

Module 6 : Reaction Kinetics and Dynamics

Lecture 27 : Experimental methods in chemical kinetics

Objectives

After studying this Lecture you will be able to do the following:

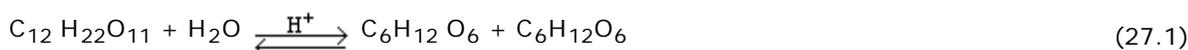
- Outline the physical and chemical (experimental) methods for determining the concentrations of the species participating in chemical reactions.
- Use optical rotation to study the evolution of a reaction when one or more of the reacting species are optically active.
- Use the conductivity of the reaction mixture to obtain the concentration of the reactants / products.
- Outline the techniques of flash photolysis.
- Describe the techniques of laser induced fluorescence. Outline the techniques involved in time resolved spectroscopy to study chemical dynamics.
- Relate the relaxation times obtained in relaxation methods to rate constants.

27.1 Introduction

In the experiments for studying chemical kinetics there are three major ingredients, namely, the method for initializing the reaction, the reaction medium and thirdly the method for detecting the extent of reaction that has occurred. The initiation may consist of simple mixing of reactants, thermal activation (heating), electrical discharge, chemical activation, photoactivation (with light of wavelength 120 nm to 700 nm) and so on. The reaction medium can either be static (such as a test tube with a solvent medium, a gas bulb, living cell etc) or a flow system wherein atoms /ions /molecules are formed in a continuous discharge and the reaction occurs during the flow process. The last and the most important aspect is the technique for measuring concentration changes. The classical techniques (for times in the range of 0.1 sec to greater than an hour) include pressure measurements for gas phase reactions, conductance measurements, polarimetry, polarography, gas chromatography, chemical trapping and so on. The main criteria here is that the time to analyse the concentration changes must be much smaller than the time scale of the reaction. For shorter time scale (10^{-5} s to 1s), the method like flash photolysis, pulse radiolysis, nuclear magnetic resonance, temperature jump, pressure jump and electrochemical methods are useful. For the time in the range of 10^{-5} s to 10^{-8} s, acoustical methods and electrical pulses are useful. Fluorescence decay is useful for the time span of 10^{-6} s to 10^{-10} s. For shorter times, pico second techniques (10^{-11} s to 10^{-13} s) and femtosecond methods (10^{-15} s to 10^{-14} s) have been developed recently. In this lecture, we will consider only a few representative techniques among the methods mentioned above, which illustrate the principles involved in detecting concentrations at different time scales.

27.2 Polarimetry

This method is useful when reactants/products are optically active. Optically active compounds contain asymmetric centers (e.g., a carbon atom to which four distinct groups / atoms are attached). Such molecules rotate the plane of polarization of polarized light. In a plane polarized light the electric and magnetic fields of radiation oscillate in a given plane (unlike the usual light from a torch or a light bulb wherein the radiation is not polarized, i.e., different photons coming out have different planes of polarization). A polarized light can be separated from an unpolarized beam of light by using appropriate prisms (polarizers) which permit only polarized light to pass through. The method is illustrated for the following reaction



sucrose + water → dextrose + levulose

Sucrose rotates the plane of polarized light to a particular angle (clockwise rotation, dextrorotatory). Let us denote this by α_0 . As the hydrolysis starts, the plane of polarization starts tilting away from α_0 because the products have a different degree of polarization.

As the reaction reaches a final equilibrium, the polarization (degree to which the polarimeter has to be rotated to allow the light to pass through) reaches a value α_∞ . At each stage of the reaction, the plane of polarization may be denoted by α_t as illustrated in the following figure.

Figure 27.1 Different planes of polarization at times a) $t = 0$, b) $t \neq 0$, c) $t \rightarrow \infty$

The angle ($\alpha_\infty - \alpha_t$) may be taken as proportional to the concentration of sucrose. The rate of the reaction may be written as

$$d[\text{sucrose}] / dt = d\alpha / dt = -k \alpha \quad (27.2)$$

by plotting $\log \left[\frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_t} \right]$ vs time t , the rate constant for the hydrolysis (or inversion in this case) of sucrose can be determined.

