Faculty of Science

Unit 2:
Kinetics

CHEM 1523
Principles of Chemistry

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Unit 2: Kinetics

Overview

Kinetics, the study of the rates of chemical reactions, is part of the general field of "chemical dynamics" that also includes mechanisms, the pathways and steps the reaction follows, and molecular dynamics, the study of the motion of individual atoms in reactions. This latter is a relatively new field of study; it is very complex and will not be discussed in this unit. This unit includes some simple mechanisms where it is possible to predict how the reaction occurs and to test these predictions experimentally.

Most of this unit is concerned with kinetics. Rates of reaction can range from hundreds or thousands of years down to seconds or microseconds. In 1963, the German chemist Manfred Eigen was awarded the Nobel Prize in Chemistry for measuring the rate of one of the fastest reactions known:

$$H_3O^+ \;+\; OH^- \;\rightarrow\; 2H_2O$$

This process takes place in about 37 microseconds!

This unit introduces various methods of handling kinetic data. In many cases you will be expected to analyze results graphically and use your graphs to calculate various reaction concentrations and reaction times. You should make sure you have a supply of proper graph paper, that is, graph paper divided into 1-cm blocks and into 1-mm blocks within these divisions. Also make sure you draw your graphs accurately. Lack of attention to detail and sloppy drawing can lead you to wrong conclusions from the graph. This unit will also supply examples for application, if you are using a graphing calculator.

Kinetic studies are extremely important in industrial processes. While thermodynamics is able to predict that a reaction will occur, it does not give an indication of how fast the reaction will occur. Hydrogen and oxygen combine to form water

$$H_2 \;+\; \frac{1}{2}O_2 \;\rightarrow\; H_2O$$
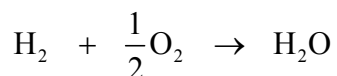
Since this reaction is extremely exothermic, you might be tempted to predict that it will proceed very quickly to completion. Yet hydrogen and oxygen can be kept in contact with one another for a very long time without producing any noticeable amounts of water. This is an example of a chemical reaction where the speed of the reaction governs whether the formation of the product will or will not be observed. Kinetics can be used to determine ways of speeding up a reaction (for the commercial production of chemicals) or slowing down a reaction (for controlling the growth of microorganisms that spoil food).

The factors that control the rate of a chemical reaction can be summarized as follows:

a. The nature of the reactants and products

b. The concentrations of the reacting species

c. The temperature

d. The effect of outside agents (catalysts)

This unit will consider each of these factors. To follow the rate of a chemical reaction, you have to be able to measure a change in the **concentration** of a reactant or product during the course of the reaction. This is usually done by monitoring some property that is unique to a given substance, such as its colour, electrical conductivity, or absorption of electromagnetic radiation. If a gas is produced during the reaction, the increase in pressure can be measured. If a colour change occurs, then the change can be monitored by means of a colorimeter. Other spectral changes that can be followed may be in the infrared or ultraviolet portions of the electromagnetic spectrum. There are sophisticated spectroscopic techniques that can detect very small changes in chemical or physical properties of the reaction system. Examples of these are nuclear magnetic resonance spectroscopy and atomic absorption spectroscopy. If an aqueous reaction produces or uses hydrogen ions, its rate can be monitored by titration or by a pH meter. A change in the ionic concentration of a solution can be followed by measuring the conductivity throughout the reaction.

In this unit you will not be expected to propose mechanisms for the pathways that reactions might follow. That would need more chemical and kinetic experience than what is required for a first-year course. However, you will be asked to comment on the validity of simple mechanisms that have been proposed for reactions. This is done by seeing if the proposal fits the kinetic data supplied. You should note that a mechanism is a proposal by a chemist of what he or she thinks is happening during the reaction. The kinetic data is the experimental result that may indicate how the reaction occurs. A proposed mechanism can be excluded by showing that it cannot lead to the observed kinetics. However, kinetic experiments *cannot prove* that a certain mechanism is the correct one.

Radioactive decay, although not strictly a chemical process, follows the same simple kinetic law observed in many chemical reactions. The subject of nuclear chemistry is not covered in this course. If you have not had any previous courses covering the basics of radioactivity, read Sections 19.1 and 19.3 in your textbook.

You should understand (as a minimum) such terms as **parent** and **daughter nuclide**; -, -, and -**decay**; and **radioactive series**. The rate of decay of a radioactive isotope can be found by measuring the number of particles given off in unit time.

Instruments such as scintillation counters or Geiger counters are used for this purpose. The **half-life**, that is, the time taken for one-half of the atoms to disintegrate, is known for many radioactive isotopes. This information, along with kinetic laws, is used in age estimations of rocks and the technique of "carbon dating" as discussed later in this unit.

Learning Outcomes

Once you have finished this unit, you should be able to:

- Calculate, from reaction stoichiometry, rates of appearance of products or disappearance of reactants, given one of these rates.

- Determine the rate law from a series of kinetic runs.

- Determine graphically the order of a reaction for first-, second-, or zero-order reactions from the data of one kinetic run.

- Explain kinetic terms such as average rate, instantaneous rate, molecularity, rate-determining step, elementary reaction.

- Distinguish between differential and integral rate equations.

- Calculate half-lives, per cent reaction, and time taken for a reaction, knowing the rate constant and the order of the reaction.

- Determine, from given possibilities for a reaction, a mechanism that fits the kinetic data.

- Use the Arrhenius equation to determine activation energies from rate constants at various temperatures, and vice versa.

- Explain the effect of a catalyst on a reaction mechanism.

Rates of Reactions

Study Section 13.1 in your textbook.

Average and Instantaneous Rates

For almost every chemical reaction the rate decreases with time. This is because reaction rate depends on the concentrations of the reactants. Once you start to use up these reactants, the rate drops. This is logical considering that for a chemical reaction to occur, the molecules or atoms or ions involved must collide with each other, and the fewer the collisions, the slower the reaction. This is shown graphically in Figure 2.1 below.
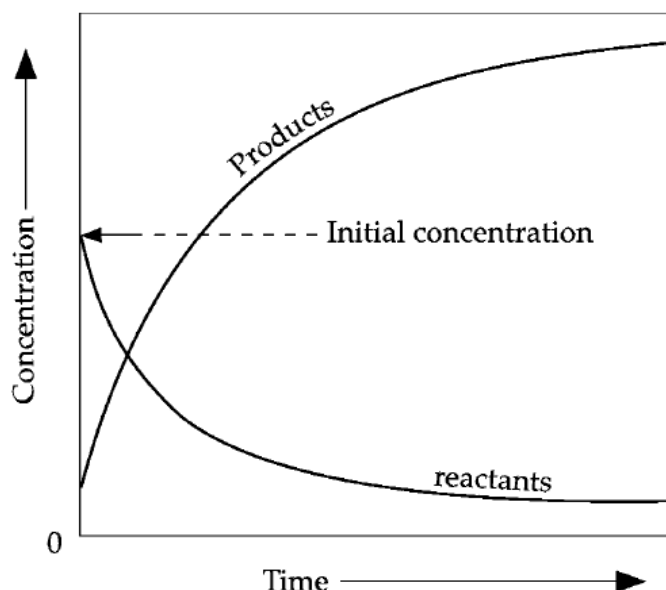

Figure 2.1: Graph of the concentration of products and reactants against time. The concentration of reactants decreases more rapidly at the beginning of the reaction. The concentration of products, initially zero, increases rapidly at the beginning of the reaction (i.e., exponential functions). These rates of increase and decrease fall with increasing time.

