

# Chemical Kinetics

## Bsc Part-II, Chemistry (Gen) paper-III

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At our previous class we have learnt about the direction, spontaneity of a chemical reaction from thermodynamics. It is also important to know the time period of a chemical reaction. But thermodynamics does not give any information about what time a reaction will take to complete. In this chapter we shall learn about the rate of a chemical reaction and we can calculate concentration of a species at any time.

During progress of a reaction amount of  $i_{th}$  species is given by the relation

$$n_i = n_i^0 + \nu_i \xi, \quad (1)$$

where,  $n_i$  is mole numbers of  $i_{th}$  species after  $\xi$  moles advancement of the reaction,  $n_i^0$  is the initial mole numbers and  $\nu_i$  is the stoichiometry of this species. For example, in the reaction  $2H_2 + O_2 = 2 H_2O$  stoichiometry of  $H_2$ ,  $O_2$  and  $H_2O$  are -2, -1 and 2 respectively. If the reaction advances by 1 mole or one mole reaction occur then on consumption of 2 moles  $H_2$  and 1 mole  $O_2$  2 moles  $H_2O$  forms.

### Rate ( $\nu$ ):

Let us start with a general chemical reaction  $3A + B = 2P$  (2)

If we calculate change of amount of a particular chemical species with unit time then by differentiating equation (1) we get

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi_i}{dt} \quad (3)$$

Which term of equation (3) is rate? If the left hand side of the equation is rate then it is not unique for a reaction as it is defined in terms of a particular species of the reaction. For example, in the reaction 2 when one mole of B is consumed with consumption of three moles of A i.e. consumption of A is 3 times faster than B. The rate would also be different if we start with a test tube full of reaction mixture and a large vessel full of reaction mixture. So both side of equation 3 must be divided by reaction volume in order to make the rate of the reaction a unique term. So we should use concentration, rather than mole number. As advancement of a reaction is unique it will be more logical if we express the rate in terms of advancement of reaction. *The rate of a chemical reaction is defined as the rate of change of advancement of the reaction in unit volume with time.*

$$\nu = \frac{1}{V} \frac{d\xi_i}{dt} = \frac{1}{\nu_i} \frac{dC_i}{dt} \quad (4)$$

where  $C_i$  is concentration of  $i_{th}$  species expressed in mole per unit volume. For reaction 2 the rate of the reaction can be written as

$$\text{rate}(v) = -\frac{1}{3} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2} \frac{d[P]}{dt} \quad (5)$$

### (b) 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

$$v = k[A][B] \quad (6)$$

with each concentration raised to the first power. The coefficient  $k$  is called the **rate constant** for the reaction. The rate constant is independent of the concentrations but depends on the temperature. An experimentally determined equation of this kind (eqn 6) is called the **rate law** of the reaction. More formally, 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 at some time:

$$v = f([A],[B], \dots) \quad (7)$$

For homogeneous gas-phase reactions, it is often more convenient to express the rate law in terms of partial pressures, which are related to molar concentrations by  $p_J = RT[J]$ . In this case, we write

$$v = f(p_A, p_B, \dots) \quad (8)$$

The rate law of a reaction is determined experimentally, and cannot in general be inferred from the chemical equation for the reaction. The reaction of hydrogen and bromine, for example, has a very simple stoichiometry,  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{HBr}(\text{g})$ , but its rate law is complicated:

$$v = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]} \quad (9)$$

In certain cases the rate law does reflect the stoichiometry of the reaction, but that is either a co-incidence or reflects a feature of the underlying reaction mechanism (see later).

A practical application of a rate law is that, once we know the law and the value of the rate constant, we can predict the rate of reaction from the composition of the mixture. Moreover, as we shall see later, by knowing the rate law, we can go on to predict the composition of the reaction mixture at a later stage of the reaction. Moreover, a rate law is a guide to the mechanism of the reaction, for any proposed mechanism must be consistent with the observed rate law.

