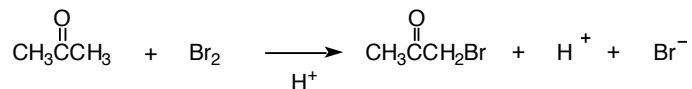


Experiment 3: A Kinetic Analysis of the Bromination of Acetone

Reading: SGN: p. 604-610; 676-679

Many of the reactions encountered in chemistry occur so quickly that we get used to ignoring the time component. However, sometimes the time component is important, and contains information that can not be obtained from steady state experiments. In this experiment you will characterize the kinetics of the acid-catalyzed reaction between acetone and bromine:



The ultimate goal of this experiment is to use the experimentally determined rate law to gain some insight about the mechanism of the reaction. A mechanism is a series of **elementary steps**, in which each elementary step represents an actual collision or rearrangement event. Very few reactions occur as a single elementary step. In the case of the acid-catalyzed bromination of acetone, the accepted mechanism involves three elementary steps, shown in Figure 1.

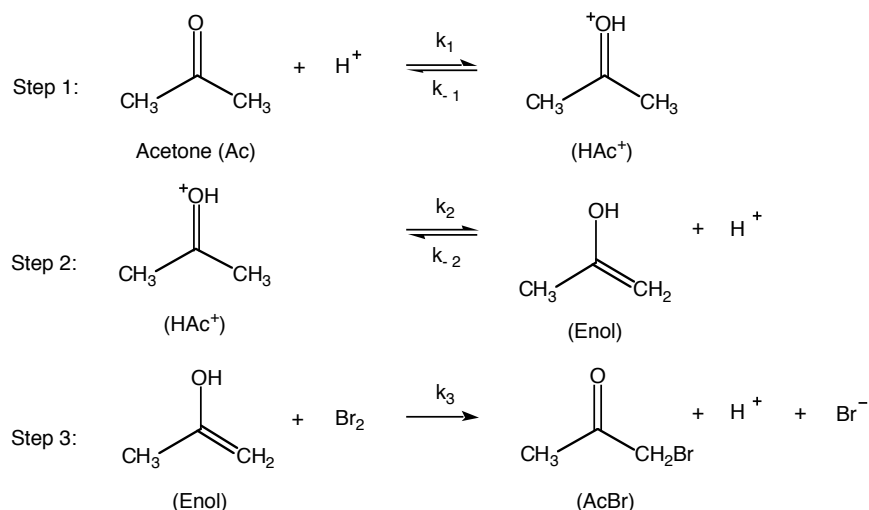


Figure 1: Mechanism for the acid-catalyzed bromination of acetone.*

A mechanism can be evaluated by comparing the experimentally observed rate law to the theoretical rate law that is derived from the mechanism. If the forms of the rate law agree, then the mechanism is supported. If not, then a new mechanism must be proposed. If the mechanism is supported, then experiments can be designed that reveal other interesting aspects of the mechanism, such as the identity of the rate-determining step (RDS). The RDS is the step that limits the rate of reaction, and is therefore a very important piece of information. In this experiment, you will be able to characterize step 3 as either very slow (the RDS) or very fast.

* As might be expected, the base-catalyzed reaction has a different mechanism.

The Experimental Rate Law

Rate laws can take many forms. The simplest form is a power law, where the rate of the reaction is proportional to the concentrations of the reactants raised to some integer powers. In this case, we will assume a power law of the form:

$$\text{Rate} = -\frac{d[\text{Br}_2]}{dt} = k_{\text{obs}} [\text{Br}_2]^m [\text{Ac}]^n [\text{H}^+]^p \quad (1)$$

where the square brackets denote molar concentrations of reactants, *Ac* represents acetone, and k_{obs} is the experimentally observed rate constant, which is strongly temperature dependent (as you saw in Experiment 1). The exponents are called the **orders** of the reactants, and the overall reaction order is the sum of the reactant orders. Reactant orders must be determined experimentally and cannot be assumed to be equal to the stoichiometric coefficients. Notice that the acid catalyst is included in the initial form of the rate law. While the order of the catalyst (or indeed any species) might be zero, catalyst concentrations do sometimes have non-zero orders. Product concentrations can also appear in rate laws. However, because the overall reverse reaction in the bromination of acetone is negligible we will not include the products in the rate law.