The average reaction rate depends on when during the reaction the measurement is taken and how large a time interval (Δt) is chosen. The rate over a time range is the average rate; the rate at any one instant is the instantaneous rate. It is possible to approximate an instantaneous rate provided the time interval is small.

The smaller the time interval is, then the closer the approximation to an instantaneous rate. When the time interval becomes infinitesimal, the average rate is the same as the instantaneous rate.

Figure 2.2 of this unit is a graph of the data from Table 1.1 (below) for the gaseous reaction $2O_3 \rightarrow 3O_2$.

Table 1.1: Data for $[O_3]$ vs. time graph.

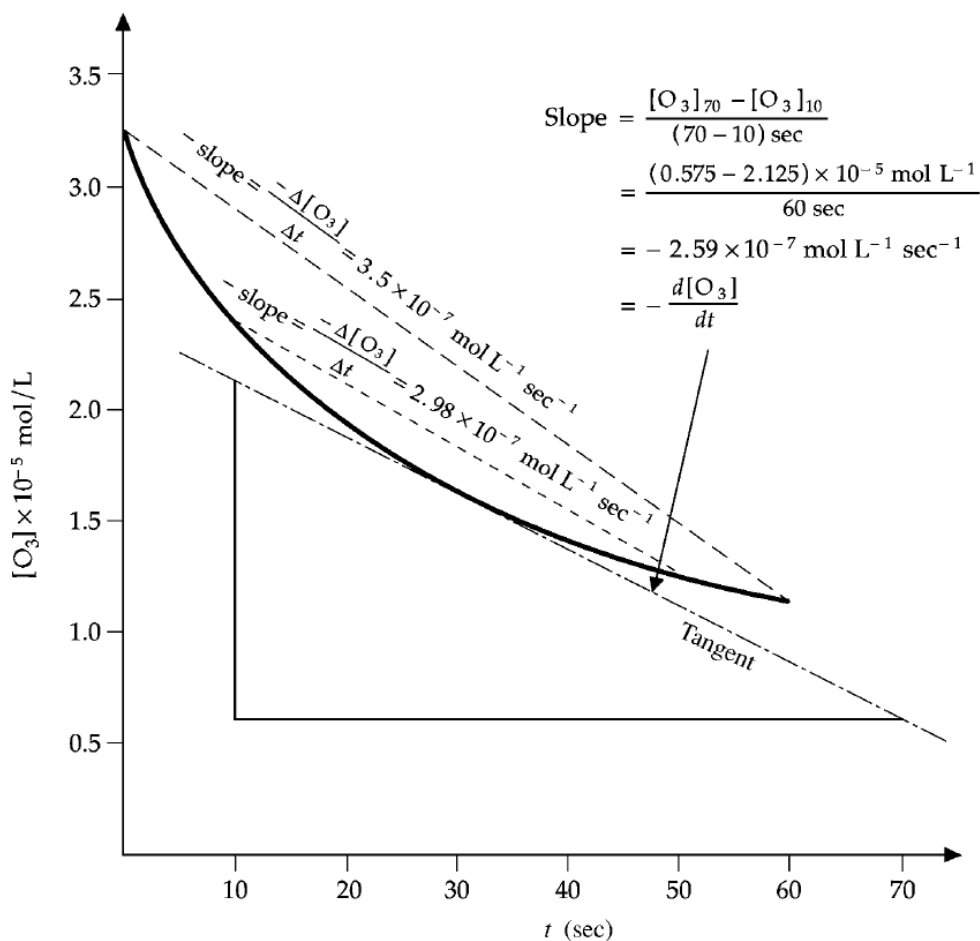| time (s)	$[O_3]$
0.0	3.20×10^{-5}
10.0	2.42×10^{-5}
20.0	1.95×10^{-5}
30.0	1.63×10^{-5}
40.0	1.40×10^{-5}
50.0	1.23×10^{-5}
60.0	1.10×10^{-5}

Figure 2.2: Rate of disappearance of O_3 with time. As the time interval decreases, the average rate approached the instantaneous rate. $-d[O_3]/dt$ is found at 30 seconds from the slope of the tangent at that point.

Also calculated here is a value for the slope of the tangent at the point where time equals 30 seconds. The accuracy of this value depends on how accurately the tangent is drawn.

The symbol $-\Delta[A]/\Delta t$ is used to represent the average rate of disappearance of the reactant A in the reaction

$$A \longrightarrow B$$
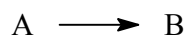
To indicate the instantaneous rate, the notation $-d[A]/dt$ is used. When following the appearance of B, you would write $d[B]/dt$ for the instantaneous rate. If you have done any calculus you will recognize this as a derivative. While knowledge of calculus is not essential for this unit on kinetics, it will help in relating rate expressions to the kinetic data. If you have not encountered calculus before this will not affect your ability to understand kinetics and do kinetic problems at this level, just skip those parts that refer to calculus derivations. In this unit, we will use the *results* of calculus procedures, not the calculus methods themselves. If you have not had calculus you should know that $d[B]$ does not mean d times B. You can translate the symbol d very loosely as "a minutely small change in."

Reaction Rate and Stoichiometry

You should understand that a reaction rate is always positive. If you follow the *decrease* in one of the reactants, then the rate is expressed as $-\Delta[x]/dt$ because here $\Delta[x]$ is itself negative. A decrease in concentration is negative so you have to use a negative decrease to maintain a positive reaction rate. Also note that the rate of appearance of one product may not be the same as the rate of appearance of another product. This depends on the reaction stoichiometry as given in the general equation

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$
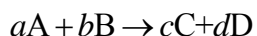
Rates for this reaction are

$$\frac{1}{a}\frac{-\Delta A}{\Delta t} = \frac{1}{b}\frac{-\Delta B}{\Delta t} = \frac{1}{c}\frac{\Delta C}{\Delta t} = \frac{1}{d}\frac{\Delta D}{\Delta t}$$

The best way to make sure you can write down correct rates of appearance and disappearance is to do some examples. Work through Example 13.1 and its practice exercise in your textbook. The answers to the practice questions are at the very end of the chapter.

The following problems will give you further practice in writing rates.

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Problem: For the reaction

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

The rate of appearance of NO_2 gas is 6.30×10^{-2} atm/sec at a particular temperature. Calculate the rate of appearance of $O_2(g)$ and the rate of disappearance of $N_2O_5(g)$ under these conditions.

Solution: The rate of appearance of O_2 is ¼ that of NO_2, since you get only one O_2 for every four NO_2 produced. Thus,

$$\frac{\Delta P_{O_2}}{\Delta t} = 1.58 \times 10^{-2} \text{ atm / sec}.$$

Since you get $4NO_2$ molecules for every 2 molecules of N_2O_5 used up, the rate of disappearance of N_2O_5 is 2/4 of the rate of appearance of NO_2. Thus,

$$\frac{-\Delta P_{N_2O_5}}{\Delta t} = 3.15 \times 10^{-2} \text{ atm / sec}.$$

Problem: The rate of appearance of I_2 in aqueous acid solution when I^- is oxidized by H_2O_2 is found to be 1.2×10^{-4} mol L^{-1} sec^{-1} over a set time period. Find the rate of disappearance of the reactants involved.

