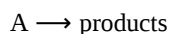


## 3.2: Day 19- Integrated Rate Law

Instead of using the method of initial rates, you can use the **integrated rate law** method to determine the rate law and rate constant from experimental data. An integrated rate law relates the concentration of a reactant or product to the elapsed time of the reaction. Thus, it can be used to determine the concentration of a reactant or product present after a certain period of time or to estimate the time required for a reaction to proceed to a certain extent.

For a given rate equation, calculus can be used to derive an appropriate integrated rate law. If you are not familiar with calculus and integration, don't worry—you can still use the integrated rate law for a reaction without deriving it yourself.

For a generic reaction:



The rate of the reaction can be expressed as:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^m$$

In calculus, the definition of a derivative is:

$$\frac{d[A]}{dt} = \lim_{\Delta t \rightarrow 0} \frac{\Delta[A]}{\Delta t}$$

So a rate law for the reaction can be written as:

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

Rearranging gives:

$$-\frac{d[A]}{[A]^m} = k dt$$

Integrating both sides of this equation gives:

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

Assuming that the reaction starts at  $t = 0$ , the right side integration simply becomes  $kt$ . And then multiplying both sides by  $-1$  gives:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^m} = -kt$$

$[A]_0$  is the initial reactant concentration and  $[A]_t$  is the reactant concentration at time  $t$ . The solution to the left side integration has a different mathematical form depending on the order of the reaction with respect to A (value of  $m$ ). We will explore cases where  $m = 1, 2$ , and  $0$ , in the next three sections.

### D19.2 First-Order Reaction

When  $m = 1$ , the integrated rate law for the reaction " $A \longrightarrow \text{products}$ " becomes:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \ln[A]_t - \ln[A]_0 = -kt$$

This integrated rate law for a first order reaction can be alternatively expressed as:

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

It is easier to use this form of this equation when trying to calculate the time required for a reaction to proceed to a certain extent.

On the other hand, if you raise  $e$  (the base of the natural logarithm system) to the power of each side of the equation, it gives:

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

It is easier to use this form when trying to determine the concentration of reactant left after a certain period of time.

The integrated rate law for a first order reaction can be rearranged to have a standard linear equation format:

$$\begin{aligned} \ln[A]_t &= -kt + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

Hence, if a reaction “A → products” is first order in [A], a plot of “ln[A]<sub>t</sub> vs. t” must give a straight line. The slope of such a plot would be  $-k$  and the y-intercept would correspond to  $\ln[A]_0$ . If the plot is *not* a straight line, the reaction is *not* first order in [A].

### Activity 1: First-order Rate Constant from Graph

## D19.3 Second-Order Reaction

When  $m = 2$ , the integrated rate law for the reaction “A → products” becomes:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^m} = \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -\frac{1}{[A]_t} - \left( -\frac{1}{[A]_0} \right) = -kt$$

This integrated rate law for a second order reaction can be alternatively expressed as:

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

The integrated rate law for second-order reaction also has a standard linear equation format:

$$\begin{aligned} \frac{1}{[A]_t} &= kt + \frac{1}{[A]_0} \\ y &= mx + b \end{aligned}$$

Hence, if a reaction “A → products” is second order in [A], a plot of

$$\frac{1}{[A]_t}$$

vs  $t$  should be a straight line, where the slope equals  $k$  and the y-intercept is

$$\frac{1}{[A]_0}$$

If the plot is *not* a straight line, then the reaction is *not* second order with respect to [A].

### Activity 2: Order from Integrated Rate Law

## D19.4 Zeroth-Order Reaction

The “A → products” reaction that is zeroth-order ( $m = 0$ ) in [A] exhibits a constant reaction rate regardless of the concentration of A:

$$\text{Rate} = k[A]^0 = k$$

The integrated rate law for such a zeroth-order reaction is:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^m} = \int_{[A]_0}^{[A]_t} d[A] = [A]_t - [A]_0 = -kt$$

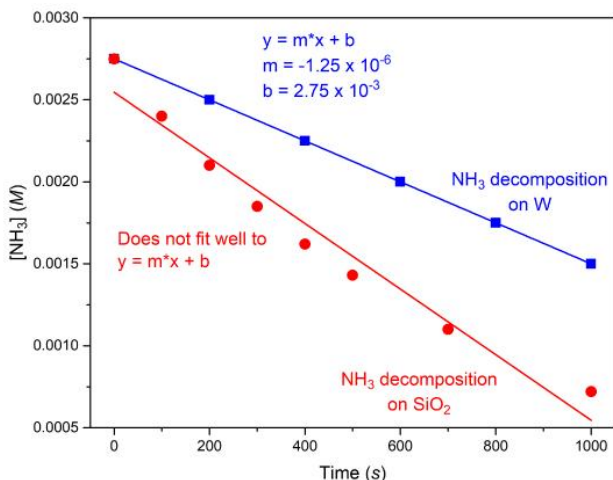
This integrated rate law also has a standard linear equation format:

$$[A]_t = -kt + [A]_0$$

$$y = mx + b$$

A plot of  $[A]_t$  vs  $t$  for a zeroth-order reaction is a straight line with a slope of  $-k$  and a y-intercept of  $[A]_0$ .

Figure 1 shows two plots, both are for the decomposition reaction of ammonia. One reaction occurred on a hot tungsten (W) surface, while the other reaction occurred on a hot quartz ( $\text{SiO}_2$ ) surface.



