4

RELATIONSHIP BETWEEN RATES AND MECHANISMS

PRÉCIS

The objective of this chapter is to examine the relationship between rates and mechanisms. So far in this book we have treated rate equations as empirical relationships that are fit to rate data. However, in fact, rate equations have a more fundamental basis. The form of the rate equation is determined by the elementary chemical reactions that occur as a reaction proceeds. The rate constants are related to the rate of the elementary reactions.

The objective of this chapter is to explore the relationship between rates and mechanisms. We will introduce the concept of a mechanism, and show how one can use the mechanism and the pseudo-steady-state approximation to calculate a rate equation for a given reaction. Most of the students who take our course already know that reactions obey distinct mechanisms, and many have seen the pseudo-steady-state approximation previously. However, most students do not know where the pseudo-steady-state approximation comes from, when it works, and when it fails. The objective of this chapter is to extend students' knowledge so that they will know how the pseudo-steady-state approximation arises, and where it fails. We will also define some more key terms that we will use later in the book.

4.1 INTRODUCTION

Studies of the relationship between rates and mechanisms have had a long history. Work started with Dobereiner (1829) and Wilhelmy (1850), who supposed that rates of reaction would be simply related to the stoichiometry of the reaction. However, in 1878, Van't Hoff showed that the rate of reaction had little correlation to stoichiometry. For example, Table 2.5 (page 14) shows the rate equation for several reactions discussed by Van't Hoff. Notice that the rate of phosphine oxidation is first-order in the phosphine concentration and half-order in the oxygen concentration. Yet during the reaction, each phosphine reacts with two oxygens to yield products. Further, one needs two phosphines to yield each P_2O_5.

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This example shows that there is no relationship between the rate equation for a reaction and the stoichiometry of the reaction.

The purpose of this chapter is to try to understand the molecular basis of the rate equation, and in particular why rates do not correlate with stoichiometry. Section 4.2 will discuss the idea that reactions actually occur by a complex series of chemical reactions. Sections 4.3 and 4.4 will review the rates of elementary reactions and how the rates are related to the stoichiometry of the reactions.

Next, we will examine rate equations. In Section 4.5 we will show that if one knows the mechanism one will be able to derive a set of differential equations for the change in concentration of all of the species in the reactor. The differential equations are the fundamental rate equations for a chemical reaction, and they fully determine the behavior. We will briefly review the behavior to give the reader a qualitative picture of the results. Next, we describe the pseudo-steady-state approximation and see how it can be used to determine a rate equation. We will also discuss the rate-determining-step approximation. Finally, we will close by discussing the failure of the methods, and what one does in such a case. The discussion will assume that the reader has had an introduction to these topics before. If you have not had an introduction, please look back over the kinetics section of your physical chemistry text before proceeding with this chapter.

4.2 HISTORICAL OVERVIEW

To start, it is useful to review some history. In the 1896 edition of his book, *l'Etudes Dynamique Chemie*, Van't Hoff speculated why the kinetics of a reaction did not correspond to the stoichiometry of the reaction. Van't Hoff supposed that when only one molecule participated in a critical step of reaction, the reaction would be first-order. In contrast, if two molecules participated in some critical step of a reaction, the reaction would be second-order. Consequently, Van't Hoff proposed that the kinetics of a reaction were related to what Van't Hoff termed the **molecularity** of a reaction, where the molecularity was loosely defined as the number of molecules participating in some critical step in the reaction.

For further reference, we will need to know that there are **unimolecular** reactions, where only one reactive molecule participates; **bimolecular** reactions, where two molecules participate; and **termolecular** reactions, where three molecules participate. An example of a unimolecular reaction is

$$\text{Cyclopropane} \Longrightarrow \text{propylene} \tag{4.1}$$

where one cyclopropane molecule rearranges to yield propylene. An example of a bimolecular reaction is

$$\mathrm{OH} + \mathrm{C_2H_6} \Longrightarrow \mathrm{H_2O} + \mathrm{C_2H_5} \tag{4.2}$$

where a hydroxyl grabs a hydrogen from an ethane molecule. An example of a termolecular reaction is

$$\mathrm{CH_3} + \mathrm{CH_3} + \mathrm{N_2} \Longrightarrow \mathrm{C_2H_6} + \mathrm{N_2} \tag{4.3}$$

This example is more complex; two methyl radicals are reacting to form ethane. However, no reaction occurs unless a nitrogen collides with the two methyls. The nitrogen facilitates the reaction.

Van't Hoff proposed that all first-order reactions are unimolecular, all second-order reactions are bimolecular, and all third-order reactions are termolecular.

If one looks at the stoichiometry of the reaction, though, one finds that complicated reactions have simple rate equations. For example, according to the information in Table 2.1 (page 14) the reaction

$$4\mathrm{PH_3} \Longrightarrow \mathrm{P_4} + 6\mathrm{H_2} \tag{4.4}$$

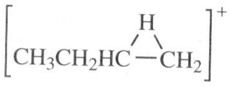
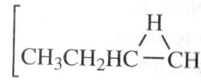
is first-order in the phosphine pressure. Yet, it is hard to imagine how reaction (4.4) could be a unimolecular reaction. After all, one needs four phosphines to produce a single P_4. Van't Hoff tried to get around this difficulty by assuming that only one molecule was participating in some critical step in reaction (4.4). However, when Van't Hoff's book was written (1896), it was not obvious how it was possible to have only a single phosphine molecule participate in the reaction when four phosphines are needed to produce a P_4.

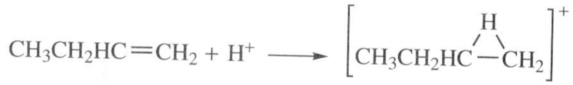
In the time between 1890 and 1919, a number of papers were written that looked at the details of many different reactions. An attempt was made to try to understand how the kinetics of a reaction was related to the stoichiometry of the reaction. David Chapman (1913) Muriel Chapman, and Max Bodenstein (1907) examined the kinetics of HCl formation. They showed that the reaction

$$\mathrm{H_2} + \mathrm{Cl_2} \Longrightarrow 2\mathrm{HCl} \tag{4.5}$$

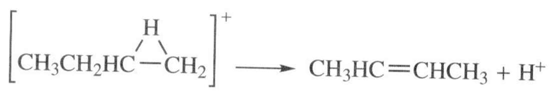
did not occur via a direct reaction between molecular chlorine and molecular hydrogen. Instead, the chlorine needed to dissociate into atoms before the reaction proceeded. Slowly a consensus emerged that the reactants are not directly converted into products during a chemical reaction. Rather, the reactants are converted into species called **reactive intermediates**, and then the reactive intermediates are converted into products. For example, during the acid-catalyzed isomerization of 1-butene to 2-butene in solution

$$\mathrm{CH_3CH_2HC{=}CH_2} \overset{\mathrm{H^+}}{\Longrightarrow} \mathrm{CH_3HC{=}CHCH_3} \tag{4.6}$$

