Department of Chemistry
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Kinetics Unit Activity - Chemical Kinetics **KEY**

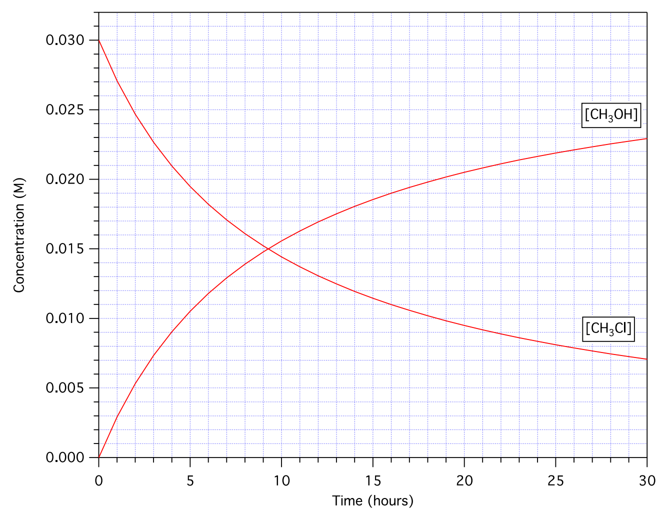
The purpose of this activity is to develop concepts of chemical kinetics: Specifically to look at reaction rate laws. First, it is important to understand rates.

Consider the following reaction

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

Below is a graph of concentration of CH_3Cl and CH_3OH as a function of time.

1. Where is the rate of change in concentration the highest?



The rate of change is highest in the very beginning. This is seen by observing the slope of the line, which is the steepest initially.

2. Write down an expression for the rate of the chemical reaction both in terms of the change in concentration of CH_3Cl and CH_3OH.

$$rate = -\frac{\Delta[CH_3Cl]}{\Delta t} = \frac{\Delta[CH_3OH]}{\Delta t}$$

3. Use the graph to estimate the initial rate of the reaction (yes, you will need to read numbers off the graph)

Let's select two easy to read points from the line of CH_3OH that are also close to the initial time of 0 hours. Then, we can find the slope between these two points to approximate the initial rate How about (0 hr, 0 M) and (1 hr, 0.003 M).

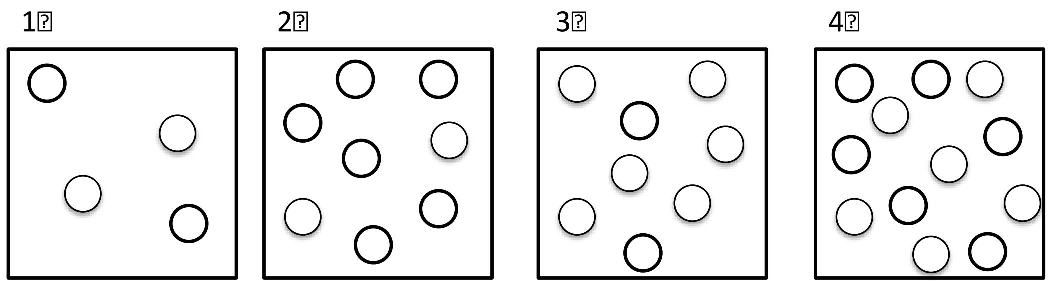
$$rate = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.003 - 0}{1 - 0} = \frac{0.003}{1} = 0.003\ M/hr$$

$$rate = \frac{rise}{run}$$

Name:_______________

For this reaction, the rate is thought to be determined by the collision between a hydroxide ion and the CH_3Cl molecule. When they collide there is a chance they will react. The more collisions, the faster the rate of the reaction.

Let's imagine four solutions from four distinct experiments that contain different initial concentrations of CH_3Cl (the gray circles) and OH^- (the white circles). Below are a few "snap shots" of some small portion of the 4 different solutions **before** the reaction begins.



4. How do the concentrations of each species compare in each experiment? Which experiment has the lowest total concentration? Which experiments have the same concentration of CH_3Cl and OH^-? What are the ratios of those two species in the other experiments?

1 has the lowest total concentration (lowest number of total circles)
4 has the highest total concentration (highest number of total circles)
2 and 3 have the same total concentration (mid-number of total circles)

Both 1 and 4 have the same concentrations of CH_3Cl and OH^-

In 2 there is a 3:1 ratio of OH^-:CH_3Cl
In 3 there is a 1:3 ratio of OH^-:CH_3Cl

5. According to our assumption that the two species will react when they collide, in which solution do you think the rate of the reaction will be the **fastest**?

4. It has the highest concentration of both (more molecules), so it is more likely that there will be a collision (more collisions) and likely that one OH^- and one CH_3Cl will collide.

