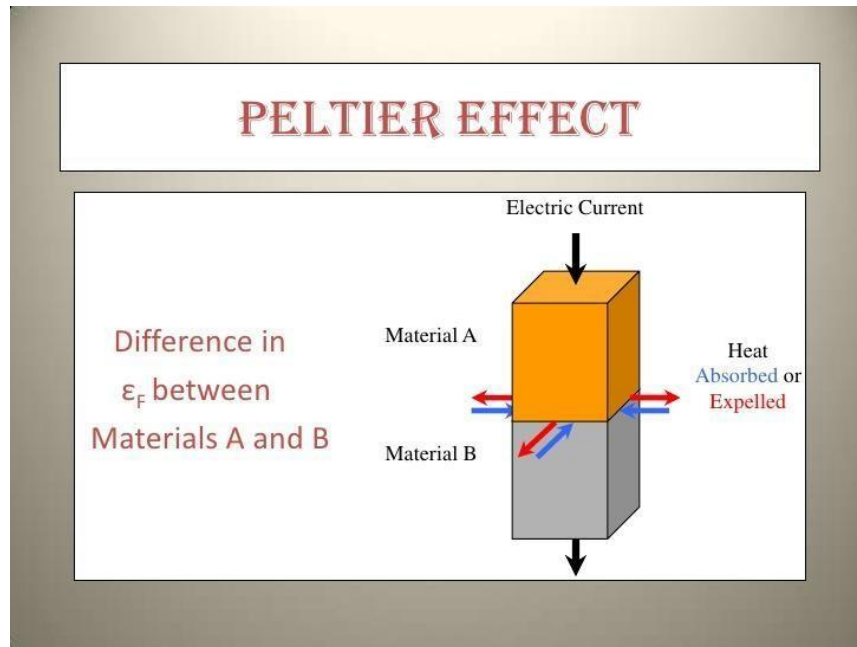
Vapor

When a gaseous substance is below its critical temperature, it is called vapor. It can be liquefied by applying pressure.

Gas

When a gaseous substance is above its critical temperature, it is called gas. A gas cannot be liquefied by applying pressure.

Difference between Gas & Vapour

- Gas :
  it is the state of substance in which the evaporation from the liquid state is complete.
- Vapour :
  it is the homogeneous mixture of minute liquid particles in suspension with true gas of the same substance.

- With changes in t & p, gas remains in its gaseous state (except under extreme conditions)
- With changes in t & p, a vapour can undergo condensation or evaporation.
- Gas obey the gas laws whereas vapour doesn't.

Kinetic Theory of Gases

The kinetic theory of gases describes a gas as a large number of small particles (atoms or molecules), all of which are in constant, random motion. The rapidly moving particles constantly collide with each other and with the walls of the container. Kinetic theory explains macroscopic properties of gases, such as pressure, temperature, and volume, by considering their molecular composition and motion.

Postulates of Kinetic(-Molecular) Theory

- All gases are made up of particles
  - Usually molecules
- The particles are in constant, random motion, colliding with each other and with the walls of the container.
- All collisions are perfectly elastic
- Volume of the particles is insignificant
- There are no interactions between particles (attraction/repulsion)
- The average kinetic energy of the particles is a function of only absolute temperature
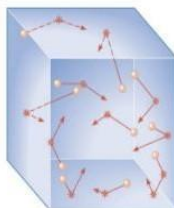
Fundamental assumption / postulates of kinetic theory of gases

1. The gas consists of very small particles known as molecules.

2. These particles have the same mass.

3. The number of molecules is so large that statistical treatment can be applied.

4. These molecules are in constant, random, and rapid motion.

5. The gas molecules are not affected by gravity.

6. Except during collisions, the interactions among molecules are negligible. (That is, they exert no forces on one another.)

7. The rapidly moving particles constantly collide among themselves and with the walls of the container. All these collisions are perfectly elastic. This means, the molecules are considered to be perfectly spherical in shape, and elastic in nature.

8. The average kinetic energy of the gas particles depends only on the temperature of the system.

9. The time during collision of molecule with the container's wall is negligible as compared to the time between successive collisions.

Mean velocity

The average between two or more velocities is called the mean velocity. Let a closed container contain n number of molecules of a gas. If the velocities of the molecules be c_1, c_2, c_2, …….. c_n, then the mean velocity is

$$\bar{c} = \frac{c_1 + c_2 + c_3 + \ldots\ldots\ldots c_n}{n}$$

Mean square velocity

It is defined as the mean of the square of all molecular velocities. Let the velocities of the molecules be c1, c2, c2, …….. cn, then the mean square velocity is

$$\overline{c^2} = \frac{c_1^2 + c_2^2 + c_3^2 + \ldots\ldots\ldots + c_n^2}{n}$$

Root mean square velocity

It is defined as the square root of the mean square velocity of the molecules.

Let the velocities of the molecules be c1, c2, c2, …….. cn, then root mean square velocity is

$$c = \sqrt{\overline{c^2}} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \ldots\ldots\ldots + c_n^2}{n}}$$

Mean free path

The mean free path is the mean path length that a molecule traverses between two successive impacts with other molecules. It depends upon molecular diameter dm and temperature T.

