

Numerical Integration of Rate Equations

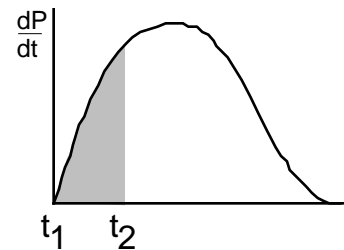
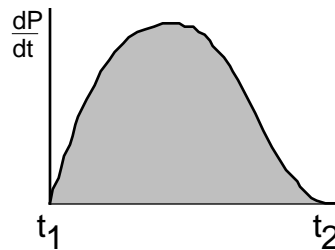
Traditional approaches to kinetics have relied on manipulating the system into a form in which the rate law can be integrated analytically (that is, via integration of the rate law to produce an explicit equation for the appearance of product (or other species) as a function of time. Often the calculus can become quite complex, and even more often, the integral simply cannot be evaluated analytically.

Numerical integration is an approach toward simulating and fitting kinetic data of any complexity. Its beauty lies in its simplicity. Although conceptually, this is an old approach, it has only become practical in recent times, with the advent of very fast computers.

To begin, we must remember that the derivative and the integral are inter-related. We can see how this applies to reaction kinetics by comparing the method applied to changes in distance and to changes in concentration. In both cases, the rate of change of the quantity is given by the velocity.

Distance vs. Time	Concentration vs. Time
<p>Remember: velocity x time interval = change in distance</p> $\frac{dx}{dt} \cdot t = x$ <p>Or more precisely:</p> $\text{Net } x = \int_{t_1}^{t_2} \frac{dx}{dt} dt = \int_{t_1}^{t_2} v(t) dt$	<p>Remember: velocity x time interval = change in conc</p> $\frac{dC}{dt} \cdot t = C$ <p>Or more precisely:</p> $\text{Net } C = \int_{t_1}^{t_2} \frac{dC}{dt} dt = \int_{t_1}^{t_2} v(t) dt$

Going back to our math training, we remember that the integral of a function is simply the area under the curve when the function is plotted versus time. The left curve shows the integration across the entire graph, the area under the curve is the integral of the function from time t_1 to time t_2 .

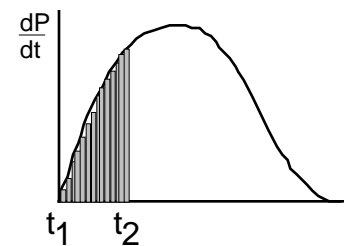
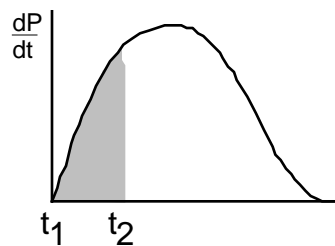


The right curve shows the same thing, but t_2 is a shorter time.

So if we have the expression for velocity, dC/dt , then we can determine the total change in concentration (or distance) at any time by evaluating the integral.

This is what we do when we take $\frac{dA}{dt} = -kA$

and integrate it analytically, to get concentration as a function of time for a first order reaction. But what if we can't do the integral? We can instead find the area under the curve, as shown at right.



This is called numerical integration.

In its simplest form, we simply evaluate the velocity at each of a series of steps (the height of each box) and multiply it by the corresponding small Δt (the width of each box). At each point, this gives us the area of the box.

Summing all of the boxes, and approaching a very small box width, we approach the area under the curve shown at left.

Application to simple kinetics

We have already seen, that given the mechanism of a reaction, it is easy to write the velocity for any given species in the reaction (it is often not at all easy to integrate those equations).

For the reaction mechanism $A \rightarrow B$, we have $\frac{dA}{dt} = -kA$

So at the initial time, the concentration of A is A_0 . At that point in time, the velocity will be $-kA_0$, so we can determine that over some small time window Δt , the concentration of A will decrease by $kA_0 \cdot \Delta t$. So the new concentration of A will be $A_0 - kA_0 \cdot \Delta t$.

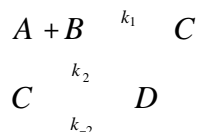
So we decrease the concentration of A by that amount, and increase the concentration of B by the same amount (the mechanism tells us the stoichiometry).

We're now ready to continue the process, moving to the next "box" in the plot above right. The concentration of A has changed, but we know by how much. Consequently, we can evaluate a new velocity at the new time point.

We continue this process through until the final time desired. At that point, we will have known concentrations of A and B.

Application to more complex kinetics

Now take a more complex reaction:



We can easily write down the velocities for each species:

$$\frac{dA}{dt} = -k_1AB$$

$$\frac{dB}{dt} = -k_1AB$$

$$\frac{dC}{dt} = k_1AB - k_2C + k_{-2}D$$

$$\frac{dD}{dt} = k_2C - k_{-2}D$$

Then we do exactly as we did above. At time t_1 , we know the concentrations of all species (perhaps finite amounts of A and B, with no C or D, but it really doesn't matter). Over the first very short time interval, we:

Change the concentration of A (and B) by $-k_1AB \cdot \Delta t$
 Change the concentration of C by $(k_1AB - k_2C + k_{-2}D) \cdot \Delta t$
 Change the concentration of D by $(k_2C - k_{-2}D) \cdot \Delta t$

Remember:

$$\frac{dC}{dt} \Delta t = \Delta C$$

At this point, starting with these new concentrations of A, B, C, and D, we simply reevaluate the above expressions and find still newer concentrations of A, B, C, and D.

This is very simple, but very tedious. To do this correctly, one wants to use a very small value for Δt . This means looping through the above simple set of calculations thousands of times. Difficult on a calculator, but trivial on a reasonable computer.