



## Department of Chemistry

### **Material Chemistry**

## **LIQUID CRYSTALS**

When a solid is heated, the thermal agitation overcomes the cohesive force of attraction till it reaches its melting point and changes into liquid form.

But, when long chain organic molecules are heated one or more phase transitions take place in passing from solid to liquid phase and are called '**Intermediate phases**' or '**Mesophases**' or '**Mesogens**'. The molecular ordering in mesophases lies between that of a solid and a liquid.

**“An ordered fluid mesophase of an organic long chain molecule both solid like molecular order and liquid like character is known as Liquid Crystal”**

OR

**“Liquid Crystal state may be defined as any state of matter where the molecules are orientationally ordered but yet are in dynamic motion”.**

Liquid crystals exhibit optical anisotropy. That is they possess different optical properties when light is incident in different directions.

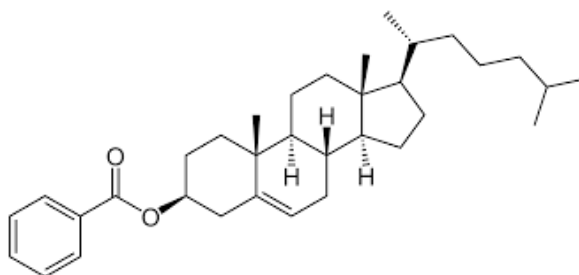
The study of liquid crystals began with an observation made by an Austrian Botanist Freindrich Reinitzer, in 1888.

He found that solid Cholesteryl Benzoate melts at  $145.5^{\circ}\text{C}$  giving a turbid appearance or hazy liquid of red colour and on further heating, turns into a clear transparent liquid of blue colour, at  $178.5^{\circ}\text{C}$ .

On cooling, the reverse changes occurred exactly at the same temperatures.

Cholesteryl benzoate	$145.5^{\circ}\text{C}$	Cholesteryl benzoate	$178.5^{\circ}\text{C}$	Cholesteryl benzoate
<b>Solid, crystal</b>	→	<b>liquid crystals</b>	→	<b>liquid</b>
<b>(colourless)</b>	←	<b>(red)</b>	←	<b>(blue)</b>

Cholesteryl benzoate is said to exist as liquid crystal between  $145.5^{\circ}\text{C}$  and  $178.5^{\circ}\text{C}$  and its structure is



**Cholesteryl benzoate**



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The temperature at which the solid Cholesteryl benzoate converts to liquid crystal state i.e.,  $145.5^{\circ}\text{C}$  is the **melting point** and the temperature at which the transition from liquid crystal state to isotropic liquid, i.e.,  $178.5^{\circ}\text{C}$ , takes place is referred to as **clearing temperature**.

Thus, liquid crystal state is a distinct phase observed between crystalline state and isotropic liquid state.

#### **Classification of Liquid Crystals:**

Liquid crystals are classified into two main categories such as

- Thermotropic liquid crystals and
- Lyotropic liquid crystals

#### **1) Thermotropic Liquid Crystals:**

The class of compounds that exhibit liquid crystal behaviour on **variation of temperature alone** are referred to as **Thermotropic Liquid crystals**.

The temperature ranges at which some liquid crystals are stable are given below:

Compound	Solid	Liquid Crystal	Liquid
Cholesteryl benzoate		$145.5^{\circ}\text{C}$	$178.5^{\circ}\text{C}$
p-azoxy phenetole		$137^{\circ}\text{C}$	$167^{\circ}\text{C}$
p-azoxy anisole (PAA)		$116^{\circ}\text{C}$	$135^{\circ}\text{C}$
p-methyl benzylidene – p' - n butyl aniline (MBBA)		$21^{\circ}\text{C}$	$47^{\circ}\text{C}$

The liquid crystal state can be observed by carefully raising the temperature of a solid or by lowering the temperature of a liquid.

