

4.1 Heating Effect of Electric Current: Joule's Law

The electric current in a conductor is due to the motion of electrons. During their motion, electrons collide with the oscillating positive ions in the conductor and impart part of their energy to them. Ions oscillate faster and their increased energy is manifested as heat.

The heat energy released in a conductor on passing an electric current is called the "Joule heat" and effect is called the 'Joule effect'.

The potential difference of V volt applied between two ends of a conductor means that V joule of electrical energy is utilized and converted into heat when one coulomb charge passes through the conductor.

If Q coulomb charge passes through the conductor in t seconds resulting in current I , the heat energy produced is

$$\begin{aligned} W &= VQ \quad \text{joule} \\ &= VIt \quad \text{"} \\ &= I^2 R t \quad \text{"} \quad (\because V = IR \text{ according to Ohm's law}) \\ &= (V^2/R)t \quad \text{"} \end{aligned}$$

The electric power, i.e., the electrical energy supplied per unit time or converted into heat energy per unit time in a resistance R , is

$$\begin{aligned} P &= VI \quad \text{joule/second (= watt)} \\ &= I^2 R \quad \text{"} \\ &= (V^2/R) \quad \text{"} \end{aligned}$$

Thus, mechanical unit of energy, joule = watt. second which is an electrical unit of energy. This being too small, kilowatt-hour (kwh) = 3.6×10^6 joule is used as a practical unit of electrical energy.

R is the Ohmic resistance of the conductor value of which does not depend upon V or I . Considering R as a constant,

$$P \propto I^2 \text{ or } I^2 \propto P$$

In fact, all electrical appliances are rated to operate for a given potential difference and hence in household wiring, they are connected in parallel. Therefore, V is same for all whereas I varies. Hence, it is more convenient to use the formula $P = (V^2/R)$.

Joule's Law: "The heat produced per unit time, on passing electric current through a conductor at a given temperature, is directly proportional to the square of the electric current".

To express heat produced in calories, the following relation given by Joule is used.

$$\begin{aligned} W &= JH, \text{ where } W \text{ is mechanical energy in joule,} \\ &\quad H \text{ is heat energy in calorie and} \\ &\quad J = 4.2 \text{ joule/calorie is Joule's constant or mechanical equivalent of heat.} \end{aligned}$$

$$\therefore H \text{ (cal)} = \frac{I^2 R t \text{ (joule)}}{J}$$

4.2 Practical Applications of Joule Heating

Joule heat is used in domestic appliances such as electric iron, toaster, oven, kettle, room heater, etc. It is also used in electric bulbs to produce light. The temperature of the filament of the bulb rises considerably when current flows through it and it emits light. Hence it should be made of a metal of high melting point such as tungsten whose melting point is 3380°C . Also it should be thermally isolated from the surrounding as far as possible. Only a small fraction of electrical power supplied to the bulb is converted into light. Normally a bulb emits 1 candela of light per watt of electrical power consumed.

Another common application of Joule heat is fuse wires used in circuits. It consists of a piece of metal wire having low melting point (such as aluminium, alloy of tin / lead, copper etc.) and is connected in series with an appliance. If a current larger than a specified value flows, the fuse wire melts and breaks the circuit thus protecting the appliance.

4.3 Chemical Effects of Electric Current

4.3 (a) Introduction

- Solid and molten metals are good conductors of electricity due to free electrons. When current flows through metals, only heating occurs and no chemical effect is observed.
- Most liquids have no free electrons and hence do not conduct electricity, e.g., water.
- When an acid, base or an inorganic salt is added to water it dissociates into positive and negative ions which conduct electricity. The solutions which conduct electric current are called electrolytes and the vessel containing it along with electrodes is called an electrolytic cell.
- Inorganic salts like NaCl and KNO_3 conduct electricity in molten form.
- Silver iodide (AgI) conduct electric current even in solid form.
- Normally, the solutions of organic compounds are non-conductors.
- In NaCl crystal, Na^+ and Cl^- ions are bound to each other due to electrostatic attraction. About 1.6 eV ($1\text{ eV} = 1.6 \times 10^{-19}$ joule) energy is required to separate them. Only 0.03 eV thermal energy is available at room temperature which is insufficient to break NaCl crystal.

