ChemQuest 57

Intro to Reaction Rates

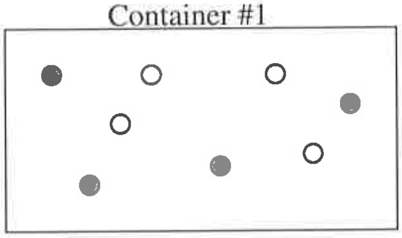
Name: ____________________
Date: ____________
Hour: _____

Information: Rate of Reaction

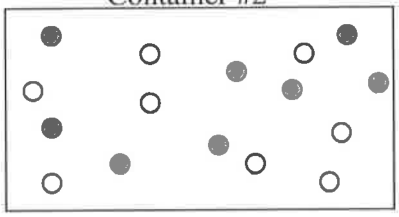
Since "time is money" in the business world, it is very important to know how fast a reaction will occur. Whether a company is producing a medicine, plastic, or adhesive, the speed of reaction will greatly impact the amount of money that the company can earn.

Chemical kinetics is a term that refers to how fast chemical reactions take place. Some reactions take place very quickly, seemingly instantaneously. Other reactions take place very slowly. Consider for a moment two hypothetical gaseous reactants—A and B—reacting together:

Container #1



Container #2



In the above two containers, two different substances are reacting together. Each particle is moving randomly in the container. *A reaction occurs when one particle from substance A collides with a particle from substance B **if** the collision is a strong enough collision.* Sometimes, a gentle "bump" won't have enough energy to cause a collision.

Critical Thinking Questions

1. Which container—#1 or #2—should have the most collisions between particles? #2

2. Which container—#1 or #2—do you think will have the faster rate of reaction? Explain why.
   #2 because more collisions will lead to more reactions

3. Which of the below scenarios will have the fastest rate of reaction? Why? Recall that Molarity (M) is a unit of concentration.

Scenario #1	Scenario #2
200 mL of 0.75 M HCl reacts with 200 mL of 0.75 M NaOH.	200 mL of 0.95 M HCl reacts with 200 mL of 0.95 M NaOH.

   Scenario #2 because of the greater concentration of particles leading to more collisions.

4. What will happen to the speed of the particles if you heated up the containers?
   The particles will move faster.

5. If the particles are heated up, what will happen to the energy of the particles' collisions? Will the collisions have more energy or less energy?
   Each collision will have more energy.

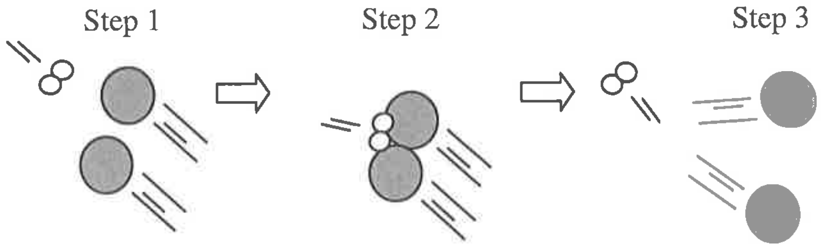
6. Again, consider heating up a container of particles. Will there be more collisions or fewer collisions after heating them up?
   There will be a greater number of collisions.

7. a) Given your answers to questions 4-6, what happens to the rate of the reaction if you increase the temperature of the reactants?
   The rate increases.

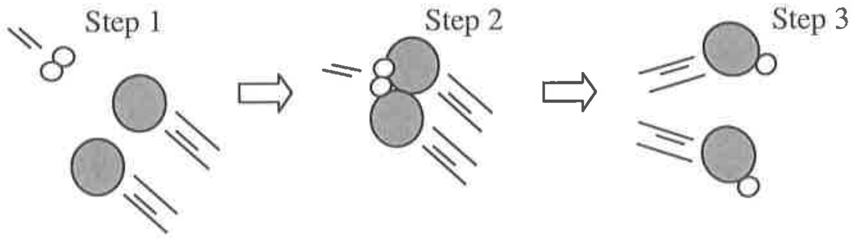
   b) Try to think of two reasons WHY and write them down. (Hint: questions 4-6 should contain the two reasons.)
      1) There will be more collisions between particles.
      2) Each collision will be more energetic and have a greater chance of leading to a reaction.