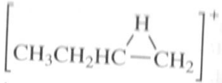
The H^+ reacts with the 1-butene to produce a  $\left[\mathrm{CH_3CH_2HC}\overset{\mathrm{H}}{\diagup\diagdown}\mathrm{CH_2}\right]^+$ intermediate where the hydrogen is held in a three-center two-electron bond. The  $\left[\mathrm{CH_3CH_2HC}\overset{\mathrm{H}}{\diagup\diagdown}\mathrm{CH_2}\right]^+$ intermediate then loses a 3-proton to form 2-butene. The sequence of reactions is



$$\mathrm{CH_3CH_2HC{=}CH_2} + \mathrm{H^+} \longrightarrow \left[\mathrm{CH_3CH_2HC}\overset{\mathrm{H}}{\diagup\diagdown}\mathrm{CH_2}\right]^+ \tag{4.7a}$$



$$\left[\mathrm{CH_3CH_2HC}\overset{\mathrm{H}}{\diagup\diagdown}\mathrm{CH_2}\right]^+ \longrightarrow \mathrm{CH_3HC{=}CHCH_3} + \mathrm{H^+} \tag{4.7b}$$

There are two reactions in mechanism (4.7): 1-butene is the reactant,  $\left[\mathrm{CH_3CH_2H}\overset{\mathrm{H}}{\overbrace{\mathrm{C{-}CH_2}}}\right]^+$ is the intermediate, and 2-butene is the product. Each of the steps in mechanism 4.7 are called **elementary reactions**, while reaction (4.6) is called the **overall reaction**, or the **stoichiometric reaction**.

> More precisely, an elementary reaction is defined as a chemical reaction going from reactants to products without going through any *stable* intermediates. In this context, a species is said to be stable if it has a lifetime longer than ~10^{-11} seconds (i.e., much longer than vibrational or collisional times).

There are some important notations. We will use a single arrow → to designate an elementary reaction but a double arrow ⇒ to designate an overall reaction. In this notation, the reaction

$$H_2 + Br_2 \Longrightarrow 2HBr \tag{4.8}$$

will be an overall reaction, while the reaction

$$H + Br_2 \longrightarrow HBr + Br \tag{4.9}$$

will be an elementary reaction.

In the gas phase, most elementary reactions are of the type

$$A + B \longrightarrow C + D \tag{4.10}$$

where at least two reactants come together to produce at least two products. Examples include

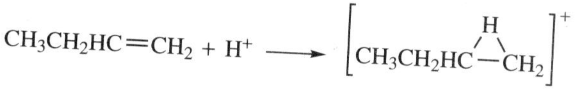
$$H + HBr \longrightarrow H_2 + Br \tag{4.11}$$

and

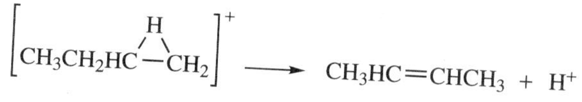
$$X + H_2 \longrightarrow 2H + X \tag{4.12}$$

where X is a something called a **collision partner**. The collision partner is a species that collides with the H_2 and initiates the reaction.

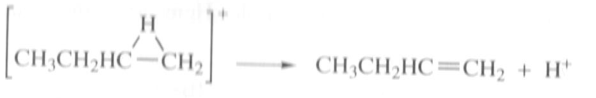
Next, we want to define a concept called the **mechanism** of a reaction. The mechanism of a reaction is defined as the sequence of elementary reactions that occur at appreciable rates when the reactants come together and react to form products. For example, if one actually runs reaction (4.6) in solution, one finds that four elementary reactions can occur:



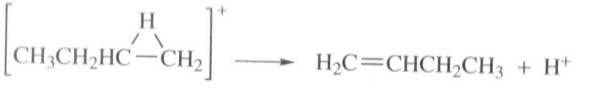
$$\mathrm{CH_3CH_2HC{=}CH_2} + \mathrm{H^+} \longrightarrow \left[\mathrm{CH_3CH_2H}\overset{\mathrm{H}}{\overbrace{\mathrm{C{-}CH_2}}}\right]^+ \tag{4.13a}$$



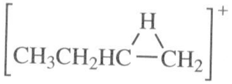
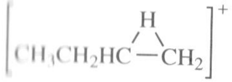
$$\left[\mathrm{CH_3CH_2H}\overset{\mathrm{H}}{\overbrace{\mathrm{C{-}CH_2}}}\right]^+ \longrightarrow \mathrm{CH_3HC{=}CHCH_3} + \mathrm{H^+} \tag{4.13b}$$



$$\left[\mathrm{CH_3CH_2H}\overset{\mathrm{H}}{\overbrace{\mathrm{C{-}CH_2}}}\right]^+ \longrightarrow \mathrm{CH_3CH_2HC{=}CH_2} + \mathrm{H^+} \tag{4.13c}$$



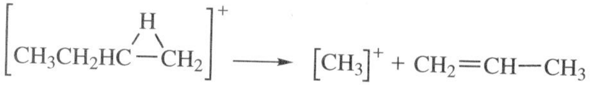
$$\left[\mathrm{CH_3CH_2H}\overset{\mathrm{H}}{\overbrace{\mathrm{C{-}CH_2}}}\right]^+ \longrightarrow \mathrm{H_2C{=}CHCH_2CH_3} + \mathrm{H^+} \tag{4.13d}$$

The first two steps in (4.13) are the steps listed in reaction (4.7). The last two steps are processes where the  $\left[\mathrm{CH_3CH_2H}\overset{\mathrm{H}}{\overbrace{\mathrm{C{-}CH_2}}}\right]^+$ intermediate loses a proton to produce either 1-butene or the equivalent 3-butene. Note that the proton that leaves the  $\left[\mathrm{CH_3CH_2H}\overset{\mathrm{H}}{\overbrace{\mathrm{C{-}CH_2}}}\right]^+$ intermediate in steps (4.13c) and (4.13d) may be different from the proton which reacts in step (4.13a).[1]

The sequence of elementary reactions listed in (4.13) is called the *mechanism of acid-catalyzed isomerization* of 1-butene and 2-butene.

There are two subtle points in the definition of a mechanism that students often miss. First, notice that there are four elementary reactions in equation (4.13). However, only the first two of the four lead from reactants to products. The other two steps lead back to the reactants. Therefore, it is incorrect to think of the mechanism as consisting of just the steps leading from reactants and products. Rather, the mechanism includes the steps that lead from reactions to products, plus other steps that either lead to new products or convert the intermediates back to the reactants.

A second subtlety is that when someone reports a mechanism in the literature, they do not necessarily list all of the reactions that would occur. They list only reactions that occur at appreciable rates. For example, during reaction (4.6), one also gets the reaction



$$\left[\mathrm{CH_3CH_2H}\overset{\mathrm{H}}{\overbrace{\mathrm{C{-}CH_2}}}\right]^+ \longrightarrow [\mathrm{CH_3}]^+ + \mathrm{CH_2{=}CH{-}CH_3} \tag{4.14}$$

Reaction (4.14) is much slower than reactions (4.13a)–(4.13d). Consequently, people often ignore reaction (4.14) even though it occurs at a nonnegligible rate. The mechanism of a reaction, then, does not necessarily include all reactions that occur. Rather, they include only reactions that occur at nonnegligible rates.

