Chapter 18. Chemical Kinetics

18.1. The Kinetic-Molecular Theory Paradox

The two grand questions of chemical reactions are *where are the reactants headed*, and *how fast are they getting there*? Where the reactants are headed is the subject of chemical thermodynamics. In this chapter we will investigate how *fast* chemical reactions occur, the subject of **chemical kinetics**, or **chemical rates**. Since, as we shall see, chemical kinetics has a firm basis in the kinetic-molecular theory, developed in great detail during the last half of the Nineteenth Century, principally by J. Clerk Maxwell and Ludwig Boltzmann, most of the analysis is quantitative in nature. Consequentially, most of the algorithms of this unit will involve mathematical equations and numerical analysis.

One of the disturbing features of Nineteenth Century kinetic-molecular theory was the prediction that chemical reactions should take place almost instantaneously! This result, known as the ‘‘paradox of kinetic molecular theory’’, could not resolve the known frequency of molecular collisions with measured rates of chemical reactions, assumed to be the result of such molecular encounters. Nitrogen and oxygen molecules under room conditions travel on average about 300 m/s and experience about 10 billion collisions per second (see Example 15.5). On this basis, the average lifetime of a nitrogen molecule should thus be only one ten-billionth of a second in the atmosphere! Yet we know that (fortunately for us) the atmosphere does not spontaneously convert itself into nitrogen oxides, at least with any haste under ordinary conditions. On the other hand, elemental hydrogen released into the atmosphere doesn’t last very long, and can be converted into water with explosive speed.

Why does oxygen tolerate the presence of nitrogen, but not hydrogen? Since chemical reactions result from the breaking of reactant-molecule bonds and the formation of new bonds in the products, a clue comes from considering the chemical bonding of the molecules involved in the reaction. Recall that diatomic oxygen has unpaired electrons (is paramagnetic) contributing to its electronegativity and chemical reactivity. (See Example 12.12 in Section 12.10 on Molecular Orbital Bond Theory.) The encounter between an oxygen molecule and a hydrogen molecule can be therefore productive in producing the more stable bonding arrangement found in water. Dinitrogen, on the other hand, has filled octets and a triple bond, rendering it fairly inert to chemical attack. A second clue comes from the observation that under the right conditions nitrogen *does* burn rapidly in the atmosphere. Such conditions are found in lightning thunder storms, and inside internal combustion engines (where the principle chemical process is supposed to be combustion of petroleum fuel). What do these conditions have in common? Both involve the availability of intense energy, sufficient to disrupt the strong chemical bond of dinitrogen. On the basis of these considerations, it should be easy to understand why every encounter between molecules may not be effective in producing products.

18.2. The Collision Rate Model

The key to reconciling observed rates of chemical reactions with the kinetic-molecular prediction that molecules experience on average about 10 billion collisions per second, is the phrase "on average"; *average* molecular collisions do not have sufficient energy to produce a chemical reaction. However, the kinetic-molecular theory is not limited to describing average behavior only. The complete theory recognizes that even if all the molecules in a system started out with the same speed, in a very short time random collisions would result in some molecules moving slower than the average, and some faster, resulting in a *distribution* of molecular speeds, the *Maxwell-Boltzmann distribution*. Since kinetic energy is related to speed, a certain fraction of the molecules will have the necessary speed to bring sufficient kinetic energy to the collision to cause a chemical reaction. This amount of energy is called the **activation energy** of the reaction, which is of the order of magnitude of chemical bond energies, characteristic of the reaction taking place. The kinetic-molecular paradox was resolved when the fraction of molecules having kinetic energy at least equal to the activation energy was calculated. A typical value for the fraction of neutral molecules would be 10^{-18}.[1] In addition, molecules must approach each other in the correct orientation to transfer the kinetic energy into the proper bond to cause a chemical reaction to occur. The fundamental notion of chemical kinetics is: *chemical reactions occur between molecules undergoing effective collisions (sufficient kinetic energy and proper orientation).* In quantitative terms the reaction rate (r) = collision frequency (Z) times the fraction with favorable energy (f_{E_a}) times

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[1] This corresponds to Boltzmann distribution factor of $e^{-\frac{E_a}{RT}}$, with E_a = 100 kJ/mol at T = 300 K (Section 13.9). Ions might be attractive, thus lowering the value of E_a and raising the fraction having sufficient energy to react.

