

## ***Chemical Kinetics***

Chemical Kinetics - The study of reaction rates

### ***What affects reaction rates??***

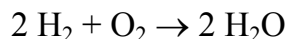
1. Concentration of reactants. Reaction rates are usually dependent on the concentration of reactant present. However, the rate may not depend on the concentration of a reactant as long as it is present.
2. Concentration of catalyst. A CATALYST is a substance that increases the rate of reaction without being consumed in the reaction. Catalysts do not appear in the balanced overall equation.
3. Temperature of the reaction. Usually reaction rates increase with increases in temperature. A “rule of thumb” is that the rate will double for every 10°C increase in temperature.
4. Surface area of reactant of catalyst. If a reaction involves a solid with a gas or liquid, the surface area of the solid will affect the rate of the reaction. A solid which is ground up will react faster than a solid that is in one large chunk.

### ***Definition of Reaction Rate***

- increase in molar concentration of products per unit time or the decrease in molar concentration of reactants per unit time.

Unit of Reaction Rate - mol L<sup>-1</sup>s<sup>-1</sup>

For a reaction:



The rate is defined as  $\Delta[\text{H}_2\text{O}]/\Delta t$ . This is actually an average rate over the time interval  $\Delta t$ . If the time interval is arbitrarily short then the equation will give the instantaneous rate, the rate at a particular point in time.

The rate can also be given as  $-\Delta[\text{H}_2]/\Delta t$  or  $-\Delta[\text{O}_2]/\Delta t$ . Note the presence of the minus sign in these expressions. This is because the rate has to be positive and to show the decrease in concentration of reactant.

### ***How are all of these rates related???***

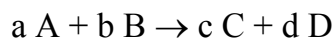
Looking at the above equation we see that for every oxygen molecule consumed 2 hydrogen molecules are also consumed and 2 molecules of water are produced. Using this fact we can relate the rates of the reaction in terms of different species. Since 2 molecules of water are produced for every molecule of oxygen consumed water is produced at a rate that is 2 times the rate at which oxygen is consumed. In other words:

$$\Delta[\text{H}_2\text{O}]/\Delta t = -2 \Delta[\text{O}_2]/\Delta t$$

or

$$-\Delta[\text{O}_2]/\Delta t = \frac{1}{2} \Delta[\text{H}_2\text{O}]/\Delta t = -\frac{1}{2} \Delta[\text{H}_2]/\Delta t.$$

In general, for a reaction:



the rate of the reaction is:

$$\text{Rate} = -1/a \Delta[\text{A}]/\Delta t = -1/b \Delta[\text{B}]/\Delta t = 1/c \Delta[\text{C}]/\Delta t = 1/d \Delta[\text{D}]/\Delta t.$$

### ***Calculation of average rate***

If we know the concentration of a reactant or product at at least two different times we can calculate the average rate.

Example.

For the above reaction (for water), if we knew that the concentration of hydrogen initially was 4.5 M and at a time 0.5 seconds later we knew it was 0.053 M what is the average rate of this reaction.

$$\begin{aligned} \text{Average rate} &= -\Delta[\text{H}_2] / \Delta t = - (0.053 \text{ M} - 4.5 \text{ M}) / (0.5 \text{ s} - 0.0 \text{ s}) \\ &= - (- 4.447 \text{ M}) / 0.5 \text{ s} = 8.894 \text{ M/s} \end{aligned}$$

### ***Experimental determination of rate***

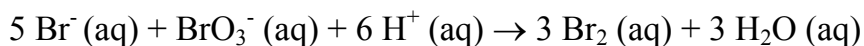
1. pH behavior of a solution. Changes in pH can be monitored for relatively slow reactions and the concentration of one of the species can be followed over a period of time.
2. Changes in physical properties. The total pressure of a system can be monitored. The pressures of the individual species can be related to the total pressure and monitored over time.
3. Spectroscopically. Many compounds absorb light in a variety of parts of the spectrum. The amount of light absorbed is proportional to the concentration of the compound. Thus the concentration can be monitored over time.
4. Often we can extract a sample from the reaction mixture and titrate for a particular substance. This generally requires a fairly slow reaction so the concentration of the substance does not change significantly during the course of the titration.

