Bhartiya Vaidya Bhavan's Shri I. L. Pandya Art's-Science and J. Shah Commerce College, Dakor

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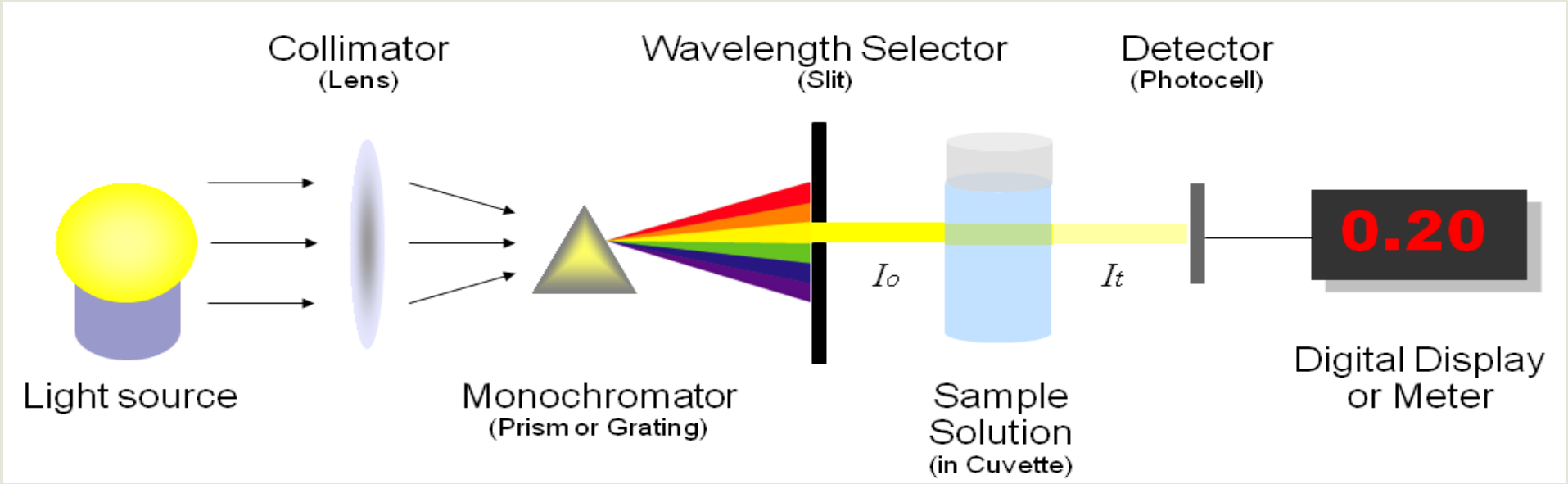
**TITLE OF PAPER : PHYSICAL CHEMISTRY**

# MONOCHROMETER

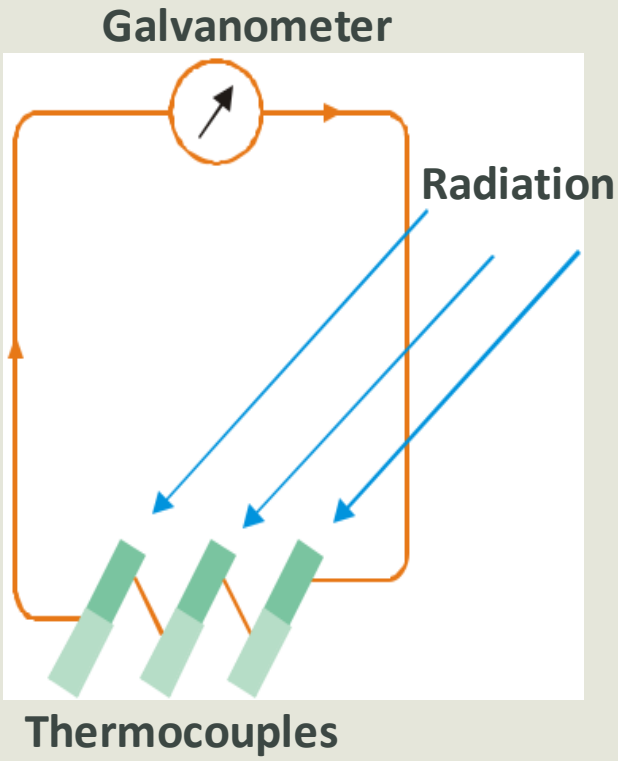
- A photochemical reaction occurs by the absorption of photons of light by the molecules.
- Therefore, it is essential to determine the absorbed intensity of light for a study of the rate of reaction.