When NaCl is added to water, polar water molecules get arranged in space between the ions which reduce attraction between them. Also, due to a specific distribution of charge inside them, some water molecules stick to each other forming a cluster around the ions. Each cluster is electrically polarized which reduces the strength of electric field between the ions. For this reason, dielectric constant, K , of water is very high which reduces the electric field between Na^+ and Cl^- ions to $1/K$ times and they get dissociated. Due to its high dielectric constant, water acts as a good solvent. Ions dissociated this way participate in conduction of electric current.

- At room temperature, electrical conductivity of electrolytes is 10^{-5} to 10^{-6} times that of metals because
 - (i) the number density of ions is less as compared to the number density of electrons in metals,
 - (ii) viscosity of solution increases electrical resistance and
 - (iii) drift velocity of ions is less compared to electrons due to their larger mass.

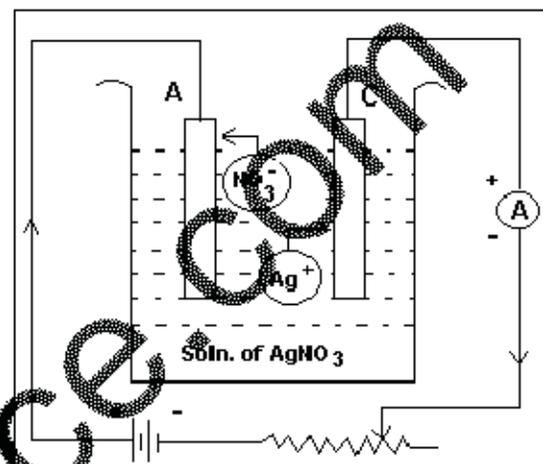
4.3 (b) Electrolysis

The device in which electrolysis occurs is called an electrolytic cell or voltameter which is used to study the chemical effects of electric current.

Refer to the figure shown to understand the working of an electrolytic cell.

Here aqueous solution of AgNO_3 is used as an electrolyte and two plates A and C of silver are partially immersed in it which are the electrodes. The electrodes are connected to a battery from which current enters the electrolyte through A and leaves through C.

AgNO_3 dissociates into Ag^+ and NO_3^- ions in the electrolyte. NO_3^- ions (anions) move towards the anode A and Ag^+ ions (cations) move towards the cathode C.



Each Ag^+ ion, on reaching the cathode, picks up an electron from it and reduces to become a neutral atom of silver and deposits on cathode. ($\text{Ag}^+ + e^- \rightarrow \text{Ag}$). This process of plating of Ag on the cathode is called electroplating.

NO_3^- ion reaching the anode oxidizes Ag to Ag^+ ion and the electron so released goes to the positive terminal of the battery through the wire. AgNO_3 formed dissociates maintaining concentration of Ag^+ and NO_3^- ions ($\text{Ag} + \text{NO}_3^- \rightarrow \text{Ag}^+ + \text{NO}_3^- + e^-$). Thus, Ag^+ ion lost at the cathode is obtained back at the anode.

Summarizing,

- (1) Electric current is due to the motion of electrons in the external conducting wire and due to the motion of ions in the electrolyte.
- (2) Anode loses silver which gets deposited on the cathode.
- (3) Concentration of AgNO_3 is maintained.
- (4) Cathode is made of the metal which is to be plated, e.g., for silver-plating of copper, cathode is made of copper.
- (5) Anode is made of the metal of which plating is to be done and electrolyte must be a compound of that metal.

4.3 (c) Faraday's Laws of Electrolysis

Law 1: "Mass m of the substance liberated at the electrode from the electrolyte, on passing electric current through the electrolyte, is directly proportional to the amount of charge (Q) passing through it."

Thus, $m \propto Q$. $\square m = ZQ = ZIt$, where I is the current for time t .

" Z is called electrochemical equivalent of the substance liberated and is defined as the mass of the substance liberated from an electrolyte on passing one ampere current for one second, i.e., one coulomb of charge."

Its unit is g/C or kg/C .

Law 2: "When the same current is passed for the same time through different electrolytes, the masses of elements liberated at electrodes are directly proportional to their respective chemical equivalents."