### ***Dependence of rate on concentration***

It has been determined that the rates of reactions depend on the concentrations of the certain reactants as well as any catalysts that may be present. This relationship is usually expressed as a rate law.

Rate law - an equation that relates the rate of the reaction to the concentration of certain reactants and catalysts raised to some power.

The rate law must be experimentally determined. For example, for the reaction



the *experimentally determined* rate law is

$$\text{Rate} = k [\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2.$$

In this equation the exponents of the concentration of the reactants are not necessarily the same as the coefficients of the same reactants in the balanced overall equation.

The exponents must be *experimentally determined*.

The  $k$  is the **rate constant** and is a constant of proportionality between the rate of the reaction and the concentrations of the reactants.

It is a constant at a given temperature but varies with temperature.

Because the units of rate are  $\text{mol L}^{-1} \text{s}^{-1}$  the units of the rate constant are dependent on the form of the rate law.

The exponents in the rate law usually are integers but need not be so.

### ***Reaction order***

The order of a reaction with respect to a particular substance is the exponent of the concentration of that substance in the experimentally determined rate law.

In the above rate law the order with respect to Bromide ion is 1.

In the above rate law the order with respect to Bromate ion is 1.

In the above rate law the order with respect to Hydrogen ion is 2.

The overall order is the sum of all the exponents in the experimentally determined rate law.

In the above rate law the overall order is 4.  $(1 + 1 + 2)$

If a reactant does not appear in the rate law the order with respect to that substance is zero (0).

Overall orders can be positive (usually are 1 or 2), negative or zero.

### ***Determination of rate laws***

We determine the rate law experimentally by the method of initial rates. We do several experiments and measure the initial rate of the reaction. The concentrations of the reactants are changed in a systematic way between experiments. We then look at experiments where all variables except one are held constant. The variable that changes is the one that will have its exponent determined. If the rate doubles when the concentration doubles the order is 1. Let's look at this.

$$\frac{[x]_1^m}{[x]_2^m} = \left(\frac{1}{2}\right)^1$$

Let's solve for the exponent,  $m$ . Remember that  $[x]_2 = 2 [x]_1$ . This leaves us with:

$$\left(\frac{1}{2}\right)^m = \left(\frac{1}{2}\right)^1$$

Solving for  $m$  is done as follows:

- Take logarithms of both sides. This should give an equation that is linear.
- Solve the linear equation for  $m$ .

Looking at this gives.

$$\log\left[\left(\frac{1}{2}\right)^m\right] = \log\left[\left(\frac{1}{2}\right)^1\right]$$

which reduces to:

$$m \log\left(\frac{1}{2}\right) = 1 \log\left(\frac{1}{2}\right)$$

When we solve this, we find that  $m=1$ . We do a similar analysis for each of the other reactants and ***any catalysts that are present***. Once we have all of the exponents in the rate law we can use any one of the experiments to determine the rate constant by plugging the data into the rate law.

### ***Changes in concentration with time***

#### *Zero order reactions*

In a zero order reaction the rate of the reaction does not depend on the concentrations of the reactants.

$$\text{Rate} = k = -\frac{\Delta[A]}{\Delta t}$$

if the changes in concentration and time are small enough the differences can be expressed as differentials.

$$k = -\frac{d[A]}{dt}$$

This needs to be rearranged before we can arrive at an expression that relates concentration and time. The rearranged expression is:

$$d[A] = -kdt$$

If we then integrate both sides of this equation we arrive at an expression that shows how the concentration of a reactant in a zero order reaction changes with time.

$$\begin{aligned} [A]_t - [A]_0 &= -kt \\ [A]_t &= -kt + [A]_0 \end{aligned}$$

*Example:*

A zero order reaction has a rate constant of  $6.58 \times 10^{-2} \text{ M s}^{-1}$ . How many seconds will it take for the concentration of the reactant to drop from 0.100 M to 0.00100 M?

