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1. Learning Outcomes

After studying this module, you shall be able to

- Know types of Flow Systems and calculate order and rate constant for reactions
- Know about different techniques for the study of kinetics of fast reactions
- Derive relaxation time for temperature jump method
- Calculate rate constant for temperature jump method

2. Introduction

Fast reactions can be studied by flow systems. We have seen so far rate equations for reactions of various orders for static systems, i.e. a reaction system in which reactants are put in a reaction vessel and their concentration changes as the reaction continues as the reaction continues. For some cases, though, it is necessary to study the kinetics of reactions in flow systems where the reaction mixture is flowing via a reaction vessel called as a reactor. In such kinds of flow systems kinetic measurements are usually done beneficial when the reactants are at very low pressures or concentrations.

Those reactions which carried out in short span of time than the time required to mix up the reactants cannot be examined by conventional methods. Those reactions are known as fast reactions. For studying the kinetics of such reactions powerful experimental techniques have been developed by the German chemist Manfred Eigen in 1950. In this module, we will emphasis on the various methods to study the kinetics of fast reactions.

3. Types of Flow Systems

Flow systems can be categorized into two types on the basis of state of reaction mixture: In the first type, where no stirring takes place in the reactor is called the plug flow. In the second type, stirring takes place which does completely mixing in the reactor. This is called stirred flow.

3.1 Plug Flow System

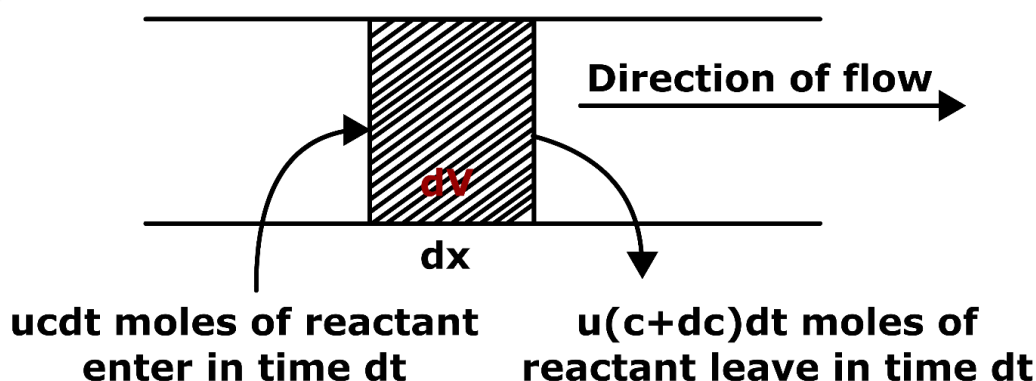**$k_n C^n dV dt$ moles leave by the chemical reaction in time dt**

Direction of flow

dV

dx

ucdt moles of reactant enter in time dt

u(c+dc)dt moles of reactant leave in time dt

Fig. 1 shows the schematic representation of the plug flow.

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In the system the reaction mixture is passed through the reactor at a volumetric flow rate (unit- $m^3 \, s^{-1}$) equal to u.

Let us consider an element of volume dV in the reactor. Assume that the reaction rate depends upon the concentration c of a single reactant. It is known that, for an nth-order reaction, the rate of consumption of the reactant is given by $r = k_n C^n$. Hence, the rate of consumption of the reactant in volume $dV = k_n c^n dV$.

After some time, a steady state is acquired, i.e., there is no further change in the concentration of the reactant occurring with time in the volume element dV.

Three processes that contribute to the steady state are as follows. These are:

1. The reactant molecules enter the slab (shown by slanting lines) through the left face, the amount entering in time dt being $ucdt$.
2. The molecules leave the slab by the right face, the amount leaving in time dt being $u(c+dc)dt$
3. Molecules disappear by chemical reaction. For an nth-order reaction, the amount consumed in time dt is $k_n c^n dV dt$.

