TEACHING KINETICS WITH THE LANDOLT IODINE CLOCK RXN

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CHEMICAL CONCEPTS

Chemical Kinetics

- Measuring reaction times
- Predicting the influence changing the concentration of a reactant species has on the time of reaction
- First-order kinetics

Scientific Process Skills

- Making qualitative and quantitative observations
- Making qualitative and quantitative predictions based on observations
- Experimental design

Stoichiometry

- Interpreting chemical equations
- Limiting reactant

HOW DEMONSTRATION ADDRESSES THE CONCEPTS

The measurement of reaction rates involves the determination of the time required for a specific quantity of reactant to be consumed or product to be formed. In this demonstration the time required for the sodium bisulfite ion to be consumed by the potassium iodate is determined. This requires a "signal" that indicates that the species has been consumed. In the Landolt iodine clock reaction the sudden change from colorless to blue-black indicates the bisulfite ion has been consumed. Having the students "measure time" by counting at a constant rate from the first moments the two solutions come in contact until the formation of the blue-black starch-iodine complex involves them in measuring the rate of reaction.

Based on their observations of the time required for the first mixture to react, the students are asked to make a qualitative prediction of the time required to react if the iodate concentration is cut in half and to explain their reasoning. The reaction is then carried out and the students are able to test their prediction by counting out the time to react. Then, based on their observations of the time for the first and second reaction mixtures to react, the students are to make a quantitative estimate of the time required to react if the iodate concentration is now one-fourth that in the first mixture. Again, their predictions are tested by carrying out the reaction, which should be four times longer than the time for the first reaction mixture.

From their observations students should be able to derive a "rule" that expresses the influence the concentration of a reactant species has on the overall reaction rate. Since the reaction is first-order with respect to the iodate ion concentration and the times clearly reflect this, the idea of first-order reactions can be developed through discussion.

The discussion of what is happening on the molecular level takes place after performing the first reaction mixture. The bisulfite ion is the limiting reactant and through the discussion the students should be able to understand why it must be the limiting reactant (the formation of the tri-iodide ion will not occur if the bisulfite is in excess preventing the formation of the starch-iodide complex that signals the end of the reaction).

The students are involved in experimental design when they are asked to design an experiment that could possibly be used to determine the effect of changing the bisulfite ion concentration has on the overall reaction rate, and to determine the influence temperature has on the rate.

PREPARING AND PERFORMING THE DEMONSTRATION

Safety

- Potassium iodate is mildly toxic by ingestion and is irritating to body tissues. Avoid contact.
- Sodium bisulfite is slightly toxic by ingestion and is a severe body tissue irritant. Avoid contact.
- Sodium thiosulfate is slightly toxic by ingestion and is a body tissue irritant. Avoid contact.
- Iodine is generated in this demonstration. Those who know they are allergic to iodine or do not know whether they are should avoid contact. Wear protective gloves.
- Safety goggles should be worn while doing this demonstration. Protective gloves are recommended.

Equipment and Materials (for one presentation)

- 2.60 grams of sodium bisulfite
- 100-mL volumetric flask
- 5.35 grams of potassium iodate
- 250-mL volumetric flask
- 5.0 grams of soluble starch
- Distilled (or de-ionized) water
- Crushed ice
- One 1000-mL beaker

- Four 600-mL beakers
- Three 250-mL beakers
- One 50-mL beaker
- Parafilm
- Volumetric transfer pipets of various sizes or four titration burettes
- Waste container (at least 2-L)
- 10-20 grams of sodium thiosulfate pentahydrate (for waste treatment)

Preparation of Solutions

- Dissolve 5.35 grams of potassium iodate in 200 mL of water (250-mL volumetric flask) and dilute to 250 mL. The potassium iodate solution is 0.10 M.
- Heat 250 mL of water to boiling in a 600-mL beaker. In a 50-mL beaker, make slurry of 5.0 grams of soluble starch in 10 mL of distilled water. Pour the slurry into the boiling water and boil for 5 minutes. Place 225 g of crushed ice in a 1000-mL beaker. Pour the hot starch mixture over the ice. When all the ice has melted, dilute the mixture to 500 mL. The starch solution is 1% starch.
- Dissolve 2.60 grams of sodium bisulfite in 60 mL of water (100-mL volumetric flask) and dilute to 100 mL. NOTE: this solution decomposes over time and should be made fresh (less than three days prior to presentation). The sodium bisulfite solution is 0.25 M.

