Ch. 3. Chemical kinetics

THE rate at which a chemical reaction occurs is a critical parameter at an industrial and laboratory-level as the faster the speed the sooner one can commercialize or sell a given chemical product. Slow chemical reactions are, in general, less desirable as it takes more time for the reagents to react. On the other hand, too fast chemical reactions can also be less desirable. Think, for example, in an explosion in which gas and a spark quickly generate carbon dioxide with water and a lot of heat in a way that is not easy to control. This chapter deals with the rate of reactions. You will learn how to calculate what we call a rate law which is a mathematical formula that gives the numerical rate value. You will also learn the collision theory that explains the factors that affect the speed of chemical reactions.

3.1 Rate of reaction

Some chemical reactions are fast such as the explosive reaction between cooking gas and oxygen, happening almost instantaneously. Other reactions are slow such as the rusting of iron, taking months to occur. Chemical kinetics is a chemistry discipline that studies the speed of chemical reactions and the factors that affect this measure. The overall goal here is to understand the factors that control the rate of reactions with the ultimate goal of maximizing the generation of products. This section covers the principles of reaction rates, defining two different types of rates, and showing how to interconvert rates of reaction.

Two different ways of defining the reaction rate When a chemical reaction proceeds, reactants decompose into products. Therefore, the concentration of reactants decreases with time as reactant molecules become products, and the concentration of products increases with time as products are being formed. This change in concentration with time is what we call reaction rate. There are two different ways of defining the rate of a reaction. We can define the average reaction rate $\overline{r}$ as the change in concentration with time or as an instantaneous rate r when the time interval is very small (we call this derivative):

$$\overline{r} = \frac{\Delta c}{\Delta t} \quad \text{or} \quad r = \lim_{\Delta t \to 0} \frac{\Delta c}{\Delta t} = \frac{dc}{dt} \tag{3.1}$$

Both types of rates are not numerically the same. The average rate is an average change in concentration between two different times. At the same time, the time interval for the average can be large or small. Differently, the instantaneous rate is calculated as the slope in the concentration vs. time plot at a given time–using mathematical terms

we call this the derivative. Instantaneous rates represent more accurately the changes in concentration happening in a reaction. For this reason, from now on, whenever we describe a reaction rate we will refer to the instantaneous rate.
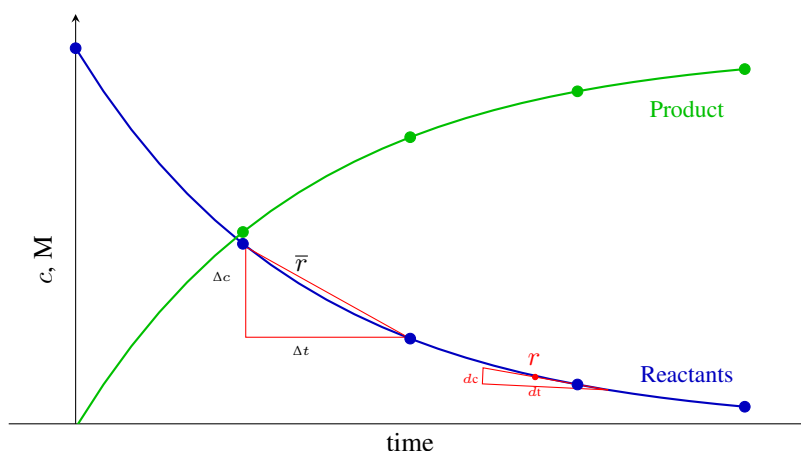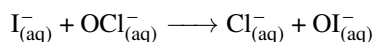

Figure 3.1 Change of the concentration of reactants and products with time showing the average and instantaneous velocity.

Rate of appearance and disappearance At the beginning of a reaction, the molecules of reactants will be consumed while the molecules of products will form (see Figure 3.1). There are three different ways to measure the reaction rate. We can measure the amount of reactants that disappear per unit of time and this would give you the rate of disappearance of a reactant. We can also measure the amount of products formed per unit of time and that would give you the rate of appearance of a product. As a note, rates of disappearance are negative (as the molarity of reactants decreases with time) whereas rates of appearance are positive. Finally, we can measure the amount of reactants the interconvert into products and that would give you the overall rate of reaction, which is always a positive number. Overall, by measuring concentration changes of reactants and products we can compute three types of rates: rates of disappearance, rates of appearance, and rates of reaction. Let us work on a sample reaction:

$$I^-_{(aq)} + OCl^-_{(aq)} \longrightarrow Cl^-_{(aq)} + OI^-_{(aq)}$$

We can think of the rate of disappearance of $I^-_{(aq)}$ that should be written as:

$$r_{I^-} = \frac{d[I^-]}{dt}$$

Similarly, we have that the rate of appearance of Cl^- is:

$$\overline{r}_{Cl^-} = \frac{d[Cl^-]}{dt}$$

As chemical rates represent the change of concentration of a given reactant with time, the units for a chemical rate are M/s.

Relating rates of appearance and disappearance We can relate the rates of any two reactants or products in a chemical reaction and, at the same time, we can relate the rate of reaction with the rate of any product or reactant–remember there is a single rate of reaction and multiple rates of appearance and disappearance of products and reactants. For example, for the following reaction:

$$4\,NH_{3(g)} + 5\,O_{2(g)} \longrightarrow 4\,NO_{(g)} + 6\,H_2O_{(g)}$$
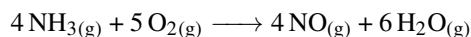
We can relate r_{NH_3} and r_{H_2O}:

$$-\frac{1}{4}r_{NH_3} = +\frac{1}{6}r_{H_2O}$$

Overall, a negative sign should be included before the rate of any reactant and a positive sign before the rate of any product. You also need to divide by the stoichiometric coefficients of each reactant and product. Similarly, we can relate r_{O_2} with the rate of reaction r:

$$-\frac{1}{5}r_{O_2} = r$$

For a general equation such as:

$$aA + bB \longrightarrow cC + dD$$
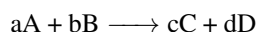
we have that the general relationship between any rate and the overall reaction rate is:

$$\boxed{r = -\frac{1}{a}r_A = -\frac{1}{b}r_B = +\frac{1}{c}r_C = +\frac{1}{d}r_D} \qquad (3.2)$$

Sample Problem 1

For the reaction below, the rate of disappearance of A is -0.1M/s. Calculate: (a) The rate of disappearance of B. (b) The rate of appearance of C. (c) The rate of appearance of D. (d) The rate of reaction.

$$2\,A + 3\,B \longrightarrow 4\,C + 5\,D$$
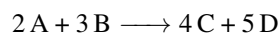
SOLUTION

In order to calculate the rate of disappearance of B, we will use the following relationship, in which the rate of disappearance of A and B have a negative sign and carries the respective stoichiometric coefficient

$$-\frac{1}{2}r_A = -\frac{1}{3}r_B$$

We know r_A and hence we can solve for r_B:

$$-\frac{1}{2}(-0.1) = -\frac{1}{3}r_B$$

We have that r_B is -0.15M/s. We will now use a similar relationship to calculate r_C:

$$-\frac{1}{2}(-0.1) = +\frac{1}{4}r_C$$

We have that r_C is +0.2M/s. Finally, we will calculate r_D and r:

$$-\frac{1}{2}(-0.1) = +\frac{1}{5}r_D \text{ and } -\frac{1}{2}(-0.1) = r$$

We have that r_D is +0.25M/s and r is 0.05M/s. Mind the rate of disappearance of reactants are negative, whereas the rate of appearance of products and the overall rate of reaction are positive numbers.

◈ STUDY CHECK

For the reaction below, the rate of appearance of C is 0.3M/s. Calculate: (a) The rate of disappearance of A and B. (b) The rate of appearance of D. (c) The rate of reaction.

$$5\,A + 2\,B \longrightarrow C + 2\,D$$

▶Answer: r_A=-1.5M/s, r_B=-0.6M/s, r_D=0.6M/s, and r=0.3M/s

| | 0 min | 5 min | 10 min | 500 min |

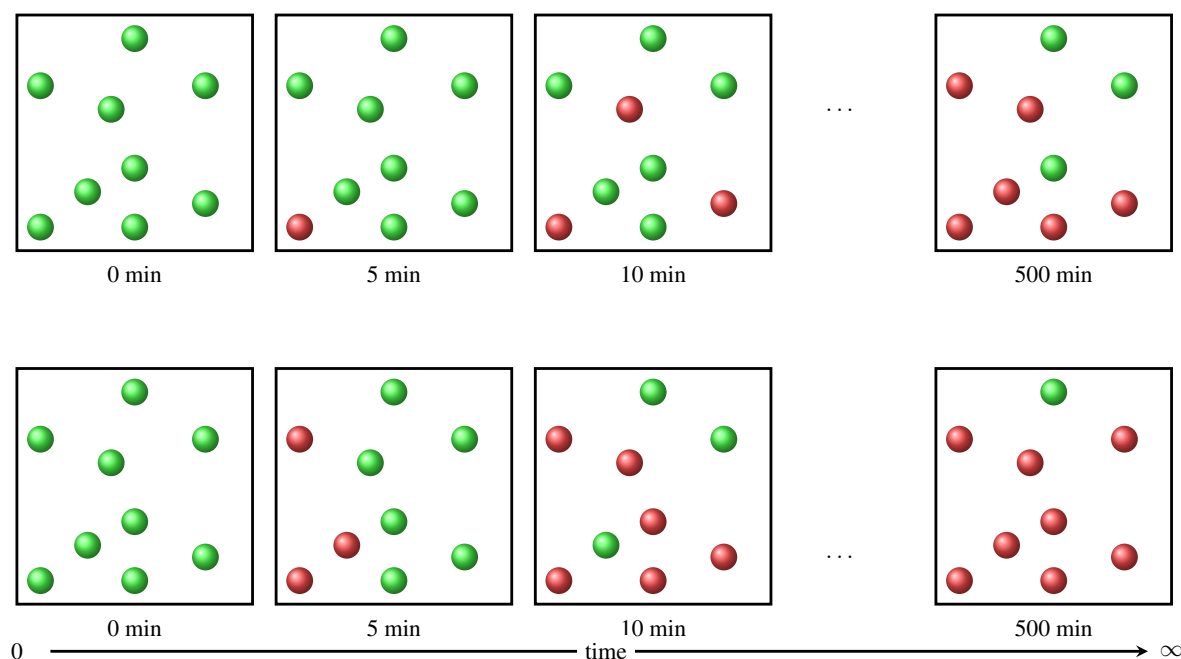0 min   5 min   10 min   500 min

0 ——— time ——— ∞

Figure 3.2 A fast and a slow reaction

3.2 Rate law

Some chemical reactions double their rate by increasing the concentration of reactants, whereas, for the same change of concentration, others quadruple their rate. The rate law of a reaction is an experimental formula that explicitly includes the power dependence of the rate of reaction on the concentration of reactants and products. You can find rate laws in a differential form and in an integrated form. On one hand, the differential rate law, or simply the rate law, is convenient when we want to assess the impact of concentration on the rate of reaction. On the other hand, integral rate laws give the time dependency of the concentration, being convenient to track how the reactants disappear with time. This section will cover how to interpret rate laws and how to differentiate rate laws from integral rate laws. It will also introduce the concept of the partial and the total order of reaction, as well as the idea of reaction rate constant.