A sketch of the reaction set up is shown in Fig 27.2

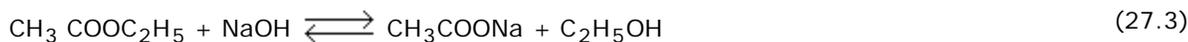
Figure 27.2 The polarimeter set up for the inversion of sucrose.

The role of the nicol prism is to produce two beams of plane polarized light which differ by a phase difference of half wavelength. This allows for an easy detection of plane of polarization at the telescope, where one half of the view is fully bright and the other half, dark.

One of the main advantage of this physical method is that the reactant concentration can be measured without disturbing the system. This is possible because a physical property is used to measure the concentration. In chemical methods, a small part of the reaction mixture is removed, the reaction process stopped (quenched) and the concentration of one or more of the species is measured by a chemical reaction, such as a titration.

27.3 Conductometry

This method can be used when the conductance of the reaction mixture changes significantly during the course of a reaction. A common example is the saponification of an ester, ethyl acetate.



In the reaction mixture, the conductances of the ester and the alcohol are negligible as they do not ionise. NaOH has a very high value of conductance and the conductance of sodium acetate is much smaller. The conductance of the reaction decreases as the reaction proceeds. The conductance (or the resistance) of the reaction mixture can be measured in a conductivity cell.

The above reaction is known to be second order and the rate constant can be determined by taking initially equal concentrations of NaOH and ethyl acetate. If the initial conductance is C_0 final conductance is C_∞ and the conductance at time t , UC_t , then the rate constant can be obtained from eq (27.4)

$$k = (1/t) \times [a(a-x)] \quad (27.4)$$

Where a is the initial concentration (proportional to C_0), x is the amount reacted ($= C_0 - C_t$) and $(a-x)$ is the amount remaining ($= C_t - C_\infty$).

The operation of conductance cells and their calibration is done by using a conductivity bridge and do look up this material in reference books.

The measurements of polarization and conductance and several other physical properties are useful when the rate constants are small enough so that the values of these properties do not change during the time period of measurement (which is typically at least a few seconds.) The rest of the chapter deals with methods which are useful to study fast kinetics. As mentioned in the introduction, we will outline only some among the large number of techniques available in chemical kinetics.

27.4 Flash Photolysis:

Introduced by Norrish and Porter in 1950, this method was one of the early departures from the classical methods. A Schematic diagram illustrating the principles involved is given in Fig 27.3.

Figure 27.3 A flash photolysis apparatus.

The reaction is initiated by an intense flash of visible or ultraviolet light generated by a photoflash lamp. The duration of the flash, about 5 to 15 microseconds (μs) is shorter than the reaction time scale. The intermediates generated can be probed in real time using spectroscopic methods. The absorption spectrum of the intermediate has to be determined at fixed intervals after the initial flash. This is best accomplished by repeating the experiment after different time delays.

The reaction cell (RC) is a quartz cylinder of length up to 1 m. Both the ends of the cylinder are plane windows. The photoflash lamp tube is parallel to the reaction cell. Suitably placed reflectors increase the intensity of light falling on the sample. The photoflash lamp has a capacitor connected to the two electrodes of the lamp. For short flashes (ns) the energy dissipated from the lamp is small (μJ , microjoules) for millisecond flashes, the energy dissipated is several hundred joules.

The absorption spectrum of intermediates/products is obtained using a second lamp (the spectroflash) at one end of the reaction cell. The spectroflash energy and duration have to be adjusted so that it does not interfere with the ongoing photochemistry in the reaction cell, but has sufficient intensity to be detected in the detector, kept at the other end.

Today, pulsed lasers have replaced the conventional photoflash lamps, as they give light with higher power and of a much greater time resolution. This is in addition to the coherent and monochromatic light beams of the laser. The trigger enables in starting the discharge of the capacitor as well as timing the spectroflash output signals of the spectrum. Laser flash photolysis has been used to study a number of reactions including radical radical recombinations (e.g., $^{\circ}\text{CH}_3 + ^{\circ}\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$), unimolecular decay, atom - atom, atom - molecule and radical - molecule reactions. It has also helped in detecting excited states of atoms, molecules, ions and radicals.

