

## Module 6 : Reaction Kinetics and Dynamics

### Lecture 26 : Integrated Rate Laws

#### Objectives

In this Lecture you will learn to

- Define the reaction rate and the rate constant (coefficient).
- Distinguish between molecularity and order of a reaction.
- Obtain the integrated rate laws for orders  $n = 1, 2$  and  $3$ .
- Define half lives and decay times for reactions.
- Give a few examples of the orders of magnitudes of rate coefficients.

#### 26.1 Integrated Rate Laws

So far in our course, we have been mainly concerned with molecular structures or bulk matter in equilibrium. Quantum theory and spectroscopic methods (modules 1, 2 and 3) give a very good idea of the structure of molecules and diffraction methods (module 4) help us in understanding the structure of solids and liquids. Thermodynamics gives a satisfactory description of the states of matter at equilibrium and gives an unambiguous picture of the direction of changes in nature. (module 5).

Simply knowing the direction of change, in a chemical reaction such as



is hardly satisfactory because the rate of this transformation can be as fast as  $10^{10}$  (in suitable units such as the number of D molecules produced per second) or can be as slow as  $10^{-10}$  (where there is barely any perceptible change). Therefore, studying the rates of reactions experimentally (empirically) or predicting the reaction rates (theoretical modeling) has always remained a fascinating task. With the advent of ultrafast lasers (sub - picosecond) one can address and answer questions such as " How long lived is the transition state ( the state intermediate between reactants and products) of this reaction?" In this module we shall slowly go over from a macroscopic description of chemical changes to a microscopic description involving details of the energy levels of the reactants and products. Let us begin with the definitions of the reaction rate and the rate constant.

#### 26.2 The reaction rate and the rate constant.

In reaction represented by eqn (20.1), for each mole of A reacting with two moles of B, one mole of D and three moles of C are produced. In terms of moles per liter the rate of production of C is three times the rate of production of D and is equal to three times the rate of disappearance of A.

To avoid the roles of stoichiometric coefficients and to obtain a unique definition of the rate, the reaction rate of a reaction such as,



is defined as

rate =

$$\frac{1}{\nu_C} \frac{d[C]}{dt} = \frac{1}{\nu_D} \frac{d[D]}{dt}$$

$$= -\frac{1}{\nu_a} \frac{d[A]}{dt} = -\frac{1}{\nu_b} \frac{d[B]}{dt} \quad (20.3)$$

Here  $\nu_a, \nu_b, \dots$  are the stoichiometric coefficients and  $[A], [B], \dots$  represent the concentrations of the respective reactants or products in convenient units such as moles / liter. In later chapters, we will also use units such as number of molecules per  $\text{cm}^3$  of volume per unit time for the reaction rate.

Once the methods for determining the reaction rates (such as conductance measurements, spectrophotometry, optical rotation and so on, just to name a few) were established, a large amount of data was generated (similar to the P, V, T data for gases and liquids) and it became imperative to organize this data in a compact form.

The rate of a reaction is, in general, a complicated function of the concentration of the reactants, temperature, pressure and so on. A simple way to represent this dependence was to find a relation between the rates of reactions and the concentrations of the reacting species.

$$\frac{1}{\nu_a} \frac{d[A]}{dt} \propto [A]^\alpha [B]^\beta \quad (20.4)$$

where  $\alpha$  and  $\beta$  are the parameters to be determined experimentally (empirically) for each reaction. Here,  $\alpha$  is called the order of the reaction with respect to A and  $\beta$  is the order with respect to B. Please distinguish between the order  $\alpha$  and the symbol representing proportionality.

The proportionality constant in eqn (26.4) is called the rate constant or the rate coefficient and is commonly denoted by k. For  $\nu_a = 1$ , we have,

$$\frac{d[A]}{dt} = k [A]^\alpha [B]^\beta \quad (26.5)$$

### 26.3 Order and Molecularity

The central task in experimental chemical kinetics is to determine k,  $\alpha$  and  $\beta$ . A special situation or simplification occurs when  $\alpha = \nu_a$  and  $\beta = \nu_b$ , i.e., the stoichiometric coefficient of a species equals the order to which the concentration of that species has to be raised in eqn (26.5).

