

LITTLE FLOWER COLLEGE

**DEPARTMENT OF
CHEMISTRY**

***TOPIC : KINETICS OF FAST
REACTIONS***

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FAST REACTION

- Reaction which go to equilibrium in a few seconds are known as fast reactions.
- This reaction even proceed in less time can not be kinetically studied by conventional methods.
- The reasons for inability are as follows–
- A] The time it takes to make a measurement of concentration may be significant as compared to its half-life.
- B] The time it takes to mix reactants or to bring them to a desired temp may be significant as compared to the half-life of the reaction. An appreciable error creeps in because the initial time cannot be accurately determined.

Methods



- Relaxation methods
- Flash photolysis
- Molecular beams

Fast Reactions

Experimental methods for fast reactions

Flash photolysis method

The gaseous or liquid sample is exposed to a brief photolytic flash of light and then the contents of the reaction chamber are monitored. Both emission and adsorption spectroscopy may be used to monitor the reaction, and the spectra are observed electrochemically or photographically at a series of times following the flash.

FLASH PHOTOLYSIS METHOD

- It was first used by “PORTER”.
- This method has been used for the study of reactions in solution as well as those in gaseous phase.
- PHOTOCHEMICAL DISSOCIATION OF IODINE–If iodine vapour is illuminated with light of suitable wavelength , the dissociation occurs .