The rate itself can be expressed in terms of any of the components in the reaction equation. Since we are using visible absorption spectroscopy to detect concentrations and bromine is colored, we are expressing the rate in terms of the bromine concentration (it is our *observable species*). According to Beer's law:

$$A = abc \quad (2)$$

where *A* is the absorbance of the bromine in solution, *a* is the molar absorption coefficient, *b* is the cell path length, and *c* is the molar concentration of bromine in solution. The molar absorption coefficient is dependent on the wavelength of the incident light. Useful values of *a* for aqueous bromine are given in Table 1.

Table 1: Molar absorption coefficients for Br₂ (aq)¹

λ (nm)	<i>a</i> (M ⁻¹ cm ⁻¹)
400	160
450	100
500	30
550	8

1. Daniels, F., et al, *Experimental Physical Chemistry*, 7th Ed., McGraw-Hill, New York, 1970.

Determination of the rate law involves determining the reactant orders and the rate constant. We will use two methods to obtain the orders of the reactants: the **Integral rate method** will be used to determine *m* (the order of Br₂), and the **Differential rate method** will be used to determine *n* and *p* (the orders of Ac and H⁺). Once the orders are known, the rate constant can be calculated.

The Integral Rate Method:

This method is the simpler of the two methods, but has several limitations.

- (1) The IRM can only be used to determine the order of an *observable* species.
- (2) The observable species must be integral order.
- (3) The observable species must be the *limiting reagent*, and all other species that appear in the rate law must be *flooded*.
- (4) The reverse reaction must be negligible.

A species is **flooded** if its concentration does not change appreciably over the course of the reaction. This is achieved by using a large excess of that species relative to the observable (limiting) species. Condition 1 requires that we can only use this method for the determination of m , the order of bromine. Conditions 2 and 4 have been shown in the literature to be true. Condition 3 will be set by flooding the experimental concentrations of Ac and H^+ relative to Br_2 .

The central idea behind the integral rate method is that since the concentrations of all species except for the observable remains essentially constant, a pseudo rate constant, k' , can be defined that includes the constant concentrations of the flooded species:

$$k' = k_{obs} [Ac]^n [H^+]^p \quad (3)$$

The rate law then becomes:

$$Rate = -\frac{d[Br_2]}{dt} = k'[Br_2]^m \quad (4)$$

which is an integrable differential equation. This is more clearly seen by rewriting equation (4) as:

$$\frac{d[Br_2]}{[Br_2]^m} = -k' dt \quad (5)$$

Equation (5) can be integrated for several values of m to obtain the **integrated rate laws** (Table 2). Keep in mind that the pseudo rate constant k' is not a true rate constant, because it depends both on temperature *and* on the initial concentrations of the flooded species. A true rate constant is independent of all concentrations.

Table 2: Integrated rate laws for a pseudo α -order reaction.^a

m	Rate Law
0	$[Br_2] = [Br_2]_0 - k't$
1	$\ln[Br_2] = \ln[Br_2]_0 - k't$
2	$\frac{1}{[Br_2]} = \frac{1}{[Br_2]_0} + k't$

a. $[Br_2]_0$ denotes the concentration of bromine at time $t=0$.

To determine m , the concentration of the observable species is monitored as a function of time for a single reaction solution. The data is plotted according to the zeroth, first and second order integrated rate laws in Table 2. The plot that is linear indicates the order of bromine (all others should be curved). The value of k' can be obtained from the slope of the linear (m^{th} order) plot.

The Differential Rate Method:

Condition 1 for the integral rate method requires that a different method be used to determine the orders of the flooded (non-observable) species in the reaction. The differential method is one possible method for doing this; while it is somewhat less straightforward than the integral method, it is also more flexible. The only limitations of the differential method are:

- (1) The observable species must be the *limiting reagent*, and all other species that appear in the rate law must be *flooded*.
- (2) The order of the observable species must be known.
- (3) The reverse reaction must be negligible.