The rate law The rate law is an experimental expression, a formula that comes from an experiment, relating the rate of reaction with the concentration of the chemicals that impact the rate. An example of a rate law would be:

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

where:

r is the overall rate of reaction

k is the rate constant

$[NO]$ is the molarity of NO

$[O_2]$ is the molarity of O_2

So, what is the purpose of a rate law? Let us use the following rate law as an example:

$$r = 0.002[NO]^2[O_2]$$

By means of the rate law above, we can compute the numerical value of the rate of reaction for different concentrations. As such, rate laws help predict the value of the reaction rate.

Partial and overall reaction orders The powers in the rate law are called reaction order. For example, in the rate law below

$$r = k[NO]^2[O_2]$$

the order of NO is 2 as the power of NO in the rate law is 2. Similarly, the partial order of O_2 is 1 as the power of O_2 in the rate law is 1. The overall reaction order it 3, and this number results in adding all partial orders. Regarding the way we describe the reaction order, if the reaction order is one, we would say that the reaction is first order. Similarly, if the reaction order is two, we would say the reaction is second order, and so on. The reaction order can also be zero when the power in the rate law is zero. Reaction orders tend to be integer numbers such as 0, 1, or 2, mostly in educational problems. However, using realistic kinetic data, the partial and total orders can be any number and even have a negative sign. The reaction orders are very important as they indicate how the reaction rate responds to changes in concentration. For example, using the rate law above, if we double the concentration of O_2 the rate law will double, but if we double the concentration of NO, the reaction rate would quadruple, that is, it would be four times larger.

The rate constant, k The rate constant is a critical parameter of a rate law as it tells how the reaction responds to changes on molarity. For example, look this two different rate laws:

$$r_A = 0.01[N_2O_5] \qquad \text{and} \qquad r_B = 0.001[N_2O_5]$$

We have that as the rate constant in r_A is larger the changes in the concentration of N_2O_5 will have a stronger impact on the rate than in r_B.

Sample Problem 2

Given the following rate law. Indicate: (a) The rate constant giving the correct units. (b) The partial order of all species. (c) The total order of the reaction. (d) If $[F_2]$ is doubled how would the reaction rate be affected?

$$r = 0.002[Cl_2][F_2]^3$$

SOLUTION

Given the information provided in the rate law, we have that the reaction is first

order with respect to Cl_2 and third order with respect to F_2. The overall reaction order is four. The rate constant is 0.002 $1/M^2$s.

◈ STUDY CHECK

Given the following rate law. Calculate: (a) The rate constant giving the correct units. (b) The partial order of all species. (c) The total order of the reaction. (d) If $[A]$ is doubled how would the reaction rate be affected?

$$r = 0.056[A]^4[B]^2[C]^2$$

▶Answer: Orders: A(4), B(2), C(2), overall(8); k=0.056 $1/M^7$s; 16 times larger

The rate constant units The units of a rate constant are determined by the reaction order. In other words, given a reaction order, we will have a given unit for the rate constant. At the same time, given the units of a rate constant, we can also determine the order of the reaction. The following formula gives the constant units for a given reaction order n:

$$\boxed{\frac{M^{1-n}}{s}} \tag{3.3}$$

where:

$$n \text{ is the reaction order}$$

For example, for first-order reaction (n=1) the units of the reaction constant are 1/s and for a second-order reaction, the units are 1/Ms. For a reaction of zero-order, the units of the constant are M/s. This formula results from a dimensional analysis given that the units of reaction rate r are M/s and the units of concentration is molarity, M. As a side note, here we will use second as a unit of time, however, one can envision a similar formula for different time units.

Sample Problem 3

Given the following rate constants indicate the reaction order: (a) k=0.04 M/s (b) k=0.09 1/M·s (c) k=0.03 $1/M^4$·s

SOLUTION

We will use Formula 3.3 to calculate the reaction order. We have that 0.04 M/s is order zero, 0.09 1/Ms is second order and 0.03 $1/M^4$s is fifth order.

◈ STUDY CHECK

Given the following rate constants indicate the reaction order: (a) k=0.03 1/s (b) k=3×10^{-4} L/s·mol (c) k=3×10^{-5} 1/s·M^2

▶Answer: (a) Order 1 (b) Order 2 (c) Order 3

Integral reaction law The reaction law is more specifically called a differential reaction law as it represents a differential equation–this is a mathematical term to describe equations in terms of derivatives. For a differential rate law, there is an integral rate law. The integral rate law is obtained using a mathematical technique called integration–this technique is out of the scope of this class. For example, below we have an example of a differential and integral rate law for a first-order reaction.

$$r = 0.01[N_2O_5] \qquad \text{and} \qquad Ln[N_2O_5] = -0.01 \cdot t + Ln(0.1)$$

In the differential rate law, we have the explicit reaction rate r accompanied by molarities ($[N_2O_5]$), whereas in the corresponding integral rate law we have molarities ($[N_2O_5]$) accompanied of time. The integral rate law gives the change of the concentration with time, whereas the differential rate law gives the change of the reaction rate with concentration. Each type of law has its purpose and differential rate laws are more common and used when we have experimental data in terms of reaction rates and molarities. The integrated rate law is used when we have data in terms of molarity and time. Overall, differential rate laws and integral rate laws are exchangeable. To convert a differential rate law into its corresponding integral rate law we just need the initial concentration of the species involved in the law, $[A]_0$. For example, the corresponding differential and integral rate law for a zeroth-order reaction are: Table 3.1 reports the corresponding differential and integral rate laws for different orders.

Table 3.1 Corresponding differential, integral rate laws and half-life formulas

Order	Differential rate law	Integral rate law	Hal-life ($t_{1/2}$) formula
0	$r = k$	$[A] = -k \cdot t + [A]_0$	$\frac{[A]_0}{2k}$
1	$r = k[A]$	$\text{Ln}[A] = -k \cdot t + \text{Ln}[A]_0$	$\frac{0.693}{k}$
2	$r = k[A]^2$	$\frac{1}{[A]} = k \cdot t + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$

Sample Problem 4

Identify the following rate law as differential or integral and switch into the other form.

$$\frac{1}{[C_2H_6]} = 4 \times 10^{-4} \cdot t + \frac{1}{0.03}$$

SOLUTION

As the equation contains time this would be a integrated rate law. We can use Table 3.1 to identify the order and compute the differential law. This is a second order reaction with rate constant 4×10^{-4} 1/s, therefore:

$$r = 4 \times 10^{-4}[C_2H_6]$$

◈ **STUDY CHECK**

Identify the following rate law as differential or integral and switch into the other form for an initial concentration of 0.3M.

$$r = 5 \times 10^{-2}$$

▶Answer: $[A] = -5 \times 10^{-2} \cdot t + 0.3$

Half-life, $t_{1/2}$ When a reaction starts to happen, the concentration of reactants decreases with time. Half-life is the time at which the initial concentration of reactants

is half its initial value. Reactions with small half-life are fast, as they take a short time to reduce the concentration of reactants to half. Differently, reactions with large half-life are slow as they need longer times to proceed. This way, the numerical value of half-life helps you compare the speed of reactions. At the same time, the half-life is a transformation of the rate constant into a time value. That is, by rate constants can be converted into half-lives. There is a single half-life formula for each reaction order and Table **??** reports some half-life formulas. If you wonder, where these formulas come from, one can obtain all these formulas by using $[A] = [A]_0/2$ in any integral rate law. For example, for a first order reaction we have that:

$$\text{Ln}[A] = -k \cdot t + \text{Ln}[A]_0$$

When $[A] = [A]_0/2$ we have that $t = t_{1/2}$ and therefore:

$$\text{Ln}\left(\frac{[A]_0/2}{[A]_0}\right) = -k \cdot t_{1/2}$$

that leads to

$$t_{1/2} = -\frac{\text{Ln}(0.5)}{k}$$

Sample Problem 5

Calculate the half-life for a second order reaction with initial concentration of 5.99×10^3 M if the rate constant is 0.005 1/Ms?

SOLUTION

As we deal with a second order reaction, we will use $\frac{1}{k[A]_0}$ given that $[A]_0 = 5.99 \times 10^3$M and k=0.005 1/Ms. We have that

$$t_{1/2} = \frac{1}{0.005 \cdot 5.99 \times 10^3} = 0.03s$$

◈ **STUDY CHECK**

Calculate the half-life for a first order reaction with initial concentration of 5.99×10^3 mol/L if the rate constant is 0.02 1/s?

▶Answer: 34.65s

3.3 The differential and integral methods for obtaining rate laws

Up to now, we analyzed the importance of using rate laws. However, before this point, all rate laws were given. This section will cover how to experimentally obtain rate laws by analyzing experimental data. There are two main methods for obtaining rate laws: the differential method and the integral method and each method differs not only on the nature of the experimental data gathered but also on how this data is processed.

The differential method The differential method also called the method of the initial rates measures velocities for different concentrations, and in particular, measures initial velocities. These are velocities at very short times after the reaction starts. This method is convenient when there are parasite reactions that compete with the reaction one wants to study. By using initial rates, we can minimize the impact of competing reactions on the kinetic data. In this method, by comparing different velocities for

different concentrations one can calculate the reaction order and the rate constant, that is, one can construct the rate law. The next example will show you how to use this method. As a note, one can only use the differential method when reaction rates data is supplied.