Solution: The balanced equation for this reaction is

$$2I^- + H_2O_2 \longrightarrow I_2 + 2H_2O$$
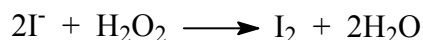
For this reaction

$$\frac{\Delta[I_2]}{dt} = \frac{1}{2}\frac{-\Delta[I^-]}{dt} = \frac{-\Delta[H_2O_2]}{dt} = \frac{1}{2}\frac{-\Delta[H^+]}{dt}.$$

Thus, the rate of disappearance of H_2O_2 is also 1.2×10^{-4} mol L^{-1}sec^{-1}. The rate of disappearance of both H^+ and I^- is 2.4×10^{-4} mol L^{-1} sec^{-1}.

Reaction Rate and Concentration

Study Sections 13.2 and 13.3 in your textbook.

A summary of kinetics in one phrase would be that *rate is proportional to concentration*. This should be self-evident. The more often molecules collide, the more likely there is to be a chemical reaction. Of course, *rate is proportional to concentration* oversimplifies the situation. You also want to know to what concentration the rate is proportional. It is assumed that the concentration refers to a reactant and not to a product, but it may involve more than one reactant or more than one molecule of a reactant—something that can only be determined experimentally.

TRU Open Learning

This is an important point and bears repeating. *The relationship between rate and concentration for a given reaction can be established only by experiment*. It is possible to look at the stoichiometry of a reaction such as

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$
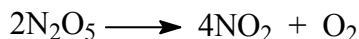
and say that the rate of production of O_2 is ¼ the rate of production of NO_2 and ½ the rate of disappearance of N_2O_5. But looking at the stoichiometry does not tell you how the rate depends on the concentration. For that you have to do a kinetic experiment.

Since rate is proportional to concentration, this can be written as the **rate law**

$$\text{rate} = k\,[\text{concentration}]$$

where k is a proportionality constant known as the **reaction rate constant**. The rate may be dependent on more than one concentration or on the square, cube, and so on, of that concentration. The sum of the exponents of the concentration terms in a rate law is known as the **order** of a reaction. If the general rate law is

$$\text{rate} = k\,[\text{A}]^x\,[\text{B}]^y$$

then

$$\text{order} = x + y.$$

First- and second-order reactions are by far the most common. Third-order and fractional-order reactions do exist, but this unit deals with only first- and second-order kinetics in any detail.

One other order of reaction is zero-order, where the rate is considered independent of the concentration of any reactant.

$$\text{rate} = k\,[\text{concentration}]^0 = k$$

This means that the rate is constant (the same value as the rate constant). In fact, true zero-order chemical reactions are nonexistent, but some reactions follow zero-order kinetics until all but a small fraction of the reacting molecules are consumed. These are the reactions that are considered to be zero-order. Examples are reactions catalyzed by solids and enzymatic reactions. In solid-catalyzed reactions, once all the surface catalytic sites are occupied the reaction proceeds at a constant rate irrespective of the concentration of the reactants. Enzyme-catalyzed reactions show the same kinetic behaviour. Once all the enzymatic sites are occupied, the rate of the reaction is independent of the concentration of substrate. We will learn more about these catalyzed reactions later in this unit.

The rate law, and thus the order of the reaction, can be found in the following manner. If a concentration of a reactant is doubled and the rate also doubles, then the rate is first order with respect to this reactant. Note that you need to run a series of different experiments to determine reaction order this way. Each experiment can be referred to as a "kinetic run." Each will give you an initial rate and it is these initial rates that are usually compared. If initial rates are not used, then you must make sure that you are using a rate that makes your comparison valid. Work through Example 13.2 and its practice exercise from your textbook and the following problem. You should then be able to determine the order of a reaction, given data from a number of kinetic runs.

Problem: The reaction

$$H_2O_2 + 3I^- + 2H^+ \longrightarrow I_3^- + H_2O$$

is independent of [H$^+$] at a pH of 3 and higher. At 25°C, the following rate data were collected.

[H$_2$O$_2$]	[I$^-$]	Initial rate of formation of I$_3^-$ (M min^{-1})
0.10	0.10	6.9×10^{-4}
0.05	0.10	3.4×10^{-4}
0.10	0.20	1.4×10^{-3}

   a.   What is the rate law for this reaction?
   b.   Calculate the rate constant for this reaction at 25°C.
   c.   What is the rate of formation of I$_3^-$ in M min^{-1} when initial concentrations of H$_2$O$_2$ and I$^-$ are both 0.05 M?

Solution:

a.   When the concentration of I$^-$ is held constant and the concentration of H$_2$O$_2$ is halved (0.10 to 0.05 M), the reaction rate is also halved. Thus the rate is proportional to the concentration of H$_2$O$_2$. When the concentration of H$_2$O$_2$ is held constant and the concentration of I$^-$ is doubled (0.10 to 0.20 M), the reaction rate is doubled (6.9×10^{-4} to 1.4×10^{-3} M min^{-1}). Thus, the rate is also proportional to [I$^-$]. The reaction rate law is

$$\text{rate} = k\,[H_2O_2]\,[I^-]$$

The reaction is overall second-order; it is first-order in H$_2$O$_2$ and first-order in I$^-$.

b.   Using the first kinetic run data and substituting in the rate law,

$$6.9 \times 10^{-4} \text{ M min}^{-1} = k \times 0.10 \text{ M} \times 0.10 \text{ M}$$

so

$$k = 6.9 \times 10^{-4} \text{ M}^{-1} \text{ min}^{-1}.$$

(You could have used the data from any of these three kinetic runs and obtained the same value for k, within experimental error. k is a constant at a given temperature for any given reaction.)
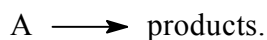
c. $$\text{rate} = k\,[H_2O_2]\,[I^-]$$

$$= 6.9 \times 10^{-2} \times (0.05) \times (0.05)$$

$$= 1.7 \times 10^{-4} \text{ M min}^{-1}$$

First-Order Reactions

The rate law for a first-order reaction has the form

$$\text{rate} = k\,[A]$$

for the reaction

$$A \longrightarrow \text{products.}$$

This can be written as

$$\frac{-\Delta A}{dt} = k\,[A].$$

On rearranging, this equation becomes

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

but this is for an average rate. For an instantaneous rate

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

On integration (a calculus procedure) this **first-order differential rate equation** becomes

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

or

$$\ln\frac{[A]_0}{[A]_t} = k\,t\,.$$

This is also sometimes written as

$$\log \frac{[A]_0}{[A]_t} = \frac{kt}{2.303}$$

with $\log_{10}$ instead of ln, the natural logarithm, where $\ln x = 2.303 \log x$. This is known as the **first-order integrated rate equation**. $[A]_t$ and $[A]_0$ are the concentration of A at time t and time 0, respectively. You do not need to worry about the calculus derivation of this equation. What is important is that you know how to apply this equation to kinetic data. Normally the integrated rate equation is used to determine a reaction rate constant. This means that the error in measuring an instantaneous rate (from a tangent to a curve) is eliminated.

