PHYSICAL CHEMISTRY

CHEMICAL KINETICS

This chapter introduces the principles of chemical kinetics, the study of reaction rates,by showing how the rates of reactions may be measured and interpreted.

The rate of a chemical reaction might depend on variables under our control, such as the pressure, the temperature,and the presence of a catalyst, and we may be able to optimize the rate by the appropriate choice of conditions. The study of reaction rates also leads to an understanding of the mechanisms of reactions, their analysis into a sequence of elementary steps

1- *Empirical chemical kinetics*

The first steps in the kinetic analysis of reactions are to establish the stoichiometry of the reaction and identify any side reactions. The basic data of chemical kinetics are then the concentrations of the reactants and products at different times after a reaction has been initiated. The rates of most chemical reactions are sensitive to the temperature, so in conventional experiments the temperature of the reaction mixture must be held constant throughout the course of the reaction. This requirement puts severe demands on the design of an experiment. Gas-phase reactions, for instance, are often carried out in a vessel held in contact with a substantial block of metal.

Liquid-phase reactions, including flow reactions, must be carried out in an efficient thermostat. Special efforts have to be made to study reactions at low temperatures, as in the study of the kinds of reactions that take place in interstellar clouds

1-1   Experimental techniques

The method used to monitor concentrations depends on the species involved and the rapidity with which their concentrations change. Many reactions reach equilibrium over periods of minutes or hours, and several techniques may then be used to follow the changing concentrations

1-1-1-Monitoring the progress of a reaction

A reaction in which at least one component is a gas might result in an overall change in pressure in a system of constant volume, so its progress may be followed by recording the variation of pressure with time.

Spectrophotometry, the measurement of absorption of radiation in a particular spectral region, is widely applicable, and is especially useful when one substance in the reaction mixture has a strong characteristic absorption in a conveniently accessible region of the electromagnetic spectrum .Other methods of determining composition include emission spectroscopy, mass spectrometry, gas chromatography, nuclear magnetic resonance, and electron paramagnetic resonance

1-1-2-Flow method

In a real-time analysis the composition of the system is analysed while the reaction is in progress. Either a small sample is withdrawn or the bulk solution is monitored. In the flow method the reactants are mixed as they flow together in a chamber (Fig. 1).
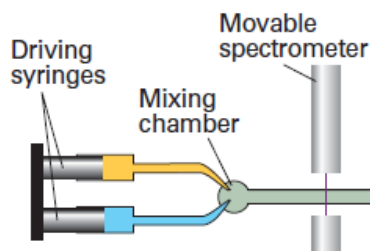
The reaction continues as the thoroughly mixed solutions flow through the outlet tube, and observation of the composition at different positions along the tube is equivalent to the observation of the reaction mixture at different times after mixing. The disadvantage of conventional flow techniques is that a large volume of reactant solution is necessary. This makes the study of fast reactions particularly difficult because tospread the reaction over a length of tube the flow must be rapid. This disadvantage is avoided by the stopped-flow technique, in which the reagents are mixed very quickly in a small chamber fitted with a syringe instead of an outlet tube (Fig. 2).
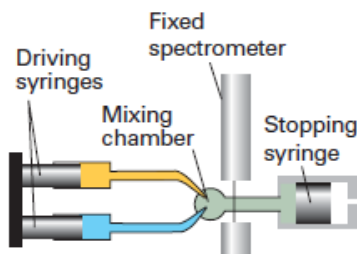
The flow ceases when the plunger of the syringe reaches a stop, and the reaction continues in the mixed solutions. Observations, commonly using spectroscopic techniques such as ultraviolet–visible absorption, circular dichroism, and fluorescence emission, are made on the sample as a function of time. The technique allows for the study of reactions that occur on the millisecond to second timescale. The suitability of the stopped flow method to the study of small samples means that it is appropriate for many biochemical reactions.

1-1-3-Flash photolysis

Very fast reactions can be studied by flash photolysis, in which the sample is exposed to a brief flash of light that initiates the reaction and then the contents of the reaction chamber are monitored. Most work is now done with lasers with photolysis pulse widths that range from femtoseconds to nanoseconds . The apparatus used for flash photolysis studies is based on the experimental design for time-resolved spectroscopy . Reactions occurring on a picosecond or femtosecond timescale may be monitored by using electronic absorption or emission, infrared absorption, or Raman scattering. The spectra are recorded at a series of times following laser excitation. The laser pulse can initiate the reaction by forming a reactive species, such as an excited electronic state of a molecule, a radical, or an ion

2-Rates of reactions

The rate of a reaction tells as to what speed the reaction occurs. Let us consider a simple reaction