- Light beam from a suitable source (tungsten filament or mercury vapour lamp) is rendered parallel by the lens.
- The beam then passes through a ‘filter’ or monochrometer which yields light of one wavelength only.
- The monochromatic light enters the reaction cell made of quartz. The part of light that is not absorbed strikes the *detector.*
- Thus the intensity of light is measured first with the empty cell and then the cell filled with the reaction sample.
- The first reading gives the incident intensity, $I_0$, and the second gives the transmitted intensity, $I$. The difference, $I_0 - I = I_a$, is the absorbed intensity.

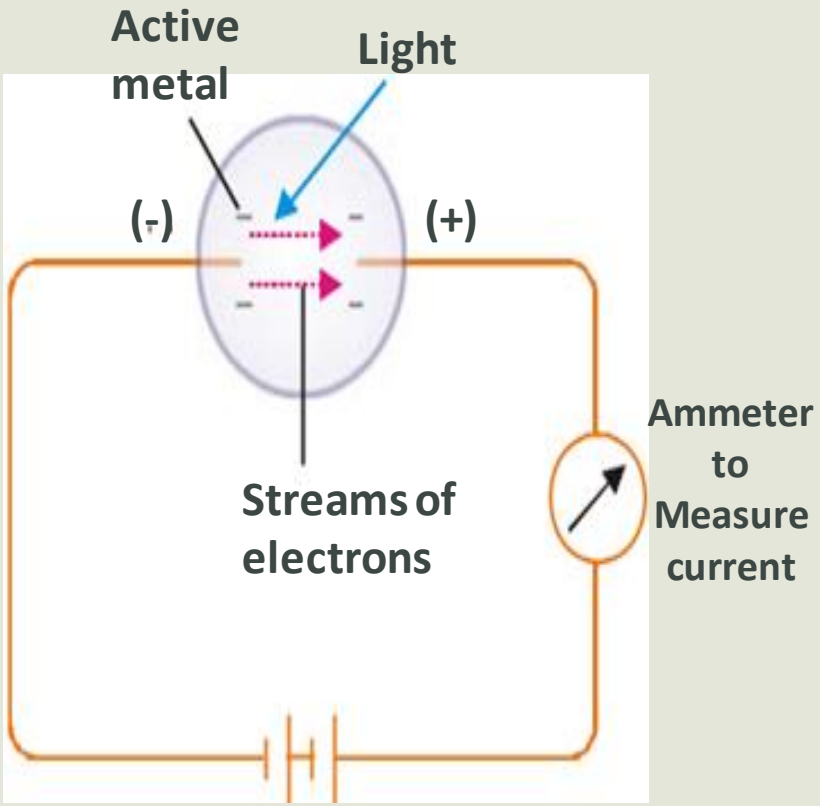
# THERMOPILE

- It is made of a series of thermocouples in which unlike metals such as bismuth and silver are joined together.
- One end of the couple is blackened with lamp black and the other end is left as such.
- When the radiation strikes the black end it absorbs energy and is heated up.
- The temperature difference between the two ends causes a current to flow in the circuit as indicated by the galvanometer.
- **The current is proportional to intensity of radiation.** The thermopile is previously calibrated against a standard source of light.