We can obtain the steady- state equation, by equating the rate of entry of reactant into the slab (by process1) to the sum of the rates of its removal (by processes 2 and 3)
$$ucdt = u(c+dc)dt + k_n c^n dV dt \quad or \quad -dc/c^n = dVk_n/u \tag{1}$$

The above equation needs to be integrated over the volume V_0 of the reactor. At the entrance to the reactor $V = 0$ and $c = c_i$ (the initial concentration) while at the exit $V = V_0$ and $c = c_f$ (the final concentration of the reactant) Hence,
$$-\int_{c_1}^{c_1} \frac{dc}{c^n} = \frac{k_n}{u} \int_0^{v_0} dV \tag{2}$$

For a first-order reaction $(n=1)$, integration of Eq. 1yields
$$-ln(c_f/c_i) = k_1 V_0/u \quad or \quad c_f = c_i \exp(-k_1 V_0/u) \tag{3}$$

Comparing this equation with that for a static first-order reaction, viz., $c_f = c_i \exp(-k_1 t)$, we see that the two are equivalent if V_0/u is replaced by t. The quantity V_0/u is called the contact time for the reaction. The contact time is the average time that a molecule takes to pass through the reactor. Eq.170 may be tested by varying V_0/u (by changing either the volume of the reactor or the flow rate), just as time is varied in a static system. Reaction those are too fast for suitable examination in a static system can be studied in a flow system, the contact time being reduced by using a high flow rate and a small volume.

For a nth-order reaction ($n>1$), integration of Eq. 1 yields
$$\frac{1}{n-1}\left[\frac{1}{c_f^{n-1}}\right] = \frac{k_n V_0}{u} \tag{4}$$

This equation can be compared with the equation for the rate constant of a static nth-order reaction with $V_0/u = t$.

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We have supposed above that there is no volume change takes place during the progress of the reaction, any such alteration will cause the volumetric flow rate to vary. The concern of volume change, however, complicates the integration of the rate equation.

3.2 Stirred Flow-reactor System (Shown in Fig. 2)

In this type of reactant system, the reactants are added from the the inlet point A and are mixed at a high speed (about 3000 rpm). Due to the fast mixing (in seconds) the concentration of the mixture can be maintained uniformly. After acquiring a stable state, the product mixture is removed from B. The rate of flow of reactants into the reactor is uc_i and the rate of flow out is uc_f. The difference of the two gives the rate of reaction in the reaction in the reactor which is rV which gives the rate per unit volume. Hence,
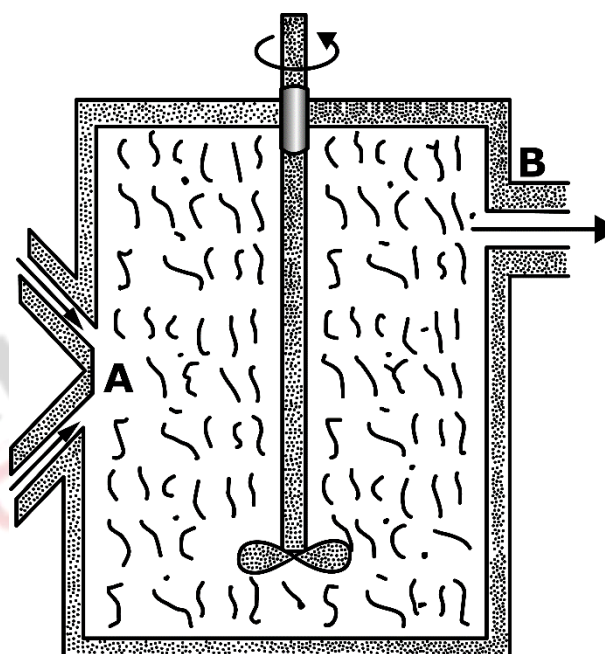

Fig. 2 A stirred-flow Reaction

$$uc_i - uc_f = rV \quad or \quad r = u(c_i - c_f)V \tag{5}$$

We can measure reaction rate, by measuring c_i and c_f at a given flow rate. The order of the reaction and the rate constant can also evaluated by working at different initial concentration and flow rates.

The stirred-flow reactor has application in the study of transient reaction intermediates, whose concentration in a static system might rapidly reach a maximum and then fall to zero. You will be amaze to know that, there is similarity between a living cell and a continuous stirred-flow reactor. The theoretical principles of kinetics are the same in both case. However, there is no obvious internal stirrer in the case of a cell, the process of diffusion of molecules across the cell can maintain the 'well-stirred' conditions. Further there are no such inlets and outlets in a cell as are in the case of a reactor, the entire cell wall sufficiently carryout functions.

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Example 1. An equimolar mixture of NO and Cl_2 in an inert carrier gas is passed through a tubular furnace whose radius is 0.01 m and length 0.30 m, at 973°C and 1 atm pressure, at a rate of 0.01 $m^3 s^{-1}$. The reaction is second-order with rate constant $k_2 = 8.0 \times 10^5 \, dm^3 mol^{-1} s^{-1}$. If Cl_2 constitutes 1.0% of the gas stream at the entry to the furnace, calculate the percentage of Cl_2 in the stream at the exit $\left(1 atm = 101 \times 10^3 \, Nm^{-2}\right)$.

