Chemical Kinetics - Iodine Clock Reaction

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Abstract

The purpose of this experiment was to investigate the effects of concentration, temperature, and the presence of a catalyst on the rate of a reaction. Using the method of initial rates, the order with respect to each reactant, the overall order of the reaction, the rate constant, and the activation energy were determined in this experiment. This was done using a controlled amount of thiosulfate in the reaction to consume the iodine created in the slower, main reaction. This technique is the “clock” that prevents the solution from turning blue too soon before the desired amount of iodine has been produced. It was determined experimentally that as concentration and temperature increase, the rate of the reaction also increases. It was also discovered that adding a catalyst increases the rate of the reaction significantly by lowering the activation energy needed for a molecular collision to occur. Based on the value of the rate constants, k, all medium values, we can conclude that the reactions were all normal/fast while the reaction with the catalyst was very fast. We discovered the activation energy for the rate law, **$R = [I^-]\ [BrO_3^-]\ [H^+]^2$ was 45 kJ with a rate constant of 31.64 $M^{-3}* s^{-1}$.**

Introduction

Chemical kinetics applies to the speed of a reaction, concentration of product that appears (or of reactant that disappears) per unit of time. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. The factors that affect reaction rates include the surface area of a reactant, concentration or pressure of a reactant, temperature, nature of the reactants, and the presence or absence of a catalyst.

The rates of chemical reactions, and especially the ability to control those rates is an important area of chemistry to understand due to the importance of many such reactions to our health, well-being, and comfort. Chemical kinetics relates, for example, to how quickly a medicine is able to work, whether the formation and depletion of ozone in the upper atmosphere are in balance, industrial problems such as the development of catalysts to synthesize new materials, and to successful rocket launches, which depend on the rate at which fuel burns. In some cases it would be advantageous to slow down reactions such as with food spoilage and rust formation, while in other cases it would be beneficial to speed them up such as quick acting medicines and the conversion of organic matter to fossil fuels.

In the collision model, a chemical reaction occurs after a sufficiently energetic collision between two reactant molecules. Moreover, the rate of a reaction is governed by the collision theory. In order for a reaction to occur, there must be a collision between reactant molecules, and this reaction must have enough energy to break and form the appropriate bonds as well as have the correct orientation when colliding. If we can increase or decrease the conditions that enable a chemical reaction to occur, then we can manipulate the reaction rate.

The rate of a chemical reaction often depends on the concentration of one or more of the reactants, and is measured as a change in the amounts of reactants or products (usually in concentration units) divided by the change in time given by Equation (1) below:

$$\mathbf{Rate = -1/a\,\Delta[A]/\Delta t = -1/b\,\Delta[B]/\Delta t = +1/c\,\Delta[C]/\Delta t = +1/d\,\Delta[D]/\Delta t} \tag{1}$$

From the definition, we can see that knowing the rate of change in the concentration of any one reactant or product at a point in time allows us to determine the rate of change in the concentration of any other reactant or product at that point in time (from the balanced equation). In order to study kinetics, we must have an experimental way to measure the concentration of at least one of the reactants or products as a function of time. Common techniques include three continuous monitoring methods: polarimetry, spectroscopy, and pressure measurement. Polarimetry measures the change in the degree of rotation of plane-polarized light caused by one of the components over time, spectroscopy measures the amount of light of a particular wavelength absorbed by one component over time, and in pressure measurement the total pressure of a gas mixture is stoichiometrically related to partial pressures of the gases in the reaction.

The rate law or rate equation shows how the rate of a reaction depends on the concentrations of the reactions and is expressed by Equation (2) below:

$$\mathbf{Rate = k[A]^m[B]^n} \qquad (2)$$

where [A] and [B] are the molarities of the reactants, m and n are the orders of the reaction with respect to [A] and [B], and k is the rate constant which we can determine once we know the concentration of [A] and [B], the order of [A] and [B], and the rate of the reaction.

If we are unsure about how the initial rate is changing with the initial reactant concentration, or if the numbers are not obvious, to determine the rate order (n) we use Equation (3) below:

$$\mathbf{Rate\ 2/Rate\ 1 = k[A]^n{}_2/k[A]^n{}_1} \qquad (3)$$

Knowing the reaction order can help chemists to predict how the reaction speed will change over time, as well help them to know how much or little to change the experimental conditions that influence the rate of the reaction.