The average distance traveled by a molecule between two successive collisions is called mean free path. It is denoted by λ. Let, the distance from A to B = S1, the distance from B to C = S2, the distance from C to D = S3.

If the molecule collides N times in traveling a distance S, then the mean free path, λ of that molecule, is

$$\lambda = \frac{S_1 + S_2 + S_3 + \ldots\ldots\ldots\ldots + S_n}{N} = \frac{S}{N} = \frac{\text{Total distance travelled}}{\text{Number of collisions}}$$
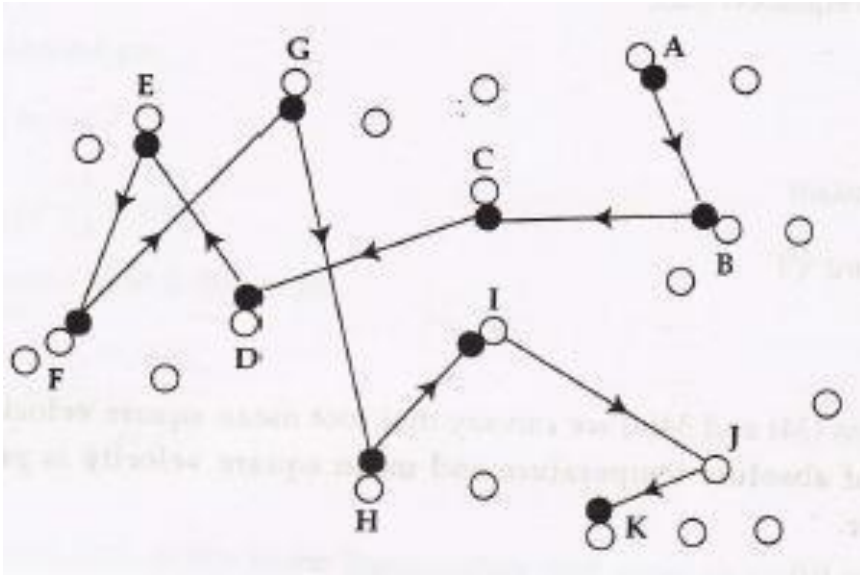
Mean Free Path

all particles, including photons, suffer from collisions with other particles such that their path through space is very short the higher the densities. This typical path length is called the mean free path.
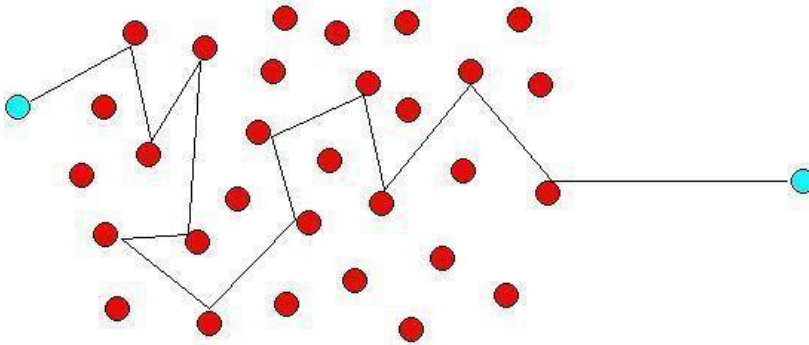
Ideal gas law

The **ideal gas law** is the equation of state of a hypothetical ideal gas. It is a good approximation to the behavior of many gases under many conditions, although it has several limitations. It was first stated by Émile Clapeyron in 1834 as a combination of Boyle's law and Charles's law. The ideal gas law is often written as

$$PV = nRT$$

where the letters denote pressure, volume, amount (in moles), ideal gas constant, and temperature of the gas, respectively.

Ideal Gas Law

$$PV = nRT$$

- P = pressure in atm
- V = volume in liters
- n = moles
- R = proportionality constant
  = 0.08206 L atm/ mol·K
- T = temperature in Kelvins

Holds closely at $P < 1$ atm

The Ideal Gas Law

- An *ideal gas* is an idealized model for real gases that have sufficiently low densities.
- The condition of low density means that the molecules are so far apart that they do not interact except during collisions, which are effectively elastic.
- At constant volume the pressure is proportional to the temperature.

$$P \propto T$$
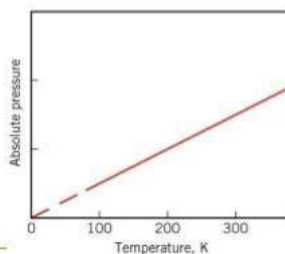
Derivation of the ideal gas equation (PV=nRT) from the kinetic theory of gases

According to the kinetic theory of gases, the heat energy of a gas is the result of the kinetic energy of its molecules. At absolute zero temperature the heat energy of the molecules is zero. As a result the kinetic energy is zero and hence the magnitude of root mean square velocity is also zero. If heat is applied to a gas it appears as kinetic energy,

$$\therefore \text{K.E.} = \frac{1}{2}mnc^2 = \frac{1}{2}Mc^2$$

But we know the average kinetic energy of the molecules of a gas is proportional to absolute temperature.

$$\therefore \frac{1}{2}mnc^2 \propto T$$

Or, $\frac{1}{2}Mc^2 \propto T$ [M is the total mass of the gas]

Or, $\frac{1}{2}Mc^2 = KT$ ... ... (1)[K is proportionality constant]

Again we know from the kinetic theory of gases,

$$PV = \frac{1}{3}mnc^2 \qquad \text{(P is the pressure \& V is the volume)}$$

Or, $PV = \frac{1}{3}Mc^2 = \frac{2}{3} \times \frac{1}{2}Mc^2 = \frac{2}{3}KT$ [using (1)]

$\therefore$ PV = RT   [where R = $\frac{2}{3}$K = gas constant]

This is the equation of an ideal gas. And this is for 1 gm-mole gas.

