

## 2.1: Kinetic Rate Laws

Kinetics deals with the rates of chemical processes *i.e.* how rapidly is a reactant consumed and a product formed? In this chapter, we will first define the reaction rate as the instantaneous change in concentration with respect to the time. Often we are interested in how the reaction rate depends on the concentrations of the species involved. This depends on the order of the reaction and leads to the various differential rate laws. On the other hand, if we are interested in how the concentration of species changes with time, we integrate the differential rate laws to obtain the integrated rate laws. Given an initial concentration and a kinetic rate constant, the integrated rate laws allow us to calculate the concentration at any future time.

### Learning Objectives

- Understand the definition of the reaction rate and be able to write down a differential equation for any proposed mechanism.
- Understand the difference between the differential vs. integrated rate laws and be able to recognize the order of a reaction from a plot of either rate vs. concentration or concentration vs. time.
- Be able to use the integrated rate laws to solve for the half life.
- Be able to solve the integrated rate laws algebraically, given the initial concentration, to find the concentration at a later time.

### The Reaction Rate

The **rate of a reaction** is the change in concentration of either the reactant or product with respect to time. During the course of a reaction, the concentration of the reactants will decrease and the concentration of the products will increase as shown in **Figure II.1.A**.

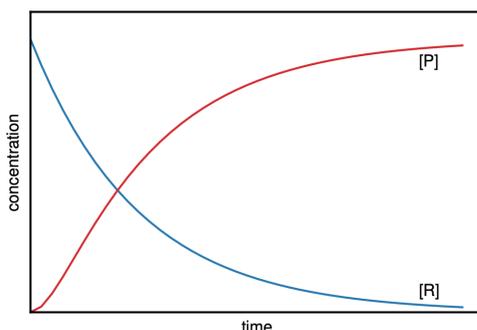
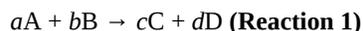


Figure II.1.A. Schematic depiction of the concentration of the reactants [R] and the concentration of products [P] as a function of time for a hypothetical reaction. The reactant [R] is consumed while the production [P] is formed. The rate at any given time is related to the slope of the concentration vs. time curve.

The rate of change of reactant and product is related to the slope of the concentration curves shown in **Figure II.1.A**. In general, for the reaction:



where the coefficients ( $a$ ,  $b$ ,  $c$ , and  $d$ ) are the stoichiometric coefficients, the **rate** can be expressed in terms of any of the reactants or products as:

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \quad (2.1.1)$$

where the expression in brackets refers to the concentration at a given time  $t$ . Notice that the rate expression in terms of the reactants contains a negative sign because the reactant is being used up, so its concentration is decreasing, whereas the concentration of the product is increasing.

## Reaction Order

The rate of a reaction usually (but not always) depends on the concentration. Conceptually, it makes sense that the reaction rate increases with concentration because the frequency of collisions between reactive species will be greater at higher concentrations. However, the precise relationship between concentration and the reaction order must be determined experimentally. In most cases, for the general reaction of the form of **Reaction 1**, the reaction rate can be expressed in terms of the concentrations as:

$$\text{rate} = k[A]^n[B]^m \quad (2.1.2)$$

where  $k$  is called the **rate constant** and  $n$  and  $m$  are the **order** of the reaction with respect to A or B and must be determined experimentally.

### Note

The reaction orders  $m$  and  $n$  in Equation 2.1.2 are *not* the same as the stoichiometric coefficients and must be determined from experiment.

Equation 2.1.2 is known as the *rate law* and the overall **reaction order** is determined by the sum of the orders  $n$  and  $m$  for each reactant. We will now consider a few cases.

### Zero-Order Reaction

Consider the reaction of the form:



If the reaction is **zero order**, the rate law (Equation 2.1.2) is given by:

$$\text{rate} = k[A]^0 \quad (2.1.3)$$

Substituting the definition of the rate from Equation 2.1.1 we have:

$$\begin{aligned} -\frac{d[A]}{dt} &= k[A]^0 \\ -\frac{d[A]}{dt} &= k \end{aligned} \quad (2.1.4)$$

where the negative sign is because the concentration of reactant A is decreasing. Equation 2.1.4 gives us a first-order differential equation for the concentration [A]. This is known as the *differential rate law* since it is in differential form. For a zero-order reaction, the rate constant  $k$  is in units of  $M s^{-1}$ .