Sample Problem 6

Use the data below to calculate the rate law of the following reaction:

$$A \longrightarrow B$$
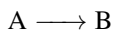
Experiment	r (M/s)	$[A]$, (M)
1	0.5	0.5
2	0.72	0.6

SOLUTION

As they provide values of $[A]$ the rate law should be $r = k[A]^n$. In order to calculate the rate law we need the values of k and n. We will apply the rate law two the two different experiments and divide:

$$\left.\begin{array}{l} 0.5 = k0.5^n \quad \text{(Experiment 1)} \\ 0.72 = k0.6^n \quad \text{(Experiment 2)} \end{array}\right\} \frac{0.5}{0.72} = \frac{\cancel{k}}{\cancel{k}} \cdot \left(\frac{0.5}{0.6}\right)^n$$

This approach will cancel k leaving only n.

$$0.694 = (0.833)^n$$

Remember that if we divide two numbers with the same exponent we can combine the numbers and share the exponents. In order to solve for n we need to apply natural logarithms (or simply log) to both sides of the equation in order to move the exponent down:

$$Ln(0.694) = n \cdot Ln(0.833) \text{that gives } n = \frac{Ln(0.694)}{Ln(0.833)} = 1.99 = 2$$

Remember the orders are normally integer numbers so you can round to the closes integer. Now that we have the order, we can use the rate law again to obtain the rate constant using for example: r=0.5M/s and $[A]$ =0.5M, and given that now we know n=2

$$0.5 = k0.5^2$$

Solving for k we have k=2 1/Ms. We have that the reaction law is: $r = 2[A]^2$

◈ STUDY CHECK

Use the data below to calculate the rate law of the following reaction: $A \longrightarrow B$

Experiment	r (M/s)	$[A]$, (M)
1	0.5	2.5
2	0.6	3.0

▶Answer: $r = 0.2[A]^1$

The differential method with two reactants This previous example

was useful to obtain the rate law using data involving only the concentration of one reactant. In other words, the previous example was useful to obtain simple rate law such as:

$$r = k[A]^x$$

The next example will cover how to calculate the rate law when the data provided involved the concentration of two reactants and therefore the rate law contains the orders of two species. In other words, the next example will show how to obtain more complex rate laws such as:

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

in which we do not know the reaction constant and two of the order.

Sample Problem 7

Use the data below to calculate the rate law of the following reaction: A + B $\longrightarrow$ C

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.5	0.2	0.25
2	0.6	0.2	0.36
3	0.5	0.3	0.375
4	0.6	0.3	0.54

SOLUTION

As they provide values of $[A]$ and $[B]$ the rate law should be $r = k[A]^n[A]^m$. In order to calculate the rate law we need the values of k, n and m. We will apply the rate law two the two different experiments and divide. But this time we will sort the data appropriately. In order to calculate the order or A we will select the data with different values of $[A]$ and the same value of $[B]$:

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.5	0.2	0.25
2	0.6	0.2	0.36

Again, we will apply the rate law to each Experiment:

$$\left. \begin{array}{l} 0.25 = k0.5^n0.2^m \quad \text{(Experiment 1)} \\ 0.36 = k0.6^n0.2^m \quad \text{(Experiment 2)} \end{array} \right\} \frac{0.25}{0.36} = \frac{\cancel{k}}{\cancel{k}} \cdot \left(\frac{0.5}{0.6}\right)^n \cdot \left(\frac{\cancel{0.2}}{\cancel{0.2}}\right)^m$$

This approach will cancel k and $[B]$ leaving only n giving

$$0.694 = (0.833)^n$$

In order to solve for n we need to apply natural logarithms (or simply log) to both sides of the equation in order to move the exponent down:

$$Ln(0.694) = n \cdot Ln(0.833) \text{that gives } n = \frac{Ln(0.694)}{Ln(0.833)} = 1.99 = 2$$

Again, remember the orders are normally integer numbers so you can round to the closes integer. In order to calculate the order or B we will select the data with different values of $[B]$ and the same value of $[A]$:

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.5	0.2	0.25
3	0.5	0.3	0.375

Again, we will apply the rate law to each Experiment:

$$0.25 = k0.5^n0.2^m \quad \text{(Experiment 1)}$$
$$0.375 = k0.5^n0.3^m \quad \text{(Experiment 3)}$$

$$\frac{0.25}{0.375} = \frac{\cancel{k}}{\cancel{k}} \cdot \left(\frac{\cancel{0.5}}{\cancel{0.5}}\right)^n \cdot \left(\frac{0.2}{0.3}\right)^m$$

We have that $0.666 = (0.66)^m$. The order of B is $m=1$. Now that we have the order, we can use the rate law again to obtain the rate constant using any of the experiments:

$$0.25 = k0.5^20.2^1 \quad \text{(Experiment 1)}$$

r=0.5M/s and $[A]$ =0.5M, and given that now we know n=2

$$0.5 = k0.5^2$$

Solving for k we have k=2 1/M^{2}s. We have that the reaction law is: $r = 2[A]^2[B]^1$

◈ STUDY CHECK

Use the data below to calculate the rate law of the following reaction: A + B $\longrightarrow$ C

Experiment	$[A]$ (M)	$[B]$ (M)	r (M/s)
1	0.5	0.2	2×10^{-4}
2	0.6	0.2	2×10^{-4}
3	0.5	0.3	4.5×10^{-4}
4	0.6	0.3	4.5×10^{-4}

▶Answer: $r = 5 \times 10^3[B]^2$

Table 3.2 The integral method					
Order	y	x	Slope	Slope Sign	Intersect
0	$[A]$	t	$-k$	$-$	$[A]_0$
1	$Ln([A])$	t	$-k$	$-$	$Ln([A]_0)$
2	$\frac{1}{[A]}$	t	$+k$	$+$	$\frac{1}{[A]_0}$

The integral method: an introduction The integral method is used to calculate the rate law if data reporting concentration and time are given. To understand the use of the integral method, it is convenient to learn more about integral rate laws. Let us analyze the integral rate law for a zeroth-order reaction:

$$[A] = -k \cdot t + [A]_0$$

If you look carefully you could notice that this integral rate law is indeed a linear relationship. The term $[A]_0$ and k are constants. Differently, the terms A] and t are variables. Linear relationships are mathematical relationships with an independent variable represented in the horizontal axes and a dependent variable represented in the

vertical axis. In the rate law above the independent variable is t and the dependent variable is [A] and for every value of t we would have a given value of [A]. Moreover, $-k$ is the slope of the relationship, and $[A]_0$ is the intersect. Let us analyze another integral rate law, this time for a first-order reaction:
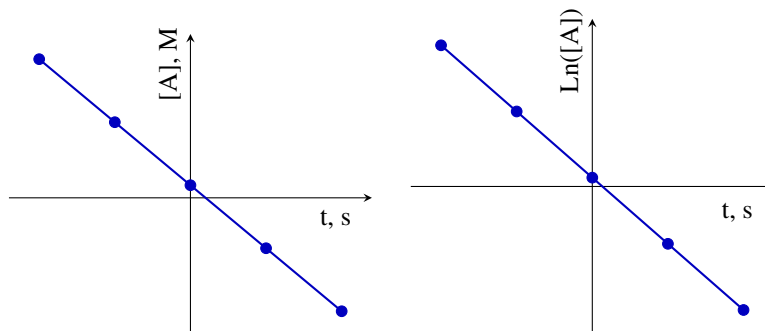
$$Ln[A] = -k \cdot t + Ln[A]_0$$

we have that this law also represent a linear relationship as well, with t as independent variable (the x) and $Ln([A])$ as the dependent variable (the y). The slope is $-k$ and the intersect is $Ln([A]_0)$. Overall, we have that all integral rate laws are linear relationship with t as the x and different properties as the y: [A] for a zeroth-order, $Ln([A])$ for a first-order reaction and $\frac{1}{[A]}$ for a second-order reaction. We also have that the slope of the lines in absolute value always gives k. This information is summarized in Table 3.2.

The integral method is based on plotting some kinetic data, for example, concentration vs. time, and fitting the data into a linear relationship. If the quality of the fit is good enough, by reading the slope of the line and the intersect one can compute the rate law that rules the reaction. To associate the experimental data into a line we use linear regression, a statistical tool that gives the equation of the best line that fits the experimental data. At the same time, linear regression gives an estimate of the goodness of the fit through a regression parameter, r or r^2, depending on the statistics software employed. Overall, is good to keep in mind that every plot ([A] vs. t, Ln[A] vs. t or $1/[A]$ vs. t) is associated to a specific order.

The integral method: associating a linear plot with an order

The base of the integral method is to create three different plots: (a) [A] vs. t (b) $Ln[A]$ vs. t and (c) $\frac{1}{[A]}$ vs. t. In all plots, time is always indicated in the horizontal axis. Based on the data, only one of the plots will be the best linear plot with a regression coefficient r^2 closer to one. The perfect linear plot will be associated with an order (here, either 0, 1, or 2). If the plot [A] vs. t gives a perfect line the reaction will be zeroth-order. If the plot $Ln([A])$ vs. t gives a perfect line the reaction will be first order. If the plot $\frac{1}{[A]}$ vs. t gives a perfect line the reaction will be second-order. It is convenient to practice identifying the different plots and associating them with an order. The following example covers just that.

> **Sample Problem 8**
>
> The following plots results from processing kinetic data by means of the integral method. They are all perfect lines with r^2=0.99. Indicate the order of the reaction.
>
>
>
> **SOLUTION**
> We will inspect the linear plot and based on what is represented on the vertical and horizontal axis we will conclude the reaction order. The plot on the left represents molarity on the vertical axis and time on the horizontal. This is a

zeroth-order reaction. On the other hand, the plot on the right represents the logarithm of molarity on the vertical axis and time on the horizontal axis. This is a first-order reaction.