#### **2) Lyotropic Liquid Crystals:**

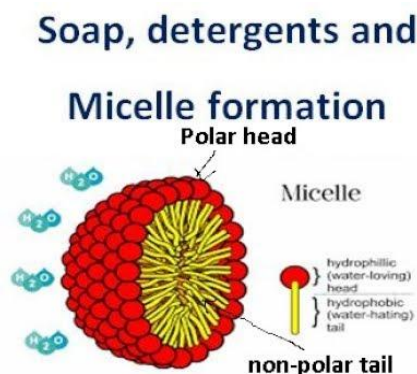
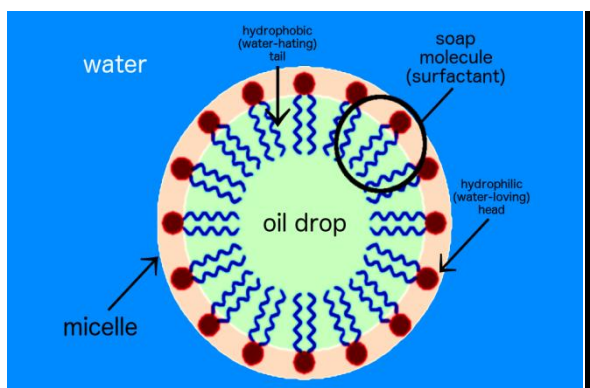
**Lyotropic liquid crystals** are obtained by **mixing the two components** and **increasing the concentration of one of the components** till liquid crystal phase is observed.

Example: Soap molecules (Soap - water mixture) and phospholipids (phospholipids - water mixture)

Lyotropic liquid crystals are typically obtained from amphiphilic compounds compressing of both lyophilic (solvent loving / attracting) and lyophobic (solvent heating / repelling) ends in the same molecule. In the presence of a solvent, lyophobic ends come together while lyophilic ends are directed towards solvent forming '**micelles**'.

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The formation of micelles takes place only beyond a certain concentration (50 to 100 molecules of amphiphilic compounds) of the solution called, critical micelle concentration (CMC). When the concentration of the solution is increased beyond CMC, the micelles swell or increase in size and eventually coalesce to form liquid crystals phase.

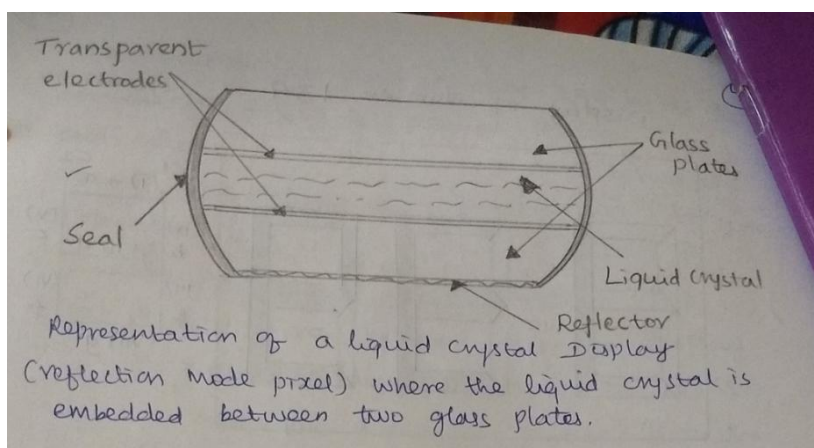
## LIQUID CRYSTAL DISPLAY (LCD)

Liquid crystals are unique class of long chain organic compounds exhibiting interesting polymorphic behaviour and properties and as such find wide applications in display systems.

### Information displays:

The electro optic effect of liquid crystals controls brightness / darkness of the light emerging from its elements and this property of liquid crystals are used in information displays. Information is passed on to the user using liquid crystals which controls the brightness/darkness of the parts of display.

Numerical display has 7 segments, whereas alphabets are displayed using 14 segments. Light from the area of each of the seven segments is controlled independently and creation of any of ten digits becomes possible. A representation of a LCD segment or reflection mode pixel where the liquid crystal is embedded between two glass plates is given below.



