UNIT 1A - PAPER 2

WRITTEN BY

MR. ANIKET BHARDWAJ

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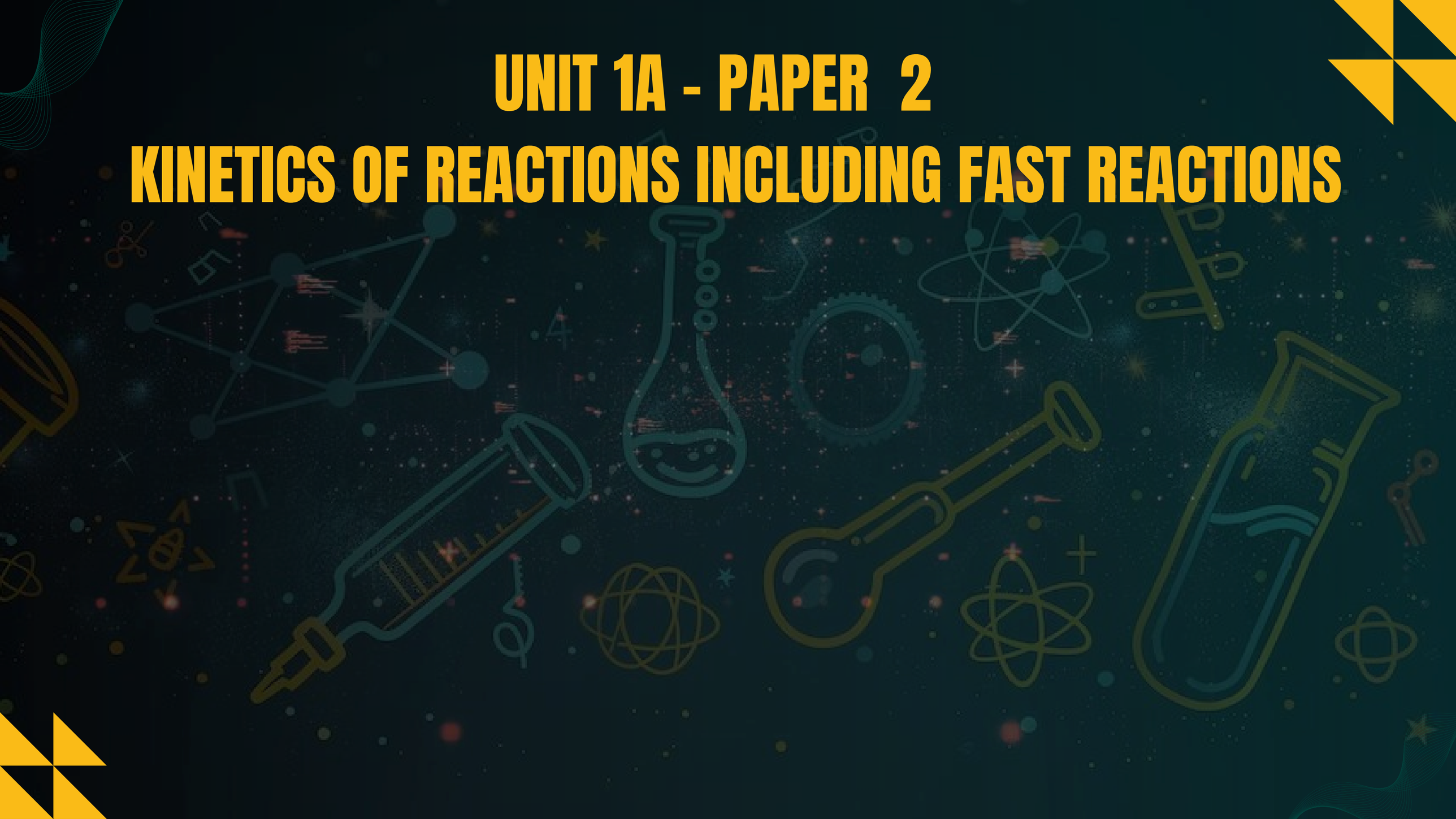
DWARKA, NEW DELHI, INDIA
9212149491

