

KINETICS OF FAST REACTIONS

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10.1 INTRODUCTION

In the previous block you have learnt about the kinetics of reactions in gaseous and in solution phase. The time frame of these reactions is of the order of a few seconds to several minutes to hours. In this unit we will take up fast reactions, for which the time scale is of the order of a fraction of a second. You have learnt in your earlier classes that in a typical kinetic measurement, the reactants are mixed, homogenised by shaking, and the progress of the reaction that follows is measured as a function of time. These measurements are spread over a long period of time relative to the time of mixing of the reactants. However, in case of fast reactions such a difference in time of mixing and measurement is not possible because the reaction may get over even before the conventional mixing of the reactants. Therefore, we need to modify our strategy to study such reactions and it forms the subject of this unit.

We will begin the unit by defining fast reactions and outline the strategies that may be followed for studying them. Thereafter, we will take up flow techniques, one of the experimental strategies of studying fast reactions. In this context we will discuss different types of flow techniques in terms of their principle, method and the merits and limitations. This will be followed by a discussion on relaxation methods-another approach to study fast reactions. Herein, we will explain the principle of relaxation methods, relate relaxation time with the rate of reaction and describe the methods. We will also briefly state how the spectroscopic methods can be used to study fast reactions.

In the next unit you will learn about the kinetics of enzyme reactions.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define fast reactions;
- ❖ list different strategies used for studying fast reactions;
- ❖ define flow methods and list different flow methods used for studying fast reactions;
- ❖ explain the principle and describe the experimental set up of different flow methods used for the determination of the rate of fast reactions;
- ❖ discuss the merits and limitations of flow methods;
- ❖ define and classify relaxation methods used for studying fast reactions;
- ❖ derive an expression relating the relaxation time with the rate constants for a reaction involving a single equilibrium;
- ❖ explain the principle and describe the experimental set up of different relaxation methods used for studying fast reactions; and
- ❖ explain the principle of spectroscopic methods used for studying fast reactions.

10.2 WHAT ARE FAST REACTIONS?

As stated above, in a typical conventional kinetic measurement, the reactants are mixed; homogenised by shaking, and the progress of the reaction that follows is measured as a function of time. However, in certain reactions, it may so happen that the time required to mix reactants, may be larger in comparison with the half-life of the reaction. Therefore, we cannot determine the initial time accurately and there will be a large error in the rate determination. On the other hand, in some cases the time required to make concentration measurement may be large as compared to the half-life of the reaction. Here again, we cannot perform a reliable kinetic determination by conventional kinetic methods. You may have guessed that such issues will arise when the reaction is fast. How do we ascertain that a given reaction is fast?

As you know that in a typical conventional kinetic measurement, the reactants are mixed; homogenised by shaking, and the progress of the reaction that follows is measured as a function of time.

Whether a given reaction is fast or slow is a little difficult to state as these terms are relative and subjective. The question is, how fast is fast- a reaction getting over in a minute, a second or a millisecond or how do we ascertain? Alternatively, one may say that a reaction with a large value of rate constant is a fast reaction. This again raises the question of how large? Also, as you know that the rate constant is temperature dependent. Therefore, a reaction at high temperature may be fast but is relatively slow at low temperature.

Therefore, a reasonable basis to define fast reactions is whether it can be studied by conventional methods or not? A reaction whose kinetics cannot be studied by conventional methods at ambient temperature and moderate concentrations may be termed as **fast reaction**. Alternatively, a fast reaction may also be visualised as the one whose half-life is of the order of the mixing time for reactants i.e., less than a second at room temperature.

Thus, to study fast reactions as defined above, it is important to ensure that there is rapid mixing of reactants, quick initiation and fast analysis of the reactants (or products). For this a number of special strategies have been employed. Some of these are to:

- a) decrease the rate of the reaction by decreasing the temperature or the concentration of reactants.
- b) decrease the time required for mixing of the reactants. This can be achieved by using flow methods;
- c) quickly perturb the reaction equilibrium, and follow the changes occurring during the relaxation of the system to the same or a new equilibrium.
- d) observe competition between the desired reaction and a fast process of known rate

In this unit we will take up the techniques based on two of these strategies listed at b) and c) above. These are

- Flow techniques
- Relaxation methods

Let us learn about these techniques in details in the next section. However, before that answer the following simple question to assess your understanding.

SAQ 1

The conventional kinetic methods cannot be used to study fast reactions. Explain.

10.3 FLOW METHODS

Flow method was the first technique invented to study fast-reaction and is an important method used till today. The method was introduced by Hartridge and Roughton in 1923 in their study of the reaction between haemoglobin and oxygen and makes use of a continuous-flow system. Since then, a number of variants of flow methods have been employed to study the fast reactions. These have been used to study the kinetics of reactions in liquid and gas phases and are applicable for the reactions both with small or large equilibrium constants. Let us learn about the different flow methods.

10.3.1 Continuous Flow Method

The first apparatus based on flow method designed by Hartridge and Roughton, consisted of a mixing chamber from which the reactants were made to flow down a tube at high speed. A schematic diagram of the apparatus is given in Fig. 10.1. The principle of the method is that the reactants are forced under constant pressure into a mixing chamber from where they continuously flow into a uniform tube called **detection tube**. The concentrations of the reactants (or that of the products) are then determined as a function of distance along this tube. These determinations are done by measuring

physical properties of the species being determined employing suitable techniques. Generally absorption spectrophotometry, electrochemical, thermal or some other measurement is used for the purpose. For this method to be successful the half-life of the reaction needs to be more than mixing time and the detector response time needs to be much smaller as compared to the mixing time.

