**How Can I Start My Campfire Faster?**

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After a round of tough exams and tired of your cramped dorm room, you and a group of friends have taken advantage of a gorgeous weekend and the close proximity of the Adirondacks to go camping. As the sun begins to set and the air begins to cool, you all agree that a campfire would be nice. While some of you have been camping before with your families, none of you has ever been responsible for building a campfire on your own.

You all gather whatever good sized pieces of dead wood you can find and stack them in the fire pit. One of you lights a match and places the burning match on the logs. After a short while, the match goes out without getting any of the logs to burn. Picturing in your mind the steps you’ve seen your dad go through, you suggest that you pile a bunch of twigs and dry leaves underneath the logs and light those first.

At first, when a new lighted match is placed near them, the leaves and twigs begin to burn rapidly. As the match is consumed, the flames from the twigs and leaves begin to fade. Not wanting to have to use another match from your small supply, you lean down and start blowing on the fire which increases the size of the flames. Since the logs are just beginning to smolder and most of the twigs and leaves have burned, your friends start tossing more twigs and leaves on the fire while you continue to blow.

Eventually, the logs start burning. As you sit back, soaking up the warmth and gazing into the fire, you start to wonder about the process (hey, you’re a chemistry student, it’s hard not to). Why did the twigs and leaves start burning before the logs even though they are made up of the same compounds? Why did blowing on the fire make the flames get bigger? What else can be done to make the fire burn faster or slower?

**Background**

One of the burning questions for chemists has always been why do some chemicals react when mixed together while others do not. While the elements present in the reactants give them specific properties which play a major role in determining whether or not a reaction can occur, some reactions do not occur at any level we can measure while others need encouragement to get started. Once a reaction gets going, it may go at different speeds under different conditions. Just as the speed you drive is influenced by many things (your habits, number and speed of other vehicles, presence of a cop, condition of the road), so too is the speed of a chemical reaction. In addition to the properties of the reactants, some of the things that can influence a reaction are:

1. concentration of reactants (think oxygen increase by blowing)
2. surface area especially for solids (think twigs versus logs)
3. temperature
4. other chemicals that are not part of the overall reaction

When you are driving your car, your speed is determined by measuring how many miles you travel (Δ distance) over the time it takes (Δ time) with units of miles/hour. For a chemical reaction, how fast a reaction goes (rate) is really how many molecules of reactant are consumed or molecules of product are produced in a specific amount of time. As you are well aware by now, we cannot count individual molecules very easily so we need a more accessible method to define our rates. Since concentration is a measure of how many molecules are present, it makes sense to use the change in concentration over time to define the rate of a reaction (equation 1). Because the amount of reactant present decreases as the amount of product increases, the change in concentration for a reactant is a negative number, so we take the negative of the change to give rate as a positive number.

 (1)

In order to sort out how different factors influence the rate, we need to conduct experiments designed to look at only one particular factor at a time. The one that we will be looking at today is the concentration of the reactants. The relationship between the changes in rate of reaction and changes in concentration of reactants is referred to as the order of the reaction. If the rate doubles when the concentration of a reactant doubles it is said that the reaction is first order with respect to that reactant. If it quadruples when the reactant is doubled then it is second order with respect to that reactant. Sometimes changing the concentration of a reactant has no effect at all on the rate and thus is zero order with respect to that reactant. Since the rate responds in a consistent manner to changes in the concentration of reactants, this relationship can be expressed mathematically in terms of the rate law (equation 2) where the exponents are the orders with respect to each reactant and k is a constant that is specific for the reaction conditions (temperature, ion concentration, etc.). The orders for each of the reactants are added together to give the overall reaction order.

rate = k[A]x[B]y (2)

Knowing the rate law is extremely important because it helps us understand how the reaction happens. For example, if the reaction is first order with respect to A but zero order with respect to B, then we know the reaction must be at least a two step process where the slower step involves A but not B even though both are necessary to create the final product. The “how” is the mechanism of the reaction and combined with rate is referred to as the kinetics of the reaction.

The reaction we will study today is the reaction of peroxydisulfate ion with iodide ion to make iodine and sulfate ions (equation 3). Rate can be expressed either in terms of increase in the concentration of iodine or decrease in the concentration of S2O82−.

S2O82−+ 2 I− I2 + SO42− (3)

In order measure the rate we need to be able to measure the amount of either a product or a reactant*.* When starch is added to the solution any iodine produced will combine with some of the iodide ions to form I3− which complexes with starch to produce a blue to blue-black color. This is great for showing us whether or not we have made I2 but is not so good for telling us how much has been made. To get around this problem we are going to make use of a second reaction which occurs at a much faster rate than our reaction of interest. Thiosulfate ions react instantaneously with iodine to produce iodide ions (equation 4) which keeps the solution from turning blue until all of the S2O32− has been used up.

2S2O32− + I2 2I− + S4O62− (4)

Based on the amount of the sodium thiosulfate added and the stoichiometric ratios from the balanced equations we can calculate the moles of iodine produced and the moles of S2O82− used up at the moment when the solution turns blue. Since rate is the change in concentration over time, when we divide the moles for either iodine or S2O82− by the total volume (L) and the time (s) it took to turn blue we get the rate of reaction. If we add more Na2S2O3 as soon as the solution turns blue, it will rapidly become colorless and by measuring the time from blue to blue we can get a second rate for the same initial concentrations. As long as the concentration of peroxydisulfate ions remains relatively large, we can continue repeating the process.

