Initial Rates Method (but not Table Logic) of Determining Rate Laws

Introduction

The study of reaction rates is called kinetics. On a molecular basis, the collision theory of chemical reactions predicts that reacting particles must collide in a particular way to allow a reaction to occur. The collision will be an effective one only if the reacting particles collide with sufficient kinetic energy to allow the rupture of an existing bond. Further, the reacting particles must strike each other in an orientation that allows a new chemical bond to form. Only if both of these criteria are met will an effective collision occur, and a chemical reaction will be completed. The vast majority of collisions that occur in a reaction mixture will be ineffective and do not lead to a completed chemical reaction. A step-by-step description of the reaction process is called a reaction mechanism.

The factors that alter the rate of a reaction include:

- concentration
  - ‣ Increasing *concentration* of a reactant means that more particles are available to collide, potentially leading to more effective collisions.
- temperature
  - ‣ Increasing the *temperature* of a system should cause a greater fraction of reacting particles to carry enough kinetic energy to break existing bonds.
- chemical characteristics
  - ‣ Some reactants are more likely to react quickly because of *chemical characteristics* unique to each particular element or molecule. Those characteristics are related to the reduction/oxidation potentials of various elements.
- surface area of solid reactants
  - ‣ The s*urface area* of the reactants will greatly affect the number of molecules that can come in contact with each other.
- presence of a catalyst
  - ‣ A *catalyst* is a substance that alters the rate of a reaction. Most catalysts cause an increase in rate, however, some chemicals may have the opposite effect and slow the reaction. These negative catalysts are called *inhibitors*. While much about catalysts is not know, it is believed that the catalyst interacts with the reactants allowing for the formation of a lower energy activated complex which makes it easier (usually) for the collisions to be effective.
  - ‣ In general, catalysts fall into two groups, depending on phase. Homogeneous catalysts are the same phase as the reacting substances, and heterogeneous catalysts are a different phase.

Because the rate of a chemical reaction is influenced by the concentration of the reactants, a rate law (differential rate law) can be written to quantify the general relationship between the concentration of reactants and rates:

$$\text{rate} = k \, [\text{reactant A}]^x \, [\text{reactant B}]^y$$

where x and y are the orders of the reactants. Any reactant is said to be first order if a change in its concentration causes a direct corresponding change in the rate of reaction; hence doubling the concentration would cause a doubling of the reaction rate. Any second order reactant causes an exponential change; hence, doubling the concentration of a second order reactant will cause a 2^2, or fourfold increase in the reaction rate. Changing the concentration of a zero order reactant causes no change in the reaction rate. The order of a reaction must be determined experimentally and is not determined by the coefficients of the balanced chemical equation.

Procedure Overview

In this lab you will gather data to determine the differential rate law experimentally by altering the concentration of the reactants in a predictable fashion, then measuring the changes in initial rates that occur as a result of the adjustments t the starting concentrations. Thus multiple trials are necessary both to compare the changes of two different reactants and to have enough trials to smooth out lab error and eliminate outliers. The trials can be compared and the order of the reactants can be determined.

In this lab you will study the catalyzed decomposition of hydrogen peroxide. While hydrogen peroxide is unstable and disproportionates into water and oxygen gas over time, it does so too slowly for us to gather any meaningful data in a class period, thus the use of catalysts will speed up the process. Three different catalysts will be used; solid pyrolusite, a solution of potassium iodide, and then a third catalyst called; Katalyst.

Using a simple apparatus, the rate of decomposition can be monitored by counting the number of oxygen bubbles formed during a certain time period. This count will serve as a measure of the rate of formation of oxygen. It is assumed that the pressure inside the reaction flask builds to a high enough level at which the gas is able to push out through the small opening and bubble up through the water reservoir. Any additional oxygen formed will create more pressure and force bubbles up through the opening.

Materials per tray
- bottle _____% hydrogen peroxide
- 125 ml bottle with 0.10 M KI solution
- plastic vial with a few pieces of pyrolusite
- 2× tweezers
- 2× 10 ml cylinder

- 2× 25 ml cylinder
- 2× water squirt bottle
- 2× flasks with bubble apparatus
- 2× stirring bar
- 2× stirring plate
- you may use your phone as a timer

Heterogeneous Catalyst − Procedure 1

Procedure 1 − **Varying [H₂O₂] while using the same piece(s) of pyrolusite**
In these trials, the size, shape, and amount of solid catalyst will be held constant, and
the amount of hydrogen peroxide will be adjusted. You can do this by diluting with
water as demonstrated in the data table to the right.