Solution: $P = 1 atm = 101 \times 10^3 \, Nm^{-2}$. There is no stirring in the reactor and, therefore, this is a plug flow.

For the given second-order reaction, $r = dx/dt = k_2 (a-x)^2$ and the integrated rate law is

$$k_2 = \frac{1}{t} \frac{x}{a(a-x)} \qquad \qquad \text{…(i)}$$

The contact time t, is given by

$$t = V/u = \pi (0.01m)^2 (0.30)/0.01 m^3 s^{-1} = 9.4 \times 10^{-3} s$$

Assuming that the gas mixture behaves ideally, $PV = nRT$

The initial concentration of the reactants is

$$a = \frac{n}{V} = \frac{P}{RT} = \frac{\left(10^{-2}\right)\left(101 \times 10^3 \, Nm^{-2}\right)}{\left(8.314 \, JK^{-1} mol^{-1}\right)(1200K)} = 0.10 mol m^{-3} = 1.0 \times 10^{-4} \, mol \, dm^{-3}$$

From Eq. (i)

$$\left(8.0 \times 10^5 \, dm^3 mol^{-1} s^{-1}\right)\left(9.4 \times 10^{-3} s\right) = \frac{x}{1.0 \times 10^{-4}\left(1.0 \times 10^{-4} - x\right)}$$

Which on solving gives, $x = 0.43 \times 10^{-4} \, mol \, dm^{-3}$. Hence the amount of Cl_2 in the carrier gas leaving the exit is 0.43%.

4. Methods to Study Kinetics of Fast Reactions

4.1 Relaxation Methods

Eigen and his coworkers used relaxation methods to examine fast reactions in solution. In these methods, the reaction system in equilibrium is exposed to an abrupt change in some physical parameter on which the equilibrium constant of the reaction depends. If the change is applied suddenly there will be a time lag while the system modifies (releases towards) new state of chemical equilibrium. This time lag, called Relaxation time, can be related to forward and reverse rate constant which is then examined. Relaxation studies are takes place with parameters such as temperature, pressure and electric field.

Fig. 3 shows the device for the **'temperature jump'** method. There is a high-voltage power supply that charges a capacitor C. On attaining a certain voltage, the spark gap G breaks down, discharging the capacitor and transferring a strong current over the cell arranging the reactive system at equilibrium, in a conducting aqueous solution. With the passage of current, the temperature of the system increases by about 10°C in a few microseconds, in the equilibrium value suitable to the temperature jump. Consequently, the intensity of the light beam parting the cell and arriving the detector (the photomultiplier tube, PM) is modified. The output of the photomultiplier tube is exhibited on the vertical axis of the oscilloscope. In this manner, the curve showing the variation of concentration versus time, is presented on the oscilloscope screen.
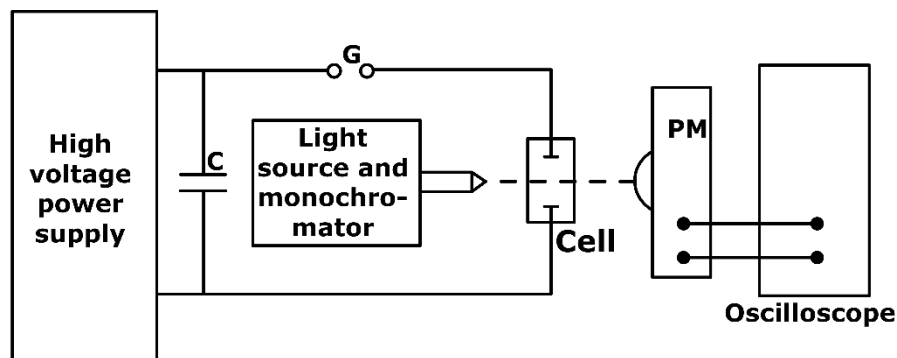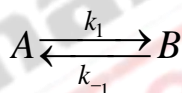
Fig. 3 Apparatus for the temperature jump method

We shall now deduce expression for the rate constants of fast reaction. In case of displacement from equilibrium is very insignificant, the rate of relaxation, i.e., restoration of equilibrium, always follows first-order kinetics. Consider a reversible first- order reaction:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