# PHOTOELECTRIC CELL

- A photoelectric cell can be conveniently used for measuring intensity of light.
- The light striking the active metal electrode (cesium, sodium or potassium) causes the emission of electrons.
- A current flows through the circuit which can be measured with an ammeter.
- The intensity of light is proportional to the current.



# CHEMICAL ACTINOMETER

- A chemical actinometer uses a chemical reaction whose rate can be determined easily. One such simple device is **Uranyl oxalate actinometer.**
- It contains 0.05 M oxalic acid and 0.01 M uranyl sulphate in water.
- When it is exposed to radiation, oxalic acid is decomposed to $CO_2$, CO and $H_2O$.

$$UO^{2+}_2 + h\nu \rightarrow (UO^{2+}_2)^*$$

$$(UO^{2+}_2)^* + \begin{vmatrix} COOH \\ | \\ \text{oxalic acid} \end{vmatrix} \rightarrow UO^{2+} + CO_2 + CO + H_2O$$

- The concentration of oxalic acid that remains can be found by titration with standard $KMnO_4$ solution.
- The used up concentration of oxalic acid is a measure of the intensity of radiation.

# PHOTOPHYSICAL PROCESSES

- If the absorbed radiation is not used to cause a chemical change, it is re-emitted as light of longer wavelength.
- The three such photophysical processes which can occur are：

a) Fluorescence

b) Phosphorescence

c) Chemiluminescence

# FLUORESCENCE

- **Certain molecules (or atoms) when exposed to light radiation of short wavelength (high frequency), emit light of longer wavelength.** The process is called **fluorescence** and the substance that exhibits fluorescence is called florescent substance.
- Florescence stops as soon as the incident radiation is cut off.
- **Examples :** (*a*) a solution of quinine sulphate on exposure to visible light, exhibits blue fluorescence.

  (*b*) a solution of chlorophyll in ether shows blood red fluorescence.

Figure : Fluorescent minerals, shown under ultraviolet light.



Figure : Tonic water is clear under normal light, but vividly fluorescent under ultraviolet light, due to the presence of the quinine used as a flavouring.

Figure : A solution of chlorophyll in ether solution shows blood red fluorescence.

- **Explanation :** When a molecule absorbs high energy radiation, it is excited to higher energy states. Then it emits excess energy through several transitions to the ground state. Thus the excited molecule emits light of longer frequency. The colour of fluorescence depends on the wavelength of light emitted.

# PHOSPHORESCENCE

- **When a substance absorbs radiation of high frequency and emits light even after the incident radiation is cut off, the process is called phosphorescence.** The substance which shows phosphorescence is called **phosphorescent substance.**
- Phosphorescence is chiefly caused by ultraviolet and visible light. It is generally shown by solids.
- **Examples :** (*a*) Sulphates of calcium, barium and strontium exhibit phosphorescence.

  (*b*) Fluorescein in boric acid shows phosphorescence in the blue region at 5700 Å wavelength.