UNIT 1A - PAPER 2

KINETICS OF REACTIONS INCLUDING FAST REACTIONS



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KINETICS OF FAST REACTION

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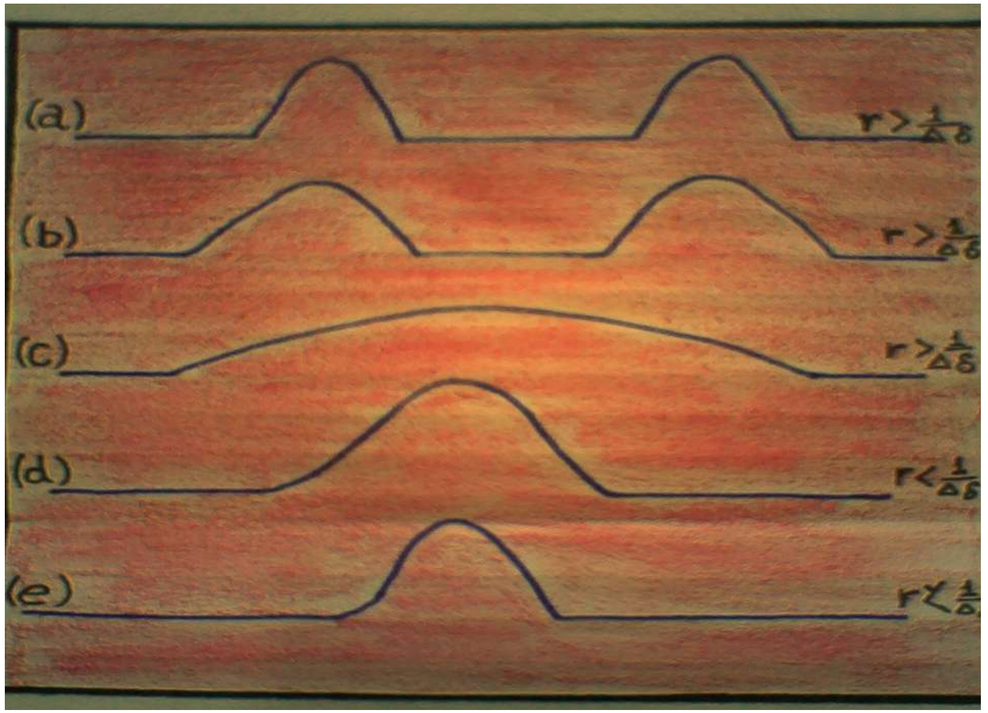
FAST REACTION

- 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-

1. The time it takes to make a measurement of concentration may be significant as compared to its half-life.
2. 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.