In this situation, the order of the reaction with respect to a given species is the same as the molecularity of that species in the equation for the reaction (20.2). Very high orders such as 3 or 4 are indeed rare, and more often than not, orders and molecularities are different.

#### Example 26.1

In a reaction  $A + B + C \rightarrow \text{products}$ , doubling the initial concentration of A increases the reaction rate by a factor of 2; doubling the concentration of B increases the rate four fold and increasing the concentration of C by a factor of 4 doubles the rate. What is the order of the reaction with respect to each of the reactants?

#### Solution :

The rate of the reaction may be written as  $-d[A]/dt = k[A]^\alpha[B]^\beta[C]^\gamma$

When the initial concentration of B is doubled, the rate is increased by a factor of four i.e.,

$$-4 \frac{d[A]}{dt} = k [A]^{\alpha} [2B]^{\beta} [C]^{\gamma}$$

Comparing the two equations, we get  $2\beta = 4$  or  $\beta = 2$ ; i.e the order of the reaction with respect to B is 2.

Using similar arguments, show that the order w.r.t. (with respect to) A is 1 and the order w. r. t. C is 1/2.

## 26.4 Integrated Rate Laws for First and Second order Reactions

In a first order reaction,



The rate of decrease in the concentration of A is given by

$$\frac{-d[A]}{dt} = k[A]^1 \quad (26.7)$$

In this equation the rate of the reaction depends on the first power of A.

A typical example is the isomerization of methyl isocyanide



Rearranging and integrating eqn (26.7), we get,

$$-\int \frac{d[A]}{[A]} = k \int dt \quad (26.9a)$$

$$\text{or } -\ln[A] = kt + \text{constant} \quad (26.9b)$$

The constant of integration can be eliminated by a proper choice of initial condition. At time  $t = 0$ ,  $[A] = [A]_0$ , the initial concentration of A. At time  $t$ , the concentration of  $[A]$  may be written as  $[A]_t$ . Integrating (26.9a) from  $t = 0$  ( $[A] = [A]_0$ ) to a final value of  $t$  ( $[A] = [A]_t$ ), we get

$$-(\ln[A]_t - \ln[A]_0) = kt \quad (26.10)$$

or the value of constant in eq (26.9b) is  $\ln[A]_0$ .

Rewriting (26.10),

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \text{or}$$

$$[A]_t = [A]_0 e^{-kt} \quad \text{or}$$

$$\frac{[A]_t}{[A]_0} = e^{-kt} \quad (26.11)$$

Eqn (26.11) indicates that the concentration of  $[A]$  decreases exponentially with time for this process. The time required for  $[A]_0$  to decrease by a factor of  $e$ , i.e., the time when  $[A]_t / [A]_0 = 1/e$ , is called as the

decay time  $\tau$  or a relaxation time. We see from eqn (26.11) that when  $t = 1/k$ ,  $[A]_t / [A]_0 = 1/e$ . Therefore

$$\tau = 1/k \quad (26.12)$$

A more common time is the half life for the reaction  $t_{1/2}$ .

This is the time required for the initial concentration  $[A]_0$  to decrease by a factor of 2. From eq (26.11), when

$$[A]_t = (1/2) [A]_0,$$

$$\ln \frac{[A]_t}{[A]_0} = - \ln \frac{[A]_0}{[A]_t} = - \ln 2 = -k t_{1/2} \quad (26.13)$$

$$\text{or } t_{1/2} = \ln 2 / k \quad (26.14)$$

A consequence of this equation is that the half life for a first order reaction is independent of the initial concentration of A,  $[A]_0$ . This equation provides an easy criterion to determine the order. A straightforward method to determine  $k$  is suggested by eq (26.11)

$$\ln [A]_t = \ln [A]_0 - kt \quad (26.15a)$$

or

$$\log_{10} [A]_t = \log_{10} [A]_0 - kt / 2.303 \quad (26.15b)$$

In the second equation (26.15b) above, logarithms have been taken to the base 10. Before the proliferation of hand calculators or computers, this was the more common equation which was in use. Plotting  $\log_{10} [A]_t$  vs  $t$  for a first order reaction will give a straight line with a slope  $= -k / 2.303$  and the intercept on the  $t = 0$  axis will be  $\log_{10} [A]_0$

