

## Rate Laws

1. Kinetics is the study of the **rates of reaction**.
2. What is a Rate Law?

The equation that defines the rate of a particular reaction at a particular temperature.

- a. How is a rate law determined?

It must be experimentally determined.

3. What are the two types of rate law and what does each compare?

- a. **Differential Rate Law**

This rate compares how the rate of the reaction changes as the concentrations change.

- b. **Integrated Rate Law**

This rate compares how the concentrations change with time.

4. The general appearance of a differential rate law is:

$$\text{Rate} = k [\text{Reactant}]^n$$

- a. Where k represents the **rate constant**.

- i. What are the units for k?

The units for k change depending on the rate of reaction. The units for k can be worked out using the following equation:

$$k \text{ units} = \frac{\text{L}^{n-1}}{\text{mol}^{n-1} \text{ s}}$$

- b. Where n represents the **order of reaction**.
- If  $n=1$  this is said to be a **first order** reaction.
  - If  $n=2$  this is said to be a **second order** reaction.
  - If  $n=0$  this is said to be a **zero order** reaction.
- c. If there is more than one reactant in a rate law you must **add** their n values to determine the overall order of the reaction.
5. For a zero order reaction
- a. What does zero order tell us with respect to concentration & rate?

When a reaction is zero order with respect to some species a change in its concentration has no effect on the rate of reaction (the rate remains unchanged).

- b. Differential Rate Law

$$\text{Rate} = k$$

### c. Integrated Rate Law

$$[A] = -k t + [A]_0$$
$$y = mx + b$$

- [A] : concentration of A at time t  
[A]<sub>0</sub>: initial concentration of A  
-k : rate constant and slope of line.

#### i. How can we utilize this information?

An important point about the format of the equation is that a reaction is zero order if a graph of [A] vs. t yields a straight line.

### d. Half Life Equation

$$t_{1/2} = \frac{[A]_0}{2k}$$

## 6. For a first order reaction

### a. What does first order tell us with respect to concentration & rate?

When a reaction is first order with respect to some species that means that if you double the concentration of the reactant, the rate of the reaction will double as well. If you were to quadruple the concentration of reactant the rate would quadruple as well. In a first order case, the rate will change by the same factor that the concentration of the reactant changes.

### b. Differential Rate Law

The general appearance of the first order rate law looks like:

$$\text{Rate} = k [A]$$

c. Integrated Rate Law

$$\ln[A] = -kt + \ln[A]_0$$

$$y = mx + b$$

[A] : concentration of A at time t

[A]<sub>0</sub>: initial concentration of A

-k : rate constant and slope of line.

- i. What format is this equation written in? How can we utilize this information?

The important thing about the format of the equation is that a reaction is first order if a graph of  $\ln [A]$  vs.  $t$  yields a straight line.

d. Half Life Equation

$$t_{1/2} = \frac{0.693}{k}$$

From this you can see that the half-life of a first order reaction is constant.

7. For a second order reaction

- a. What does second order tell us with respect to concentration & rate?

When a reaction is second order with respect to some species that means that if you double the concentration of the reactant, the rate of the reaction will quadruple. If you were to triple the concentration the rate would be nine times as large. In the second order case the change in the rate of reaction is equal to the factor of concentration change squared.

- b. Differential Rate Law

The general appearance of the second order rate law looks like:

$$\text{Rate} = k [A]^2$$

c. Integrated Rate Law

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

$$y = mx + b$$

[A] : concentration of A at time t

[A]<sub>0</sub>: initial concentration of A

k : rate constant and slope of line.

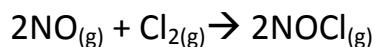
- i. What format is this equation written in? How can we utilize this information?

The important thing about the format of the equation is that you can tell if a reaction is second order if a graph of 1/[A] versus t yields a straight line.

d. Half Life Equation

$$t_{1/2} = \frac{1}{k[A]_0}$$

8. Determine the differential rate law and rate constant for



given:

[NO] <sub>0</sub> (mol/L)	[Cl <sub>2</sub> ] <sub>0</sub> (mol/L)	Initial Rate (mol/Lmin)
0.10	0.10	0.18
0.10	0.20	0.36
0.20	0.20	1.45

The technical method for solving this sort of problem is using the formula:

$$\frac{\text{rate of experiment a}}{\text{rate of experiment b}} = \frac{\overbrace{k[\text{reactant A}]^n[\text{reactant B}]^m}^{\text{concentrations from experiment a}}}{\underbrace{k[\text{reactant A}]^n[\text{reactant B}]^m}_{\text{concentrations from experiment b}}}$$

Where n represents the order of the reaction with respect to reactant A and m represents the order of reaction with respect to reactant B. Our goal when using this formula is usually to determine n and m.