Chemical equivalent (e) of any element is the ratio of its atomic mass to its valency. It is also called gram equivalent.

Let e_1 and e_2 be the chemical equivalents of two substances and m_1 and m_2 be their masses liberated at the electrodes when the same current i passes through two electrolytic cells for the same time t . Then,

$$\frac{e_1}{e_2} = \frac{m_1}{m_2} = \frac{Z_1 It}{Z_2 It} \quad \therefore \frac{e_1}{Z_1} = \frac{e_2}{Z_2} = F$$

where F is Faraday's constant having value 96500 coulomb/mole. This means that 96500 C charge is required to liberate, through electrolysis, 1 mole of an element having valency 1. It also means that the amount of substance liberated at the electrode when 96500 C charge is passed through an electrolyte is

$$m = \frac{\text{atomic mass}}{\text{valency}} = \text{chemical equivalent}$$

4.4 Electrochemical Cells

The device used to convert chemical energy into electrical energy is called an electrochemical cell.

When a metal plate (electrode) is immersed into an electrolyte, positive or negative ions from the electrolyte move towards it and a net e.m.f. is developed between it and the electrolyte. When two electrodes of different metals are immersed into the electrolyte, a net e.m.f. is generated between them. The electrode at higher electric potential is called the positive electrode and the one having lower potential is called the negative electrode. Steady electric current flows on completing the electric circuit by connecting the two electrodes with a conducting wire. Such a device is called an electrochemical cell.

Electrochemical cells are of two types:

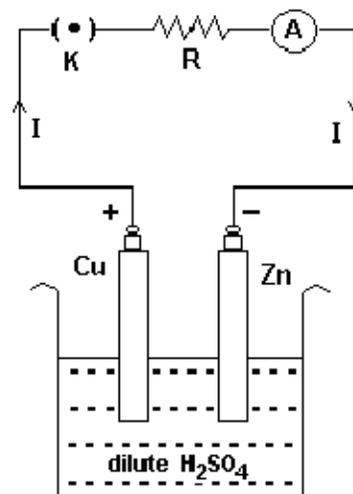
1) **Primary cells:** The cells that get discharged only and cannot be recharged after use are called the primary cells.

2) **Secondary cells:** The cells which can be recharged after use and restored to original condition are called the secondary cells.

Voltaic Cell:

Italian scientist Volta prepared such a cell for the first time. Hence it is known as voltaic cell in his memory.

Dilute H_2SO_4 is used as an electrolyte. Positive charge deposits on copper electrode and negative charge on zinc electrode. So copper electrode is at a higher potential than the zinc electrode.



On connecting the electrodes with a conducting wire, current (conventional) starts flowing from copper to zinc. Inside the cell, flow of current is due to motion of positive ions towards the copper electrode and negative ions towards the zinc electrode.

Volta observed that the e.m.f. developed depends on the type of metals used and the electrolyte and not on the size of electrodes. He also found that by connecting them in series a large p.d. can be obtained. Such a connection of cells is called a Voltaic battery or Voltaic pile.

Daniel Cell:

In this cell, solution of CuSO_4 is filled in a copper container. Copper wall of the cell acts as positive terminal. A porous porcelain pot containing zinc electrode and dilute solution of H_2SO_4 is kept inside the copper container as shown in the figure. The porous pot allows ions to pass through but does not allow the solution to get mixed up.

Following reactions occur:



Zn^{2+} ions enter CuSO_4 solution through the porous pot and combine with SO_4^{2-} to form ZnSO_4 whereas $2e^-$ remain on the Zn electrode. Cu^{2+} gain two electrons from the copper wall and reduce to Cu which deposits on the walls of the copper container. Zn electrode acts as anode and copper container as cathode. An emf of 1.1 V is obtained in this cell.