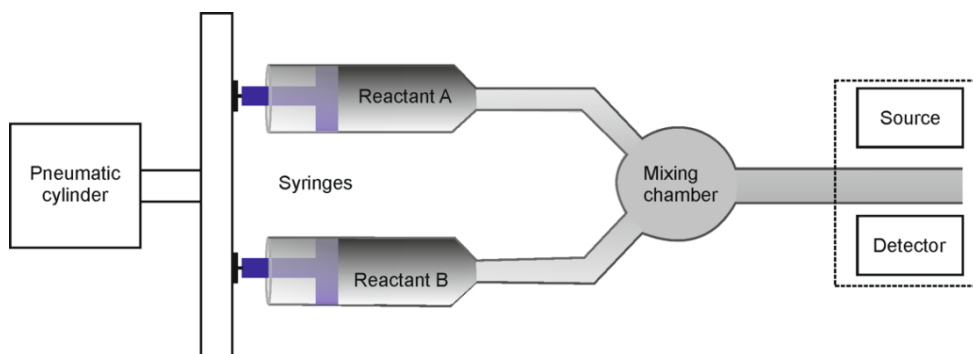


Fig.10.1: A schematic diagram of the continuous flow apparatus.

In a typical measurement using continuous flow method, the reactants are injected continuously into the mixing chamber. As a consequence, the profile of concentration of reactants and products along the detection tube, does not change with time. In other words, the composition of the reaction mixture varies as a function of the distance from the mixing chamber and not the time of measurement.

If we know the rate of flow and the diameter of the tube leading from the mixing chamber, we can relate the reaction time to the distance between the mixing chamber and the place where the reactants (or products) are measured / detected along the tube. In a way, *in the flow techniques, the clock as a timer in conventional methods is replaced by distance along the detection tube*. The rate of change of concentration of a reactant (say A) with time can be obtained by dividing the rate of change in its concentration with distance by the flow rate i.e.,

$$-\frac{dA}{dt} = \frac{-\frac{dA}{dx}}{\frac{dx}{dt}} = \frac{-\frac{dA}{dx}}{\text{Flowrate}} \quad \dots(10.1)$$

The measurement at a distance of 10 cm from the mixing chamber in a system having a flow rate of 10 m s^{-1} corresponds to a reaction time of 0.01 second. Similarly, the measurements at a distance of 20 cm, 50 cm and 1m along the detection tube will correspond to a time of 0.02, 0.05 and 0.1 s respectively. The reaction mixture is analysed at different points along the observation tube and is a measure of the progress of the reaction at different times. Using the measurements made at different distances (representing different times) we can prepare a concentration versus time plot, which in turn, can provide the rate constant for the reaction being studied.

Limitations of continuous flow method

Though the continuous flow method is quite simple and provides good results it has a few limitations such as

- We can study reactions having a half-life of $\geq 10^{-3}$ s only. Increasing the flow rate may permit the measurement at a still lesser time, however, then the flow will no more be lamellar and the results will not be reliable.
- We need to use high pressures to study gaseous reactions by continuous flow method. It is so because we need to measure the concentration changes due to reaction only. In case of low pressures the reaction mixture moves slowly along the detection tube. This may also allow the diffusion of the reactants and products thereby affecting their concentrations leading to an error in the determination of the kinetic parameters.
- We need a large volume of the reactant. The earlier experiments, required 3-4 dm³ of reactants per run. This becomes an issue when the reactants are somewhat expensive. However, with the use of narrow-bore tubing and mechanically-operated hypodermic syringes, the requirements of the reactant volumes have been considerably reduced.

In a variant of the continuous flow method, the rate of flow is continuously varied and the analysis is made at a fixed point along the observation tube. The method is called **accelerated flow method**. In such a case, as the rate of flow changes with time, the reactants reach at the fixed observation point at different times. The measured value of the concentration at different times helps generate a time-concentration plot which can then be used for the rate study. The advantage of this method is that it requires very small quantities of the reactant and is useful for studying enzyme reactions.

10.3.2 Stopped Flow Method

The stoppered flow technique, developed for solutions, is an improvement over the continuous flow method and addresses the issue of the requirement of large volume of the reactants. In this method, the solutions containing the reactants are taken in separate syringes and their pistons are pushed rapidly by a mechanical system to inject the reactants simultaneously into the mixing chamber, where the reaction starts. This acts as an efficient and rapid mixing device. The reaction mixture then exits into a tube and the flow of the reaction mixture is suddenly (in about 10^{-3} s) stopped. This is achieved by interrupting the flow by a stop syringe, which also controls the volume of the reaction mixture studied. A schematic diagram of the stoppered flow apparatus is given in Fig. (10.2). The smaller the distance from the mixing chamber at which the flow is stopped, the shorter is the time from the start of the reaction at the time of mixing. The reaction between the reactants continues here and the changes in the concentrations of reactants (or products) are followed in real time.

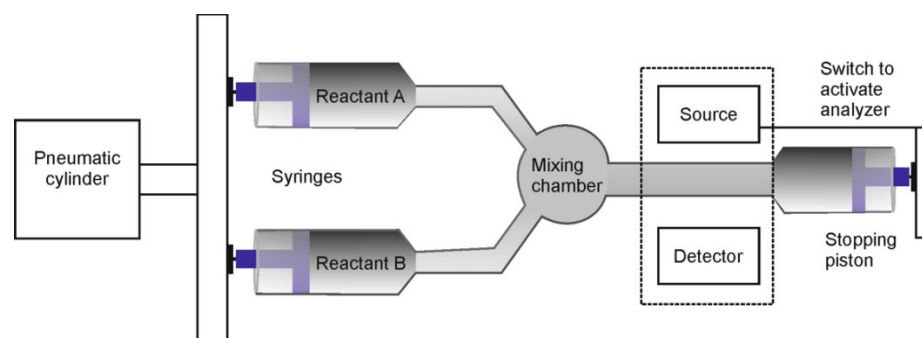


Fig.10.2: A schematic diagram of the stoppered flow apparatus.