When using this formula, our intent is to plug in experimental data for circumstances where only one of the concentrations of reactants changes. This way we are able to see how the concentration of one of the reactants affects the rate of reaction.

For example, if we look at the highlighted boxes

[NO] <sub>0</sub> (mol/L)	[Cl <sub>2</sub> ] <sub>0</sub> (mol/L)	Initial Rate (mol/Lmin)
0.10	0.10	0.18
0.10	0.20	0.36
0.20	0.20	1.45

The [NO] remains constant at 0.10 M and [Cl<sub>2</sub>] changes. That means that the change in [Cl<sub>2</sub>] is the cause of the change in the rate of reaction. So what we want to do is plug in the information from those 2 experiments into the formula given above. It does not matter what you call “experiment a” or “experiment b”.

$$\begin{aligned}
 \frac{\text{rate of experiment 2}}{\text{rate of experiment 1}} &= \frac{\text{concentrations of experiment 2}}{\text{concentrations of experiment 1}} \\
 \frac{0.36 \text{ mol/Lmin}}{0.16 \text{ mol/Lmin}} &= \frac{(0.10)^n(0.20)^m}{(0.10)^n(0.10)^m} = \frac{(0.20)^m}{(0.10)^m} = 2^m \\
 \frac{0.36 \text{ mol/Lmin}}{0.16 \text{ mol/Lmin}} &= 2^m \\
 2 &= 2^m \\
 m &= 1
 \end{aligned}$$

So from this we have found that the rate of reaction with respect to  $[\text{Cl}_2]$  is first order. Now we need to do the same calculations, but in terms of  $[\text{NO}]$ . So in this case we will look at the highlighted experiments:

$[\text{NO}]_0$ (mol/L)	$[\text{Cl}_2]_0$ (mol/L)	Initial Rate (mol/Lmin)
0.10	0.10	0.18
0.10	0.20	0.36
0.20	0.20	1.45

Let's plug the given information into the equation:

$$\begin{aligned}
 \frac{\text{rate of experiment 3}}{\text{rate of experiment 2}} &= \frac{\text{concentrations of experiment 3}}{\text{concentrations of experiment 2}} \\
 \frac{1.45 \text{ mol/Lmin}}{0.36 \text{ mol/Lmin}} &= \frac{(0.20)^n(0.20)^1}{(0.10)^n(0.20)^1} = \frac{(0.20)^n}{(0.10)^n} = 2^n \\
 \frac{1.45 \text{ mol/Lmin}}{0.36 \text{ mol/Lmin}} &= 2^n \\
 4 &= 2^n \\
 n &= 2
 \end{aligned}$$

So from this we have found that the rate of reaction with respect to  $[\text{NO}]$  is second order. Now we need to combine the information into one rate law...

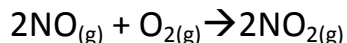
$$\text{Rate} = k [\text{NO}]^2 [\text{Cl}_2]$$

In order to solve for the value of  $k$ , all we need to do is plug in the data from one of the experiments and solve for  $k$ .

Using the data from the first experiment:

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{Cl}_2]} = \frac{0.18}{(0.1)^2 (0.1)} = 180 \text{ M}^{-2} \text{ min}^{-1}$$

9. Determine the rate law for



given:

$[\text{NO}]_0$ (mol/L)	$[\text{O}_2]_0$ (mol/L)	Initial Rate (mol/Lmin)
$1.66 \times 10^{-9}$	$1.66 \times 10^{-9}$	$3.32 \times 10^{-11}$
$4.98 \times 10^{-9}$	$1.66 \times 10^{-9}$	$2.99 \times 10^{-10}$
$4.15 \times 10^{-9}$	$4.15 \times 10^{-9}$	$5.20 \times 10^{-10}$

In the case of this problem, we are not given 2 fixed data points. We are given only a fixed concentration for  $\text{O}_2$ , which makes it very easy to calculate the order of reaction with respect to  $[\text{NO}]$ . It is not as clear for  $\text{O}_2$  however.

Let's try and determine the order with respect to  $[\text{NO}]$  without using the formula and simply evaluating how the concentrations change and how the corresponding rates change.