If gas contain n gm-mole, then the above equation becomes

$$PV = nRT$$

Real gas doesn't always obey the ideal gas equation, PV = nRT. Only at high temperature and at low pressure it follows the ideal gas equation.

Boyle's law:

At a fixed temperature, the pressure of a fixed mass of a gas is inversely proportional to the volume of the gas.

∴ **P** $\propto \frac{1}{V}$ **[when T is fixed]**

⇒ **P= constant** $\times \frac{1}{V}$

⇒ **PV = constant**

Charles's law:

At constant pressure, the volume of a fixed amount of a gas is directly proportional to the absolute temperature.

∴ **V** $\propto$ **T , when P is constant**

⇒ $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ **= constant.**

All the Law's Combined

Boyle's Law
PV – k

Charles' Law
$\frac{V}{T}$ – k

Ideal Gas Law
PV = nRT

Combined Gas Law
$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ – k
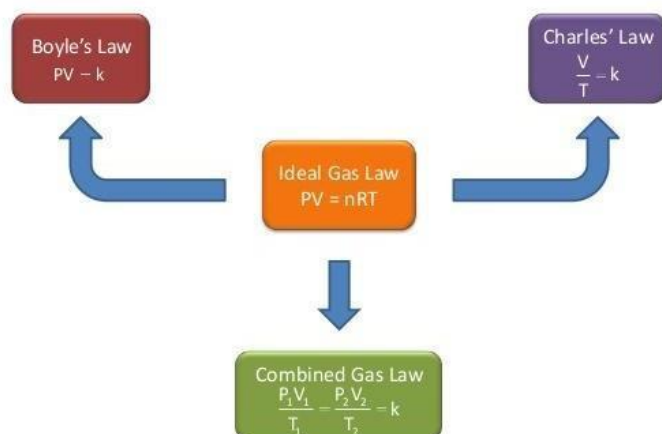
❑ **Show that the root mean square velocity of a gas molecule is directly proportional to the square root of absolute temperature.**

According to the kinetic theory of gases, we have

PV = $\frac{1}{3}$ Mc² … … … (1)

Here, M = mass of one gm-mole of a gas

For ideal gas, PV = RT … … … … (2)

∴ from equation (1) we get,

$\frac{1}{3}$ Mc² = RT Or, c² = $\frac{3RT}{M}$ Or, c = $\sqrt{\frac{3RT}{M}}$ … … … (3)

Here, c is the root mean square velocity.

Since R and M are constant

Therefore,

$$C \propto \sqrt{T} \qquad \text{[showed]}$$

Origin of Van der Waals equation

While deriving ideal gas equation, the molecule of a gas is considered as point masses, i.e., the volume of the gas molecules are not considered. Besides, the attractive forces between gas molecules are ignored.

Famous scientist Van der Waals made necessary corrections taking into consideration the finite volume of

the gas molecules and intermolecular force between the molecules. He corrected the ideal gas equation as,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Here, a and b are constant for particular gas.

So, we can say the origin of Van der Waals equation are,

i) Intermolecular force of attraction

ii) Finite size of the molecules

The van der Waals Equation

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Corrects for molecular volume

Corrects for molecular attraction

General form of the van der Waals equation:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Critical temperature

The **critical temperature** of a substance is the temperature at and above which vapor of the substance cannot be liquefied, no matter how much pressure is applied.

Every substance has a critical temperature. Some examples are shown below.

Substance	Critical temperature (^{o}C)
NH_3	132
O_2	-119
CO_2	31.2
H_2O	374

Critical Pressure

The **critical pressure** of a substance is the pressure required to liquefy a gas at its critical temperature. Some examples are shown below.

Substance	Critical pressure (atm)
NH_3	111.5
O_2	49.7
CO_2	73.0
H_2O	217.7

Root mean square velocity of a gas is directly proportional to the square root of absolute temperature of the gas

According to kinetic theory of gases, we have

$$PV = \frac{1}{3} M \cdot c^2 \qquad \text{............. (1)}$$

Where, M is the mass of one gm-mole of a gas. For ideal gas $PV = RT$ ………….. (2)

From equation number (1)

$$RT = \frac{1}{3} M \cdot c^2$$

$$c^2 = \frac{3RT}{M}$$

$$c = \frac{3RT}{M}$$

Where, c is the root mean square velocity. Since, R and M are constant, then

$$C \propto T$$

So, the Root mean square velocity of a gas is directly proportional to the square root of absolute temperature of the gas.

Isothermal Change

When a gas undergoes a change in pressure and volume at constant temperature, the gas is said to undergo an isothermal change, and the process in which the change takes place is called isothermal process.