Notice from Equation 2.1.4 for a zero-order reaction, the rate is simply a constant  $k$  and does not depend on the concentration. A plot of the rate vs. concentration for a zero-order reaction gives a horizontal line as shown in **Figure II.1.B (a)**

Integrating both sides of Equation 2.1.4 from concentration  $[A]_0$  at  $t = 0$  to concentration  $[A]$  at  $t = t$  gives

$$\begin{aligned} \int_{[A]_0}^{[A]} d[A] &= -k \int_0^t dt \\ [A] - [A]_0 &= -kt \\ [A] &= [A]_0 - kt \end{aligned} \quad (2.1.5)$$

Equation 2.1.5 is the *integrated rate law* for a zero-order reaction and gives an expression for the time-dependence of the concentration [A]. From Equation 2.1.5 we see that for a zero-order reaction, a plot of the concentration [A] vs. time yields a straight line with slope  $-k$ . A plot of Equation 2.1.5 is shown in **Figure II.1.B (b)**

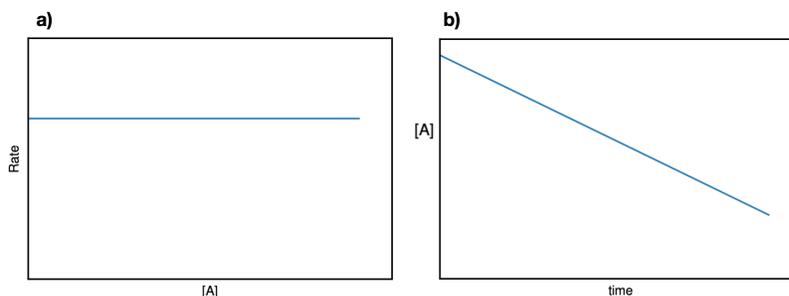


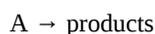
Figure II.1.B. Zero-order reaction. **(a)** For a zero-order reaction, the rate is independent of time and a plot of the rate vs. concentration is a constant. **(b)** The integrated rate law for a zero-order reaction exhibits a linear dependence of the concentration with respect to time.

### First-Order Reaction

In a first-order reaction, the rate is proportional to the concentration.

$$\text{rate} = k[A]$$

Again, for a reaction of the form of **Reaction 2:**



we have:

$$-\frac{d[A]}{dt} = k[A] \quad (2.1.6)$$

For a first-order reaction, the rate constant  $k$  has units of  $s^{-1}$ . A plot of Equation 2.1.6 is shown in **Figure II.1.C (a)** showing a linear dependence of the rate vs. time with a slope of  $-k$ . The first order differential equation of Equation 2.1.6 can be solved by *separation of variables* to obtain the *integrated rate law*:

$$\begin{aligned} \frac{d[A]}{[A]} &= -kdt \\ \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} &= -k \int_0^t dt \\ \ln \frac{[A]}{[A]_0} &= -kt \\ [A] &= [A]_0 e^{-kt} \end{aligned} \quad (2.1.7)$$

Notice that in a first-order reaction, the initial concentration decays *exponentially* with time. **Figure II.1.C (b)** shows the concentration vs. time for a first-order reaction.

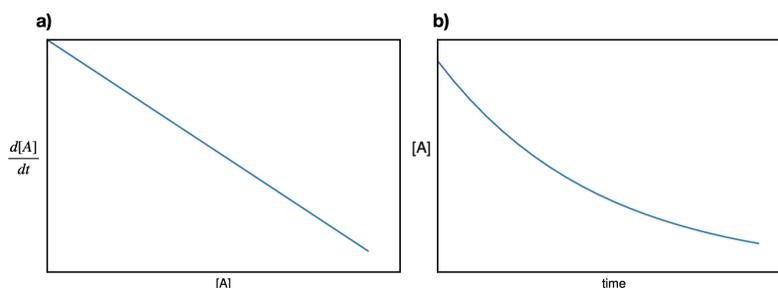


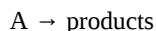
Figure II.1.C First-order reaction. **(a)** In a first-order reaction, the rate depends linearly on the time with the magnitude of the slope equal to the rate constant. **(b)** A plot of the concentration with respect to time for a first-order reaction is an exponential function.

## Second-Order Reaction

There are two types of reactions we will consider that are second-order.

### Case 1: Reaction of the type $A \rightarrow \text{products}$

The first type of second-order reaction that we will consider is for a reaction of the form of **Reaction 2**:



For a second-order reaction of this type, the rate is:

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2 \quad (2.1.8)$$

For a second-order reaction of this type, the rate constant  $k$  has units of  $M^{-1} s^{-1}$  and the rate is proportional to the concentration raised to the power of two. A plot of Equation 2.1.8 is shown in **Figure II.1.D (a)** showing a quadratic dependence of the rate vs. time. Equation 2.1.8 is a *second* order differential equation that can be solved by *separation of variables* to obtain the *integrated rate law*:

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

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad (2.1.9)$$

Notice that for a second-order reaction of this kind, the *inverse* of the concentration is linear with time with a slope of  $k$ . **Figure II.1.D (b)** shows the concentration vs. time for a second-order reaction.

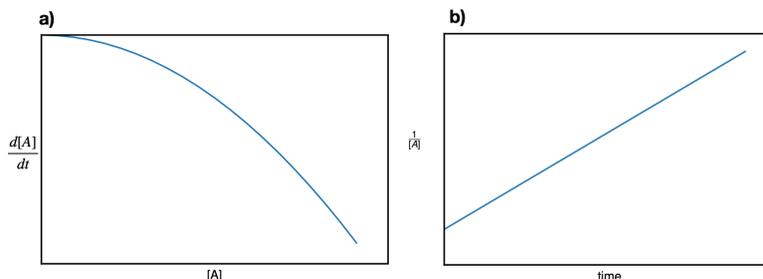


Figure II.1.D. Second order reaction. (a) For a second-order reaction describing **Reaction 2**, the rate has a quadratic dependence on the time. (b) A plot of the *inverse* concentration with respect to time gives a straight line.