*Solution:*

We use the integrated rate law (above) to solve for time. We know  $k$ ,  $[A]_t$ , and  $[A]_0$ . If we rearrange the integrated rate law solving for time we get:

$$\begin{aligned} [A]_t - [A]_0 &= -kt \\ \frac{[A]_t - [A]_0}{-k} &= t \\ \frac{0.00100 \text{ M} - 0.100 \text{ M}}{-6.58 \times 10^{-2} \text{ M s}^{-1}} &= 1.504559271 \text{ s} = 1.50 \text{ s} \end{aligned}$$

*First order reactions*

In a first order reaction the rate law is

$$\text{Rate} = k[A] = -\frac{\Delta[A]}{\Delta t}$$

Again, if the changes in concentration and time are small enough the differences can be expressed as differentials.

$$k[A] = -\frac{d[A]}{dt}$$

We can rearrange this expression to make it easier to solve:

$$\frac{d[A]}{[A]} = -kdt$$

Integration of both sides of this equation gives us the relationship between concentration and time:

$$\begin{aligned}\ln\left(\frac{[A]_t}{[A]_0}\right) &= -kt \\ \ln[A]_t - \ln[A]_0 &= -kt \\ \ln[A]_t &= -kt + \ln[A]_0\end{aligned}$$

*Example*

A 1<sup>st</sup> order reaction has the following chemical equation:



If the rate constant for this reaction is  $1.43 \times 10^{-2} \text{ s}^{-1}$  and the initial concentration of A is 0.567 M, what is the concentration of A 2.5 minutes later.

*Solution*

Start with the integrated rate law.

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

In this equation  $[A]_0 = 0.567 \text{ M}$ ,  $k = 1.43 \times 10^{-2} \text{ s}^{-1}$ , and  $t = 2.5 \text{ min} = 1.5 \times 10^2 \text{ s}$ . If we plug these numbers into the equation we have.

$$\begin{aligned}\ln[A]_t &= -kt + \ln[A]_0 \\ \ln[A]_t &= -(1.43 \times 10^{-2} \text{ s}^{-1})(1.5 \times 10^2 \text{ s}) + \ln(0.567) \\ &= -2.712395975 \\ [A]_t &= e^{-2.712395975} = 0.0664 \text{ M}\end{aligned}$$

Does this answer make sense?? The concentration at 2.5 min is lower than at the start so this answer does make sense.

*Example*

For the same reaction at the same temperature how long does it take for the concentration to drop from 0.500 M to 0.00463 M?

*Solution*

Use the integrated rate law.

$$\ln \frac{[A]_t}{[A]_0} = -kt$$
$$t = -\frac{\ln \frac{[A]_t}{[A]_0}}{k}$$

If we plug our numbers into this equation we have

$$t = -\frac{\ln \frac{0.00463}{0.500}}{0.0143\text{s}^{-1}} = 327.4\text{s} = 327\text{s}$$

*Second Order Reaction*

Now we'll look at the relationship between concentration of reactant and time for a second order reaction. The rate law is:

$$\text{Rate} = k[A]^2 = -\frac{\Delta[A]}{\Delta t}$$

Again if we make the changes small enough we can use the methods of calculus to determine the relationship that we are seeking.

$$k[A]^2 = -\frac{d[A]}{dt}$$
$$-\frac{d[A]}{[A]^2} = kdt$$
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

*Example:*



A second order reaction has a rate constant of  $5.32 \text{ M}^{-1}\text{s}^{-1}$ . If the concentration of the reactant is  $1.545 \text{ M}$  initially, what is the concentration after 65 seconds have passed?