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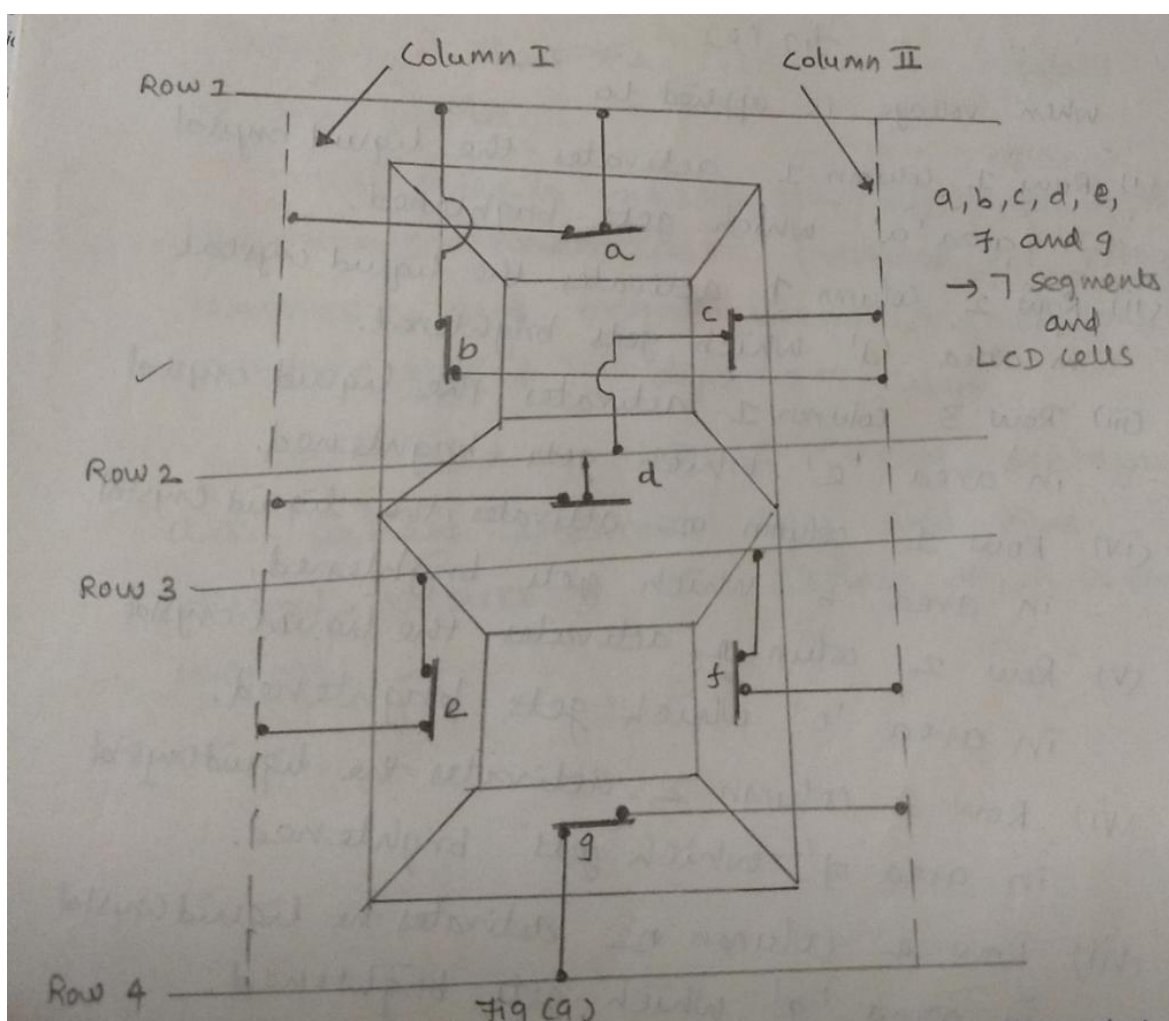
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When an electric field is applied to a segment, the liquid crystal in that segment undergoes deformation (is activated) and when polarized light is incident, the segment gets brightened.

Consider a typical LCD cell (reflection mode) and the electrical circuit with 4 rows and 2 columns for a digit to appear.

#### Seven segment LCD for a digit:

Each row is connected to two segments and each column is connected to three or four segments and **a, b, c, d, e, f & g** are LCD cells.