An important point is that

> Every overall chemical reaction can be divided into a sequence of elementary reaction.
> Every reaction has a mechanism.

Sometimes reactions have more than one mechanism. This occurs when there are, for example, competing reaction pathways.

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[1] If reaction (4.13) would occur in the gas phase, one would need collision partners. For the purposes here, we will ignore the collision partners, since in solution, the solvent can act as a collision partner.

The mechanism in (4.13) is relatively simple. Here are some other examples. The reaction

$$H_2 + Br_2 \Longrightarrow 2HBr \tag{4.15}$$

follows the following mechanism:

$$\begin{aligned}
Br_2 &\xrightarrow{1} 2Br \\
Br + H_2 &\xrightarrow{2} HBr + H \\
H + Br_2 &\xrightarrow{3} HBr + Br \\
2Br &\xrightarrow{4} Br_2 \\
H + HBr &\xrightarrow{5} H_2 + Br
\end{aligned} \tag{4.16}$$

The reaction

$$2H_2 + O_2 \Longrightarrow 2H_2O \tag{4.17}$$

follows a complex mechanism with over 30 steps. However, one can get the structure of the solution by assuming that the reaction obeys the following mechanism:

$$\begin{aligned}
H_2 + O_2 &\xrightarrow{1} 2OH\bullet \\
OH\bullet + H_2 &\xrightarrow{2} H_2O + H\bullet \\
H\bullet + O_2 &\xrightarrow{3} OH\bullet + O: \\
O: + H_2 &\xrightarrow{4} OH\bullet + H\bullet \\
H\bullet &\xrightarrow{5} \text{wall} \\
H\bullet + O_2 + X &\xrightarrow{6} HO_2\bullet + X \\
HO_2\bullet + X &\xrightarrow{7} \text{wall} \\
2HO + X &\xrightarrow{8} H_2O_2 + X
\end{aligned} \tag{4.18}$$

Notice that even through the overall reactions in (4.15) and (4.17) appear to be simple, the mechanisms are not simple. This is typical. Physically, what is happening is that reactive intermediates are, by definition, reactive. They undergo many reactions. As a result, there are usually many reactions in an overall mechanism.

Let's repeat that again because it is really important.

Reactive intermediates are by definition reactive. They undergo many reactions.

We will describe the mechanisms of many different reactions in Chapters 5 and 12. However, the thing to remember for now is that a typical chemical reaction occurs via a number of elementary steps. One needs to understand the kinetics of those individual steps to determine the mechanism of a reaction.

4.3 KINETICS OF ELEMENTARY REACTIONS

Next, we want to discuss how the mechanism of a reaction is related to the kinetics of the reaction. We will assume for the moment that you already know the mechanism of a reaction, and ask how one can determine the rate equation of reaction from the mechanism.

We will start with some material that we will eventually derive in Chapter 9. Consider an elementary reaction between an atom or molecule, A, and another atom or molecule, B, to form two product atoms or molecules, P and Q:

$$A + B \longrightarrow P + Q \tag{4.19}$$

In Chapter 9, we will show that r_2, the rate of reaction (4.19), is given by

$$r_2 = k_2[A][B] \tag{4.20}$$

Similarly, the rate of formation of A is given by

$$r_A = -k_2[A][B] \tag{4.21}$$

where [A] and [B] are the concentrations of A and B, respectively, and k_2 is a constant. Equation (4.20) is a key result. It says that if we know the stoichiometry of an elementary reaction, we also know the rate equation for the reaction. Notice that the rate equation for an elementary reaction is proportional to the product of the concentrations of the reactants of the elementary reaction. However, the rate does not depend on the concentrations of the products of the elementary reactions.

One can also consider elementary reactions of the form

$$2A \xrightarrow{4} P + Q \tag{4.22}$$

In this case the rate of reaction, r_4, obeys

$$r_4 = k_4[A]^2 \tag{4.23}$$

Similarly, the rate of formation of A, r_A is given by

$$r_A = -2k_4[A]^2 \tag{4.24}$$

where k_4 is the rate constant for reaction (4.22).

The factor of 2 in equation (4.24) is very important. The factor of 2 arises because two molecules of A are destroyed every time reaction (4.22) goes once. Students often forget the factors of 2 when they derive rate equations. The reader should be very careful to avoid that error.

One way to avoid this error is to use the definitions from Chapter 2 to quantify the rate of formation of any species. For example, consider species A participating in a group of reactions numbered 1, 2, . . . , i. One can show that the net rate of formation of the species, r_A, is given by

$$\boxed{r_A = \beta_{A,1}r_1 + \beta_{A,2}r_2 + \cdots + \beta_{A,i}r_i} \tag{4.25}$$

where r_i, $r_2, \ldots, r_i$ are the rates at reactions $1, 2, \ldots, i$, respectively, and $\beta_{A,1}$, $\beta_{A,2}, \ldots, \beta_{A,i}$ are the stoichiometric coefficients of species A in reaction 1, 2, . . . , i. Again, we remind you that in our definition, the stoichiometric coefficient is negative for a reactant and positive for a product. In reaction (4.22), $\beta_{A,4.26}$ is −2, which is why there is a −2 in equation (4.24). When I am deriving rate equations, I find it easier to remember that the coefficient in the rate equation is ALWAYS the stoichiometric coefficient instead of having to work out the coefficient every time.

Equation (4.20) applies only to elementary reaction of the form in (4.19). However, people often generalize equations (4.20) to first- and third-order reactions. For example, with an elementary reaction of the form

$$A \longrightarrow P \tag{4.26}$$

it is often *incorrectly* assumed that the reaction obeys

$$r_A = k_1[A] \tag{4.27}$$

where [A] is the concentration of A and k_1 is a constant. Similarly, with an elementary reaction of the form

$$A + B + C \longrightarrow \text{products} \tag{4.28}$$

it is often assumed that the reaction obeys:

$$r_A = -k_3[A][B][C] \tag{4.29}$$

where [A], [B] and [C] are the concentration of A, B, and C, respectively, and k_3 is a constant.