Rearranging the first-order integrated rate equation gives

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

or you may prefer to use the form

$$\log [A]_t = -\frac{kt}{2.303} + \log [A]_0$$

These have the form of the straight line equation, $y = mx + c$. A graph of $\ln [A]_t$ against time gives a straight line with slope –k. In this case the line will have a negative slope, so k will be positive. If you graph $\ln ([A]_0/[A]_t)$ against time, the slope of the straight line will be positive and equal to k.

This unit includes a number of graphical examples and exercises. You should be able to handle kinetic data graphically. Once you have done a few examples, you will find that a graph simplifies kinetic calculations. Remember that a graph takes the raw experimental data from one kinetic run and allows determination of k. (The previous method for order determination required a number of kinetic runs.) The following problem demonstrates the graphical method for a first-order reaction.

Problem: The decomposition of azomethane

$$CH_3 - N = N - CH_{3(g)} \longrightarrow N_{2(g)} + C_2H_{6(g)}$$
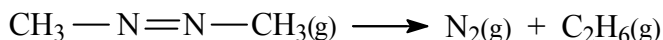
was followed by measuring the decrease in the partial pressure (P) of $(CH_3)_2N_2$.

time (sec)	0	100	150	200	250	300
$P_{(CH_3)_2N_2}$ (mm Hg)	284	220	193	170	150	132

Does this data fit first-order kinetics? If so, determine the reaction rate constant, k, graphically.

Solution: The partial pressure of azomethane is proportional to the concentration of azomethane. If the reaction is first-order, then a graph of $\ln(P_0/P_t)$ against time will give a straight line.

time (sec)	0	100	150	200	250	300
$\dfrac{P_0}{P}$	$\dfrac{284}{284}$	$\dfrac{284}{220}$	$\dfrac{284}{193}$	$\dfrac{284}{170}$	$\dfrac{284}{150}$	$\dfrac{284}{132}$
$\ln\dfrac{P_0}{P}$	0	0.255	0.386	0.513	0.638	0.766

Figure 2.3 in this unit shows that the result of graphing of $\ln(P_0/P)$ of azomethane against t is a straight line. Thus the data fits first-order kinetics.

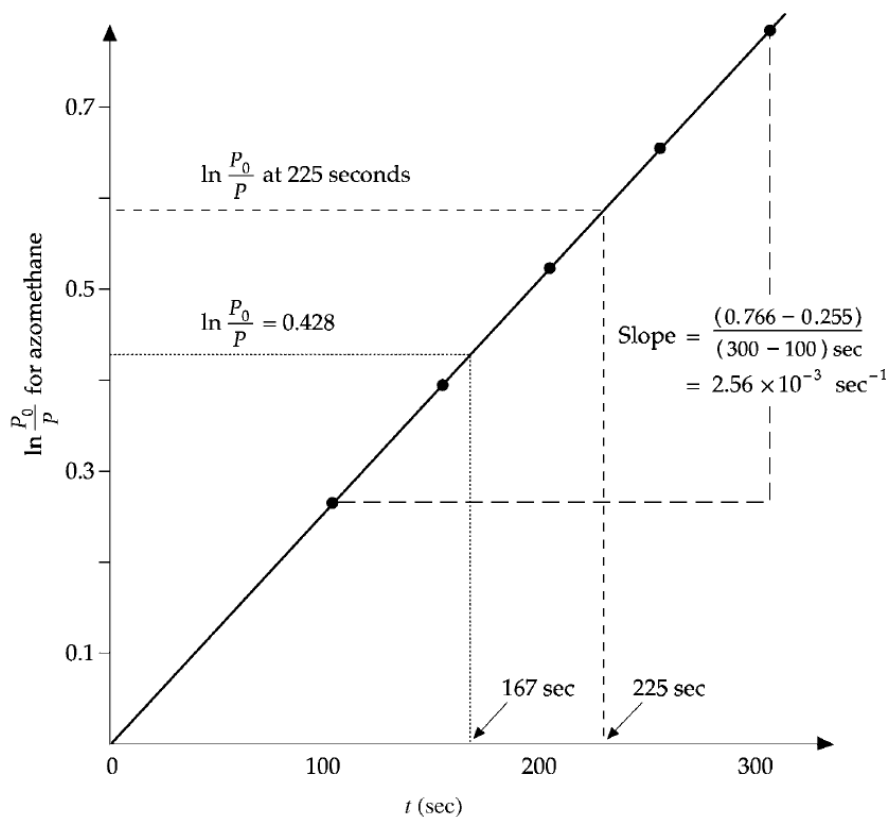From Figure 2.3, slope = 2.56×10^{-3} sec^{-1} = k

Figure 2.3: First-order graph of $\ln(P_0/P)$ against time for the decomposition of azomethane.

Note that units of the first-order rate constant are reciprocal time. When you are graphing such kinetic data, always use proper graph paper and work accurately. It is often not until you have graphed the last few points that you can be certain you have a straight line. Also, choose your scale carefully.

Make sure that the graph is of reasonable size. This minimizes errors in measuring the slope. Once you have a graph, it is possible to use it to determine a concentration at any time or the time needed to arrive at a particular concentration.

Problem:

a. Use the graph in Figure 2.3 above to determine the partial pressure of azomethane after 225 seconds.

b. How much time is required for the partial pressure of azomethane to drop to 185 mm Hg?

Solution:

a. Reading off the graph at 225 seconds, the ln (P_0/P) value is 0.58.

Therefore P_0/P = 1.78.

Since P_0 = 284 then P = 284 ÷ 1.78 = 160 mm Hg.

This could have been calculated without the graph, using the k value determined previously, and the integrated first-order rate equation.

b. At 185 mm Hg, ln (P_0/P) = ln (284/185) = 0.428. Reading off the graph in Figure 2.3, this gives a value for t of 167 seconds. Again, this could also have been calculated mathematically using the integrated rate equation.

The time taken for half of the initial concentration of a reactant to be used up is known as the **half-life** of the reaction. For a first-order reaction this half-life is independent of the initial concentration. You can show this by substituting various values for $[A]_t$ and $[A]_0$ in the integrated rate equation. But when $[A]_t$ equals ½ of $[A]_0$, the ratio ln ($[A]_0 / [A]_t$) always equals ln 2. Then

$$\ln ([A]_0 / [A]_t) = kt$$

yields

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

or

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

$$t_{1/2} = 0.693 / k .$$

Radioactive decay is an example of a first-order reaction. The concept of a half-life is used in the technique of radiocarbon dating, explained in the Chemistry in Action box in Section 13.3 of the textbook. You should be able to do calculations on determining age of artifacts using carbon-14 dating, since this is an application of the principles of first-order kinetics.

Other radioactive isotopes also act as "natural clocks" and allow geologists to estimate the age of rocks. An example is the uranium / lead clock. If the "daughter" lead atoms created by disintegration of "parent" radioactive uranium atoms have not escaped from the rock, they may be chemically extracted in a laboratory and the ratio of parent / daughter measured. For example, the decay of

$$^{238}U \text{ to } ^{206}Pb$$

is known to a have a half-life of forty-five hundred million (4.5×10^9) years. Measurement of the ratio uranium-238 / lead-206 allows geologists to estimate the age of the rock, using this half-life. Older rocks would have lower ratios, because more of the uranium has decayed to lead. The rubidium / strontium and potassium / argon "clocks" are used in a similar manner.