In isothermal process the relation between pressure and volume of a gas follows the Boyle's law, i.e.

A practical example of this is some heat engines which work on the basis of the Carnot cycle. The Carnot cycle works on the basis of isothermal.

ISOTHERMAL PROCESS
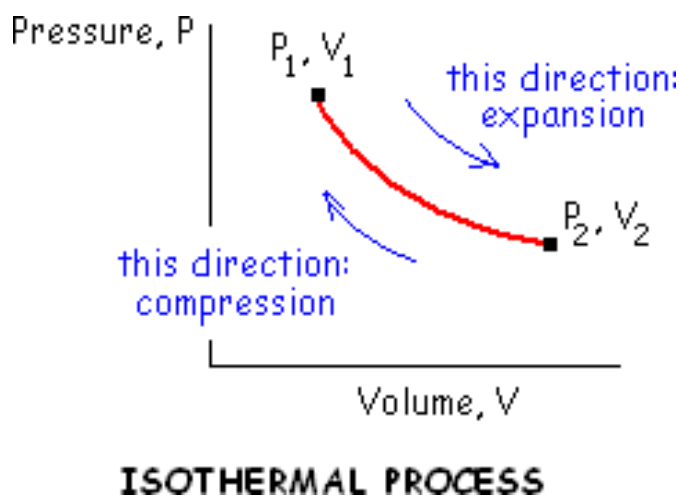
Conditions for isothermal change

The following conditions are to be satisfied for isothermal process

(i)   Container of the gas must be good conductor of heat.
(ii)   Thermal capacity of the surroundings should be high.
(iii)   Change of pressure should be made very slowly.
(iv)   By absorption or rejection of necessary heat the temperature is to be kept constant.

Adiabatic Change

The process in which a system neither receives heat nor rejects heat is called adiabatic process. In this process a gas undergoes changes in pressure, volume and temperature under thermal isolation.

Alternatively, when no heat is allowed to enter or leave the gas, it is called an adiabatic process and change under this process is called adiabatic change. In case of adiabatic process, Boyle,s law does not apply.

The relation between pressure and volume in adiabatic process is PV^γ = constant. Pressure versus volume curve is called adiabatic curve [Fig. 2]. The adiabatic curve is steeper than isothermal curve.

The compression and expansion strokes in an internal- combustion engine are both approximately adiabatic processes. What little heat transfers outside of the system is negligible and virtually all of the energy change goes into moving the piston.

Air is made up of a mixture of gases that is subject to adiabatic heating when it is compressed and adiabatic cooling when it is expanded.

Pressure, P

P_1, V_1

this direction: expansion

this direction: compression

P_2, V_2

Volume, V
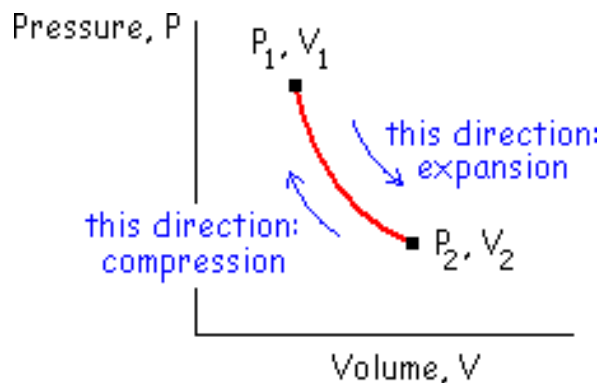
ADIABATIC PROCESS
no heat, Q, in or out

Conditions for adiabatic change

The following conditions are to be satisfied for adiabatic change

(i)   The container of the gas should be non-conducting.
(ii)   Thermal capacity of the surrounding should be low.
(iii)   Change of pressure of the gas must be very rapid so that heat exchange with the surrounding does not take place.

Difference between isothermal and adiabatic change

Sl. No.	Isothermal change	Adiabatic change
1	The change of pressure and volume of a gas at constant temperature is called isothermal change.	The change of pressure and volume of a gas by keeping the total heat content of the gas fixed is called adiabatic change.
2	In this change necessary heat is taken or rejected to keep the temperature constant.	Change of temperature takes place in this process.
3	It is very slow process.	It is very fast process.
4	The container of the gas should be good conductor of heat.	The container of the gas should be non- conducting.
5	It follows Boyle's law.	It does not follow Boyle's law.

Figure 6
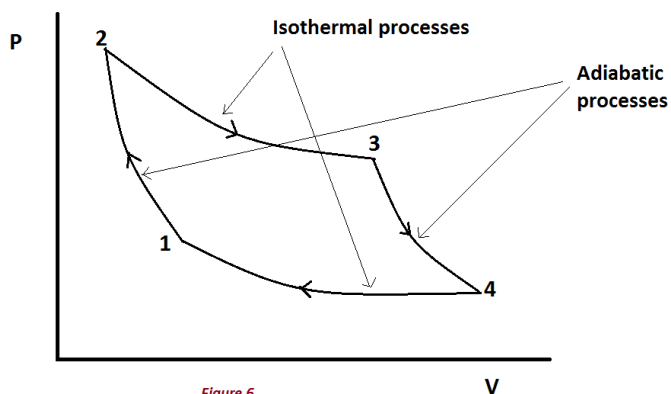
Reversible Process

A reversible process is one which can be retraced in the opposite direction so that the working substance passes through exactly the same state in all respects as in the direct process.