◈ STUDY CHECK

The following plots results from processing kinetic data by means of the integral method. They are all perfect lines with r^2=0.99. Indicate the order of the reaction.
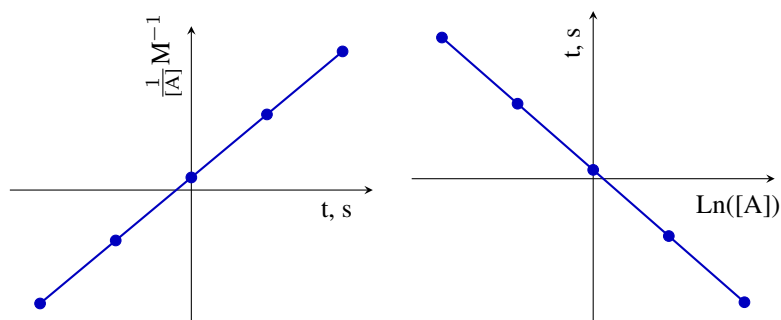
▶Answer: Left (order 2), right (order 1)

How to carry out a linea regresion with a calculator First and foremost, to carry out a linear regression, you need a graphing calculator. In general, Casio calculators are very user-friendly and easy to use. Differently, Texas calculators tend to be hard to employ. Here I will show how to carry out a linear regression displaying the correlation coefficient r^2 parameter on the screen first using a Casio calculator and then using a Texas calculator. You need to follow the following steps to carry out a linear regression in a Casio fx 9750GII:

1 **Step one:** Enter the data: start the calculator and press menu+2 (stat) to access the list menu. You will follow all the steps on this menu. Type the X values in List 1 and Y in List 2.

2 **Step two:** Press Calc (F2) on the bottom menu of the screen, then press Reg (F3) to press X (F1) and then $ax + b$ (F1).

3 **Step three:** At this point, you will have all the results from the regression on the screen.

You need to follow the following steps to carry out a linear regression in a TI 84:

1 **Step one:** Enter the data: press Stat and Enter. Type the X values in List 1 and Y in List 2.

2 **Step two:** Press Second and Zero to access the catalg. Now, go down the menu until you find DiagnosticOn and select it.

3 **Step three:** Now carry out the regression by pressing Stat and Calc. Now go down on the menu until you find $ax + b$ and press it.

4 **Step four:** At this point, you will have all the results from the regression on the screen.

*The integral method: extracting data from linear regressions*
We will practice the integral method by extracting the rate constant and the initial reactant concentration from the linear regression data. Linear regression software will

give the equation of a line and the associated r coefficient. We will have to read the slope and the intercept of the equation and infer the rate constant and the initial reactant concentration $[A]_0$. The rate constant will be obtained from the slope of the line, whereas $[A]_0$ is related to the intercept. For all cases, the absolute value of the slope of the line equation will correspond to the rate constant k. The relationship between $[A]_0$ and the intercept differs based on the order. For a zeroth-order plot, the intersect directly corresponds to the initial concentration. Differently, for a first-order reaction, the intercept corresponds to $Ln([A]_0)$. Therefore, to obtain $[A]_0$ you will have to compute the exponential of the intersect: $[A]_0 = e^{Intersect}$. Finally, for a second-order reaction, the slope will correspond to the inverse of the initial concentration, and hence, to obtain $[A]_0$ we will have to compute the inverse of the intersect: $[A]_0 = \frac{1}{Intersect}$. The following example shows how to obtain the rate constant and $[A]_0$ using regression results.

Sample Problem 9

The following plots results from processing data by means of the integral method. Interpret the linear regressions and indicate the rate law.

$$y=-0.005x+0.3 \; r^2=0.99$$

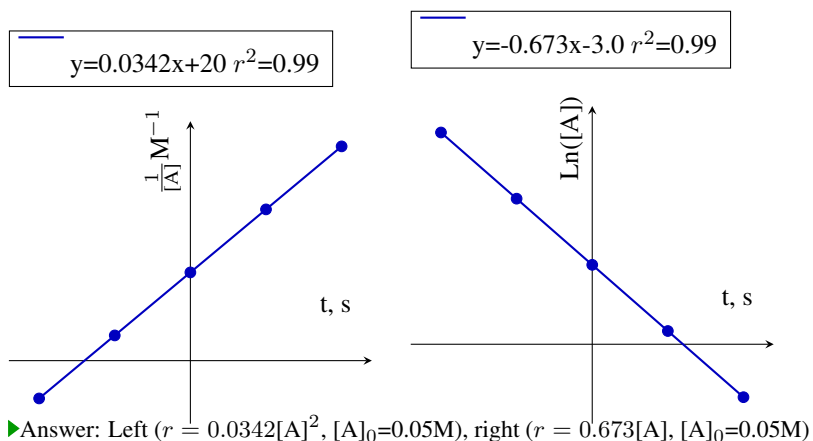$$y=-0.012x+0.006 \; r^2=0.99$$
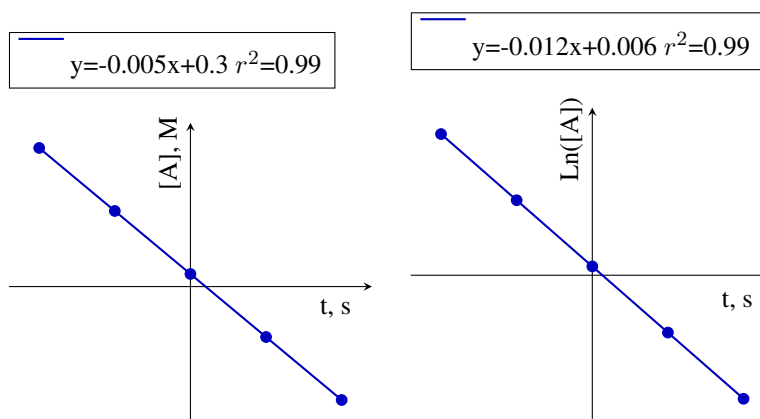
SOLUTION

We will inspect the linear regression to identify the reaction order. From the absolute value of the slope, we will obtain the rate constant. The plot from the left represents molarity and hence this is a zeroth-order reaction with a rate constant k=0.005M/s. The rate law would be: $r = 0.005$. The plot from the right displays the logarithm of the concentration and hence this would be a first-order reaction, with a rate constant k=0.012 1/s. The rate law would be: $r = 0.012[A]$. We can also calculate the initial concentration for each plot. On the left plot, we have that as this is a zeroth-order reaction the intercept directly gives you the initial concentration of reactants: $[A]_0$=0.3M. On the right plot, we have that as this is a first-order reaction the intercept gives you the logarithm of the initial concentration of reactants. We have that $Ln([A]_0)$=0.006 and hence $[A]_0=e^{0.006}$=1.006M.

◈ STUDY CHECK

The following plots results from processing data by means of the integral method. Interpret the linear regressions and indicate the rate law and the initial concentration of reactants.

y=0.0342x+20 r^2=0.99

y=-0.673x-3.0 r^2=0.99

$\frac{1}{[A]}$M^{-1}

Ln([A])

t, s

t, s

▶Answer: Left ($r = 0.0342[A]^2$, $[A]_0$=0.05M), right ($r = 0.673[A]$, $[A]_0$=0.05M)

▼Speed is a critical concept in chemistry
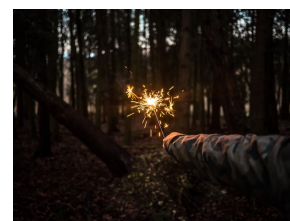
© www.wallpaperflare.com

▼Explosions are fast reactions

© www.wallpaperflare.com

▼Sparks can activate reactions

© www.wallpaperflare.com

Sample Problem 10

Using the following data, apply the integral method to calculate the order and rate constant and write down the rate law.

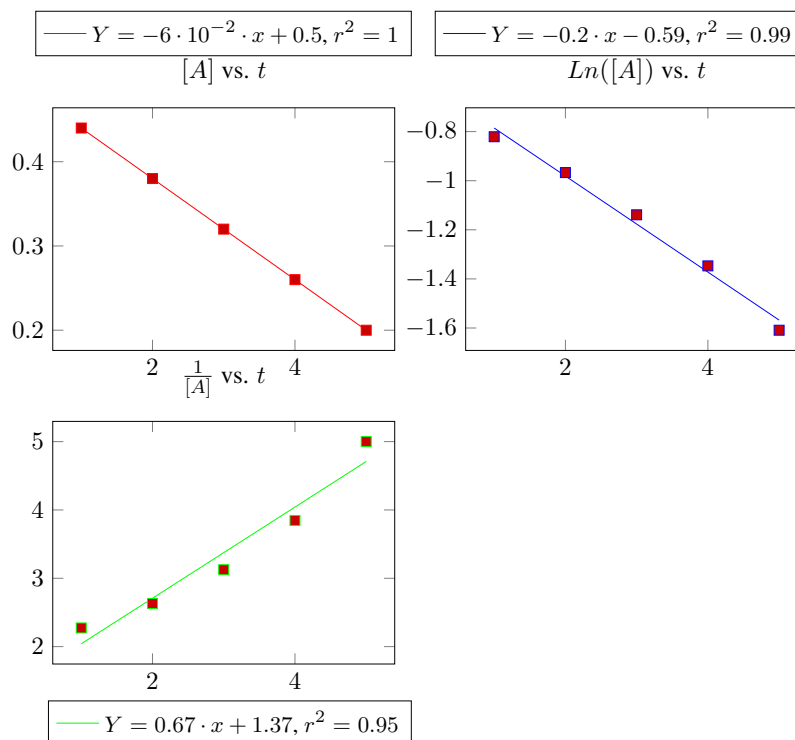| t (s)	1	2	3	4	5
$[A]$, (M)	0.44	0.38	0.32	0.26	0.20

SOLUTION

We will apply the integral method and will process the data calculating the logarithm of the molarity and the inverse of molarity. It is recommended to use three digits in order for the regression to be consistent:

t (s)	$[A]$, (M)	$Ln([A])$	$\frac{1}{[A]}$, (M^{-1})
1	0.440	-0.821	2.273
2	0.380	-0.967	2.631
3	0.320	-1.139	3.125
4	0.260	-1.347	3.846
5	0.200	-1.609	5.000

Now we will create three different plots and carry linear regressions for each:

Legend: $Y = -6 \cdot 10^{-2} \cdot x + 0.5, r^2 = 1$ — $[A]$ vs. t; $Y = -0.2 \cdot x - 0.59, r^2 = 0.99$ — $Ln([A])$ vs. t; $\frac{1}{[A]}$ vs. t; $Y = 0.67 \cdot x + 1.37, r^2 = 0.95$

We have the the reaction can be order zero or order one, as for both cases r^2 is larger or equal to 0.99. However, the fir for zeroth-order is better, so we will choose that possibility. For an oder zero plot, the absolute value of the slope gives the rate constant. The final rate law would be: $r = 6 \times 10^{-2}$.