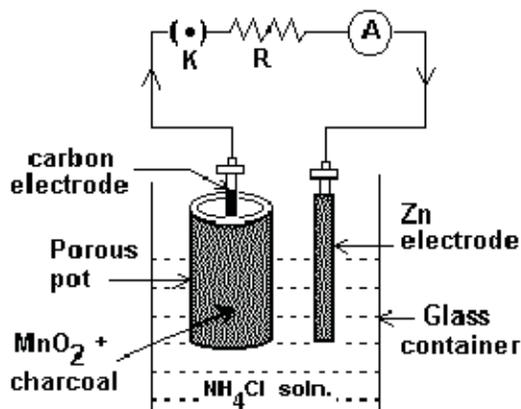
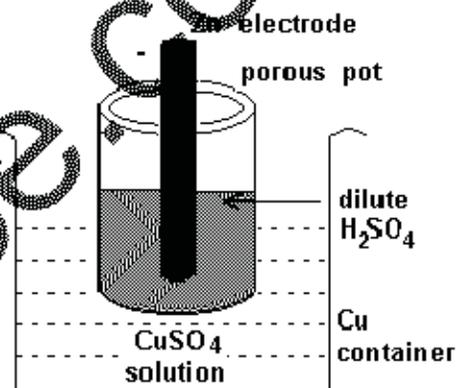
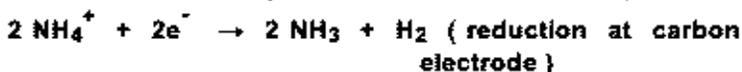
Hydrogen produced due to electrolysis forms a layer of hydrogen gas on the copper container which increases the internal resistance of the cell and finally the cell stops working. This phenomenon known as polarization, reduces the efficiency of the cell. To avoid it, substances which oxidize hydrogen are added in Leclanche and dry cells.

(Note: The electrode where oxidation occurs is called anode and where reduction occurs is called cathode.)

Leclanche Cell:

This cell consists of a glass container filled with NH_4Cl as an electrolyte. Zn electrode and a porous pot containing carbon electrode are partially immersed in it. The porous pot contains MnO_2 and charcoal powder. Charcoal powder is used for better electrical conduction as MnO_2 is a poor conductor.

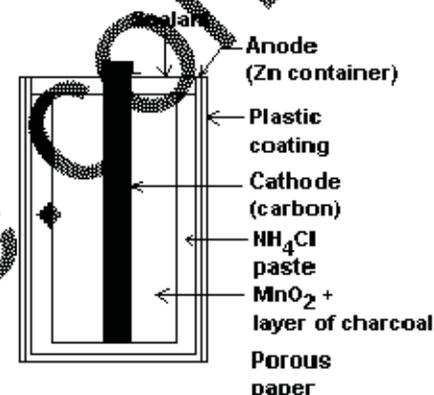
Following reactions occur:



Zn^{2+} ions combine with Cl^- ions forming ZnCl_2 while going towards carbon electrode. H_2 combines with MnO_2 forming Mn_2O_3 and water thus preventing it from collecting around the carbon electrode and reducing its efficiency. This process is called depolarizing action. However, this action being slow, H_2 collects around the carbon electrode reducing efficiency and voltage of the cell. If the cell is switched off, H_2 gets removed and the cell can be used again. Thus the cell is useful for short duration use. Emf of this cell is 1.5 V.

Dry Cell:

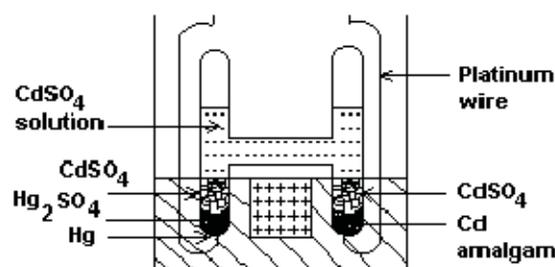
Dry cell is a type of portable Leclanche cell. The figure shows sectional view of the dry cell. Zn pot acting as a negative terminal is anode. It contains electrolyte NH_4Cl in the form of a paste. MnO_2 mixed with charcoal is packed around central carbon rod which is a positive terminal (cathode). MnO_2 acts as a depolarizer to which charcoal is added for better electrical conductivity. The whole arrangement is sealed at the top with a sealant. The brass cap on top of carbon rod has a hole to allow H_2 gas produced to escape. Outer surface of Zn pot except the bottom is covered with plastic coating.



Standard Cell:

Normally, the electrodes used in cells corrode with time and cannot provide a constant emf for a long time. But some cells, known as standard cells, can provide a constant emf for a very long time. One such cell, known as Weston cell is shown in the figure.