Example

A given mass of ice changes to water when a certain amount of heat is absorbed by it and the same mass of water changes to ice when the same quantity of heat is removed from it.
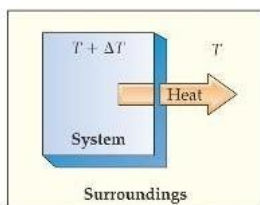
Irreversible Process

An irreversible process is one which cannot be retraced in the opposite direction by reversing the controlling factor. All changes which occur suddenly like the explosion etc may be considered as irreversible. Some examples of irreversible process are

1. Sudden unbalanced explosion of a gas either isothermal or adiabatic.
2. Heat produced by friction.
3. Heat generated when a current flows through an electrical resistance.

Irreversible Processes
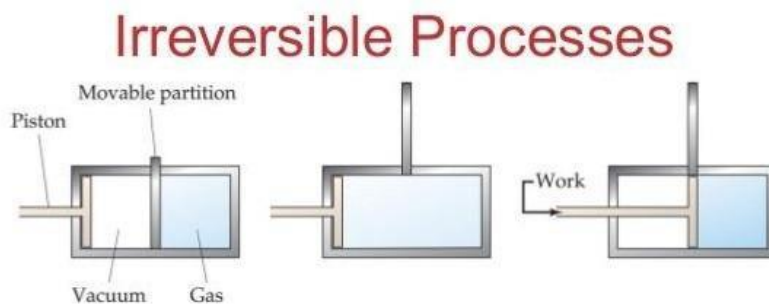
- Irreversible processes cannot be undone by exactly reversing the change to the system.
- All **Spontaneous** processes are **irreversible**.
- All **Real** processes are **irreversible**.

Laws of thermodynamics

The four laws of thermodynamics define fundamental physical quantities (temperature, energy, and entropy) that characterize thermodynamic systems. The laws describe how these quantities behave under various circumstances, and forbid certain phenomena (such as perpetual motion).

The four laws of thermodynamics are

Zeroth law of thermodynamics

If two bodies are separately in thermal equilibrium with a third body then the first two bodies must be in thermal equilibrium with each other".

First law of thermodynamics

Famous scientist Joule first established the relation between heat and work and expressed the relation in terms of law. The law is stated below:

"When work is transformed into heat or heat is transformed into work, then work and heat is directly proportional to each other".

Explanation

If Q be the amount of heat produced due to transformation of W amount of work, then according to first law of thermodynamics.

Here J is proportionality constant. It is called mechanical equivalent of heat or Joule's equivalent. This law is a special form of the principle of conservation of energy.

General form of first law of thermodynamics

Clausius expressed the first law of thermodynamics in a general form. He expressed the law in the following way.

"If some heat is supplied to a system which can do work, then the quantity of heat absorbed by the system is equal to the sum of the increase in internal energy of the system and the external work done by the system".

If dQ be the amount of heat absorbed by a system and dU be the change in the internal energy and dW be the work done by

the system due to absorption of heat, according to the first law of thermodynamics, dQ = dU + dW. This is the special form of the principle of conservation of energy. It is valid for any system.

In above equation, dQ,dU and dW may be positive or negative.

1. dQ is positive when the system absorbs heat and is negative when it loses heat,

2. dU is positive when the internal energy of the system increases and is negative when it decreases,

3. dW is positive when the system does work on the environment and is negative when the surrounding does work on the system.

Significance of the 1st law of thermodynamics:

1. It establishes the relation between heat and work,

2. Heat and work are equivalent to each other,

3. It is nothing but the principle of conservation of energy,

4. Work or heat cannot be obtained from nothing,

5. It is impossible to design a machine of perpetual motion without spending energy.

Second law of thermodynamics

Clausius's statement

It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the substance.

Kelvin's statement

Continuous flow of energy cannot be obtained from an object cooling it from its surrounding.

Plank's statement

It is impossible to construct an engine which can extract heat continuously from a heat source and completely transforms into work.

Carnot's statement

No engine can be built which can extract a fixed amount of heat and will convert totally into work.

Third law of thermodynamics

The entropy of a system approaches a constant value as the temperature approaches zero. The entropy of a system at absolute zero is typically zero, and in all cases is determined only by the number of different ground states it has. Specifically, the entropy of a pure crystalline substance at absolute zero temperature is zero.

Relation between pressure and volume of a gas in adiabatic change:

Let dQ amount of heat be supplied in 1 mole of an ideal gas. Due to this temperature of the gas will increase and the gas will do some work i.e., the supplied heat will be used in two ways.

Let the change in volume and temperature be dV and dT respectively

So, from the first law of thermodynamics we get, dQ = du + dW

dQ = Cv dT + P dV………………. (1) Here

Cv = Specific heat of the gas at constant volume

 PdV =Work done due to the expansion of gas at constant pressure.