NUCLEAR MAGNETIC RESONANCE

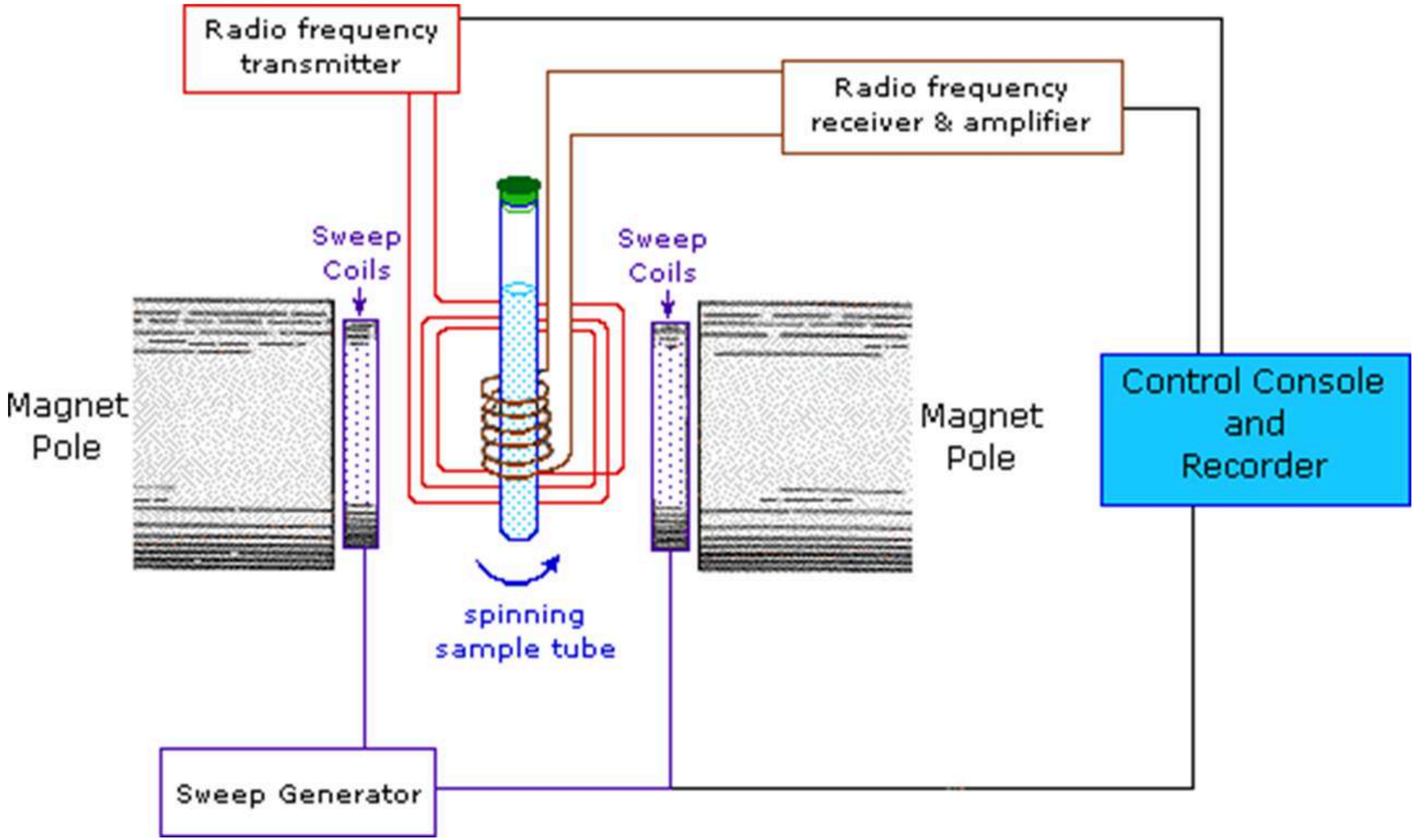
- Kinetic data on reactions in solution are obtained by NMR methods.
- This method is based on the fact that when two compounds with different NMR chemical shifts change rapidly from one to another, their two NMR peaks merge into one.



NUCLEAR MAGNETIC RESONANCE

- The NMR method is a relaxation method in which the systems studied are usually close to equilibrium, and those molecules which are excited by the absorption of radiation lose their excess energy rather quickly due to collisions.
- With relaxation methods, the rate constants of second order reactions with numerical values appreciably above Dd may be studied when the concentrations of reactants are substantially below ı M.

NMR SPECTROPHOTOMETER



FLOW METHOD

- Flow method is also known as “mix and shake” method in which the reactants are mixed within a fraction of a second.
- It was first developed by “ROUGHTON and HASTRIDGE” ,are used to measure the reaction half-time in the range from 1/10 sec to 1/1000 sec.

APPARATUS

- With flow of completely mixed solution at a constant rate , reaction occurs at a certain extent at a position along the observation tube.
- This condition exist because each position along the observation tube corresponds for a particular flow rate to the lapse of some definite time interval after mixing.
- Measurement of light absorption may be used conveniently in this type of experiment to determine the extent of reaction if the absorption spectrum of the product differs from that of the reactant.

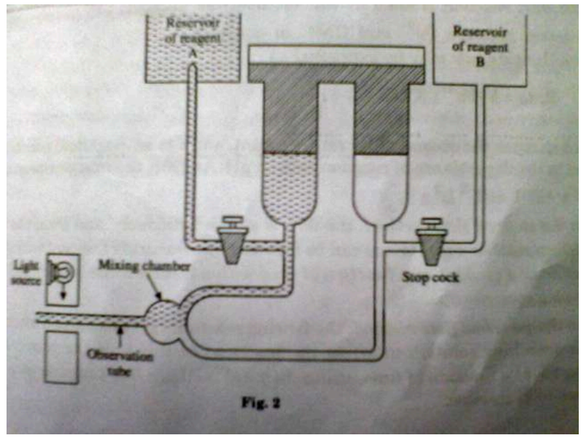


Fig. 2

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 DISSOSIATION OF IODINE-If iodine vapour is illuminated with light of suitable wavelength , the dissociation occurs .