In this cell, mercury (Hg), which acts as cathode, kept in contact with a paste of mercurous sulphate (Hg_2SO_4) (which acts as a depolarizing agent) is filled in one part of a glass tube of H-shape.



The other part of this tube is filled with cadmium mixed with mercury and it acts as anode. Concentrated solution of CdSO_4 is used as an electrolyte.

Bottom of both the parts of this tube is sealed with platinum wires and thus connecting terminals are prepared, so that the cell can be connected in external circuits.

At 20°C , the emf of this cell is 1.0183 V and it remains constant over a wide range of temperatures.

Standard Cell: Lead Storage Cell (accumulator)

Unlike primary cell, the secondary cell can be recharged and reused. Lead storage cell is the most widely used secondary cell in practice.

The positive terminal of a lead storage cell is of PbO_2 and the negative terminal is of Pb. The dilute solution of H_2SO_4 is the electrolyte. In fully charged condition, the specific gravity of the electrolyte is 1.285 which can be measured by a device called hydrometer. The emf of the cell is 2.1 V. During discharge, PbSO_4 deposits on both the electrodes. In fully discharged state, the specific gravity falls to 1.15.

Charging:

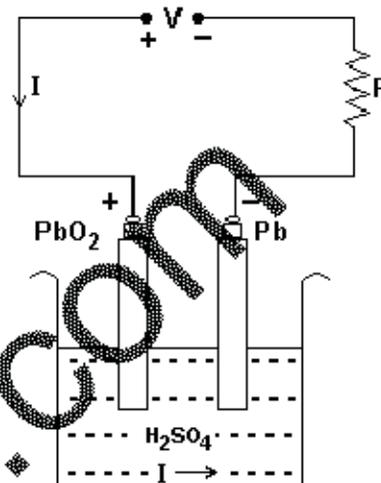
For charging the cell, direct current is passed through it by connecting positive electrode with positive terminal and negative electrode with negative terminal of the D.C. source as shown in the figure. During charging PbO_2 is formed at the positive terminal and Pb is formed at the negative terminal and at the same time H_2SO_4 is also generated which restores the concentration of the electrolyte. Hence the cell is ready for reuse. As the cell is being charged,

$$V = \epsilon + I(R + r) \quad \therefore Vit = \epsilon It + I^2(R + r)t$$

Here, Vit = electrical energy used from charging battery

ϵIt = electrical energy stored in the cell being charged

and $I^2(R + r)t$ = electrical energy lost as heat in resistance.



Solid State Cell:

Cells using liquid electrolytes have the following disadvantages:

- (i) leakage after long storage,
- (ii) corrosion due to acidic or alkaline solution,
- (iii) short life,
- (iv) small wattage per unit mass of the cell and
- (v) difficulty in making them in smaller size.

Solid state cells do not have these problems. Such cells are prepared using solid electrolytes in the form of jelly, polymer, composite polycrystalline solids or thin film in which ions are mobile.

Figure 1 shows a schematic diagram of such a cell. Any one or both of M^+ (cations) and X^- (anions) are mobile.

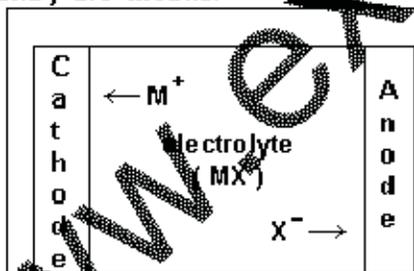


Fig. 1

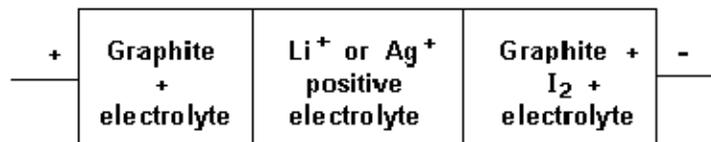


Fig. 2

Figure 2 shows lithium solid state cell. Chemical reaction occurring at Iodine (I_2) electrode



To reduce polarization at electrodes, the electrolyte is mixed with the material of electrodes.