A. Set up a data table to record your trials. Do not fill in your quantities until you
    test to get an appropriate set to measure.
B. Measure the desired quantity of H_2O_2 in the 25 ml grad cylinder and then add
    the appropriate amount of water on top of the peroxide in the same grad
    cylinder, pour into the flask, then drop in the stirring bar and adjust the speed
    of the stirrer. (It is important to keep the stirring as consistent as possible among the trials.) Do NOT handle the
    pyrolusite with your hands. Use tweezers. The oils on your hands may block its catalytic capabilities. Select a small
    piece of pyrolusite and put into the flask, and then insert the stopper securely into the mouth of the flask and pour water
    into the bulb to the same level for each trial. Count the number of bubbles for a set amount of time (perhaps 30 seconds).
    Record the rate of bubbles in BPM (bubbles per minute).
C. Perform the first trial to be sure the rate is slow enough that you can count bubbles − if it is too fast, you'll need to adjust
    your starting quantities and dilute from there. If it is too slow, you could increase the amount of peroxide (while
    adjusting the water as appropriate). Make note of the position of the stirrer control so you can stir all of your trials at the
    same rate.
D. Perform *at least* three measurable trials, don't worry about how good or bad your data seems; you can do more later if
    you have time. Record the data for the trials.

Procedure 1			
trial	vol of ___% H₂O₂ (ml)	vol water	bubbles per minute
1	10	15	
2	9	16	
3	8	17	
etc			

Homogeneous Catalyst − Procedures 2, 3, and 4

Procedure 2 − **Varying [H₂O₂] while holding [I⁻] constant**
Set up a data table as shown to the right that allows you to record the volume of
hydrogen peroxide, KI, and water used for each trial. The total volume will be held
constant at 25 ml of solution. The amounts of KI and H_2O_2 will be varied in a
systematic way to adjust their concentrations. Enough water will be added each
time to make the total volume equal to 25 ml.

E. Set up a table to record the volumes for your various trials. Again, do not
    fill in your quantities until you test to get an appropriate set to measure.
F. Measure H_2O_2 in the 25 ml grad cylinder and add water to it. Pour into the flask and adjust the speed of the stirrer. It is
    important to keep the stirring as consistent as possible among the trials.
G. Measure out the 0.10 M potassium iodide with the 10 ml cylinder, pour into the flask and then insert the stopper securely
    into the mouth of the flask and pour water into the bulb to the same level for each trial. Wait 15-20 seconds after mixing
    and covering before starting your bubble count. Count the number of
    bubbles for a set amount of time (perhaps 30 seconds). Record the rate of
    bubbles in BPM (bubbles per minute).
H. Repeat enough trials so that you have *at least* three measurable trials.
    Again don't worry about how good or bad your data seems; you can do
    more later if you have time. Record the data for the trials.

Procedure 2				
trial	vol of ___% H₂O₂ (ml)	vol KI (ml)	vol water (ml)	bubbles per minute
1	10	3	12	
2	9	3	13	
3	11	3	11	
etc				

Procedure 3 − **Varying [I⁻] while holding [H₂O₂] constant**
I. Repeat the procedure *at least* three more times (more if you have time)
    adjusting the KI while holding the amount of hydrogen peroxide and
    total volume constant. Again, wait 15-20 seconds after mixing and
    covering before starting your bubble count.

Procedure 3				
trial	vol of ___% H₂O₂ (ml)	vol KI (ml)	vol water (ml)	bubbles per minute
1	10	5	10	
2	10	6	9	
3	10	4	11	
etc				

Procedure 4 − **Varying [Katalyst] while holding [H₂O₂] constant**
J. Repeat the procedure *at least* five more times (more if you have
    time) adjusting the special Katalyst while holding the amount of
    hydrogen peroxide and total volume constant.

Procedure 4				
	vol of ___% H₂O₂ (ml)	vol Katalyst (ml)	vol water (ml)	bubbles per minute
1	10	10	0	
2	10	9	1	
3	10	8	2	
etc		7		

adapted from Hostage & Fossett, Lab Investigations in AP® Chemistry and and Zipp, Ragsdale, and Vanderhooft, JCE 1998

Process The Data

In the various procedures, the total volume is held constant by adding water when the volume of the reactant/catalyst is changed. *Thus the changing volume is proportional to concentration changes. This allows the data to be analyzed using the changing volumes without the need to convert to concentrations.* Use your google LAD sheet to set up a table with volume and rate data. On your Google sheet, use the =log( ) function to calculate the log of the volume and log of BPM. Make four separate graphs, one for each procedure; log(rate) on y-axis and log(vol) on x-axis. Put Proc 1&2 on one sheet and Proc 3&4 a separate sheet.

