Technique Primer

Pseudo-first Order Kinetics – Determination of a rate law

One of the primary goals of chemical kinetics experiments is to measure the rate law for a chemical reaction. There are many ways to do this, but one of the most often used is the method of pseudo-first order conditions. This method is sometimes also referred to as the method of isolation or the method of flooding.

The perennial problem in kinetic studies is that every reactant concentration changes over time as the reaction proceeds. Thus measuring the rate of change of one reactant independent of the rate of change of another reactant requires some clever experimental design. Let us imagine that we have a reaction between two reactants:

$$A + B \rightarrow \text{products} \qquad \text{(A)}$$

We expect the rate law to be of the form:

$$r = k[A]^n[B]^m \qquad (1)$$

If we want to isolate the effect of changing the concentration of reactant A while keeping the concentration of B the same throughout the time course of the reaction we will need to devise a way that B will not get used up when A reacts to become products.

Let us imagine doing this reaction with a large excess (x100 or more) of reactant B so that reactant A is the limiting reagent throughout the course of the reaction.

	A +	B →	products
initial:	$[A]_o$	$100[A]_o=[B]_o$	0
change:	$-[A]_o$	$-[A]_o$	$[A]_o$
final:	0	$(100-1)[A]_o$	$[A]_o$

From the above limiting reagent calculation we can see that we only use up 1% of the amount of B we started with while we use up ALL of the A we started with. Thus we should be able to assume that the concentration of B has not changed to any appreciable amount or $[B] = [B]_o$ at all times.

This strategy of *flooding* the reaction mixture with one reactant allows us to *isolate* the effect of the other reactant on the rate of change or reaction rate. Thus we call this the *method of flooding* or the *method of isolation*.

Let us now examine the form of our expected rate law for this reaction knowing that the concentration of B is not going to change (is a constant).

$$r = k[A]^n[B]^m = (k[B]_o^m)[A]^n = k_{obs}[A]^n \qquad (2)$$

Note that we have combined the actual (true) rate constant for the reaction (k) with the constant concentration of B ($[B]_o$) to form a new constant that we have called k_{obs}.

$$k_{obs} = k[B]_o^m \qquad (3)$$

This new constant is called k_{obs} because this will be the rate constant that we “observe” in our experiment.

Now, if we assume a value for the order of the reaction with respect to the concentration of A (n) then we can determine the *integrated rate law* under these conditions where we have flooded the reaction mixture with B.

Most often we are working with first order reactions so we will examine only that case. In this case we call the reaction a pseudo-first order reaction.

For the first order case we have:

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

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

$$-\int_{[A]_o}^{[A]_t} \frac{d[A]}{[A]} = \int_0^t k_{obs}dt$$

$$-\ln\left(\frac{[A]_t}{[A]_o}\right) = k_{obs}t$$

$$[A]_t = [A]_o e^{-k_{obs}t} \qquad (4)$$

If our reactant A absorbs light at a given wavelength (and the products and the other reactant don't) then we can use the absorbance to determine the concentration of reactant A as a function of time.

$$[A]_t = [A]_o e^{-k_{obs}t}$$

$$Abs_t = \varepsilon b[A]_t \qquad and \quad Abs_o = \varepsilon b[A]_o$$
$$Abs_t = \varepsilon b[A]_o e^{-k_{obs}t}$$
$$Abs_t = \varepsilon b\left(\frac{Abs_o}{\varepsilon b}\right)e^{-k_{obs}t}$$
$$Abs_t = Abs_o e^{-k_{obs}t} \tag{5}$$

From this we can see that a plot of absorbance as a function of time will decay exponentially from some initial absorbance value down to zero. Thus we should be able to fit our experimental data curves to this function. Alternatively we can write this in the form of a straight line by taking the natural log of both sides to obtain:

$$\ln(Abs_t) = \ln(Abs_o) - k_{obs}t \tag{6}$$

Equation (6) suggests that a plot of ln(Abs) vs. time will yield a straight line and the slope will be equal to k_{obs}.

Note that we have learned two things from plotting the data this way. 1) We have confirmed that the reaction is indeed first order in A (otherwise we wouldn't get a straight line); and 2) we have learned the value of the observed rate constant for the particular temperature and concentration of B that we used to do the reaction.

If we now repeat this experiment with a different concentration of B, making sure that it is still large enough to be in at least 10x excess of the amount of A, we will obtain a new value of k_{obs} because, according to equation (3), k_{obs} depends on the concentration of B we used to flood the reaction mixture. If we do at least 5 or 6 experiments all with different excess concentrations of B then we can graph the k_{obs} values (obtained from the slopes of the plots of ln(Abs) vs time) as a function of the concentration of B ($[B]_o$) to determine the actual or true rate constant for the reaction.

Recall that $k_{obs} = k[B]_o^m$. Thus if the order of the reaction with respect to B (m) is one then we would expect k_{obs} vs $[B]_o$ to be a straight line. If the order of reaction with respect to B is anything other than one (second (2) or third (3) order) then the graph of k_{obs} vs. B will be a curve (not straight). By plotting the data in this way we again learn two things. 1) We can confirm the reaction order with respect to B from the shape of the curve (first order = linear, second order = parabola, etc.); and 2) we obtain the actual or true rate constant from the slope of the line (curve).