27.5 Laser induced Fluorescence

When the life - times of the excited states of molecules (which are produced by short laser pulses) are short compared to collision times, the excited molecules decay to their stable ground states by fluorescence (which is the process by which excess energy is irradiated to the surroundings). This technique is of course restricted to molecules that fluoresce (rather than give away their energy by radiationless processes) and are spectroscopically well characterized. Suitable lasers should be available in the required frequency range. The Schematic diagram is shown in figure 27.4 below.

Figure 27.4 Schematic diagram for Laser Induced Fluorescence (LIF).

The fluorescence is detected using efficient photomultiplier tubes (PMTs) and photon counting techniques. Gated photon counting synchronized to a pulsed laser further enhances the signal to noise ratio. This technique can detect lower concentrations of species, even in the range of 10^6 to 10^{10} molecules/cm³. Variety of reactions between atoms with molecules, radicals with molecules as well as unimolecular reactions can be studied by this method. The time resolution extends from μ s to ns (nanoseconds).

Examples of species detected by LIF are hydrogen halides, NO, CN, NO₂, CF₂, NO₃, CH₃O and so on. Having low lying excited states increases the fluorescing ability of molecules.

The fluorescence intensity (which is proportional to the concentration or the population of the fluorescing states) is plotted versus time to get the appropriate rate constant.

27.6 Time Resolved Spectroscopy and Dynamics

From the earlier sections we can infer that if we excite molecules by short pulses (now pulses of the duration of a few femtoseconds from femtosecond lasers are available) we can initiate a chemical or a physical process. The progress of this process can be studied at intermittent times by using a second, less intense light beam (so that the ongoing process is not disturbed) to assess the time evolution of an intermediate or a product by different spectroscopic methods.

The typical processes involved at short time scales may be represented as



→

[27.5a to 27.5f]

[AB] → D (products of a reaction)

A schematic diagram of a time-resolved spectroscopy apparatus is given below.

Figure 27.5 A time resolved spectroscopy apparatus.

A strong and short pulse, called the pump, excites the molecules A in the sample cell. The possible sequence of reactions of A are given in eq (27.5) above. The beam splitter takes part of the initial beam through an alternative route so that this beam can be used to probe the time dependent reactive processes. By passing this second beam through an appropriate liquid such as H₂O or CCl₄ a wide distribution of frequencies (continuum generation) can be obtained. From this continuum, frequencies useful to analyse the products can be obtained by using suitable filters. A time delay between the initial pump light and the probe beam can be introduced by allowing the probe beam to travel an additional distance. If the additional distance is 1 mm, the time delay $\delta t = 1\text{mm} / c$, which is 3.3ps. Different time delays are obtained by moving the prisms on a motorized stage. The difference in the probe beam resulting after its passage through the sample is analysed by the detector.

When one considers a duration of less than a pico second, molecules normally do not complete even one vibration. Using pulses of 10 to 100fs (A pulsed Ti³⁺ sapphire laser can produce 10fs pulses), it is possible to monitor the detailed dissociation of a molecule into different possible products. We will illustrate this using the example of NaI dissociation which was first reported by Zewail who has pioneered the work in femtochemistry. The reaction sequence may be written as



The potential energy diagram for NaI dissociation is given in fig 27.6

Figure 27.6 The ionic(V_1) and covalent (V_0) potential energies of NaI as a function of the NaI distance, r .

For the two dissociation products (covalent : Na + I and ionic: Na⁺ + I⁻) there are two surfaces V_0 and V_1 . The two surfaces "cross" near 6.9 \AA . In this case, crossing from one surface to another is avoided. This region of avoided crossing is also the transition state. Beyond this distance, the molecule can be considered to be dissociated.

When the molecule is vertically excited from its minimum energy in V_0 , it gives to the surface V_1 and can oscillate in the upper V_1 surface for a few vibrational periods. The progress of the reaction can be studied by a probe pulse of wavelength near 589 nm (corresponding to the sodium D absorption). It is observed that the fluorescence intensity does not rise smoothly but there are several undulations of a period about 1.2 ps (Fig 27.7)

Figure 27.7 Fluorescence intensity of Na and NaI as a function of time.

At 589nm, the fluorescence intensity of Na grows to the largest value after about 8 ps. The lower curve shows the fluorescence of bound sodium in NaI. The molecule undergoes 6 to 7 vibrations before the covalent dissociation is complete. The rise and fall in intensity is due to the NaI molecule (which is represented as a wave packet in Fig 27.7) going back and forth in the upper curve V_1 .