### Example 26.2

Two reactions, a)  $N_2O_5(g) \rightarrow 2NO_2(g) + 1/2 O_2(g)$  and b)  $NOBr(g) \rightarrow NO(g) + 1/2 Br_2(g)$  are studied kinetically by measuring the concentrations of  $N_2O_5(g)$  and  $NOBr(g)$  respectively, as a function of time. Find the order of the reaction with respect to the reactants.

Reaction (a)		Reaction (b)	
Time / min	$[N_2O_5] / \text{mol dm}^{-3}$	Time / sec	$[NOBr] / \text{mol dm}^{-3}$
0	0.0124	0	0.0250
20	0.0068	6.2	0.0191

40	0.0037	10.8	0.0162
60	0.0020	14.7	0.0144
80	0.0011	20.0	0.0125
100	0.0006	24.6	0.0112

For reaction (a) the values of the log of the concentration of  $[\text{N}_2\text{O}_5]$  in  $\text{mol dm}^{-3}$  at the six values of time, namely - 4.39, - 4.99, - 5.60, - 6.21, - 6.81 and - 7.42 are plotted against time as shown below in Fig (26.1). We observe that the graph is a straight line with a slope =  $k = 3.04 \times 10^{-2} \text{ min}^{-1}$ , indicating that the reaction is first order with respect to  $\text{N}_2\text{O}_5$ . A similar plot against time for the second reaction with the values of  $\log ([\text{NOBr}] / \text{mol dm}^{-3})$ , namely, -2.584, -3.353, -4.123, - 4.433, and, does not give a straight line. In such a situation we have to systematically try the plots for other orders one by one. Plotting the six  $1/ [\text{NOBr}]$  values of 40.0, 52.3, 61.7, 69.9, 80.0 and 89.3 vs time as shown in fig (26.2) gives a straight line with slope of  $2.01 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , which is the second order rate constant for the reaction.

**Figure 26.1 First order plot for reaction (a) above.**

**Figure 26.2 Second order plot for reaction (b) above.**

For the second order reactions, we have two distinct cases. In the first case, both the reactants are identical. This is shown in equation (26.16).



The rate equation for this process is

$$\text{rate} = - \frac{1}{2} \frac{d[A]}{dt} = k [A]^2 \quad (26.17)$$

Rearranging and integrating between the limits  $[A]_0$  at  $t = 0$  and  $[A]_t$  at time  $t$ , we have,

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = 2k \int_0^t dt \quad (26.18)$$

integrating the equation, we get

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} - 2k t \quad (26.19)$$

A plot of the reciprocal the concentration,  $[A]_t^{-1}$  vs  $t$  will give a straight line with a slope equal to  $-2k$  and intercept of  $1/[A]_0$ .

Typical examples of reactions of type (26.16) are  $H + H \rightarrow H_2$ ,  $CH_3 + CH_3 \rightarrow C_2H_6$ ,  $2Br \rightarrow Br_2$  and so on.

When both reactants are not identical, the reaction is given as



The extent of the progress of the reaction may be measured by using a variable  $x$  which measures the extent of progress of the reaction

$$x = [A]_0 - [A]_t = [B]_0 - [B]_t \quad (26.21)$$

Here  $[A]_0$  and  $[B]_0$  are the initial concentrations of A and B and their concentrations at time  $t$  are  $[A]_t$  and  $[B]_t$  respectively.