In actual practice, elementary reactions of the form in equation (4.26) are never seen experimentally and reactions of the form in equation (4.28) are rarely seen. In Chapter 8, we will show that the rate constant for any elementary reaction of the form in (4.26) (i.e., where one reactant is converted into one product without colliding with any other molecule in the system) is ZERO, which means that elementary reactions of the form in equation (4.26) are impossible. Similarly, we will show that the rate constant for reactions of the form in equation (4.28) is very small. Therefore, in practice, one rarely sees reactions of the form in equations (4.26) and (4.28). One can, however, see reactions of the form

$$A + X \longrightarrow P + X \tag{4.30}$$

where X is any other molecule in the system that can collide with A. We call X the *collision partner*. Reaction (4.30) obeys

$$r_A = -k_2[A][X] \tag{4.31}$$

where [A] and [X] are the concentrations of A and X, and k_2 is a constant. Equation (4.31) is very similar to equation (4.27) in cases where [X] does not change during the reaction. As a result, people often say that the kinetics of a reaction like that in reaction (4.30) obey (4.27) approximately, even though they do not fit exactly.

There is an important point I want to repeat here that for emphasis. One can never have an elementary reaction with only one reactant or only one product. It looks as though you only have one reactant or one product in some elementary reaction. There will always be some other species, X, contributing to the reaction. Therefore, the elementary reactions are

$$A + X \longrightarrow B + C + X$$
$$A + B + X \longrightarrow P + X$$

and NOT

$$A \longrightarrow B + C$$
$$A + B \longrightarrow C$$

4.4 THE RELATIONSHIP BETWEEN KINETICS AND EQUILIBRIUM (MICROSCOPIC REVERSIBILITY)

Before we proceed, it is useful to point out that the results in Section 4.3 imply that there is a simple relationship between the kinetics of a reaction and the equilibrium constant for the reaction. Consider the simple reversible elementary reaction:

$$A + B \underset{2}{\overset{1}{\rightleftharpoons}} C + D \tag{4.32}$$

The equilibrium constant for the reaction, $K_{1,2}$, is given by

$$K_{1,2} = \frac{[C][D]}{[A][B]} \tag{4.33}$$

where [A], [B], [C], and [D] are the concentrations of A, B, C, and D. There is a principle called **microscopic reversibility**, which states

> At equilibrium, the rate of any forward chemical reaction (elementary or not) must equal the rate of the reverse chemical reaction. (4.34)

Principle (4.34) implies that at equilibrium, the rate of all processes must equal the rate of the backward processes.

If we apply principle (4.34) to our example, we conclude that at equilibrium, the rate of the forward reaction 1 should be equal to the rate of the reverse reaction 2. Therefore

$$k_1[A][B] = k_2[C][D] \tag{4.35}$$

where k_1 and k_2 are the rate constants for reactions 1 and 2. Rearranging equation (4.35) yields

$$\frac{[C][D]}{[A][B]} = \frac{k_1}{k_2} \tag{4.36}$$

Substituting equation (4.36) into equation (4.33) yields

$$K_{1,2} = \frac{k_1}{k_2} \tag{4.37}$$

Consequently, the equilibrium constant for a reversible elementary reaction is equal to the ratio of the forward and reverse rate constants for the reaction.

One can generalize this result to a more complex reaction:

$$A + B \underset{-1}{\overset{1}{\rightleftarrows}} C + D \underset{-2}{\overset{2}{\rightleftarrows}} E + F \underset{-3}{\overset{3}{\rightleftarrows}} G + H \underset{-4}{\overset{4}{\rightleftarrows}} I + J \underset{-5}{\overset{5}{\rightleftarrows}} L + M \tag{4.38}$$

At equilibrium

$$\frac{[E][F]}{[A][B]} = \frac{k_1k_2}{k_{-1}k_{-2}} \tag{4.39}$$

$$\frac{[L][M]}{[A][B]} = \frac{k_1k_2k_3k_4k_5}{k_{-1}k_{-2}k_{-3}k_{-4}k_{-5}} \tag{4.40}$$

$$\frac{[L][M]}{[G][H]} = \frac{k_4k_5}{k_{-4}k_{-5}} \tag{4.41}$$

where [A], [B], [E], [F], [G], [H], [L], and [M] are the concentrations of A, B, E, F, G, H, L, and M, respectively, and k_1, k_{-1}, and so on are the rate constants for reactions 1, −1, and so forth. I find that a good mnemonic to remember these results is that if I want to calculate the equilibrium concentration of two species G and H and two other species C and D, I say that the product of the concentration of G and H divided by the concentrations of C and D is equal to the product of all the rate constants leading from C and D to G and H divided by the rate constants for the reverse reactions. There are two rate constants leading from C and D to G and H, k_2 and k_3. Therefore

$$\frac{[G][H]}{[C][D]} = \frac{k_2k_3}{k_{-2}k_{-3}} \tag{4.42}$$

Similarly, I say that the product of the concentration of C and D divided by the concentrations of G and H is equal to the product of all of the rate constants leading from G and H to C and D divided by the rate constants for the reverse reactions. There are two rate constants leading from G and H to C and D, k_{-2} and k_{-3}. Therefore

$$\frac{[C][D]}{[G][H]} = \frac{k_{-2}k_{-3}}{k_2k_3} \tag{4.43}$$

4.5 RATES OF OVERALL REACTIONS

Next, we will change topics slightly and use the results in Section 4.2 to derive a rate equation for an overall reaction. Our approach will be to consider the mechanism in equation (4.13) and derive an equation. We will then generalize to a mechanism.

Consider the mechanism in equation (4.13). During the mechanism in reaction (4.13), 1-butene reacts with a proton to yield an intermediate. The intermediate then decomposes to either form 2-butene or decomposes back to form 1-butene. If we call 1-butene, "A", 2-butene "P", and the intermediate "I", then one can view the reaction as follows:

$$A + H^+ \underset{2}{\overset{1}{\rightleftarrows}} I \xrightarrow{3} P + H^+ \tag{4.44}$$

where we have ignored the collision partners since we are running the reaction in solution.

In equation (4.44), we call the reaction that converts A into I "reaction 1". The reaction that converts I back to A is called "reaction 2". The reaction that converts I to P is called "reaction 3".

Next, we will to derive a general equation for the change in the concentration of all of the species in the system. Our approach will be to use equation (4.25) to derive a differential equation for the production rate of all of the species. We will then integrate the differential equation to compute all of the rates.

4.5.1 Derivation of a Differential Equation for the Concentration

First, we derive a general differential equation for the rate of production of each of the species. The general approach will be to plug into equation (4.25) to obtain a differential equation for each species.

Consider the intermediate I. The intermediate I is formed in reaction 1 and destroyed in reactions 2 and 3. Therefore, according to equation (4.25), one can write the change in the concentration of the intermediate I as

$$\frac{d[I]}{dt} = r_1 - r_2 - r_3 \tag{4.45}$$

where r_1, r_2, and r_3 are the rates of reactions 1, 2, and 3 respectively; [I] is the concentration of the intermediate I; and t is time. Similarly, [A], the concentration of A, obeys:

$$\frac{d[A]}{dt} = r_2 - r_1 \tag{4.46}$$

where r_1, and r_2 are the rates of reactions 1 and 2, respectively.