Let 'a' be the total concentration of reactant and product (A+B) and x be the concentration of B at any instant. Then

$$r = dx/dt = k_1 (a - x) - k_{-1} x \tag{1}$$

If x_e is the equilibrium concentration, then

$$\Delta x = x - x_e \ or \ x = \Delta x + x_e \tag{2}$$

Since $d(\Delta x)/dt = dx/dt$, we have

$$d(\Delta x)/dt = k_1 (a - x_e - \Delta x) - k_{-1}(x_e + \Delta x) \tag{3}$$

At equilibrium, $dx/dt = 0$ and $x = x_e$. Hence, form Eq.1

$$k_1 (a - x_e) = k_{-1} x_e \tag{4}$$

Substituting in Eq.3, we have

$$d(\Delta x)/dt = -(k_1 + k_{-1})\Delta x = -k_r \Delta x \tag{5}$$

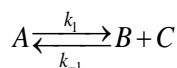Where $k_r = (k_1 + k_{-1})$ is the relaxation rate constant.

Eq. 5 can be integrated to give

$$\Delta x = \Delta x_0 \exp(-k_r t) \tag{6}$$

The reciprocal of k_r viz., $(k_1 + k_{-1})^{-1}$ is called the relaxation time, τ i.e.,

$$\tau = 1/(k_1 + k_{-1}) = 1/k_r \tag{7}$$

Let us now consider a somewhat more complicated case involving a first-order forward reaction with a second-order reverse reaction

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$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B + C$$

Let 'a' be the total concentration and x be the concentration of B which is equal to the concentration of C. Then, the rate law is given by $r = dx/dt = k_1(a-x) - k_{-2}x^2$ \hfill (8)

Now $\Delta x = x - x_e$, where x_e is the equilibrium concentration.

Hence,
$$d(\Delta x)/dt = k_1(a - x_e - \Delta x) - k_{-2}(x_e + \Delta x)^2$$
$$= k_1(a - x_e) - k_1\Delta x - k_{-2}x_e^2 - 2k_{-2}x_e\Delta x - k_{-2}(\Delta x)^2 \hspace{2em} (9)$$

At equilibrium, $dx/dt = 0$ and $x = x_e$ or $\Delta x = 0$; hence from Eq. 9
$$k_1(a - x_e) = k_{-2}x_e^2 \hfill (10)$$

Substituting Eq. 10 in Eq. 9 and simplifying, we get
$$d(\Delta x)/dt = -k_1\Delta x - 2k_{-2}x_e\Delta x - k_{-2}(\Delta x)^2 \hfill (11)$$

Assuming that Δx is very small, therefore $k_{-2}(\Delta x)^2$ can be neglected w.r.t first two terms, giving
$$d(\Delta x)/dt = -(k_1 + 2k_{-2}x_e)\Delta x = -k_r\Delta x \hfill (12)$$

Where $k_r = (k_1 + 2k_{-2}x_e)$ is the relaxation rate constant.

Eq.12 can be integrated to give
$$\Delta x = \Delta x_0 \exp(-k_r t) \hfill (13)$$

The relaxation time τ
$$\tau = (k_1 + 2k_{-2}x_e)^{-1} \hfill (14)$$

Example 1. The relaxation time for the fast reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$ is $10\,\mu s$ (i.e., microseconds and the equilibrium constant is 10×10^{-3}. Calculate the rate constants for the forward and the reverse reaction.

Solution. From Eq. 7,
$$\tau = 1/(k_1 + k_{-1}) = 10 \times 10^{-6}\,s = 10^{-5}\,s \hspace{3em} \ldots(i)$$
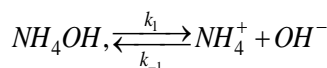$$K = k_1/k_{-1} = 10 \times 10^{-3} \hspace{4em} \ldots(ii)$$
$$k_1 = 10 \times 10^{-3} k_{-1}$$

Since $k_1 \ll k_{-1}$, therefore, k_1 can be neglected in comparison to k_{-1} in Eq (i) so that
$$1/k_{-1} = 10^{-5}\,s \quad or \quad k_{-1} = 10^5\,s^{-1}$$
$$k_1 = 10^3\,s^{-1}$$

Example 2. Calculate the rate constant involved in the dissociation of NH_4OH, viz.

$$NH_4OH, \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NH_4^+ + OH^-$$

The following data is given: A 0.01 molar solution of NH_4OH is subjected to a sudden temperature jump termination at $25°C$, at which temperature, the equilibrium constant is $1.8 \times 10^{-5}\,mol\,dm^{-3}$. The observed relaxation time is $0.109\mu s$ and $x_e = 4.1 \times 10^{-4}\,mol\,dm^{-3}$.