◈ **STUDY CHECK**

Using the following data, apply the integral method to calculate the order and rate constant and write down the rate law.

t (s)	0	6	12	18	24
$[A]$, (M)	1.0000	0.5000	0.2500	0.1250	0.0625

▶Answer: $r = 0.115[A]$

The integral method in action Now we are ready to work from scratch on a set of data from the integral method. Normally, data involving concentration and time will be given. To apply the integral method, we need to process these data into three different columns, reporting the concentration, the logarithm of the concentration, and the inverse of the concentration. Next, we will do three plots and we will obtain the regression line for each plot. We will compare the goodness of the fit by assessing the value of r^2. The closer this value to one the better the fit. This analysis will lead to the reaction order. Finally, after we have selected the plot that corresponds to the best fit, we will analyze the regression line and extract the rate constant and initial molarity of reactants.

The integral method for more than one reactant The integral methods can also be applied to obtain rate laws involving more than one reactant (e.g. $r = k[A][B]^x$). For this case we will obtain pseudo rate-constants. In general rate constants only depend on the temperature and not on concentration. However, let us assume we want to calculate a rate law that depends on two reactants ($[A]$ and $[B]^x$),

and we start the experiment by using a very large molarity of one of them so that during the reaction this value do not change much. On the other hand, we use a smaller molarity for the other reactant and we want to apply the integral method to his molarity. We will have that [A] is approximately constant (let us call this $[A]_0$), whereas [B] is not. We can include the constant molarity in the rate law (as it is constant) so that we have

$$r = k[A]_0[B]^x \simeq k'[B]^x$$

And we have that

$$k' = k[A]_0$$

Applying the integral method we can find out the order of B and the pseudo rate constant. Once we have the pseudo constant, as we control $[A]_0$ we can always obtain the real rate constant.
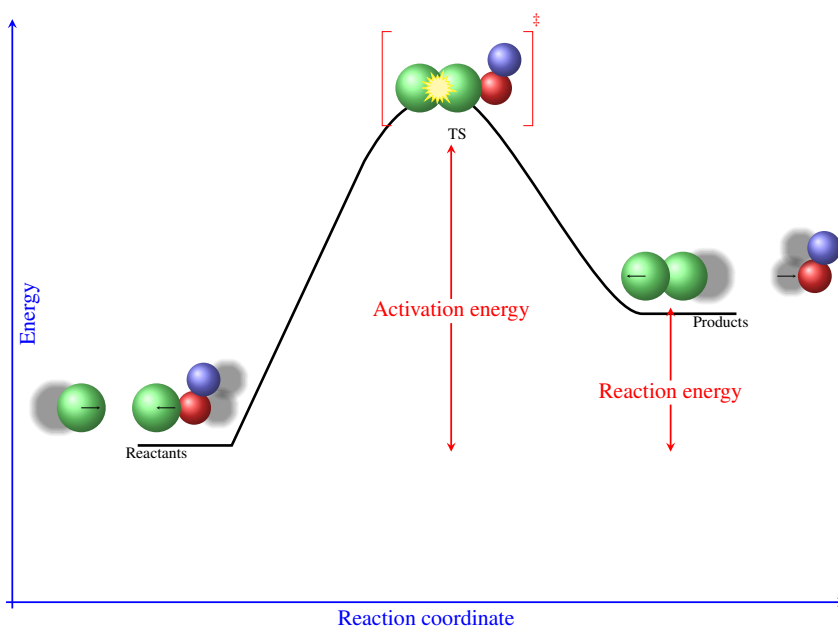

**Figure 3.4** Energy diagram showing the conversion of reactants into products

3.4 Collision theory

The rate of reaction depends on temperature and reactions proceed at a higher speed at higher temperatures. This is the reason we use refrigerators and freezers to keep food for a longer time. The collision theory provides a microscopic understanding of chemical reactions. A pivotal element of this theory is the transition state also called the activated complex. This is an ephemeral state between reactants and products so that if the reaction proceeds until this point, reactants will certainly evolve into products. The energy difference between the reactants and the transition state of a reaction is called the activation energy. Energy diagrams are useful representations of the energy changes involved in a reaction. By analyzing an energy diagram we can predict whether a reaction is endo of exothermic and estimate the energy involved in the activation of a reaction. This section covers the fundamental principles of collision theory.

Collision theory Chemical reactions proceed at a molecular level by means of the collision of reactant molecules. The frequency of collisions is directly related to the reaction rate so that the more collisions per second the faster the reaction would proceed

as the higher would be the chance for a reaction to occur. The collision theory of the chemical reactions associates the rate to the frequency of collisions. By increasing the concentration of reactants the number of collisions would increase and that is the reason why there is a concentration dependency on the reaction rate. However, not all collisions are equally effective and only effective collisions will contribute to chemical reactions. Two main factors control the effectiveness of the molecular collisions. First, the orientation of the collisions is critical and only certain orientations will produce successful collisions. The second factor is the energy of the molecules colliding. Only molecules with energy beyond a threshold will be able to form products. In other words: a successful collision should have the right orientation while having enough energy. Let us elaborate on the role of the orientation for the reaction:

$$Cl + NOCl \longrightarrow Cl_2 + NO$$
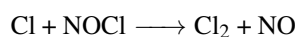
We have that a Cl atom reacts with a NOCl molecule to produce Cl_2, as represented in the image below. Only with the Cl atoms hit the NOCl molecule through the Cl atom, the collision will proceed with the right orientation in order to produce the Cl_2 molecule. At the same time, if the orientation is correct and the molecules have enough energy a transition state will form. We will discuss more this state during the next sections.

Transition state and activation energy We have discussed that the energy of reactants is a key parameter during a reaction. The minimum energy needed to activate the reactants so that they can produce products is called activation energy. The higher the activation energy the more energy is needed for a reaction to happen and hence the lower the reaction rate will be. When reactants get together they increase their energy from reactants until a state of maximum energy before producing the products. This state of maximum energy is called an activated complex or transition state. Transition states are very ephemeral states that exist for a very short amount of time in comparison to reactants and products. An example of activation happens during the ignition of a gas burner. Cooking gas and oxygen can react together to produce water and carbon dioxide only with the help of a spark. A spark is needed to activate the reactants so that their molecules can reach the transition state and hence produce products. Transition states are normally indicated with a ‡ sign to indicate they have a very different nature than normal molecules. The figure below represents two reaction pathways with different activation energy.
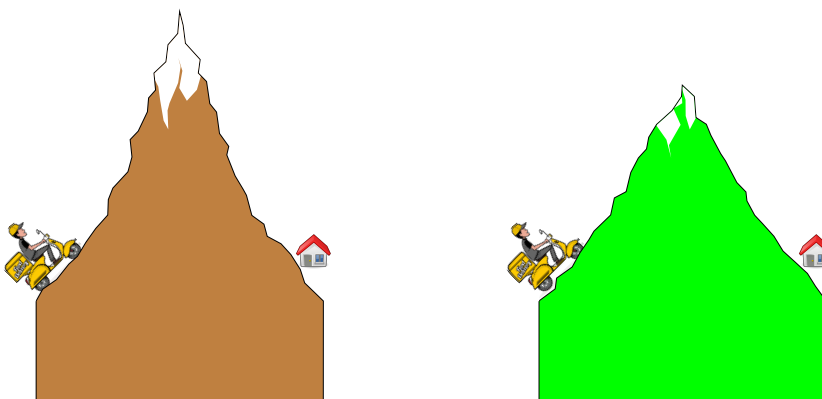

Effect of temperature As temperature increases the kinetic energy of the molecules reacting increases as well and with this the energy involved in the collisions also increases. Molecules move faster at higher temperature and hence the frequency of collisions between reactants and molecules increases with temperature.

Overall, the reaction rate increases with temperature. In other words, we can speed up chemical reactions by increasing temperature.

Concentration of reactants Another way to favor the collision between the molecules of reactants is to increase its concentration. The larger the concentration of reactants the higher the probability of their molecules to collide with each other potentially producing products.

Sample Problem 11

Methane (CH_4) reacts with oxygen (O_2) to produce carbon dioxide (CO_2) and water (H_2O) according to the following reaction

$$CH_4(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$
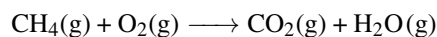
(a) What happens to the number of collision between CH_4 and O_2 when you add extra oxygen?; (b) How would increasing temperature impacts the rate of the reaction?

SOLUTION

(a) The more reactants the mode collisions between their molecules. (b) Increasing temperature would increase the rate of the combustion reaction, as increasing temperature increases collisions.

◈ **STUDY CHECK**

How would the following changes affect the rate of this reaction:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$
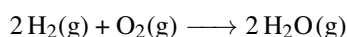
(a) Removing oxygen; (b) Decreasing temperature
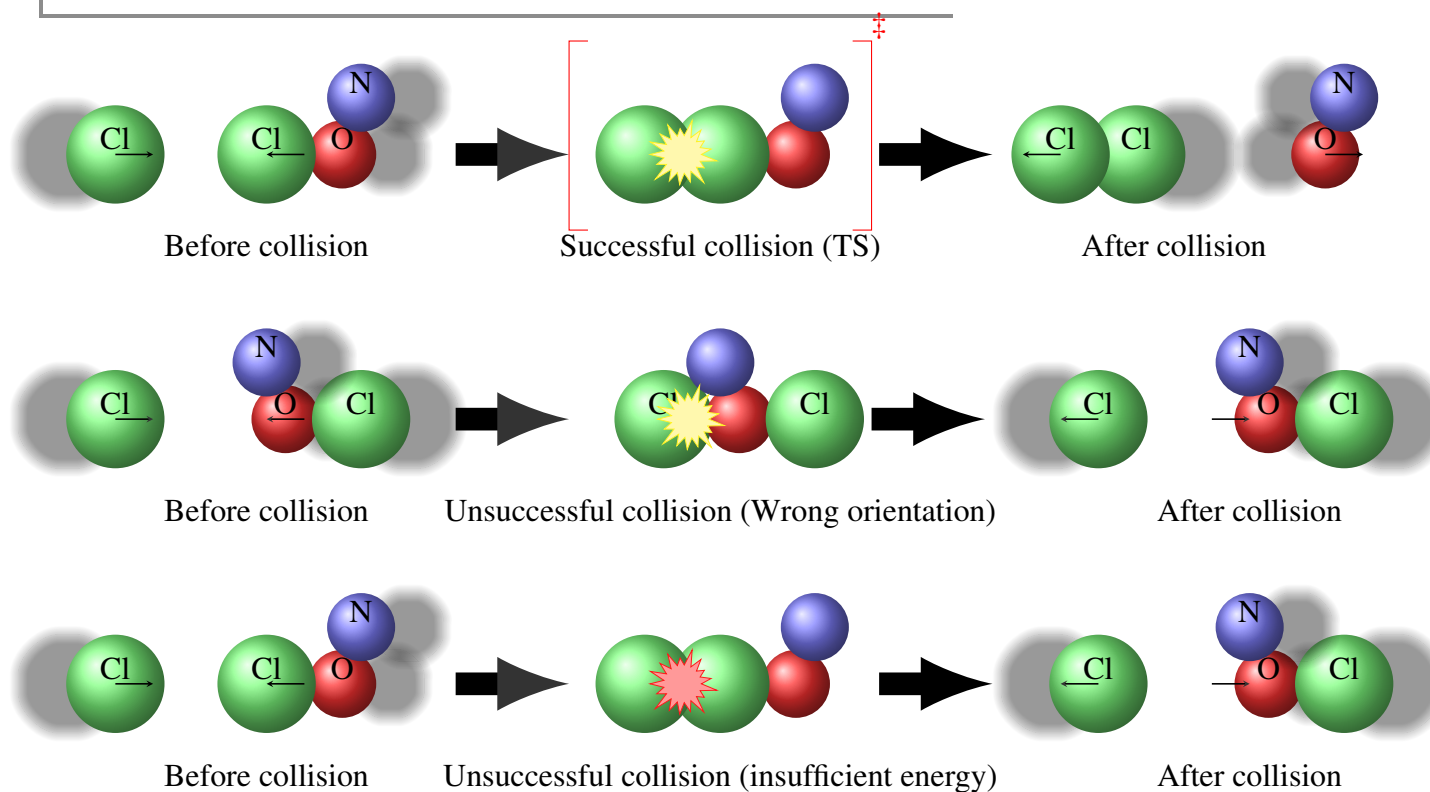
▶Answer: (a) slow down; (b) slow down.