The Iodine Clock Reaction is a classical experiment clock demonstration experiment to display chemical kinetics in action. Discovered by Heinrich Landolt in 1886, the purpose of the experiment is to investigate the effects of concentration, temperature, and the presence of a catalyst on the rate of a reaction. Using common sense, we should expect to see slower rates and times at lower concentrations and temperatures, and faster rates and times at higher concentrations and temperatures. One should also expect to see faster rates when a catalyst is used because it is a substance that modifies the transition state to lower the activation energy and increase the rate of a reaction. The term “chemical clock” refers to a reaction where the concentration of one of the chemical components undergoes an abrupt change in concentration after a time period and leads to a sudden change in color to blue. The reaction in this experiment is termed an *iodine clock reaction* because it is the molecular iodine (I_2) that undergoes the sudden concentration change that we are only able to see because of the starch that is used in the experiment turning blue from reaction with iodine. In the experiment, a reaction between iodide ions and bromate ions also takes place according to Equation (4) below:

$6I^-(aq) + BrO3^-(aq) + 6H^+(aq)$ ✏ $3I_2(aq) + Br^-(aq) + 3H_2O(l)$ **(4)**

In order to determine the dependence of the reaction rate on concentration, temperature, and a catalyst, experiments were performed according to the slow reaction in Equation (4). The results then allowed you to determine the orders of the iodide ion, bromate ion, and hydrogen ion as well as the value of the rate constant k by the method of initial rates, expressed in the rate law form of Equation (5) below:

$$\text{Rate} = k[I^-]^x[BrO_3^-]^y[H^+]^z \qquad (5)$$

Once we know the concentrations, rate order, and rate constant (k) of the reactions, we are able to use integrated rate laws which show the relationship between the concentrations of the reactants and time and allow us to make predictions on how long reactions will take as well as predictions on how concentrations may vary over time. The integrated rate laws are expressed mathematically by Equation (6) below:

$$\text{Zero-Order} = [A]_t = -kt + [A]_0 \qquad (6)$$
$$\text{First Order} = \ln[A]_t = -kt + \ln[A]_0$$
$$\text{Second-Order} = 1/[A]_t = kt + 1/[A]_0$$

In order to have the experiment go right and have the appropriate data collected, a predetermined amount of thiosulfate was used to control the amount of I_2 formed in the main reaction. The purpose of this was to not have the starch present turn blue too quickly from the I_2, as that would give us a premature reaction and therefore the wrong data. Ideally, the blue color will not appear until the thiosulfate is consumed, and that is when we know the desired amount of I_2 has been formed. This is a simultaneous, fast-second reaction given by Equation (7) below:

$$\mathbf{I_2(aq) + 2S_2O_3^{2-}(aq) \leftrightarrow 2I^-(aq) + S_4O_6^{2-}\,(aq)} \qquad \textbf{(7)}$$

The experiment then consisted of measuring the time it takes for the blue color to appear as a function of varied concentrations of each of the three reactants/ions given in Equation (4). In all of the reaction mixtures, the same number of moles of BrO_3^- had reacted once the color changes. In order to use the number of moles reacted to calculate the rate of reaction of $BrO_3^{-,}$ however, Equations (3 & 6) were combined first to account (through stoichiometry) for the mole to mole ratio of bromate to thiosulfate, using the number of moles of thiosulfate reacted to convert to moles of bromate reacted. This is shown by Equation (8) below:

$$\mathbf{\frac{3\ mol\ I_2}{1\ mol\ BrO_3^-} \times \frac{2\ mol\ S_2O_3^{2-}}{1\ mol\ I_2}\quad \text{accounts for}\quad \frac{\Delta\,[BrO_3^-]}{\Delta t} = \frac{1}{6}\frac{\Delta\,[S_2O_3^{2-}]}{\Delta t}} \qquad \textbf{(8)}$$

Once the moles of thiosulfate were converted to moles of BrO_3^-, the rate of the reaction was determined by dividing the time (in seconds) by the mol/L of the bromate reacting expressed by Equation (9) below:

$$\mathbf{Rate = -\Delta[BrO_3^-] = 3.33 \times 10^{-5}\,(mol/L) \div \Delta t} \qquad \textbf{(9)}$$