We know, in adiabatic process no heat exchange takes place with the surroundings, so dQ = 0………………………….. (2)

From equation (1),
$$C_V dT + PdV = 0 \quad\text{………………….. (3)}$$
Again, for an ideal gas, PV=RT, here R is molar gas constant.
By differentiating Eq. (3) we get,
$$PdV + VdP = RdT$$
$$\Rightarrow\ dT = \frac{PdV + VdP}{R}$$
From Eq. (3),
$$C_V\left(\frac{PdV + VdP}{R}\right) + PdV = 0$$

$$\Rightarrow C_v PdV + C_v VdP + RPdV = 0$$
$$\Rightarrow C_v PdV + C_v VdP + (C_p - C_v)PdV = 0 \quad \text{[since R}=C_p - C_v]$$
$$\Rightarrow C_v PdV + C_v VdP + C_p PdV - C_v PdV = 0$$
$$\Rightarrow C_v VdP + C_p PdV = 0$$
$$\Rightarrow VdP + \frac{C_p}{C_v}PdV = 0 \quad \text{[dividing by } C_v]$$
$$\Rightarrow VdP + \gamma PdV = 0 \quad\quad [\frac{C_p}{C_v} = \gamma]$$
$$\Rightarrow \frac{dP}{P} + \gamma\frac{dV}{V} = 0 \quad\quad\quad \text{[dividing by PV]……… (4)}$$

By integrating Eq. (4), we get,

$\log_e$ P+ γ $\log_e$ V= Constant= $\log_e$ K, here K=Constant

$\Rightarrow \text{Log}_e$ P + $\log_e V^\gamma$ = $\log_e$ K

$\Rightarrow \text{Log}_e PV^\gamma$ = $\log_e$ K

$\Rightarrow PV^\gamma$ =K=Constant

This is the relation between pressure and volume for adiabatic process.

Relation between temperature and volume of a gas in adiabatic change:

We know, for an ideal gas, PV=RT

=> P=RT/V

Again we know, $PV^\gamma = Constant$

Putting the value of P in the above equation, we get,

$$\frac{RT}{V} \times V^\gamma = Constant$$

$$=> TV^{\gamma-1} = Constant$$

This is the relation between volume and temperature in adiabatic process.

13.16 Difference between C_p and C_v for an ideal gas

In order to find the difference between C_p and C_v, let us take a cylinder C with a frictionless movable piston D [Fig. 13.4]. Both the cylinder and the piston are bad conductors of heat. Consider that an amount of n moles of an ideal gas is kept in the cylinder at volume V and pressure P. Keeping the volume fixed, the temperature of the gas is raised by dT, by supplying heat. So heat required,
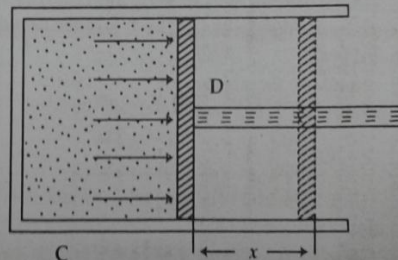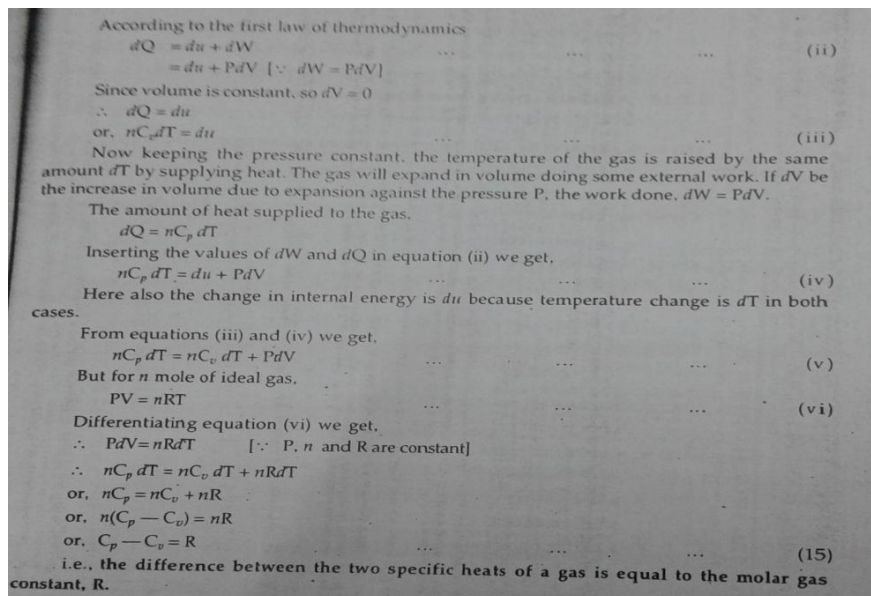
$dQ = nC_v dT$ ... ... (i)

Fig. 134

where C_v is the molar specific heat at constant volume.

According to the first law of thermodynamics

$dQ = du + dW$ ...   .   (ii)

$\quad = du + PdV \quad [\because dW = PdV]$

Since volume is constant, so $dV = 0$

$\therefore \quad dQ = du$

or, $\quad nC_v dT = du$ ...   .   (iii)

Now keeping the pressure constant, the temperature of the gas is raised by the same amount dT by supplying heat. The gas will expand in volume doing some external work. If dV be the increase in volume due to expansion against the pressure P, the work done, $dW = PdV$.