**“Seven segment LCD for a digit; Each row is connected to two segments and Each column is connected to three or four segments; a, b, c, d, e, f & g are LCD cells”**

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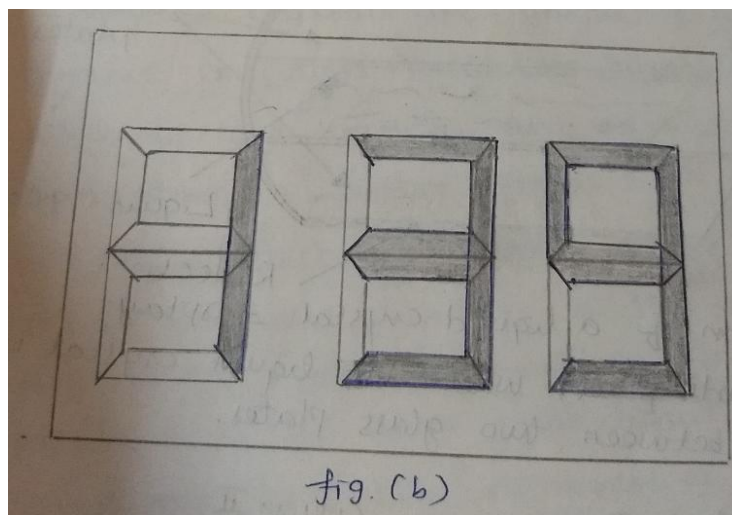
When voltage is applied to a particular row and corresponding column, the respective liquid crystal in that area gets brightened according to the table given below.

Voltage applied to : Rows↓	Area where LC gets activated and brightened	
	columns ↓	
	C1	C2
R1	‘a’	‘b’
R2	‘d’	‘c’
R3	‘e’	‘f’
R4		‘g’

When voltage is applied to:

- Row 1 Column 1 activates the liquid crystal in area ‘a’ which gets brightened
- Row 2 Column 1 activates the liquid crystal in area ‘d’ which gets brightened
- Row 3 Column 1 activates the liquid crystal in area ‘e’ which gets brightened
- Row 1 Column 2 activates the liquid crystal in area ‘b’ which gets brightened
- Row 2 Column 2 activates the liquid crystal in area ‘c’ which gets brightened
- Row 3 Column 2 activates the liquid crystal in area ‘f’ which gets brightened
- Row 4 Column 2 activates the liquid crystal in area ‘g’ which gets brightened

#### Display of Number 139





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- For example, to get a number 139 on the display an electric field should be applied to **row 2** and **column 2** ('c') and **row 3** and **column 2** ('f') to give '1' on the display.
- For the second digit, an electric field should be applied to **row 1** and **column 1** ('a'), **row 2** and **column 2** ('c'), **row 2** and **column 1** ('d'), **row 3** and **column 2** ('f') and **row 4** and **column 2** ('g') to give '3' on the display.
- For the third digit, an electric field should be applied to **row 1** and **column 1** ('a'), **row 1** and **column 2** ('b'), **row 2** and **column 2** ('c'), **row 2** and **column 1** ('d'), **row 3** and **column 2** ('f') and **row 4** and **column 2** ('g') to give '3' on the display.

In order to enhance the difference in the brightness between dark (turned OFF, voltage removed) and bright areas (turned ON, voltage applied), dyes are used. Dyes used in liquid crystal displays are called dichroic dyes and give desired colours to the displays with a good contrast.

### Applications:

Liquid crystal displays operate at low voltages and consume less power as compared to other display systems.

- Liquid crystal displays are used in calculators, watches, mobile telephones, laptop computers and related electronic gadgets.
- Liquid crystal displays are used in Automobile dashboards, airplane cockpits, traffic signals, advertisement boards and petrol pump indicators.
- Liquid crystal displays are used in pH meter, conductometer, colorimeter, potentiometer Blood pressure instruments, digital thermometers and TV channel indicators.
- Liquid crystals are useful in the detection and determination of size and shape of subcutaneous tumours because the skin in these areas will be warmer than in other areas.
- Using the variation in colour of liquid crystals with change in temperature, the paths of arteries and veins can be detected, because the portion of skin above the veins and arteries are at slightly higher temperature than at other areas. This helps in detection of blockage in veins and arteries.
- Information about the effect of certain drugs on circulations system can also be studied.
- The points of failure of electronic components can be detected using LCs. Failure at certain points in the components leads to localized heating at these spots and can be detected by the change in colour of cholestric liquid crystals.
- The liquid crystals have been used to detect the impurities in the atmosphere. The colour of the liquid crystals changes in the presence of impurities.





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# FLOURESCENCE AND PHOSPHORESCENCE

According to Grotthus - Droper law of photochemistry, also called the principle of photochemical activation, “**only the light which is absorbed by a system (substance / material) can bring about a photochemical change**”.

However, it is not essential that the light which is absorbed must bring about a chemical change. The absorption of light may result in two phenomena.

