Lecture 2 & 3-Reaction Order, Rate Constants and the Experimental Determination of Velocity

We will now turn our attention to the experimental and theoretical basis needed to determine rate constants.

I. REACTION ORDER

First Order Reaction.

The simplest chemical reaction is the one in which reactant A forms product P

$$A \rightarrow P \quad \text{(unimolecular)}$$

One can study the course of this reaction by observing the formation of product or the disappearance of reactant. The velocity of a reaction is defined as the increase in product /time

$$v = \frac{d[P]}{dt}$$

or the decrease in reactant/time

$$v = -\frac{d[A]}{dt}$$

A first order (or unimolecular) reaction then is one in which the velocity of the reaction is proportional to the concentration of one reactant. By using a proportionality constant or *rate constant, k*, one can say that the velocity of the reaction to form P is given by:

$$d[A]/dt = -k[A]$$

An important point to note here is the units of the rate constant for a first order reaction are time^{-1}. This really means the number of *events* per *time*. But what is this event and why does it take time to occur? Let us consider the second question first. To do this let us think about the units of 1/k, which are time/event. The time for an event to occur, in this case the breakdown of A to P is really a summation the time it takes for A to gain energy and go to that activated A* (we'll call this τ_A^{Act}) plus the time to lose/use that energy to breakdown A* to products (we'll call this τ_{A*}^{Bkd}). Thus, the time for an event is

$$\tau_{A\rightarrow P} = \tau_A^{Act} + \tau_{A*}^{Bkd}$$

Thus, the τ values are really 'lifetimes'-how long a species exists, on average. Since the time to lose energy is very short, the $\tau_{A\rightarrow P} \cong \tau_A^{Act}$. This makes sense in what we already know about transition state theory in that the rate constant for the reaction exponentially related to the ΔG^{+}.

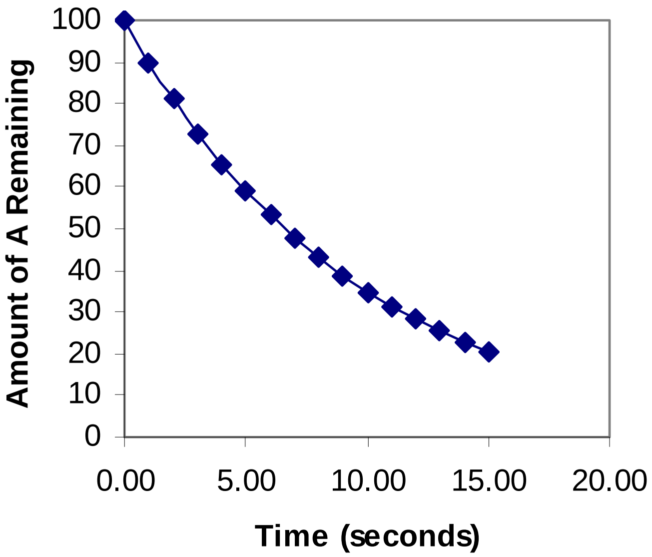
In the reaction:

$$A \rightarrow P$$

the *event* we are measuring is the breakdown of A (or the formation of P). If it takes A, on average 20 sec to reach the energy state of A*, every second a molecule of A has a 1/20th of a chance to go to A* or a 5% probability. Thus, if the average lifetime of A is 20 seconds/event, the rate constant for the reaction is 0.05 (events) $\sec^{-1}$. Similarly if the average lifetime of A is 10 seconds/event, every second a molecule of A has a 0.1% a chance to go to A* or a 10% probability, hence the rate constant for the reaction is 0.1 (events) $\sec^{-1}$

Suppose now that we begin with 100 molecules of A and $k=0.1\ \sec^{-1}$. Each molecule has a 10% chance of reacting in the subsequent second, how will the plot of remaining A as a function of time look?

Time	**Amount of A**	**Loss**
0.00	100.00	10.00
1.00	90.00	9.00
2.00	81.00	8.10
3.00	72.90	7.29
4.00	65.61	6.56
5.00	59.05	5.90
6.00	53.14	5.31
7.00	47.83	4.78
8.00	43.05	4.30
9.00	38.74	3.87
10.00	34.87	3.49
11.00	31.38	3.14
12.00	28.24	2.82
13.00	25.42	2.54
14.00	22.88	2.29
15.00	20.59	2.06



Notice that *the actual amount of A released (the velocity-amount/time) decreases as a function of time, but the percentage of A that is converted to product remains constant at 10%.* Thus how frequently an event is observed depends on the concentration of the reactant. Hence the velocity is given as # of product molecules/time (e.g. moles/second), but the actual intrinsic rate constant denotes the chemical probability of reaction and that amount is a constant!