*Solution:*

Using the integrated rate law and plugging in our numbers gives:

$$\begin{aligned}\frac{1}{[A]_t} &= kt + \frac{1}{[A]_0} \\ \frac{1}{[A]_t} &= (5.32 \text{ M}^{-1}\text{s}^{-1})(65\text{s}) + \frac{1}{1.545\text{M}} \\ \frac{1}{[A]_t} &= 346.447 \text{ M}^{-1} \\ [A]_t &= 0.002886 \text{ M} = 0.0029 \text{ M}\end{aligned}$$

*Example:*

How long will it take for the concentration of A to drop to 25% of its initial value?

*Solution:*

$$[A]_t = 0.25 [A]_0$$

Substituting this into our integrated rate law we get

$$\begin{aligned}\frac{1}{[A]_t} - \frac{1}{[A]_0} &= kt \\ t &= \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{k} = \frac{\frac{1}{0.25[A]_0} - \frac{1}{[A]_0}}{5.32 \text{ M}^{-1}\text{s}^{-1}} = \frac{\frac{1-0.25}{0.25[A]_0}}{5.32 \text{ M}^{-1}\text{s}^{-1}} = \frac{\frac{3}{1.545\text{M}}}{5.32 \text{ M}^{-1}\text{s}^{-1}} = 0.365\text{s}\end{aligned}$$

### ***Half Life of a Reaction***

The **half-life** of a reaction is the amount of time it takes for the concentration of the reactant to drop to  $\frac{1}{2}$  of its initial value.

### ***Zero order reactions***

The integrated rate law for a zero order reaction is:

$$[A]_t = -kt + [A]_0$$

If we impose the restriction that  $[A]_t = \frac{1}{2} [A]_0$  we get:

$$\begin{aligned} [A]_t &= -kt + [A]_0 \\ \frac{1}{2}[A]_0 - [A]_0 &= -kt \\ -\frac{1}{2}[A]_0 &= -kt \\ t_{\frac{1}{2}} &= \frac{[A]_0}{2k} \end{aligned}$$

So we see that the half-life depends on the initial concentration of the reactant. Each successive half-life will be shorter than the one that came before, because the concentration at the end of each half-life will be smaller than at the beginning.

### *First order reactions*

For a first order reaction we have shown the integrated rate law to be:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

If we are trying to find the half-life of the reaction we need  $[A]_t = \frac{1}{2} [A]_0$ . Substituting this into our integrated rate law and simplifying we find that:

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

For a first order reaction we see that the half-life is independent of the initial concentration of the reactant. This means that the time it takes for the reaction to proceed to the half-way point is the same as it takes for it to proceed from the half-way point to the  $\frac{3}{4}$  point, and so on.

### *Second order reaction.*

For a second order reaction we know that the integrated rate law is:

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

Imposing the same conditions on the concentrations as before and doing a bit of algebra we arrive at:

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

This shows that the half-lives are not constant as they are for a first order reaction. In a second order reaction the half-life gets progressively longer as the reaction proceeds.

### *Example*

A first order reaction has a rate constant of  $0.667 \text{ s}^{-1}$ . What is the half-life of this reaction?

### *Solution*

Because we know that the half-life of a first order reaction is  $\ln 2 / k$ , we find that the half-life of this reaction is  $(0.693)/0.667 \text{ s}^{-1} = 1.039 \text{ s} = 1.04 \text{ s}$ . This reaction will be half-over in 1.04 seconds.

### ***Graphical methods for kinetic problems***

Both of the integrated rate laws we have looked at can be written in a form that can be interpreted as being a linear equation.

$$\begin{aligned}y &= mx + b \\[A]_t &= -kt + [A]_0 \\ \ln[A]_t &= -kt + \ln[A]_0 \\ \frac{1}{[A]_t} &= kt + \frac{1}{[A]_0}\end{aligned}$$

These equations indicate that

- For a zero order reaction, a plot of concentration versus time will give a straight line with a slope equal to  $-k$  and an intercept equal to the initial concentration of the reactant.
- for a first order reaction, if we plot the natural log of the concentrations versus time we get a straight line that has a slope of  $-k$  and an intercept of  $\ln[A]_0$ .
- for a second order reaction, a plot of the inverse of the concentrations versus time gives a straight line with a slope of  $k$  and an intercept of  $1/[A]_0$ .