It is important that the time of analysis must be very rapid and an inbuilt timing device is required. That is the detector response time must be much shorter than the reaction half-life. The time intervals at which concentration measurements are made is determined by the speed at which successive analyses are allowed by the detection method. The technique permits to follow changes in optical (or other) properties of solutions with a time resolution in the range of milliseconds to seconds. The concentration of the sample is normally measured by using spectroscopic methods; the detector is placed at the position of halting.

The advantages of the stopped flow method over continuous flow method are as under:

- small volumes of solutions are required,
- If the mixing is proper, the rate and character of flow does not affect the study
- Concentration-time plot is obtained that gives a complete record of the progress of reaction
- The rate equations for modelling the reactions are equivalent to those used in conventional methods.

The flow methods are good but have limitations of their applicability to study reactions having reaction times of the order of 1ms. For faster reactions we need to use relaxation methods. Let us learn about them. However, before that answer the following simple questions to assess your understanding of flow methods.

SAQ 2

Outline the limitations of continuous flow method.

SAQ 3

In an accelerated flow experiment the spectrophotometric concentration determinations are made at a fixed point located at 1 cm from the mixing chamber along the observation tube. If the initial flow rate of 2.0 m s^{-1} , is accelerated progressively to 4.0, 6.0, 8.0 and 10.0 m s^{-1} calculate the corresponding reaction times.

10.4 RELAXATION METHODS

The flow methods discussed above can be employed to study fast reactions having a timescale of about a millisecond. For reactions faster than that we need to use relaxation methods. The concept of chemical relaxation was first introduced by German physical chemist, Manfred Eigen in 1954 for which he was awarded the Nobel Prize in 1967. In this method of studying fast reactions, a reaction at equilibrium is quickly perturbed to a non-equilibrium position and is allowed to come back to the same or a new equilibrium. This process is then followed to determine the rate.

Since the equilibrium state corresponds to minimised free-energy state, it is called the 'relaxed' state.

The perturbation of the equilibrium could be brought about either by change of a state parameter or by some other external forces influencing the equilibrium. These include temperature, pressure, electric field, and chemical potential etc. Further the perturbations can be applied as a single impulse, or in a periodic manner. Since in the process of regaining equilibrium, the system relieves itself of the applied stress, it is referred to as **relaxation**. The concentration changes occurring during the relaxation process are rapid and are followed as a function of time. This is achieved by using a rapid detection method like, spectroscopy, mass spectrometry or chromatography etc. The rate at which the new equilibrium is established can be utilised to determine the rate of the reaction.

Relaxation methods are so designed that the rates and times of mixing of the reactants do not control the reaction. These methods are used in the kinetic study of reversible reactions and deal only with rate processes that are close to equilibrium because in such a situation, the mathematical procedures involved are quite simple. These are represented by linear relationships like, differential equations of first order. These linear relaxational processes are characterised by a time constant called the '**relaxation time**'. For a single step process under defined external conditions the relaxation time is related to the rate constants.

The principle of the relaxation method

The principle of the relaxation method can be understood by considering a simple equilibrium reaction as follows:



Where, k_1 and k_{-1} are the rate constants for the forward and the reverse reactions respectively. Initially at equilibrium, the reactant and product have certain concentrations that do not change with time until the equilibrium is disturbed, the temperature is suddenly increased or decreased i.e., the temperature jump occurs. At temperature jump, the concentration changes to a new value which will be higher or lower than the initial value depending on the sign of ΔH° for the reaction. The concentration-time plot during the relaxation process, can be used to determine the sum of the rate constants, $(k_1 + k_{-1})$, as shown by the following treatment. Also, the equilibrium constant for the reaction, determined separately, provides the ratio k_1/k_{-1} . These can then be used to determine the individual rate constants k_1 and k_{-1} . It is important to note that for the mathematical analysis of the data to be valid, the rates must be studied very close to equilibrium, i.e., the displacement from the equilibrium must be small. Further, when a single equilibrium is involved, then the relaxation to the new equilibrium position always simulates first order behaviour as discussed below. However, for systems with multi-step equilibria or equilibrium reactions involving consecutive steps the behaviour may or may not conform to first order. This aspect will not be taken up any further in this course.

Relationship between relaxation time and rate constants

Let us assume that we start with 'a' as the initial concentration of the reactant A and let the system come to the equilibrium with the concentration of B = x_e . The concentration of A at the equilibrium would be $(a - x_e)$. We can write the rate expression as

$$-\frac{dA}{dt} = k_1(a - x_e) - k_{-1}x_e \quad \dots (10.4)$$

Since at equilibrium the rate = 0, we can write

$$k_1(a - x_e) - k_{-1}x_e = 0 \quad \dots (10.5)$$

or

$$k_1(a - x_e) = k_{-1}x_e \quad \dots (10.6)$$

Once the perturbation is applied, the system is no more at equilibrium. Let us define the deviation from the equilibrium Δx , as

$$\Delta x = x - x_e \quad \dots (10.7)$$

Where, x is the new value of the the concentration of B; i.e., Δx represents deviation from the equilibrium. The system will recover now and the rate of change of the deviation (Δx) from equilibrium as a function of time will be given as

$$\frac{d\Delta x}{dt} = \frac{d(x - x_e)}{dt} \quad \dots (10.8)$$

$$\frac{d(\Delta x)}{dt} = \frac{dx}{dt} - \frac{dx_e}{dt} \quad \dots (10.9)$$

As the second term in Eq. (10.9) = 0, we can write

$$\frac{d(\Delta x)}{dt} = \frac{dx}{dt} \quad \dots (10.10)$$

Now since at any time t , the concentration of B is x , therefore the concentration of A will be $(a - x)$ we can write,

$$\frac{d(\Delta x)}{dt} = \frac{dx}{dt} = k_1(a - x) - k_{-1}x \quad \dots (10.11)$$