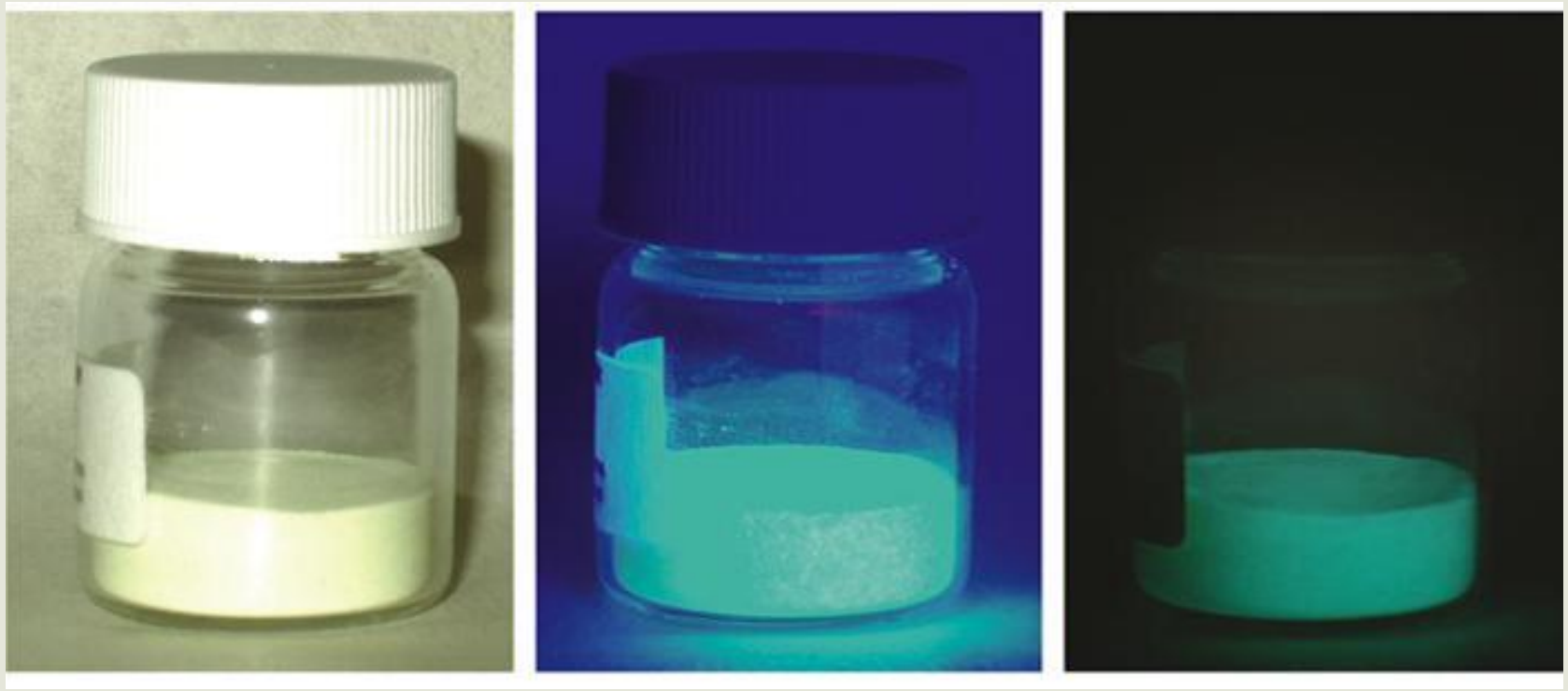


**Figure : Phosphorescent powder under visible light, ultraviolet light, and total darkness**

- **Explanation :** As in fluorescence, a molecule absorbs light radiation and gets excited. While returning to the ground state, it emits light energy of longer wavelength. In doing so the excited molecule passes from one series of electronic states to another and gets trapped. This shows the emission of light which persists even after the removal of light source. Thus **phosphorescence could be designated as delayed fluorescence.**

$$A + h\nu \rightarrow A^* \xrightarrow{slow} h\nu'$$

# CHEMILUMINESCENT

- Some chemical reactions are accompanied by the emission of visible light at ordinary temperature.
- **The emission of light as a result of chemical action is called Chemiluminescence.** The reaction is referred to as **a chemiluminescent reaction.**
- Such a reaction is the reverse of a photochemical reaction which proceeds by absorption of light. The light emitted in a chemiluminescent reaction is also called **'cold light'** because it is produced at ordinary temperature.
- **Examples :** (*a*) The glow of fireflies due to the aerial oxidation of *luciferin* (a protein) in the presence of enzyme *luciferase.*

  (*b*) The oxidation of 5-*aminophthalic* cyclic hydrazide (*luminol*) by hydrogen peroxide in alkaline solution, producing bright green light.

**Figure : Chemiluminescence of fireflies and luminol**

- **Explanation :** In a chemiluminescent reaction, the energy released in the reaction makes the product molecule electronically excited. The excited molecule then gives up its excess energy as visible light while reverting to ground state.


Thank You