The amount of heat supplied to the gas,

$dQ = nC_p dT$

Inserting the values of dW and dQ in equation (ii) we get,

$nC_p dT = du + PdV$ ...   .   (iv)

Here also the change in internal energy is du because temperature change is dT in both cases.

From equations (iii) and (iv) we get,

$nC_p dT = nC_v dT + PdV$ ...   .   (v)

But for n mole of ideal gas,

$PV = nRT$ ...   .   (vi)

Differentiating equation (vi) we get,

$\therefore \quad PdV = nRdT \quad [\because P, n \text{ and } R \text{ are constant}]$

$\therefore \quad nC_p dT = nC_v dT + nRdT$

or, $\quad nC_p = nC_v + nR$

or, $\quad n(C_p - C_v) = nR$

or, $\quad C_p - C_v = R$ ...   .   (15)

i.e., the difference between the two specific heats of a gas is equal to the molar gas constant, R.

Entropy

Entropy is the physical property of an object which remains constant in adiabatic process. It is represented by S.

Entropy has tremendous importance and significance in thermodynamics. It tells us about the direction of heat flow and helps in determining the thermodynamic condition. Entropy is measured by the rate of change of heat absorbed or rejected with respect to temperature of the system.

The change in entropy (ΔS) of a system was originally defined for a thermodynamically reversible process as

$$\Delta S = \int \frac{dQ_{rev}}{T},$$

Where T is the absolute temperature of the system, dividing an incremental reversible transfer of heat into that system (dQ). (If heat is transferred out the sign would be reversed giving a decrease in entropy of the system.)

16.8.1 Significance of entropy

Entropy is very significant in thermodynamics. The significances are mentioned below :

1. Entropy is a physical quantity. It is equal to the ratio of heat absorbed or rejected to the temperature.

2. It indicates the direction of heat flow.

3. It helps in determining the thermodynamic state of an object.

4. Like temperature, pressure, volume, internal energy, magnetic behaviour it expresses the state of a body.

5. The orderliness of an object decreases with the increase of entropy.

6. Like temperature or pressure it cannot be felt.

16.9 Change of entropy in a reversible process

Let $abcd$ be a complete reversible Carnot's cycle. It is shown in fig. 16.4. In that cycle ab and cd are two isothermal graphs and bc and da are two adiabatic graphs. Let the working substance absorb an amount of heat Q_1 from the heat source at temperature T_1 while moving from a to b along the isothermal graph ab. Let the working substance reject Q_2 amount of heat to the heat sink at temperature T_2 while going from c to d along the isothermal graph cd. But graphs bc and da are adiabatic, hence no heat will be absorbed or rejected along these graphs. Consequently, there will be no change of entropy.
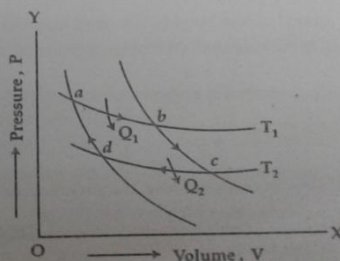
Fig. 16.4

So, increase of entropy in isothermal process $ab = \dfrac{Q_1}{T_1}$

and decrease of entropy in isothermal process $cd = \dfrac{Q_2}{T_2}$

∴ Total change of entropy in the complete cycle $= \dfrac{Q_1}{T_1} - \dfrac{Q_2}{T_2}$

But, as the cycle is reversible, so, $\dfrac{Q_1}{T_1} = \dfrac{Q_2}{T_2}$

∴ Change of entropy, $\Delta S = \dfrac{Q_1}{T_1} - \dfrac{Q_2}{T_2} = 0$

$$\text{or, } \Delta S = \Sigma \dfrac{Q}{T} = 0$$

Conclusion : In reversible process the change of entropy is zero.

16.10 Change of entropy in an irreversible process

Let an irreversible engine take up Q_1 amount of heat from a source at temperature T_1 and t Q_2 amount of heat to the sink at temperature T_2. So, the efficiency,

$$\eta' = \dfrac{Q_1 - Q_2}{Q_1}$$

But the efficiency of a reversible cycle (Carnot's cycle) working within the above perature limit is

$$\eta = \dfrac{T_1 - T_2}{T_1} \qquad \cdots \qquad \cdots \qquad \cdots \qquad (7)$$

Now, according to Carnot's theorem, $\eta > \eta'$

∴ $\dfrac{T_1 - T_2}{T_1} > \dfrac{Q_1 - Q_2}{Q_1}$

or, $1 - \dfrac{T_2}{T_1} > 1 - \dfrac{Q_2}{Q_1}$

or, $\dfrac{Q_2}{Q_1} > \dfrac{T_2}{T_1}$

or, $\dfrac{Q_2}{T_2} > \dfrac{Q_1}{T_1}$

or, $\dfrac{Q_2}{T_2} - \dfrac{Q_1}{T_1} > 0$

So, if the working system is considered as a whole, we find that the heat source loses opy $\dfrac{Q_1}{T_1}$ and the heat sink gains entropy $\dfrac{Q_2}{T_2}$.

Hence, the net gain of entropy $= \dfrac{Q_2}{T_2} - \dfrac{Q_1}{T_1}$, the value of which is positive.