According to equation (4.21), r_1 is given by

$$r_1 = k_1[A][H^+] \tag{4.47}$$

where k_1 is the rate constant for reaction 1, [A] is the concentration of A, and $[H^+]$ is the concentration of protons. Similarly, r_2 and r_3 are given by

$$r_2 = k_2[I] \tag{4.48}$$

$$r_3 = k_3[I] \tag{4.49}$$

(4.47) and (4.48) into equation (4.46) yields

$$\frac{d[A]}{dt} = k_2[I] - k_1[A][H^+] \tag{4.50}$$

Similarly, substituting equations (4.47)–(4.49) into equation (4.45) yields

$$\frac{d[I]}{dt} = k_1[A][H^+] - (k_2 + k_3)[I] \tag{4.51}$$

Equations (4.50) and (4.51) are the fundamental differential equations for the behavior of the system. They are the key results in this section.

4.5.2 Integration of the Rate Equation

Next, we want to integrate the equations to calculate the overall rate of reaction. There are three approaches:

- Analytic integration of the differential equations
- Numerical integration of the differential equations
- Approximate integration of the rate equation

In this section we will concentrate on the analytic treatment. Numerical integration is discussed in the supplementary material. An approximation scheme is discussed in Section 4.7. In order to simplify the algebra, we will assume that $[H^+]$ is constant [equation (4.50)] and that we start with pure A (no intermediate or product) so that

$$[A] = [A]^0 \qquad [I] = 0 \qquad [P] = 0 \qquad \text{at } t = 0 \tag{4.52}$$

One can then solve equations (4.50) and (4.51) simultaneously to calculate the concentration of A and I as a function of time. The algebra is complex, but the answer is

$$[A] = [A]^0 \left\{ \frac{(k_4 - k_6)\exp(-k_5 t) - (k_5 - k_6)\exp(-k_4 t)}{(k_4 - k_5)} \right\} \tag{4.53}$$

$$[I] = [A]^0 \left\{ \frac{(k_4 - k_6)(k_6 - k_5)}{k_2(k_4 - k_5)} \right\} \{\exp(-k_5 t) - \exp(-k_4 t)\} \tag{4.54}$$

where $[A]^0$ is the initial concentration of A and

$$k_4 = \tfrac{1}{2}(k_6 + k_2 + k_3 + \sqrt{(k_6 + k_2 + k_3)^2 - 4k_6 k_3}) \tag{4.55}$$

$$k_5 = \tfrac{1}{2}(k_6 + k_2 + k_3 - \sqrt{(k_6 + k_2 + k_3)^2 - 4k_6 k_3}) \tag{4.56}$$

$$k_6 = k_1[H^+] \tag{4.57}$$

Note that every mole of A that is used up must be converted into P or I. The number of moles of A used up is the initial concentration of A minus the current concentration of A. Therefore, the sum of the number of moles of I and P is given by

$$[P] + [I] = [A]^0 - [A] \tag{4.58}$$

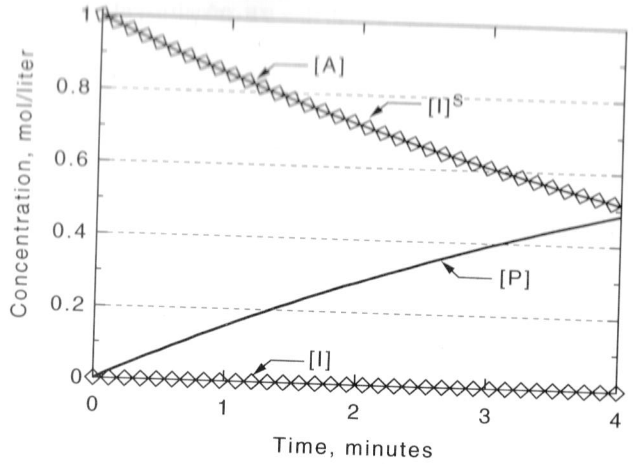

Figure 4.1 [A], [I], and [P] as a function of time calculated from equations (4.53), (4.54), and (4.58), respectively, with $k_1[H^+] = 0.2$/minute, $k_2 = 5.7 \times 10^6$/minute, and $k_3 = 3.8 \times 10^7$/minute.

where [A], [I], and [P] are the concentrations of A, I, and P, respectively, at any time during the reaction, and $[A]^0$ is the initial concentration of A. Equation (4.58) can be used to calculate [P]. One should verify equations (4.53) and (4.54) before proceeding with this chapter.

Figure 4.1 shows a plot of [A], [I], and [P] as a function of time calculated from equations (4.53), (4.54), and (4.58), respectively, for some typical values of the parameters. Typically $k_1[H^+]$, the rate constant for the formation of the reactive intermediate, will be much less than k_2 and k_3, the rate constants for the destruction of the reactive intermediate. If one substitutes values into equation (4.54), one finds that the concentration of the intermediates is small.

4.5.3 An Approximation

For future reference, Figure 4.1 also provides a plot of another quantity, $[I]^S$, where $[I]^S$ is defined by

$$[I]^S = [I]\left(\frac{k_2 + k_3}{k_1[H^+]}\right) \tag{4.59}$$

Notice that $[I]^S$ and [A] are almost equal, except near $t = 0$.

Next, we will compute a new quantity, where $[I]^X$ is an approximation to [I], by substituting [A] for $[I]^S$ in equation (4.59), substituting $[I]^X$ for [I] and rearranging. The result is

$$[I]^X = [A]\left(\frac{k_1[H^+]}{k_2 + k_3}\right) \tag{4.60}$$

Figure 4.2 compares [I] calculated from equation (4.54) to $[I]^X$ computed from equation (4.60). The left curve shows the behavior from $t = 0$ to $t \leq 10^{-7}$ minutes; the right curve shows the behavior from 2×10^{-2} minutes on. Notice that there are some deviations for $t < 10^{-7}$ minutes. However, the two curves are virtually identical when $t > 10^{-7}$ minutes.

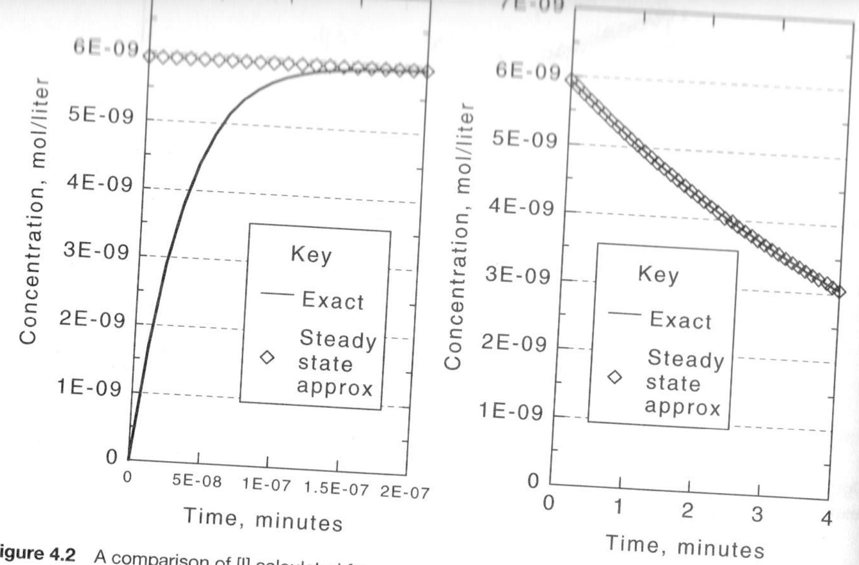

Figure 4.2 A comparison of [I] calculated from equation (4.54) and $[I]^X$ computed from equation (4.60).