Below is a set of actual data obtained using this method and analyzed as described above. This example is meant to help you understand how to handle data obtained from a flooding or isolation kinetic experiment.

The overall reaction shown below as Scheme B was run with different concentrations of hydroxide (different pH's were used).

$$Co(NH_3)_5Cl^{2+}_{(aq)} + {}^{-}OH_{(aq)} \rightarrow Co(NH_3)_5OH^{2}_{(aq)}{}^{+} + Cl^{-}_{(aq)} \quad \text{(B)}$$

The cobalt amine chloride absorbs visible light at a wavelength where the cobalt amine hydroxide does not. Thus the absorbance at the wavelength corresponding to the cobalt amine chloride was used to monitor the progress of the reaction. When the natural log of the absorbance vs. time was plotted, the linear relationships shown in figure 1 were obtained.

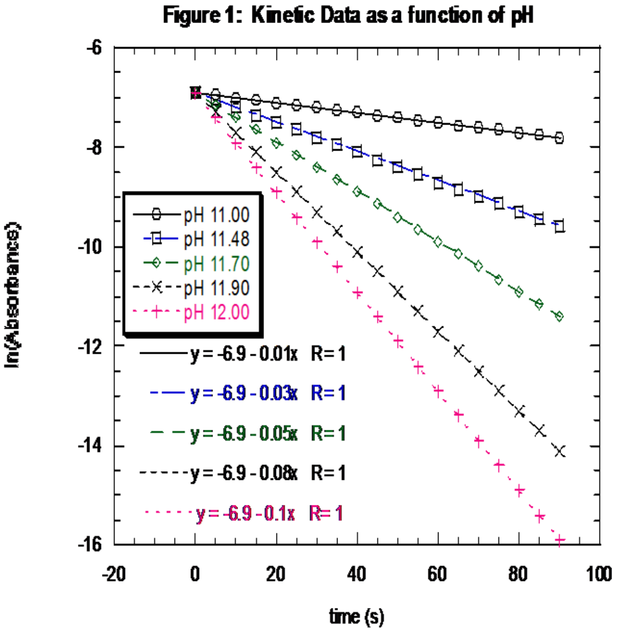

Figure 1: The natural log of the absorbance of $Co(NH_3)_5Cl^{2+}$ plotted as a function of time for reactions run at various pH's. Each reaction shows a linear relationship indicating a first order reaction with respect

to the $Co(NH_3)_5Cl^{2+}$. The slope of each straight line relationship is the value of the observed rate constant (k_{obs}) for the pH ($[OH^-]$) used in that reaction.

The values of the observed rate constants extracted from the slopes of the best fit lines to the data in figure 1 were plotted as a function of the hydroxide concentration. These data are shown in figure 2 and indicate that the reaction is first order in hydroxide resulting in an overall second order reaction. These data are consistent with the experimental rate law shown in equation (7).

$$r = k[OH^-][Co(NH_3)_5Cl^{2+}] \qquad (7)$$

with k = 10 $M^{-1}s^{-1}$.

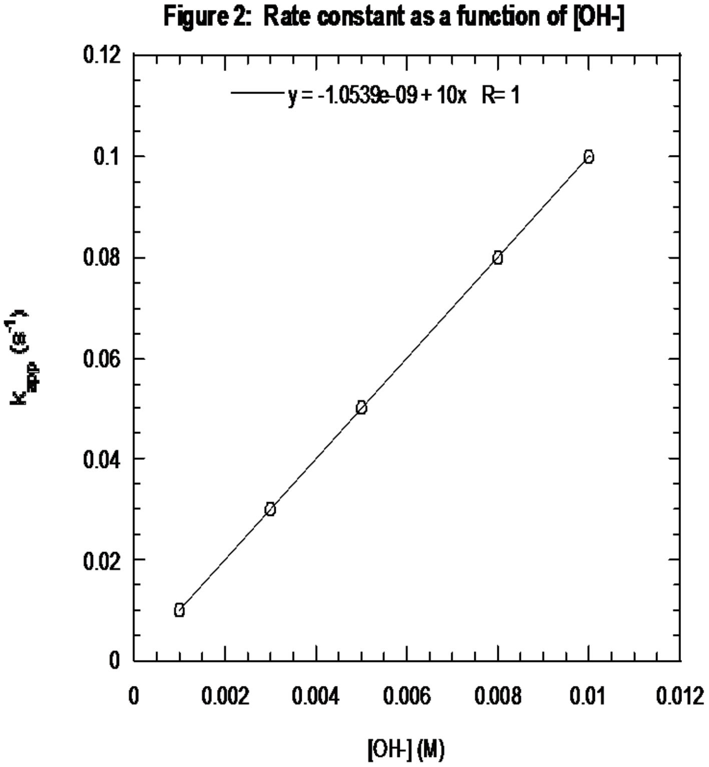

Figure 2: The observed (or apparent) rate constants for the reaction between cobalt amine chloride and hydroxide as a function of the concentration of excess hydroxide used. The observed rate constants are a linear function of the hydroxide concentration indicating that the reaction is first order in hydroxide. The slope of the best fit line provides a second order rate constant of 10 $M^{-1}s^{-1}$.