Work through Examples 13.3, 13.4, and 13.5 and their practice exercises in your textbook.

Second-Order Reactions

The rate law for the second-order reaction

$$A \longrightarrow \text{products}.$$

is

$$\text{rate} = k\,[A]^2\,.$$

This can be rearranged to

$$-\frac{dA}{dt} = k[A]^2$$

Integration of this expression gives the second-order integrated rate equation

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

where $[A]_t$ and $[A]_0$ are the concentrations of A at time t and time zero, respectively. Note that $[A]_0$, and hence $1/[A]_0$, are constant for any one particular kinetic run. Thus the second-order integrated rate equation also has the form of a straight line. For second-order reactions, a graph of the reciprocal of concentration against time will give a straight line of slope equal to k. The rate constant can be found graphically as shown in the following problem.

Problem: The decomposition of gaseous NO_2 at 300ºC,

$$NO_{2(g)} \longrightarrow NO_{(g)} + 1/2 O_{2(g)}\,,$$

was followed by monitoring the [NO_2] at various times. From the results can you say that the reaction is second order? If so, determine the reaction rate constant, k, at 300ºC.

time (sec)	0	60	120	180	240	300	360
$[NO_2]$ (M) (all $\times 10^{-2}$)	1.00	0.683	0.518	0.418	0.350	0.301	0.264

Solution: Figure 2.4 in this unit shows the results of graphing $1/[NO_2]$ against time as a straight line.

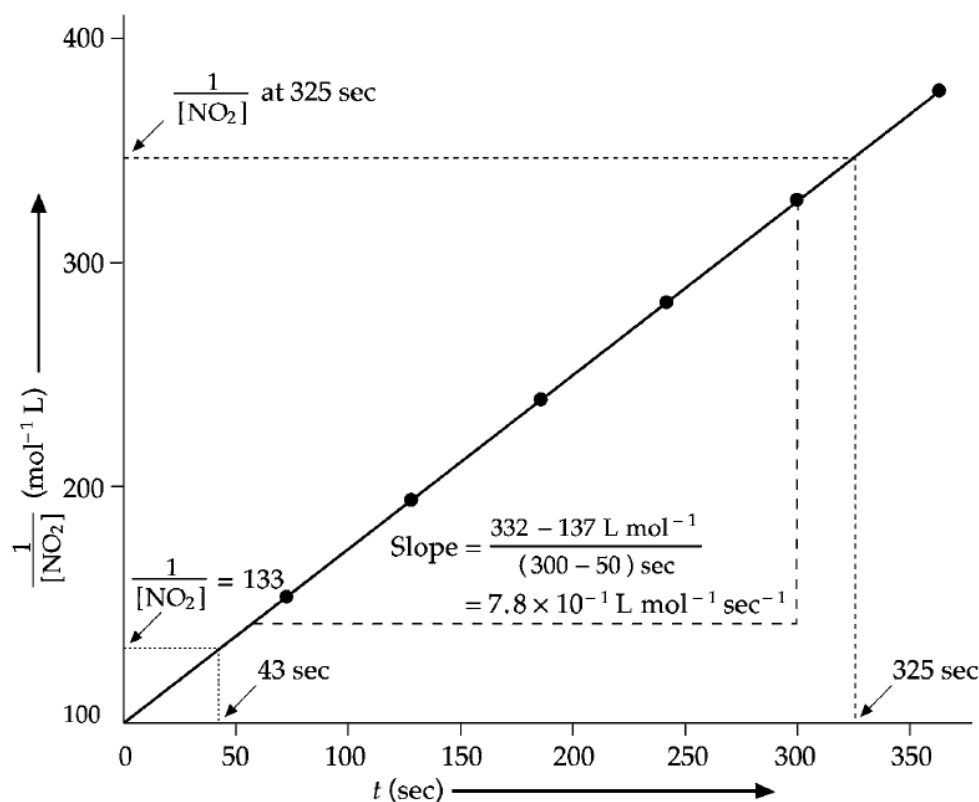| time (sec)	0	60	120	180	240	300	360
$\dfrac{1}{[NO_2]}$	100	146	193	239	286	332	379

Figure 2.4: Second-order graph of 1/[conc.] against time for the decomposition of NO_2.

Thus, this reaction fits second-order kinetics. The slope (from Figure 2.4) is 7.8×10^{-1} L mol^{-1} sec^{-1}, and this is the reaction rate constant, k.

Units of k for a second-order reaction are reciprocal molarity × reciprocal time. You could use this graph to determine concentration at any particular time or time required to reach a specific concentration, as shown in the following calculation.

Problem:

    a. Use the graph in Figure 2.4 to determine [NO_2] after 325 seconds.

    b. How much time is required for 25% of the NO_2 in this reaction to decompose?

Solution:

    a. Reading off the graph in Figure 2.4 at 325 seconds,

$$1/[NO_2] = 350$$

    so $[NO_2] = 1/350 = 2.86 \times 10^{-3}$ mol L^{-1}

    b. When 25% of the NO_2 has decomposed, 75% still remains. Thus,

$$[NO_2] = 0.75 \times 1.00 \times 10^{-2} = 7.5 \times 10^{-3}$$

    and $1/[NO_2] = 133$ L mol^{-1}.

From the graph in Figure 2.4, this gives a time reading of 43 sec.

Both of these values could have been determined mathematically (from the second-order integrated rate equation) as well as graphically.

Unlike that of a first-order reaction, the half-life of a second-order reaction does depend on the initial concentration, that is,

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

Work through Example 13.6 and its practice exercise in your textbook.
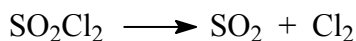
Determination of Reaction Order

Table 2.2 in this unit summarizes the relevant equations for first- and second-order reactions and also gives you the equivalent formulas for zero-order reactions. Figure 2.5, below, shows in graphical form the difference between zero-, first-, and second-order reactions.

Table 2.2: Summary of zero-, first-, and second-order reactions; c = concentration of A at time t and c_0 = concentration of A at time zero in the reaction A → products.

Reaction order	Rate law	Differential rate equation	Integrated rate equation	Straight line graph	Units of k	Half-life
zero	rate $= k$	$-dc/dt = k$	$c = kt$	c vs. t	Mt^{-1}	$t_{1/2} = c/2k$
first	rate $= k[\text{conc}]$	$-dc/dt = kc$	$\ln c_0/c = kt$	$\ln c_0/c$ vs. t	t^{-1}	$t_{1/2} = 0.693/k$
second	rate $= k[\text{conc}]^2$	$-dc/dt = kc^2$	$1/c - 1/c_0 = kt$	$1/c$ vs. t	$M^{-1}t^{-1}$	$t_{1/2} = 1/kc_0$

If you are given data for one kinetic run and asked to determine the order of the reaction, you would normally do this graphically. It can be done mathematically, using the integrated rate equations and testing to see if a calculated rate constant remains the same over a spread of points. But it is usually determined faster and more readily from a graph. If you have a graphing calculator, you will probably find this very straightforward. In this unit you will be given only zero-, first-, and second-order (from one reactant) data.