- NON-PHOTOCHEMICAL RECOMBINATION OF IODINE ATOM–

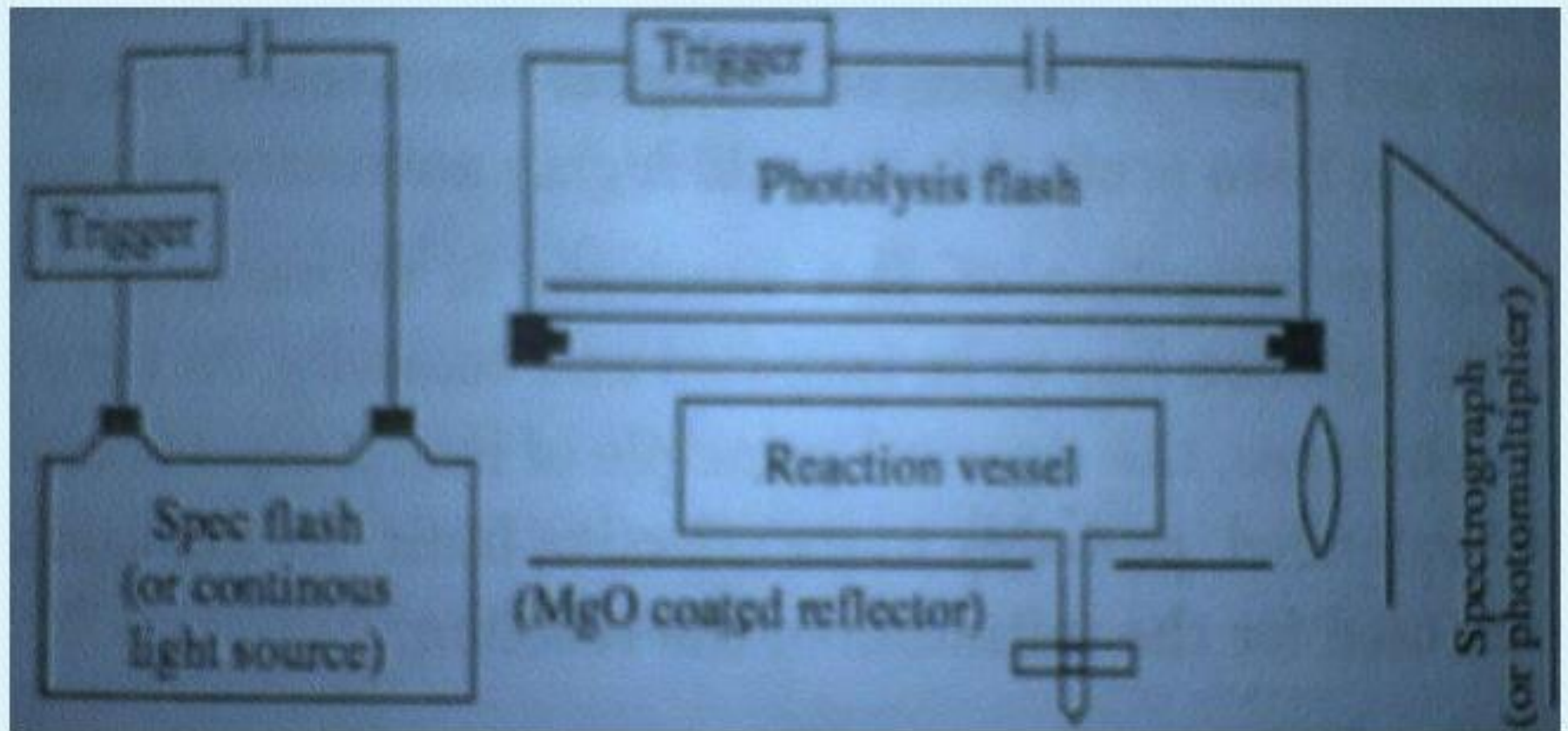


- ▶ Under steady illumination with light of moderate intensity , steady state is reached with only a very small fraction of iodine dissociated into atoms.
- ▶ This steady state is obtained when the rate of photochemical dissociation of iodine molecules and non-photochemical recombination of iodine atoms equals each other.

FLASH PHOTOLYSIS

- ▶ Flash photolysis is a commonly used fast reaction technique for photochemical reactions. For reactions with a moderate rate, flash lamps provide sufficient time response.
- ▶ To maintain nanosecond range flash photolysis technique is used.