- Many solids are developed for anode, cathode and electrolytes used in solid state cells. The lithium (Li^+) battery used in mobile phones consists of such electrolytes.
- Lithium button cells are used in pacemakers for controlling heart beats which contain the mixture of LiI and Al_2O_3 as an electrolyte.
- Polymer Li -batteries and H^+ -batteries are being developed to run electric cars.

4.5 Thermoelectricity

4.5 (a) Seebeck Effect

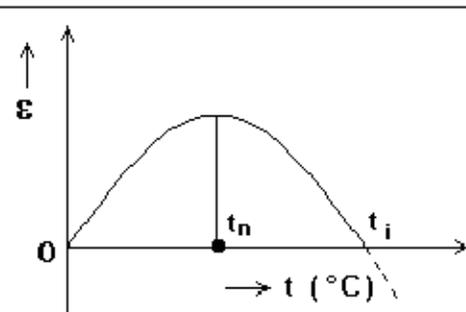
In 1821, German scientist, John Seebeck, showed experimentally that when two junctions prepared by connecting ends of two different appropriate metals, are kept at different temperatures, e.m.f. is developed. This phenomenon is called Seebeck effect. The device prepared in this manner is called thermocouple and metals or alloys used in it are called thermoelements.



The junction at lower temperature (t_R) is called reference junction and the junction at higher temperature (t_t) is called test junction. The e.m.f. developed is called thermoelectric e.m.f. (thermo e.m.f. in short) or Seebeck e.m.f. which is of the order of $\mu\text{V}/^\circ\text{C}$. Its direction depends on the type of metals used and temperature of junctions.

Metals, which exhibit thermoelectric effect, are arranged in a definite series known as thermoelectric series. It starts with Antimony (Sb), Nichrome, Iron (Fe),..... and ends with Nickel (Ni), Constantan, Bismuth (Bi). At cold junction, the direction of electric current is from a metal to the metals coming after it in the above series. In Bi-Sb thermocouple, the direction of electric current at cold junction is from Sb to Bi. On reversing the temperatures of the junctions, the direction of the current also reverses. More the separation of metals in the series, more is the value of the thermo e.m.f. developed in the thermocouple made from them.

On plotting the e.m.f. (ϵ) obtained on varying the test junction temperature (t), keeping reference junction temperature fixed at 0°C , against the test junction temperature, a parabolic graph as shown in the figure is obtained. For thermocouples prepared from some metals, this graph is an inverted parabola.



For reference junction temperature at 0°C , the relation between ϵ and t is given as under.

$$\text{Thermo emf, } \epsilon = \alpha t + \frac{1}{2} \beta t^2$$

$$\frac{d\epsilon}{dt} = \alpha + \beta t$$

The rate of change of thermo emf with temperature ($d\epsilon/dt$) is called thermoelectric power. Its unit is $\mu\text{V}/^\circ\text{C}$. Unit of α is $\mu\text{V}/^\circ\text{C}$ and that of β is $\mu\text{V}/^\circ\text{C}^2$.

The constants α and β depend upon the type of metals forming the thermocouple. Both emf and thermoelectric power depend on the type of metals forming the thermocouple and the temperature.

The temperature at which the thermo emf is maximum is called the "neutral temperature", t_n , and the temperature at which thermo emf changes its direction is called the "inversion temperature", t_i .

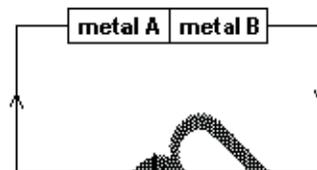
$$\text{At } t = t_n, \quad \frac{d\epsilon}{dt} = 0 \Rightarrow t_n = -\alpha/\beta$$

Thus, for a given thermocouple, the value of neutral temperature is fixed but the value of inversion temperature depends on the reference junction temperature as given by

$$t_n = \frac{t_R + t_i}{2}$$

4.5 (b) Peltier Effect

As shown in the figure, when electric current is passed through a junction of two different metals, heat is exchanged between the junction and surrounding (environment). This is known as Peltier effect. Thus Peltier effect is the reverse of Seebeck effect.



On reversing the direction of current, heat exchange also reverses. This means that if heat was absorbed at the junction, it will be evolved on reversing the current. Thus Peltier effect is reversible. When heat is absorbed at the junction, heat energy is converted into electrical energy and vice versa.