Figure 3.5 Example of three collisions, a successful collision that leads to a transition state and the products and two unsuccessful collisions due to an ineffective molecular arrangement and insufficient energy.

Catalysts Catalysts are chemicals that are not directly involved in a reaction–they are neither reactants nor products and as such, they are not consumed during a reaction. Still, they have the ability to increase the rate of reactions. Each catalyst is specific to a given reaction. As such, a catalyst can speed up a reaction without affecting other reactions. Enzymes are biological catalysts that support chemical reactions happening in the body. Most of the biological reactions involved in the chemistry of life are very slow. It is only with the help of biological catalysts that these reactions can indeed happen at reasonable rates. Every single metabolic reaction has associated an enzyme responsible for speeding up the process. Similarly, catalysts are well-known compounds in the chemical industry. The production of chemicals in the industry is also supported by the help of catalysts which make the chemical processes more economically beneficial. For example, catalysts are used in the manufacturing of margarine from vegetable oils. In the same line, the synthesis of ammonia is catalyzed by iron, the manufacturing of sulfuric acid uses catalysts based on nitrogen(II) oxide and platinum, and the oxidation of hydrocarbons in automobile exhausts are catalyzed by platinum. Enzymes are also added to detergents in order to speed up the breaking of protein molecules in stains. How do catalysts work? Catalyst function by providing alternative reaction pathways with more favorable–normally lower–activation energy. This way, in the presence of a catalyst, reactions proceed by means of two different reaction pathways, the catalyzed and non-catalyzed pathways. Still, as the catalyzed pathway is more favorable the overall speed of the reaction is higher. Catalysts can be classified as homogeneous, heterogeneous, and acid catalysts.
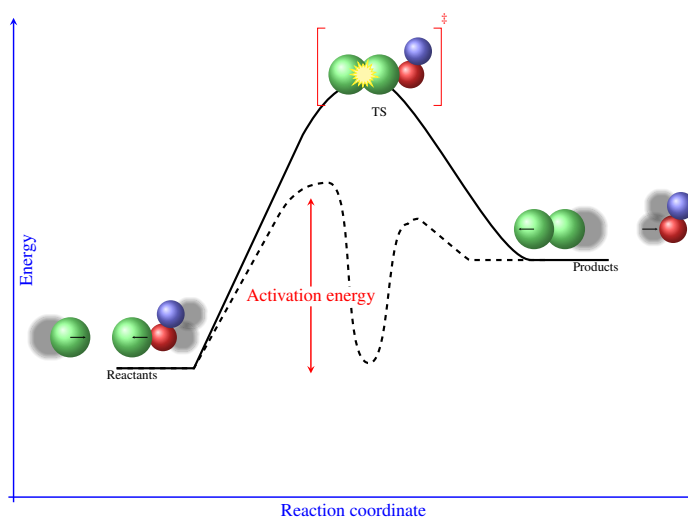

Figure 3.6 Energy diagram showing the catalyzed and non-catalyzed pathways

Heterogeneous catalysis A heterogeneous catalyst is a material with catalytic properties which has a different state of matter than the main reaction. For example, the synthesis of ammonia is carried in the chemical industry by means of reacting has hydrogen and nitrogen. The catalyst for this process is iron, which is a solid. The reaction proceeds in a gas phase, whereas the catalyst employed is solid. This is an example of heterogeneous catalysis. Another example of the hydrogenation of alkenes by means of molecular hydrogen. This process is used for example in the production of saturated fats or shortenings such as Crisco. As hydrogen hardly dissociates in gas, this reaction proceeds at a very low rate without the help of a catalyst. Differently, in the presence of platinum, the dissociation energy of hydrogen is lower what makes the process function at a faster rate. The necessary steps for a reaction to happen on

a heterogeneous catalyst are: (a) the adsorption of the reactants on the surface (the words adsorption refers to the attachment of a gas onto a solid) (b) the activation of the reactants in which its molecular geometry changes due to the adsorption (c) the migration of the adsorbed reactants (d) the surface reaction (e) the desorption of the products
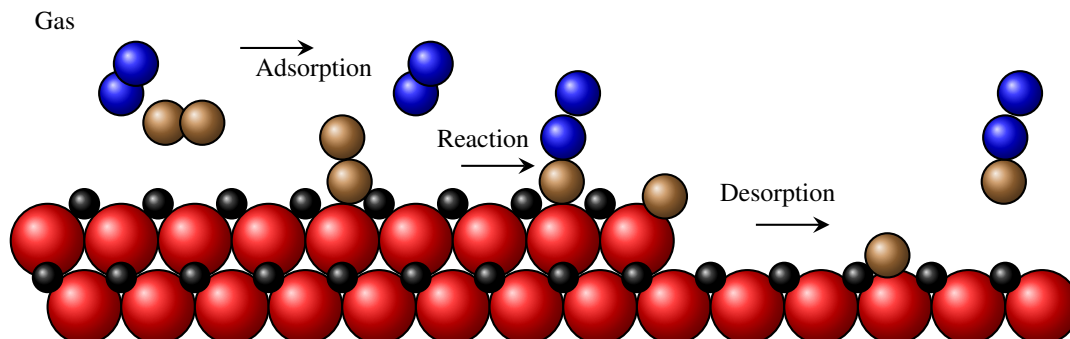

Figure 3.7 Steps in a heterogeneously catalyzed reaction

3.5 Use of energy diagrams

Energy diagrams Energy profile, or energy diagrams, are a visual representation of the advancing of a reaction (see Figure 3.4). Reactions advance through changes in the geometry of the reaction and during a reaction, for example, some bonds are being formed while others are being broken. The horizontal axis of the diagram represents the reaction coordinate, representing how the reaction proceeds, from reactants on the left to products on the right. The vertical axis represents the energy, oftentimes the enthalpy of the different steps of the reaction. Transitions states are maxima in the energy diagrams, that is, points between two minima connecting reactants and products.
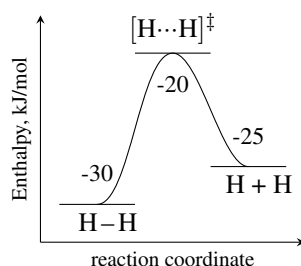

We can extract two types pf properties from energy diagrams. First, the reaction energy ΔH_R is the difference in energy between the products and reactants. If this value is negative, the reaction will be exothermic, releasing heat. The opposite is true for an endothermic reaction that consumes heat. Second, we can obtain the activation energy as the energy of the transition state with respect to the energy of the reactants. The activation energy will always be a positive number which value is related with the reaction rate: in general small activation energies lead to fast reactions and large activation energies lead to slow reactions. Below are two examples showing an exothermic and endothermic reactions, as well as a diagram showing the activation energy.

Sample Problem 12

For the energy profile below
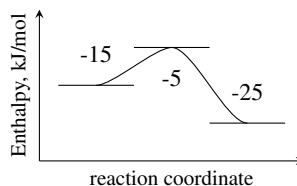
Calculate (a) The energy of the reactants (b) The energy of the products (c) The energy of the transition state (d) The activation energy (e) The reaction energy (f) Indicate whether the reaction is endothermic or exothermic

SOLUTION

We have that the energy of the reactants is -15kJ/mol, the energy of the products is -25kJ/mol and the energy of the transition state (TS) is -5kJ/mol. The reaction energy represents the energy of the products concerning the reactants: $-25 - (-15) = -10$kJ/mol. This is an exothermic reaction. The activation energy represents the energy of the TS concerning the reactants: $-5 - (-15) = 10$kJ/mol.