A ⎯⎯→ B

The concentration of the reactant A decreases and that of B increases as time passes. The rate of reactions is defined as the change in concentration of any of reactant or products per unit time. For the given reaction the rate of reaction may be equal to the rate of disappearance of A which is equal to the rate of appearance of B.
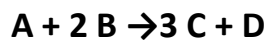
Thus

**rate of reaction = rate of disappearance of A**

= rate of appearance of B

Or:

$$\text{rate} = -\frac{d[A]}{dt}$$

$$= +\frac{d[B]}{dt}$$

Reaction rates depend on the composition and the temperature of the reaction mixture. Consider a reaction of the form

A + 2 B →3 C + D

in which at some instant the molar concentration of a participant J is [J] and the volume of the system is constant. The instantaneous rate of consumption of one of the reactants at a given time is **−d[R]/dt**, where R is A or B. The rate of formation of one of the products (C or D, which we denote P) is **d[P]/dt** (note the difference in sign). This rate is also positive. It follows from the stoichiometry for the reaction

A + 2 B →3 C + D
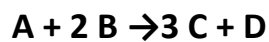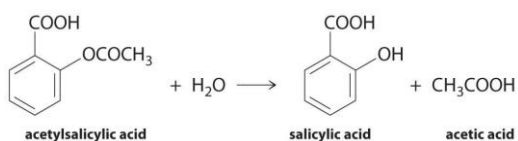
That

$$\frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$
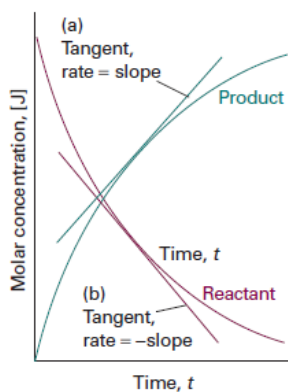
reaction rates of homogeneous reactions are reported in moles per cubic decimetre per second **(mol dm^{-3} s^{-1})** or related units

Example/Determining the Reaction Rate of Hydrolysis of Aspirin

COOH

OCOCH$_3$ COOH

                   OH

+ H$_2$O $\longrightarrow$ + CH$_3$COOH

acetylsalicylic acid   salicylic acid   acetic acid

Data for the hydrolysis of a sample of aspirin are in the Table below

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

The graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data In the Table
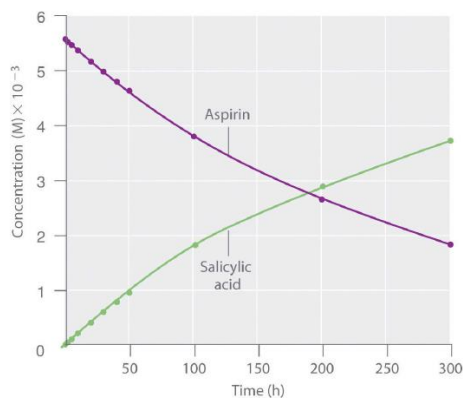
Example/ If the rate of formation of NO in the reaction 2 NOBr(g) → 2 NO(g) + Br2(g) is

reported as 0.16 mmol dm^{-3} s^{-1}, we use vNO = +2 to report that The rate of the reaction:

v = 0.080 mmol dm^{-3} s^{-1}.

Because vNOBr = −2 it follows that

d[NOBr]/dt = −0.16 mmol dm^{-3} s^{-1}.

The rate of consumption of NOBr is therefore 0.16 mmol dm^{-3} s^{-1}

3-Rate laws and rate constants

The rate of reaction is often found to be proportional to the concentrations of the reactants raised to a power. For example, the rate of a reaction may be proportional to the molar concentrations of two reactants A and B, so we write

v = k[A][B]

with each concentration raised to the first power. The coefficient **k** is called the **rate constant** for the reaction. An experimentally determined equation of this kind is called the **rate law** of the reaction

A **rate law** is an equation that expresses the rate of reaction as a function of the concentrations of all the species present in the overall chemical equation for the reaction.

4-Order of a Reaction

The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

Let us consider the example of a reaction which has the rate law

rate = k [A]^m [B]^n ...(1)

The order of such a reaction is (m + n).

The order of a reaction can also be defined with respect to a single reactant. Thus the reaction order with respect to A is m and with respect to B it is n. The overall order of reaction (m + n) may range from 1 to 3 and can be fractional

RATE LAW	REACTION ORDER
rate = $k\,[N_2O_5]$	1
rate = $k\,[H_2]\,[I_2]$	1 + 1 = 2
rate = $k\,[NO_2]^2$	2
rate = $k\,[[H_2]\,[NO]^2$	1 + 2 = 3
rate = $k\,[CHCl_3]\,[Cl_2]^{1/2}$	$1 + \dfrac{1}{2} = 1\dfrac{1}{2}$

5- *Molecularity of a Reaction*

Chemical reactions may be classed into two types :

(a) Elementary reactions and (b) Complex reactions

An elementary reaction is a simple reaction which occurs in a single step.