The amount of heat exchanged at the junction (ΔH) is directly proportional to the amount of charge (ΔQ) passing through that junction.

$$\Delta H \propto \Delta Q \Rightarrow \Delta H = \pi_{AB} \Delta Q$$

π_{AB} is called Peltier emf (or Peltier coefficient) which is defined as the amount of heat exchanged at the junction per unit electric charge passing through it. The value of π_{AB} depends on the type of metals and the temperature of the junction.

Comparison of Peltier and Joule Effects

Joule Effect	Peltier Effect
1) Heat is evolved for any direction of current through the resistor	1) Heat is evolved at the junction with current in one direction and absorbed when the direction of current is reversed.
2) Rate of heat evolved is proportional to the square of the current through the resistor.	2) Rate of heat exchanged is proportional to the current through the junction or total amount of heat evolved is proportional to the amount of charge passing through the junction.
3) Heating takes place throughout the resistor.	3) Peltier heating is observed only at the junction.

4.5 (c) Thomson Effect

In 1851, William Thomson (later known as Lord Kelvin) observed that when different parts of a conducting wire are kept at different temperatures and electric current passed through it, heat either evolves or gets absorbed in different parts of the wire. This phenomenon is called Thomson effect. Heat produced or absorbed is called Thomson heat which is in addition to the Joule heat produced on passing the current.

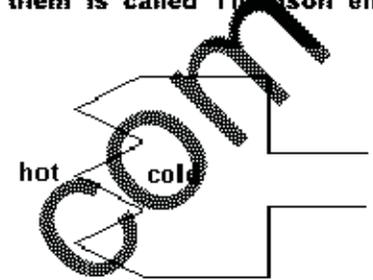
The amount of Thomson heat (ΔH) emitted or absorbed in any part of the conductor is directly proportional to the amount of charge (ΔQ) passing and temperature difference (ΔT) between two ends of that part of conductor.

$$\Delta H = \sigma (\Delta Q)(\Delta T) \Rightarrow \sigma (\Delta T) = \frac{\Delta H}{\Delta Q} = \frac{\text{Thomson heat}}{\text{Electric charge}}$$

where σ is constant for any metal at a given temperature and is called Thomson coefficient. Its unit is volt / °C. The emf, $\sigma (\Delta T)$, developed due to temperature difference between different points of a conductor per unit charge passing between them is called Thomson emf.

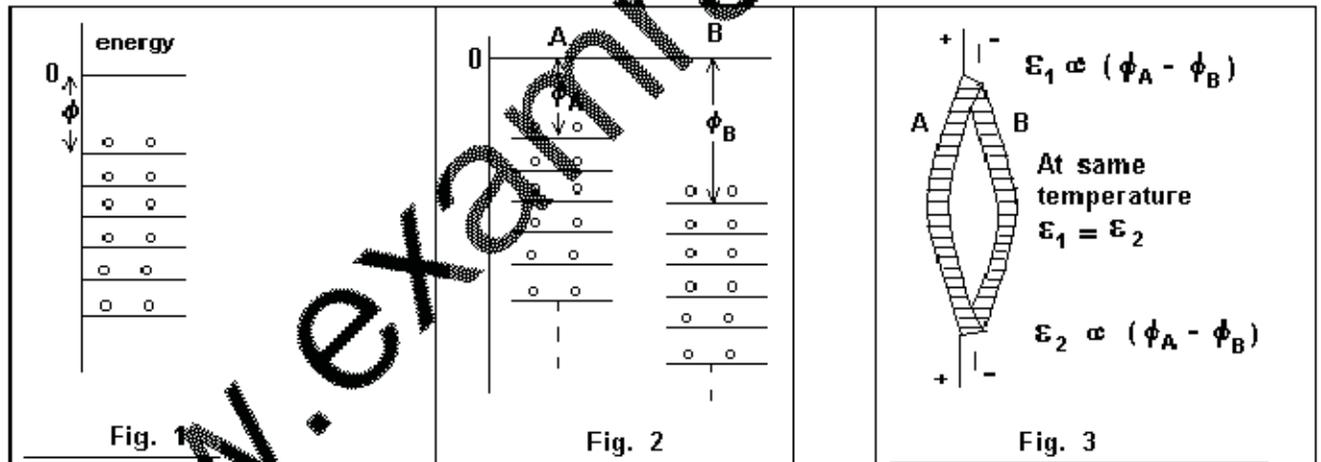
4.5 (d) Thermopile:

The device, shown in the figure, prepared by connecting a number of thermocouples in series to obtain larger emf is known as thermopile.