Apparatus

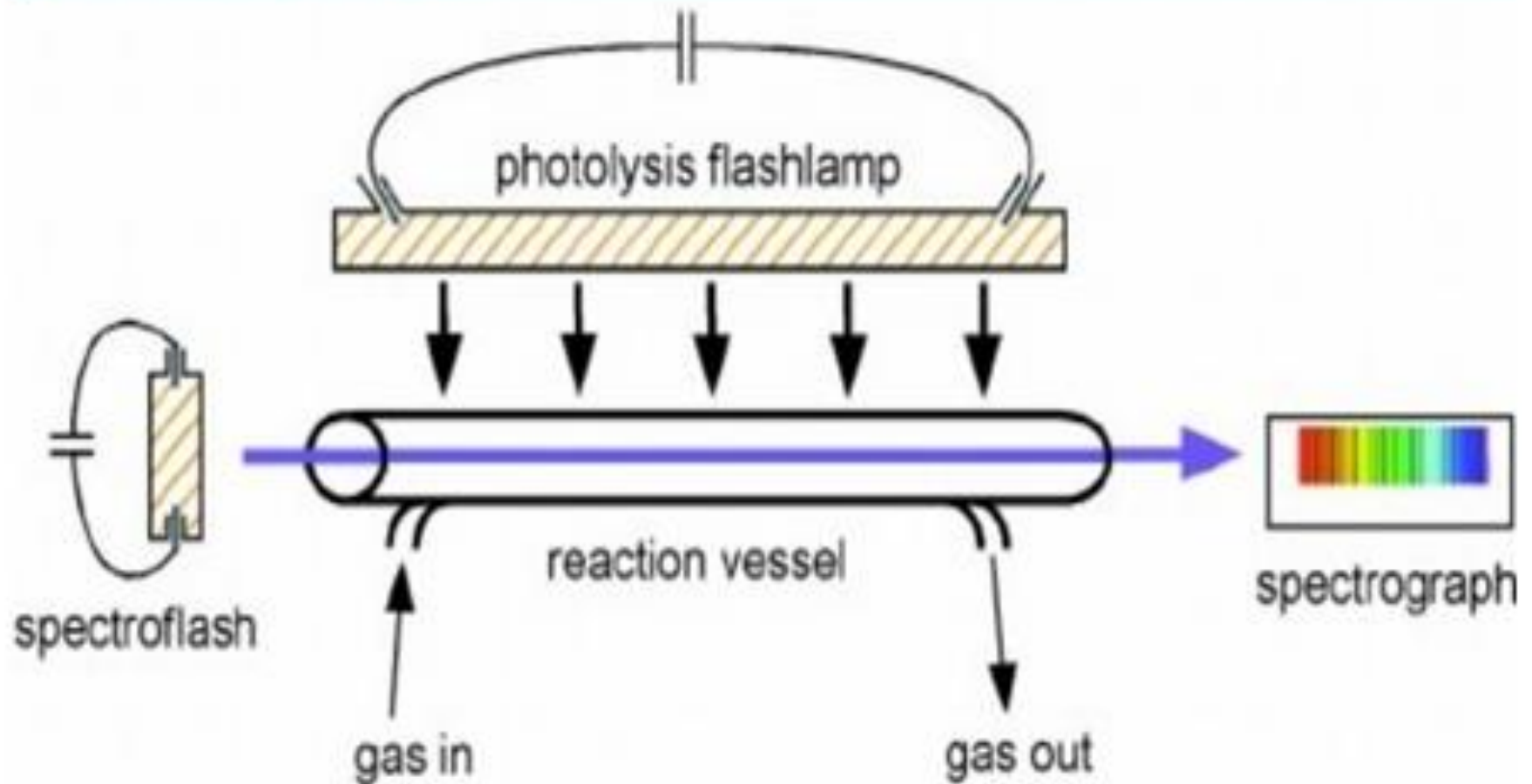




- ▶ In actual experiments , the peak intensity of a flash may build up in 10^{-5} sec and their decay over a period of 4×10^{-4} sec or even less.
- ▶ After the decay of light intensity from the flash , light of low intensity can be used in a spectrophotometric arrangement to follow the increase in concentration of molecular iodine.

PRINCIPAL OF FLASH PHOTOLYSIS

The principle of flash photolysis. A gas mixture flows into the reaction vessel, and reactions are initiated by a burst of intense radiation from a flash lamp. A second flash lamp acts as a source for measurement of the absorption spectrum of the resultant gas mixture.