(i) The light absorbed may cause only a decrease in the intensity of the incident radiation, which is governed by **Lambert - Beer law** resulting in the increase in the rate of absorption with concentration.

(ii) The light absorbed may be reemitted almost instantaneously (within  $10^{-8}$  sec) known as **Fluorescence**, which ceases with the removal of the source of light.

Sometimes, the light absorbed is given out slowly and even long after the removal of the source of light known as **Phosphorescence**.

**Fluorescence:** When a beam of light is incident on certain substances, they emit visible light or radiations and they stop emitting light or radiations as soon as the incident light is cut off. This phenomenon is known as **fluorescence**. Such substances which emit radiations during the action of stimulating light are called **fluorescent substances**.

**Phosphorescence:** When a light radiation is incident on certain substances, they emit light continuously even after the incident light is cut off. This type of delayed fluorescence is called **phosphorescence** and the substances are called **phosphorescent substances**.

### Theory of Fluorescence & Phosphorescence :

Some terminologies (quantum) need to be clarified in order to understand the theory of Fluorescence and Phosphorescence.

**Spin multiplicity:** Most molecules have an even number of electrons and thus in the ground state all the electrons are spin- paired.

The quantity  $2S + 1$  is the total spin and it is known as the spin multiplicity of a state.

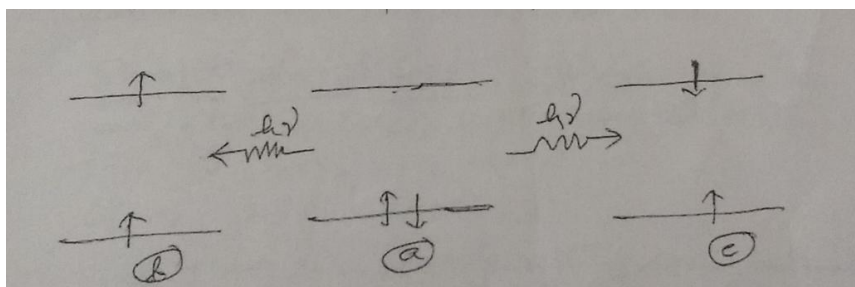


Fig 'a' – singlet ground state; Fig 'b' – Triplet excited state; Fig 'c' – singlet excited state



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#### **Singlet ground state:**

When the spins are paired as in (fig. 'a'), the upward orientation of the electron spin is cancelled by the downward orientation of electron spin, so that  $S = 0$ .

- $S_1 = +\frac{1}{2}$  and  $S_2 = -\frac{1}{2}$
- $S = S_1 + S_2 = \frac{1}{2} + (-\frac{1}{2}) = 0$ .
- Spin multiplicity  $= 2S + 1 = (2 \times 0) + 1 = 1$ .

Thus, **spin multiplicity of the molecule is 1** and the **molecule is in the singlet ground state**.

Hence, if the spin multiplicity of the molecule is 1 in the ground state, it is called as **singlet ground state**.

#### **Triplet excited State:**

When upon the absorption of a photon of a suitable energy,  $h\nu$ , one of the paired electrons goes to a higher energy level or excited state and the spins are parallel, as in (fig. 'b'), then  $S = 1$ .

- $S = S_1 + S_2 = (+\frac{1}{2}) + (+\frac{1}{2}) = 1$
- Spin multiplicity  $= 2S + 1 = (2 \times 1) + 1 = 3$ .

Thus, **spin multiplicity of the molecule is 3** and the **molecule is in the triplet excited state**.

Hence, if the spin multiplicity of the molecule is 3 in the excited state, it is called as **triplet excited state**.

#### **Singlet Excited State:**

When upon the absorption of a photon of a suitable energy,  $h\nu$ , one of the paired electrons goes to a higher energy level or excited state and if the spins are anti parallel as in (fig. 'c'), in the excited state, then  $S = 0$ .

- $S = S_1 + S_2 = (+\frac{1}{2}) + (-\frac{1}{2}) = 0$
- Spin multiplicity  $= 2S + 1 = (2 \times 0) + 1 = 1$ .

Thus, the **spin multiplicity of the molecule is 1** and the molecule is in the **singlet excited state**.

Hence, if the spin multiplicity of the molecule is 1 in the excited state, it is called as the **singlet excited state**.