Before using Equation (9) to calculate the rate, however, it was necessary to account for the dilution in concentration of each reagent as well as the deionized water since the total volume in all the reactions was 50 mL. To calculate and account for the dilution, Equation (10) below was used to do so:

$$\mathbf{M_1V_1 = M_2V_2} \quad \mathbf{(10)}$$

The experiment also investigates the rate of a reaction as a function of temperature in order to determine the activation energy, E_a for the reaction. The activation energy is calculated from the Arrhenius Equation (11) below:

$$\mathbf{\ln k = E_a/R\ (1/T) + \ln A} \quad \mathbf{(11)}$$

where A is a constant, T = temperature in Kelvin, and R = 8.314 J/mol*k. The value of E_a was then determined by first graphing ln k vs. 1/T and then using Equation (12) below:

$$\mathbf{Slope = -E_a/R} \quad \mathbf{(12)}$$

Experimental

The study consisted of three different experiments: Part 1 – Find the dependence of the reaction rate of concentration, Part 2 – Determine the dependence of reaction rate on temperature, & Part 3 – Observe the dependence of reaction rate on a catalyst. To gain the data necessary for our observations and results, the execution of the experiment was very straightforward which was to perform several solution mixtures and swirl the contents until it turned blue at which point you would take note of the time it took for the reaction (iodine to turn starch blue) to take place. The reaction mixtures consisted of potassium iodide, sodium thiosulfate, potassium bromate, hydrochloric acid, starch, and distilled water for reaction mixture 1 only. The same amount (10 mL) of thiosulfate was used in each mixture as the “clock” of the reaction by controlling the amount of $I_{2,}$ thus preventing the I_2 from turning the starch blue too soon. Once the thiosulfate was used up, the I_2 present would turn the starch blue, which is the time we wanted to note for our experiment. By using the same amount of thiosulfate in each mixture, this allowed us to convert (through stoichiometry) the amount of moles in the thiosulfate used up to the amount of moles in bromate that reacted. Once we knew our moles of bromate, we then converted the moles to mol/L to use to calculate our rate of the reaction.

Table 1 below shows the volume (in mL) and the initial concentration of each of the reagents that were used to mix for each trial:

	Reaction Flask 1 (125 mL)			Reaction Flask 2 (125 mL)		
Mix	0.010M KI	0.0010 M $Na_2S_2O_3$	H_2O	0.040 M $KBrO_3$	0.10 M HCl	Starch
1	10 mL	10 mL	10 mL	10 mL	10 mL	3 drops
2	20 mL	10 mL	0 mL	10 mL	10 mL	3 drops
3	10 mL	10 mL	0 mL	20 mL	10 mL	3 drops
4	10 mL	10 mL	0 mL	10 mL	20 mL	3 drops
5	0 mL	10 mL	0 mL	5 mL	15 mL	3 drops

Table 1: Volume & Concentrations of reagent to be mixed

For Part 1, five different trials were conducted, each corresponding to the respective row from Table 1. Using two separate flasks, the given amount of each reagent and water was poured into their respective flasks. It is important to note that either you used two different graduated cylinders to measure the reagents, or made sure to rinse out the graduated cylinder with deionized water before measuring the contents for the second flask. This was to ensure that the reagents didn’t start to react prematurely. Once both flasks were filled with the proper contents, we then poured the contents of flask 2 into flask 1. At this point we started our timers and began to swirl the mixture until it turned blue. Once that reaction took place, we carefully noted the time it took for the iodine to turn the starch blue. This process was repeated for four more trials. Trial 1 was repeated a second time as a way to check for consistency and to make sure the experiment was being performed correctly.

Some key points to make about Part 1 are that the temperature of the experiment was held constant at room temperature around 23.7 °C, as well as the concentrations of each trial were varied in order to obtain the orders of each reaction. This is a technique used to find the dependence of reaction rates on concentration. In trial 1 the measure of each content was the same (10 mL), and this was used as a comparison for trials 2, 3, & 4. In trials 2, 3, and 4 one of the reagent's concentration was varied while the other two reagent's concentrations were held constant. Also, deionized water was not added to trials 2-4. In trial 5, only the thiosulfate and starch were held constant, while the other three reagent's concentrations as well as the volume of deionized water were varied. This trial was used as a prediction trial for the results that were obtained from trial 1-4.