We rarely care about the first 10^{-7} minutes in a process that takes several minutes. Consequently, the approximation in (4.60) works quite well in most practical cases.

4.6 GENERALIZATION TO OTHER REACTIONS

Next, we want to generalize these results to other reactions. First, it is important to note that there is nothing special about the example we considered in Section 4.4. If we start with any reaction, we can always set up a series of differential equations similar to equations (4.50) and (4.51), and then solve the equations to predict the behavior of the system. In a general case, the differential equations can be complex. However, one can always numerically integrate the differential equations to calculate all of the concentrations. There are some details that one needs to worry about when one does the numerical integrations because initially the intermediate concentration changes much more quickly than does the reactant concentration. Still, the equations can be solved numerically, using standard commercial software as shown in the solved examples at the end of this chapter. Consequently, if one knows the rate equations for a mechanism, one can always solve the rate equations to calculate the behavior of the reacting system. Algorithms are given in Example 4.B.

The algorithms are very general, and can be used for any rate equation. Generally, the numerical solution is the most accurate way to understand the behavior of a reaction.

4.7 THE PSEUDO-STEADY-STATE APPROXIMATION

Often however, one needs an analytical expression for the rate equation that one then uses in, for example, a reactor design. In order to get the approximation, we will generalize the approximation in equation (4.60) and use that approximation to estimate the concentrations of all the intermediates. In particular, we will derive what is called the *pseudo-steady-state approximation* for the intermediate concentrations and see how this approximation works.

I know that most of our readers have already seen the pseudo-steady-state approximation. However, I was not sure whether people know where this approximation comes from. Therefore, I decided to "derive" this approximation rather than just present it.

We will start by computing the size of the various terms in equation (4.51). Figure 4.3 is a plot of the various terms in equation (4.51) calculated by substituting equations (4.53) and (4.54) into equation (4.51). Notice that the first term on the right side of equation (4.51) is between 0.1 and 0.2 over the entire range at times shown. The second term on the right side of equation (4.51) is between 0.1 and 0.2 after 2×10^{-8} minutes. In contrast, while the derivative on the left side of equation (4.51) is significant for the first 10^{-7} minutes, the derivative decreases rapidly so that after the first 2×10^{-7} minutes, it is much smaller than the other two terms in the equation. In fact, on the scale shown, after the first 10^{-7} minutes, the derivative appears to be virtually zero.

One can use the fact that the derivative in equation (4.51) is almost zero to compute useful quantities. Let's assume, for the moment, that we can set the derivative in equation (4.51) to zero. In that case, equation (4.51) becomes

$$0 = k_1[A][H^+] - (k_2 + k_3)[I] \tag{4.61}$$

Rearranging equation (4.61) yields

$$[I] = [A]\left(\frac{k_1[H^+]}{k_2 + k_3}\right) \tag{4.62}$$

Notice that equations (4.60) and (4.62) are virtually the same. According to Figure 4.2, [I] calculated from equation (4.62) will be virtually identical to [I] computed from the exact

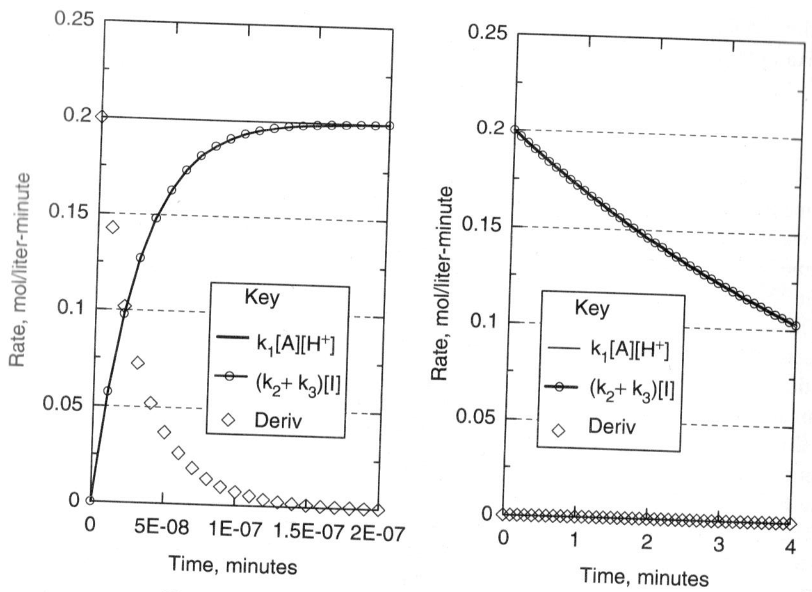

Figure 4.3 The size of various terms in equation (4.51).

result, equation (4.54), except at t = 0. Therefore, one can compute useful properties by assuming that the derivative in equation (4.51) is zero.

Physically, the derivative is the *net* rate of formation of the intermediate. If we set the derivative equal to zero, we are in effect assuming that the intermediates react as soon as they form. Physically, even though the intermediates form relatively quickly, they react very quickly, too, so that the net rate of formation of the intermediates is small.

One can easily generalize this result using something called the **pseudo-steady-state approximation**, discussed above. Most of our readers have already seen the pseudo-steady-state approximation. However, I want to state it a little differently than you have seen before

> According to the pseudo-steady-state approximation, one can compute accurate values of the concentrations of all of the intermediates in a reaction by assuming that the net rate of formation of the intermediates is negligible (i.e., the derivatives with respect to time of the concentrations of all intermediates are negligible).

Note that there is a subtle point here. One is not actually assuming that the derivatives are exactly zero. Rather, one is assuming that the derivatives are much smaller than the other terms in the rate equations, so that the intermediates are consumed as quickly as the intermediates are formed. Consequently, the net rate of formation of the intermediates (i.e., the difference between the rate that the intermediates are formed and destroyed) can be neglected when one uses the rate equation to compute the concentration of all of the intermediates.

Physically, what is happening is that the concentrations of the intermediates are usually tiny, so the derivatives of the intermediate concentrations are tiny, too. Consequently, the derivatives of the intermediate concentration can be ignored in equation (4.51).

One needs to be careful because one **cannot** just ignore all of the terms in the rate equation containing the intermediate concentration; one can ignore only the derivatives. For example, in equation (4.51), there is a term:

$$r_3 = k_3[I] \tag{4.63}$$

If one proceeded naively, one might guess that according to equation (4.62), the intermediate concentration in equation (4.63) is tiny, so r_3 is tiny, too. However, note that we plotted r_3 in Figure 4.3, and r_3 is not tiny. The reason is that even though the intermediate concentration is tiny (6×10^{-9}), k_3 is huge ($2.8 \times 10^{+7}$). Consequently, r_3 is not negligible.