Problem: The reaction

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

at 320°C was followed by measuring the concentration of SO_2Cl_2 at various time intervals. From the results below, determine (graphically) the order of the reaction and calculate the specific reaction rate constant, k, at 320°C.
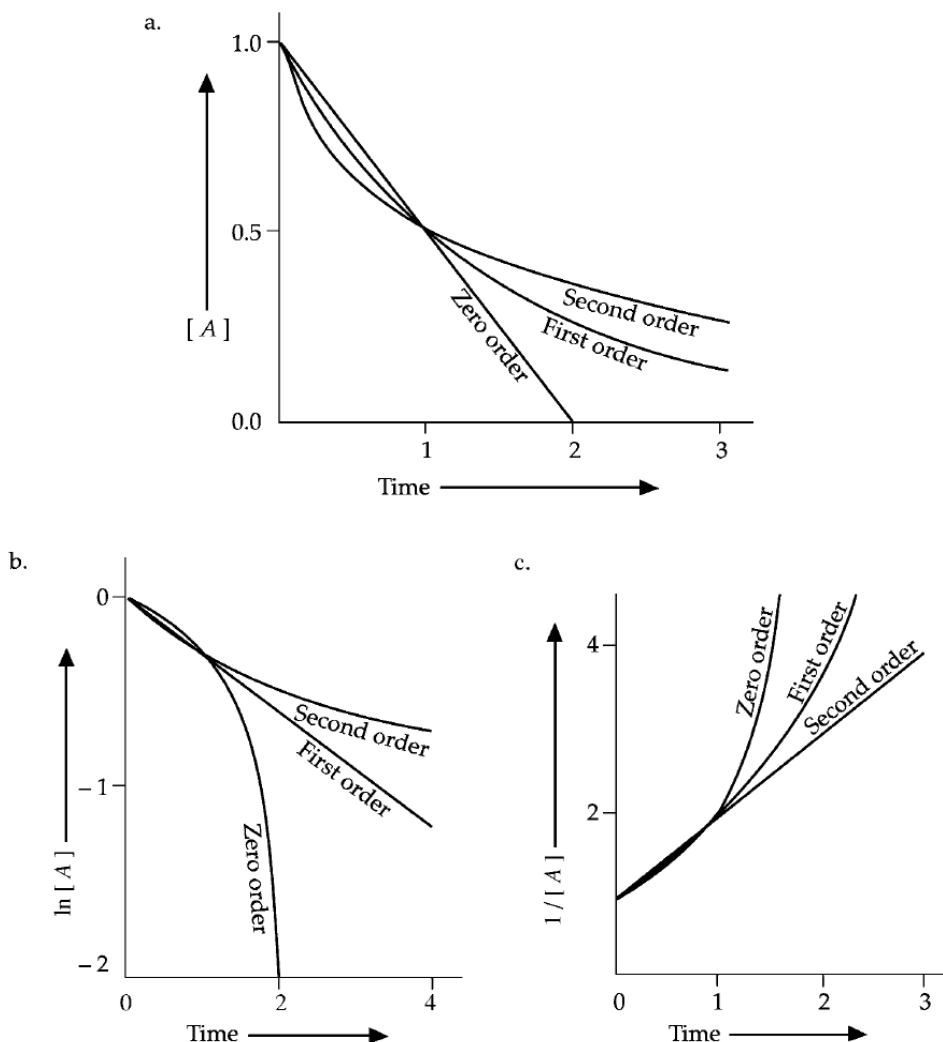

Figure 2.5: Summary of direct plots of degree of advancement versus time.

a. [A] vs. time gives a straight line for zero order.

b. ln [A] vs. time gives a straight line for first order.

c. 1 / [A] vs. time gives a straight line for second order. The primary limitation of this method is that curves for more complicated laws may not differ enough to be experimentally distinguishable.

time (hr)	0.00	1.00	2.00	3.00	4.00
$[SO_2Cl_2]$ (M)	1.200	1.109	1.024	0.946	0.874

Solution: First calculate ln $[SO_2Cl_2]$ and 1 / $[SO_2Cl_2]$ for these points.

time (hr)	0.00	1.00	2.00	3.00	4.00
ln $[SO_2Cl_2]$	0.1824	0.1035	0.0237	-0.0555	-0.1347
1/$[SO_2Cl_2]$	0.8333	0.9017	0.9766	1.057	1.144

Figure 2.6, below, shows the result of graphing $[SO_2Cl_2]$, ln $[SO_2Cl_2]$, and the reciprocal of $[SO_2Cl_2]$ against time. The dashed lines show that treating this data as zero- or second-order does not lead to a straight line. Only the graph of ln $[SO_2Cl_2]$ is a straight line, and so the reaction is first order.
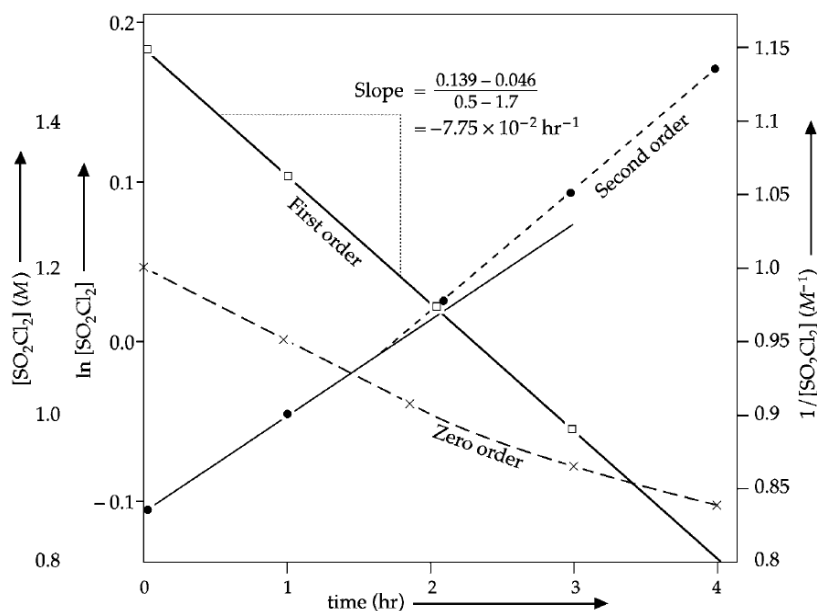

Figure 2.6: Determination of the order of the reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$. A straight line is obtained only when ln $[SO_2Cl_2]$ is graphed against time. Therefore, the reaction is first order.

In this example, we rearrange the integrated rate equation

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

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

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

Since $[A]_0$ is a constant, a graph of $\ln [A]_t$ against time gives a straight line with a negative slope. This is illustrated in Figure 2.6. This also means that you do not need to know an initial concentration to determine the order of a reaction. From Figure 2.6,

$$\text{slope} = -7.75 \times 10^{-2} = -k$$

so $k = 7.75 \times 10^{-2} \text{ hr}^{-1}$.

Further practice on determining reaction rate order is available in the problems at the end of Chapter 13 of your textbook and in the practice exercise with this unit.