$$I_2 + hv \rightarrow 2\ I$$

- NON-PHOTOCHEMICAL RECOMBINATION OF IODINE ATOM-

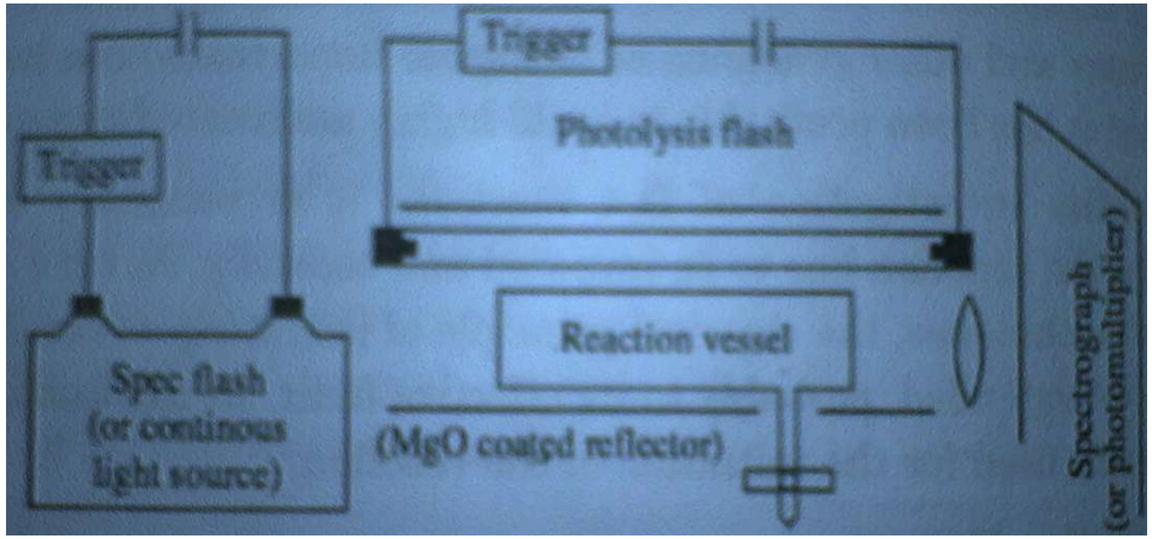
$$2I \rightarrow I_2$$

FLASH PHOTOLYSIS METHOD

- 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.

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 law intensity can be used in a spectrophotometric arrangement to follow the increase in concentration of molecular iodine.