*Example*

Use the following data to determine if the reaction is first order or second order.

Time (s)	[A] (M)
0.00	1.0
120.0	0.91
300.0	0.78
600.0	0.59
1200.0	0.37
1800.0	0.22
2400.0	0.13
3000.0	0.082
3600.0	0.050

*(Graphing solution)*

***Temperature and reaction rate: 2 theories***

*Theory 1: Collision theory*

Assumption: In order for a reaction to occur the reactants must collide with a energy greater than some minimum and with the proper orientation. The minimum of energy required is called the **activation energy,  $E_a$** . The value of the activation energy depends on the reaction.

In this theory the rate constant is a product of three factors:

1.  $Z$ , the collision frequency, how often the reactants collide with one another at a given temperature.
2.  $f$ , the fraction of molecules having an energy greater than  $E_a$  at a given temperature.
3.  $p$ , the fraction of collision that have the molecules aligned correctly for a reaction to occur.

The first 2 of these factors is temperature dependent. The last is not.

The collision frequency depends on temperature but it will not, by itself, explain the dependence of reaction rates on temperature. The dependence here is merely because as the temperature increases the speed of the molecules also increases. As a result, the number of collisions between molecules in a given period of time increases. The frequency is related to the root-mean-square speed of the molecules which is dependent on the square root of the Kelvin temperature. A  $10^\circ\text{C}$  increase in temperature results in an increase in collision frequency of around 2-5%. Most reactions, however, have rates that increase by a factor of 200-300% for a similar temperature increase.

The fraction of molecules above  $E_a$  must be the major factor in determining the temperature dependence of reaction rates. The speed, and therefore energy, distribution of molecules is given by an inverse exponential distribution.

$$f = e^{-E_a/RT}$$

In this equation  $e = 2.7182818\dots$ ,  $R = 8.31 \text{ J/mol K}$ . For the reaction of  $\text{NO}$  and  $\text{Cl}_2$   $E_a = 8.5 \times 10^4 \text{ J/mol}$ . At  $25^\circ\text{C}$  the fraction of molecules above this energy is  $1.2 \times 10^{-15}$ . At  $35^\circ\text{C}$  the fraction is  $3.8 \times 10^{-15}$  or about 3 times higher. This is a much more likely reason for the increase of reaction rates with the increase in temperature. From the above equation the fraction of molecules and the activation energy are inversely related. Reaction with a high activation energy have a low fraction of molecules above that energy and, therefore, a low reaction rate constant.

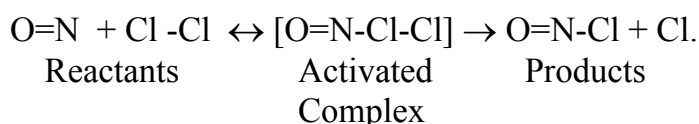
The third term in the rate constant is the orientation factor,  $p$ . This is important for the reaction to occur but is not temperature dependence. For the reaction between  $\text{NO}$  and  $\text{Cl}_2$ , in order for the reaction to occur the molecules have to meet with the Nitrogen end of the molecule pointed towards the  $\text{Cl}_2$ . If it isn't oriented in this manner, the reaction will not occur.

## *Theory 2: Transition-state theory*

Transition-state theory explains the reaction from the collision of two molecules in terms of an **activated complex**.

An **activated complex** is an unstable grouping of atoms that can break up to form products or the original reactants.