Simplifying,

$$\frac{d(\Delta x)}{dt} = k_1a - (k_1 + k_{-1})x \quad \dots (10.12)$$

Substituting for x from Eq. (10.7), we get

$$\frac{d(\Delta x)}{dt} = k_1a - (k_1 + k_{-1})(x_e + \Delta x) \quad \dots (10.13)$$

Simplifying, we get

$$\frac{d(\Delta x)}{dt} = k_1 a - k_1 x_e - k_{-1} x_e - k_1 \Delta x - k_{-1} \Delta x \quad \dots (10.14)$$

$$\frac{d(\Delta x)}{dt} = k_1 (a - x_e) - k_{-1} x_e - (k_1 + k_{-1}) \Delta x \quad \dots (10.15)$$

Substituting for $k_{-1} x_e$ from Eq. (10.6), we get

$$\frac{d(\Delta x)}{dt} = -(k_1 + k_{-1}) \Delta x \quad \dots (10.16)$$

Thus, we note that the quantity Δx varies in the same way as the concentration in the first order reaction with rate constant as $(k_1 + k_{-1})$.

Rearranging Eq. (10.16) we get

$$\frac{d(\Delta x)}{\Delta x} = -(k_1 + k_{-1}) dt \quad \dots (10.17)$$

Integrating Eq. (10.17) we get

$$\ln \Delta x = -(k_1 + k_{-1}) t + \text{const.} \quad \dots (10.18)$$

Since at $t = 0$, $\Delta x = \Delta x_0$ we get

$$\ln \Delta x_0 = \text{const.} \quad \dots (10.19)$$

Substituting in Eq. (10.18), we get

$$\ln \frac{\Delta x}{\Delta x_0} = -(k_1 + k_{-1}) t \quad \dots (10.20)$$

$$\frac{\Delta x}{\Delta x_0} = e^{-(k_1 + k_{-1}) t} \Rightarrow \Delta x = \Delta x_0 e^{-(k_1 + k_{-1}) t} \quad \dots (10.21)$$

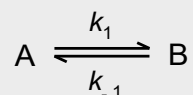
$$\text{When, } t = \frac{1}{(k_1 + k_{-1})}, \quad \Delta x = \Delta x_0 e^{-1} = \frac{1}{e} \Delta x_0 \quad \dots (10.22)$$

i.e., the value of Δx becomes $\frac{1}{e}$ of Δx_0 . This time is defined as **relaxation time** and is denoted as τ . Thus, *the relaxation time is defined as the time in which the deviation from equilibrium reduces to $\frac{1}{e}$ of its initial value.*

$$\text{Relaxation time} = \tau = \frac{1}{(k_1 + k_{-1})} \quad \dots (10.23)$$

Therefore, the determination of the relaxation time provides us the value of $(k_1 + k_{-1})$. As mentioned before, the ratio of the rate constants can be obtained from the equilibrium constant. Using this information, we can calculate the individual rate constants. Let us take an example to understand the application of relaxation method.

Example 10.1: The relaxation time of an equilibrium reaction of the type



determined by T-jump method is found to be $10 \mu\text{s}$.

If the equilibrium constant for the reaction determined separately is found to be 1×10^{-4} , calculate the values of rate constants for the forward and backward reactions.

Solution: As per Eq. (10.23), the expression for the relaxation time for the given fast reaction is:

$$\tau = \frac{1}{(k_1 + k_{-1})}$$

Substituting the value of relaxation time, we get

$$\frac{1}{(k_1 + k_{-1})} = 10 \mu\text{s} = 10 \times 10^{-6} \text{ s} = 10^{-5} \text{ s}$$

Now since the value of the equilibrium constant is given as 1×10^{-4} , we can say that the value of k_{-1} is far greater than k_1 (i.e., $k_{-1} \gg k_1$). Thus, ignoring, k_1 in comparison to k_{-1} , we can write

$$\frac{1}{k_{-1}} = 10^{-5} \text{ s}$$

Rearranging, we get

$$k_{-1} = \frac{1}{10^{-5} \text{ s}} = 10^5 \text{ s}^{-1}$$

Now, the equilibrium constant (K) for the given reversible reaction is given as:

$$K = \frac{k_1}{k_{-1}} \Rightarrow k_1 = K \times k_{-1}$$

Substituting the values of the equilibrium constant and k_{-1} , we can get the value of k_1 as

$$k_1 = (1 \times 10^{-4}) \times 10^5 \text{ s}^{-1} = 10^{-9} \text{ s}^{-1}$$

Different relaxation methods differ primarily in the type of stress applied to the system. The time range covered by relaxation methods includes more than nine orders of magnitude. The advantage with relaxation methods is that since the reaction is initially at equilibrium, we accurately know the time of start of the reaction which is an important consideration in case of fast reactions. Also, since the reactants are premixed and reaction is initiated by the applied impulse, there is no need for rapid mixing.

The Relaxation methods are classified into three groups based on the extent of perturbation applied to the reaction at equilibrium. These are:

1. Small Perturbation Methods e.g., Temperature jump and Pressure jump methods
2. Large Perturbation Methods e.g., Shock tube and Flash photolysis methods
3. Periodic Perturbation Methods e.g., Ultrasonic method

Let us learn about these relaxation methods.