the fraction with favorable orientation ($f_{\text{orientation}}$)

$$r = Z \times f_{E_a} \times f_{\text{orientation}} \tag{18.1}$$

Considering molecules to be approximate spheres, a collision occurs when molecules pass by each other close enough to touch. The appropriate model is a 2-body problem (Section 5.4) consisting of an effective molecule with reduced mass (μ_{AB})of the two interacting molecules A and B moving with relative velocity v_{AB}. As this molecule travels it sweeps through molecules colliding with those within distance $r_A + r_B$, where r_A and r_B are the radii of the molecules. In a given time t a disc of effective target area

$$A_{AB} = 4\pi(r_A + r_B)^2 \tag{18.2}$$

sweeps out a cylinder of length $L_{AB} = v_{AB}/t$.[2] The collision frequency Z is equal to the number of collisions per unit time and depends on the concentrations of projectile (say, A) and target molecules (say, B):

$$Z = \frac{\text{number of collisions}}{\text{time}} = \frac{\text{number of molecules}}{\text{volume}} \times \frac{\text{volume}}{\text{time}} = C_A C_B \times \frac{A_{AB} L_{AB}}{t} = C_A C_B A_{AB} v_{AB} \tag{18.3}$$

The kinetic molecular theory provides a formula for the mean velocity of molecules:[3]

$$v_{AB} = \sqrt{\frac{RT}{2\pi\mu_{AB}}} \tag{18.4}$$

where μ_{AB} is the reduced mass of A and B. For n-ary collisions between a molecules of type A, b molecules of type B, representing the chemical reaction aA + bB + cC ..., the total number of collisions is proportional to the concentration of molecules of each type colliding. The total collision frequency becomes

$$Z = 4\pi(r_A + r_b)^2 \sqrt{\frac{RT}{2\pi\mu_{ABC}\cdots}}\, C_A^a C_B^b \cdots \tag{18.5}$$

where C_i is the concentration of species i.

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[2] Useful analogies are collecting rain in a bucket or running mindlessly through a crowd with the ability to change direction only on bumping into someone else.

[3] This velocity is in one direction and differs somewhat from that for three-dimensional motion given in Section 15.6.

The Boltzmann distribution Eq. (13.23) gives the number of molecules with sufficient energy to rearrange bonds. All molecules with at least that energy will contribute to f_{E_a}

$$f(E \geq E_a) = e^{-E_a/kT} \tag{18.6}$$

The total reaction rate expression is

$$r = 4\pi(r_A + r_b)^2 \sqrt{\frac{RT}{2\pi\mu_{ABC}\cdots}} \times f_{orientation} \times e^{-E_a/kT} C_A^a C_B^b \cdots \tag{18.7}$$

which has the general form

$$\boxed{r = A(T)\, e^{-E_a/kT} C_A^a C_B^b \cdots \equiv k(T) C_A^a C_B^b \cdots \qquad (18.8)}$$

where k is called the (specific) *rate coefficient*[4] The temperature dependence of the rate coefficient is expressed in the *Arrhenius equation*

$$\boxed{k(T) = A(T)\, e^{-E_a/kT} \qquad (18.9)}$$

The *preexponential factor* is the product of the collision frequency and the orientation factor:

$$A(T) = 4\pi(r_A + r_b)^2 \sqrt{\frac{RT}{2\pi\mu_{ABC}\cdots}} \times f_{orientation} \tag{18.10}$$

The preexponential factor is seen to have some temperature dependence, but it is insignificant compared to the exponential term in Eq. (18.9).

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[4] Sometimes called the rate "constant" because it plays the role of a proportionality constant between the rate and the concentration terms. The term constant is unfortunate however, as k clearly is a function of the temperature.

18.3. Rate Laws

Consider the general reaction

$$aA + bB + cC + \cdots \longrightarrow \text{Products} \qquad (18.11)$$

It should be apparent that increasing the concentration of A molecules will increase the number of collisions they experience, and also increase the number of *effective* collisions to produce reaction as well. The same holds for the other reactant molecules. Thus rates of reaction in general depend on concentrations of reactants. From the effective collision model it is seen that the rate of reaction should depend on the temperature too (which determines the kinetic energy distribution). Rates of reaction thus depend on concentrations of reactants and temperature; these are referred to as *rate variables*. However, reactions do not have to proceed in a single collision encounter. Multiple-step processes affect the observed concentration dependence of rates. Determining the mathematical dependence of rate on concentrations and temperature is the basic task of experimental chemical kinetics.