The phenomenon of fluorescence and phosphorescence can readily be followed by **Jablonski diagram**.



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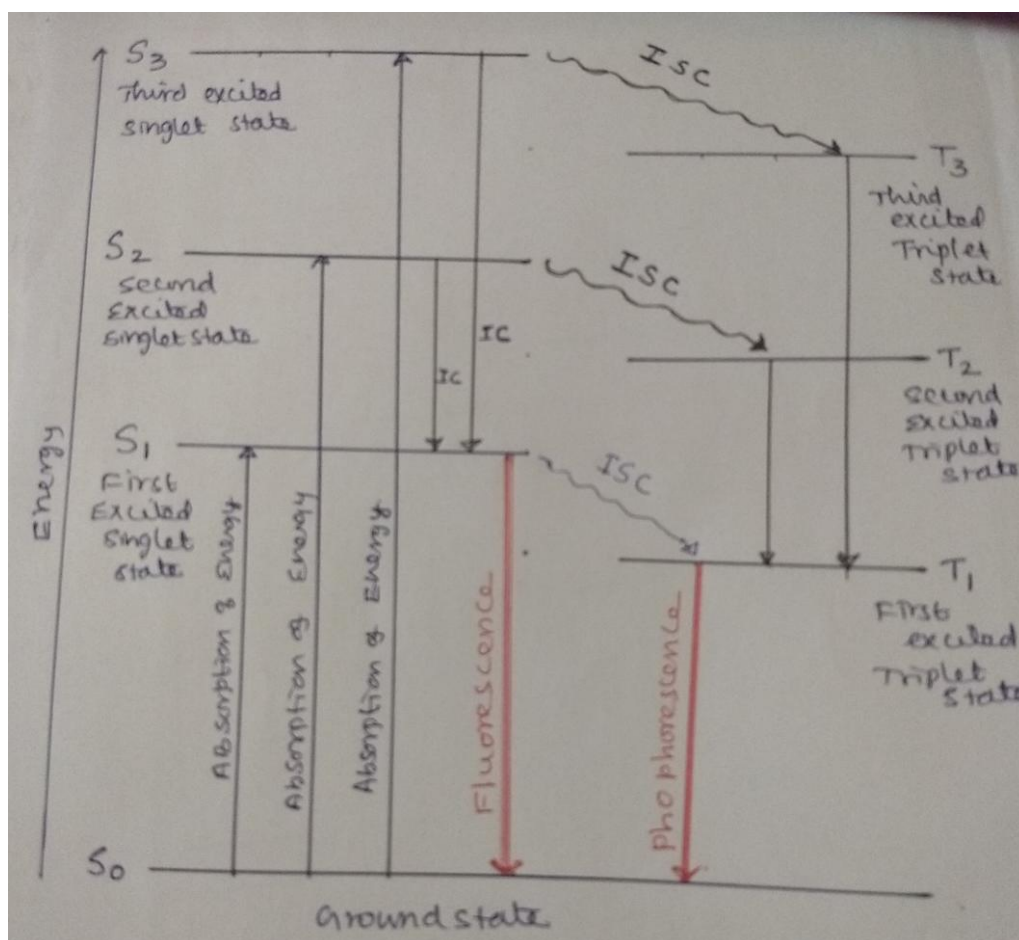
Since the electron can jump to any of the higher electronic states depending upon the energy of the photon quantum absorbed, it is possible to get a series of singlet excited states,  $S_n$  ( $n = 1, 2, 3, \dots$ ) and a series of triplet excited states  $T_n$  ( $n = 1, 2, 3, \dots$ ).

In other words  $S_1, S_2, S_3$ , etc., are known as first singlet excited state, second singlet excited state, third singlet excited state etc., and  $T_1, T_2, T_3$  etc., are known as first triplet excited state, second triplet excited state and third triplet excited state, etc.

It has been shown quantum mechanically that a singlet excited state has higher energy than the corresponding triplet excited state. Accordingly, the energy sequence is:

$$ES_1 > ET_1; \quad ES_2 > ET_2; \quad ES_3 > ET_3, \text{ etc.}$$

On absorption of light photon, the electron of the absorbing molecule may jump from  $S_0$  to  $S_1, S_2$  or  $S_3$  singlet excited state, depending upon the energy of the light photon absorbed, as shown in the following Jablonski diagram for various photo physical processes.