The rate of the reaction in terms of the progress variable is

$$- \frac{d[A]_t}{dt} = \frac{dx}{dt} = k[A]_t [B]_t = k([A]_0 - x)([B]_0 - x) \quad (26.21)$$

For integrating eq ( 26.21 ) rewrite it as

$$\int_{x_0}^{x_t} \frac{dx}{([A]_0 - [B]_0)([B]_0 - x)} = k \int_0^t dt \quad (26.22)$$

The quadratic term in  $x$  in the denominator can be simplified by using the method of partial fraction as

$$= \int \frac{dx}{([A]_0 - [B]_0)([B]_0 - x)} - \int \frac{dx}{([A]_0 - [B]_0)([A]_0 - x)} \quad (26.23)$$

Integrating (26.23) and equating it to  $kt$  from eq (26.22) , we get

$$\frac{1}{([A]_0 - [B]_0)} \ln \left( \frac{[B]_0 [A]_t}{[A]_0 [B]_t} \right) = kt \quad (26.24)$$

To obtain  $k$ , we need to plot the logarithm of the product in parenthesis of eq (26.24) against time. The equation will fail if  $[A]_0 = [B]_0$ . In this case, since  $[A]_t = [B]_t$ , eq (26.19) can be used to obtain  $k$ .

Typical examples of reactions of type (26.20) are  $\text{H} + \text{Cl} \rightarrow \text{HCl}$ ,  $\text{CH}_3 + \text{Cl} \rightarrow \text{CH}_3\text{Cl}$  and so on.

Table 26.1 gives a list of integrated rate laws for integer orders. Here,  $x$  = concentration of a product, rate  $r = dx / dt$ .  $M$  = moles.  $L$  = liter.

Order	Reaction	Rate Law		Units of k	Half life (t <sub>1/2</sub> )
		Differential form	Integrated form		
0	A → Products	r = k [A] <sup>0</sup>	x = kt for x ≤ [A] <sub>0</sub>	M L <sup>-1</sup> s <sup>-1</sup>	[A] <sub>0</sub> / 2k
1	A → Products	r = k [A]	kt = ln [A] <sub>0</sub> / [A] <sub>0</sub> - x	s <sup>-1</sup>	Ln 2 / k
2	A → Products	r = k [A] <sup>2</sup>	kt = x / [A] <sub>0</sub> ( [A] <sub>0</sub> - x)	L M <sup>-1</sup> s <sup>-1</sup>	1 / k [A] <sub>0</sub>
2	A → Products	r = k [A] [B]	kt = 1 / ( [A] <sub>0</sub> - [B] <sub>0</sub> ) ln ([B] <sub>0</sub> ( [A] <sub>0</sub> - x) / [A] <sub>0</sub> ( [B] <sub>0</sub> - x)) {See Eq (26.24)}	L M <sup>-1</sup> s <sup>-1</sup>	
				(LM <sup>-1</sup> ) <sup>n-1</sup> s	2 <sup>n-1</sup> - 1 /

$n \geq 2$	$A \rightarrow \text{Products}$	$r = k [A]^n$	$kt = ([A_0] - x)^{-(n-1)} - [A_0]^{-(n-1)} / (n-1)$	-1	$(n-1)k[A_0]^{n-1}$
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In many reactions, the concentrations of all but one of the reactants is in large excess. In such a situation, it is easier to follow the changes in concentration of this particular species. E.g., in the reaction  $A + B \rightarrow \text{Products [P]}$ ,  $dP/dt$  may be actually  $k [A] [B]$ , but if  $[B]$  is in large excess, the concentration of  $B$  is likely to remain a constant  $= [B]_0$  for a considerable length of time. In this situation, the rate law may be written as

$$\frac{d[P]}{dt} = k [A] [B]_0 = k' [A] \text{ where } k' = k [B]_0 \quad (26.25)$$

The above reaction is said to follow a pseudo first order rate law.