Experimentally, it is found that rates of reaction have rather simple concentration dependencies, specifically, *rates of reactions at a given temperature are proportional to powers of reactant concentrations*. The particular set of powers depend on the reaction, and specifying the values determines the **rate law** (or **rate equation**) for the reaction. The rate law for the general reaction aA + bB + cC + ... ⟶ Products, is expressed mathematically in the form:

$$r(\vec{C},T) = k(T){C_A}^{n_A}{C_B}^{n_B}{C_C}^{n_C}\cdots \qquad (18.12a)$$

$$r(\vec{C},T) = k(T)\prod^{\text{reactants}} {C_i}^{n_i} \qquad (18.12b)$$

where C_i is the concentration of the i-th reactant.[5] By convention the units of concentration are $C_i = M_i \equiv [i]$ (molarity) for solutions and $C_i = P_i = \frac{M_iRT}{V}$ (partial pressure) for gases. Each of the powers of concentration n_i is called the **order of reaction with respect to the reactant i**. The sum of the powers (orders) is called the **overall** or **total order** of the

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[5] Rate laws ordinarily (but not exclusively) involve only reactants.

reaction. The proportionality factor, k, is the rate coefficient of the reaction. Its value depends on the temperature and two parameters, A and E_a (Eq. (18.8) above), but at a given temperature it remains constant.

18.4. Reaction Mechanisms

Clearly the collision rate is proportional to the number of molecules of each reactant, and since the number in a given volume is the concentration, the rate of reaction will also be proportional to the *concentration* of each reactant. This generates an observed overall, or total (mixed) order of two. In fact, most gas-phase collisions are bimolecular because the probability of three or more molecules finding themselves at the same place at the same time is quite small.[6] On the other hand, many chemical reactions involve several species with coefficients greater than one in the balanced reaction. Such processes are most likely to proceed in stages, or *steps* involving a series of **elementary processes**, such as bimolecular collisions leading to products. Along the way, temporary *intermediate species*, or substances may be produced in one of the steps, only to be consumed in another. Although the sum of the steps must add up to the overall reaction equation, these intermediates cancel out and therefore don't appear in the total balanced reaction.[7] The series of elementary reactions leading from reactants to products is called the **mechanism** of the reaction. While it may not be possible to deduce a definitive mechanism from an observed rate law, the opposite is a straightforward process, that is, deriving the rate law from a given mechanism. The fundamental rule of mechanisms is that *in each elementary step of a reaction the orders (powers of concentration) equal the stoichiometric coefficients of that step*. It logically follows that *reactions for which the orders equal the stoichiometric coefficients* **may** *proceed in one elementary step; reactions for which the orders do not equal the stoichiometric coefficients* **must** *proceed by way of a mechanism involving a sequence of more than one elementary step*. The qualification for the case where the orders equal the stoichiometric coefficients derives from the fact that it is possible for some multi-step mechanism to generate the same

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[6] Have you ever encountered an acquaintance in a strange place? How many times have you encountered *two* other acquaintances (who were unacquainted themselves) in the same place?

[7] However, fleeting intermediates may be (and have been) detected with sufficiently sensitive equipment. Establishing their existence provides experimental evidence in support of a suggested mechanism.

rate law as a one-step mechanism.[8]

Generating a mechanism to account for all the information known about a given chemical reaction may be an uncertain process at best; more evidence may arrive at some future time precipitating a reevaluation. Nevertheless, mechanisms are the frosting on the cake of kinetics. In deducing the steps in a mechanism, much speculation can be (and is) made about the way the molecules interact to break and form bonds by chemical detectives. The tools of the trade here are based on experience and guesswork, aided by chemical intuition about bond strengths, molecular vibrations and rotations. Reasoning by analogy serves the same purpose here as it does in reading the periodic table.[9]

Due to the complexity of the subject of chemical mechanisms, introductory treatments are usually limited to the sure subject of *analysis of a given mechanism.* In any valid proposed mechanism, the sum of the steps must equal the overall reaction equation. Each step in a proposed mechanism is assumed to be a simple collision process, for which the orders of reaction equal the stoichiometric coefficients of the step.[10] In the process, a *rate-limiting* slowest step is identified, which restricts the rates of all the steps; the observed rate should equal the rate of the rate-limiting step. If the rate-limiting slow step is not the first step in the mechanism, intermediate species may be involved. They must be eliminated in order to compare the rate law derived from the mechanism with the experimentally derived rate law (which is expressed solely in terms of reactant concentrations). A method for eliminating intermediates mathematically is to assume that all the elementary processes (steps) preceding the slow, rate-limiting step are *reversible*, and achieve *equilibrium* between their reactants

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[8] Despite the arguments given above from the kinetic-molecular collision model for reactions, it may be speculated that there are in fact *no* reactions which proceed by a simple bimolecular single-step mechanism. The classic textbook example of the reaction between dihydrogen and diiodine, for which the rate law was determined in the Nineteenth Century to be mixed second order, was shown by John Sullivan in 1967 to proceed by a multistep process.