As in the integral method, the concentration of the observable species is monitored as a function of time the differential rate method. The data is then plotted according to the correct m^{th} order integrated rate law in order to obtain the value of the pseudo rate constant, k' . Let us examine the dependence of k' on the concentrations of the flooded species in more detail. Taking the natural logarithm of both sides of equation (3), we obtain:

$$\ln k' = \ln k_{\text{obs}} + n \ln [\text{Ac}] + p \ln [\text{H}^+] \quad (6)$$

According to equation (6), $\ln k'$ is linearly dependent on n and on p . Therefore, if k' is measured for a variety of Ac (or H^+) concentrations, we can plot $\ln k'$ versus $\ln[\text{Ac}]$ (or $\ln[\text{H}^+]$) to obtain n (or p). However, we must make sure that we have only one dependent variable at a time – that is, we only want $\ln[\text{Ac}]$ *or* $\ln[\text{H}^+]$ to vary in a single plot. Thus, many reaction solutions are needed to obtain the orders of acetone and acid.

In total, two sets of experiments must be performed. In the first set, a series of reaction solutions are studied in which the *initial* concentration of H^+ is kept constant while the *initial* concentration of Ac is varied. (Of course, both species are flooded with respect to bromine, so their concentrations do not change appreciably over the course of a single reaction.) The value of n can be then obtained from a plot of equation (6) using the data in this set of experiments. The second set is similar to the first, except that the initial concentration of Ac is kept constant while the initial concentration of H^+ is varied, leading to a value for p .

The Theoretical Rate Law

The theoretical rate law can be derived from a reaction mechanism using the fact that the orders of the reactants for an elementary step are equal to the stoichiometric coefficients. This is true *only* for elementary steps because elementary steps represent actual collisions, but is not true for the overall reaction equation or overall rate law. Typically the theoretical rate law is derived in terms of the rate of appearance of product, although any species could be used. In this case, we will derive the theoretical rate law using the rate of appearance of bromoacetone (AcBr). From step 3 (Figure 1), we have:

$$\text{Rate} = \frac{d[\text{AcBr}]}{dt} = k_3[\text{Enol}][\text{Br}_2] \quad (7)$$

Equation (7) cannot be compared with an experimental rate law because it contains an unstable intermediate whose concentration cannot be measured (i.e.: a species that does not appear in the overall reaction equation - in this case, *Enol*). The bulk of a rate law derivation usually involves getting rid of terms involving intermediates. For unstable intermediates (those that are not long-lived), we can invoke the **steady state approximation**. The SSA says that since the species is unstable, its concentration should be fairly small. Furthermore, it should be used up about as quickly as it is produced. Therefore, rate of change of its concentration is approximately equal to zero (it appears to be in a "steady state").

We will use the SSA to eliminate the *Enol* term from equation (7). In doing so, we must recognize that *Enol* is involved in three elementary steps in this mechanism: 2-forward (production of enol), 2-reverse (destruction of enol), and 3 (destruction of enol). Therefore the rate law in terms of *Enol* concentration is:

$$\text{Rate} = \frac{d[\text{Enol}]}{dt} = -k_3[\text{Enol}][\text{Br}_2] + k_2[\text{HAc}^+] - k_{-2}[\text{Enol}][\text{H}^+] \approx 0 \quad (8)$$

Solving for $[\text{Enol}]$, we obtain:

$$[\text{Enol}] = \frac{k_2[\text{HAc}^+]}{k_3[\text{Br}_2] + k_{-2}[\text{H}^+]} \quad (9)$$

which can be substituted into equation (7). The result is still unacceptable, however, because another intermediate (HAc^+) now appears in the rate law. This unstable intermediate can also be eliminated using the SSA. The final (acceptable) expression for the theoretical rate law is given in equation (10).

$$\text{Rate} = \frac{k_1 k_2 k_3 [\text{Ac}][\text{H}^+][\text{Br}_2]}{k_3(k_{-1} + k_2)[\text{Br}_2] + k_{-1} k_{-2}[\text{H}^+]} \quad (10)$$

⇒ Do the following in your notebook before you come to lab on **day 1**:

1. Write out the expression for the rate of production of HAc^+ based on the mechanism (i.e.: one similar to equation (8)), and solve for $[\text{HAc}^+]$.
2. Use the expressions for $[\text{HAc}^+]$ and $[\text{Enol}]$ to derive equation (10).