8. Consider the following two scenarios where different particles are colliding:

Scenario #1:



Scenario #2:



   a) During which scenario is there enough energy for a reaction to occur? Scenario #2

   b) Which scenario involves molecules moving at a faster speed? Scenario #2

   c) Which scenario do you think occurs at the highest temperature? Scenario #2

9. Consider the two scenarios from question 8. Which of the following balanced chemical reactions could be occurring?
   A) $2\ H_2 + O_2 \rightarrow 2\ H_2O$
   [✓ B)] $2\ Na + Cl_2 \rightarrow 2\ NaCl$
   C) $Cl_2 + O_2 \rightarrow 2\ ClO$

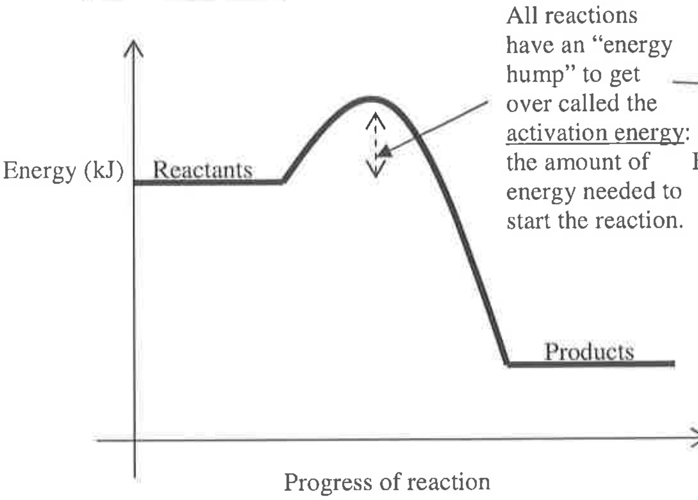
10. An "activated complex" is a very unstable arrangement of atoms that forms for a very brief moment during a reaction. The activated complex will then turn into a product or into a reactant. There is an equal chance of either option occurring. When did an activated complex occur in the scenarios from question 8—Step 1, 2, or 3?

    Step #2

11. The "activated complex" is sometimes called the "transition state." Think about what the word "transition" means. Why do you think the activated complex is called the transition state?

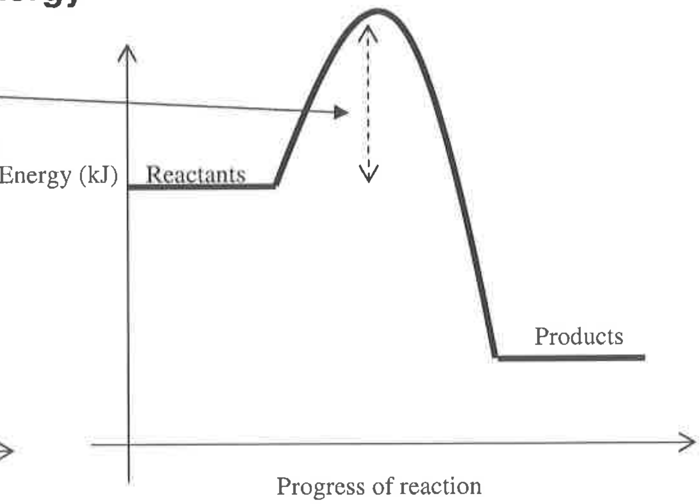
    The activated complex is turning into, or transitioning into, the products.

Information: Rate and Activation Energy



All reactions have an "energy hump" to get over called the activation energy: the amount of energy needed to start the reaction.

Reaction X



Reaction Y

Critical Thinking Questions

12. Consider the two diagrams above of reactions X and Y. Which one has the higher activation energy?

    Y

13. True or False: Reaction X and Reaction Y have the same ΔH value. True

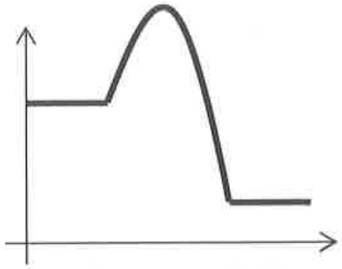
14. Consider the two diagrams above of reactions X and Y. Reaction X is a faster reaction than Reaction Y. Offer an explanation.

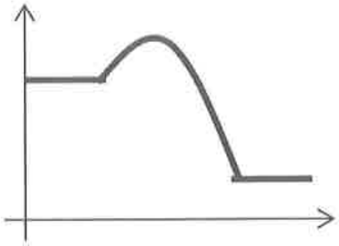
    A lower activation energy must lead to a faster reaction.