As the molecules come together, a bond starts to form between the reactants. At the same time the bonds within the reactants start to weaken. This can be represented for the reaction between NO and Cl<sub>2</sub> as:



These systems can be represented by **potential energy diagrams**. These are diagrams that show the potential energy of the system as a function of the **reaction coordinate**; how far into the reaction is the system. We can look at this for the reaction as follows:



Where NOCl<sub>2</sub><sup>‡</sup> denotes the activated complex.

The potential energy diagram indicates whether the reaction is endothermic or exothermic. It shows what the activation energies for the forward and reverse reactions are.

### ***Arrhenius Equation***

Most rate constants follow the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

which shows the temperature dependence of the rate constant. A is known as the frequency factor and is dependent on the reaction. The frequency factor is related to the product pZ from the collision theory. It has slight temperature dependence, but this dependence can usually be ignored. E<sub>a</sub> is the activation energy and is also dependent on the reaction. R is the ideal gas constant and T is the kelvin temperature.

We can take the logarithm of both sides of this equation and get a linear equation from it:

$$\ln k = \ln A - \frac{E_a}{RT}$$

We can use this relationship at two different temperatures to find a useful relationship between temperature and the rate constant.

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

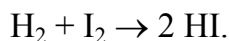
The  $\ln A$  terms are the same since they have only a very small dependence on temperature (even smaller than the  $A$  value has). If we then subtract equation 2 from equation 1 we get the relationship between temperature and the rate constant.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

This is the form of the Arrhenius equation we will use.

### *Example 1*

Calculate the rate constant at 780 K for the following reaction if the rate constant is  $3.5 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$  at 550 K. The activation energy is 188 kJ/mol.



### *Solution*

We can assign either  $k_1$  or  $k_2$  to be the rate constant we are seeking. It does not matter which. What matter is that we get the temperatures in the right places and the units to work out correctly. Let's solve for  $k_1$ . We can rearrange the equation to be:

$$\ln k_1 = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) + \ln k_2$$

We can now plug in our numbers. Keeping in mind that the ideal gas constant is in J/mol K and the activation energy is in kJ/mol. This gives us:

$$\ln k_1 = \frac{188 \times 10^3 \text{ J/mol}}{8.314 \text{ J/molK}} \left( \frac{1}{550 \text{ K}} - \frac{1}{780 \text{ K}} \right) + \ln(3.5 \times 10^{-7})$$

$$\ln k_1 = -2.742$$

$$k_1 = 0.0644 \text{ M}^{-1} \text{ s}^{-1}$$

### *Example 2*

Calculate the Activation energy for the decomposition of  $\text{N}_2\text{O}_5$  if the rate constant at  $25^\circ\text{C}$  is  $1.52 \times 10^{-5} \text{ s}^{-1}$  and at  $45^\circ\text{C}$  is  $3.83 \times 10^{-3} \text{ s}^{-1}$ .

### *Solution*

Now we need to rearrange the Arrhenius equation to find the activation energy. Doing so gives:

$$E_a = \frac{R \ln \frac{k_1}{k_2}}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$

When we plug in our numbers we find that the activation energy has the value of  $217818.9 \text{ J/mol} = 218 \text{ kJ/mol}$ .

## ***Reaction Mechanisms***

### *Elementary Reactions*

Most reactions occur via more than one step. These individual steps are called **elementary reactions**. An elementary reaction is a single molecular event, such as the collision of two molecules, which results in a reaction. The product of the elementary reaction can be either a product or an **intermediate**, a species that is produced by an elementary reaction that is later used by another elementary reaction and, as a consequence, does not appear in the overall chemical reaction. The overall chemical reaction is obtained by adding all of the individual elementary reactions.



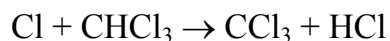
The **molecularity** of an elementary step in a mechanism is the number of molecules that act as reactants in the elementary step.

- A **unimolecular** reaction involves the breakup of a single molecule.
- a **bimolecular** reaction involves a reaction between two molecules.
- a **termolecular** reaction is extremely rare and involves the simultaneous collision between three molecules resulting in a reaction.