It might appear from a comparison of equations (1) and (10) that the experimental and theoretical rate laws could not agree, since the rate law in equation (10) does not look like a power law. However, there are two limiting cases for which equation (10) can be reduced to a power law form. Both of these limiting cases have physical interpretations that can reveal information on the mechanism itself.

$$\text{Case 1: } k_3(k_{-1} + k_2)[Br_2] \gg k_{-1}k_{-2}[H^+]$$

If this limitation holds true, then the second term in the denominator of equation (10) can be ignored, and the rate law reduces to:

$$\text{Rate} = \frac{k_1 k_2 [Ac][H^+]}{(k_{-1} + k_2)} \quad (11)$$

which indeed looks like a power law ($m=0$, $n=1$, $p=1$). In this case, the observed rate constant is a combination of rate constants from steps 1 and 2.

$$k_{obs}^{case1} = \frac{k_1 k_2}{(k_{-1} + k_2)} \quad (12)$$

Since k_3 does not appear in the expression for k_{obs} , then we can at least say that if equation (11) agrees with the experimental rate law, then step 3 is fast (not the rate determining step since it does not influence the observed rate constant). We would need other experiments to actually identify the rate determining step in this case. You will need to think about the physical meaning of this limit in your discussion.

$$\text{Case 2: } k_3(k_{-1} + k_2)[Br_2] \ll k_{-1}k_{-2}[H^+]$$

If this limitation holds true, then the first term in the denominator of equation (10) can be ignored, and the rate law reduces to:

$$\text{Rate} = \frac{k_1 k_2 k_3 [Ac][Br_2]}{k_{-1}k_{-2}} \quad (13)$$

which also looks like a power law ($m=1$, $n=1$, $p=0$). In this case, the observed rate constant is a combination of rate constants from all three steps.

$$k_{obs}^{case2} = \frac{k_1 k_2 k_3}{k_{-1}k_{-2}} = K_{eq,1} K_{eq,2} k_3 \quad (14)$$

The appearance of the equilibrium constants for steps 1 and 2 indicates that these reactions are at equilibrium (recall that $K_{eq} = k_f/k_r$ for any elementary reaction). Therefore, only step 3 has a rate constant that influences k_{obs} , so it must be the rate determining step.

Thus, assuming that this reaction behaves according to one of the two limiting cases, you should be able to identify the role of step 3 in the mechanism for the acid-catalyzed bromination of acetone. Of course, this reaction has been chosen specifically because it does behave according to one of these cases. Keep in mind, however, that not all reactions appear to follow a power law, and some can be quite complicated. The process of characterizing a reaction mechanism is something of an art, and generally is associated with a subfield of chemistry called Physical Organic chemistry.

Experimental Procedure:[†]

Apparatus: Spectronic 21 visible absorption spectrometer and cuvettes; thermostated temperature bath; volumetric ware; saturated aqueous bromine solution; acetone; 1.00 M HCl solution.

Safety Considerations: Bromine is a strong lachrymator (causes tearing and irritation of the eyes) and can burn the skin. Handle bromine solutions in the fume hood as much as possible, and avoid skin contact. Keep all bromine solutions covered to avoid bromine vaporization.

Rate constants are strongly temperature dependent ($k=Ae^{-E_a/RT}$), so great care must be taken to maintain all solutions at a constant temperature. A thermostated bath is available for this purpose. Prepare the bath before you begin preparing the solutions so that the water has time to equilibrate. Be sure to record the temperature of the bath after it has reached equilibrium.

Prepare 250 mL each of ~4 M acetone and ~0.02 M bromine. You have available pure acetone ($d=0.792$ g/mL) and a saturated bromine solution (~0.2 M). You will need to know the concentration of the acetone solution to at least 3 significant figures. Since you will determine the concentration of the bromine solution spectroscopically, a simple 1/10 dilution of the stock solution is sufficient. Keep both solutions covered (they will vaporize) and place them in the water bath to equilibrate. Also place a container of 1.00 M HCl and a container of distilled water in the bath to equilibrate.

Part A: Determination of the Order of Bromine

In order to determine the order of bromine, you need to monitor the decay in bromine absorbance due the reaction of bromine with acetone for a period of roughly 10 minutes. The absorbance should decay by at least a factor of two in order to observe a significant slope in the integral rate plots. We will monitor the absorbance at 450 nm, where there is minimal interference from other intermediate species in the reaction. The best data will be obtained when the initial absorbance is ~1, which means that the initial bromine concentration in the reaction solution should be ~0.01 M (a 1/2 dilution of your 0.02 M stock). You will need to experiment with the acetone and acid concentrations in order to find the concentrations that produce a good reaction rate with this amount of bromine. The total volume of your reaction solution will be 100 mL.