15. A catalyst is a substance that speeds up a reaction when it is added to the mixture of the reactants. A catalyst speeds up a reaction by doing something to the activation energy. What do you think a catalyst does to the activation energy?

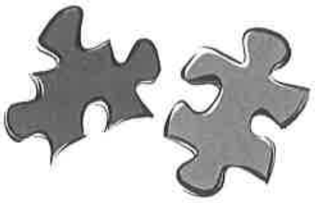
    A catalyst lowers the activation energy.

16. Below is an energy diagram for a certain reaction. Redraw the energy diagram to depict what happens after a catalyst is added. Note: the energy of the reactants and products stays the same; only the activation energy changes.





Information: Factors Affecting Rate

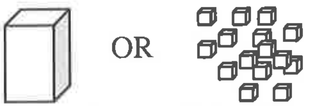


We have already looked at how concentration (question 3) and temperature (questions 4-7) affect the rate of reactions. It is important to note that for a reaction to happen, particles must have sufficient energy when they collide AND they also must be oriented in the correct way. Just as puzzle pieces must be oriented correctly, so also particles must be oriented correctly to bond.

Two other factors in reaction rates are particle size (or surface area) and the pressure at which the reaction is carried out.

Critical Thinking Questions

17. Consider the two amounts of sugar shown below. Both amounts have the same weight.

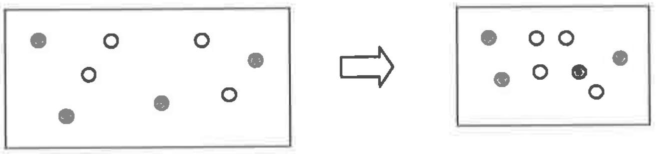


a) Which version of the sugar has the greatest surface area—the cube or the crushed?
Crushed

b) Which would dissolve fastest in water—the cube or the crushed sugar?
Crushed

c) The greater the surface area of the substance, the faster (faster OR slower?) the reaction rate.

18. Consider a container of gas molecules that is being compressed. The temperature is the same in both containers:



a) True or False: As the volume of the container decreases, pressure increases. True

b) True or False: The molecules move faster after the container is compressed. False

c) True or False: The reaction rate is faster after the container is compressed. True

d) Explain your answer to part c. There is less space for the molecules to move around and therefore a greater number of collisions between molecules.

ChemQuest 58

Rates of Reactions Calculations

Name: ____________________

Date: _______________

Hour: _____

Information: Average Rate of Reaction

Recall that during a chemical reaction reactants are transformed into products: A + B → C + D. A very important question is: how fast do such processes happen? For example, we need to know how long it will take for a medicine to work in our bodies and how long will it take to produce chemicals in industry.

How fast do reactants A and B disappear? How fast do products C and D form? We can express such questions in the form of an equation as shown below.

$$\text{rate of disappearance of reactant A} = -\frac{\text{change in molarity of reactant A}}{\text{change in time}} = -\frac{\Delta[\text{reactant A}]}{\Delta\text{time}}$$

Keep in mind that all rates are written as positive numbers; thus, the function for the negative sign in the above equation is to yield a positive result for the rate.

Critical Thinking Questions

1. What is molarity?
   Molarity is a measure of the moles of solute per liter of solution.

2. What do the symbols Δ and [ ] mean in the above equation?
   Δ means "change" and [ ] means concentration in molarity.

3. What units would you expect for the rate of disappearance of a reactant? (Assume time is measured in seconds.)
   Molarity per second

4. How is the change in molarity of a reactant calculated? Would this be a positive or a negative number?
   Final molarity minus initial molarity. It would be a negative number because the molarity of a reactant decreases as the reaction proceeds.

5. How is the change in molarity of a product calculated? Would this be a positive or a negative number?
   Final molarity minus initial molarity. It would be a positive number because the molarity of a product increases as the reaction proceeds.

6. When writing the equation for the rate of formation of a product, the negative sign in the above equation is not needed. Explain why.
   The only purpose of the negative sign is to give a positive number and the negative sign is only needed for calculating the change in concentration for a reactant because the change will be a negative number, as mentioned in our answer to question 4.