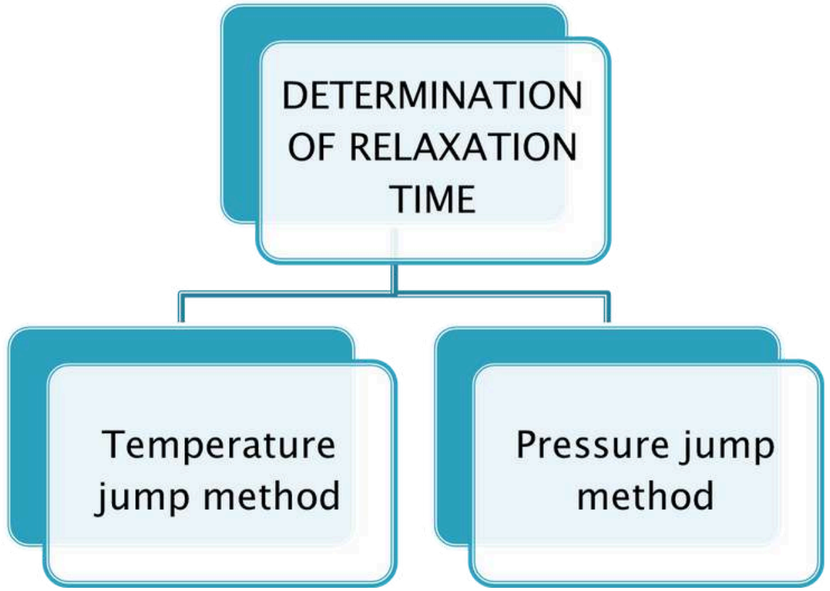


CHEMICAL RELAXATION METHOD

- 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

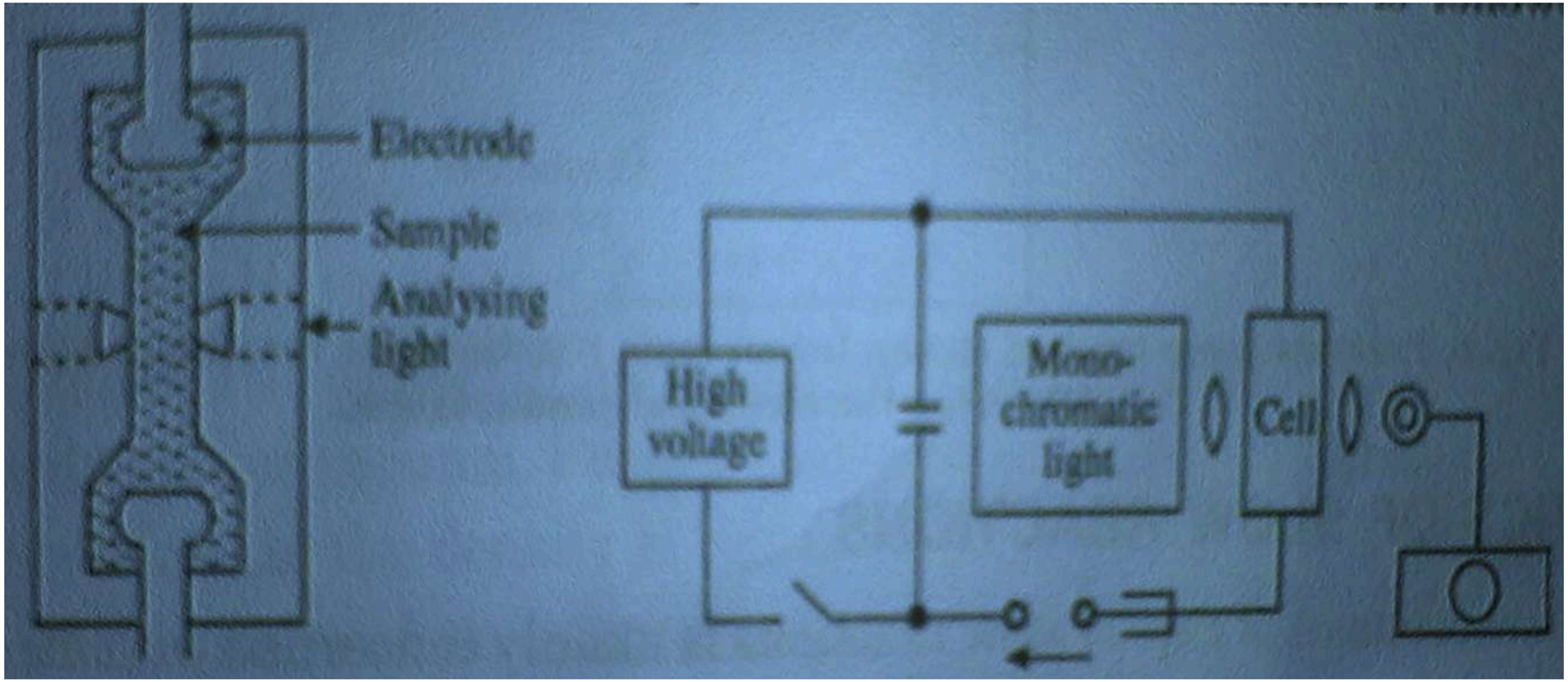
- In all relaxation method, a chemical equilibrium is perturbed by a rapid change in one of several possible external parameters, like electric field intensity , temperature and pressure.
- The equilibrium process is then followed by spectrophotometric or conduct photometric method.



TEMPERATURE JUMPMETHOD

- A temperature change of several degrees [ो c] in [¯ो 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 1degree centigrade has been found to change the equilibrium concentration by about 3%.