Solution: $\tau = 0.109\mu s = 1.09 \times 10^{-7}\,s$; $k_r = 1/\tau = 9.2 \times 10^6\,s^{-1}$

For the given reaction which is first-order forward and second- order reverse, we have
$$k_r = k_1 + 2k_{-2}x_e \text{ which can be simplified to}$$
$$k_r = k_1[1 + 2(k_{-2}/k_1)x_e] = k_1(1 + 2x_e/K)$$

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Where the equilibrium constant $K = k_1 / k_{-2}$

$$k_1 = k_r / (1 + 2x_e / K) = \frac{9.2 \times 10^6 \, s^{-1}}{1 + \left(2 \times 4.1 \times 10^{-4} \, mol \, dm^{-3} / 1.8 \times 10^{-5} \, mol \, dm^{-3}\right)} = 2 \times 10^5 \, s^{-1}$$

$$k_{-2} = k_1 / K = 2 \times 10^5 \, s^{-1} / 1.8 \times 10^{-5} \, mol \, dm^{-3} = 1.1 \times 10^{10} \, dm^3 mol^{-1} s^{-1}$$

Example 3. For the dissociation of water, $H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+ + OH$, the relaxation time obtained from the temperature jump method is $40\mu s$ at $25^\circ C$, at this temperature, $K_w = \left[H^+\right]\left[OH\right] = 1.0 \times 10^{-14} \left(mol \, dm^{-3}\right)^2$. Calculate the rate constants k_1 and k_{-2}.

Solution:
$$\tau = 40\mu s = 40 \times 10^{-6} \, s = 4.0 \times 10^{-5} \, s$$
$$k_r = 1 / \tau = 2.5 \times 10^4 \, s^{-1}$$

Since
$$k_w = \left[H^+\right]\left[OH\right] = x_e^2 = 1.0 \times 10^{-14} \left(mol \, dm^{-3}\right)^2$$
$$x_e = 1.0 \times 10^{-7} \, mol \, dm^{-3}$$

For water $K = \dfrac{K_W}{\left[H_2O\right]} = \dfrac{10 \times 10^{-14} \left(mol \, dm^{-3}\right)^2}{55.5 \, mol \, dm^{-3}} = 1.8 \times 10^{-16} \, mol \, dm^{-3} = k_1 / k_{-2}$

Proceeding as in the last example,

$$k_1 = \frac{k_r}{1 + \left(2x_e / K\right)} = \frac{2.5 \times 10^4 \, s^{-1}}{1 + \left(2 \times 10^{-7} \, mol \, dm^{-3} / 1.8 \times 10^{-16} \, mol \, dm^{-3}\right)} = 2.5 \times 10^{-4} \, s^{-1}$$

$$k_{-2} = \frac{k_1}{K} = \frac{2.5 \times 10^{-5} \, s^{-1}}{1.8 \times 10^{-16} \, mol \, dm^{-3}} = 1.4 \times 10^{11} \, mol^{-1} s^{-1}$$