Reaction Rate and Temperature

Study Section 13.4 in your textbook. How fast a chemical reaction occurs depends on three factors:

a. The number of collisions per unit time (concentration of reactants)
b. The orientation of the collision (steric factor)
c. The energy of the colliding species (temperature)

Depending on the particular reaction, any one of these factors may be more important than the others. (For reactions taking place in solution, there is the added factor of fluid resistance of the solvent.)

The **activation energy**, symbol E_a, is more than simply the amount of energy required to overcome natural repulsions between molecules. In order to react, most molecules must be jostled into a "disturbed" state where bonds are stretched or twisted in such a way that the electron distribution between the atoms is no longer the most stable one. Instead of returning to the original state, the atoms and electrons arrange themselves into a new low-energy configuration: the reaction product. This explains why the geometry of the collision has to be appropriate to the interacting electron orbitals of reacting species. The orientational or geometric factor depends greatly on the complexity of the reacting molecules and may be completely absent if the reacting species are atoms.

An actual example of what we have been discussing may make these concepts more understandable. The oxidation of gaseous hydrogen bromide by oxygen gas is easily followed by measuring the light absorption of the reddish-brown bromine gas produced.

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$
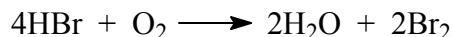
If the reactants are brought together in a stoichiometric ratio, at 750 K and a total pressure of 10 torr, the reaction will be only 1% complete after 25 minutes. Calculations show this means that only one in a million million collisions will result in a reaction. If the temperature is raised to 825 K, it takes only 2.5 minutes for 1% of the molecules to react. The reaction rate has increased tenfold with a 75-degree temperature increase. However, at this temperature the collision rate has increased by only 5%. What is important here is that a larger fraction of the molecular collisions now has a kinetic energy greater than the threshold energy necessary for a reaction to occur. This is shown in Figure 2.7 below.
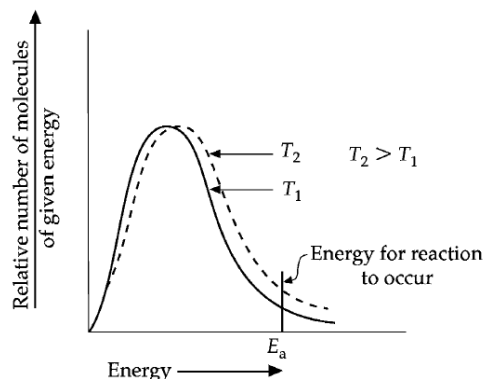

Figure 2.7: At a higher temperature, more molecules have enough energy to overcome
the activation energy barrier. While the mean energy of all the molecules
increases only slightly, when the temperature rises, the fraction of molecules
that are energetic enough to react increases substantially.

At temperatures where the distribution of molecular velocities tail into the activation energy, a relatively small change in temperature will have a large effect on the reaction rate. Figure 2.7 is a Maxwell-Boltzmann distribution curve (see Unit 2, CHEM 1503). Remember that increased temperature does not change the activation energy. More molecules will now have enough energy to overcome the activation energy barrier.

At temperatures so low that very few molecular collisions possess the required activation energy, reaction rates are negligible. For HBr / O₂ oxidation at room temperature, we can calculate that a successful molecular encounter will occur once every three hours. There would be no detectable change after one million years! This is also the explanation for why hydrogen and oxygen can be kept together infinitely without any observable production of water, despite the large free energy decrease for this reaction.

Although you do not need to memorize the Arrhenius equation in its different forms, you should be aware of what they mean and how they are used. Once you have calculated an activation energy from two rate constants at different temperatures, you can use it to estimate the reaction rate at any other temperature. The **Arrhenius law**, written as

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

shows a straight line form, where A is a constant for a particular reaction and incorporates the orientation or steric factor. E_a is the activation energy. We can assume that both A and E_a remain unchanged over normal temperature ranges. If $\ln k$ is graphed against the reciprocal of temperature (in K) you get a straight line of slope $-E_a / R$. Thus, knowing rate constants at two or more different temperatures, you can determine a value for the activation energy of the reaction. This can be done graphically, as shown in Example 13.8 of your textbook and in the following problem.

Problem: The rate of decomposition of N_2O_5 was followed at various temperatures. The following results were obtained.

t (°C)	k (sec^{-1})
0	7.86×10^{-7}
10	3.20×10^{-6}
25	3.46×10^{-5}
35	1.35×10^{-4}
45	4.98×10^{-4}
55	1.50×10^{-3}
65	4.87×10^{-3}

Deduce graphically the activation energy for the reaction.

Solution: Set up a table of the reciprocal values of T and the ln values of k.

t (°C)	T (K)	$1/T$ (K^{-1})	k (sec^{-1})	$\ln k$
0	273	3.66×10^{-3}	7.86×10^{-7}	-14.0
10	283	3.53×10^{-3}	3.20×10^{-6}	-12.6
25	298	3.36×10^{-3}	3.46×10^{-5}	-10.3
35	308	3.24×10^{-3}	1.35×10^{-4}	-8.91
45	318	3.14×10^{-3}	4.98×10^{-4}	-7.60
55	328	3.05×10^{-3}	1.50×10^{-3}	-6.50
65	338	2.96×10^{-3}	4.87×10^{-3}	-5.32

The result of graphing $\ln k$ against $1/T$ is shown below in Figure 2.8.

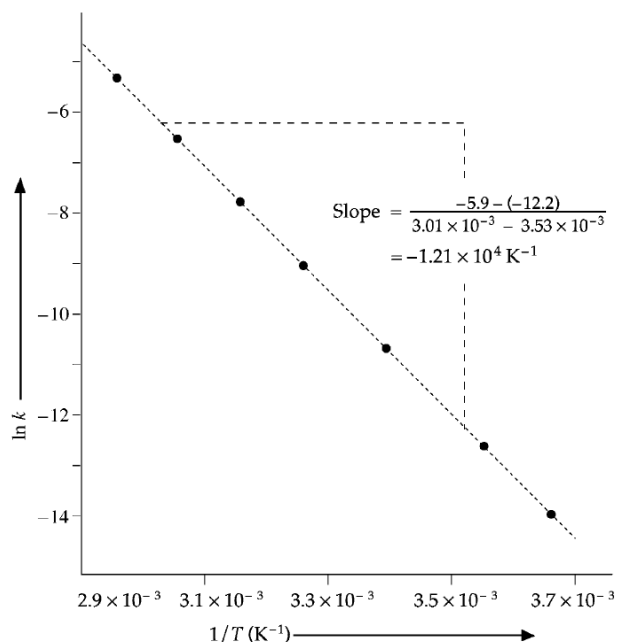**Figure 2.8:** Graph of $\ln k$ against $1/T$ for the decomposition of N_2O_5 gas.

The slope of the straight line obtained is -1.21×10^4 K^{-1}. Since

$$\text{slope} = -E_a / R,$$

we have
$$E_a = -R \times \text{slope}$$

$$= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (-1.21 \times 10^4 \text{ K}^{-1})$$

$$= 101 \text{ kJ mol}^{-1}$$

In a problem where you are given rate constants at only two temperatures it is usual to use the Arrhenius equation as shown in Example 13.9 in your textbook. Do the practice exercises associated with Examples 13.8 and 13.9.