10.4.1 Small Perturbation Methods

As the name suggests, in these methods the system at equilibrium is disturbed to a small extent by using suitable perturbation. These perturbations could be sudden changes in temperature, pressure, or electrical field. Here, we are going to take up two different methods based on the perturbations in terms of temperature and pressure respectively.

1. Temperature Jump Method

Among all the relaxation techniques developed for the study of fast reactions, the temperature jump method is probably the most widely used. The prerequisite for the applicability of this method is that the reaction must have a large value of ΔH . The change can be explained by using the relationship between temperature and equilibrium constant given by the van't Hoff equation.

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^0}{RT^2} \quad \dots(10.24)$$

This method can be used to study a large variety of reactions of organic, inorganic, and biochemical nature having a wide range of relaxation times from about $1\mu\text{s}$ to 1 s. The temperature jump (or T -jump) method is based on rapidly disturbing a chemical equilibrium through a sudden change of the temperature of the system. It involves rapidly heating the system to disturb the equilibrium and requires a method that heats the system faster than its chemical relaxation time. It is possible to increase the temperature of a small cell containing the reaction mixture by a few degrees in as small a time as about 100 ns. Such a sudden increase of temperature in an electrically conducting medium can be obtained by a fast input of electrical energy. This is generally done by the discharge of a capacitor that is charged by a high voltage power supply. The energy stored in the high voltage capacitor is suddenly released across the electrodes of a cell containing the solution under investigation. Such a short pulse (of the order of $1\mu\text{s}$) of electrical discharge at suitably high voltage can induce a temperature rise of up to 10°C within a few microseconds. This method of producing heating effect is referred to as **Joule Heating**.

A schematic representation of the experimental set up developed by Eigen and his Co-workers is given in Fig. 10.3.

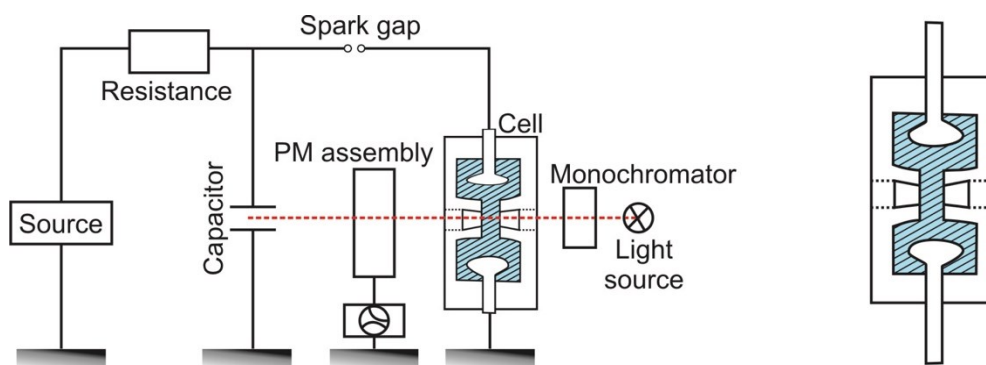


Fig.10.3: A schematic representation of the experimental set up for temperature jump method.

In a typical experiment the condenser is charged to a high voltage of the order of 20 to 100 kV. The capacitor is then discharged through the cell containing the experimental solution by firing the spark gap. This causes the temperature of the solution to increase by about $5\text{-}10^\circ$ within about $1\mu\text{ sec}$.

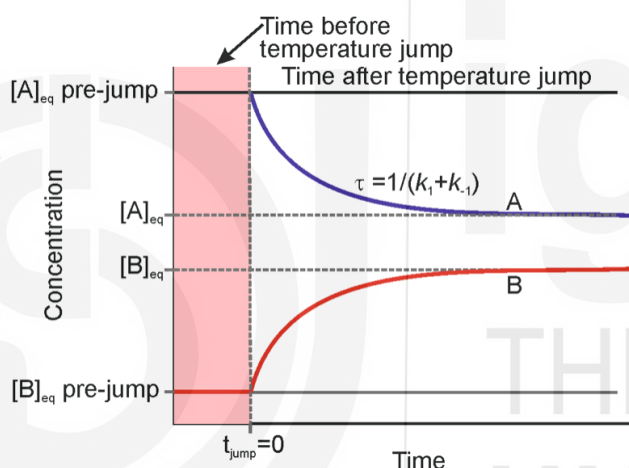


Fig.10.4: A typical concentration-time plot for T-jump method.

The subsequent change in the concentration manifested in terms of change in colour is followed by spectrophotometry or spectrofluorimetry using fast response detectors and suitably processing the obtained signal. These absorbance or fluorescence signals are related to the concentration of the species involved in the reaction. A typical concentration-time plot obtained in this method is given in Fig. 10.4.

2. Pressure Jump Method

This relaxation method is applicable to reactions that are sensitive to changes in pressure and can be utilised to study reactions having relaxation times of greater than 5×10^{-5} s. This method utilizes a sudden perturbation of a reaction at equilibrium by a rapid increase or decrease in pressure. When the reaction at equilibrium is exposed to such a large and sudden change in pressure, the reaction adjusts to a new equilibrium controlled by the rate constant(s) for the reaction. This approach to the new equilibrium is followed by sensitive conductimetric measurements.

In one of the methods, to induce a rapid jump in the pressure the reaction vessel at atmospheric pressure is separated from another vessel at extremely high pressure by using a diaphragm. Suddenly breaking the diaphragm increases the pressure on the reaction by upto a hundred atmospheres in a very short time of the order of a hundred microseconds. This method is like the shock tube discussed later.