27.8 Relaxation Methods

When a reaction system at equilibrium is disturbed by a sudden change in temperature or pressure, the concentrations of the species change in response to this change. After some time, the reactant concentrations reach a new equilibrium from the initial non-equilibrium (caused by pressure/temperature jump, or electric/ magnetic/ultrasonic disturbances) The process of relaxing to a new equilibrium is called the relaxation process. Consider the following process which is at an initial old equilibrium.



The ratio of concentrations $[B]_{eq,old} / [A]_{eq,old}$ is the initial equilibrium constant. This equilibrium is shifted by a change/jump in in one of the reaction conditions mentioned above. Let the rate constants after this jump be k_f (forward reaction) and k_b (reverse reaction) and $[A]_{eq,new}$ and $[B]_{eq,new}$ be the new equilibrium values of A

Figure 27.8

$$x = [A] - [A]_{new, eq}, \quad x_0 = [A]_{eq,old} - [A]_{eq,new}, \quad [B] = [B]_{eq,new} - x \quad (27.8)$$

$$\begin{aligned} d[A]/dt &= -k_a[A] + k_b[B] \\ &= -k_a\{x + [A]_{eq,new}\} + k_b\{[B]_{eq,new} - x\} \end{aligned} \quad (27.9)$$

But since $[B]_{eq,new} / [A]_{eq,new} = k_a / k_b$

$$k_b [B]_{eq,new} = k_a [A]_{eq,new} \text{ and}$$

$$d[A]/dt = -(k_a + k_b)x = dx/dt$$

$$\text{or } -d\ln x = (k_a + k_b) dt \quad (27.10)$$

$$\text{or } x = x_0 e^{-t/\tau}$$

$$\text{Where } 1/\tau = (k_a + k_b) \quad (27.11)$$

The time required for x_0 to reach the value $(1/e)x_0$ is called the relaxation time τ . After a few relaxation times, x becomes very small and the new equilibrium is established.

For other equilibria too, expressions for relaxation times can be derived. For example, for the reaction



the relaxation time τ is given by

$$\tau = 1 / k_1 ([A]_{\text{eq, new}} + [B]_{\text{eq, new}}) + k_{-1} \quad (27.13)$$

Given in the following table are the values of k_1 and k_{-1} for a few reversible acid base reactions.

Table 27.1 values of k_1 and k_{-1} for some reversible acid base reactions at 298 K

Reaction	k_1 (in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	k_{-1} (in s^{-1})
$\text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$	1.4×10^{11}	10^{-3}
$\text{H}^+ (\text{aq}) + \text{CH}_3\text{COO}^- (\text{aq}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq})$	4.5×10^{10}	7.8×10^{-5}
$\text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3 (\text{aq})$	4.7×10^{10}	8×10^6
$\text{H}^+ (\text{aq}) + \text{C}_6\text{H}_5\text{COO}^- (\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{COOH}(\text{aq})$	3.5×10^{10}	2.2×10^6

For the reaction $A \rightleftharpoons B$, τ is calculated from k_f and k_r . For the reactions in the table, in addition to k_1 and k_{-1} , we need the equilibrium constants of the reactions to get τ . For the reaction $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$, the conductivity of the solution increases with a temperature jump. Measuring the time dependent conductivity, the value of τ has been found to be 3.7×10^{-5} s. The value of $[\text{H}^+][\text{OH}^-] = K_w$ for water is 10^{-14} and the value of $K_c = [\text{H}_2\text{O}] / [\text{H}^+][\text{OH}^-] = [\text{H}_2\text{O}] / K_w = 5.5 \times 10^{15} \text{mol}^{-1} \text{dm}^{-3}$. Using these values, show that $k_1 = 1.4 \times 10^{11} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

Relaxations methods work best when equilibria are disturbed by small amounts to get new equilibria. These methods combine the methods of thermodynamics and kinetics.