Before you begin to prepare solutions, zero the spectrometer at 450 nm using a cuvette filled with distilled water. Be sure to use the same cuvette for the rest of the experiment so that you do not have to recalibrate the spectrometer.

The timing of the reaction is important for obtaining good data. Since the reaction will begin as soon as the bromine comes in contact with the acetone, the addition of bromine should be left to the last minute. To prepare your reaction solution, add the acetone, acid, and approximately half of the water that will be needed to a 100 mL volumetric flask. Place the flask in the water bath while you pipet the bromine solution. Have a water bottle ready for topping off the reaction solution to the mark after the bromine is added. When you are ready, add the bromine and start the stopwatch as soon as the first drop hits the acetone/acid solution. Fill to the mark with water as quickly as possible, mix well, and place the flask in the water bath.

To begin measurements, rinse the cuvette once with the reaction solution, then fill it to the top. Cover the cuvette with parafilm and keep it in the water bath when not taking a measurement.

[†] From: Sime, R.J., "Physical Chemistry: Methods, Techniques and Experiments", CSU Publishers, Sacramento CA.

Be sure to wipe off all excess water when taking a measurement since stray water droplets will cause artifacts in the measurement. Press the lap button on the stopwatch at the moment when you take the absorbance reading, then return the cuvette to the water bath. Record a measurement approximately once every minute. Periodically check the water bath temperature to be sure that it stays constant. If not, record the temperature at regular intervals to get a sense of the size of the fluctuations.

You will probably have to try several different acid/acetone combinations before you achieve a working reaction solution. Nevertheless, be sure to record all of your observations in your notebook, particularly since they will be useful in the design of the next section of the experiment.

⇒ **Do the following in your notebook before you come to lab on day 2:**
Determine the order of Br₂ using the instructions for the calculations for Part A.

Part B: Determination of the Orders of Acetone and Acid

If you are working on this part on a new day, you will need to (1) make sure the water bath has equilibrated to exactly the same temperature as on day 1 (this may take some time to achieve), (2) prepare new bromine and acetone solutions, and (3) make sure that the three stock solutions and some distilled water has equilibrated to the correct temperature in the water bath.

To determine the orders of the flooded species (Ac, H⁺), you will need to prepare two sets of four solutions. In the first set, the initial concentration of H⁺ is constant, but the initial concentration of Ac is varied. In the second set, the initial concentration of Ac is constant, but the initial concentration of H⁺ is varied. You can start to design your experiment while the stock solutions are coming to temperature. The initial bromine concentration should be the same in all solutions as it was in Part A. For the varying [Ac] series, use the initial concentration of H⁺ from the solution in Part A so that you can include that point data in your analysis. Likewise, use the initial concentration of Ac from Part A in the varying [H⁺] series. Try to vary the concentration of Ac or H⁺ in the solutions by at least an order of magnitude over the series.

For all eight solutions, monitor the decrease in bromine absorbance at 450 nm as a function of time. The criteria for an acceptable solution can be somewhat relaxed in this part: the absorbance must decay by at least 10%, and you must be able to obtain at least 5-6 absorbance readings (i.e.: the reaction must last for ~5-6 minutes). Try to obtain as wide a range of reaction rates as possible for each set of solutions. Once again, periodically check the water bath temperature to be sure that it stays constant. If not, record the temperature at regular intervals to get a sense of the size of the fluctuations. Data obtained during large fluctuations should be discarded.

Calculations:

Part A: Determination of the Order of Bromine

Enter the absorbance versus time data for your “good” solution from Part A into three linear least squares spreadsheets (it is a good idea to place them in a single workbook). Calculate the concentration of bromine using Beer’s Law ($b=1.00$ cm) and the data in Table 1. Fit the data using the three integral rate law forms from Table 2. Make plots of the data to visualize the results. The most linear plot will be the one that (a) looks most linear (!), and (b) has the smallest error in the LLS fit. This plot indicates the value of m . Record the results (qualitative and quantitative) in your notebook.

Print a copy of all three plots on a single page to hand in with your report. Please conserve toner and use a white background on your plots, as usual. Also print a copy of each spreadsheet (use "Fit to 1 Page" in **Page Setup** for each one).