### Jablonski Diagram

- **Non – radiative Transition:** IC: Internal conversion; ISC – Intersystem crossing.
- **Radiative Transition:** Fluorescence and Phosphorescence.



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- For each singlet excited state ( $S_1, S_2, S_3$ , etc.), there is a corresponding triplet excited state ( $T_1, T_2, T_3$ , etc.)
- The molecule whether is in singlet or triplet excited state is said to be activated.



Where  $A_0$  is the molecule in the ground state and  $A^*$  is the molecule in the excited state. The activated molecule returns to the ground state by dissipating its energy through the following transitions.

#### **1. Non-radiative Transition:**

- These involve the return of the activated molecules from higher energy states ( $S_3, S_2$  or  $T_3, T_2$ ) to the first excitation states ( $S_1$  or  $T_1$ ).
- During these transitions, the energy of the activated molecules is dissipated in the form of heat through molecular collisions but don't involve in the emission of radiations and are therefore referred to as **non-radiative** or **radiationless** transitions. The process is called **internal conversion, IC**, and occurs in less than about  $10^{-11}$  sec.
- The molecules may also lose their energy by another process called **intersystem crossing, ISC**, which involves transitions between states of different spins, i.e., different multiplicity, as for example from  $S_3$  to  $T_3$  or  $S_2$  to  $T_2$  or  $S_1$  to  $T_1$  and occur at relatively slow rates. These transitions are also known as non-radiative or radiationless and are forbidden, spectroscopically. However they do occur though at relatively slow rates.

#### **2. Radiative Transition:**

- These involve the return of activated molecules from the singlet excited state  $S_1$  & triplet excited state  $T_1$  to the ground state  $S_0$ . Such transitions are accompanied by the emission of radiation.
- Spectroscopically the transition from  $S_1$  to  $S_0$  state is an allowed transition and it occurs in about  $10^{-8}$  sec. The emission of radiation in this transition is called **Fluorescence**.
- The transition from  $T_1$  to  $S_0$  is rather slow as it is a spectroscopically forbidden transition and has longer life time of the order of  $10^{-3}$  sec to 20 sec or greater, since this transition involves spin inversion which needs time for its occurrence. The emission of radiation in this transition is called **Phosphorescence**.
- Both fluorescent and phosphorescent radiations are of shorter frequencies than the exciting light. This is obvious because some part of light energy absorbed by the molecules is dissipated in the form of heat during the non-radiative transitions.



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#### **Characteristics of the phenomenon of Fluorescence:**

- It is an instantaneous phenomenon, i.e., it starts immediately re-emitting excess radiation within  $10^{-8}$  sec of absorption of light and stops as soon as the incident light is cut off.
- It is stimulated by light of the visible or UV regions of the spectrum.
- It is a general phenomenon and is exhibited by gases, liquids and solids. No fluorescence will be observed in gases unless the pressure is low.
- Different substances fluoresce with light of different wave lengths.
- Example: Fluorspar fluoresces with blue light and chlorophyll with red light.

#### **Examples of Fluorescent substances:**

- Chlorophyll present in green leaves, a naturally occurring substance show the phenomenon of fluorescence. i.e., when leaves are strongly illuminated in presence of  $O_2$ , they emit fluorescent light whose intensity changes with time of irradiations.
- Petroleum hydrocarbons (paraffin's and olefins), acetone,  $I_2$  and vapours of Na have been found to fluoresce in UV light.

#### **Characteristics of the phenomenon of Phosphorescence:**

- It is a non-instantaneous phenomenon. That is it reemits the excess radiation within  $10^{-3}$  to 20 seconds or longer. Thus, the life time of phosphorescence is much longer than fluorescence.
- It is stimulated chiefly by UV and Violet parts of the spectrum.
- Different colours may be obtained by mixing different phosphorescent substances.
- Example: Many phosphors are prepared by mixing alkaline earth metals with about 2.5% alkali chlorides and a trace of sulphide of some heavy metal.

#### **Examples of Phosphorescent substances:**

- The common substance that exhibit phosphorescence phenomenon are sulphides of Ca, Ba and Sr.
- Ruby and Emerald are the interesting examples of minerals which exhibit phosphorescence phenomenon.