⬧ STUDY CHECK
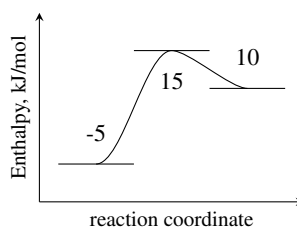
For the energy profile below

Calculate (a) The energy of the reactants (b) The energy of the products (c) The energy of the transition state (d) The activation energy (e) The reaction energy (f) Indicate whether the reaction is endothermic or exothermic

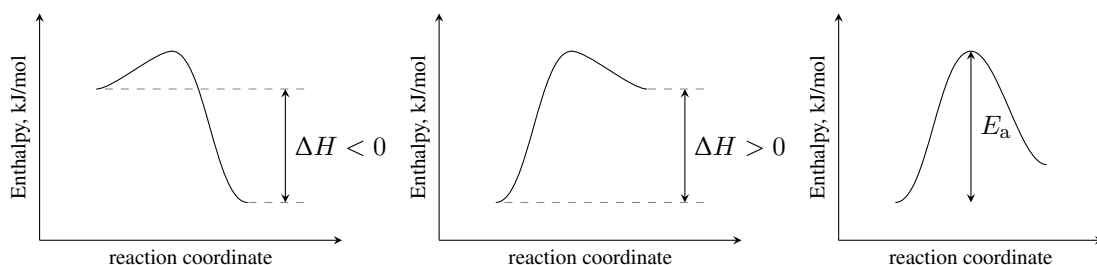▶Answer: (a) -5kJ/mol (b) 10kJ/mol (c) 15kJ/mol (d) 20kJ/mol (e) 15kJ/mol
(f) Endothermic

Figure 3.8 A set of reaction energy profiles

3.6 The Arrhenius equation

The Arrhenius equation on its exponential form The   Arrhenius equation gives the dependency of the rate constant with the frequency factor and the activation energy. We will introduce this equation in two forms: an exponential and a linear form. However, in this section we will focus on the exponential form of this equation:

$$k = A e^{\left(-\frac{E_a}{RT}\right)} \quad \text{and} \quad Ln(k) = Ln(A) - \frac{E_a}{R} \cdot \left(\frac{1}{T}\right) \qquad (3.4)$$

where:

r is the overall rate of reaction

A is the frequency (or pre-exponential) factor

E_a is the activation energy in kJ/mol

R is the constant of the gases in energy units (8.314J/molK)

T is the temperature in Kelvins

Based on Arrhenius equation, the larger the activation energy the smaller the rate constant. Similarly, as the temperature increases the rate constant increases, and therefore the reaction rate increases too. The following example shows how to use this equation in its exponential form. The linear form of the equation results simply from applying logarithms to both sides of the regular Arrhenius equation and is useful to obtain data graphically as it represents a linear relationship with $\frac{1}{T}$ as x and $Ln(k)$ as y. The slope of the resulting line is $-\frac{E_a}{R}$ (mind the negative sign) and the intercept is $Ln(A)$. In the Arrhenius equation, the pre-exponential factor represents the frequency of collision between molecules, in s^{-1}.

Sample Problem 13

The rate constant at 325K for the decomposition reaction $C_4H_8 \longrightarrow 2\,C_2H_4$? is 6.1×10^{-8} s^{-1}, and the frequency factor is 3.9×10^{-5} s^{-1}. Calculate: (a) the activation energy (b) the rate constant at 200K

SOLUTION

We will use the Arrhenius equation on its exponential form:

$$k = A e^{\left(-\frac{E_a}{RT}\right)}$$

As we know the frequency factor ($A = 3.9 \times 10^{-5}$ s^{-1}) and the rate constant at a given temperature ($k = 6.1 \times 10^{-8}$ s^{-1} at 325K), we can solve for the activation energy:

$$6.1 \times 10^{-8} = 3.9 \times 10^{-5} e^{\left(-\frac{E_a}{8.314 \cdot 325}\right)}$$

We have that

$$1.56 \times 10^{-3} = e^{\left(-\frac{E_a}{8.314 \cdot 325}\right)}$$

Using logarithms to solve for E_a:

$$Ln(1.56 \times 10^{-3}) = -\frac{E_a}{8.314 \cdot 325}$$

And solving for E_a:

$$Ln(1.56 \times 10^{-3}) = -\frac{E_a}{8.314 \cdot 325}$$

we have that E_a=17463.5J/mol in another words17kJ/mol.

◈ **STUDY CHECK**

The Arrhenius parameters for the gas-phase reaction below are 6×10^{-12} s^{-1} and 665J/mol.

$$H_2S + OH \longrightarrow HS + H_2O$$

Calculate: (a) the rate constant at 300K. (b) the temperature in Kelvins at which the rate constant is 5×10^{-12} s^{-1}

▶Answer: (a) 4.6×10^{-12} s^{-1} (b) 439K

The following example shows how to use rate constant and temperature data in order to graphically compute the Arrhenius parameters.

Sample Problem 14

Using the following data, calculate the Arrhenius parameters (the activation energy and the frequency factor) for the following gas-phase reaction using the graphic method:

$$HS + O_3 \longrightarrow HSO + O_2$$
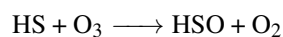
T (K)	$k, (s^{-1})$
100	5.8×10^{-13}
200	2.3×10^{-12}
300	3.7×10^{-12}
400	4.7×10^{-12}

SOLUTION

As they provide with rate constant and temperature data, we will use the linearized form of Arrhenius equation in order to calculate the activation energy and the frequency factor. We will first process the data and compute the natural logarithm of the rate constant and the inverse of temperature.

T (K)	$\frac{1}{T}$ (K^{-1})	$k, (s^{-1})$	$Ln(k)$
100	1.0×10^{-2}	5.8×10^{-13}	-28.17
200	5.0×10^{-3}	2.3×10^{-12}	-26.80
300	3.3×10^{-3}	3.7×10^{-12}	-26.32
400	2.5×10^{-3}	4.7×10^{-12}	-26.08

Now we are ready to graph the Arrhenius plot with $\frac{1}{T}$ in the horizontal (x) axis and $Ln(k)$ in the vertical (y) axis.

$Y = -277.57 \cdot x - 25.4, r^2 = 1$

$Ln(k)$ vs. $\frac{1}{T}$
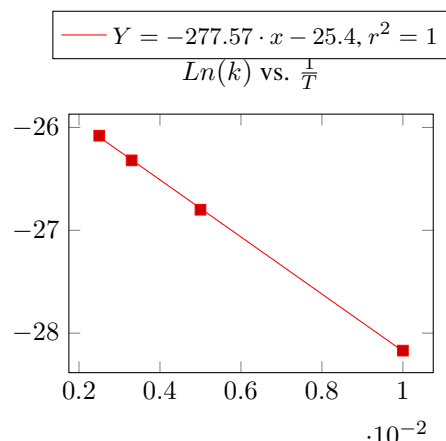
From the slope of the graph we will calculate $-\frac{E_a}{R}$ and from the intersect we will calculate $Ln(A)$. We have that $\frac{E_a}{R} = 227.57$ and $Ln(A) = -25.4$. We have that the Arrhenius parameters are: $E_a = 1892 J/mol$ and $A = 9.3 \times 10^{-12}$ s^{-1}.

◈ STUDY CHECK

Using the following data, calculate the Arrhenius parameters (the activation energy and the frequency factor) for the following gas-phase reaction using the graphic method:
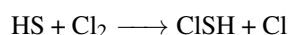
$$HS + Cl_2 \longrightarrow ClSH + Cl$$

T (K)	$k, (s^{-1})$
100	1.1×10^{-15}
200	1.4×10^{-13}
300	6.9×10^{-13}
400	1.5×10^{-12}

▶Answer: $E_a = 7990 J/mol$, $A = 1.7 \times 10^{-11}$ s^{-1}.

3.7 Reaction mechanisms

Most chemical reactions do not occur in a single step but in a series of steps that connect reactants with products in the form of a reaction mechanism. Some of the steps of the mechanism are slow–heavily impacting the experimentally measured rate law–others proceed quickly or are equilibrated hence going backwards. A proper reaction mechanism will justify the experimental rate law while matching the overall reaction stoichiometry. This section will gain insight into the different nuances involving reaction mechanisms, first giving an example of a reaction mechanism, then describing to of the most important steps of mechanisms: the rate-limiting step and the equilibrated steps. The first step gives the experimental rate law whereas the second is useful to calculate the concentration of reaction intermediates.

An example of a reaction mechanism Let us analyze the reaction between nitrogen dioxide and carbon monoxide, with the experimental rate law indicate below:

$$\text{NO}_{2(g)} + \text{CO}_{(g)} \longrightarrow \text{NO}_{(g)} + \text{CO}_{2(g)} \qquad\qquad r^{Exp} = k^{Exp}[\text{NO}_2]^2$$
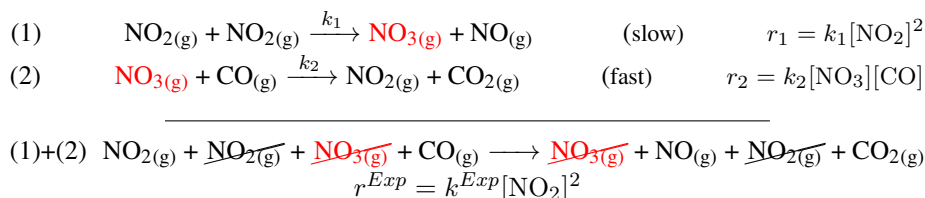
The experimental rate law demonstrates that this is a second order reaction. The reaction mechanism associated with the overall reaction is shown below. It consists of two steps. The first step involve the reaction of two nitrogen dioxide molecules (NO_2)–one of the reactants–to produce a molecule of nitrogen trioxide and a nitrogen monoxide molecule (NO_3)–one of the products. The second step involves the reaction of nitrogen trioxide (NO_3) and carbon monoxide (CO)–a second reactant–to produce nitrogen dioxide and carbon dioxide–the second product.

