Chemical Reaction Rates I

Solving Kinetics Problems Involving Differential Rate Law

Chemical kinetics is the study of the speed or rate of a chemical reaction under various conditions. Collisions must occur in order for chemical reactions to take place. These collisions must be of sufficient energy to make and break bonds. The collisions must also be “effective” which means they not only have sufficient energy during the collision but that the molecules also collide in the proper orientation. The speed of a reaction is expressed in terms of its rate — some measurable quantity is changing with time.

\[
\text{Rate} = \frac{\text{Change in concentration of a reactant or a product}}{\text{Change in time}}
\]

Most commonly, we discuss four different types of rate when discussing chemical reactions: relative rate, instantaneous rate, differential rate, and integrated rate. Although these sound complicated, they are actually quite simple. This activity will focus primarily on the last two types, differential rate and integrated rate.

First, we need to discuss factors that affect the rate of a chemical reaction:
1. **Nature of the reactants**—Some reactant molecules react quickly, others react very slowly.
2. **Concentration of reactants**—more molecules in a given volume means more collisions which means more bonds are broken and more bonds are formed.
3. **Temperature**—“heat ’em up & speed ’em up”; the faster the molecules move, the more likely they are to collide and the more energetic those collisions will be.
   - An increase in temperature produces more successful collisions because more collisions will meet the required activation energy. There is a general increase in reaction rate with increasing temperature.
   - In fact, a general rule of thumb is that increasing the temperature of a reaction by 10°C doubles the reaction rate.
4. **Catalysts**—accelerate chemical reactions by allowing for more effective collisions, thus lowering the activation energy. The forward and reverse reactions are both accelerated to the same degree. Catalysts are not themselves transformed in the reaction, so they may be used over and over again.
5. **Surface area of reactants**—exposed surfaces affect speed.
   - Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases.
   - The greater the surface area exposed, the greater the chance of collisions between particles, hence, the reaction should proceed at a much faster rate. Example: coal dust is very explosive as opposed to a piece of charcoal. Solutions provide the ultimate surface area exposure!
DIFFERENTIAL RATE
This is sometimes referred to as the “differential rate law” or simply “rate law”. In most reactions once molecules begin colliding, product molecules are formed and are now available to initiate the reverse reaction. To simplify matters, we will deal only with the initial rates of the forward reaction throughout our discussions.

Differential rate laws or “rate expressions” express how a measured rate depends on reactant concentrations. To find the exact relation between rate and concentration, we must do some experiments and collect information.

Consider this generalized reaction:

\[ aA + bB \rightarrow xX \]

The rate expression will always have the form:

\[ \text{Initial reaction rate} = k[A]_o^m[B]_o^n \]

- \( k \) = rate constant
- \([A] = \) concentration of reactant A in mol/L
- \([B] = \) concentration of reactant B in mol/L
- \( m = \) order of reaction for reactant A
- \( n = \) order of reaction for reactant B

the little subscript “o” means “original” or initial concentration at time “zero”.

Exponents \( m \) and \( n \) can be zero, whole numbers or fractions and must be determined by experimentation!

The rate constant, \( k \), is temperature dependent and must be evaluated by experiment. The order with respect to a certain reactant is the exponent on its concentration term in the rate expression. The overall order of the reaction is the sum of all the exponents on all the concentration terms in the rate expression. The significance of the most common orders is explained below:

1. **Zero order**: The change in concentration of reactant has no effect on the rate. These are not very common. General form of rate equation: \( \text{Rate} = k \)

2. **First order**: Rate is directly proportional to the reactants concentration; doubling \([\text{reactant}]\), doubles the rate. These are very common. Nuclear decay reactions usually fit into this category. General form of rate equation: \( \text{Rate} = k [A] \)

3. **Second order**: Rate is quadrupled when reactant concentration (symbolized by \([\text{reactant}]\)) is doubled and increases by a factor of 9 when \([\text{reactant}]\) is tripled etc. These are common, particularly in gas-phase reactions. General form of rate equation: \( \text{Rate} = k [A]^2 \)

Now that we have mastered the format and the lingo, let’s apply what we have learned!
Experiments were performed involving reactants A and B and the following data was collected:

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial Rate mol/(Lx hr)</th>
<th>Initial concentration [A]₀</th>
<th>Initial concentration [B]₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50 x 10⁻²</td>
<td>0.50</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>0.50 x 10⁻²</td>
<td>0.75</td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td>0.50 x 10⁻²</td>
<td>1.00</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>1.00 x 10⁻²</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td>5</td>
<td>1.50 x 10⁻²</td>
<td>0.50</td>
<td>0.60</td>
</tr>
</tbody>
</table>

When analyzing a set of data, you should be aware of the following:

In any well designed experiment, there should be a control. In experiments 1, 2 & 3, the concentration of reactant B was held constant at 0.20 M while the concentration of reactant A was varied. Controls are good starting places!

A good experimenter then reverses the variables and varies B while holding A constant. Experiments 1, 4 & 5 held the concentration of reactant A constant and varied the concentration of reactant B. When this has been done properly, deducing the orders of the reactions is simplified.

Start by attacking the controls! Focus only on those experiments and how the varied reactant concentration affected the rate. Ignore the concentration of the controlled reactant since it is not changing and thus not contributing to any change in the rate.

Look for a doubling, the number 2 is easy to work with, you can easily multiply by, divide by, square or cube the number 2.

**Question**: “Where do I start?”  **Answer**: “With the controls!” Experiments 1, 2 & 3 hold [B] constant, start there. . . The rate stays the same regardless of how the concentration of [A] changes, therefore, it is zero order with respect to A. Also, scan the exponents on the rates. If any of the exponents are different, make an adjustment to the numbers so that all of the exponents are the same.
### Experiment Table

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial Rate mol/(L×hr)</th>
<th>Initial concentration [A]₀</th>
<th>Initial concentration [B]₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50 x 10⁻²</td>
<td>0.50</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>0.50 x 10⁻²</td>
<td>0.75</td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td>0.50 x 10⁻²</td>
<td>1.00</td>
<td>0.20</td>
</tr>
</tbody>
</table>

### Question

**“Now what?”**

**Answer:** “Move on to Experiments 1, 4 & 5 where the concentration of reactant A is held constant.” Compare experiments 1 & 4. The [A] is held constant and the rate doubles with a doubling of [B]. Think: rate = $k[B]^{0.5}$ which becomes $2\text{(rate)} = k[2B]^{0.5}$ once each are doubled. The only possible value for the exponent we seek is 1, since it’s the only way $2 = [2]^{1}$. Since the exponent is one, the reaction is first order with respect to reactant B.

For further proof, compare Experiments 1 & 5 and you see that the rate triples with a tripling of [B]. This indicates a **direct relationship** and therefore, the rate is first order with respect to [B].

### Summary

Initial reaction rate = $k[A]₀[B]₀^{1} = k[B]₀^{1}$; remember any number raised to the zero power is one!

The overall reaction order is 1 because the sum of all the exponents is 1.

Next, we need to solve for the numerical value of the rate constant, $k$.

Use a set of the data from the table above to calculate $k$:

#### FROM EXPERIMENT 1:

$$
\text{rate} = k \ [B]^{1}
$$

$$
0.0050 \frac{\text{mol}}{\text{L} \cdot \text{hr}} = k \ [0.20 \frac{\text{mol}}{\text{L}}]^{1}
$$

Therefore, 

$$
k = \frac{2.5 \times 10^{-2}}{\text{hr}}
$$

You should get the same value with any set of data!
What if all that logic gives you a headache? You can always rely on good old algebra skills. This method is especially useful if the experiment was designed poorly resulting in one reactant’s concentration never being held constant. You still have to compare two experiments and controls are good starting points.

Here’s the algebraic setup:

\[
\frac{\text{rate 1}}{\text{rate 2}} = \frac{k[\text{reactant}]^m[\text{reactant}]^n}{k[\text{reactant}]^m[\text{reactant}]^n}
\]

Select a trial where one reactant concentration is held constant SO THAT IT CANCELS; the \(k\)'s will also cancel

Using trials 1 & 4:

\[
\frac{0.50 \times 10^{-2}}{1.00 \times 10^{-2}} = \frac{k[0.50]^m[0.20]^n}{k[0.50]^m[0.40]^n}
\]

so… \(\frac{1}{2} = [\frac{1}{2}]n\) and \(\therefore n\) must be ONE to make that true!