A theoretical equation that describes the velocity of a process is called a *rate law*. As we stand on the outside and study the reaction of A→P, we can only measure the velocity of the reaction, but are unable to measure the rate constant. This is, however, easily done by rearranging the equation and integrating:

$$\int d[A]/[A] = -k\int dt$$

or

$$\ln [A] = -kt + \text{constant}$$

If we integrate between the initial concentration of A_o and the concentration of A at time t, the constant is equal to the A_o, the initial concentration of A, thus we can write,

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

Thus a plot of ln [A] vs time is a straight line and the rate constant is its slope.

For the data given above, the data table would look like:

Time	Ln of A
0.00	4.61
1.00	4.50
2.00	4.39
3.00	4.29
4.00	4.18
5.00	4.08
6.00	3.97
7.00	3.87
8.00	3.76
9.00	3.66
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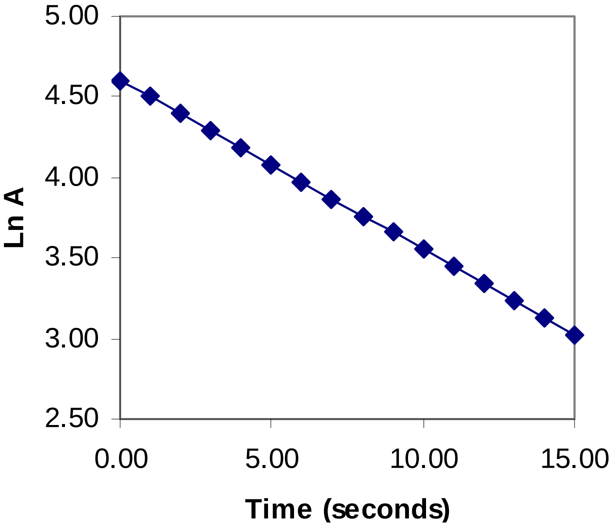
11.00	3.45
12.00	3.34
13.00	3.24
14.00	3.13
15.00	3.02



By taking the antilog the this equation, we have:

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

Thus a first order process is one in which the concentration of reactant decreases exponentially with time-exactly as we have seen.

If we also integrate the equation

$$\int d[A]/[A] = -k\int dt$$

between t=0 and time, t we can write:

$$\ln \quad [A]/[A]_o = -kt$$

or

$$\ln[A]_o/[A] = kt$$

Thus the plot of $\ln A_o/A$ vs t is a straight line whose slope is k. Occasionally it is desirable to express the rate of reaction as a *half-life*, $t_{1/2}$; the time it takes to reduce the concentration of A to half its initial value. At $t_{1/2}$ for a first order reaction, $[A]=[A]_o/2$, thus:

$$\ln[A]_o/2=kt_{1/2}$$

rearranging

$$t_{1/2} = \ln 2/k$$

this is also a quick way to determine a rate constant from a plot of product decrease vs time since

$$k = \ln 2/t_{1/2}$$

Reversible processes: Unimolecular

In the mathematical treatments of the reactions we have been considering thus far, we have ignored the idea that not only can A→P, but also the P→A. Thus:

$$A \underset{k_{PA}}{\overset{k_{AP}}{\rightleftarrows}} P$$

Therefore, every time a molecule of A converts to P, that newly created P molecule can convert back to P with the probability equal to the rate constant k_{PA}. Thus, to describe the change in amount of A per time, we need to consider BOTH the forward AND reverse reactions:

$$\frac{d[A]}{dt} = -k_{AP}\,[A] + k_{PA}[B]$$

This is a differential rate equation. The minus sign in front of k_{AP} denote that this term expresses the decrease in A, the plus sign in front of k_{PA} indicates that this pathway creates A.