4.2 Flow Methods

The most popular flow method is the stopped- flow method. The schematic diagram of its experimental set up is shown in Fig. 4. Two syringes A and B contains distinct reactant and are fixed with proper valves. The common drive mechanism D consists of an air-driven piston by which the solution is forced into the mixing chamber M. Another syringe on the right receives the effluent solution and is arranged to establish the time origin. The time scale is provided by the sweep frequency of the oscilloscope, which displays a plot of the transmitted light intensity against time. In this arrangement the distance between the mixing region and the observation point P (i.e. the point at which absorption of light is monitored) is small. The method of detection operates the ultraviolet/ visible spectrophotometer.
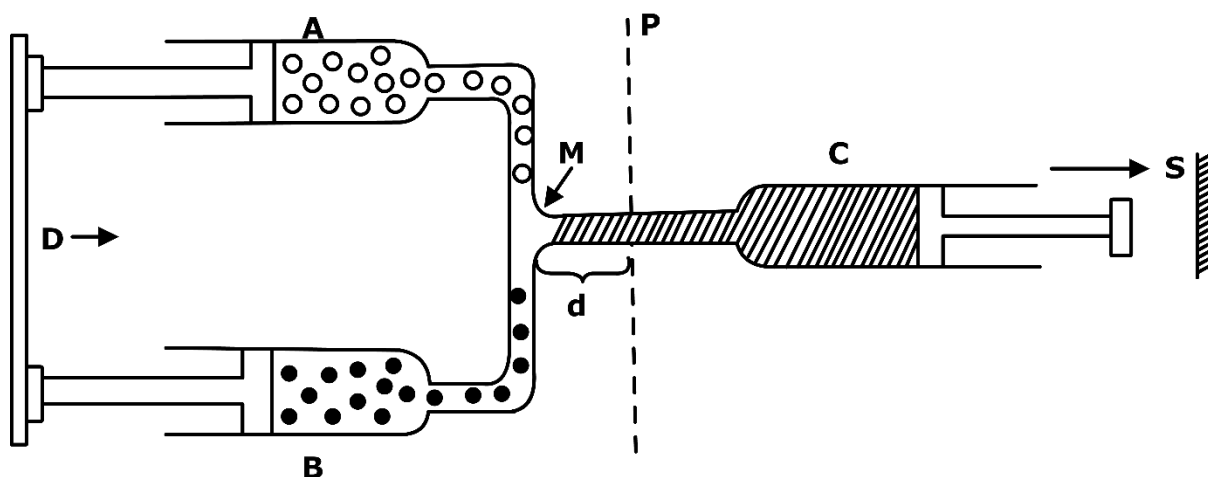
Fig. 4: Schematic diagram of a stopped-flow apparatus

Kinetic data are acquired by determining the values of a suitable physical property as determined at several times after mixing with the aid of an appropriate technique, kinetic date are obtained.

Being less popular in the former methods, the continuous-flow and quenched-flow methods are also used, in which measurements are made at different distances down the flow tube (i.e., at varying distances d in Fig.4).

There is no utilization of stopping syringe. The principle of this procedure uses the information that the measurements along the flow stream amount in effect to determination at different times. With a known and constant flow rate, the time corresponding to each reading is known. By placing several detectors alongside the tub or moving a single detector to different positions the measurement can be made. There is a minor perfection in time resolution in the continuous-flow method as compared with the stopped-flow methods.

As, though, the continuous-flow method utilizes large quantities of solution, it is less usually used. In the quenched flow process, samples of the reaction mixture are quickly mixed with a quenching mixture, followed by the analytical determination that can be made at ease. Different samples can be having different timings by different flow rates of different distances along the flow stream. This method is best appropriate to the study of exchange reactions which takes place too fast for the typical sampling techniques.

4.3 Pulse Methods

Pulse method is also utilized for studying the fast reactions. Short pulse of electromagnetic radiation using light, ultraviolet radiations, X-rays or charged particles (usually electrons) start the reaction by creating very high concentrations of excited state molecules. If, a powerful flash of visible or UV radiation is utilized, the method is called flash photolysis. While, on the other hand, from a generator charged particles (electrons) are used, the method is known as pulse radiolysis.

4.4 Flash photolysis.

This method was pioneered by R.G.W. Norrish and G Porter in 1949. The apparatus for flash photolysis studies is shown below schematically in Fig. 5. The sample is exposed to a very intense flash that have energy of the order of $10^5 J$ and duration of $10\mu s$ (i.e., microseconds.). The flash is so powerful that in