Advanced Preparation

- Label three 600-mL beakers *Set 1A, Set 2A*, and *Set 3A*. Label three 250-mL beakers *Set 1B, Set 2B,* and *Set 3B.*
- Using transfer volumetric pipets or titration burettes measure accurately the quantities of reagents shown in the table below and place them in the appropriate beakers. Cover the beakers with parafilm.

Beaker	**KIO_3**	**H_2O**	**Starch**		**Beaker**	**$NaHSO_3$**	**Water**
Set 1A	100 mL	100 mL	50 mL		Set 1B	20 mL	130 mL
Set 2A	50 mL	150 mL	50 mL		Set 2B	20 mL	130 mL
Set 3A	25 mL	175 mL	50 mL		Set 3B	20 mL	130 mL

Performing the Demonstration

- For each set of solutions, one set at a time, add the solution in beaker B to the solution in beaker A and measure the time from first mixing to when the mixture turns blue-black. See the section “Pedagogical Strategies” for more detail.

Handling of Waste

- The waste mixture consists primarily of iodine, starch, sodium ions, potassium, ions, and sulfate ions. Combine the waste mixtures of the three sets into a large container. Add 10-20 grams of sodium thiosulfate pentahydrate, swirl, cap the container, and let stand for 10-15 minutes. The mixture should now appear murky white. If the blue-black coloration is still visible, add more sodium thiosulfate. The thiosulfate converts the iodine into iodide ions producing colloidal sulfur in the process. This mixture can be safely disposed of down the sink flushed with plenty of water. Check your local regulations before disposing of waste in the sink.

PEDAGOGICAL STRATEGIES FOR FOSTERING LEARNING AND UNDERSTANDING OF THE CONCEPTS

- I begin the demonstration with a discussion of what is involved in measuring reaction rates bringing out that one is measuring the time it takes for a particular reactant species to disappear or a product species to appear. I then bring out that some reactions allow us to easily make this measurement of time because there is a clear signal indicating the reaction is complete, as they will see shortly.
- Next I tell them that I will perform a reaction by mixing two solutions together and they are to measure the time for the reaction to occur by counting out loud at a steady rate. We practice counting and I congratulate them on their ability to count (a little humor goes a long ways). I then tell them that they are to begin counting from when the first drop of solution in beaker B meets the solution in beaker A until a sudden change is observed. I purposefully do not tell them what the change will actually be (a little anticipation of the unknown is good for keeping attention on the demonstration).
- I then perform the demonstrations beginning the counting process with them but once they are going I fade out. The time required for the reaction to occur is usually around 10-14 seconds depending upon the freshness of the bisulfite ion solution (older solutions take less time). The time required to react is written on the board.
- Then with the aid of a poster board, Velcro®, and signs with the formulas of the various species in the reaction mixture, I discuss what is happening on the molecular level. Initially only iodate and bisulfite ions, and starch molecules are present in the reaction mixture with the iodate ions in excess. These are displayed on the poster board. I begin the discussion stressing the bisulfite is the limiting reagent and that they will see why this is necessary as I discuss what is happening. I then state that the iodate and bisulfite ions react to form iodide and sulfate ions (a redox process). I remove one pair of signs “iodate ions” and “bisulfite ions” and replace them with “iodide ions” and “sulfate ions”. I next tell them that the iodate ions also react with iodide ions to convert them to tri-iodide ions. Again, I remove a pair of signs, “iodate ions” and “iodide ions”, and put a sign “tri-iodide ions” in their place. However, this is not a problem because the bisulfite ions rapidly react with the tri-iodide ions converting them back into iodide ions while oxidizing to sulfate ions. Again, I replace signs for “tri-iodide ions” and “bisulfite ions” with “iodide ions” and “sulfate ions”. I stress that these processes continue to cycle through until the bisulfite runs out (there are no more signs for bisulfite