For each set of data show the *linear* trend-line and the equation for the trend-line. This is important because the slope will indicate the order of the reaction with respect to the reactant/catalyst that is being varied in each procedure.

> **Google Sheet Alert**
>
> Google will plot the first column of data on the x-axis, and the second column on the y-axis

Graph Procedure 1 − Graph log(BPM) vs log(vol of H_2O_2) (No need to put *units* on either axes.)

- Since the rate equation is: rate $= k\,[H_2O_2]^m$
  (the concentration of the solid catalyst does not vary thus the solid catalyst does not show up in the rate law)

- Taking the log of both sides of the equation above and using both of the Handy Log Rules shown in the box, yields:
  (Let's be really clear, this is NOT use of the integrated rate laws as in LAD E2, this is simply use of Handy Log Rules)

  Per Rule#1: $\log(\text{rate}) = \log k + \log[H_2O_2]^m$

  and Per Rule#2: $\log(\text{rate}) = \log k + m \times \log[H_2O_2]$

> **Handy Log Rules**
>
> Rule#1: $\log(A \times B) = \log A + \log B$
>
> Rule#2: $\log(A)^m = m \times \log A$

- Algebraically rearrange to give: $\log(\text{rate}) = m \times \log[H_2O_2] + \log k$
- This is of course: $y = m\,x + b$
- The *slope* of the graph will indicate the *order* of the reaction with *respect to H_2O_2*

Graph Procedure 2 − Graph log(BPM) vs log(vol of H_2O_2) (No need to put *units* on either axes.)

- Since the rate equation is: rate $= k\,[H_2O_2]^m\,[I^-]^x$ and since $[I^-]^x$ is held constant,
- The *slope* of the graph will indicate the *order* of the reaction with *respect to H_2O_2*.

Graph Procedure 3 − Graph log(BPM) vs log(vol of I^-) (No need to put *units* on either axes.)

- Since the rate equation is: rate $= k\,[I^-]^m\,[H_2O_2]^y$ and since $[H_2O_2]^y$ is held constant,
- The *slope* of the graph will indicate the *order* of the reaction with *respect to I^-*.
- Assume the order with respect to H_2O_2 does not change from what you learned in Procedures 1 & 2.

Graph Procedure 4 − Graph log(BPM) vs log(vol of Katalyst) (No need to put *units* on either axes.)

- Since the rate equation is: rate $= k\,[\text{Katalyst}]^m\,[H_2O_2]^z$ and since $[H_2O_2]^y$ is held constant,
- the *slope* of the graph will indicate the *order* of the reaction with *respect to the Katalyst*.
- Again, assume the order with respect to H_2O_2 does not change from what you learned in Procedures 1 & 2.

To be turned in: *(stapled in the following order)*

1. Typed cover sheet:

    • Name, LAD #, title,

    • the reaction (*Take the time to learn to make subscripts.*),

    • the purpose, (*This should be short 2−3 sentences at the very most.*)

    • a labeled diagram/sketch of the apparatus and how/why it worked as a method to collect rate data,

    • order of the reaction with respect to _____, with a brief explanation of how you are able to make such conclusions from your graphs, while marking/highlighting the important information directly on your graphs.

    • write out three rate laws; one for Procedure 1, one for Procedures 2 & 3, and one for Procedure 4

2. Two printed sheets:
    (*Be sure the graphs have correct and complete descriptive titles − not just Proc 1,2,etc, labeled axes, trend line, and the equation for trend line. After printing, take a red pen and mark/highlight what about the graph allowed you to make the conclusions that you made.*)

    • one with graphs from Procedures 1 & 2,

    • a second with graphs from Procedures 3 & 4.

3. This LAD protocol.

To save typing, this data is available on the shared Google sheet. You can cut and paste to your own Google LAD document.

Procedure 1		Procedure 2		Procedure 3		Procedure 4	
solid MnO_2 catalyst while changing H_2O_2		KI catalyst while changing H_2O_2		changing KI catalyst while holding H_2O_2 constant		changing volume of Katalyst while holding H_2O_2 constant	
Vol of H_2O_2	BPM	Vol of H_2O_2	BPM	Vol of I^-	BPM	Vol of Katalyst	BPM
10	89	10	136	10	175	10	109
9	81	9	120	9	168	9	90
8	73	8	103	8	151	8	72
7	60	7	95	7	130	7	48
6	53	6	85	6	121	6	39
5	40	5	72	5	100	5	26
4	30	4	54	4	72	4	17
3	22	3	40	3	57	3	8
2	17	2	27	2	37	2	4

adapted from David Hostage & Martin Fossett Lab Investigations in AP® chemistry and Arden Zipp in JCE