Higher molecularities are not encountered due to the extremely low probability of more than three molecules coming together simultaneously.

#### *Rate equation for elementary steps*

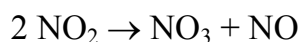
For an elementary reaction only, the rate is proportional to the product of the concentrations of the reactants. For example if an elementary step in a mechanism is the following:



the rate equation would be:

$$\text{Rate} = k[\text{Cl}][\text{CHCl}_3].$$

For this reaction:



the rate equation would be:

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

#### ***The Rate Law and Mechanisms***

The mechanism cannot be observed. Only circumstantial evidence can point to whether or not the proposed mechanism is likely to be correct. Data about the rate and the conditions of the reaction can point to one mechanism being correct over another. Once a mechanism is proposed a rate law can be derived. If the derived rate law does not agree with the experimental rate law the mechanism is not correct. Observations about the way the reaction proceeds can give information that can be used to propose a mechanism.

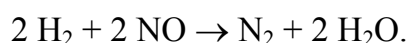
The rate of a reaction is regulated by one of the steps in the reaction. This step is called the **rate limiting step** or **rate determining step**. The rate determining step

is the slowest step in the mechanism. Think about a freeway on-ramp to understand why the rate determining step is the slowest step. The rate at which cars can enter the freeway is determined by the slowest of the cars on the on-ramp.

The rate determining step is the step in the mechanism used to start to derive the rate law for the reaction. Because the rate law for an elementary step is determined from the stoichiometry of that step we can start with the rate law for the rate determining step. After starting with this step we need to eliminate any intermediates that may appear in the rate law, because they do not appear in the overall chemical equation. Any species that are not represented in the overall chemical equation cannot be in the rate law.

### *Mechanisms with an initial slow step*

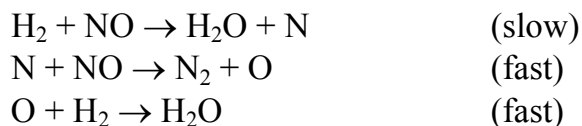
Look at the following chemical equation:



This chemical reaction has the following experimental rate law:

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

Does the data support this mechanism?

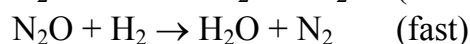
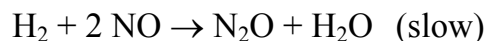


First check to make sure that it gives the correct overall equation. It does. Next, look at the rate law that is indicated by this mechanism. The first step is the slow step so we can start with that. The rate law for this step is:

$$\text{rate} = k_1[\text{H}_2][\text{NO}]$$

Because there are no intermediates in this rate law, this is the rate law according to this mechanism. It does not match the experimental rate law however, so this mechanism is not correct.

Does the data support this mechanism?



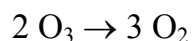
This mechanism also gives the correct overall chemical equation. But does it give the correct rate law? The rate law for this mechanism, from the rate determining step, is:

$$\text{rate} = k_1[\text{H}_2][\text{NO}]^2.$$

This is the same as the experimental rate law so the data does support this mechanism.

### *Mechanisms with a fast initial step*

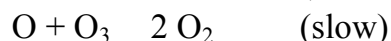
The decomposition of ozone is indicated by the following reaction:



and has the following rate law:

$$\text{rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

Let's derive the rate law from this mechanism:



The slow step here is the second one. It indicates the rate law should be:

$$\text{rate} = k_2[\text{O}][\text{O}_3].$$

This rate law contains an intermediate that must be resolved. We can do this by looking at the first equilibrium step. Because it is at equilibrium, the forward and reverse rates are the same.

$$k_1[\text{O}_3] = k_{-1}[\text{O}][\text{O}_2]$$

This can be rearranged to solve for [O].

$$[O] = \frac{k_1 [O_3]}{k_{-1} [O_2]}$$

This can then be substituted into the rate law:

$$\begin{aligned} \text{rate} &= k_2 \left( \frac{k_1 [O_3]}{k_{-1} [O_2]} \right) [O_3] \\ \text{rate} &= \frac{k_2 k_1 [O_3]^2}{k_{-1} [O_2]} = k \frac{[O_3]^2}{[O_2]} \end{aligned}$$

where, in the last step we have collected all of the constants into one constant. This rate law is the same as the experimental rate law which indicates this proposed mechanism could be valid.