27.8 Problems

- 27.1) List the names of a few molecules which are levorotatory and dextrorotatory. Do they all have to have asymmetric carbon atoms?
- 27.2) Among the following, which one has the highest value of molar conductance, KCl, NaCl, HCl and CH₃F ? List them in the decreasing order of molar conductivity.
- 27.3) In a flash photolysis experiment a beam is split into two by a beam splitter. A part of the beam goes directly to the reaction cell. Another part goes through a longer path (reflected by a mirror, passed through a fluorescent solution which converts the beam into continuous radiation in the visible range so that this can be used to analyse the products) so that it can reach the reaction vessel after a time delay to analyse the products. For a time delay of 10⁻⁷s, the additional path to be traveled by the second analysing beam is $c \cdot t = 2.988 \times 10^{10} \text{cm/s} \times 10^{-7} \text{s} = 2998 \text{cm}$. What is the smallest time delay that can be achieved in this set up?
- 27.4) Can you suggest ways for determining the rates of the following reactions?
- 2 NO(g) + 2H₂(g) → N₂(g) + 2H₂O(g)
 - A reaction with a half life of 10⁻¹⁰s
 - S₂O₄²⁻(aq) + I₂⁻(aq) → 2SO₄²⁻(aq) + I₂(aq), and
 - Bromination of CH₃COCH₃
- 27.5) Conductance measurements were used to study the hydrolysis of CH₃COOCH₃ by NaOH at 25 ° C in the reaction $\text{NaOH} + \text{CH}_3\text{COOCH}_3 \xrightarrow{\text{CH}_3} \text{COONa} + \text{H}_2\text{O}$ The initial concentrations of both the reactants were 0.004 mol / lit. The molar conductivity κ at different times was measured as follows

Time (in minutes)	1000 * κ (in ohm ⁻¹ cm ⁻¹)
0	1.24
10	1.04
20	0.92
30	0.84
40	0.78
∞ (very large times)	0.44

Initially the conductivity is mainly due to OH⁻ and at the end, the conductivity is mainly due to CHCOO⁻ ions. Find the concentrations of OH⁻ and CH₃COO⁻ as a function of time. Determine the reaction order with respect to OH⁻ by plotting log [a/ (a-x)] vs time.

- 27.6) The dimerization of $2\text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}_2(\text{g})$ was studied by noting the decrease in pressure of the reacting mixture as a function of time

P total (in mm Hg)	631	590	532	482	445	416
Time (in min)	0	10	30	60	100	150

Find the partial pressure of the monomer as a function of time. If P_0 is the initial pressure of NO and the partial pressure of NO has decreased by x at time t , then the pressure of remaining NO is $P_0 - x$ and the partial pressure of N_2O_2 is $x/2$ and the total pressure P_{total} at t is $P_0 - x/2$ or $x = 2(P_0 - P_{\text{total}}(t))$ and the partial pressure of the monomer remaining is $P_0 - x = 2P_{\text{total}} - P_0$. Plot $\ln P_0 / (2P_{\text{total}} - P_0)$ vs time to see if the reaction is first order with respect to $\text{NO}(\text{g})$

- 27.7) Look up the detailed meanings of fluorescence, phosphorescence, chemiluminescence and give examples of molecules who have dominantly these properties.
- 27.8) Try and find out how short pulses of the durations of a few pico seconds or a few femtoseconds are generated.

Recap

In this Lecture you have learnt the following

Summary

In this lecture, you have been introduced to some of the common techniques employed in experimental chemical kinetics. In all these methods, the concentration of some or all of the species involved in a chemical reaction need to be measured as a function of time. If reactants/products are optically active, a physical property such as optical rotation can be used to measure changes in concentration. If the conductance of the reaction mixture changes significantly (because of the conductance of the reactants/products being significantly large), then it is a good measure for assessing time dependent concentrations. A time tested classical chemical method to study the extent of a reaction is to take out a small portion of the reaction mixture (such as half or one milliliter), freeze or quench the progress of the reaction and estimate the concentration of one of the species. Modern kinetics is progressing towards studying faster and even faster chemical events.

Flash photolysis combined with absorption spectroscopy can study reactions on a microsecond time scale. Laser induced fluorescence extends the measurements to nanosecond time scales. It has been possible to extend the time resolution to pico seconds and femtoseconds using very short laser pulses (pump) to initiate a reaction and then use a second laser pulse (probe) to monitor the extent or the progress of the reaction. These techniques have been briefly described towards the end of the lecture. All these methods involve a very high degree of experimental sophistication involving precision optics, electronics and spectroscopy