### (c) Reaction order

Many reactions are found to have rate laws of the form

$$v = k[A]^a[B]^b \dots \quad (10)$$

The power to which the concentration of a species (a product or a reactant) is raised in a rate law of this kind is the **order** of the reaction with respect to that species. A reaction with the rate law in eqn 6 is **first-order** in A and first-order in B. The **overall order** of a reaction with a rate law like that in eqn 10 is the sum of the individual orders,  $a + b + \dots$ . The rate law in eqn 6 is therefore second-order overall. A reaction need not have an integral order, and many gas-phase reactions do not. For example, a reaction having the rate law

$$v = k[A]^{1/2}[B] \quad (11)$$

is half-order in A, first-order in B, and three-halves-order overall. Some reactions obey a **zero-order rate law**, and therefore have a rate that is independent of the concentration of the reactant (so long as some is present). Thus, the catalytic decomposition of phosphine ( $\text{PH}_3$ ) on hot tungsten at high pressures has the rate law

$$v = k \quad (12)$$

The  $\text{PH}_3$  decomposes at a constant rate until it has almost entirely disappeared. Zero-order reactions typically occur when there is a bottle-neck of some kind in the mechanism, as in heterogeneous reactions when the surface is saturated and the subsequent reaction slow and in a number of enzyme reactions when there is a large excess of substrate relative to the enzyme. When a rate law is not of the form in eqn 11, the reaction does not have an overall order and may not even have definite orders with respect to each participant. Thus, although eqn 9 shows that the reaction of hydrogen and bromine is first-order in  $\text{H}_2$ , the reaction has an indefinite order with respect to both  $\text{Br}_2$  and  $\text{HBr}$  and has no overall order. These remarks point to three problems. First, we must see how to identify the rate law and obtain the rate constant from the experimental data. We concentrate on this aspect in this chapter. Second, we must see how to construct reaction mechanisms that are consistent with the rate law.

#### (d) The determination of the rate law

The determination of a rate law is simplified by the **isolation method** in which the concentrations of all the reactants except one are in large excess. If B is in large excess, for example, then to a good approximation its concentration is constant throughout the reaction. Although the true rate law might be  $v = k[A][B]$ , we can approximate  $[B]$  by  $[B]_0$ , its initial value, and write

$$v = k'[A], \quad k' = k[B]_0 \quad (13)$$

which has the form of a first-order rate law. Because the true rate law has been forced into first-order form by assuming that the concentration of B is constant, eqn 13 is called a **pseudofirst-order rate law**. The dependence of the rate on the concentration of each of the reactants may be found by isolating them in turn (by having all the other substances present in large excess), and so constructing a picture of the overall rate law.

## Integrated rate laws

Because rate laws are differential equations, we must integrate them if we want to find the concentrations as a function of time. Even the most complex rate laws may be integrated numerically. However, in a number of simple cases analytical solutions, known as **integrated rate laws**, are easily obtained, and prove to be very useful. We examine a few of these simple cases here.

### (a) First-order reactions

For first order reaction the rate law is

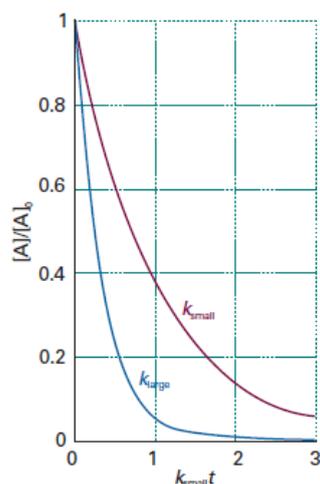
$$\frac{d[A]}{dt} = -k[A] \quad (14)$$

Rearranging we have  $\frac{d[A]}{[A]} = -kt$

This expression can be integrated directly because  $k$  is a constant independent of  $t$ . Initially (at  $t = 0$ ) the concentration of A is  $[A]_0$ , and at a later time  $t$  it is  $[A]$ , so we make these values the limits of the integrals and write

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

And we obtain immediately  $\ln\left(\frac{[A]}{[A]_0}\right) = -kt$  (15a) and  $[A] = [A]_0 e^{-kt}$  (15b) where  $[A]_0$  is initial concentration of A (at  $t=0$ ).



**Figure 1:** The exponential decay of the reactant in a first-order reaction. The larger the rate constant, the more rapid the decay: here  $k_{\text{large}} = 3k_{\text{small}}$

### (b) Half-lives and time constants

A useful indication of the rate of a first-order chemical reaction is the **half-life**,  $t_{1/2}$ , of a substance, the time taken for the concentration of a reactant to fall to half its initial value. The time for  $[A]$  to decrease from  $[A]_0$  to  $1/2[A]_0$  in a first-order reaction is given by eqn 15a

$$kt_{\frac{1}{2}} = -\ln\left(\frac{1/2[A]_0}{[A]_0}\right) = -\ln\frac{1}{2} = \ln 2$$

Hence  $t_{\frac{1}{2}} = \frac{\ln 2}{k}$  (16)

( $\ln 2 = 0.693$ .) The main point to note about this result is that, for a first-order reaction, the half-life of a reactant is independent of its initial concentration. Therefore, if the concentration of A at some *arbitrary* stage of the reaction is [A], then it will have fallen to  $1/2$  [A] after a further interval of  $(\ln 2)/k$ .