If a reaction begins with no P and 1 M A, then in the first time interval, some A is converted to P. At this time the reverse *velocity* is zero. At a second time interval, the same fraction of A is converted to P, BUT now some fraction of P is converted to A. This process continues until the *velocities* of the forward and reverse reactions are equal, i.e.,

$$\frac{d[A]}{dt} = 0$$

the change in the concentration of A over time is zero. This DOES NOT MEAN that A is not being converted to P, it is just that the velocity at which A → P is equal to P→A. This state is known as dynamic EQUILIBRIUM. Thus at equilibrium:

$$\frac{d[A]}{dt} = 0 = -k_{AP}\,[A] + k_{PA}[B]$$

rearranging

$$k_{AP}\,[A]_{EQ} = k_{PA}[B]_{EQ}$$

thus

$$\frac{k_{AP}}{k_{PA}} = \frac{[B]_{EQ}}{[A]_{EQ}} = K_{EQ}$$

Second Order Reactions

A second order reaction in one that obeys the rate law

$$v = k\,[A]^2 \text{ or } k[A][B]$$

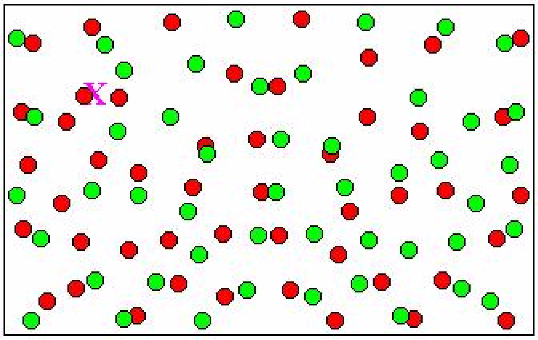
for the reactions

$$2A \rightarrow P \text{ or } A + B \rightarrow P\text{, respectively.}$$

That is the velocity is dependent on the concentration of both reactants. In order to understand the effect of concentration on rate, we must recall the three critical things that must happen if a chemical reaction is to occur. These are:

Molecules must collide
Collisions must bring the reactive sites together
Collisions must have sufficient energy to break and remake bonds

Concentration effects the number of molecular collisions that occur in any given period of time. To understand this we can consider a simple container filled with two types of gas. If we ask the question what is the probability of a red gas molecule and a green gas molecule being at some point in the container at the same time, it is clear that this total probability is simply the product of the two individual probabilities. Since each of these individual probabilities is proportional to the concentration, the overall probability is proportional to the product of the concentrations.



Probability of Collisions Between Two Reactants

If we have two sets of molecules in a container, each has a probability of being at some spot at a given time. The probability of a collision (one of each being at this spot simultaneously) must then be the product of these two probabilities. The overall probability is then proportional to:
Total Prob $\propto$ [red][green]

We will not bother going thru the calculus to get us to the full analytical expressions that are used in studying second order reactions. The units of a second order rate constant are M^{-1} $time^{-1}$, since the velocity of the reaction is proportional to the second power of concentration, i.e., the rate describes a collisional as well as a decompositional process.

At a given temperature most molecules may all have the appropriate kinetic energy for particular reaction. Since most chemical reactions involve steps that require two molecules to collide and since the probability of these events is directly proportional to concentration, why don’t they all just react upon collision, with the same intrinsic rate constant? The key is that all collisions do not occur with the appropriate orientation!

If a chemical reaction is to occur
Molecules must collide (a concentration dependent process).
Collisions must bring the reactive sites together
Collisions must have sufficient energy to break and remake bonds

The second of these requires that the reactive parts of the molecule must be brought together. The more complex the molecule, the less likely it will be for two reacting species to come together at the right place. To illustrate this point, let's look at two molecules that are very different in size and complexity, but will undergo identical chemical reactions. The smaller molecule is methylacetate, very similar to the compound in nail polish remover, and the second is a lipid, a molecule that resembles fat molecules in the body.

One simplifying and common practice which allows the determination of a rate constant for a second order reaction which involves two different molecules [A] and [B] is to have one of the reactants, for example B, present in great excess over the other. The concentration of B then decreases negligibly over the course of the reaction and can be considered constant. We can then treat the resulting velocity data as a first order process or more correctly called a *pseudo first order* reaction. The rate constant for this reaction determined in this way is a *pseudo first order* rate constant, k_{obs}. The second order constant can thus be determined by determining the k_{obs} at several concentrations of B and plotting k_{obs} vs B.

Since for the reaction A+B->P,

$$-d[A]/dt = k [A][B]$$

and qualitatitvely the pseudo first order reactions follow the rate law

$$-d[A]/dt = k_{obs}[A];$$

and

$$k_{obs}[A]=k[A][B]$$

then

$$k_{obs}= k[B].$$

Thus the slope of the line is equal to the second order rate constant.

Zero order reactions

A zero order reaction obeys the rate law:

$$-d[A]/dt = k,$$

and the velocity of the reaction is thus independent of the concentration of the reactants. This type of reaction is important in enzyme catalyzed reactions as we shall see later.