Heat Transfer

Heat transfer describes the exchange of thermal energy, between physical systems depending on the temperature and pressure, by dissipating heat. The fundamental modes of heat transfer are conduction or diffusion, convection and radiation.

The exchange of kinetic energy of particles through the boundary between two systems which are at different temperatures from each other or from their surroundings. Heat transfer always occurs from a region of high temperature to another region of lower temperature. Heat transfer changes the internal energy of both systems involved according to the First Law of Thermodynamics. The Second Law of Thermodynamics defines the concept of thermodynamic entropy, by measurable heat transfer.

Thermal equilibrium is reached when all involved bodies and the surroundings reach the same temperature. Thermal is the tendency of matter to change in volume in response to a change in temperature.

The fundamental modes of heat transfer are

Conduction or diffusion

The transfer of energy between objects that are in physical contact. Thermal conductivity is the property of a material to conduct heat and evaluated primarily in terms of Fourier's Law for heat conduction.

Convection

The transfer of energy between an object and its environment, due to fluid motion. The average temperature is a reference for evaluating properties related to convective heat transfer.

Radiation

The transfer of energy from the movement of charged particles within atoms is converted to electromagnetic radiation.
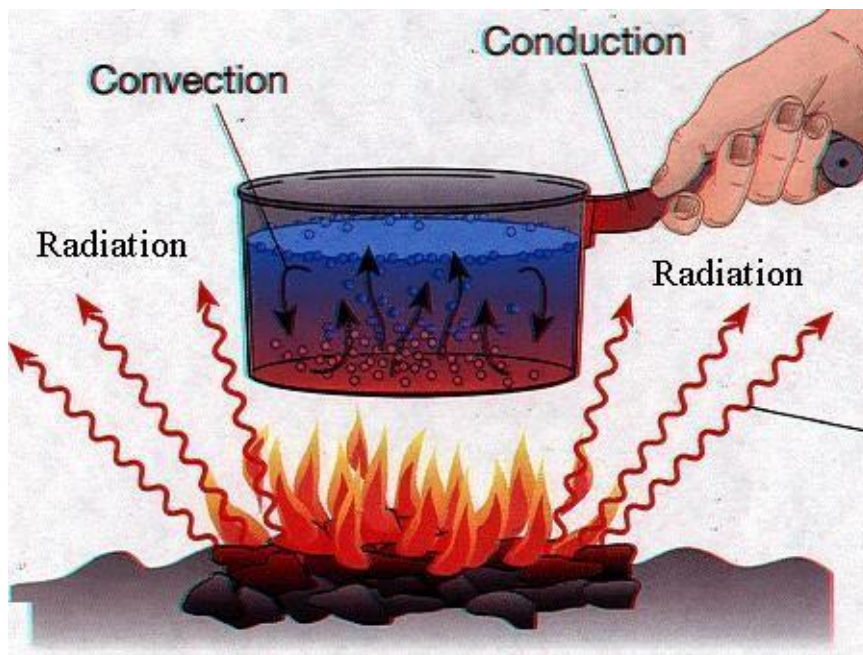
Thermal Conductivity

<u>Laws of Radiation</u>

❑ <u>Stefan - Boltzmann's Law</u>

The **Stefan–Boltzmann law**, also known as **Stefan's law**, describes the power radiated from a black body in terms of its temperature.

This law states that - "The amount of heat radiated by a perfectly black body per unit area per second is directly proportional to the fourth power of its absolute temperature"

Let the amount of heat radiated from a perfectly black body per second per unit area at absolute temperature T be E. Then according to Stefan's Boltzmann's Law

$E \propto T^4$

$E = \square \, T^4$

Where, $\square$ is a constant. It is called Stefan–Boltzmann constant. Its value is 5.67×10^{-8} Wm^{-2} K^{-4}.

❑ <u>Newton's law of cooling</u>

The rate of cooling of a hot body by radiation is directly proportional to the difference of temperature between the hot body and the surrounding.

Let the temperature of the hot body and the surrounding be $\square_1$ and $\square$ respectively. Let the rate of cooling of the hot body be $\frac{dQ}{dt}$. Then according to Newton's law of cooling

$$\frac{dQ}{dt} \propto (\square - \square)_1$$

$$\frac{dQ}{dt} = K (\square - \square)$$

Where, K is a proportional constant. Minus sign indicates the rate of cooling of the hot body.

☐ **Wien's Displacement Law**

The wavelength corresponding to the maximum radiant energy of a black body radiation is inversely proportional to the absolute temperature of the black body.

If λ_m be the wavelength corresponding to the maximum radiant energy of a black body and T, the absolute temperature of the black body, then according to this law

$$\lambda_m \propto \frac{1}{T}.$$

$$\lambda_m \times T = \text{constant}$$

The value of this constant is 28.98×10^{-4} mK.

☐ **Wien's Distribution Law or fifth power law**

The maximum relative emissive power of a black body is proportion to the fifth power of absolute temperature of the body.

Let E_m be the maximum relative emissive power of a black body and T is the absolute temperature of the body. Then according to this law

$$E_m \propto T^5$$

$$\frac{E_m}{T^5} = \text{constant}$$

The value of this constant is 28.98×10^{-4} mK.