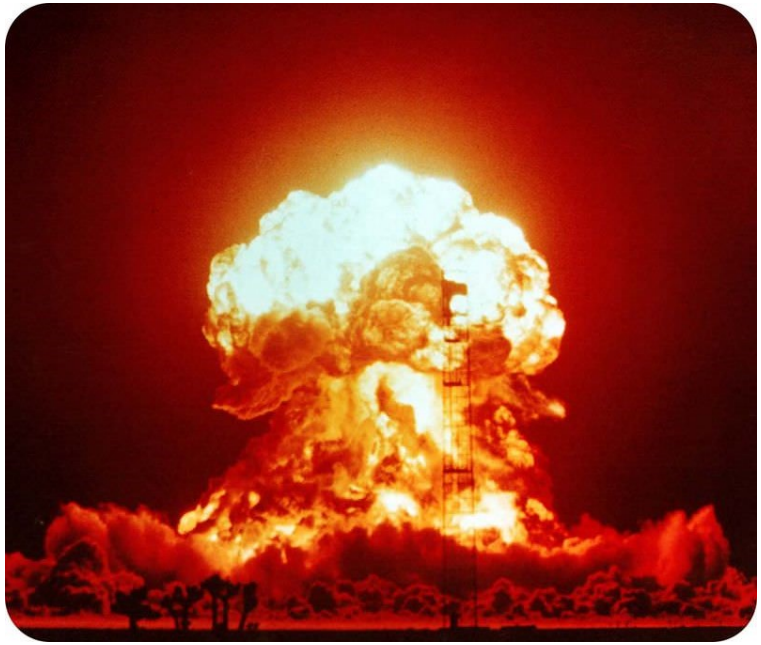
Fast Reactions



17 FAST REACTIONS

Fast reactions are reactions which take just a fraction of a second to complete. The kinetics of fast reactions are expressed in femtoseconds (10^{-15} s), picoseconds (10^{-12} s), nanoseconds (10^{-9} s), microseconds (10^{-6} s) or milliseconds (10^{-3} s). As these reactions take place in times shorter than the time required in mixing the reactants so these reactions cannot be investigated by conventional methods.

Study of fast reactions. The following techniques can be used :

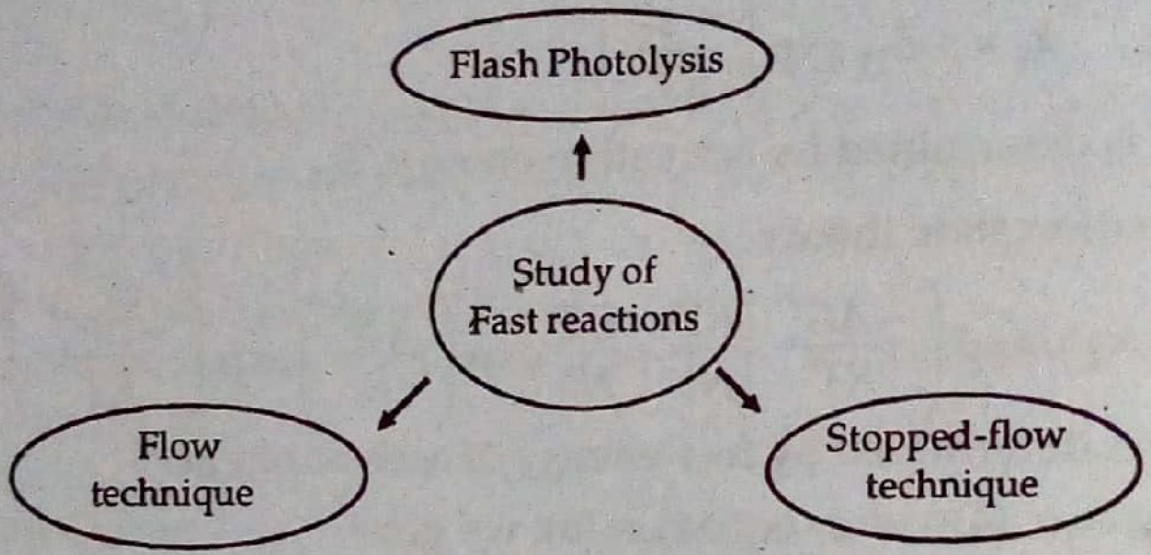


Fig. 18. Summary of techniques used to study fast reactions.

(*i*) ***Flash photolysis.*** In this technique, the liquid or gaseous sample is exposed to a brief photolytic flash of light with lasers, and then the contents of the reaction chamber are monitored spectrophotometrically. To monitor the reaction, either absorption or emission spectroscopy can be used and the spectra are recorded electronically at a series of times following the flash.