A word about the units for \(k\…\)

The units on \(k\) are very important. They are also simple to deduce if you respect the fact that \([A]\) translates to the “concentration of reactant A” in \(M = \frac{\text{mol}}{\text{L}} = \text{mol L}^{-1}\). Rate on the other hand, is ALWAYS communicated as a change in molarity (or atmospheres) per unit time. Think of it as \(\frac{\text{M}}{\text{time}} = \text{M time}^{-1} = \text{mol L}^{-1} \text{time}^{-1}\). The rate constant, \(k\) MUST have the units assigned to it that make BOTH sides of the equation end up as M/time!
<table>
<thead>
<tr>
<th>Rate Law Expression showing the correct units on $k$ where $k$ is a numerical value determined from experimental data analysis.</th>
<th>Reasoning for the units on $k$ : Initial Rate = $k$ [reactant(s)]$^{\text{order(s)}}$</th>
<th>M/t = M/t The units on $k$ MUST make this true!</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{M}{\text{time}} = \frac{k}{\text{time}}$</td>
<td>$[\text{A}]$</td>
<td>$\frac{M}{\text{time}} = k \cdot M ;$ the right side is currently just $M$, so $k$ must have the reciprocal time unit attached to it so that the right side becomes M/t. $k$ is reported as a number/time unit.</td>
</tr>
<tr>
<td>$\frac{M}{\text{time}} = \frac{k}{M \cdot \text{time}}$</td>
<td>$[\text{A}]^2$</td>
<td>$\frac{M}{\text{time}} = k \cdot M^2 ;$ the right side is currently $M^2$, so $k$ must have the reciprocal time unit attached to it AND a reciprocal molarity so that the right side becomes M/t. $k$ is reported as a number/M • time unit.</td>
</tr>
<tr>
<td>$\frac{M}{\text{time}} = \frac{k}{M \cdot \text{time}}$</td>
<td>$[\text{A}]\cdot[B]$</td>
<td>$\frac{M}{\text{time}} = k \cdot M^2 ;$ the right side is also currently $M^2$, so $k$ must have the reciprocal time unit attached to it AND a reciprocal molarity so that the right side becomes M/t. $k$ is reported as a number/M • time unit.</td>
</tr>
<tr>
<td>$\frac{M}{\text{time}} = \frac{k}{M^2 \cdot \text{time}}$</td>
<td>$[\text{A}]\cdot[B]^2$</td>
<td>$\frac{M}{\text{time}} = k \cdot M^3 ;$ the right side is currently $M^3$, so $k$ must have the reciprocal time unit attached to it AND a reciprocal molarity squared so that the right side becomes M/t. $k$ is reported as a number/M$^2$ • time unit.</td>
</tr>
</tbody>
</table>

**PURPOSE**

In this activity you will determine the order of a reactant from concentration-rate data using the method of differential rate law.

**MATERIALS**

- calculator
- paper and pencil

**PROCEDURE**

Solve the problems found on your student answer page. Be sure to show all work paying attention to the proper use of significant digits and units.
Chemical Reaction Rates I
Solving Kinetics Problems Involving Differential Rate Law

CONCLUSION QUESTIONS
1. The rate of the reaction between CO and NO₂

\[ \text{CO}(g) + \text{NO}_2(g) \rightarrow \text{CO}_2(g) + \text{NO}(g) \]

was studied at 650 K starting with various concentrations of CO and NO₂, and the data in the table were collected.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial Rate ( \text{mol/(Lx h)} )</th>
<th>Initial concentration [CO]</th>
<th>Initial concentration [NO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 3.4 \times 10^{-4} )</td>
<td>0.510</td>
<td>0.0350</td>
</tr>
<tr>
<td>2</td>
<td>( 6.8 \times 10^{-4} )</td>
<td>0.510</td>
<td>0.0700</td>
</tr>
<tr>
<td>3</td>
<td>( 1.7 \times 10^{-4} )</td>
<td>0.510</td>
<td>0.0175</td>
</tr>
<tr>
<td>4</td>
<td>( 6.8 \times 10^{-4} )</td>
<td>0.102</td>
<td>0.0350</td>
</tr>
<tr>
<td>5</td>
<td>( 10.2 \times 10^{-4} )</td>
<td>0.153</td>
<td>0.0350</td>
</tr>
</tbody>
</table>

a. Write the rate law that is consistent with the data.