### Case 2: Reaction of the type $A + B \rightarrow \text{products}$

We can also consider a second type of second-order reaction that is represented by two different molecular species (A and B) coming together to form products:



The rate is given by:

$$\text{rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \quad (2.1.10)$$

In this case, the rate is first-order with respect to A and first-order with respect to B, but the overall reaction order is second-order. An example of this type of second-order reaction is the renaturation of DNA from two complementary single-stranded DNA chains to form double-stranded DNA.

The integrated rate law from Equation 2.1.10 is

$$\frac{1}{[B]_0 - [A]_0} \ln \left( \frac{[B][A]_0}{[A][B]_0} \right) = kt \quad (2.1.11)$$

where  $[A]_0$  is the initial concentration of species A at time  $t = 0$  and  $[B]_0$  is the initial concentration of species B at time  $t = 0$ . A plot of Equation 2.1.11 is shown in **Figure II.1.E**

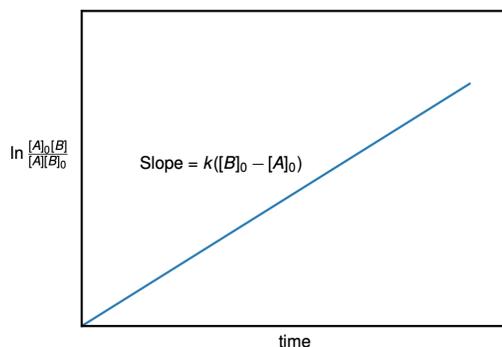


Figure II.1.E. Integrated rate law for a second-order reaction of the type according to Reaction 3. In this type of reaction, two different species A and B react to form a product. The reaction is first order with respect to both A and B, so the overall reaction order is two.

**Key Result:** **Table II.2.i** summarizes the various *rate laws* for a zero, first, and second order reaction

Table II.2.i

order	differential form	integrated form	units of k
0	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$	$M s^{-1}$
1	$\frac{d[A]}{dt} = -k[A]$	$[A] = [A]_0 e^{-kt}$	$s^{-1}$
2	$\frac{d[A]}{dt} = -k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$M^{-1} s^{-1}$
2 <sup>a</sup>	$\frac{d[A]}{dt} = -k[A][B]$	$\frac{1}{[B]_0 - [A]_0} \ln \frac{[B][A]_0}{[A][B]_0} = kt$	$M^{-1} s^{-1}$

a)  $A + B \rightarrow$  products

## The half-Life

The **half-life** of a reaction is the time required for the concentration of a reactant to decrease to half of its initial concentration. To find the half-life of any reaction, we can substitute the quantity:

$$\frac{1}{2}[A]_0 = [A] \quad (2.1.12)$$

into any of the integrate rate laws in **Table II.2.i** and solve for the time  $t$ . For example, for a first order rate law given by Equation 2.1.7:

$$[A] = [A]_0 e^{-kt} \quad (2.1.13)$$

Substitution of  $\frac{1}{2}[A]_0$  for  $[A]$  gives:

$$\begin{aligned} \frac{1}{2}[A]_0 &= [A]_0 e^{-kt_{1/2}} \\ \frac{1}{2} &= e^{-kt_{1/2}} \\ -kt_{1/2} &= \ln 2 \\ t_{1/2} &= \frac{\ln 2}{k} \end{aligned} \quad (2.1.14)$$

Notice that for a *first-order* reaction, the half-life does not depend on the initial concentration since  $[A]_0$  does not appear in the expression for  $t_{1/2}$ .

The half-lives for the other reaction orders can be solved in a similar way for each of the integrated rate laws in **Table II.1.i**. The expression for the half-lives for reaction orders 0, 1, and 2 are summaries in **Table II.1.ii**.

**Table II.1.ii. Half life for some common reactions**

Table II.2.ii

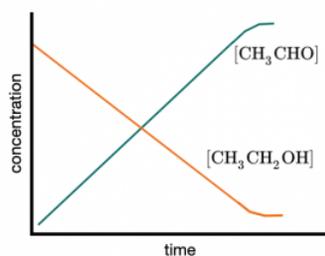
order	half life
0	$t_{1/2} = \frac{[A]_0}{2k}$
1	$t_{1/2} = \frac{\ln 2}{k}$
2	$t_{1/2} = \frac{1}{k[A]_0}$

## Practice problems

**Problem 1.** The first step in the metabolism ethanol is the conversion of ethanol into acetaldehyde by the enzyme ethanol dehydrogenase according to the reaction:



The figure below shows the concentration of the reactant ethanol and the product acetaldehyde. What is the order of the reaction? Sketch a plot of the rate of alcohol metabolism vs. concentration of ethanol.



**Problem 2.** For a certain first order reaction, the reaction is 40% complete after 120 min at 298 K. What is the value of the rate constant?

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