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several cases about all the molecules of the sample are excited and due to which most of the molecules are broke into free radicals. Powers of the order of 50 megawatt can be obtained for a few microseconds. In recent years, high intense pulsed laser light sources have been utilized in flash photolysis. The concentration of the intermediated formed by flash photolysis is followed as a function of time by absorption photometry.
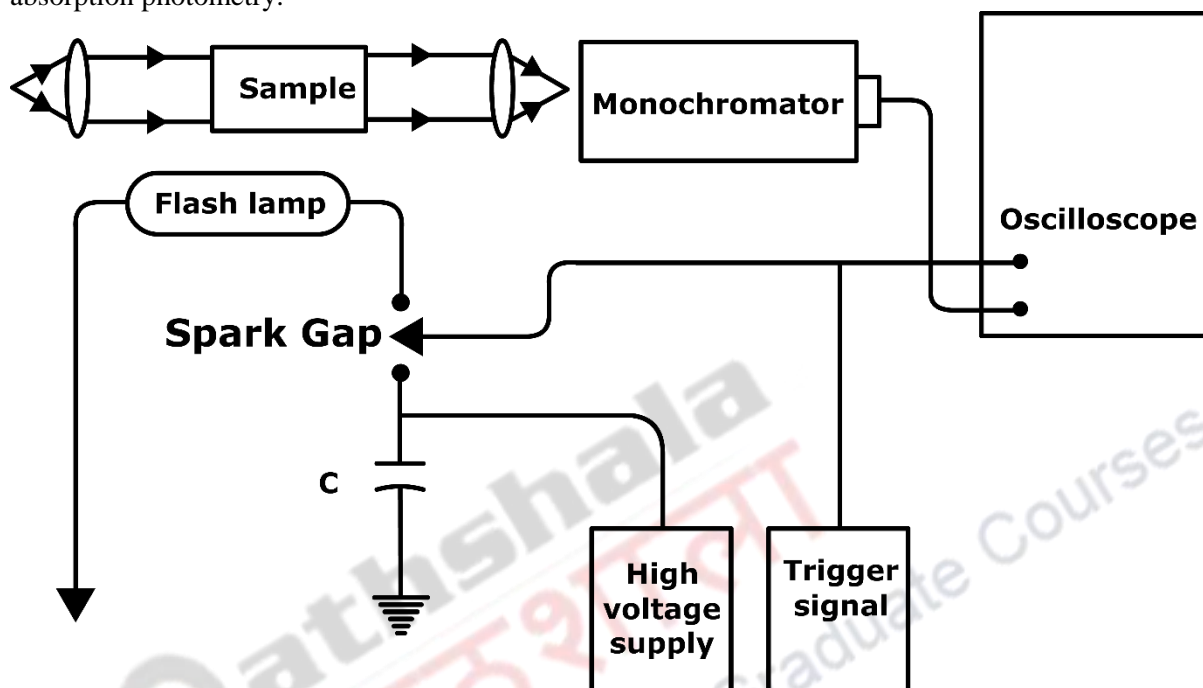

Fig. 5 Apparatus for flash photolysis

From Fig 3, a condenser of high microfarad capacity is charged to 10,000 volt-by a high voltage supply. Through the trigger signal, a spark is created in the spark gap which allows quick passage of current via the flash lamp. The condenser discharges in a few microseconds. The lasers can create a flash of the period of a few nanoseconds. Immediately after the capacitor discharges, the flash lamp is spontaneously triggered off. The rate of the fading of excited molecules or free radicals is followed by the rate of increase in the monochromatic transmitted light as calculated with an oscilloscope and photomultiplier.

The spectrometer is fixed such that the light moving via the illuminated cell is of the wavelength that is absorbed by the excited molecule or free radical. This technique is known as kinetic spectroscopy.

Eigen, Norrish and Porter shared the 1967 Chemistry Nobel Prize for contributions to fast reaction kinetics "by disturbing the equilibrium by means of very short pulses of energy."

Flash photolysis has been used for deducing the absorption spectra of free radicals such as NH_2, CH_3 and ClO, whose concentration may be as small as $10^{-6} M$.

4.5 Pulse Radiolysis.

By utilizing Pulse radiolysis transient species can be generated by direct ionizing radiation. If a beam of high-energy electrons imposes on water, quantities of stable and unstable species are generated. They start from the energy transmitted to water molecule by the electron beam. It is normal to express the
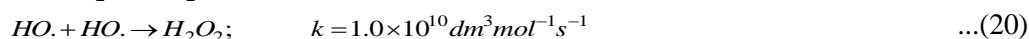
amount of each species by a G-value, which signifies the number of species formed per 100 eV of energy absorbed by water. The species made in the pulse radiolysis of water, with the G-value displayed as the coefficient of each species, are given by the equation

$$4.0H_2O \rightarrow 2.6e^-(aq) + 2.6HO. + 0.6H. + 2.6H^+ + 0.4H_2 + 0.7H_2O_2 \qquad ...(15)$$
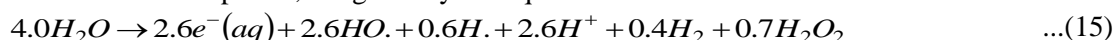
The first three are highly reactive entities. The hydrated electron and the hydrogen atom are strong reducing agents and the hydroxyl radical $HO.$ is a very powerful oxidizing agent. In the absence of suitable scavengers, the species rapidly decay by reactions of the following types:

$$e^-(aq) + H_3O^+ \rightarrow H. + H_2O; \quad k = 2.2 \times 10^{10} dm^3 mol^{-1} s^{-1} \qquad ...(16)$$

$$e^-(aq) + 2H_2O \rightarrow H_2 + 2OH; \quad k = 5.5 \times 10^{9} dm^3 mol^{-1} s^{-1} \text{ if OH radical then no e- } ...(17)$$