In order to do this we are going to evaluate  $[\text{NO}]$  from the information in experiment 1 and experiment 2. Remember that I am choosing these values because  $[\text{O}_2]$  is held constant, so I know that any changes in the rate are due to changes in the concentration of  $\text{NO}$ .



The [NO] has tripled from experiment 1 → experiment 2.

The rate is nine times as large from experiment 1 → experiment 2.

Because 9 is the square of 3... I am able to determine that the reaction is second order with respect to [NO].

If this method does not sit well with you, then simply plug into the formula like we did for problem 8.

Now for determining the order with respect to [O<sub>2</sub>], we are not able to use the method above. We have to plug into the formula (this is why it is good to understand both methods).

Taking the following experiments (it doesn't really matter which 2 you choose)

[NO] <sub>0</sub> (mol/L)	[O <sub>2</sub> ] <sub>0</sub> (mol/L)	Initial Rate (mol/Lmin)
1.66 × 10 <sup>-9</sup>	1.66 × 10 <sup>-9</sup>	3.32 × 10 <sup>-11</sup>
4.98 × 10 <sup>-9</sup>	1.66 × 10 <sup>-9</sup>	2.99 × 10 <sup>-10</sup>
4.15 × 10 <sup>-9</sup>	4.15 × 10 <sup>-9</sup>	5.20 × 10 <sup>-10</sup>

We will plug into the formula:

$$\begin{aligned}
 \frac{\text{rate of experiment 3} \left( \frac{5.20 \times 10^{-10} \text{ mol/Lmin}}{2.99 \times 10^{-10} \text{ mol/Lmin}} \right)}{\text{rate of experiment 2} \left( \frac{1.72 \times 10^{-17} (4.15 \times 10^{-9})^m}{2.48 \times 10^{-17} (1.66 \times 10^{-9})^m} \right)} &= \frac{\text{concentrations of experiment 3} \left( \frac{(4.15 \times 10^{-9})^2 (4.15 \times 10^{-9})^m}{(4.98 \times 10^{-9})^2 (1.66 \times 10^{-9})^m} \right)}{\text{concentrations of experiment 2} \left( \frac{5.20 \times 10^{-10} \text{ mol/Lmin}}{2.99 \times 10^{-10} \text{ mol/Lmin}} \right)} = 1.739 \\
 (2.5)^m &= 2.5 \\
 m &= 1
 \end{aligned}$$

From this we have determine the rate of the reaction with respect to [O<sub>2</sub>] =

1

We are now able to combine all the information into our rate law:

$$\text{Rate} = k [\text{NO}]^2[\text{O}_2]$$

10. A certain reaction has the following general form



At a particular temperature and  $[\text{A}]_0 = 2.80 \times 10^{-3} \text{ M}$  concentration versus time data were collected and a plot of  $1/[\text{A}]$  versus time resulted in a straight line with a slope value of  $+3.60 \times 10^{-2} \text{ L/mol}\cdot\text{min}$

- a. Determine the differential and integrated rate laws and the value of the rate constant.

Based on the fact the graph of  $1/[\text{A}]$  versus time yields a straight line, we know that this reaction must second order with respect to A. We know that the rate law relates only to A because we are only considering reactants at this point.

Thus we obtain:

Differential Rate Law:

$$\text{Rate} = k[\text{A}]^2$$

Integrated Rate Law:

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

In order to determine the value of k, we remind ourselves that slope of the line is equal to the value of k. Based on the question, the, we are able to solve for k:

$$k = 3.60 \times 10^{-2} \frac{\text{L}}{\text{mol min}}$$

b. Calculate the half-life for this reaction.

$$t_{1/2} = \frac{1}{[A]_0 k} = \frac{1}{(3.60 \times 10^{-2} \text{ min}^{-1} \text{ M}^{-1})(2.8 \times 10^{-3} \text{ M})} = 9921 \text{ min}$$

c. How much time is required for the concentration of A to decrease to  $2.50 \times 10^{-3} \text{ M}$ ?

In order to solve this problem you will need to plug into the integrated rate law. Remember it is the integrated rate law that relates how concentration changes with time.

We will use:

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

Where :

$$[A] = 2.50 \times 10^{-2} \text{ M}$$

$$k = 3.60 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$$

$$[A]_0 = 2.80 \times 10^{-3} \text{ M}$$

$$t = ?$$

Plugging in we get:

$$\frac{1}{0.00250 \text{ M}} = (3.60 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}) (t) + \frac{1}{0.0028 \text{ M}}$$

$$t = 1109 \text{ minutes}$$

11. The decomposition of hydrogen peroxide was studied and the following data was obtained

Time(s)	[H <sub>2</sub> O <sub>2</sub> ] (mol/L)
0	1
120	0.91
300	0.78
600	0.59
1200	0.37
1800	0.22
2400	0.13
3000	0.082
3600	0.05

- a. Determine the integrated rate law, the differential rate law, and the value of the rate constant.