**Figure 1.** The decomposition of  $\text{NH}_3$  on a tungsten (W) surface is a zeroth-order reaction because the concentration data fit the equation  $y = mx + b$ . However, when data are collected for a quartz ( $\text{SiO}_2$ ) surface, there is curvature: the reaction is not zeroth-order.

We can see from this set of data that the reaction on tungsten is zeroth-order; the plot of  $[\text{NH}_3]$  vs  $t$  is a straight line. From the slope, we find that the rate constant for this reaction under the experimental conditions is:

$$-\text{slope} = k = 1.25 \times 10^{-6} \frac{\text{M}}{\text{s}}$$

The decomposition on hot quartz, on the other hand, is not zeroth-order (analysis of the data shows that it is first order).

Equations for zeroth-, first-, and second-order reactions are summarized in Table 1.

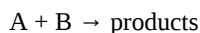
Property	Zeroth-Order	First-Order	Second-Order
rate law	$\text{rate} = k$	$\text{rate} = k[A]$	$\text{rate} = k[A]^2$
units of rate constant	M/s	1/s	1/M s
integrated rate law	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$1/[A]_t = kt + 1/[A]_0$
linear plot	$[A]$ vs. $t$	$\ln[A]$ vs. $t$	$1/[A]_t$ vs. $t$
relationship between slope of linear plot and rate constant	$k = -\text{slope}$	$k = -\text{slope}$	$k = +\text{slope}$

**Table 1.** Summary of Rate Laws for Zeroth-, First-, and Second-Order Reactions

### D19.5 Flooding Method: Pseudo-Order Reaction

The integrated rate laws are quite useful when determining the reaction order and rate constant using all the data from a single experimental trial. However, thus far we have only considered example reactions involving one reactant, whereas most reactions involve two or more reactants. How can we use integrated rate laws to find the reaction order and rate constants for those reactions?

Let's consider a generic reaction:



where:

$$\text{Rate} = k[A]^m[B]^n$$

**Flooding** refers to *running a reaction that involves two or more reactants with a large excess of all but one reactant*. For example, we can run the reaction above with a *large excess* of B so that A is the *limiting reactant* by a significant amount. In that case,  $[B]_0 \gg [A]_0$ , and the concentration of B would effectively remain constant during the course of the reaction. (If  $[B]_0 = 0.100 \text{ M}$  and  $[A]_0 = 0.00100 \text{ M}$ , then at a time  $t$  when all the A has reacted,  $[B]_t = (0.100 - 0.00100) \text{ M} = 0.099 \text{ M}$ , which is essentially no change in the concentration of B.)

Under this condition of  $[B]_t \approx [B]_0 = \text{constant}$ , the rate law becomes:

$$\text{Rate} = k[A]^m[B]_0^n = k_{\text{obs}}[A]^m$$

where  $k_{\text{obs}}$ , the rate constant we observe during the flooded experiment, is  $k_{\text{obs}} = k[B]_0^n$ . This new rate equation allows us to use the integrated rate laws we've just discussed to determine the reaction order with respect to [A], and also to determine  $k_{\text{obs}}$  and  $k$ . The order of the reaction,  $m$ , is called a **pseudo order** because it is *obtained under flooding conditions and is not necessarily the overall order of the reaction*. If  $m = 1$ , we say the reaction is pseudo first order and  $k_{\text{obs}}$  is called a pseudo-first-order rate constant.

Here is an example experiment: For trial 1, flood the reaction mixture with a large excess of reactant B

$$[B]_{01}$$

and measure  $[A]_t$  as the reaction progresses. Then plot  $\ln[A]_t$  vs  $t$ . If the graph is a straight line, then the reaction is first-order with respect to [A]. (In this case, the flooded reaction a pseudo-first-order reaction.) The slope of this graph is

$$-k_{\text{obs}1}$$

For trial 2, flood the reaction mixture with a *different* large excess of B

$$[B]_{02}$$

The plot of  $\ln[A]_t$  vs  $t$  has a different slope corresponding to

$$-k_{\text{obs}2}$$

The ratio of the two  $k_{\text{obs}}$  allows us to determine  $n$ , the reaction order with respect to [B]:

$$\frac{k_{\text{obs}2}}{k_{\text{obs}1}} = \frac{k([B]_{02})^n}{k([B]_{01})^n} = \left( \frac{[B]_{02}}{[B]_{01}} \right)^n$$

In the above equation, all the variables aside from  $n$  are known or have been experimentally determined.

Finally, the actual rate constant for the reaction,  $k$ , can be determined from the relationship  $k_{\text{obs}} = k[B]_0^n$ . The data all trials should be averaged to get the best value of  $k$ .

### Activity 3: Determining a Rate Constant Using Flooding

#### Day 19 Pre-class Podia Problem: Integrating a Rate Law

In Activity 1, earlier in today's work, data are given for the decomposition of hydrogen peroxide. Hydrogen peroxide decomposes to form oxygen and water. Write a balanced chemical equation for decomposition of hydrogen peroxide. How is the equation you wrote for hydrogen peroxide different from the chemical equation  $A \rightarrow \text{products}$  that was used to derive the integrated rate law in Section D19.1?

Now define the rate of reaction for decomposition of hydrogen peroxide using the method given in [Section D18.2](#) and derive the integrated first-order rate law, following the derivation in Sections D19.1 and D19.2. Use your mathematical work to show that the rate constant calculated in Activity 1 for the first-order decomposition of hydrogen peroxide is twice as big as it should be.

*Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.*

**Comments.** If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day's material. We appreciate your comments.

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