In another method, first the pressure on the system under study is raised to a very high value and the system is allowed to attain equilibrium. The perturbation is caused by suddenly dropping the pressure back to the ambient pressure. For this, the experimental cell is placed in an external pressure vessel and a high pressure is set up in the pressure vessel. Once the equilibrium is set up, the pressure vessel is suddenly punctured and in a short time of about 1 ms the pressure is reduced to one atmosphere. A schematic of the experimental set up for this method is given in Fig. 10.5. Thereafter, the recovery of the system is followed by measuring a suitable physical property e.g., the electrical conductance is one of the commonly used physical property. A typical concentration-time plot so obtained is given in Fig. 10.6.

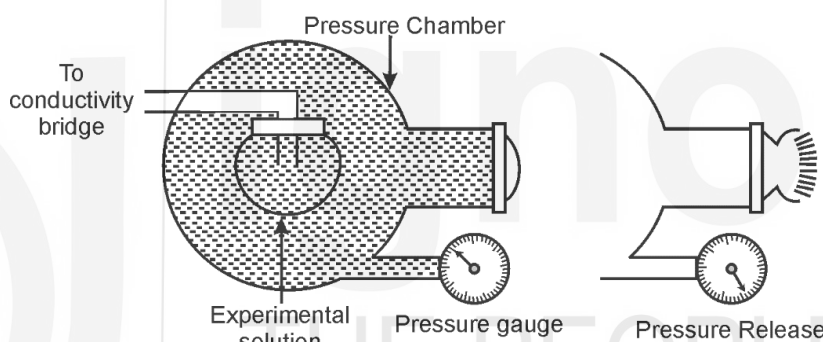


Fig.10.5: A schematic diagram of the experimental set up for pressure jump method.

The shift in equilibrium on sudden change in pressure can be described in terms of Van't Hoff equation i.e.,

$$\left(\frac{\partial \ln K}{\partial p} \right)_T = \frac{\Delta V^0}{RT} \quad \dots (10.25)$$

It may be noted that a change in pressure causes p - V work that is very small for liquids. Therefore, in liquid systems, the p -jump causes small perturbation of the equilibrium. On the other hand, in gaseous systems there may be significant perturbation. Nonetheless, the technique is used for liquid as well as gaseous systems, though it is better suited for reactions in gaseous systems.

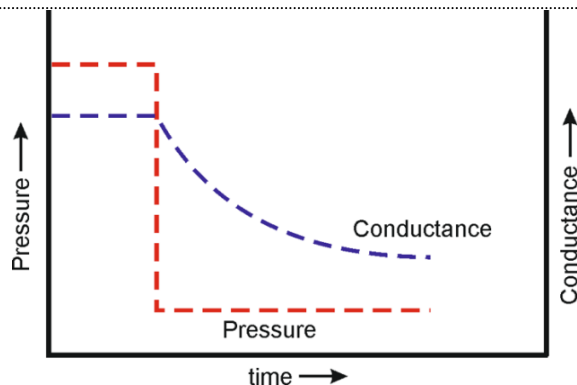


Fig.10.6: A typical concentration-time plot for P-jump method.

As discussed in case of T -Jump method, following the relaxation of the reaction, we can determine the rates. p -jump method can be used to study the kinetics of reactions like, enzyme-substrate complex formation or metal-enzyme and metal-substrate complexation reactions. A typical concentration-time plot for p -jump method using conductance as a measure of concentration is given in Fig.10.6.

10.4.2 Large Perturbation Methods

In these relaxation methods the system at equilibrium is disturbed by a large perturbation like a huge pressure shock or a strong flash of radiation. Let us learn about the relaxation methods based on these perturbations.

1. Shock Tube Method

The shock tube method has emerged as an excellent method of studying fast homogeneous gas-phase reactions at high temperatures. It allows to heat the gaseous reaction mixture to the higher temperature very quickly. It is achieved by passing a shock wave through the reaction mixture. The shock tube is a long metal tube divided into two sections separated by a diaphragm made of a metal foil or some other material that can be ruptured. The gaseous reaction mixture is placed on one side, called **driven side**, of the diaphragm at ambient pressure. On the other side, called **driver side**, the driver gas—a low molecular weight gas like helium or hydrogen, is taken at extremely high pressure. On the driven side there are several pressure gauges at different distances and optical arrangement to measure the spectral properties of the system. A schematic of the experimental set up for this method is given in Fig. 10.7.

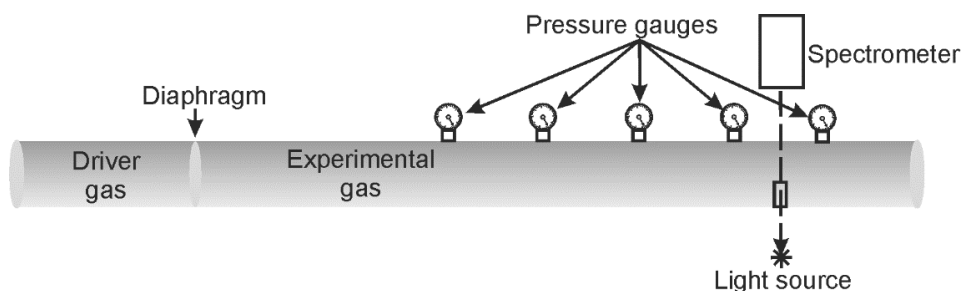


Fig.10.7: A schematic diagram of the shock tube set up.

The pressure on the driver section is increased up to a level where the diaphragm bursts. As a result, the driver and driven gases come into contact and create a contact surface that acts as a kind of piston. The released gas

produces a series of pressure waves, that start the propagation of a shock wave through the driven gas. This shock wave compresses the gas in the driven section and suddenly increases the temperature and pressure of the driven gas. This induces a flow in the direction of the shock wave. The shock wave then reflects from the wall of the shock tube at the closed end and causes further heating and compression of the reaction mixture.