ions on the poster board). At this point the iodate oxidizes the iodide ions into tri-iodide ions, which in turn react with the starch to form the blue-black complex. I remove a pair of signs for the "iodate ions" and "iodide ions" and replace them with the "tri-iodide" sign. Then I remove the "tri-iodide" and a "starch" sign and replace it with the "starch-iodide" complex sign. These reactions are summarized on the board by writing the equations for each step.

$$IO_3^{1-} + 3\ HSO_3^{1-} \rightarrow I^{1-} + 3\ SO_4^{2-} + 3\ H^{1+}$$

$$6\ H^{1+} + IO_3^{1-} + 8\ I^{1-} \rightarrow 3\ I_3^{1-} + 3\ H_2O$$

$$H_2O + I_3^{1-} + HSO_3^{1-} \rightarrow 3\ I^{1-} + SO_4^{2-} + 3\ H^{1+}$$

$$2I_3^{1-} + \text{Starch} \rightarrow \text{Starch—}I_5^{-1}\text{ complex (blue)} + I^{-1}$$

Whether the second reaction occurs at any point in the reaction or after the bisulfite ions are completely consumed is not important. The overall net effect is that the blue-black starch—iodide complex does not form until after the bisulfite ions have been consumed. Finally, I bring out the importance of keeping the bisulfite as the limiting reagent. I ask the students what will happen if it were in excess (the tri-iodide ion would not form preventing the blue-black starch—iodide complex from forming).

- The students are then asked to predict whether the time to react will be longer, shorter, or unaffected if the iodate concentration were cut in half. I give them time to think and discuss this among themselves. Then I call on students to offer their predictions and their reasons why (without judgment). Then I perform the demonstration having the students again count out loud to measure the time for reaction. Write the time on the board (should be approximately double the time for the original mixture). I allow students to verify their predictions and to discuss any predictions that were not verified by the results.
- Next I have the students predict the actual time required to react if the iodate ion concentration is now cut to one-fourth of the original concentration. Again I allow them time to think and discuss among themselves and then call on students to offer their predictions and explanations why. Then I perform the experiment and have the students count out loud (it should be approximately four times as long as the time for the first mixture). Write the time on the board.
- I ask the students to examine the data for a relationship between the time of reaction and the concentration of the iodate ion. They should see that as the concentration increases (decreases) the time to react decreases (increases) or in terms of rate, as the concentration increases so does the rate. I help them see the quantitative relationship: as the concentration of the iodate is doubled the rate is doubled, quadrupled the rate is quadrupled. Then I bring out the idea of first-order kinetics and the rate law: rate = $k[IO_3]^1$.
- Next, I have the students in small groups develop a series of experiments that could be used to determine the influence of the bisulfite ion on the reaction rate. I do this by first presenting the table that shows the volumes of each substance in

the mixture (see table in this document), bringing out the importance of keeping all variables constant except for the one of interest, including the total volume. Also, I remind them of why the bisulfite ion must be kept as the limiting reagent. I allow time for the students to develop their procedures and then have different groups present their designs. (I have not actually carried out experiments to determine the influence of changing the bisulfite concentration but it may be a good investigation for your students to actually test their designs.)

- As an extension, you can ask students to design an experiment that would test the influence of temperature on the reaction rate. Temperature effects can be done as a demonstration if you desire. The bisulfite solution will decompose when heated so only heat or cool the iodate solution.

REFERENCES

Shakhashiri, B. (1992). *Chemical Demonstrations: A Handbook for Teachers of Chemistry* (Vol. 4), Madison, WI: The University of Wisconsin Press, 3-25.