6. Comparing the solutions of experiments 1 and 2, what is different about the initial concentrations?

There are more OH^- in 2.

7. Comparing the solutions from experiments 1 and 2, which solution do you think will initially react the fastest? How much faster?

2 will react faster than 1. Because there is more OH^- available, the solution is more concentrated and collisions can occur faster. It will react 3 times faster since there is 3 times the amount of OH^- to react.

Name:________________

8. Comparing experiments 2 and 3, what is different about the initial concentrations? Which solution do you think will react faster? How much faster?

The difference is in which species has the greater concentration. In box 2 there is three times as much OH^- as there is CH_3Cl and in box 3 there is three times as much CH_3Cl as OH^-. Since the ratios of the molecules are similar, they should collide at the same rate.

Whole Class Check in

The rate of a chemical reaction and specifically how that rate depends on concentration are determined by the "mechanism" of the reaction. The mechanism is a chemist's microscopic view of how the reaction is actually happening (what bonds are breaking first, what molecules are colliding, etc…). You cannot know either the mechanism or how the rate of reaction will depend on the concentrations based on the overall reaction. This relationship between rate and concentration is called the "**empirical rate law**".

The empirical rate law is an experimental measure of how the rate of reaction depends on concentration. It is empirical as it is based purely on observation. The rate law assumes the rate is proportional to the concentration of the chemical species in the reaction raised to some power. For example, for the reaction

$$A + B \rightarrow C + D$$

The rate can be written as some function of the concentration of the reactants A and B.

$$rate = k[A]^x[B]^y$$

This expression is called the rate law where k is an unknown constant call the **rate constant**. The exponents x and y are also unknown. All of these unknown constants need to be determined from experimental data. Typically, the exponents for the concentration are whole number (0,1,2…) but they don't have to be. Typically rate laws only have reactants as species (but they don't have to).

Comprehension Check! Explain each term in the following expression in the table below:
rate=h[A]^x[B]^y

Term	Explanation
Rate	The rate of a chemical reaction is a measure of how fast the reaction is proceeding. Specifically, it is a measure of the change in the concentration of the chemical species as a function of time.
h	h (sometimes seen as "k") is our rate constant or "proportionality constant." It is dependent on the temperature of which the reaction takes place and can be determined from experimental data.

Name:_______________

[A]	This is the concentration of our first reactant, reactant "A."
x	The order of our first reactant, A, and can be determined from our experimental data. The order of a reactant can help us to determine the overall order of the reaction.
[B]	This is the concentration of our second reactant, reactant "B."
y	The order of our first reactant, B, and can be determined from our experimental data. The order of a reactant can help us to determine the overall order of the reaction.

In the previous example, we assumed the rate depended upon the two species colliding. To test this idea, we need to experimentally measure how the rate is affected by starting with different concentrations. Below is a set of data for the conditions of the four experiments we imagined previously.
For each set of conditions the initial rate of the reaction was measured.

Experiment number	**Initial [CH_3Cl]**	**Initial [OH^-]**	**Initial Rate M s^{-1}**
1	0.1 M	0.1 M	$5.0x10^{-6}$
2	0.1 M	0.3 M	$1.5x10^{-5}$
3	0.3 M	0.1 M	$1.5x10^{-5}$
4	0.3 M	0.3 M	$4.5x10^{-5}$

9. How does the initial rate depend on the initial concentration of CH_3Cl?

The initial rate is directly proportional to the initial concentration. As the concentration of CH_3Cl triples, the rate also triples. Compare experiments 1 and 3 where the concentration of CH_3Cl triples while the concentration of OH^- stays the same. The rate between these two experiments also triples.

10. How does the initial rate depend on the initial concentration of OH^-?

The initial rate is directly proportional to the initial concentration. As the concentration of OH^- triples, the rate also triples. Compare experiments 1 and 2 where the concentration of OH^- triples while the CH_3Cl concentration of stays the same. The rate between these two experiments also triples.

11. Can you write a **rate law** for this reaction?

$rate = k[CH_3Cl]^1[OH^-]^1 = k[CH_3Cl][OH^-]$

Because the rate directly triples when either CH_3Cl or OH^- triple in concentration, we can say that the reaction is first order in both of these substances (exponents of one for each).

12. Can you determine the **rate constant** for this reaction?

Simple select any experiment to work with and plug the values into the rate law equation.
Let's choose experiment 1.

Name:________________

$rate = k[CH_3Cl][OH^-]$
$5.0\bullet10^{-6} = k[0.1][0.1]$
$5.0\bullet10^{-6} = 0.01k$
$k = 5.0\bullet10^{-4}$

Since the rate must be in terms of $M\ s^{-1}$, the units of k must be whatever is required to match those units.

$Ms^{-1} = kM^2$
so k must have units of $M^{-1}s^{-1}$