Part 2 was performed similarly to Part 1, except that this time all of the trials (in this case 4) used the same volume and concentration from reaction mixture 1. The variable in this part was temperature, which was adjusted for four different trials at approximately 40 °C, 10 °C, 0 °C, and 23.7 °C. This idea of Part 2 was to determine the dependence of reaction rate on temperature. Also, with the calculated results, the value of the activation energy, E_a, was determined by plotting a graph of ln k vs. 1/T and then using Equation (11). No trials were repeated in this part as I felt confident that each trial was conducted properly, as well as the heating and cooling trials were too time consuming to redo anyhow.

Using the same principle as Part 1 and Part 2, Part 3 observed the dependence of the reaction rate on a catalyst. The experiment in this part simply compared the difference in time for the color to appear in a reaction mixture with a catalyst versus a reaction mixture without a catalyst. Just as in Part 2, reaction mixture 1 was used for the two trials. The temperature was held constant in this part at room temperature, 23.7 °C.

Results

For Part 1, the diluted concentrations for the iodide ion, bromate ion and hydrogen ion were calculated first using Equation (11) to account for the 50 mL total volume in all the reactions as provided in Table 2 below. Once the correct concentrations were calculated for each ion, the rate of the bromate ion was then calculated using Equation (9) and is also provided in Table 2 below. This was done simply by dividing the time that each mixture took to react (turn blue) by the concentration of the bromate ion, which was determined by using Equation (8 & 10). The time of each reaction was monitored with a stopwatch and given is seconds, as well as the temperature of each reaction was taken at its completion. Both values are given in Table 2 below.

Mix	Time (s)	Rate = -$\Delta[BrO_3^-]$ /Δt =3.33 * 10^{5-} (mol/L)/ ⊗t	Reactant concentration (mol/L)			Temp (°C)
			$[I^-]$	$[BrO_3^{-3}]$	$[H^+]$	
1	158.44	$2.10*10^{-7}$	0.0020	0.0080	0.020	23.7
2	83.16	$4.00*10^{-7}$	0.0040	0.0080	0.020	23.7
3	83.09	$4.00*10^{-7}$	0.0020	0.016	0.020	23.7
4	41.43	$8.04*10^{-7}$	0.0020	0.0080	0.040	23.9
5	185.98	$1.79*10^{-7}$	0.0016	0.0040	0.030	23.8

Table 2: Part 1 Results for [ ] effect

In order to determine the orders of the reaction x (iodide), y (bromate), and z (hydrogen) as shown in Equation (5), Equation (3) was used to calculate the values. For the iodide ion, rate 2 and concentration 2 were divided by rate 1 and concentration 1 since the other ions were both held constant. The result of the calculation was first-order for iodide. For the bromate ion, rate 3 and concentration 3 were divided by rate 1 and concentration 1 again because the other ions were held constant. The result of this calculation was also first-order for bromate. Lastly, rate 4 and concentration 4 were divided by rate 1 and concentration 1 for the hydrogen ion and again because the other two ions were held constant. The result of this calculation was second-order for hydrogen. The overall reaction order = 4 and put together is Rate = $k[I^-][BrO_3^-][H^+]^2$.

After determining the rate order, I next calculated the rate constant, k, using Equation (5). As expected, the rate constants calculated for mixtures 1-4 were almost identical. This is because the rate constant will remain the same unless the temperature of the reaction is changed. Because the overall reaction order is 4, the units for k = $M^{-3}*s^{-1}$. Given the average value of the rate constants, k, at 31.64 $M^{-3}*s^{-1}$ (medium size value), we can conclude that the reactions were all normal to fast reactions. Table 3 below shows the results for the rate constants and average calculated.

Mix	k	$k_{average}$
1	32.81 $M^{-3}*s^{-1}$	31.64 $M^{-3}*s^{-1}$
2	31.25 $M^{-3}*s^{-1}$	
3	31.25 $M^{-3}*s^{-1}$	
4	31.25 $M^{-3}*s^{-1}$	

Table 3: Determination of rate constant (k)

For reaction mixture 5, the value of the rate constant average, the values of the diluted concentrations, the order, and the rate of $\Delta[BrO_3^-]$ were all used to predict how long it should take (in seconds) for the color to change versus the actual time (in seconds) observed during the experiment. Using Equation (5 & 9), the calculated results were: **time predicted = 182.97 s; time; time observed = 185.98 s.** Based on the results, the data confirms consistency in the actual time the reaction took, as well as consistency with the calculated values for the reaction rate, rate constant, orders, and diluted concentrations.