$$(1) \qquad \text{NO}_{2(g)} + \text{NO}_{2(g)} \xrightarrow{k_1} \text{NO}_{3(g)} + \text{NO}_{(g)} \qquad (\text{slow}) \qquad r_1 = k_1[\text{NO}_2]^2$$

$$(2) \qquad \text{NO}_{3(g)} + \text{CO}_{(g)} \xrightarrow{k_2} \text{NO}_{2(g)} + \text{CO}_{2(g)} \qquad (\text{fast}) \qquad r_2 = k_2[\text{NO}_3][\text{CO}]$$
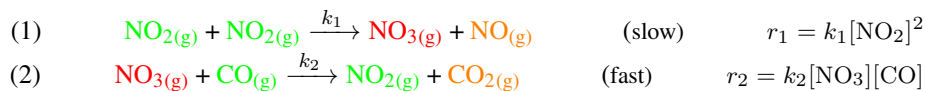
All reactions in a mechanism are called elemental steps and hence they proceed in a single step. At the same time, for each step, the number of molecules involved in the reactants is called molecularity and directly corresponds to the order or the rate law for a given step. Reactions involving a single molecule are called unimolecular, whereas reactions involving two molecules are called bimolecular. Reactions involving three molecules are called termolecular and are very rare. We have that every single step of the mechanism has a reaction constant (k_1 and k_2) and a rate law (r_1 and r_2). The rate law of each step of the mechanism simply results from multiplying the rate constant by the molarity of all reactants, using the stoichiometric coefficients are powers. For example the first step involves two NO_2 molecules and hence the rate law involve $[\text{NO}_2]^2$. At the same time, every step is characterized by a certain speed. Some steps are slower (step 1) than other (step 2). By combining the different steps and eliminating the repeated species we can obtain the overall reaction:

$$(1) \qquad \text{NO}_{2(g)} + \text{NO}_{2(g)} \xrightarrow{k_1} \text{NO}_{3(g)} + \text{NO}_{(g)} \qquad (\text{slow}) \qquad r_1 = k_1[\text{NO}_2]^2$$

$$(2) \qquad \text{NO}_{3(g)} + \text{CO}_{(g)} \xrightarrow{k_2} \text{NO}_{2(g)} + \text{CO}_{2(g)} \qquad (\text{fast}) \qquad r_2 = k_2[\text{NO}_3][\text{CO}]$$

$$(1)+(2) \quad \text{NO}_{2(g)} + \cancel{\text{NO}_{2(g)}} + \cancel{\text{NO}_{3(g)}} + \text{CO}_{(g)} \longrightarrow \cancel{\text{NO}_{3(g)}} + \text{NO}_{(g)} + \cancel{\text{NO}_{2(g)}} + \text{CO}_{2(g)}$$

$$r^{Exp} = k^{Exp}[\text{NO}_2]^2$$

Finally, there are three different types of molecules in a mechanism: overall reactants, overall products and intermediates. Overall reactants are the reactants of the overall reaction (indicated in green). Overall products are the products of the overall reaction (indicated in orange). Intermediates (indicated in red) are generated only inside the mechanism and are not involved in the overall reaction. They are very ephemeral states that exist only temporally and they are never part of any experimental rate law.

Rate limiting step The rate limiting step of a mechanism approximately corresponds to the slowest step as this step will determine the experimental rate law:
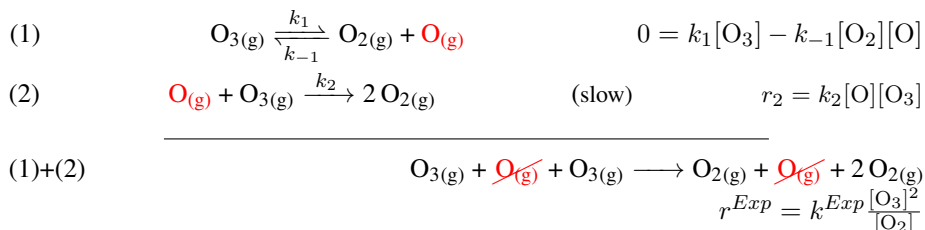
$$\boxed{r^{Exp} \sim r^{slow}} \tag{3.5}$$

The sign $\sim$ indicated that this is an approximation. Rate limiting steps represent bottlenecks of chemical mechanisms limiting the overall advance of the reaction. Hence the rate liming step is crucial to obtain the overall experimental rate law.

Equilibrated steps Often times we encounter equilibrated steps in mechanisms. Let us analyze the decomposition of ozone to produce molecular oxygen:

$$2\,\text{O}_{3(g)} \longrightarrow 3\,\text{O}_{2(g)} \qquad\qquad r^{Exp} = k^{Exp}\frac{[\text{O}_3]^2}{[\text{O}_2]}$$

This reaction proceed by means of the following mechanism the steps of which combined gives the overall reaction:

(1) $\qquad$ $O_{3(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_{2(g)} + O_{(g)}$ $\qquad$ $0 = k_1[O_3] - k_{-1}[O_2][O]$

(2) $\qquad$ $O_{(g)} + O_{3(g)} \xrightarrow{k_2} 2\,O_{2(g)}$ $\qquad$ (slow) $\qquad$ $r_2 = k_2[O][O_3]$

(1)+(2) $\qquad$ $O_{3(g)} + \cancel{O_{(g)}} + O_{3(g)} \longrightarrow O_{2(g)} + \cancel{O_{(g)}} + 2\,O_{2(g)}$

$$r^{Exp} = k^{Exp}\frac{[O_3]^2}{[O_2]}$$

The reactant is O_3, whereas O_2 is the product and O is an intermediate. The first step, the step indicated with a double arrow, is equilibrated, that means that the forward reaction ($\longrightarrow$) proceeds fast enough in order to be able to proceed backwards ($\longleftarrow$). At this point the forwards reaction is characterize by a rate constant k_1 and the backwards by another rate constant k_{-1}. Equilibrated steps are employed to compute the concentration of the reaction intermediates. As both reactions are equilibrated we have that the forwards and backwards reaction proceed at the same speed giving: $0 = k_1[O_3] - k_{-1}[O_2][O]$. We can compute the concentration of the intermediate by means of the rate law of the equilibrated step:

$$0 = k_1[O_3] - k_{-1}[O_2][O] \Longrightarrow [O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

Now let us calculate the expression of the experimental rate law in terms of the different mechanistic steps. The second step is the rate limiting reaction so we have that:

$$r^{Exp} \sim r^{slow} = k_2[O][O_3]$$

Using the concentration of the intermediate recently calculates we have:

$$r^{Exp} = \frac{k_2 \cdot k_1}{k_{-1}} \frac{[O_3]^2}{[O_2]}$$

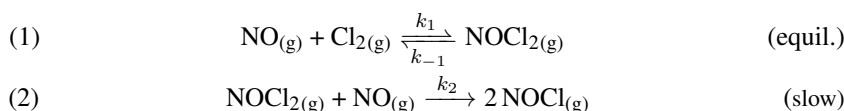We have that the mechanism justifies the experimental rate law with $k^{Exp} = \frac{k_2 \cdot k_1}{k_{-1}}$.

How to verify a possible mechanism Imagine we suggest a possible mechanism for a reaction with an experimental rate law and we want to make sure this is an appropriate mechanism. An appropriate chemical mechanism follows two rules: (a) the combination of all steps gives the overall reaction and (b) the experimental rate law can be justified by means of the mechanistic steps.

> **Sample Problem 15**
>
> Assess whether the reaction below:
>
> $2\,NO_{(g)} + Cl_{2(g)} \longrightarrow 3\,NOCl_{(g)}$ $\qquad$ $r^{Exp} = k^{Exp}[NO]^2[Cl_2]$
>
> is correctly represented by the following mechanism:
>
> (1) $\qquad$ $NO_{(g)} + Cl_{2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl2_{(g)}$ $\qquad$ (equil.)
>
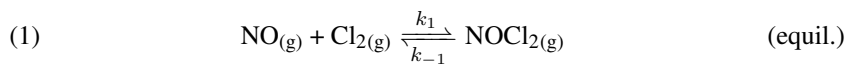> (2) $\qquad$ $NOCl2_{(g)} + NO_{(g)} \xrightarrow{k_2} 2\,NOCl_{(g)}$ $\qquad$ (slow)
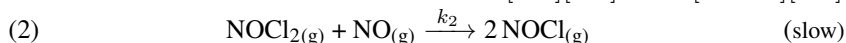>
> **SOLUTION**
>
> We will verify two criteria: that the combination of the mechanistic steps gives the overall reaction and that the rate law is correctly described by the mechanism, using the rate determining step approximation–this means that the slow step
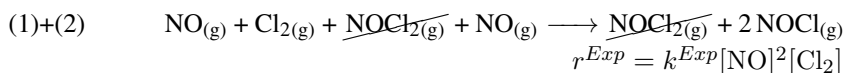
determines the experimental rate law. We will first write down the rate laws for each individual step and we will combine both steps:

(1) $$NO_{(g)} + Cl_{2(g)} \xrightleftharpoons[k_{-1}]{k_1} NOCl_{2(g)} \qquad \text{(equil.)}$$

$$0 = k_1[NO][Cl_2] - k_{-1}[NOCl_2][Cl_2]$$

(2) $$NOCl_{2(g)} + NO_{(g)} \xrightarrow{k_2} 2\,NOCl_{(g)} \qquad \text{(slow)}$$

$$r_2 = k_2[NOCl_2][NO]$$

(1)+(2) $$NO_{(g)} + Cl_{2(g)} + \cancel{NOCl_{2(g)}} + NO_{(g)} \longrightarrow \cancel{NOCl_{2(g)}} + 2\,NOCl_{(g)}$$

$$r^{Exp} = k^{Exp}[NO]^2[Cl_2]$$

We have that the first criteria is met as the overall reaction is obtained by combining both steps. Now we will use the rate liming approach in order to reproduce the experimental rate law:

$$r^{Exp} \sim r^{slow} = k_2[NOCl_2][NO]$$

and we will use the equilibrated step in order to calculate $[NOCl_2]$:

$$0 = k_1[NO][Cl_2] - k_{-1}[NOCl_2][Cl_2] \implies [NOCl_2] = \frac{k_1}{k_{-1}}[NO][Cl_2]$$

Now we are able to compute r^{slow}:

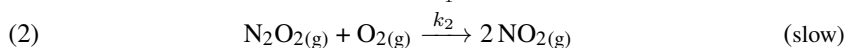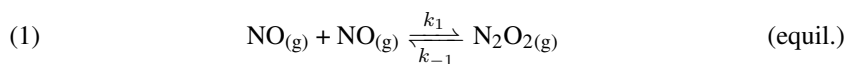$$r^{slow} = \frac{k_2 \cdot k_1}{k_{-1}}[NO]^2[Cl_2]$$

We have that the rate limiting step gives the experimental rate law. Hence this is an appropriated mechanism with $k^{Exp} = \frac{k_2 \cdot k_1}{k_{-1}}$.

◆ **STUDY CHECK**

Assess whether the reaction below:

$$2\,NO_{(g)} + O_{2(g)} \longrightarrow 2\,NO_{2(g)} \qquad\qquad r^{Exp} = k^{Exp}[NO]^2[O_2]$$

is correctly represented by the following mechanism:

(1) $$NO_{(g)} + NO_{(g)} \xrightleftharpoons[k_{-1}]{k_1} N_2O_{2(g)} \qquad \text{(equil.)}$$

(2) $$N_2O_{2(g)} + O_{2(g)} \xrightarrow{k_2} 2\,NO_{2(g)} \qquad \text{(slow)}$$

▶Answer: yes with $k^{Exp} = \frac{k_2 \cdot k_1}{k_{-1}}$