Another indication of the rate of a first-order reaction is the **time constant**,  $\tau$  (tau), the time required for the concentration of a reactant to fall to  $1/e$  of its initial value. From eqn 15a it follows that

$$kt_{\tau} = -\ln\left(\frac{1/e[A]_0}{[A]_0}\right) = -\ln\frac{1}{e} = 1$$

That is, the time constant of a first-order reaction is the reciprocal of the rate constant:

$$\tau = 1/k \quad (17)$$

### (c) Second-order reactions

For second order reaction the rate law has the form  $\text{rate} = -k[A]^2$

$$\text{Or, } \frac{d[A]}{dt} = -k[A]^2 \quad (18)$$

Rearranging we get  $\frac{d[A]}{[A]^2} = -k dt$

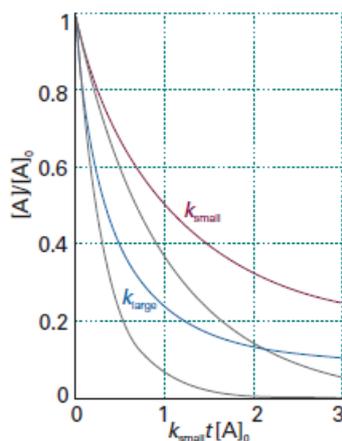
The concentration of A is  $[A_0]$  at  $t = 0$  and  $[A]$  at a general time  $t$  later. Therefore integrating both sides we get

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

Because the integral of  $1/x^2$  is  $-1/x$ , we obtain eqn 19 by substitution of the limits

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad (19) \quad \text{or } [A] = \frac{[A]_0}{1+kt[A]_0} \quad (20)$$

Equation 19 shows that to test for a second-order reaction we should plot  $1/[A]$  against  $t$  and expect a straight line. The slope of the graph is  $k$ . The rearranged form, eqn 20, lets us predict the concentration of A at any time after the start of the reaction. It shows that the concentration of A approaches zero more slowly than in a first-order reaction with the same initial rate.



**Figure 2:** The variation with time of the concentration of a reactant in a second order reaction. The grey lines are the corresponding decays in a first-order reaction with the same initial rate. For this illustration,  $k_{\text{large}} = 3k_{\text{small}}$

It follows from eqn 19 by substituting  $t = t_{1/2}$  and  $[A] = 1/2 [A]_0$  that the half-life of a species A that is consumed in a second-order reaction is

$$t_{1/2} = \frac{1}{k[A]_0} \quad (21)$$

Therefore, unlike a first-order reaction, the half-life of a substance in a second order reaction varies with the initial concentration. A practical consequence of this dependence is that species that decay by second-order reactions (which includes some environmentally harmful substances) may persist in low concentrations for long periods because their half-lives are long when their concentrations are low. In general, for an  $n$ th-order reaction of the form  $A \rightarrow \text{products}$ , the half-life is related to the rate constant and the initial concentration of A by

$$t_{1/2} = \frac{1}{k[A]_0^{n-1}} \quad (22)$$

### The temperature dependence of reaction rates

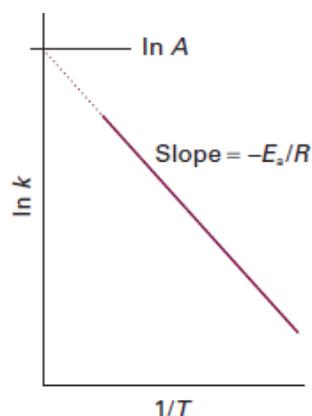
The rate constants of most reactions increase as the temperature is raised. Many reactions in solution fall somewhere in the range spanned by the hydrolysis of methyl ethanoate (where the rate constant at 35°C is 1.82 times that at 25°C) and the hydrolysis of sucrose (where the factor is 4.13).

#### (a) The Arrhenius parameters

It is found experimentally for many reactions that a plot of  $\ln k$  against  $1/T$  gives a straight line. This behaviour is normally expressed mathematically by introducing two parameters, one representing the intercept and the other the slope of the straight line, and writing the **Arrhenius equation**

$$\ln k = \ln A - \frac{E_a}{RT} \quad (23)$$

The parameter  $A$ , which corresponds to the intercept of the line at  $1/T = 0$  (at infinite temperature, Fig. 3), is called the **pre-exponential factor** or the ‘frequency factor’. The parameter  $E_a$ , which is obtained from the slope of the line ( $-E_a/R$ ), is called the **activation energy**. Collectively the two quantities are called the **Arrhenius parameters**.