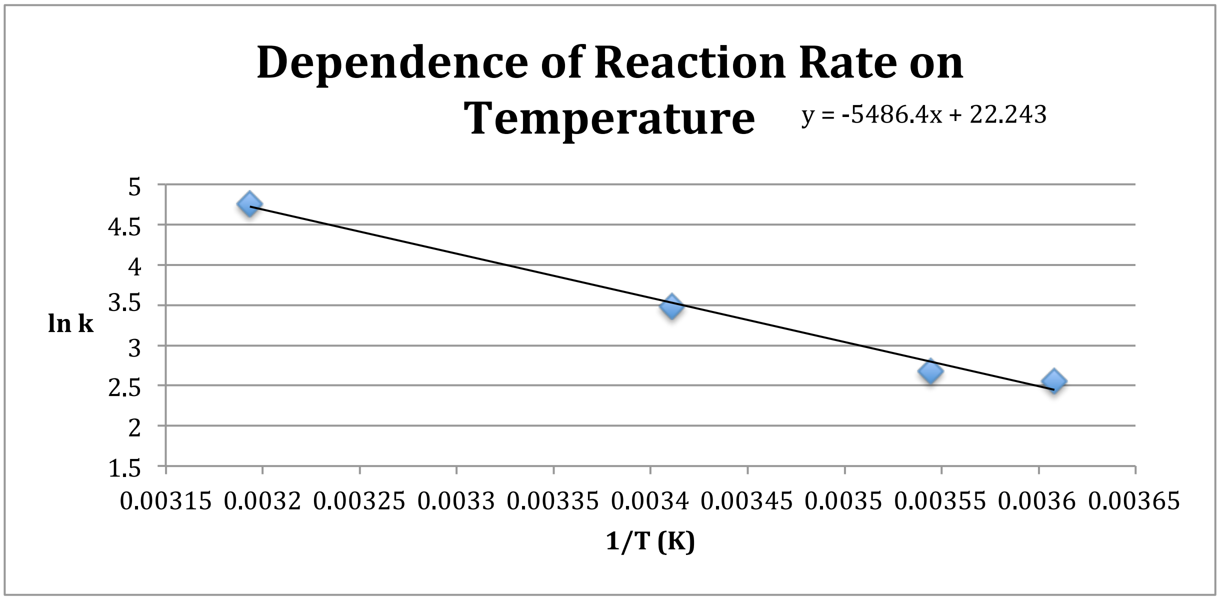
Using Equation (5) and putting the data from Part 1 together, the result is: **Rate = 31.64** $\mathbf{M^{-3} * s^{-1}[I^-] [BrO_3^-] [H^+]^2}$**, overall order = 4.** The takeaway from Part 1 is: **as you increase the concentration in a reaction, the rate of the reaction also increases.**

For Part 2, the rate of the reaction of bromate was similarly calculated as in Part 1 using Equations (8,9, &10). The adjusted bromate concentration for each trial was divided by time (in seconds) for the reaction to turn blue. After calculating the rate of bromate, again the rate constants for the mixtures were also calculated using Equation (5). As expected in this part of the experiment, the calculated rate constants varied this time since different temperatures were used in each mixture trial. Also expected, were faster rates at higher temperatures. It is important to note that the concentration was held constant as mixture 1 was used for all 4 trials, as well as the units for the rate constant again are $M^{-3}*s^{-1}$ since the overall order of the reaction = 4. The average size of the rate constant, k, remained a medium sized value, which again allows us to conclude that the reactions occurred at a normal to fast rate which is consistent with our findings in Part 1. Table 4 below summarized these results.

Mixture	Time (s)	Rate = -Δ [BrO_3^-]/Δt (mol/L-s)	Temp (°C)	Calculated k
1A	44.66	$7.46*10^{-7}$	40.2	$1.2*10^{2}$ $M^{-3}*s^{-1}$
1B	158.44	$2.10*10^{-7}$	20.4	$3.3*10^{1}$ $M^{-3}*s^{-1}$
1C	355.29	$9.40*10^{-8}$	9.1	$1.5*10^{1}$ $M^{-3}*s^{-1}$
1D	401.04	$8.30*10^{-8}$	4.3	$1.3*10^{1}$ $M^{-3}*s^{-1}$

Table 4: Part 2 Results

Using the temperature of each mixture converted to Kelvin, as well as the calculated rate constant a linear graph of ln k vs. 1/T was constructed to determine the value of the activation energy, E_a. Figure 1 below displays this graphical representation.