This is a general result. While the concentrations of all of the reactive intermediates are generally small, the intermediates are by definition very reactive; the rate constants for reactions involving the intermediates are generally huge. As a result, one cannot simply eliminate the terms involving the intermediate concentrations in the rate equation. Rather, one does have to consider the intermediate concentrations explicitly. One can, however, often eliminate terms that have to do with the derivatives of the intermediate concentration since the derivatives are usually small, except near time = 0.

There is another subtle point—the pseudo-steady-state approximation works only for reactive intermediates. If you consider a stable species such as a reactant, a product, or even a side product, you cannot assume that the species will be consumed as soon as it is formed. In most, but not all cases, radicals, hot molecules, highly strained species, or species with some unusual bonding [e.g., the three-center bonded intermediate in reaction (4.13)] will obey the pseudo-steady-state approximation. There are exceptions, of course. For example, in the upper atmosphere, OH radicals and HO_2 species are stable. More specific criteria for when the pseudo-steady-state approximation works will be given in Section 4.9. The key point, however, is that the pseudo-steady-state approximation works for most highly reactive species. Consequently, this approximation is quite useful.

4.8 APPLICATIONS OF THE PSEUDO-STEADY-STATE APPROXIMATION TO DETERMINE THE KINETICS OF A REACTION

Next, we will use the pseudo-steady-state approximation to derive a rate law for a number of example reactions. I realize that most of the readers have seen these types of derivations before. However, we needed some of the results for the discussion later in this chapter. Also, the material is a useful review.

We will start with the simple example that was discussed in Section 3.14. Consider the reaction

$$A \xrightarrow{1} I \xrightarrow{2} P \tag{4.64}$$

According to the analysis in Section 3.9, [I], the concentration of the intermediate, can be computed exactly from equation (3.84). In this section, we will use the pseudo-steady-state approximation to calculate an approximation for [I].

According to equation (4.31), r_I, the net rate of formation of the intermediate, is given by

$$r_I = k_1[A] - k_2[I] \tag{4.65}$$

where [A] and [I] are the concentrations of A and I, respectively, and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively. According to the pseudo-steady-state approximation, r_I will be much smaller than the other terms in equation (4.65). Consequently, r_I can be ignored in equation (4.65). Setting r_I to zero in equation (4.65) and solving for [I] yields

$$[I] = \frac{k_1}{k_2}[A] \tag{4.66}$$

It is useful to compare equation (4.66) to equation (3.87). The notation is different in the two equations, but otherwise the two equations are identical. Figure 3.28 shows that equation (3.87) is an excellent approximation whenever k_2/k_1 is greater than about 10. With a typical intermediate, k_2/k_1 is in the order of 10^6. Clearly, the pseudo-steady-state approximation works in such a case.

Next, let's consider a more complex example, the reaction between hydrogen and bromine to yield HBr:

$$H_2 + Br_2 \Longrightarrow 2HBr \tag{4.67}$$

The mechanism of the reaction is

$$X + Br_2 \xrightarrow{1} 2Br + X$$

$$Br + H_2 \xrightarrow{2} HBr + H$$

$$H + Br_2 \xrightarrow{3} HBr + Br \quad (4.68)$$

$$X + 2Br \xrightarrow{4} Br_2 + X$$

$$H + HBr \xrightarrow{5} H_2 + Br$$

where X is a collision partner (i.e., any other species that can collide with Br_2 as described in Section 4.2). Next, let's derive an expression for the rate that Br_2 is used up during the reaction. Note that Br_2 is formed in reaction 4 and destroyed in reactions 1 and 3. Therefore

$$r_{Br_2} = -r_1 - r_3 + r_4 \quad (4.69)$$

where r_1, r_3, and r_4 are the rates of reactions 1, 3, and 4, respectively. One can compute r_1, r_3, and r_4 from equation (4.28):

$$r_1 = k_1[X][Br_2] \quad (4.70)$$

$$r_3 = k_3[H][Br_2] \quad (4.71)$$

$$r_4 = k_1[X][Br]^2 \quad (4.72)$$

where $[Br_2]$, $[Br]$, $[H]$, and $[X]$ are respectively the concentrations of bromine molecules, bromine atoms, hydrogen atoms, and collision partners. Substituting equations (4.70)–(4.72) into equation (4.69) yields

$$r_{Br_2} = -k_1[X][Br_2] - k_3[H][Br_2] + k_4[X][Br]^2 \quad (4.73)$$

Equation (4.73) is an exact expression for the rate of consumption of bromide during the reaction. In principle, therefore, equation (4.73) can be used to calculate the concentration of all of the species in the system. In practice, however, the concentration's of bromine atoms and hydrogen atoms are tiny. Therefore, equation (4.73) is not very useful in practice.

Now, one might think that one could just ignore the second and third terms on the right side of (4.73). After all, if one runs the reaction at 1 atm and 800 K, one finds that the concentrations of hydrogen atoms and bromine atoms are less than 10^{-8} mol/liter. By comparison, the Br_2 concentration is 0.01 mol/liter under the same conditions. However, it is incorrect to ignore the second and third terms in equation (4.73) because the rate constants for the second the third terms in that equation (4.73) are large. According to the data in Benson (1976), k_3 is about 1×10^{10} Å^3/(molecule·second) at 800 K, while k_1 is only 1×10^2 Å^3/(molecule·second). Plugging in numbers shows that the second term on the right side of equation (4.73) is about 100 times bigger than the first term in the equation. A similar argument also applies to the third term on the right side of equation (4.73). As a result, it would be certainly incorrect to ignore the second and third terms on the right side of equation (4.73). Instead, one must include these two terms in the analysis.

With three terms, we have a very complicated equation. Fortunately, the pseudo-steady-state approximation can be used to get simple expressions for the bromine and hydrogen atom concentrations in equation (4.73).

Bromine atoms are formed in reactions 1, 3, and 5, and lost in reactions 2 and 4. Therefore

$$\frac{d[Br]}{dt} = 2r_1 - r_2 + r_3 - 2r_4 + r_5 \quad (4.74)$$

The factors of 2 in equation (4.74) arise because two bromine atoms are formed in reaction 1 and two atoms of bromine are lost in reaction 4. Substituting expressions similar to equations (4.70)–(4.72) into equation (4.74) yields

$$\frac{d[Br]}{dt} = r_{Br} = 2k_1[X][Br_2] - k_2[H_2][Br] + k_3[H][Br_2] - 2k_4[Br]^2[X] + k_5[H][HBr] \quad (4.75)$$

A similar analysis shows

$$\frac{d[H]}{dt} = r_H = k_2[H_2][Br] - k_3[H][HBr_2] - k_5[H][HBr] \quad (4.76)$$

(*A note for students*: Notice that I first wrote out the equations in terms of the rates of the individual reactions, and then substituted in the rate laws. In my experience, students make fewer errors if they first write down the rates in terms of $r_1, r_2, r_3, \ldots$ and then substitute the rate in terms of laws into the subsequent equations.)