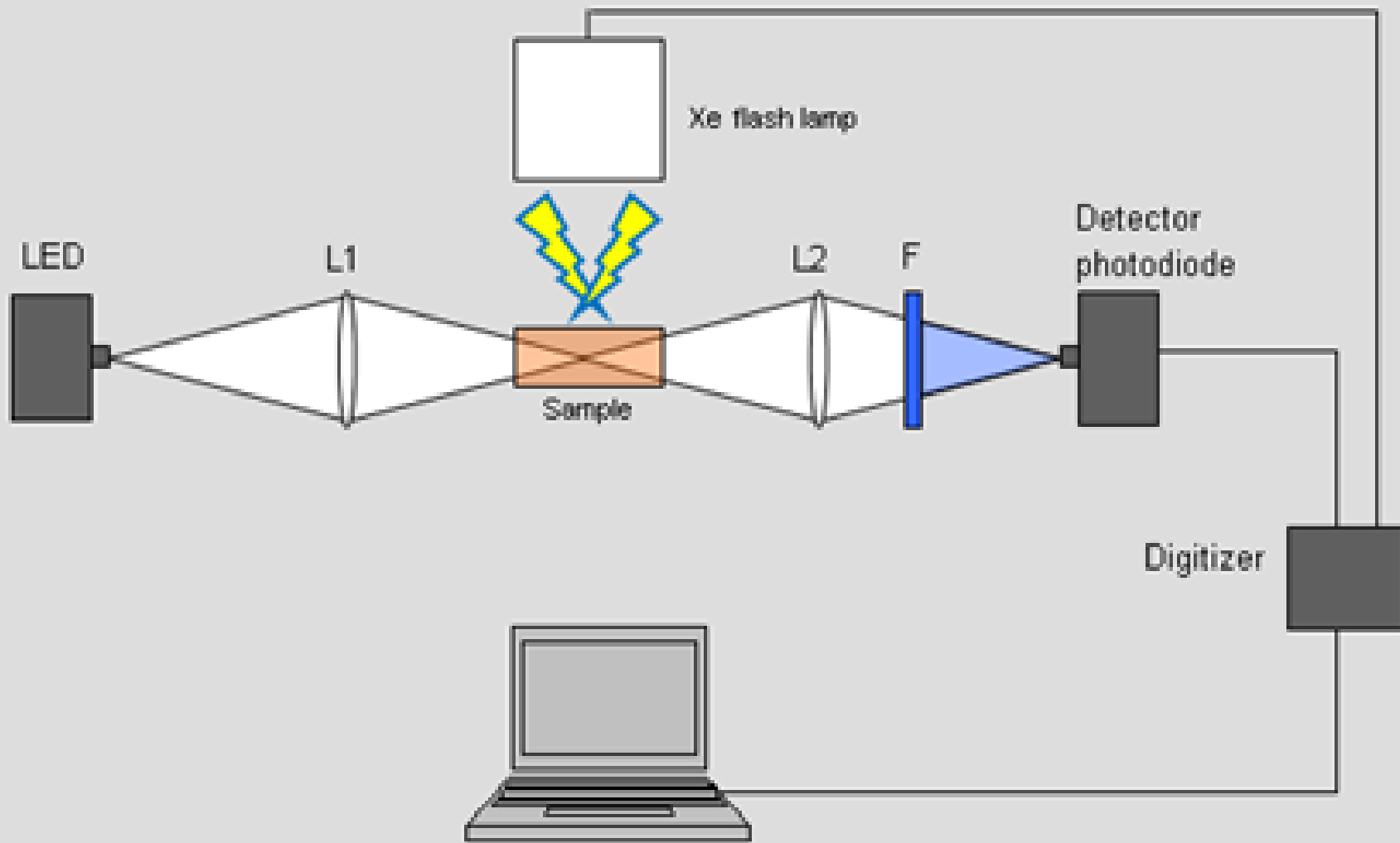


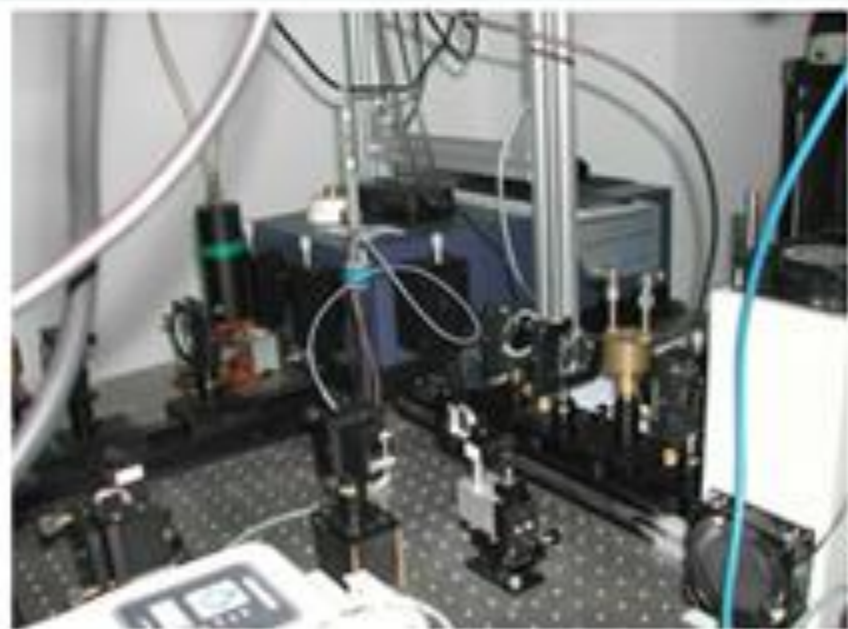
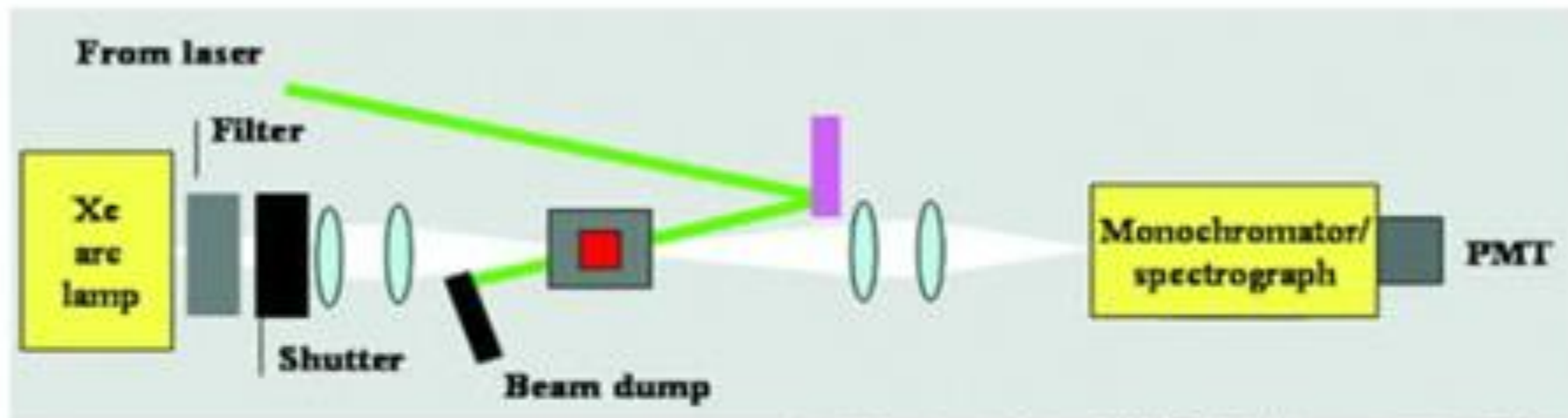
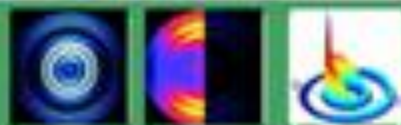
PRINCIPAL COMPONENTS OF A FLASH PHOTOLYSIS APPARATUS