Information: Stoichiometry and Average Rate

Consider the decomposition of N_2O_5 and the experimental data for the reaction taking place inside a container that has a volume of 3.0 L.

$$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$$

Time (s)	Moles N_2O_5	Moles NO_2	Moles O_2
0	0.4320	0	0
600	0.4194	0.0252	0.0063
1200	0.4104	0.0432	0.0108
1800	0.4032	0.0576	0.0144

Critical Thinking Questions

7. Calculate the change in moles of each reactant and product between 600 and 1200 seconds.

change in moles of N_2O_5:	change in moles of NO_2:	change in moles of O_2:
0.4194 – 0.4104 = 0.0090	0.0432 – 0.0252 = 0.0180	0.0108 – 0.0063 = 0.0045

8. Compare your answers in question 7. What is the relationship between the coefficients in the balanced chemical equation and the number of moles used up or produced in a reaction?
   The change in N_2O_5 is twice the change in O_2 which corresponds to the 2:1 ratio of the balanced equation. Also, the change in NO_2 is twice the change of N_2O_5, which also corresponds to the 4:2 ratio of the balanced equation.

9. Fill in the missing blanks in the table above.
   $\Delta[O_2] = 0.0144\text{-}0.0108 = 0.0036$; $\Delta[NO_2] = 4(0.0036) = 0.0144$; $\Delta[N_2O_5]=2(0.0036) = 0.0072$

10. Calculate the following values. Be sure to use molarity in your calculations.
    a) Rate of disappearance of N_2O_5 between time 0 and 600 s.

$$\frac{\frac{0.4194\ \text{mol}}{3.0\ \text{L}} - \frac{0.4320\ \text{mol}}{3.0\ \text{L}}}{600\ \text{s} - 0\ \text{s}} = \frac{0.1398 - 0.144}{600} = \boxed{-7.0x10^{-6}\ \text{M/s}}$$

    b) Rate of appearance of NO_2 between time 0 and 600 s.

$$\frac{\frac{0.0252\ \text{mol}}{3.0\ \text{L}} - \frac{0\ \text{mol}}{3.0\ \text{L}}}{600\ \text{s} - 0\ \text{s}} = \frac{0.0084}{600} = \boxed{1.4x10^{-5}\ \text{M/s}}$$

    c) Rate of appearance of O_2 between time 0 and 600 s.

$$\frac{\frac{0.0063\ \text{mol}}{3.0\ \text{L}} - \frac{0\ \text{mol}}{3.0\ \text{L}}}{600\ \text{s} - 0\ \text{s}} = \frac{0.0021}{600} = \boxed{3.5x10^{-6}\ \text{M/s}}$$

11. Compare each of the rates. What relationship exists between the rates and the coefficients in the balanced chemical equation?

    They are related by the coefficients in the balanced equation so that

    Rate O_2 = 2(Rate N_2O_5) = 4(Rate NO_2)

12. Calculate the following values. Be sure to use molarity in your calculations.

    a) Rate of disappearance of N_2O_5 between time 600 and 1200 s.

    $$\frac{\frac{0.4104\text{ mol}}{3.0\text{ L}}-\frac{0.4194\text{ mol}}{3.0\text{ L}}}{600\text{ s} - 0\text{ s}}=\frac{0.1368-0.1398}{600}\boxed{=-5.0x10^{-6}\text{ M/s}}$$

    b) Rate of appearance of NO_2 between time 600 and 1200 s.

    Rate NO_2 = 2(RateN_2O_5) = 2(5.0x10^{-6}) = 1.0x10^{-5} M/s

    c) Rate of appearance of O_2 between time 600 and 1200 s.

    Rate O_2 = 1/2(Rate N_2O_5) = 2.5x10^{-6} M/s

13. As the reaction proceeds are the rates constant? What affects the rate?

No, they are not constant. The rates are gradually slowing. For example, between 0 and 600 seconds N_2O_5 was disappearing at a rate of 7.0x10^{-6} M/s, but between 600 and 1200 seconds N_2O_5 was disappearing at a rate of 5.0x10^{-6} M/s. The other reactants also slowed. It seems that rate is dependent on concentration.

ChemQuest 59

Rate and Concentration

Name: ____________________

Date: ______________

Hour: _____

Information: Reaction Order

Below is a table of data corresponding to the following balanced equation:

$$2\ ClO_2\ (aq) + 2\ OH^-\ (aq) \rightarrow ClO_3^-\ (aq) + ClO_2^-\ (aq) + H_2O\ (l)\ .$$

Six experiments were carried out with differing concentrations of ClO_2 and OH^- in each experiment. The measurement of how quickly ClO_2 disappears is given in the table for each of the six experiments. How quickly a reactant disappears (or how quickly a product forms) is a good measurement of how fast a reaction takes place.