b. Calculate the value of the specific rate constant, \( k \), and specify units.

c. What is the overall order for the reaction?
2. The initial rate of the reaction of nitrogen monoxide and oxygen was measured at 35°C for various initial concentrations of NO and O₂.

\[ 2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g) \]

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial concentration [O₂]</th>
<th>Initial concentration [NO]</th>
<th>Initial Rate mol/(Lx s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.040</td>
<td>0.020</td>
<td>0.028</td>
</tr>
<tr>
<td>2</td>
<td>0.040</td>
<td>0.040</td>
<td>0.057</td>
</tr>
<tr>
<td>3</td>
<td>0.040</td>
<td>0.080</td>
<td>0.114</td>
</tr>
<tr>
<td>4</td>
<td>0.080</td>
<td>0.040</td>
<td>0.227</td>
</tr>
<tr>
<td>5</td>
<td>0.020</td>
<td>0.040</td>
<td>0.014</td>
</tr>
</tbody>
</table>

a. Write the rate law that is consistent with the data.

b. Calculate the value of the specific rate constant, \( k \), and specify units.

c. What is the overall order for the reaction?
3. Dinitrogen pentoxide decomposes at 45°C to yield nitrogen dioxide and oxygen gas according to the equation

\[ 2 \text{N}_2\text{O}_5 (g) \rightarrow 4\text{NO}_2 (g) + \text{O}_2 (g) \]

Data are collected in the table.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial concentration [N(_2)O(_5)]</th>
<th>Initial Rate mol/(Lx s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.75 x 10(^{-3})</td>
<td>2.06 x 10(^{-9})</td>
</tr>
<tr>
<td>2</td>
<td>3.50 x 10(^{-3})</td>
<td>8.24 x 10(^{-9})</td>
</tr>
<tr>
<td>3</td>
<td>7.00 x 10(^{-3})</td>
<td>3.30 x 10(^{-8})</td>
</tr>
</tbody>
</table>

a. Write the rate law that is consistent with the data.

b. Calculate the value of the specific rate constant, \(k\), and specify units.

c. What is the overall order for the reaction?
4. Nitrogen monoxide reacts with chlorine according to the equation

\[ 2 \text{NO}(g) + \text{Cl}_2(g) \rightarrow 2 \text{NOCl}(g) \]

The following initial rates of reaction have been observed for certain reactant concentrations:

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial concentration [NO]</th>
<th>Initial concentration [Cl(_2)]</th>
<th>Initial Rate mol/(L x h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>0.50</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>0.50</td>
<td>4.56</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>1.50</td>
<td>41.0</td>
</tr>
</tbody>
</table>

a. Write the rate law that is consistent with the data.

b. Calculate the value of the specific rate constant, \(k\), and specify units.

c. What is the overall order for the reaction?
5. Hydrogen reacts with nitrogen monoxide to form dinitrogen oxide, laughing gas, according to the equation

\[ \text{H}_2 + 2\text{NO(g)} \rightarrow \text{N}_2\text{O(g)} + \text{H}_2\text{O(g)} \]

The following data was collected:

<table>
<thead>
<tr>
<th>[NO], M</th>
<th>0.40</th>
<th>0.80</th>
<th>0.80</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H\textsubscript{2}], M</td>
<td>0.35</td>
<td>0.35</td>
<td>0.70</td>
</tr>
<tr>
<td>Initial Rate mol/(L x s)</td>
<td>5.040 \times 10^{-5}</td>
<td>2.016 \times 10^{-4}</td>
<td>4.032 \times 10^{-4}</td>
</tr>
</tbody>
</table>

a. Write the rate law that is consistent with the data.

b. Calculate the value of the specific rate constant, \(k\), and specify units.

c. What is the overall order for the reaction?