## 26.4 Examples

Every chemical reaction has a unique rate constant. Its value which depends on the external conditions such as temperature and pressure and if it is not a first order reaction,  $k$  will depend on the initial concentrations of the reactants. In this section, we will consider a few examples to get a perspective. Reactions such as precipitation reactions (e.g.,  $\text{NaCl}$  solution added to  $\text{AgNO}_3$  solution) are very fast and are controlled by the process of diffusion. Ions in solution are moving around due to the thermal forces (due to the very very large number collisions of a given particle with neighbouring particles, forcing the given particle to move in an arbitrary direction at a given time) which are omnipresent at non zero temperatures.

If the reacting particles in solution react as soon as they come close to one another, say within 2 to 3 collisions, then the rate is said to be diffusion controlled. These second order rate constants can be as high as  $10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ . The rate constants for reaction generally change if you go from the gas phase to a liquid or solution phase. E.g., the rate constant for the first order reaction  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$  at  $25^\circ\text{C}$  is  $3.3 \times 10^{-5} \text{ s}^{-1}$  in the gas phase and  $4.3 \times 10^{-5}$  in liquid bromine. The rates, of course change if you go from one solvent to another. Reaction rates within a similar group of reactions can vary widely. E.g., at 500 K, the rate constant ( $k$ ) for the isomerization cyclopropane  $\rightarrow$  propene is  $7.9 \times 10^{-14} \text{ s}^{-1}$  while  $k$  for the isomerization cyclopropane  $\rightarrow$  propyne is  $2.2 \times 10^{-14} \text{ s}^{-1}$  while  $k$  for  $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$  is  $6.2 \times 10^{-4} \text{ s}^{-1}$ .

Even for apparently very simple reactions such as electron exchange reactions of metal ions in solution(aqueous), the rates for  $\text{M}^{2+} + \text{M}^{3+} \rightarrow \text{M}^{3+} + \text{M}^{2+}$  can vary over several orders of magnitude. The rate constants for electron exchange in  $\text{Co}$  is  $10^{-5} \text{ L ml}^{-1} \text{ s}^{-1}$ , in  $\text{Fe}$ ,  $10^1 \text{ L mol}^{-1} \text{ s}^{-1}$  and  $\text{Ru}$ ,  $10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ .

All the features mentioned above are determined by the intrinsic nature of the reactants. It is well known fact that if you increase the temperature of the reaction by  $10^\circ\text{C}$ , the reaction rate doubles. the common explanation for this is that there is usually some activation barrier (activation energy  $\Delta E$ ) for most reactions and increasing the temperature increases the thermal energies of the reactants, thereby enabling them to go over the potential energy barrier more easily. It should be apparent from this brief discussion that the area of chemical kinetics and dynamics (and the associated fields such as ultrafast spectroscopy which is useful in monitoring the changes in the reactants after very small time intervals) is fascinating as well as challenging and we will take up many of these issues in the next few chapters.

## 26.5 Problems

**26.1)** Obtain the integrated rate laws for order zero and order  $n > 2$ . The final result is shown in table 26.1

**26.2)** For the reaction  $2\text{NO(g)} + \text{Cl}_2(\text{g}) \rightarrow 2\text{NOCl(g)}$ , it is found that when the concentration of chlorine is doubled, the rate of the reaction is doubled. When the concentrations of both  $\text{NO}$  and  $\text{Cl}_2$  are doubled, the reaction rate increases by a factor of 8. What is the order of the reaction with respect to nitric oxide and with respect to chlorine?



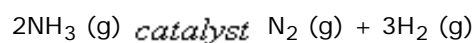
**26.3)** Show that for a third order reaction  $3A \rightarrow \text{Products}$ , the half life ( $t_{1/2}$ ) for the reaction is  $3 / (2ka^2)$  where  $k$  is the rate constant and  $a$  is the initial concentration of  $A$ .

**26.4)** The half life of  $\text{Cu}^{64}$  which emits  $\alpha$  particles is 12.8 hours. How long will it take for the radioactivity (which may be quantified as the number of disintegration in a material in unit time) of  $\text{Cu}^{64}$  to fall to 1 % of the initial value?