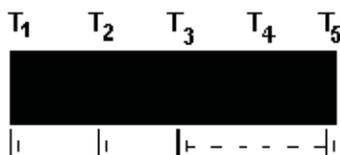
4.5 (e) Origin of Thermoelectric Effects:

Maximum two electrons are present in an orbital of an atom of the solid. Fig. 1 shows such energy levels in solids with two electrons. As can be seen from the figure, electrons have negative energies with respect to zero energy taken at infinity which means that they are bound to the nucleus. The electrons of the uppermost orbit require minimum energy (ϕ) to be liberated from the atom which is called work function of the metal.



Different metals have different work functions. Fig. 2 shows that the work function ϕ_A of metal A is less than ϕ_B of metal B which means that some electrons of metal A has more energy than maximum energy of electrons of metal B. This results into diffusion of electrons from metal A to metal B. Metal A gains positive potential on losing electrons and metal B gains negative potential. This creates potential difference, called contact potential, at the junction whose value is proportional to $\phi_A - \phi_B$ and the junction behaves like a battery. The positive terminal of this battery is towards metal A as shown in figure 3. Such contact potentials, ϵ_1 and ϵ_2 at the two junctions having different temperatures are different as the value of $\phi_A - \phi_B$ vary with temperature. This results in net emf, $\epsilon_1 - \epsilon_2$, which is called Peltier emf, π_{AB} .

If temperature gradient is maintained along the length of



a conductor of the same metal, electrons flow from the hot end to the cold. This is equivalent to the imaginary batteries formed on different small elements of the metal

connected in series as shown in the adjoining figure resulting in potential difference called Thomson emf.

The p.d. developed at the two junctions in Seebeck effect is due to Peltier emf and Thomson emf. Thus Seebeck effect is the combination of Peltier and Thomson effects.

In Peltier effect, if the charge flows in the direction of the Peltier emf at the junction, work is done by the emf. So energy is absorbed at the junction which cools it down. If the charge flows at the junction in the direction opposite to the Peltier emf, the charge uses energy that converts into heat energy and the junction gets heated.

4.6 Applications of Thermoelectricity

Some major applications of thermoelectricity are discussed as under.

Thermoelectric thermometer:

- One junction of the thermocouple is kept at a constant temperature and the other is brought in contact with the body whose temperature is to be measured. Thermo-emf produced can be calibrated to indicate the temperature of the body.
- Temperatures ranging from very low temperature to 2000 K can be measured this way.

Thermocouple

Range of temperature measured

- | | |
|---|---------------|
| 1) Copper-constantan | 50 K to 500 K |
| 2) Iron-constantan | 50 to 1000 K |
| 3) Platinum-Rhodium alloy and }
Copper-aluminium alloy | up to 2000 K |
| 4) Copper and Gold-Iron alloy | 1 K to 50 K |

- To measure low temperatures, thermocouples should be made of metals which give large emf for small differences of temperatures.

Thermoelectric generator:

- Electricity can be generated on a very small scale using Seebeck effect.
- Efficiency of thermocouples being very low (about 1%), voltage of 0.1 mV/K and power of 0.25 mW/K can be obtained using thermocouples prepared from semiconductors.
- Low power thermoelectric generators (up to 5 kW capacity) keeping one junction at room temperature and heating the other with a kerosene lamp have been developed for use in remote areas.

Thermoelectric Refrigerator:

- Thermoelectric fridge is prepared using Peltier effect with the help of junction at which temperature decreases on passing electric current.
- They can be used for cooling of small areas as they have low efficiency.
- They are noiseless as there are no moving parts like a motor.
- They are pollution-free as there is no refrigerant gas like Freon which destroys the ozone layer. Hence, there is a scope to develop such fridges by improving their efficiencies.