The basic need in this question is to determine whether [H<sub>2</sub>O<sub>2</sub>] vs. time, ln [H<sub>2</sub>O<sub>2</sub>] vs. time, or 1/[H<sub>2</sub>O<sub>2</sub>] versus time yields a straight line (meaning it has a consistent slope or k value). Remember this determination will indicate what the reaction order is. You can figure this out by plugging values into the integrated rate law for each reaction order and seeing which one results in a k value with the greatest consistency.

Check for zero order using  $[A] = -kt + [A]_0$

$$0.91 = -k(120s) + 1.00$$

$$k = 0.00075$$

$$0.13 = -k(2400) + 1.00$$

$$k = 0.00036$$

Feel free to choose whichever values of k you prefer. I tend to choose a value at the very top and a value toward the bottom... that will typically show you pretty quickly whether the values are consistent or not.

As you can see from what we plugged in, the k values vary quite heavily... so this reaction is not zero order.

Check for first order using  $\ln [A] = -kt + \ln [A]_0$ :

$$\ln (0.37) = -k (1200) + \ln (1.00)$$

$$k = 0.00083$$

$$\ln (0.05) = -k(3600) + \ln (1.00)$$

$$k = 0.00083$$

As you can see here I picked completely different number from those that I used to determine whether it was zero order. I did this just to show you that you have free choice when picking what to compare. I always referred back to the initial value because it made determining the time that much more straight forward.

Because these numbers are consistent... we can see that this *is* a first order reaction. Sometimes the numbers will not come out so exactly... but they are relatively consistent. Remember that these numbers are based on experimental results... meaning that perfect results are not achieved.

Thus, this reaction would be first order – this means that:

$$\text{Differential Rate Law - Rate} = k[\text{H}_2\text{O}_2]$$

$$\text{Integrated Rate Law - } \ln[\text{H}_2\text{O}_2] = -kt + \ln[\text{H}_2\text{O}_2]_0$$

$$\text{rate} = -\text{slope} = -(\text{average of the slopes}) = 0.00083$$

- b. Calculate the  $[\text{H}_2\text{O}_2]$  at 4000. s after the start of the reaction.

In order to do this calculation, we simply need to plug the given data into the integrated rate law and solve.

Integrated Rate Law -

$$\ln[\text{H}_2\text{O}_2] = -kt + \ln[\text{H}_2\text{O}_2]_0$$

$$\ln [\text{H}_2\text{O}_2] = ( -0.00083 \text{ s}^{-1} ) (4000. \text{s}) + \ln (1.00\text{M})$$

$$\ln [\text{H}_2\text{O}_2] = -3.32$$

$$[\text{H}_2\text{O}_2] = e^{-3.32} = 0.0362\text{M}$$

12. A first order reaction is 75.0% complete in 320. s.

From the information provided here we are able to solve for k, using the integrated rate law.

$$\ln[A] = -kt + \ln[A]_0$$

In this problem we will assume that  $[A]_0 = 1.00\text{M}$ . This means that if the reaction is 75% complete, then  $[A] = 0.25 \text{ M}$ . Let's plug in and solve:

$$\ln (0.25\text{M}) = -k (320. \text{s}) + \ln (1.00\text{M})$$

$$k = 0.00433 \text{ s}^{-1}$$

a. What are the first and second half-lives for this reaction?

Because this is a first order reaction we can use the half-life formula

$$t_{1/2} = \frac{0.693}{k}$$

Plugging in the value of k that was previously determined:

$$t_{1/2} = \frac{0.693}{0.00433 \text{ s}^{-1}} = 160 \text{ s}^{-1}$$

Because this is a first order reaction, the half-life does not change, that means each successive half-life takes 160s.

b. How long does it take for this reaction to be 90.0% complete?

Once again we are looking at how the concentration changes with time, so we will be plugging into the integrated rate law. We will also, once again, be assuming that the  $[A]_0 = 1.00\text{M}$  which would mean that the  $[A] = 0.10\text{ M}$

$$\ln(0.10\text{M}) = -(0.00433\text{ s}^{-1})(t) + \ln(1.00\text{M})$$

$$t = 531\text{ s}$$