#### **Applications:**

The phenomena of fluorescence and phosphorescence find useful applications in the development of X - ray and TV screens, fluorescent tube lights, optical brighteners, in white dress materials, luminescent dials for watches, in quantitative and qualitative analysis of inorganic and organic substances and in the sample analysis of food, pharmaceutical and medical fields.



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## **THERMOELECTRIC MATERIALS**

Certain materials allow heat to be pumped from one place using electricity. While some materials allow electricity to be generated from heat. These materials are called **Thermoelectric, TE, Materials**.

The conversion of waste heat into electrical energy play an important role in our current challenge to develop alternative energy technologies to reduce dependence on fossil fuels and reduce green house gas emissions.

### **Properties:**

The TE effect refers to a phenomenon by which either a temperature difference creates an electric potential called '**Seeback effect**' or an electric potential creates a temperature difference called '**Peltier effect**'.

The Peltier effect is the basis for many modern day refrigeration devices and Seeback effect is the basis for TE power generation devices.

### **Applications:**

- 1) **Power Generation:** Nearly 90% of world's electricity is generated by thermal power stations, i.e., by heat energy, whose efficiency is around 30-40%, thereby dissipating enormous power in the form of heat to the environment. TE devices could convert this waste heat into useful electricity. TE devices also find applications in systems such as solar thermal energy.
- 2) **Refrigeration:** TE coolers or Peltier coolers don't require refrigerant fluids, such as CFCs which can have harmful environmental effects.

TE refrigeration is an environmentally 'green' method of small scale localized cooling in computers, IR detectors, electronics and opto-electronics.

- 3) **Novel applications:** Bio thermal batteries, power heart pace makers, power generation for deep-space probes via radioisotope - TE generators.

### **Materials for TE device applications:**

Bismuth telluride,  $\text{Bi}_2\text{Te}_3$ , Bismuth selenide,  $\text{Bi}_2\text{Se}_3$  are good TE materials at room temperature and therefore suitable for refrigeration applications around 300K.

Silicon, Germanium, Si-Ge alloys are currently the best TE materials around 1000°C and are therefore used in radio- isotope - TE generation and some other high temperature applications, such as waste heat recovery.

Usability of Si-Ge alloys is limited by their high price.



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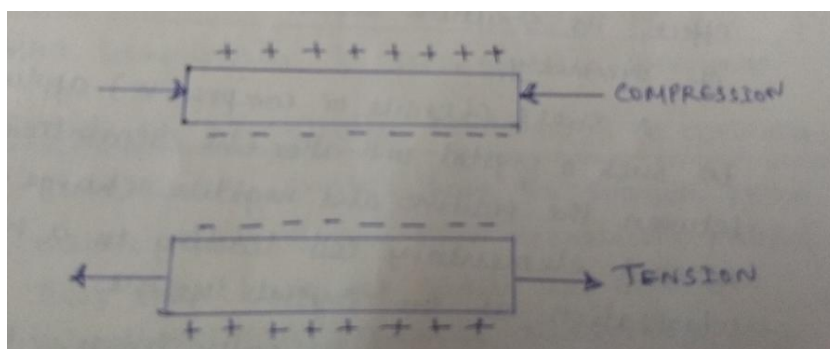
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## **PIEZO-ELECTRIC MATERIALS**

Materials when subjected to suitable force produce electrical potentials linearly related to the mechanical strains. This effect is known as '**Piezo Electric Effect**'.

These same materials deformed when they were exposed to an electric field. This has become known as '**Inverse Piezo Electric Effect**'.

Piezo electric effect is explained as:



The compression along the axis causes the upper surface to become +ve with respect to lower. If the material is subjected to a tension as a result of applied voltage or electric field along the axis, the polarity is seem to be reversed.

Since Piezo electric effect is reversible, all types of Piezo-electric microphones will function as weak sources of sound when an alternating voltage is applied.

For a crystal to exhibit the Piezo electric effect, its structure should have no centre of symmetry.

The common types of Piezo electric substances are Rochelle's salt, Ammonium dihydrogen phosphate, ADP, Lithium sulphate crystals and Barium titanate ceramic plates.

### **Application:**

Piezo electric substances have been widely used in crystal microphones that must operate over a wide range of temperature. Piezo electric microphones are widely used in public system and for hearing aids. These are highly sensitive, low in cost and small in size. These respond to frequencies ranging from 20Hz to 40Hz.