## ***Catalysis***

A catalyst is a substance that increases the rate of a reaction without being consumed in the course of the reaction. It does this by providing a lower energy path for the reaction to follow. Lower activation energy translates into a larger rate constant and, therefore, a faster reaction rate. We will examine two types of catalysis, homogeneous and heterogeneous catalysis, and then look at the special case of enzyme catalysis.

### ***Homogeneous catalysis***

A homogeneous catalyst is one that exists in the same phase as the reactants. Examples of this include enzyme catalysis, which we'll look at later, the use of aqueous acids to catalyze reactions that take place in solution such as the dehydration of alcohols or, the example used in your text, the decomposition of formic acid into Carbon Monoxide and water.

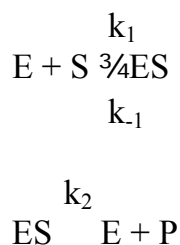
### ***Heterogeneous catalysis***

A heterogeneous catalyst is one that exists in a different phase than the reactants. This is the type of catalysis that is involved in the catalytic converter in your car. Fuel cells also use a heterogeneous catalyst to produce energy from hydrogen and oxygen gas. In heterogeneous catalysis, a solid surface acts as a site for the reaction to take place with lower activation energy. The places on the solid where this reaction is favorable are called the active sites. The reaction starts when the reactant molecules are adsorbed onto the solid surface. The reactants then diffuse

across the surface to an active site where they react. The reaction is then followed by desorption of the products from the surface.

### *Enzyme catalysis*

Enzymes are, usually, protein molecules that catalyze a very specific reaction. The operation of the enzymes follows what is known as a lock and key mechanism. The enzyme has a specific shape due to the way the protein is folded. The enzyme acts on molecules known as substrates. The shape of the substrate molecule is mirrored by the shape of the enzyme. The enzyme is the lock and the substrate is the key that opens that lock. The enzyme and substrate then combine to form a complex. The change in the chemical environment around the enzyme due to the presence of the substrate causes the shape of the enzyme to change, which, in turn, alters the substrate molecule producing the product molecules. The kinetics of this process is determined by the following two-step mechanism:



We can see that the rate of production of P (products) is determined by the second step.

$$\text{rate of production of P} = k_2 [ES]$$

If we can assume that the concentration of ES gets to the point that it doesn't change we can then see that:

$$\text{rate of formation of ES} = \text{rate of destruction of ES}$$

or

$$k_1[E][S] = (k_{-1} + k_2)[ES]$$

We do not know the concentration of free enzyme, [E], but we do know the total concentration of enzyme, [E<sub>0</sub>]. This is given by the mass balance,

$$[E_0] = [E] + [ES]$$

In other words, the total enzyme concentration is equal to the enzyme that is free and the enzyme that combines with the substrate. Substituting this into the above equation gives:

$$k_1[S]([E_0] - [ES]) = (k_{-1} + k_2)[ES]$$

$$[ES] = \frac{k_1[E_0][S]}{(k_{-1} + k_2) + k_1[S]}$$

So the rate of production of products becomes:

$$\text{rate or velocity} = \frac{k_2 k_1 [E_0][S]}{(k_{-1} + k_2) + k_1[S]}$$

If the concentration of S is very small, this becomes a simple first order reaction with respect to  $E_0$  and S. If the concentration of S is very large, it becomes first order with respect to  $E_0$  and zero order with respect to S.