Part B: Determination of the Orders of Acetone and Acid

Enter the absorbance versus time data for the eight solutions from Part B into eight linear least squares spreadsheets (it is a good idea to place them all in a single workbook). For each run, calculate the concentration of bromine using Beer's Law ($b=1.00$ cm) and the data in Table 1. Fit each set of data using the m^{th} order integral rate law equation. Plot the data by placing all of the data for the constant $[\text{Ac}]$ series on *one plot*, and all of the data from the constant $[\text{H}^+]$ series on another (*single*) plot. Since printouts will be in black-and-white, use symbols that will be distinguishable (squares, diamonds, circles, crosses; open and filled symbols, etc.) when printed. Be sure to include *meaningful* legends on your plots (i.e.: not "solution 1, solution 2, etc.).

Obtain values for the pseudo rate constant for each run from the LLS fits to the data (record these in your notebook with units and correct SF). In a new LLS spreadsheet, enter the pseudo rate constants and acetone concentrations for the constant $[\text{H}^+]$ set of data, including the solution from Part A. In your notebook, show a sample calculation for the concentration of acetone (or acid) in the reaction solution. You may perform the remaining concentration calculations in your notebook or in the spreadsheet. Fit the data using $x=\ln[\text{Ac}]$ and $y=\ln k'$, then plot y versus x according to equation (6). On your plot show the LLS fit line and the equation for the best fit line (it should agree with your result from LLS). Obtain a value for n with a 95% confidence interval from the LLS fit.

Repeat the analysis in another spreadsheet for the constant $[\text{Ac}]$ set of data to obtain a value for p with a 95% confidence interval.

Print a copy of each spreadsheet and each plot to hand in with your report (you should have 8 m^{th} order plots, and 2 $\ln k'$ plots, thus 10 LLS spreadsheets from Part B). Be sure all initial and final data in the spreadsheet have units.

Part C: Calculation of the Rate Constant, k

The value of the true rate constant, k , can be obtained from a plot of equation (3). In a new (final!) LLS spreadsheet, enter the data from all nine solutions so that $y=k'$ (with units), and $x=[\text{Ac}]^n[\text{H}^+]^p$. Use the experimental values of n and p to avoid propagating extra errors into the calculation. You can either insert a few extra columns into the LLS spreadsheet before the x and y columns, or perform the calculation of $x=[\text{Ac}]^n[\text{H}^+]^p$ in another location on the sheet. In either case, be sure to check your formulas for x to be sure that relative addressing has not played any games with your data.

At the end of the LLS area (probably column N), enter the error in k' from the LLS fits. Plot x versus y and obtain a value for k , including units and a 95% confidence interval. On your plot include:

- The LLS fit line.
- Error bars on k' (for instructions, see Appendix A).
- The value of k , including units and the 95% confidence interval.

Print a copy of the spreadsheet and the plot to hand in with your report.

Wrapping it Up:

Number and title all LLS worksheets (as Tables) and plots (as Figures) to hand in with your report. In your notebook, make a table containing the following data for all nine solutions: solution number, [Ac] in the reaction solution, [H⁺] in the reaction solution, k' , error in k' . Indicate the temperature and approximate initial bromine concentration in the title of the table. Also in your notebook, report the final experimental rate law, including 95% confidence limits and units (where appropriate) on m , n , p , and k .

In your discussion you should briefly address the following points:

- The temperature stability over the course of the experiment, and any possible ramifications.
- The quality of the determinations of m , n , p , and k . Use the final plot showing the errors in k' to support any claims that you make.
- Compare your experimental rate law to the two theoretical limiting cases. Which case is better supported by the data? How can you justify this based on your understanding of chemistry and molecular stability? What does it mean that H⁺ is flooded (i.e.: [H⁺] >> [Br₂]) in terms of the conditions for the observed limiting case? Do you think there is a way to force the other limiting case to occur (be specific)?

You will need to write an abstract for this experiment. Recall that an abstract should always contain the following five components:

- *Context (what is interesting about this experiment, or why it is interesting)*
- *What was studied/measured*
- *How it was studied/measured*
- *Results (with units and error limits if numerical)*
- *Meaningful conclusions obtained*

Read the appropriate sections of the “Notebooks and Reports” section of this manual for more detailed examples and instructions. Good writing takes practice, and writing good abstracts takes *lots* of practice. Therefore, you will have an opportunity to revise your abstract based on peer review. Remember that an abstract should be concise and to the point (no more than a paragraph long). Check your grammar and spelling *before* you hand in the first version!