So how does this help us determine the effect of the change in concentration on rate? Remember to do this mathematically, we need to complete our specific rate law (equation 5) and so we need to find the orders with respect to S2O82- and I- (x and y) and the rate constant, k.

 (5)

Since the order of the reaction depends on the mechanism rather than the stoichiometry of the reaction, we cannot simple substitute in the coefficients from the balanced equation for x and y. Instead we need to find a way to eliminate some of the unknown variables so that we can solve the equation for one variable at a time. Once we have rates for a pair of solutions where the initial concentration of one reactant changes while the other remains the same, we can determine orders by looking at the ratio of the rates.

To do this for the order with respect to S2O82−, x, look for two solutions that have the same initial concentration for I−, [I−]o. Place the rate law for one solution over the rate law for other with the actual values for the rates and concentrations filled in (6). Though you get the same answer no matter which one is on top, it is easier to do mental math if the larger rate is on top. Quickly you can see that k & [I−]oy cancel because they are the same on top and bottom.

 (6)

Now it is just a matter of solving for x. Using the rules for powers, we can divide the concentration on top by the concentration in the denominator with the result being to the x power. After dividing out the rates, we are left with equation 7. Notice at this point the numbers are unit less because the units also cancel out.

 (7)

To get x down where we can easily solve for it, we take the log of both sides (*log not ln*, equation 8). If the reduced rate and the reduced concentration are the same number, it is obvious that the order is 1 without completing the math. If however they are not identical, as is often the case, you need to solve for x.

 (8)

You can repeat the process using two solutions with the same [S2O82−]o to get the order with respect to I−(y). Substituting in the values for the concentrations, orders and rate for one solution, you can solve the rate law for k to get the rate constant. Note that the units on the rate constant vary depending on the orders of reaction. To determine what units k needs so that rate has the correct units when predicting rates, you will need to keep track of your units carefully as you solve for the rate constant.

**Procedure**

1. Get approximately 20 mL of Na2S2O3 in a clean, dry and labeled beaker.
2. To a clean and dry flask, add everything for your first solution except the (NH4)2S2O8. Place the required amount of (NH4)2S2O8 in a clean, dry and labeled beaker.
3. Add a magnetic stirbar to the flask. Place the flask on a stirplate and begin stirring at a moderate speed.
4. Quickly pour the (NH4)2S2O8 into the flask and start the timer.
5. Record the time as soon as the solution turns blue and immediately pipet in an additional 1.00 mL of Na2S2O3. Do not stop the timer.
6. Repeat step 5 until the time has been recorded four times.
7. Repeat steps 1-6 for your remaining solutions.

**Data Collection**

Copy the following tables into your notebook.

**Table 1.** Reagent amounts for solutions (insert yours).

|  |  |  |  |
| --- | --- | --- | --- |
| solution **#** |  |  |  |
| 0.2 M KI (mL) |  |  |  |
| starch (mL) |  |  |  |
| 0.4 M Na2S2O3 (mL) |  |  |  |
| 0.2 M KNO3 (mL) |  |  |  |
| EDTA (drop) |  |  |  |
| 0.2 M (NH4)2S2O8 (mL) (**in beaker**) |  |  |  |

**Table 2.** Reaction rates for solution \_\_\_\_\_.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| solution added | time when blue (min:s) | reaction time (s)  | total volume (L) | rate (mol/L sec) |
| (NH4)2S2O8 |  |  |  |  |
| Na2S2O3 |  |  |  |  |
| Na2S2O3 |  |  |  |  |
| Na2S2O3 |  |  |  |  |

**Table 3.** Reaction rates for solution \_\_\_\_.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| solution added | time when blue (min:s) | reaction time (s) | total volume (L) | rate (mol/L sec) |
| (NH4)2S2O8 |  |  |  |  |
| Na2S2O3 |  |  |  |  |
| Na2S2O3 |  |  |  |  |
| Na2S2O3 |  |  |  |  |

**Table 4.** Reaction rates for solution \_\_\_\_\_.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| solution added | time when blue (min:s) | reaction time (s) | total volume (L) | rate (mol/L sec) |
| (NH4)2S2O8 |  |  |  |  |
| Na2S2O3 |  |  |  |  |
| Na2S2O3 |  |  |  |  |
| Na2S2O3 |  |  |  |  |

**Table 5.** Average rates for solutions \_\_\_\_\_\_\_\_\_\_\_\_.

|  |  |  |  |
| --- | --- | --- | --- |
| solution | [I-]o (mol/L) | [S2O82−]o(mol/L) | ave. rate (mol/L sec) |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |

**Calculations**

1. ***PRE-LAB (as in before you come)***
	1. Calculate the number of moles of S2O82- used up each time the solution turns blue. (hint: you will need to use stoichiometric ratios from both equations 3 & 4)
	2. Calculate the [I-]o and [S2O82-]o for each solution and record in table 5.
2. IN LAB
	1. Calculate the rates for each reaction based on the moles of S2O82- used up.
	2. Calculate the average rate for each solution. If one the value for rate is far away from the others, you should not include it in your average. Use a footnote to the appropriate table to indicate any discarded values.