**26.5)** A piece of wood buried in a Himalayan glacier has only 28% of  $\text{C}^{14}$  in comparison with a recently grown piece of wood. The amount of  $\text{C}^{14}$  in the atmosphere has the value now which is the same as it was when the wood in the glacier was buried. If the half life for  $\text{C}^{14}$  is 5600 years, when was the wood buried in the glacier?

**26.6)** The rate coefficient (constant) for the hydrolysis of ethyl acetate by  $\text{NaOH}$  is  $6.36 \text{ liter mol}^{-1}$ . What fraction of the ester will be hydrolysed after a) 5 minutes and b) 10 minutes if the initial concentrations of both the ester and  $\text{NaOH}$  were 0.02 moles /liter? The reaction was carried out at  $25^\circ\text{C}$ .

**26.7)** The rate of decomposition of ammonia



with tungsten as catalyst was investigated by noting the increase in pressure of the system (at constant volume and temperature) as a function of time. At  $1100^\circ\text{C}$ , it was seen that the half life of the reaction ( $t_{1/2}$ ) varied with the initial pressure  $P_0$  as follows.

$t_{1/2}$ (mins)	$P_0$ (mm Hg)
1.7	58
3.7	130
7.6	265

Using the dependence of  $t_{1/2}$  on  $P_0$  (Table 26.1) determine the order of the reaction and the rate constant. If  $\text{NH}_3$  at 200 mm Hg is admitted into the reaction vessel at time  $t = 0$ , what is the total pressure of the reacting system after 1 min and after 3 minutes?

**26.8)** For a gaseous first order reaction  $2X \rightarrow \text{Products}$ , the rate constant at  $25^\circ\text{C}$  is  $2.8 \times 10^{-7} \text{ s}^{-1}$ . What is the half life of  $X$ ?

If the initial pressure of  $X$  is 50 kPa (kilo pascals; 1 pascal =  $1 \text{ Nm}^{-2}$ ; 1 atm = 101325 Pa; 1 bar =  $10^5$  pascals) what is the total pressure after a) 5 hours and b) 50 hrs if the reaction is initiated at  $t = 0$ ?

**26.9)** A second order reaction  $A + B \rightarrow \text{Products}$  was initiated in a solution containing  $0.1 \text{ mol L}^{-1}$  of  $A$  and  $0.15 \text{ mol L}^{-1}$  of  $B$ . After 2 hours, the concentrations of  $A$  had become  $0.1 \text{ mol L}^{-1}$ . Calculate the rate constant and the half life of each reactant.

**26.10)** The second order rate constant for the reaction  $A + 2B \rightarrow 2C + D$  is  $0.5 \text{ mol}^{-1} \text{ L s}^{-1}$ . What is the concentration of  $C$  after  $\frac{1}{2}$  minute and 10 minutes if the initial concentration of  $A$  was  $0.1 \text{ mol / L}$  and that of  $B$  was  $0.2 \text{ mol / L}$ ?

## Recap

In this Lecture you have learnt the following

## Summary

In this lecture, you have been introduced to chemical kinetics. Rate laws which relate the reaction rate to the concentrations of the species participating in the reaction were defined for reactions of different orders. The integrated rate laws for integer orders were obtained by integrating the differential forms of the rate laws. Order and molecularity were distinguished. When one of the species is present in large excess, its concentration hardly changes with time and the order of that reaction appears to be lower by one unit, as exemplified by a pseudo first order reaction. Half lives and relaxation times were defined and were computed for typical examples. It was shown that units of the rate constant depend on the reaction order. The half lives for reactions of different order depend on the initial concentrations uniquely and this dependence can be used as a method for ascertaining the orders. The main purpose of determining the rate laws, rate coefficients and half lives is to rationalize the enormous amount of kinetic data in a compact form, analogous to rationalizing the PVT data of gases and liquids into compact equations of state. Towards the end of the lecture, a few illustrative examples were given.