# The Kinetics of a Diffusion-Controlled Reaction – Modified Procedure

Several of the equations in the manual contain errors. The important ones are as follows:

## Introduction

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| p. 368 |  | (M·s-1) |  |

Note from the discussion that when the actual reaction occurs fast enough within the solvent cage (*i.e.* when k2 is very large compared to k-1), kobs ≈ k1. From the definition contained in Eq. 1 on p. 367, k1 is the rate constant for the diffusion of the reactants through the solvent. Therefore, this condition means that this *diffusion* step is actually rate limiting for the overall reaction. Once the reactants are close enough to one another, they will react almost instantaneously. This also implies that such a reaction would have essentially *no activation barrier*.

## Diffusion Mass Transport

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| p. 370 |  | (M-1·s-1) | (9) |
| p. 370 |  | (M-1·s-1) | (10) |

An important consideration in the previous two equations is the time dependence of k1. We do not typically think of rate constants as changing in time, but Eq. 9 contains a “transient term”: R/(πDt)1/2. Remember that the diffusion, or movement of the molecules through the solvent, is the slow step of this reaction and is rate determining. However, at the very beginning there will be some fraction of molecules that are already close enough together to react *without* needing to diffuse. Therefore, the apparent rate of the reaction will be faster initially. As these pairs react, this population is depleted, leaving behind reactants that are farther apart and thus need to undergo diffusion. Thus, the transient term dies out and the reaction finally reaches a purely diffusion controlled regime, described by the rate constant in Eq. 10.

Later on in the lab it will also be useful to consider the same idea in terms of the concentration of reactants, rather than the time. For very concentrated solutions, the fraction of molecules that are initially close enough to react will be large, and the transient term will be significant for a longer time. For solutions that are very dilute, there will be fewer of them and the reaction will reach steady-state conditions much faster. You can imagine that in the limit of infinite dilution, there will effectively be no transient regime, as the molecules will be so isolated that they will always need to undergo diffusion before they can react with one another.

Also, take note of the fact that the **R** in the Stokes-Einstein-Smoluchowski Equation (Equation 11, page 371) is actually the universal gas constant:

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| --- | --- | --- | --- |
| p. 370 |  | (M-1·s-1) | (11) |

**R** = 8.314 × 107 erg·mol-1·K-1

**This is the only equation in which R refers to the gas constant.** In all other equations, R is the “collision radius” of the interacting species (actually the sum of the separate collision radii). It is this collision radius that we are trying to find in this experiment, along with the rate constant k1. Also keep in mind that Eq. 11 represents an *alternative* method for estimating the diffusion rate constant k1 based on bulk parameters of the solvent, rather than detailed knowledge of the molecular parameters R (the collision radius) and D (the diffusion coefficient).

## Fluorescence Quenching

The first Stern-Volmer Equation (**Eq. 14**) in the manual, is generally applicable to because it makes no assumptions about the quenching rate constant kQ. Since we are dealing with a diffusion controlled reaction, we can identify kQ with the diffusion controlled rate constant, k1, from Eqs. 9, 10 and 11. It should therefore be straightforward to measure the fluorescence emission of some analyte (A) as we change the concentration of the quencher (Q), and fit the data to Eq. 14 to obtain a value for k1. However, this still leaves us with a question: *Does the k1 obtained in this manner correspond to Eq. 9, Eq. 10, or Eq. 11?*

Eqs. 10 and 11 do not depend on the time, t, and therefore correspond to the steady-steady state regime where the reaction is fully diffusion controlled. When combined with Eq. 14, they describe a **linear** Stern-Volmer plot in which the slope is equal to k1·τ0.

Eq. 9, however, includes a time dependence of k1. The expression cannot simply be inserted into Eq. 14 without carrying this time dependence along with it. Since we are not measuring the quenching as a function of time, this doesn’t help us at all. Instead, the Stern-Volmer Equation can be re-derived, taking into account the transient term, to obtain Eq. 15 (which is incorrect in the manual). The correct form of this equation is given here:

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| --- | --- | --- | --- | --- |
| p. 373 |  |  |  | (15) |

The correct expressions for the parameters a, b and Y are also given below.

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| --- | --- | --- | --- | --- |
| p. 373 |  |  |  | (16) |
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Eq. 15 describes a curved line due to the transient effects that take place very soon after the light source is switched on. However, this may cause some confusion, because our Stern-Volmer plots do not involve a time variable. How can the transient effects account for this curvature, if there is no explicit time dependence?

We touched on the answer to this before, but it is worth emphasizing again. The transient term arises because when the light source is first switched on there are some A/Q pairs that are close enough to react without diffusing very far. Since the overall rate of the reaction can be thought of as an average of the rates for each individual molecular collision, the faster reactions between these pairs will skew the average towards faster rates. This statistical effect will be much more significant when there is a very high concentration of one or both components, and almost negligible when the concentrations are very low. Since the slope of the Stern-Volmer plot is proportional to the rate constant, k1, this means that the slope will be large (faster rates) at high quencher concentrations, [Q], and small (slower rates) at low [Q]. We will explore how these conditions relate to the other Stern-Volmer equation (Eq. 14) in the Data Analysis section below.