(*ii*) ***Flow technique.*** In this method, either syringes or peristaltic pumps (that squeeze the fluid through the flexible tubes) are used to eject the reactants (R_1 and R_2) in the form of jet from their chambers. The reactants are then mixed as they flow together in a mixing chamber (Fig. 19). As the thoroughly mixed solutions flow through the outlet tube, the reaction continues. The different points along the outlet tube correspond to different times after the start of the reaction. Along the length of the outlet tube, a moveable spectrometer is attached. The location of the spectrometer corresponds to different times after initiation. Thus,

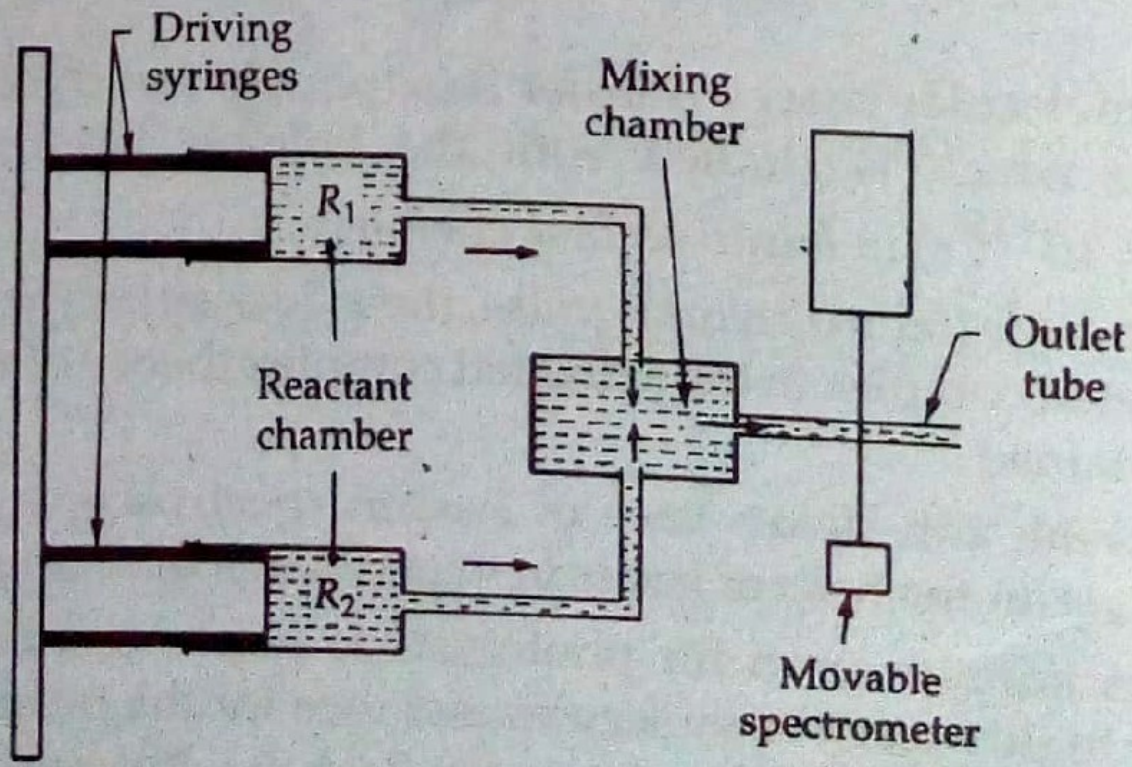


Fig. 19. The arrangement used in the flow technique for studying fast reactions.

the spectroscopic determination of the composition at different points along the outlet tube is equivalent to the determination of the composition of the reaction mixture at different times after mixing.

Note : The flow of reactants must be rapid to spread the reaction over an appreciable length of the outlet tube.

Limitation : A large volume of reactant solution is necessary, because the mixture must flow continuously through the appratus. Thus, this method is not appropriate for biochemical reactions.

(*iii*) ***Stopped-flow technique.*** In this method, the reactant solutions R_1 and R_2 are rapidly injected into a mixing chamber (Fig. 20). The design of the mixing chamber is such that it ensures turbulent flow of reactants so as complete mixing occurs very quickly. At the other end of the outlet tube, an observation cell is fitted. It has plunger that moves back as the liquid jet comes in, but it comes up against a stop after a certain volume has been admitted. the filling of the mixing chamber then corresponds to the sudden creation of an initial sample of the reaction mixture. The reaction then continues in this thoroughly mixed reactant solution & is monitored spectrophotometrically.