- ▶ The principal components of a flash photolysis apparatus, apart from a spectrograph or monochromator, are an initiating photolysis flash source, a monitoring flash source, a τ -unit which introduces a delay between these two flashes and, for subsequent kinetic work at selected wavelengths, a monitoring source with photoelectric detection system. The substantial changes which have been made in each of these components

LASER FLASH PHOTOLYSIS

- ▶ A great advantage of the laser photolysis technique is that the laser pulse and the breakdown spark are automatically synchronized to within a few nanoseconds because they originate from the same primary laser pulse. No electronic circuitry is needed other than that required for operating the laser.



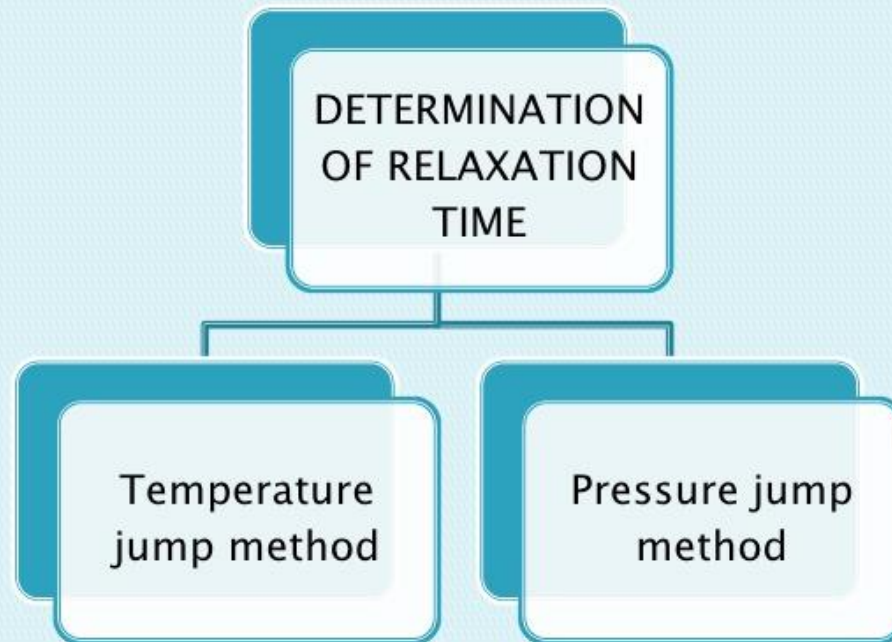


CHEMICAL RELAXATION METHOD

- ▶ In all relaxation method, a chemical equilibrium is perturbed by a rapid change in one of several possible external parameters, like electric field intensity , temperature and pressure.
- ▶ The equilibrium process is then followed by spectrophotometric or conductophotometric method.