A modern theoretical and experimental view sees reactions as more continuous processes, with the bonds extending and compressing on very short (but experimentally accessible) time scales uniformly. In this sense, the elementary chemical "act" is not so discrete as classical mechanistic models describe it to be.

[9] Time-dependent quantum mechanical calculations simulate reactions in a definitive manner, but remain currently beyond reach for all but the simplest systems.

[10] Bimolecular collisions which produce order two, and termolecular which produce order three are the most common cases.

and products. Equilibrium implies that the forward and backward process proceed at *equal* rates.

$$r_{\text{backward}} = r_{\text{forward}} \tag{18.13}$$

Since each elementary step assumes an elementary collision encounter, the rate orders equal the stoichiometric coefficients in the elementary step. Thus for aA + bB + ... = pP + qQ + ..., where one of the species is the intermediate to be eliminated:

$$k_{\text{backward}}[P]^{p}[Q]^{q}\cdots = k_{\text{forward}}[A]^{a}[B]^{b}\cdots \tag{18.14}$$

This provides an algebraic relationship which may be used to solve for the intermediate concentration, and subsequently eliminate from the slow step rate expression. There will be one equation of the form (18.14) for each intermediate in the mechanism. In this way, any of the intermediates can be eliminated from the rate law expression for the rate-determining step, and the rate law can be compared with experiment.

Mechanism to Rate Law Algorithm

Purpose: To determine the rate law (orders of reactants) from a given mechanism.

Procedure:

1. Assume each step is elementary in the sense that the orders of reactants equal the stoichiometric coefficients in the balanced step.
2. If not given, assume one of the steps, called the **rate-limiting step**, to be significantly slower than the others. The rate of the total reaction is then equal to the rate of the rate-limiting step.
3. If the rate-limiting slow step is the first step in the mechanism (or only step in a one-step mechanism), the corresponding rate law for the slow step should match the observed rate law.

   If the rate-limiting slow step is not the first step in the mechanism, it may involve intermediate species. They must be eliminated by expressing their concentrations in terms of reactant concentrations to compare the rate law for the mechanism with that derived experimentally.

   a) For each non-limiting elementary step involving an intermediate of the form $\mathrm{aA + bB} + \cdots = \mathrm{pP + qQ} + \cdots$,

   $$k_{\text{backward}}[\mathrm{P}]^{\mathrm{p}}[\mathrm{Q}]^{\mathrm{q}}\cdots = k_{\text{forward}}[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}\cdots \qquad (18.15)$$

   b) Eliminate intermediates from the rate law by solving for them from equilibrium expressions, and substituting for them in the rate-limiting rate law.

Example 18.1 Deduce the rate law for the following proposed mechanism and compare with experiment:

$$\mathrm{NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO} \qquad \text{(slow)}$$

$$\mathrm{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2} \qquad \text{(fast)}$$

1. Note first of all that the two steps of the mechanism sum algebraically to the overall chemical reaction. Thus intermediates are eliminated in overall reactions.
2. The rate-limiting step is given as the first step in the mechanism.
3. The rate law for the first step can be deduced from the balanced reaction for that step:

$$r = k_1[NO_2]^2$$

The predicted rate law for the reaction $NO_2 + CO \longrightarrow NO + CO_2$ is second order in NO_2 but independent of CO concentration (zero order in CO), which matches experimental analysis.

Example 18.2 Ozone decomposes according to the reaction $2O_3 \longrightarrow 3O_2$. Deduce the rate law for the following proposed mechanism:

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2 + O \qquad \text{(fast)}$$

$$O + O_3 \xrightarrow{k_2} 2\,O_2 \qquad \text{(slow)}$$

1. Note first of all that the two steps of mechanism sum algebraically to the overall chemical reaction. Thus intermediates are eliminated in the overall reactions.
2. The rate-limiting step is specified as the second step in the mechanism.
3. The rate law for the second step can be deduced from the balanced reaction for the step:

$$r = k_2[O][O_3]$$

In this case, the slow step involves the intermediate [O], which must be eliminated to compare the rate law with experiment.

a) Eq. (18.15) applied to the fast, reversible equilibrium of the first step gives:

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

Rearranging to solve for [O], and substituting the result into rate-limiting step rate expression gives:

$$r = \left(\frac{k_2 k_1}{k_{-1}}\right) \frac{[O_3]^2}{[O_2]}$$

with a predicted rate law which is second order in ozone and minus one order

18.5. Empirical Rate Laws

To determine the parameters of a reaction a "divide and conquer" technique is employed which reduces the rate equation to a series of equations in one unknown parameter each and collects the results together to obtain the total solution. By holding the temperature constant, k is constant and the powers (orders) can be obtained one at a time. Taking the orders (powers) as unknowns, Eq. (18.12) is just one equation in several unknowns. To convert it to one equation in one unknown, take all the concentrations but one to be constant.[11] The equation to analyze, then, is of the form

$$r = k'C^n \tag{18.16}$$

where C stands for the concentration of the reactant which is allowed to change, and k' equals k times the constant concentrations of all the other reactants raised to their powers, resulting in a new constant.[12] Knowing the orders of reaction, the temperature can be varied and the temperature dependence parameters can be obtained. In this way, all the parameters can be found and the rate law is known.

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[11] This can be realized experimentally by starting with reactant concentrations that are all large with respect to the one being varied. Although all reactant concentrations change as the reaction proceeds, the only one which changes significantly is the one with relatively small concentration.

[12] There are many equations and graphs associated with kinetics, because it is a quantitative science. Students more comfortable with the alphabet of algebra (x and y) than with other symbols may find it useful to translate the parameters and variables into "algabrize". One must at least distinguish dependent variables from independent variables, and independent variables from parameters. In Eq. (18.16), c is the independent variable upon which r depends; k' and n are parameters, effectively constant for a given system. Translated to algabrize, the equation reads $y = ax^b$.

There are several methods which may be used to determine n from Eq. (18.16), some graphical, some numerical. Some methods are limited to integer values of n, but not all reactions have integral orders. Here we will present a general algebraic method which works for all orders n. It does require knowledge of rates of reaction for given concentrations. Ordinarily in rate experiments one measures concentration as a function of time. It is necessary to derive rates from concentrations to use the algebraic method for determining orders. By definition, the **rate of reaction** is

$$\boxed{r = -\frac{1}{a}\frac{\Delta C_A}{\Delta t} = -\frac{1}{b}\frac{\Delta C_B}{\Delta t} = -\frac{1}{c}\frac{\Delta C_C}{\Delta t} = \cdots = +\frac{1}{p}\frac{\Delta C_P}{\Delta t} = +\frac{1}{q}\frac{\Delta C_Q}{\Delta t} = \cdots \qquad (18.17)}$$

where t is time and Δ means change, so that $\frac{\Delta C_A}{\Delta t}$ is the change in concentration A during a given change in time, and similarly for the other participants (P and Q are typical products). The stoichiometric quotients a,b, ... (from the balanced overall reaction) normalize the concentration changes so that the rate is *independent* of which reactant or product is used to measure it. The plus and minus signs insure that the rate is always a positive quantity, since reactants decrease and products increase with time. Rates can be determined experimentally by following a conveniently measured concentration as a function of time. The slope of a plot of concentration *vs* time (multiplied by the proper sign and divided by the proper stoichiometric coefficient) at a given concentration yields the rate for the given concentration. (See Section 3.2 on Functions and Graphs.)

Suppose the rate of reaction r is known for two values of the concentration C. Eq. 18.17 can be applied to the ratio of the rates to eliminate k, yielding a single equation in one unknown, the order of reaction n. This reasoning is the basis for the following strategy to determine the parameters of a reaction, order n and rate coefficient k:

Empirical Rate Law Algorithm

Purpose: To determine the rate law, orders (powers of concentration) and proportionality (rate) coefficient, for a reaction from rate data.

Procedure:

1. Vary the concentration, C, of each reactant, R, separately:
    A. For a set of reactant concentrations $\{C_1, C_2, C_3, \text{etc}\}$, determine a set of corresponding rates of reaction $\{r_1, r_2, r_3, \text{etc}\}$ from slopes of plots of concentrations as a function of time (Eq. (18.16)).