Table 1: Experimental data for the reaction of ClO_2

Experiment	**Initial [ClO_2]**	**Initial [OH^-]**	**Initial Rate of disappearance of ClO_2 (M/s)**
1	0.020	0.030	0.00276
2	0.040	0.030	0.01104
3	0.020	0.060	0.00552
4	0.040	0.060	0.02208
5	0.040	0.090	0.03312
6	0.120	0.030	0.09936

Critical Thinking Questions

1. What happens to the rate of a reaction as the concentrations of the reactants increases? Justify your answer with data from the table above.

   The higher the concentration of reactants, the faster the rate. For example, the rate corresponding to Experiment 4 is greater than the rate in Experiment 1 and Experiment 4 also has a greater concentration of reactants.

2. Consider the molecular level of what is happening when ClO_2 reacts with OH^- to form products. Offer an explanation for why changing the concentration of reactants changes the rate of a reaction.

   Changing the concentration changes how many molecules collide and react with each other.

3. Does the reaction depend on the concentration of ClO_2 and the concentration of OH^- equally? In other words, is the rate more dependent on ClO_2, on OH^-, or is it equally dependent on the concentration of both. Justify your answer.

   The rate depends more on the concentration of ClO_2 than on OH^-. For example, comparing experiments 1 and 2 we see that when [ClO_2] is doubled and [OH^-] held constant the rate increases by a factor of 4. When we compare experiments 2 and 4 when [OH^-] is doubled, we see that the rate only increases by a factor of 2.

4. If you wanted to know how the rate of reaction depends on the concentration of ClO_2 you could compare experiments 1 and 2. But if you compared experiments 1 and 4, you would not be able to accurately see how the reaction depends on the concentration of ClO_2. Why?

   You always need a control--one of the concentrations needs to remain constant. In experiments 1 and 4 both the $[ClO_2]$ and $[OH^-]$ change.

5. Which two experiments would you want to compare to determine how much the rate of reaction depends upon the concentration of OH^-?

   A) 1 and 4 B) 5 and 6 C) 1 and 6 [✓ D) 1 and 3]

6. Considering $[ClO_2]$ in experiments 1 and 2, complete the following sentence.

   When $[ClO_2]$ increases by a factor of 2, the rate of reaction increases by a factor of 2 to the 2nd power.

7. Considering $[OH^-]$ in the two experiments you identified in question 5, complete the following sentence.

   When $[OH^-]$ increases by a factor of 2, the rate of reaction increases by a factor of 2 to the 1st power.

8. Considering $[ClO_2]$ in experiments 2 and 6, complete the following sentence.

   When $[ClO_2]$ increases by a factor of 3, the rate of reaction increases by a factor of 3 to the 2nd power.

9. Considering $[OH^-]$ in experiments 2 and 5, complete the following sentence.

   When $[OH^-]$ increases by a factor of 3, the rate of reaction increases by a factor of 3 to the 1st power.

10. The rate dependence with respect to $[ClO_2]$ is said to be second order. Given your answers to questions 6 and 8, explain what "second order" means.

    Second order means that if the concentration increases by a factor of X, then the rate increases by a factor of X to the 2nd power.

11. The rate dependence with respect to $[OH^-]$ is said to be first order. Given your answers to questions 7 and 9, explain what "first order" means.

    First order means that if the concentration increases by a factor of X, then the rate increases by a factor of X to the 1st power.

12. Can you find the order for a reactant just by looking at the balanced equation?

    No, you must have experimental data. The orders of reactants are not the same as the coefficients in the balanced equation as can be seen in the balanced equation given at the beginning of the information section.

13. The overall "order" of the reaction for this reaction is third order. Explain how the overall order of a reaction is found.

    Overall order is found by adding the orders for each of the reactants.

Information: Rate Law

Once you know the order with respect to each reactant, you can determine the "rate law" for the reaction. Each reaction has a different rate law. The rate law is a convenient way of expressing how the rate of a reaction depends upon concentration. The rate law for the reaction we have been considering so far is

$$\text{Rate} = k[ClO_2]^2[OH^-]^1$$

Each reaction has a rate constant, given the symbol k. As you will soon see, the rate constant can be determined from experiments in a similar fashion to how you determined the orders for reactants.