You should be able to sketch energy diagrams for exothermic and endothermic products, and for elementary (one-step) reactions. You are not expected to produce scale graphs for these reactions. A sketch diagram showing $E_{products}$ higher than $E_{reactants}$ for an endothermic reaction and with appropriate labels is all that is required at this stage. At the highest point of an energy diagram the reactants are considered to be in the form of an **activated complex**.

Rate Laws and Reaction Mechanisms

Study Section 13.5 in your textbook. Make sure you understand the terms **elementary reaction**, **intermediate**, and **molecularity**. It is worth noting again that the reaction stoichiometry, that is, the overall sum of the individual steps of the complex reaction, does not give the order of the reaction. If a reaction is known to consist of only one step, then the reaction itself is an elementary reaction. Its rate law can be written directly from its stoichiometry. In most cases, kinetic experiments are required to show that the rate law is consistent with single-step reaction. It is not possible to prove that a mechanism is correct. A mechanism is a chemist's idea of how the reaction occurs and as such can never be absolutely verified. A mechanism is acceptable provided it is scientifically sound and fits the experimental evidence. Consequently, there may be more than one proposed mechanism for a reaction. Until one or other of these mechanisms is proved wrong, both are accepted.

The rate of a reaction depends on its slowest step, known as the **rate-determining step**. Of course, for an elementary reaction the slowest step is the only step and is the overall rate-determining step. In a complex reaction (more than one elementary step) where the rate-determining step is the first step, the overall rate law is the rate law of this first step. When the rate-determining step is not the first step, the derivation of the rate law is not that simple. An example of this is the reaction between hydrogen and iodine discussed in Section 13.5. Work through Example 13.10 and its practice exercise. Keep in mind that the mechanism proposed for these reactions has to fit the known experimentally determined rate laws.

Problem: The reaction

$$2O_{3(g)} \longrightarrow 3O_{2(g)}$$
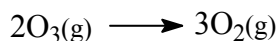
is thought to proceed by a two-step mechanism.

$$(1) \quad O_3 \longrightarrow O_2 + O$$
$$(2) \quad O_3 + O \longrightarrow 2O_2$$
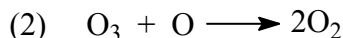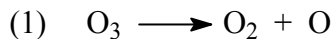
    a.   Write the rate law for the reaction if the first step is the rate-determining step.

    b.   Write the rate law for the reaction if the second step is the rate-determining step.

    c.   Suggest an experimental method for distinguishing between these two possibilities.

Solution:

a.   If the first step is the slower step, then its rate law (and the reaction rate law) is

$$\text{rate} = k\,[O_3]$$

b.   If the second step is the slower, then its rate law is

$$\text{rate} = k_2\,[O_3]\,[O]$$

The first step (fast) is considered to have reached equilibrium, so for the first step

$$K = \frac{[O_2][O]}{[O_3]}$$

and the concentration of the intermediate O can be written as

$$[O] = \frac{K\,[O_3]}{[O_2]}.$$

Substituting this value for [O] in the slow-step rate law gives

$$\text{rate} = \frac{k_2\,K\,[O_3][O_3]}{[O_2]}$$

or $$\text{rate} = k\,[O_3]^2\,/\,[O_2]\ .$$

c.   If the first step is the slow step, then the overall reaction rate is first order in O_3. If the second step is the slow step, then the overall reaction is second order in O_3. An experiment to determine the kinetics of the reaction would distinguish between these first- and second-order possibilities.

It requires a bit of experience to propose a mechanism from kinetic data. In this unit, you are not expected to propose mechanisms. You should be able to write rate laws from proposed mechanisms and explain if kinetic data could fit these mechanisms. Remember, when the rate-determining step is the first step, the remaining steps do not affect the overall rate. If the rate-determining step is not the first step, then you have to make use of the equilibrium expression for any steps before the slow step.

Catalysis

Study Section 13.6. You do not have to know details of the Haber synthesis, the manufacture of nitric acid, or catalytic converters. You can just read about these.

Catalysis is an extremely large topic. There are whole books and courses devoted to just small parts of catalysis.

An understanding of catalysis in chemical processes is vital in the chemical industry and enzyme catalysis is a cornerstone in the understanding of biochemistry. Detailed study of these, however, is beyond the scope of this course.

There are two points that you should know about catalysis and these are explained in this section. You do not need to go into details, but you should know the following.

a.   A catalyst speeds up the rate of reaction without itself being consumed. This is achieved by following a different reaction pathway. The result is a lower activation energy and hence a faster reaction rate. This is shown on the energy diagram in Figure 13.23 of your textbook.

b.   A homogeneous catalyst takes part in a chemical reaction and is then regenerated. A heterogeneous catalyst provides a surface where the reaction occurs with a lowered activation energy.

Use the summary at the end of Chapter 13 to review important concepts of kinetics.

Self-Assessment

Having reached the end of Unit 2, you should be able to:

- Calculate, from reaction stoichiometry, rates of appearance of products or disappearance of reactants, given one of these rates.

- Determine the rate law from a series of kinetic runs.

- Determine graphically the order of a reaction for first-, second-, or zero-order reactions from the data of one kinetic run.

- Explain kinetic terms such as average rate, instantaneous rate, molecularity, rate-determining step, elementary reaction.

- Distinguish between differential and integral rate equations.

- Calculate half-lives, per cent reaction, and time taken for a reaction, knowing the rate constant and the order of the reaction.

- Determine, from given possibilities for a reaction, a mechanism that fits the kinetic data.

- Use the Arrhenius equation to determine activation energies from rate constants at various temperatures, and vice versa.

- Explain the effect of a catalyst on a reaction mechanism.

Practice Exercise 2

Finish working through Unit 2 before starting this practice exercise which is found listed under the Practice Exercises section of course. The material in this unit is integrated throughout the practice exercises. The solutions to these problems will be provided once you have completed this practice exercise.

You may first want to try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can begin the practice exercises immediately. If you have no problems with this practice exercise, begin Assignment 2. If you feel that you need more practice, go to the Suggested Supplementary Exercises.

You should make a serious attempt to solve the practice exercise problems by yourself, using as a guide similar exercises from the textbook and from this unit. If your attempt is serious, you will learn a lot from the worked solutions in the Solutions to Practice Exercise 2 section of the Course Units.

Suggested Supplementary Exercises

At the end of each chapter in your textbook are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved in the concepts discussed. Fully worked solutions for most of the following exercises are given in the *Student Solutions Manual*. Other exercises at the ends of the chapters may have their answers in the back of the textbook, or a solution method is described in the *Student Solutions Manual*.

You should make a serious attempt to solve a problem by yourself before looking at a worked solution.

From Chapter 13:

13.5, 13.6, 13.7, 13.16, 13.19, 13.20, 13.24, 13.25, 13.26, 13.28, 13.38, 13.40, 13.42, 13.48, 13.53, 13.54, 13.56, 13.64, 13.74, 13.76, 13.78, 13.82, 13.84, 13.88

Assignment 2

Now refer to your *Assignments* and complete Assignment 2. Consult your Course Guide for the week this assignment is due. Send the assignment to your Open Learning Faculty Member. You may send the assignment to your Open Learning Faculty Member using the assignment tool in Blackboard or by mail with a Marked Assignment Form. Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.