After passing the shock wave the extent of reaction is determined as a function of time by absorption measurement at different points along the driven section. The appropriate beam of light is used for this purpose. This method has been successfully used to study fast reactions like, the vibrational and rotational energy transfers between gaseous molecules.

2. Flash Photolysis Method

Fast reactions, in gaseous as well as in liquid phases, can be studied by flash photolysis method. This important modern technique of studying fast reactions was developed by Norrish and Porter for which they got the Chemistry Nobel Prize in 1967. This method involves the production of radicals in the reaction mixture at relatively high concentrations. In this method, a flash of very high intensity of visible or ultraviolet radiation is produced close to the reaction vessel by a **photoflash** lamp for a very short duration ($\sim 10^{-6}$ s). This duration is lesser than the reaction time scale. The flash dissociates and excites molecules in the sample to produce atoms, free radicals, and excited species in the reaction system. These species then undergo further reactions in the system which can be followed in real time using spectroscopic tools.

Once the species of interest are produced, these need to be measured by using appropriate rapid detection method. Transient optical absorption spectroscopy is the method of choice for this and is commonly used. The absorption spectrum of the desired species is obtained by using a second lamp called **spectroflash** that is located at the other end of the reaction cell. The measurement is done at fixed intervals after the initial flash as described below. The series of spectra measured at different times after the initial flash provide important information about the course of the reaction.

A schematic diagram of the experimental set up of flash photolysis method is given in Fig. 10.8. The apparatus consists of a reaction vessel two flash lamps namely the photoflash and spectroflash lamps. The photoflash lamp is located perpendicular to the reaction cell whereas the spectroflash is in line with the reaction cell as shown in the diagram.

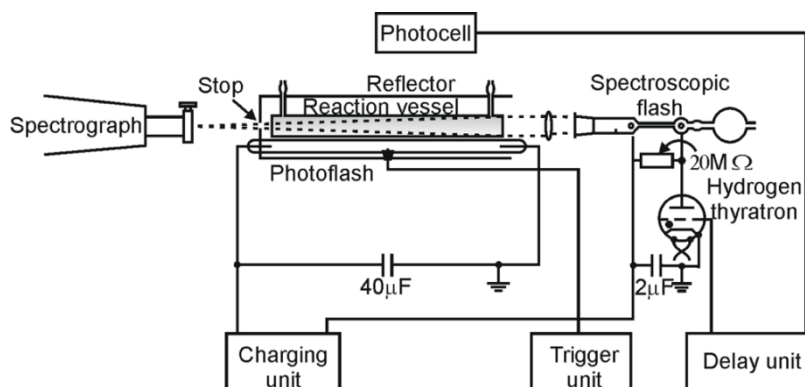


Fig.10.8: A schematic diagram of the flash photolysis apparatus set up.

The photoflash lamp generates a high-intensity light flash ($\sim 10^5\text{J}$) of about $100\ \mu\text{s}$ duration produced by discharging several condensers. This is linked by a delay unit to a spectroflash that is set to fire at time intervals of the order of about $200\ \mu\text{s}$ after the photoflash. The first flash initiates the reaction and generates the desired species whereas the second flash helps record the absorption spectrum at the predetermined time. The spectrum is captured on the photographic plate of the spectroscope at one end of the reaction vessel. It is important to note that the energy and duration of the spectroflash must be so adjusted that it does not interfere with the ongoing reaction but has sufficient intensity to be detected in the detector. The technique of flash photolysis has proved to be a useful method of studying radical-radical and radical-ion reactions.

10.4.3 Periodic Perturbation Methods

In the four relaxation methods discussed above, the applied perturbations affected the equilibrium in one direction. Here we take up ultrasonic method in which we use sound waves that cause a periodic disturbance to the reaction equilibrium.

Ultrasonic Method

This is probably the most powerful of the relaxation methods, as it can easily be used to study multi-step equilibria and provides information about the number of equilibria and the corresponding relaxation times. It can be used for reaction times of as low as $10^{-10}\ \text{s}$. In this method, a sound wave is made to pass through the reaction mixture. The frequency of sound waves is varied, and the velocity of sound or the absorption of sound is measured as a function of its frequency. We may observe an increase in the velocity of sound, or a maximum in the absorption of sound by the reaction mixture. In these experiments the reactant concentrations are usually high so that the sound velocity and the attenuation (diminution) coefficients vary measurably with the progress of the reaction.

A single inflection on the velocity–frequency plot, or a single maximum in the absorption–frequency plot is indicative of a single equilibrium i.e., only one relaxation time is involved. If there are several equilibria and their relaxation processes are well resolved we will observe corresponding number of points of inflection, or maxima in the plot. Each inflection point or maxima can be used to determine the relaxation time corresponding to the equilibrium involved. This then can be used to determine the rate constants.

SAQ 4

What are relaxation methods? How are these classified?

SAQ 5

p-Jump method is better suited for studying gaseous systems. Give reasons.

10.5 SPECTROSCOPIC METHODS

In most of the techniques of studying fast reactions as discussed above, we have used spectroscopy as a means of detecting different species or measuring their concentration. However, certain spectroscopic methods by themselves can provide useful information about the rate processes. One such technique is NMR spectroscopy.

You know that all spectroscopic lines have a natural line width that is determined by the lifetime of the excited state of the molecule. This fact is extensively exploited in spectroscopic methods. If in a reaction the lifetime of the excited state is altered, it is reflected in terms of the change in the natural line width of the transition.

If the lifetime is short the line width is broad, while longer lifetimes give more sharply defined lines. If a reaction occurs, this can alter the lifetime of the excited state and so change the natural line width of the transition. A detailed analysis of the line widths can provide information about the lifetime of the reacting species and the rate constant for the reaction. This method has proved to be useful for the reactions like proton transfers and acid/base ionization processes in solution. Let us sum up what have we discussed in this unit.