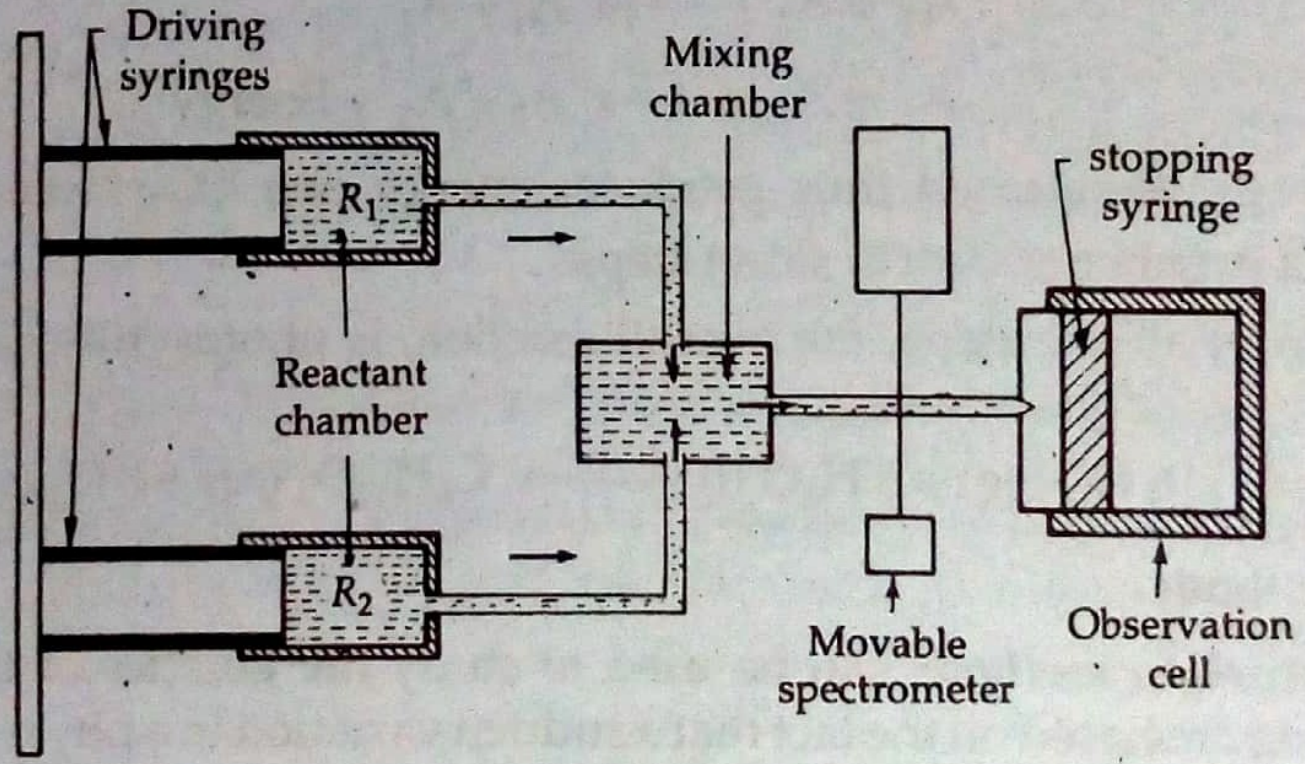


Fig. 20. The arrangement used in stopped flow technique for studying fast reactions.

Advantages of stopped-flow technique :

(*i*) It requires small reactant samples ;

(*ii*) It is more economical than the flow technique.

Applications of stopped flow technique :

This technique is preferrably used to study bio-chemical reactions as it requires small samples. Specifically speaking, it is used to study the kinetics of enzyme action.

Example 36. The activation energy of a non-catalysed reaction at 37°C is 83·68 kJ mol^{-1} and the activation energy of the same reaction catalysed by an enzyme is 25·10 kJ mol^{-1}. Calculate the ratio of the rate constants of the enzyme-catalysed and the non-catalysed reactions.

Solution : According to the Arrhenius equation, $k = Ae^{-E_a/RT}$

Let k_e and k_n be the rate constants of the enzyme-catalysed and non-catalysed reactions, respectively. Assuming that the Arrhenius pre-exponential factor A is the same in both cases, we have

$$\frac{k_e}{k_n} = \frac{e^{-E_a/RT}\,(\text{enzyme-catalysed})}{e^{-E_a/RT}\,(\text{non-catalysed})} = \exp\left(\frac{83{\cdot}68\ \text{kJ mol}^{-1} - 25{\cdot}10\ \text{kJ mol}^{-1}}{RT}\right)$$

$$= \exp\left[\frac{58{\cdot}58\ \text{kJ mol}^{-1}}{8{\cdot}314 \times 10^{-3}\ \text{kJ K}^{-1}\,\text{mol}^{-1} \times 310\ \text{K}}\right] = e^{22{\cdot}728}$$

or $\ln \dfrac{k_e}{k_n} = 22{\cdot}728$ and hence $\dfrac{k_e}{k_n} = 10^{10}$

Thus, the enzyme-catalysed reaction is about **10 billion times faster** than the non-catalysed reaction.


THANK
YOU