    B. For N pairs of subscripts (i,j) in the set $\{(r_1, C_1), (r_2, C_2), (r_3, C_3), \cdots\}$, calculate values of $n_{i,j}$ from the following equation (derived from Eq. (18.17))[13]:

    $$n_{i,j} = \frac{\log\left(r_j/r_i\right)}{\log\left(C_j/C_i\right)} \qquad (18.18)$$

    The order of reaction with respect to R is the average of the N $n_{i,j}$ values:

    $$n = \frac{\sum n_{i,j}}{N} \qquad (18.19)$$

2. Given the order of reaction for each reactant, for N pairs of values with subscript i in the set $\{(r_1, C_1), (r_2, C_2), (r_3, C_3), \cdots\}$, calculate a value of k_i from the following equation (derived from Eq. (18.15)):

    $$k_i = \frac{r_i}{C_{Ai}^{\,n_A} C_{Bi}^{\,n_B} C_{Ci}^{\,n_C} \cdots} \qquad (18.20)$$

    The average rate coefficient is then the average of the N k_i values:

    $$k = \frac{\sum k_i}{N} \qquad (18.21)$$

Note that Eq. (18.18) gives simple results for simple cases. E.g. if the rate increases fourfold when the concentration doubles, $r_2 = 4r_1$ and $C_2 = 2C_1$, so

$$n = \frac{\log(4)}{\log(2)} = \frac{\log(2^2)}{\log(2)} = \frac{2\log(2)}{\log(2)} = 2$$

For practical reasons, perhaps only a few rate measurements may be taken, perhaps the minimum number to determine the rate law (one pair of rates for each pair of concentrations). If the experiments are very precise this may be sufficient, but generally more data yields more accurate results.

Example 18.3 Determine the rate law for the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$ from the following data:

Time (min)	$P_{N_2O_5}$ (torr)
20	185.2
40	105.4
60	58.6
80	33.1
100	18.6
160	2.8

(Because the reactants are gases, concentration is expressed in pressure units: $P = (n/V)RT = MRT$.)

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[13] It doesn't matter which base of logarithms are used, because their "conversion factor" (2.302585093 in the case of ln to log) cancels in the ratio expression.

1.A. Note there is only one reactant, which simplifies the process since only one order needs to be determined. The table contains the data for step 1.A). In order to complete step 1, we need to derive rates for each concentration. Accordingly, we estimate rates as differences for adjacent pairs of entries:[14]

i	Time (min)	P_i (torr)	$r_i = -1/2\Delta P_i/\Delta t$
0	20	185.2	
1	40	105.4	2.00
2	60	58.6	1.17
3	80	33.1	0.638
4	100	18.6	0.363

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[14] Note that rate are slopes connecting *two* points. If the line is curved, which point should the rate be associated with? We have chosen to associate it with the second point in this example. Perhaps it would be more honest to associate each rate with the *average* time and concentration for each pair of times and concentrations from which the rate was obtained.

1.B. From each pair of rates Eq. (18.18) yields:

$$\boxed{\begin{aligned}
n_{1,2} &= \frac{\log(0.585)}{\log(0.569)} = 0.951\\
n_{1,3} &= \frac{\log(0.319)}{\log(0.314)} = 0.986\\
n_{1,4} &= \frac{\log(0.182)}{\log(0.176)} = 0.984\\
n_{2,3} &= \frac{\log(0.545)}{\log(0.565)} = 1.062\\
n_{2,4} &= \frac{\log(0.310)}{\log(0.317)} = 1.020\\
n_{3,4} &= \frac{\log(0.569)}{\log(0.562)} = 0.978
\end{aligned}}$$

The average of the six values of n according to Eq. (18.19) is 0.998. Given experimental error, it may be assumed that the reaction is first order ($n = 1$): $r = kP_{N_2O_5}$. This illustrates that the order of reaction does not necessarily equal the stoichiometric coefficient of the balanced overall reaction (2 in this example).[15]

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[15] Until 1925, the only known gaseous first-order reaction was the decomposition of nitrogen pentoxide.

2. The rate coefficient may now be calculated for each rate value, according to Eq. (18.20):

$$\boxed{\begin{aligned} k_1 &= \frac{2.00}{105.4} = 0.0190 \text{ torrs}^{-1} \\ k_2 &= \frac{1.17}{58.6} = 0.0200 \text{ torrs}^{-1} \\ k_3 &= \frac{0.638}{33.1} = 0.0193 \text{ torrs}^{-1} \\ k_4 &= \frac{0.363}{18.6} = 0.0195 \text{ torrs}^{-1} \end{aligned}}$$

The average value for k according to Eq. (18.21) is 0.0195 s^{-1}, so the rate law is

$$r = 0.0195 P_{N_2O_5}$$

Example 18.4 Determine the rate law for the reaction $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$ from the following kinetic data:

Exp	P_{H_2} (torr)	P_{NO} (torr)	r (torr/sec)
1	400	359	9.0
2	400	300	6.2
3	400	152	1.5
4	289	400	9.6
5	205	400	6.6
6	147	400	4.7

Step 1.A has already been done, first holding P_{H_2} constant at 400 torr and determining the rate for varying P_{NO}, then holding P_{NO} constant at 400 torr and determining the rate for varying P_{H_2}.