10.6 SUMMARY

We began the unit by defining fast reactions as the ones whose kinetics cannot be studied by conventional methods at ambient temperature and moderate concentrations or as the ones whose half-life is of the order of the mixing time for reactants i.e., less than a few seconds at room temperature. These fast reactions need special strategies to be studied. These could be decreasing the rate of the reaction by decreasing the temperature or the concentration of reactants or to decrease the time required for mixing of the reactants etc. To this effect a number of experimental methods have been devised.

In continuous flow method, the reactants are forced under constant pressure into a mixing chamber from where they continuously flow into a uniform tube called detection tube. The concentrations of the reactants (or that of the products) are then determined as a function of distance along this tube to study the reaction. On the other hand, in case of stoppered flow technique, the flow of mixed reactants is suddenly stopped as they exit into the detection tube. This is then studied as a function of time.

In relaxation methods of studying fast reactions, a reaction at equilibrium is quickly perturbed to a non-equilibrium position and allowed to come back to the same or a new equilibrium. This is then followed to determine the rate. There are several relaxation methods available. These vary in terms of the extent and nature of perturbation. As regards the extent the perturbation could be small or large and in terms of nature it could be a single pulse or a periodic perturbation. Several relaxation methods like *T*-Jump, *p*-jump, shock Tube, flash photolysis and ultrasonic Method have been discussed in terms of their principle and applicability. In addition, we have briefly outlined how

spectroscopic methods can be utilised to determine the lifetime of the excited state.

10.7 TERMINAL QUESTIONS

1. Define fast reactions.
2. What different strategies can be used to study fast reactions?
3. Give the principle of accelerated flow method. How is this method better than the continuous flow method?
4. What are the advantages of stoppered flow method over the continuous flow method?

10.8 ANSWERS

Self-Assessment Questions

1. The conventional kinetic methods cannot be used to study fast reactions because the time of mixing of reactants and the time required to measure the concentrations of reactants (or products) is more than the time taken by the fast reactions to be complete.
2. The continuous flow method has the following limitations:
 - Continuous flow methods allow the study of reactions having a half-life period of $\geq 10^{-3}$ s.
 - We need to use high pressures so that the concentration changes due to diffusion may be avoided.
 - It requires a large volume of the reactant.
3. The initial flow rate is given as 2.0 m s^{-1} i.e., the reactants travel at a rate of 200 cm s^{-1} . Now since the concentration determinations are made at a distance of 1 cm, the time taken for the reactants to reach the location will be

$$1 \text{ cm} / 200 \text{ cm s}^{-1} = 0.005 \text{ s} = 5.00 \text{ ms}$$

Similarly for other (accelerated) flow rates we can calculate the time as

$$1 \text{ cm} / 400 \text{ cm s}^{-1} = 0.0025 \text{ s} = 2.50 \text{ ms}$$

$$1 \text{ cm} / 600 \text{ cm s}^{-1} = 0.00166 \text{ s} = 1.66 \text{ ms}$$

$$1 \text{ cm} / 800 \text{ cm s}^{-1} = 0.00125 \text{ s} = 1.25 \text{ ms}$$

$$1 \text{ cm} / 1000 \text{ cm s}^{-1} = 0.001 \text{ s} = 1.00 \text{ ms}$$

4. Relaxation methods are a group of experimental methods used to study fast reactions. In these methods, a reaction at equilibrium is quickly perturbed to a non-equilibrium position and allowed to come back to the same or a new equilibrium. In this process, the system relieves itself of

the applied stress and is said to undergo relaxation. The concentration changes occurring during the relaxation process are followed as a function of time by using method like, spectroscopy, mass spectrometry and chromatography etc. The rate at which the new equilibrium is established is then utilised to determine the rate of the reaction.

The Relaxation methods are classified into three groups based on the extent of perturbation applied to the reaction at equilibrium. These are:

- Small Perturbation Methods
 - Large Perturbation Methods
 - Periodic Perturbation Methods
5. The shift in equilibrium on sudden change in pressure can be described in terms of Van't Hoff equation.

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta V^\circ}{RT}$$

The effectiveness of p -jump method will depend on the magnitude of ΔV . In case of gaseous systems, the magnitude of ΔV is much more than in case of liquid systems. Therefore p -Jump method is better suited for studying gaseous systems.

Terminal Questions

1. Fast reactions may be defined as the reactions whose kinetics cannot be studied by conventional methods at ambient temperature and moderate concentrations. These may also be defined as the reactions whose half-life is of the order of the mixing time for reactants.
2. The following strategies can be used to study fast reactions:
 - to decrease the rate of the reaction by decreasing the temperature or the concentration of reactants.
 - to decrease the time required for mixing of the reactants.
 - to quickly perturb the reaction at equilibrium, and follow the changes occurring during the relaxation of the system to the same or a new equilibrium.
 - to observe competition between the desired reaction and a fast process of known rate
3. In accelerated flow method the rate of flow of the reaction mixture is continuously varied and the analysis is made at a fixed point along the observation tube. As the rate of flow changes with time, the reaction mixture reaches at the fixed observation point at different times. The measured value of the concentration at different times helps generate a time-concentration plot which can then be used for the rate study.

This method is superior to the continuous flow method because it requires very small quantities of the reactant.

4. The stopped flow method has the following advantages over continuous flow method:
- Very small volumes of solutions are used,
 - If the mixing is proper, the rate and character of flow does not affect the study
 - We get a complete record of the progress of reaction.
 - The kinetic equations for modelling the reactions are equivalent to those used in conventional methods.

