Differential and Integrated Rate Laws

Rate laws describe the progress of the reaction; they are mathematical expressions which describe the relationship between reactant rates and reactant concentrations. In general, if the reaction is:

$$aA + bB \rightarrow cC + dD$$

We can write the following expression:

$$rate = k[A]^m[B]^n$$

Where:
k is a proportionality constant called *rate constant* (its value is fixed for a fixed set of conditions, specially temperature).

m and n are known as *orders of reaction*. As it can be seen from the above expression, these orders of reaction indicate the degree or extent to which the reaction rate depends on the concentration of each reactant. We can say the following about these orders of reaction:

1. In general, they are not equal to the coefficients from the balanced equation. Remember: they are determined experimentally (unless a reaction is what we call an *elementary reaction*, but they are the exception).
2. Each reactant has its own (independent) order of reaction.
3. Orders of reaction are often times a positive number, but they can also be zero, a fraction and in some instances a negative number.
4. The *overall reaction order* is calculated by simply adding the individual orders ($m + n$).

As it turns out, rate laws can actually be written using two different, but related, perspectives. Which are these two perspectives? What information does each provide? Read along and you will find out. On more thing – I must insist: <u>it is not possible to predict the rate law from the overall balanced chemical reaction</u>; rate laws must be determined experimentally.

Differential vs Integrated Rate Laws

Differential rate laws express the <u>*rate of reaction as a function of a change in the concentration*</u> of one or more reactants <u>*over a particular period of time*</u>; they are <u>*used to describe what is happening at the molecular level*</u> during a reaction. These rate laws help us determine the overall mechanism of reaction (or process) by which the reactants turn into products. *E.g.*:

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

On the other hand, **integrated rate laws** express the reaction <u>*rate as a function of the initial concentration and a measured (actual) concentration of one or more reactants after a specific amount of time (t)*</u> has passed; they are <u>*used to determine the rate constant and the reaction order from experimental data*</u>. *E.g.* (when $n = 1$):

$$\ln[A] = -kt + \ln[A]_0$$

Where $[A]_0$ is the initial concentration of the reactant and $[A]$ is the concentration after a time t has passed.

Although calculus is not needed for this class, on the next page you will see how to obtain the integrated rate laws for zero, first and second order rate laws because they provide important information. You <u>*do not need to memorize the method nor the equations*</u>.

Zeroth order reactions ($n = 0$)

The differential form of the rate law is (notice the presence of the negative sign since the reactant disappears):

$$Rate = -\frac{\boldsymbol{d[A]}}{\boldsymbol{dt}} = \boldsymbol{k[A]^0} = \boldsymbol{k}$$

In order to be able to integrate with ease, we can use a technique called separation of variables to get:

$$d[A] = -kdt$$

(notice how each side has a different, unique variable)

Now we can integrate both sides over the desired interval:

$$\int_{[A]_0}^{[A]} d[A] = -k\int_{t_0}^{t} dt$$

($[A]_0$ and t_0 are initial conditions, whereas $[A]$ refers to the concentration after a time t has passed)

Notice how $-k$ comes out of the integral since it is a constant. Also, recall from calculus that (you can always check a table of integrals if you don't remember):

$$\int dx = x \quad (a\ constant\ C\ is\ added, but\ we\ do\ not\ need\ it\ since\ we\ know\ the\ limits)$$

Which leads to (after evaluating over the limits, which means upper limit minus lower limit):

$$[A]\Big|_{[A]_0}^{[A]} = -kt\Big|_{t_0}^{t} \qquad \Rightarrow \qquad [A] - [A]_0 = -k(t - t_0)$$

We consider (actually define) $t_0 = 0$, and so the equation can take the form:

$$\boldsymbol{[A] = -kt + [A]_0}$$

Which looks like:

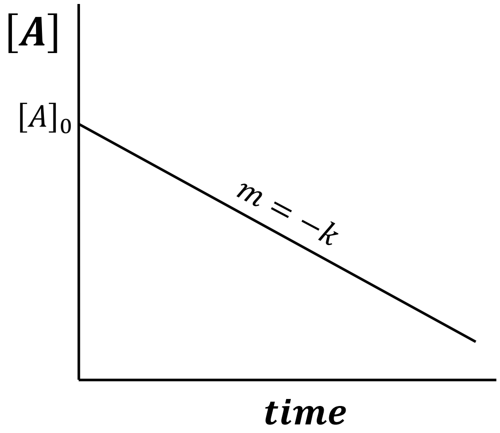
$$y = mx + b$$

Where:

$$y = [A] \quad ; \quad m = -k \quad ; \quad x = t \quad ; \quad b = [A]_0$$

If you think of it, this is a <u>*very interesting scenario*</u>! Why? If we keep plotting $[A]\ vs\ t$ for a longer and longer period of time, we will get to a point at which the concentration $[A]$ will become negative (since we have a negative slope); nevertheless, we are well aware of the fact that there is no such thing as a negative concentration, so, what is wrong here?

In actuality, nothing is wrong! What we can conclude is that a <u>*zero–order reaction model can be applied to describe a reaction just for a limited amount of time*</u>; we know the system must, at some point, change into a different kinetics model.



One more thing. The half–life is defined as the time it takes for half of the initial amount of reactant to disappear (*i.e.* a reduction of 50% its original amount). If we replace this idea on the integrated rate law we get:

$$\frac{1}{2}[A]_0 = -kt_{1/2} + [A]_0 \quad ; \quad \boldsymbol{t_{1/2} = \frac{[A]_0}{2k}}$$

This means the half–life depends on the initial concentration of reactant and the rate constant.

First order reactions ($n = 1$)

The differential form of the rate law is:

$$Rate = -\frac{\boldsymbol{d[A]}}{\boldsymbol{dt}} = \boldsymbol{k[A]}$$

After separating the variables we get:

$$\frac{d[A]}{[A]} = -kdt$$

Now we can integrate both sides over the desired interval:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k\int_{t_0}^{t} dt$$

Recall from calculus that (or check a table of integrals):

$$\int \frac{1}{x}dx = \ln x \quad and \quad \int dx = x \quad (definite\ integrals)$$

The above formulas lead to (after evaluating over the limits):

$$\ln[A]\Big|_{[A]_0}^{[A]} = -kt\Big|_{t_0}^{t} \qquad \Rightarrow \qquad \ln[A] - \ln[A]_0 = -k(t - t_0)$$

We consider $t_0 = 0$, and the equation can take the form:

$$\mathbf{ln}\boldsymbol{[A]} = \boldsymbol{-kt} + \mathbf{ln}\boldsymbol{[A]_0}$$

Which looks like:

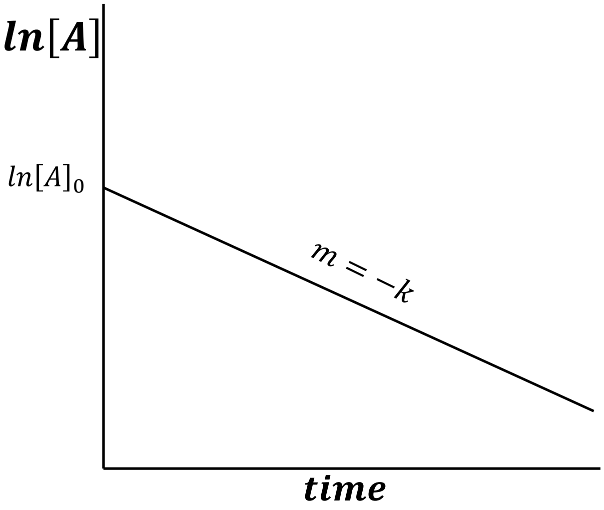
$$y = mx + b$$

Where:

$$y = \ln[A] \quad ; \quad m = -k \quad ; \quad x = t \quad ; \quad b = \ln[A]_0$$

This means that if we plot $\ln[A]\ vs\ t$, we get a line with a slope that is the negative of the rate constant. Also, using the laws of logarithms, we get:

$$\ln[A] - \ln[A]_0 = \mathbf{ln}\frac{\boldsymbol{[A]}}{\boldsymbol{[A]_0}} = \boldsymbol{-kt}$$



What is the time it takes for half of the initial concentration to disappear (the half–life or $t_{1/2}$)?