APPARATUS

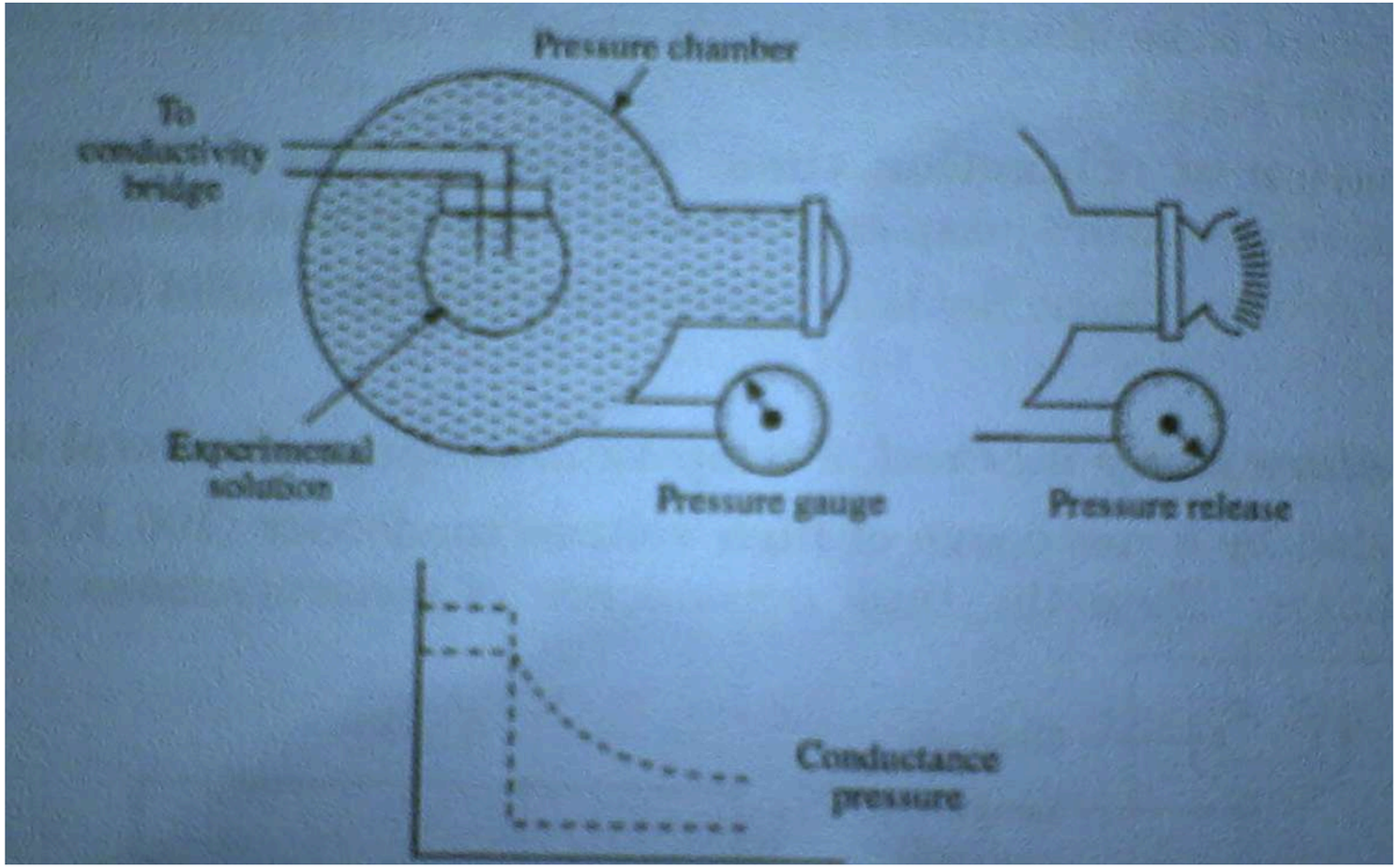


PRESSURE JUMPMETHOD

- 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 DV and is represented quantitatively by the equation

$$[\partial \ln K/\partial P]T = -Dv/RT$$

APPARATUS



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MR. ANIKET BHARDWAJ
Managing Director @ AbcChemistry

Ph.D. Chemistry (P)

AniketBhardwaj.Com

EDITOR
MRS. ABHILASHA BHARDWAJ

DESIGNER
MRS. SHWETA THAKUR