**Figure 3:** A plot of  $\ln k$  against  $1/T$  is a straight line when the reaction follows the behaviour described by the Arrhenius equation (eqn 23). The slope gives  $-E_a/R$  and the intercept at  $1/T = 0$  gives  $\ln A$

The fact that  $E_a$  is given by the slope of the plot of  $\ln k$  against  $1/T$  means that, the higher the activation energy, the stronger the temperature dependence of the rate constant (that is, the steeper the slope). *A high activation energy signifies that the rate constant depends strongly on temperature.* If a reaction has zero activation energy, its rate is independent of temperature. In some cases the activation energy is negative, which indicates that the rate decreases as the temperature is raised. We shall see that such behaviour is a signal that the reaction has a complex mechanism. The temperature dependence of some reactions is non-Arrhenius, in the sense that a straight line is not obtained when  $\ln k$  is plotted against  $1/T$ . However, it is still possible to define an activation energy at any temperature as

$$E_a = RT^2 \left( \frac{d \ln k}{dT} \right) \quad (24)$$

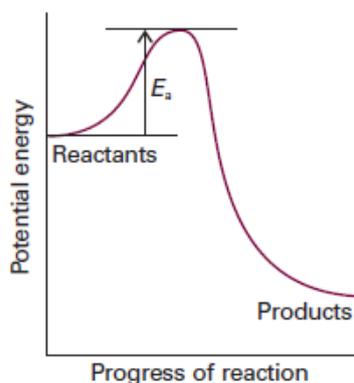
This definition reduces to the earlier one (as the slope of a straight line) for a temperature-independent activation energy. However, the definition in eqn 24 is more general than eqn 23, because it allows  $E_a$  to be obtained from the slope (at the temperature of interest) of a plot of  $\ln k$  against  $1/T$  even if the Arrhenius plot is not a straight line. Non-Arrhenius behaviour is sometimes a sign that quantum mechanical tunnelling is playing a significant role in the reaction.

### (b) The interpretation of the parameters

For the present chapter we shall regard the Arrhenius parameters as purely empirical quantities that enable us to discuss the variation of rate constants with temperature; however, it is useful to have an interpretation in mind and write eqn 23 as

$$k = Ae^{-\frac{E_a}{RT}} \quad (25)$$

To interpret  $E_a$  we consider how the molecular potential energy changes in the course of a chemical reaction that begins with a collision between molecules of A and molecules of B



**Figure 4:** A potential energy profile for an exothermic reaction. The height of the barrier between the reactants and products is the activation energy of the reaction

(Fig. 4). As the reaction event proceeds, A and B come into contact, distort, and begin to exchange or discard atoms. The **reaction coordinate** is the collection of motions, such as changes in interatomic distances and bond angles, that are directly involved in the formation of products from reactants. (The reaction coordinate is essentially a geometrical concept and quite distinct from the extent of reaction.) The potential energy rises to a maximum and the cluster of atoms that corresponds to the region close to the maximum is called the **activated complex**. After the maximum, the potential energy falls as the atoms rearrange in the cluster and reaches a value characteristic of the products. The climax of the reaction is at the peak of the potential energy, which corresponds to the activation energy  $E_a$ . Here two reactant molecules have come to such a degree of closeness and distortion that a small further distortion will send them in the direction of products. This crucial configuration is called the **transition state** of the reaction. Although some molecules entering the transition state might revert to reactants, if they pass through this configuration then it is inevitable that products will emerge from the encounter. We also conclude from the preceding discussion that, for a reaction involving the collision of two molecules, *the activation energy is the minimum kinetic energy that reactants must have in order to form products*. For example, in a gas-phase reaction there are numerous collisions each second, but only a tiny proportion are sufficiently energetic to lead to reaction. The fraction of collisions with a kinetic energy in excess of an energy  $E_a$  is given by the Boltzmann distribution as  $e^{-\frac{E_a}{RT}}$ . Hence, we can interpret the exponential factor in eqn 25 as the fraction of collisions that have enough kinetic energy to lead to reaction. The pre-exponential factor is a measure of the rate at which collisions occur irrespective of their energy. Hence, the product of  $A$  and the exponential factor,  $e^{-\frac{E_a}{RT}}$ , gives the rate of *successful* collisions.

**Book: Physical Chemistry** by Peter Atkins