1.B. For each pair of experiments, Eq. (18.18) yields:

$$\boxed{\begin{array}{l} n_{1,2} = \dfrac{\log(0.689)}{\log(0.836)} = 2.08 \\ n_{1,3} = \dfrac{\log(0.167)}{\log(0.423)} = 2.08 \\ n_{2,3} = \dfrac{\log(0.242)}{\log(0.507)} = 2.09 \\ \hline n_{4,5} = \dfrac{\log(0.688)}{\log(0.709)} = 1.09 \\ n_{4,6} = \dfrac{\log(0.490)}{\log(0.509)} = 1.06 \\ n_{5,6} = \dfrac{\log(0.712)}{\log(0.717)} = 1.02 \end{array}}$$

The orders of reaction are very close to integer second order in NO and integer first order in H_2, so the rate law is of the form:

$$r = k[NO]^2[H_2]$$

This again illustrates that the orders of reaction does not necessarily equal the stoichiometric coefficients of the balanced overall reaction.

2. Given the orders of the reaction, Eq. (18.20) yields for each experiment:

$$\boxed{\begin{aligned}
k_1 &= \frac{9.0}{359^2 \times 400} = 1.74 \times 10^{-7}\ \text{torr}^{-2}\text{s}^{-1}\\
k_2 &= \frac{6.2}{300^2 \times 400} = 1.72 \times 10^{-7}\ \text{torr}^{-2}\text{s}^{-1}\\
k_3 &= \frac{1.5}{152^2 \times 400} = 1.62 \times 10^{-7}\ \text{torr}^{-2}\text{s}^{-1}\\
k_4 &= \frac{9.6}{400^2 \times 289} = 2.07 \times 10^{-7}\ \text{torr}^{-2}\text{s}^{-1}\\
k_5 &= \frac{6.6}{400^2 \times 205} = 2.01 \times 10^{-7}\ \text{torr}^{-2}\text{s}^{-1}\\
k_6 &= \frac{4.7}{400^2 \times 147} = 1.99 \times 10^{-7}\ \text{torr}^{-2}\text{s}^{-1}
\end{aligned}}$$

The average rate coefficient for this reaction is $k = 1.86 \times 10^{-7}\ \text{torr}^{-2}\text{s}^{-1}$, and the rate law is

$$r = 1.86 \times 10^{-7}[\text{NO}]^2[\text{H}_2]$$

More consistent values for k_i should be obtained if the calculated orders of 2.08 and 1.06 are used instead of the rounded-off integer values 2 and 1 (try it!).

18.6. Temperature Dependence of Rates

Since the rate of reaction depends on effective collisions, it is reasonable to expect that as the temperature increases, the kinetic energy increases, and the rate of reaction increases as well. This agrees with experimental facts: *rates of reaction always increase with increasing temperature*. Exactly how much a rate increases for a given temperature increase depends on the reaction, but again the functional relationship between rate and temperature is relatively simple and of universal form for all rates. The temperature dependence enters into the rate coefficient k, since the concentration dependence is already explicitly accounted for in the rate law. The earliest attempts to derive the temperature effect on rates led to a second paradox. According to the kinetic-molecular theory, the number of collisions between molecules increases by about 2 percent for a ten-degree increase in temperature at ordinary temperatures. But many chemical rates were observed to increase much more, typically by an hundred percent for a ten-degree change in temperature. As discussed in the Section 1, the paradox was resolved by recognizing that the molecules that react are not average, but have exceptional high energies, at the tail end of the Maxwell-Boltzmann distribution. The form of the temperature dependence of rate coefficients based on these consideration was first derived by Svante **Arrhenius** in 1889, and bears his name:[16]

$$\boxed{k(T) = A(T)\, e^{-\frac{E_a}{RT}} \qquad (18.22)}$$

The parameter A(T) represents the **collision frequency** of reactants,[17] and E_a represents the energy of the "activation" barrier that reactants must surmount to form products. R is the molar gas constant in energy units, equal to 8.3145 J/mol-K. We will assume here that the temperature dependence of A is negligible (it is revealed experimentally in curvature of Arrhenius plots to be described below). The parameters A and E_a are unique to each reaction and together characterize the temperature dependence of the rate of the reaction.