Critical Thinking Questions

14. What is the relationship between the order of the reactant and the exponent for the reactant in the rate law?

    The order for the reactant equals the exponent in the rate law.

15. Using the data from any of the six experiments in Table 1, verify that the rate constant is 230 $1/(M^2s)$. For example, let's pick experiment 3 to use. The rate is given and so are the concentrations of ClO_2 and OH^-. Plug these given data into the rate law and solve for k. Use units in your calculation to verify that the units for k are $1/(M^2s)$.

    $\text{Rate} = k[ClO_2]^2[OH^-]^1 \rightarrow 0.00552 M/s = k\,(0.020M)^2(0.060M) \rightarrow k = 230\ 1/M^2s$

16. Now that you know the rate constant, you can calculate the rate for any concentration of reactants. For example, calculate the rate of reaction when the concentration of ClO_2 is 0.32 and the concentration of OH^- is 0.42.

    $\text{Rate} = k[ClO_2]^2[OH^-]^1 \rightarrow \text{Rate} = (230)(0.32)^2(0.42) = 9.89\ M/s$

Skill Practice

17. In a certain reaction, it is discovered that if the concentration of a reactant is tripled, then the rate of the reaction increases from 0.0670 M/s to 1.809 M/s. What is the order with respect to this reactant?

    $1.809 \div 0.0670 = 27$; $27 = 3^3$; since the exponent is a 3, the order is 3rd order.

18. Given the following data, write the rate law for the reaction. Then find the rate constant (include units).

$$H_2O_2 + 2\,HI \rightarrow 2\,H_2O_2 + I_2$$

Experiment	$[H_2O_2]$	[HI]	Rate (M/s)
1	0.1	0.1	0.0076
2	0.1	0.2	0.0608
3	0.2	0.2	0.2432

Comparing experiments 1 and 2 we see that the rate increases by a factor of 2^3 when [HI] doubles.
Comparing experiments 2 and 3 we see that the rate increases by a factor of 2^2 when $[H_2O_2]$ doubles.
Therefore we can write: $\text{Rate} = k[H_2O_2]^2[HI]^3$.
$\text{Rate} = k[H_2O_2]^2[HI]^3 \rightarrow$ (plug in data from expt. #1 $\rightarrow 0.0076 = k(0.1)^2(0.1)^3 \rightarrow k = 760\ \ 1/M^4s$

ChemQuest 60

Concentration and Time

Name: ______________________

Date: ______________

Hour: _____

Information: First Order Reactions with One Reactant

As we consider what affects the rate of reactions it is desirable to examine how the concentration of a reactant changes with time. Let us consider reactions that have only one reactant and we will further restrict our considerations to first order reactants. As an example, consider the following reaction:

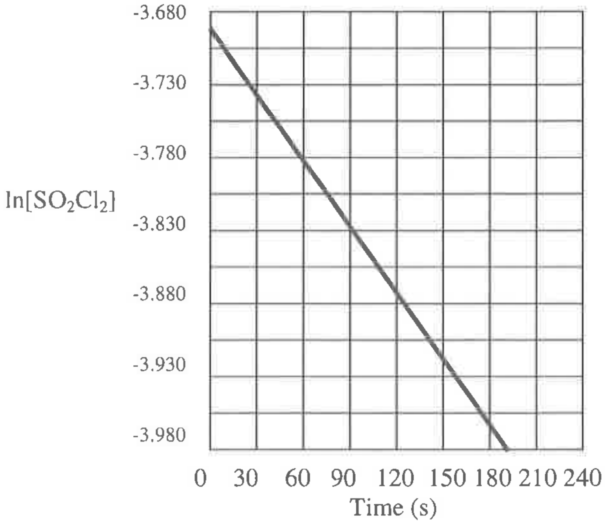
$$SO_2Cl_2 \rightarrow SO_2 + Cl_2$$

Table 1: Experimental data for the decomposition of SO_2Cl_2

Time (s)	**$[SO_2Cl_2]$**
0	0.0250
60	0.0228
120	0.0208
180	0.0190

It can be shown that the natural log of the concentration of a first order reactant varies directly with the time. So in this case $\ln[SO_2Cl_2]$ varies in direct proportion to the time.