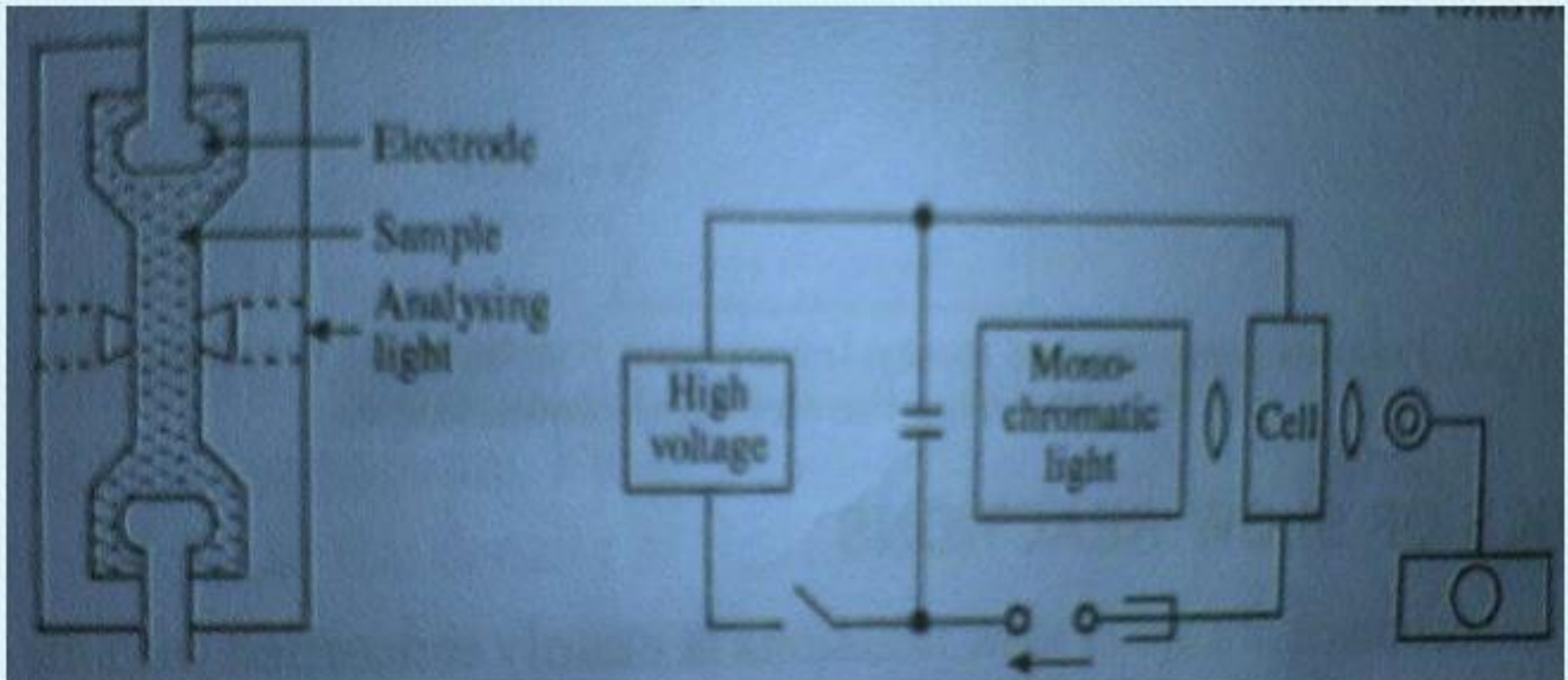
DETERMINATION OF RELAXATION TIME



TEMPERATURE JUMP METHOD

- ▶ A temperature change of several degrees [10^0c] in [10^{-5}s], is created by a discharge of high voltage condenser through a small quantity of solution . Then the time dependence of concentrations is followed by the adsorption spectroscopy.
- ▶ A temperature range of 1 degree centigrade has been found to change the equilibrium concentration by about 3%.