Figrue 1: Graph of ln k vs. 1/K

Using the equation from the graph y = -5.486.4x + 22.243, the value of E_a is calculated using Equation (12). Plugging in -5.486.4K into Equation (12) as the slope results in an activation energy of **E_a = 45.6 kJ/mol**. The takeaway from Part 2 is: **as you increase the temperature in a reaction, the rate of the reaction also increases.**

For the last Part 3, reaction mixture 1 was used for two trials. One with a catalyst added, and the other without a catalyst added. As expected, the reaction mixture with the catalyst reacted at a much faster rate and time than the mixture without the catalyst added. The results of this part are displayed in Table 5 below.

Mixture	Time (s) for color to appear
Reaction Mixture 1 with catalyst	4.19
Reaction Mixture 1 without catalyst	158.44

Table 5: Part 3 Results

The takeaway from Part 3 is: **adding a catalyst can significantly increase the rate of a reaction, and one should expect the activation energy of the catalyzed reaction to be lower. This is because a catalyst is a substance that modifies the transition state to lower the activation and increase the rate of a reaction without being consumed by it.**

Conclusion

The *iodine clock reaction* was a success. The experiments proved the theories of chemical kinetics of how different experimental conditions could influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states. The rates of chemical reactions, and especially the ability to control those rates is an important area of chemistry to understand due to the importance of many such reactions to our health, well-being, and comfort. Factors that affect reaction rates include the surface area of a reactant, concentration or pressure of a reactant, temperature, nature of the reactants, and the presence or absence of a catalyst. These important factors were all explored throughout this experiment.

Part 1 of the experiment explored the dependence of the reaction on concentration. This was successfully accomplished by running an experiment using five different trials held at constant temperature and varying concentrations of the reagents. End result is that as concentration increases, the rate of the reaction also increases and vice versa. Also, we learned that if you know the rate of change in the concentration of any one reactant or product at a point in time, this allows us to determine the rate of change in the concentration of any other reactant or product at that point in time from the balanced equation and stoichiometry. Because the value of the rate constants, k, was a medium sized number, we can conclude that the rate of the reaction happened at a normal to fast rate.

Part 2 of the experiment revealed the dependence of reaction rates on temperature. Successful again, this part used five trials held at a constant concentration and varying temperatures. The takeaway from this part of the experiment is that as temperature increases, the rate of the reaction also increases and vice versa. The results of this portion of the experiment then allowed us to make plot a graph of ln k vs. 1/T. This graph proved very useful in allowing us to then calculate the value of the activation energy of the reaction. This is important to know since the activation energy is the minimum quantity of energy that the reacting species must possess in order to undergo a reaction. The average size of the rate constant, k, remained a medium sized value, which again allows us to conclude that the rate of the reaction happened at a normal to fast rate which is consistent with our findings from Part 1.

Part 3 demonstrated the effects of a catalyst. Two trials were used, one with the presence of a catalyst and the other without. The results of this part of the experiment prove that a catalyst does in fact speed up a reaction, which was very apparent as the reaction mixture with a catalyst occurred at a much faster rate (nearly 40 times faster) than the mixture without a catalyst. Consequently, the rate constant (k) was a much larger number ($1.2*10^{3}$ $M^{-3}*s^{-1}$). This happens because a catalyst is a substance that modifies the transition state to lower the activation and increase the rate of a reaction without being consumed by it, thus allowing for molecular collisions to happen faster.

The collision theory states that a chemical reaction occurs after a sufficiently energetic collision between two reactant molecules. In order for a reaction to occur, there must be a collision between reactant molecules, and this reaction must have enough energy to break and form the appropriate bonds as well as have the correct orientation when colliding. We have learned from this experiment that we can do this by manipulating factors such as concentration, temperature, and the presence of a catalyst. Tying this into our results from the experience, it’s easy to see the ability and benefits of being able to manipulate the rates of a chemical reaction.

All in all, this experiment was a fun and easy way to see chemical kinetics in action, and watch a molecular reaction happen macroscopically because of the amazingly magical chemical reaction of iodine turning starch blue.

References

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