$$@\ t = t_{\frac{1}{2}} \quad \Rightarrow \quad [A] = \frac{1}{2}[A]_0$$

$$\ln\frac{[A]}{[A]_0} = -kt \quad or \quad \ln\frac{[A]_0}{[A]} = kt_{\frac{1}{2}}\ (reverse\ sign)$$

$$kt_{\frac{1}{2}} = \ln\frac{[A]_0}{\frac{1}{2}[A]_0} \quad ; \quad \boldsymbol{t_{\frac{1}{2}}} = \frac{\mathbf{ln\,2}}{\boldsymbol{k}} \cong \frac{\mathbf{0.693}}{\boldsymbol{k}}$$

The equation above means the half–life or $t_{1/2}$ for a first order reaction is a constant. Check the graph for $[A]\ vs\ t$ (from which you can calculate the half–life) on your textbook. ***<u>Getting ahead</u>***: we will see this half–life equation again in the nuclear chemistry chapter, although in its exponential form, which is:

$$[A] = [A]_0 e^{-kt}$$

Second order reactions ($n = 2$)

The differential form of the rate law is:

$$Rate = -\frac{\boldsymbol{d[A]}}{\boldsymbol{dt}} = \boldsymbol{k[A]^2}$$

We separate the variables and integrate over the interval:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_{t_0}^{t} dt$$

Recall from calculus that (or check a table of integrals):

$$\int x^n dx = x^{n+1}(n+1) \quad (definite\ integral)\ ; \qquad where \quad n = -2, \qquad so\text{:} \int x^2 dx = x^{-1}(-1)$$

The above formulas lead to (after evaluating over the limits):

$$-\frac{1}{[A]}\bigg|_{[A]_0}^{[A]} = -kt\Big|_{t_0}^{t} \qquad \Rightarrow \qquad \frac{1}{[A]_0} - \frac{1}{[A]} = -k(t - t_0)$$

Notice above how the limits seem changed due to the presence of a -1 on the left side. If $t_0 = 0$, then:

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

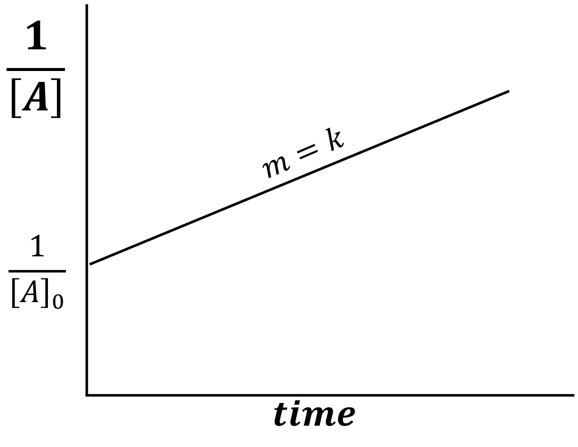
Which, again, looks like:

$$y = mx + b$$

Where:

$$y = \frac{1}{[A]} \quad ; \quad m = k \quad ; \quad x = t \quad ; \quad b = \frac{1}{[A]_0}$$

Which means that if we plot $\frac{1}{[A]}\ vs\ t$, we get a line with a slope that is the rate constant itself (not its negative!).



What is the time it takes for half of the initial concentration to disappear (the half–life or $t_{1/2}$)?

$$@\ t = t_{\frac{1}{2}} \quad \Rightarrow \quad [A] = \frac{1}{2}[A]_0$$

$$\frac{1}{[A]} = \frac{1}{\frac{[A]_0}{2}} = \boldsymbol{\frac{2}{[A]_0} = kt + \frac{1}{[A]_0}}$$

$$\boldsymbol{t_{\frac{1}{2}} = \frac{1}{k[A]_0}}$$

Notice that, as it was the case with the half–life for the zeroth order reaction, the half–life for the second order reaction also depends (albeit in a different way) from the initial concentration of the reactant (as well as on the rate constant); for this reason, the concept of half–life for second (and zeroth order) reactions are far less useful. However, the inverse relation of the half–life on the initial concentration suggests the following:

1. With a high initial concentration of reactant, we have a higher probability of the two reactant molecules interacting to form product; consequently, the reactant will be consumed in a shorter period of time.
2. Since the half–life is longer when initial concentrations are low, species following a second order kinetics may exists for a longer period of time if their initial concentrations are small.