$$e^-(aq) + HO. \rightarrow OH^-; \qquad k = 3.0 \times 10^{10} dm^3 mol^{-1} s^{-1} \qquad ...(18)$$

$$e^-(aq) + H. + H_2O \rightarrow H_2 + OH^-; \quad k = 2.3 \times 10^{10} dm^3 mol^{-1} s^{-1} \qquad ...(19)$$

$$HO. + HO. \rightarrow H_2O_2; \qquad k = 1.0 \times 10^{10} dm^3 mol^{-1} s^{-1} \qquad ...(20)$$

Due to these and various other reactions, selective practices have been developed to permit study of each of $e^-(aq), HO$ OH radical and $H.$, distinctly. For instance, if it is required to study only $e^-(aq)$ or use completely hydrate electrons to produce other species, one must work in neutral or basic solution to escape damage of $e^-(aq)$ by H_3O^+ [reaction (ii)]. The $HO.$ and $H.$ are often detached by shifting reactions such as those with formate ion or t-butyl alcohol:

$$HO.(\text{or } H.) + HCOO^- \rightarrow H_2O(\text{or } H_2) + CO_2^- \quad \text{CO}_2 \text{ radical along with minus sign}$$

$$...(21)$$

$$HO.(\text{or } H.) + (CH_3)_3COH \rightarrow H_2O(\text{or } H_2) + .CH_2C(CH_3)_2OH \qquad ...(22)$$

The hydrogen atoms in alkaline solution are converted into hydrated electrons.

$$H. + OH^- \rightarrow e^-(aq) + H_2O; \quad k = 2.0 \times 10^3 dm^3 mol^{-1} s^{-1} \qquad ...(23)$$
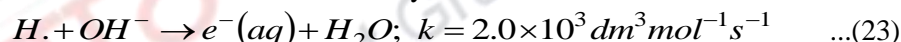
5. Summary

- Flow systems are used for learning fast reactions. There are two kinds of Flow Systems that are possible viz. Plug Flow System and Stirred-Flow reactor System
- In the Plug Flow System, final concentration of reactant falls exponentially with contact time
- In Stirred Flow method, rate of reaction changes with the difference of initial and final concentration of reactants and thus the order of the reaction and the rate constant can be measured by considering different initial concentration and flow rates.
- Various methods are there to study the kinetics of fast reactions which include Relaxation methods, Flow methods, Pulse methods, Flash Photolysis and Pulse Radiolysis
- Relaxation methods involve a sudden difference in some physical parameter such that the system moves to new state of chemical equilibrium and the rate of this change, called relaxation, is then examined
- A flow method uses ultraviolet/ visible spectrophotometer for the kinetic data. Pulse methods utilize a short pulse of electromagnetic radiation to produce excited state molecules
- In Flash Photolysis, powerful flash of high energy is utilized to produce free radicals, and its concentration is examined as a function of time by absorption photometry
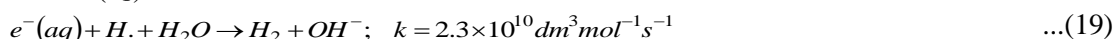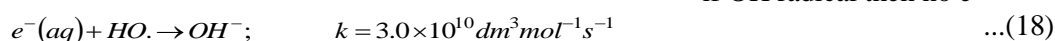 Pulse Radiolysis exploits ionizing radiation for the production of stable and unstable species.

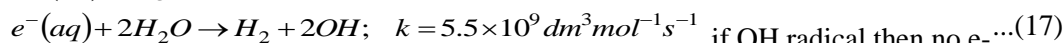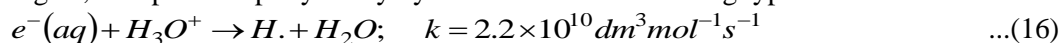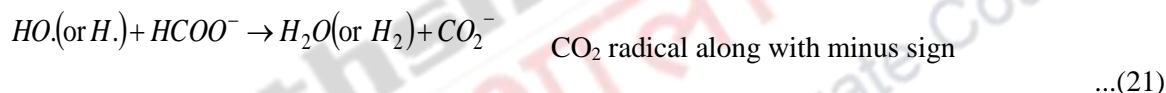| CHEMISTRY	Paper No. 10: PHYSICAL CHEMISTRY-III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)
	Module No. 32: Reactions in Flow Systems and Kinetics of Fast Reactions