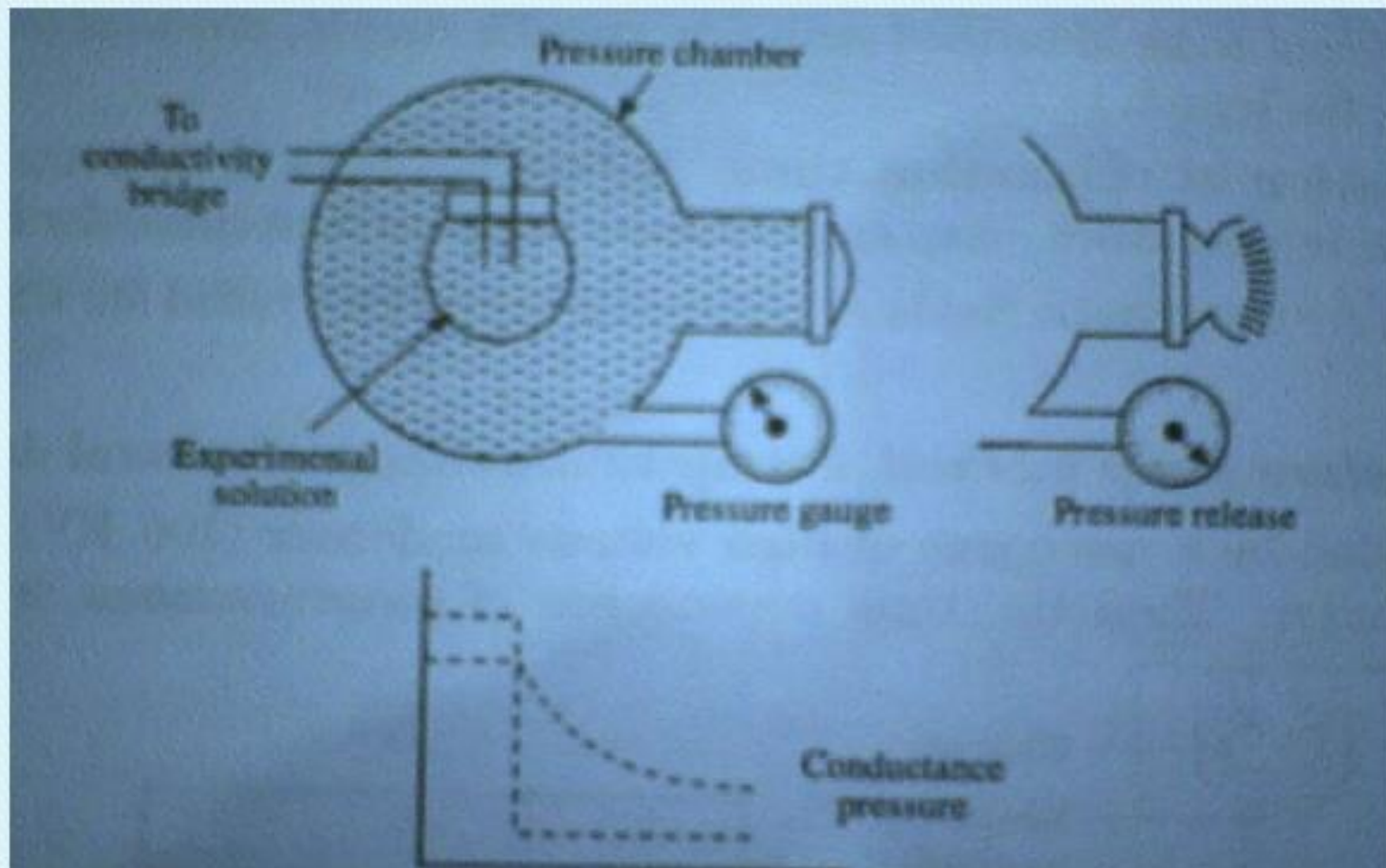
Apparatus



PRESSURE JUMP METHOD

- ▶ It involves a sudden and rapid change of pressure to displace the equilibrium.
- ▶ The sensitivity of a reaction to pressure depends on the change in volume ΔV and is represented quantitatively by the equation
- ▶
$$[\partial \ln K / \partial P]_T = -\Delta v / RT$$

Apparatus



THANK YOU