The Arrhenius equation can be transformed into linear form by taking the natural logarithm, rendering it useful for experimental analysis in determining the parameters A and E_a:

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \qquad (18.23)$$

A plot of ln(k) *vs* 1/T will thus be a straight line with slope = $-E_a/R$ and intercept = ln(A).[18] Since activation barriers are always positive, the negative slope indicates that k decreases with 1/T, or *increases* with increasing T (the fundamental qualitative behavior of rates). Application of the Arrhenius relation to pairs of rate coefficients leads to the following

---

[16] $y(x) = a\, e^{-b/x}$ in algebrize. Arrhenius derived Eq. (18.22) from the kinetic-molecular theory by summing up the total number of molecules in the Maxwell-Boltzmann distribution (Section 13.9) which have kinetic energy equal to the activation energy or greater. We will not show the derivation here; it is given in advanced courses.

[17] Perhaps times a *steric factor* to reflect the fraction of the time the collision occurs with the right orientation to disrupt the right bonds. We will assume this factor is unity.

[18] Identifying ln(k) with y, 1/T with x, m with $-E_a/R$ and ln(A) with b yields the familiar form y = b + mx. Refer to Section 3.3 on Functions and Graphs.

method for determining the parameters A and E_a:

Arrhenius Parameter Algorithm

Purpose: To determine the temperature dependence of rate coefficients (the *Arrhenius parameters* A and E_a).

Procedure:

1. From the Empirical Rate Law Algorithm, obtain values of the rate coefficient, k, for at least two temperatures.
2. For each pair of temperatures, solve two versions of Eq. (18.23) for the two unknowns E_a and A:

$$E_a = \left(\frac{T_1 T_2}{T_2 - T_1}\right) R \ln\left(k_{T_2}/k_{T_1}\right) \tag{18.24}$$

$$A = k_{T_1} e^{\frac{E_a}{RT_1}} = k_{T_2} e^{\frac{E_a}{RT_2}} \tag{18.25}$$

If there are values at more than two temperatures, obtain the best values of E_a and A by averaging.

Alternatively, if there are values at more than two temperatures, make an **Arrhenius plot** of ln(k) *vs* 1/T, based on Eq. (18.22), and determine the best slope and intercept from the data. $E_a = -R \times \text{slope}$, and $\ln(A) = \text{intercept}$.

Example 18.5 Determine the activation energy for the decomposition of nitrogen pentoxide from the following data:

Experiment	Temperature (K)	k (min^{-1})
1	273	0.0000472
2	298	0.00203
3	338	0.292

1. The rate law analysis was carried out in Example 18.3 for one temperature. Once the order of reaction is known, it remains only to find k for a number (at least one) of other temperatures. This is how the data in the table was generated.
2. Applying Eq. (18.25) to the three pairs of data in the table:

$$\boxed{\begin{aligned} E_a(1,2) &= \left(\frac{273\times 298}{298-273}\right)\times 8.3145\times \ln(0.00203/0.0000472) = 101{,}765\ \text{J/mol} \\ E_a(1,3) &= \left(\frac{273\times 338}{338-273}\right)\times 8.3145\times \ln(0.292/0.0000472) = 103{,}038\ \text{J/mol} \\ E_a(2,3) &= \left(\frac{298\times 338}{338-298}\right)\times 8.3145\times \ln(0.292/0.00203) = 104{,}023\ \text{J/mol} \end{aligned}}$$

To the proper number of significant figures, the average activation energy for the decomposition of nitrogen pentoxide is 103 kJ.

If one prefers an automated method, the Example 3.3 of Section 3.12 determines the least-squares regression slope to be −12399, from which one obtains an activation energy of −12399 x 8.3145/1000 = 103.1 kJ.

Summary

Chemical reactions occur through molecular collisions which are effective in surmounting an activation energy barrier. Multistep processes can be studied by kinetics analysis to identify the elementary steps of the mechanism.

CHEMICAL KINETICS EXERCISES

1. Determine the activation energy for the decomposition of nitrogen pentoxide from an Arrhenius plot.
2. Try to guess a reasonable mechanism which accounts for the observed rate law of nitrogen pentoxide. Derive the rate law for the proposed mechanism and compare with the experimentally derived rate law in Example 18.3.
3. What are the units of a third order rate coefficient?

CHEMICAL KINETICS EXERCISE HINTS

1. See Example 18.5 for the data.
2. Reasonable mechanisms should involve bimolecular elementary processes, not "unimolecular" "collisions".
3. Solve the appropriate rate law for k.