## Data Analysis

You can ignore the Data Analysis outlined in the manual, and just follow the steps below. There are some key differences. Keep in mind that the fluorescent analyte (A) is anthracene and the quencher (Q) is CBr4.

1. Tabulate your data as (the anthracene fluorescence at 398 or 399 nm) and [Q] (the CBr4 concentration, in M).
2. Plot a graph of . Note that is simply the value of the unquenched fluorescence peak (when [Q] = 0). This is your experimental quenching curve or Stern-Volmer plot, and we will now see how it corresponds to the two limits of the quenching model (with and without the transient term), as well as the SES equation.
3. Begin by considering the Stokes-Einstein-Smoluchowski (SES) equation (Eq. 11). Use the gas constant (**R**), the temperature (assume 25 °C) and the viscosity of *n*-hexane to calculate k1. Use the proper units as described in the manual. Once you have k1, insert it into Eq. 10 to calculate the collision radius R (don’t mix up your **R**s). To do this, you’ll need to calculate the diffusion coefficient, D, for *n*-hexane from the D known for *n*-heptane, as described in the manual. Keep track of your units. What is the collision radius calculated this way (including the unit)?
4. Using the k1 you just calculated from the SES equation, superimpose the straight line obtained from Eq. 14 onto your Stern-Volmer plot. You’ll need the lifetime, τ0, also given in the manual. Describe the relationship between this line and the experimental data points, if any.
5. Now we will consider the Stern-Volmer plot obtained when we ignore the transient term. Remember that this condition holds at low concentrations. Therefore we will be looking for the tangent to the experimental curve near the y-axis. Take a few of the experimental data points close to [Q] = 0 and have Excel (or your preferred program) fit a trendline to them and show the equation. The points you include for this should all be nearly in a straight line. If you take too many, they will begin to show the curvature and your slope will be off. From the slope of this tangent line, calculate another value for k1. You’ll need the lifetime from the manual again. From that value of k1, calculate another value for the collision radius, R, using Eq. 10. How do these values of k1 and R compare to the values calculated from the SES equation in step 3?
6. Now we can examine the entire data set, which includes effects due to the transient-term, in order to extract a third value of R directly. We will do this by fitting our data to Eq. 15 (the corrected form shown above) using a nonlinear regression analysis with R as the only parameter. You have done this a couple of times already so you should be comfortable with the procedure. Just make sure you realize that the parameter R enters into Eq. 15 directly in the numerator, as well as through the denominator *Y* due to the R dependence of *a* and *b*. Thus, you need to make sure that all of these parts of the equation refer to the same cell for R so that it is varied consistently throughout. Excel has the complementary error function, **erfc()**, built in so you can use that to calculate *Y*. Make sure that you use **erfc()** and not **erf()**. You can start with a guess of 6 Å for the radius R and have Solver vary it to fit your line. Superimpose the theoretical curve corresponding to this R value onto your data points.

**Lab Report**

Your lab report should consist of the following parts:

* **Title, Author and Date**
* **Introduction and Objective** – A paragraph describing what we hope to find in this experiment, and how.
* **Experimental Procedure** – This should be a very brief general outline of the procedure, written out as a paragraph or two. Give the make and model for any major instruments you used, as well as any important settings. For fluorescence spectroscopy, this especially means the excitation wavelength and slit widths.
* **Results & Discussion** – This should include the following:
  + A Stern-Volmer graph consisting of:
  1. Your experimental data points
  2. The straight line from step 4 corresponding to the SES
  3. The tangent line from step 5 corresponding to the steady-state regime near [CBr4] = 0.
  4. The theoretical curve from step 6 corresponding to Eq. 15.

These lines and points should all be styled uniquely to distinguish them, and the equations displayed on or near the chart. Label all axes appropriately (with units).

* + A table of k1 and R values calculated in the different ways discussed. You don’t calculate k1 from Eq. 15, so you will only have two different k1 values, but three different R values. Also give the value of D that you calculated for *n*-heptane, with proper units (this can be given in a footnote to the table, or just in the body of the discussion itself).
  + Estimate the errors in each of these tabulated values as best you can, and include them in the table. Do they agree to within the errors or uncertainty? Which value of R should be the most accurate? Which do you trust the most based on your handling of the experiment and analysis?
  + What are the approximate radii of the anthracene and CBr4 molecules? Since the observed collision radius, R, should be the sum of these two radii, do your experimental values make sense?
  + Answer any 4 of the 8 questions under “Questions and Further Thoughts” in the lab manual. This does not need to be a separate section, but can be included organically in the discussion as a way of filling it out.
* **Conclusion**
* **References**
* **Appendix** – At the very end of your report, include examples of any calculations that you did by hand. Provide digital copies of the Excel (or other) files that you used to generate your graphs.