A complex reaction is that which occurs in two or more steps.

5-1 Molecularity of an Elementary Reaction

  The molecularity of an elementary reaction is defined as : the number of reactant molecules

involved in a reaction.

Thus the molecularity of an elementary reaction is 1, 2, 3, etc., according as one, two or three

reactant molecules are participating in the reaction. The elementary reactions having molecularity 1, 2

and 3 are called unimolecular, bimolecular and termolecular respectively. Thus we have :

(a) Unimolecular reactions : (molecularity = 1)

A ⟶ product

Examples are : (i) Br_2 ⟶ 2Br

 (b) Bimolecular reactions : (molecularity = 2)

A + B ⟶ products

2 A ⟶ products

Examples are :

(i) $CH_3COOC_2H_5 + H_2O$ ⟶ $CH_3COOH + C_2H_5OH$

 (ii) 2HI ⟶ $H_2 + I_2$

(c) Termolecular reactions : (molecularity = 3)

A + B + C ⟶ products

Examples are :

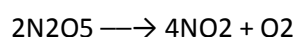$2NO + O_2 \longrightarrow 2NO_2$
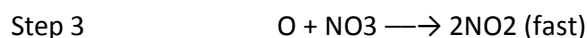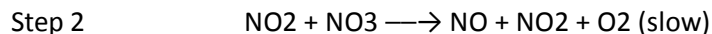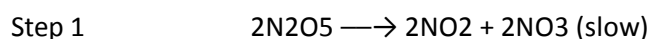
$2NO + Cl_2 \longrightarrow 2NOCl$
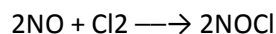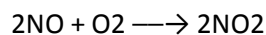
5-2 Molecularity of a Complex Reaction

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an

elementary reaction. The stepwise sequence of elementary reactions that convert reactions to products

is called the mechanism of the reaction. In any mechanism, some of the steps will be fast, others will

be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is the ratedetermining

step of the reaction.

The decomposition of N_2O_5,

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

is an example of a complex reaction. It occurs by the following steps :

Step 1 $2N_2O_5 \longrightarrow 2NO_2 + 2NO_3$ (slow)

Step 2 $NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$ (slow)

Step 3 $O + NO_3 \longrightarrow 2NO_2$ (fast)

Overall reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Each elementary reaction has its own molecularity equal to the number of molecules or atoms

participating in it. It is meaningless to give the molecularity of the overall reaction because it is made

of several elementary reactions, each, perhaps with a different molecularity. At best could be thought

of as : the number of molecules or atoms taking part in the rate-determining step.

Thus step 2 in the above mechanism is rate-determining and has molecularity '2' which could be

considered as the molecularity of the decomposition reaction of N_2O_5.

Differences Between Order and Molecularity

Order of a Reaction	Molecularity of a Reaction
1. It is the **sum of powers** of the concentration terms in the rate law expression.	1. It is number of **reacting species** undergoing simultaneous collision in the elementary or simple reaction.
2. It is an **experimentally** determined value.	2. It is a **theoretical** concept.
3. It can have **fractional** value.	3. It is always a **whole number**.
4. It can assume **zero value**.	4. It **can not have zero value**.
5. Order of a reaction **can change** with the conditions such as pressure, temperature, concentration.	5. Molecularity is **invariant** for a chemical equation.

6-PSEUDO–ORDER REACTIONS

A reaction in which one of the reactants is present in a large excess shows an order different from

the actual order. The experimental order which is not the actual one is referred to as the pseudo

order. Since for elementary reactions molecularity and order are identical, pseudo-order reactions may

also be called pseudo molecular reactions.

Let us consider a reaction

A + B ⟶ products
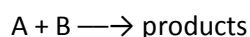
in which the reactant B is present in a large excess. Since it is an elementary reaction, its rate law can
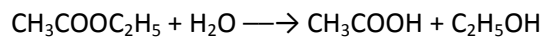
be written as

rate = k [A] [B]

As B is present in large excess, its concentration remains practically constant in the course of

reaction. Thus the rate law can be written as

rate = k' [A]

where the new rate constant k' = k [B]. Thus the actual order of the reaction is second-order but in

practice it will be first-order. Therefore, the reaction is said to have a pseudo-first order.

Example of Pseudo-order Reactions:

Hydrolysis of an ester. For example, ethyl acetate upon hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.

$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

ethyl acetate (excess) acetic acid ethyl alcohol

Here a large excess of water is used and the rate law can be written as

rate = k [CH_3COOH] [H2O]

= k' [CH3COOH]

The reaction is actually second-order but in practice it is found to be first-order. Thus it is a pseudo-first order reaction.