1. Using the above data, prove on the graph below that $\mathbf{\ln[SO_2Cl_2] = -kt + \ln[SO_2Cl_2]_0}$ is a straight line when graphed. Note the expression $[SO_2Cl_2]_0$ is the concentration of SO_2Cl_2 at a time of zero seconds. **Label the axes.**



Calculate $\ln[SO_2Cl_2]$ values and plot:

Time	**$\ln[SO_2Cl_2]$**
0	-3.689
60	-3.781
120	-3.873
180	-3.963

2. Given this relationship between concentration and time ($\ln[SO_2Cl_2] = -kt + \ln[SO_2Cl_2]_0$), find the rate constant k.

Choose values to plug into equation; I'll use at time 120:

$\ln(0.0208) = -k\,(120) + \ln(0.0250) \rightarrow k = 0.00153\ 1/s$

3. Find the half-life for this reaction. What this means is that you need to find the time it takes for half of the reactant to get used up.
   Find the time (t) when $[SO_2Cl_2] = 1/2(0.0250) = 0.0125$
   $\ln(0.0125) = -(0.00153)(t) + \ln(0.0250)$ → $t = 453$ seconds

Information: Second Order Reactions with One Reactant

Consider the following reaction: $2\ NO_2 \rightarrow 2\ NO + O_2$. The following experimental data was gathered for this reaction:

Table 2: Experimental data for the decomposition of NO_2

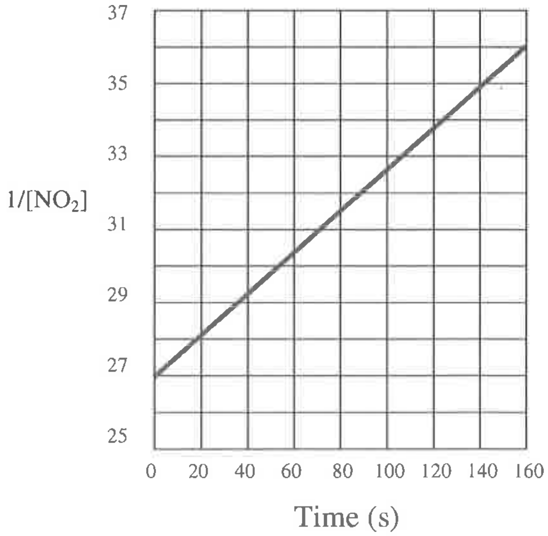
Time (s)	**$[NO_2]$**
0	0.0370
45	0.0338
90	0.0311
135	0.0288

If you attempted a plot of ln vs. t as you did in question 2 above you would not get a straight line. Instead, for second order reactants, the inverse of the concentration varies directly with time.

Critical Thinking Questions

4. Using the following graph and the above data, prove that the following equation yields a straight line.

$$\frac{1}{[NO_2]} = kt + \frac{1}{[NO_2]_0}$$



Calculate $1/[NO_2]$ and plot this data:

Time (s)	$1/[NO_2]$
0	27.03
45	29.59
90	32.15
135	34.72

5. What is the value of the rate constant, k, for this reaction?
   $1/0.0311 = k(90) + 1/0.0370$ → $k = 0.0570$ 1/Ms

6. Find the half-life for this reaction.
   Need to find the time, t, when $[NO_2] = 1/2(0.0370) = 0.0185$ M
   $1/0.0185 = (0.0570)(t) + 1/0.0370 \rightarrow t = 474$ s

Skill Practice Question

7. Given the following reaction and table of experimental data, answer the following questions.

$$2\,N_2O_5 \rightarrow 4NO_2 + O_2$$

Time (s)	$[N_2O_5]$
0	0.0200
100	0.0169
200	0.0142
300	0.0120
400	0.0101
500	0.0086
600	0.0072
700	0.0061

a) Is the reaction 1st order or second order with respect to N_2O_5? How do you know?

   It is 1st order because the data fits the equation $\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$ much more closely than it fits the 2nd order equation.

b) What is the value for the rate constant?
   Using $\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$ and plugging in data…
   $\ln(0.0086) = -k(500) + \ln(0.0200) \rightarrow k = 0.0017$ 1/s

c) What is the half life for this reaction?
   $\ln(0.0100) = -(0.0017)(t_{1/2}) + \ln(0.0200) \rightarrow t = 408$ s

d) How many seconds are required for the concentration of N_2O_5 to reach a level of 0.0025 M?
   $\ln(0.0025) = -(0.0017)(t) + \ln(0.0200) \rightarrow 1223$ s