Next, we will assume that the concentrations of the bromine atoms and hydrogen atoms follow the pseudo-steady-state approximation, that is, that the derivatives in equations (4.75) and (4.76) are negligible. Physically, we can make that assumption because the concentrations of the reactive intermediates are so small that the derivatives of the intermediate concentrations will be small, too. We note again, however, that k_2, k_3, k_4, and k_5 are huge, so one cannot assume that the other terms in equations (4.75) and (4.76) are negligible.

If one assumes that the derivatives in equations (4.75) and (4.76) are negligible, one finds

$$0 = 2k_1[X][Br_2] - k_2[H_2][Br] + k_3[H][Br_2] - 2k_4[Br]^2[X] + k_5[H][HBr] \quad (4.77)$$

$$0 = +k_2[H_2][Br] - k_3[H][Br_2] - k_5[H][HBr] \quad (4.78)$$

We now have two equations—equations (4.77) and (4.78)—and two unknowns—[H] and [Br]—so we can solve the equations simultaneously to calculate [H] and [Br].

Adding equations (4.77) and (4.78) yields

$$0 = 2k_1[X][Br_2] - 2k_4[Br]^2[X] \quad (4.79)$$

Solving equation (4.79) for [Br] yields

$$[Br] = \left(\frac{k_1}{k_4}\right)^{1/2} [Br_2]^{1/2} \quad (4.80)$$

Equation (4.80) is the pseudo-steady-state expression for the concentration of bromine atoms produced during reaction (4.67).

Next, we will obtain an expression for the concentration of hydrogen atoms. Substituting equation (4.80) into equation (4.78) yields

$$k_2[H_2]\left(\frac{k_1}{k_4}\right)^{1/2}[Br_2]^{1/2} = k_3[H][Br_2] + k_5[H][HBr] \tag{4.81}$$

Solving equation (4.81) for [H] yields

$$[H] = \frac{k_2\left(\frac{k_1}{k_4}\right)^{1/2}[H_2][Br_2]^{1/2}}{k_3[Br_2] + k_5[HBr]} \tag{4.82}$$

Equation (4.82) is the pseudo-steady-state approximation for the concentration of hydrogen atoms produced during reaction (4.67).

At this point, we have expressions for all of the unknown quantities in equation (4.73), so we can calculate an expression for the rate of destruction of bromine atoms. Substituting equation (4.82) and (4.80) into equation (4.73) and rearranging yields

$$r_{Br_2} = -\frac{k_2\left(\frac{k_1}{k_4}\right)^{1/2}[H_2][Br_2]^{1/2}}{1 + \frac{k_5}{k_3}\frac{[HBr]}{[Br_2]}} \tag{4.83}$$

Equation (4.83) is the pseudo-steady-state approximation to the rate of reaction (4.67).

The analysis above was for reaction (4.67). However, one can use an analysis similar to that above to calculate a rate equation for any reaction when one knows the mechanism of the reaction. For example, we can use the steady approximation to calculate a rate equation for the reaction between hydrogen and oxygen by assuming that the reaction follows the mechanism in equation (4.17). Generally, one has to do some algebra to solve all of the equations. However, the process is straightforward.

For the work that follows, we will need to consider one other example — the reaction between hydrogen and oxygen:

$$2H_2 + O_2 \Longrightarrow 2H_2O \tag{4.84}$$

Reaction (4.84) follows a complex mechanism with over 40 important steps. Still, one can get a reasonable approximation to the rate if one assumes that the reaction obeys the following *approximate* mechanism:

$$\begin{gathered}
H_2 + O_2 \xrightarrow{1} 2OH\bullet \\
OH\bullet + H_2 \xrightarrow{2} H_2O + H\bullet \\
H\bullet + O_2 \xrightarrow{3} OH\bullet + O{:} \\
O{:} + H_2 \xrightarrow{4} OH\bullet + H\bullet \\
H\bullet \xrightarrow{5} \text{wall} \\
H\bullet + O_2 + X \xrightarrow{6} HO_2\bullet + X \\
HO_2\bullet + X \xrightarrow{7} \text{wall}
\end{gathered} \tag{4.85}$$

In equation (4.85), the term "wall" in reactions 5 and 7 refers to processes where radicals absorb onto the walls of the vessel. We want to emphasize that reaction (4.85) is not the correct mechanism of the reaction, but one gets a reasonable rate equation anyway. In the work in the next section, we will need an expression for [H•], the concentration of the hydrogen atoms during this reaction. We will use the pseudo-steady-state approximation to get it. Let's start by deriving an equation for the rate of formation of hydrogen atoms. Hydrogen atoms are formed in reactions 2 and 4 while hydrogen atoms are lost in reactions 3, 5, and 6. Consequently, r_H, the rate of formation of hydrogen atoms is given by

$$r_H = r_2 - r_3 + r_4 - r_5 - r_6 \tag{4.86}$$

where r_2, r_3, r_4, r_5, and r_6 are the rate of reactions 2–6. Substituting the rate reactions for reactions 2–6 into equation (4.86) yields

$$\begin{aligned}
\frac{d[H\bullet]}{dt} = r_{H\bullet} &= k_2[OH\bullet][H_2] - k_3[H\bullet][O_2] \\
&\quad + k_4[O\bullet][H_2] - k_5[H\bullet] - k_6[H\bullet][O_2][X]
\end{aligned} \tag{4.87}$$

where $[H_2]$, $[H\bullet]$, $[OH\bullet]$, $[O_2]$ $[O{:}]$, and $[X]$ are the concentration of hydrogen molecules, hydrogen atoms, hydroxyl radicals, oxygen molecules, oxygen atoms, and collision partners, respectively. Similarly, the rate of formation of hydroxyl radicals and oxygen atoms, r_{OH} and r_O, is given by

$$\begin{aligned}
\frac{d[OH\bullet]}{dt} = r_{OH} &= 2k_1[H_2][O_2] - k_2[OH\bullet][H_2] \\
&\quad + k_3[H\bullet][O_2] + k_4[O{:}][H_2]
\end{aligned} \tag{4.88}$$

$$\frac{d[O{:}]}{dt} = r_O = k_3[H\bullet][O_2] - k_4[O{:}][H_2] \tag{4.89}$$

If we assume that r_{OH}, r_H and r_O are negligible, we can solve equations (4.87), (4.88), and (4.89) simultaneously to calculate expressions for [H], [OH], and [O]. Adding equation (4.87), (4.88) and 2 times equation (4.89), and neglecting r_{OH}, r_H, and r_O yields

$$0 = 2k_1[H_2][O_2] + 2k_3[H\bullet][O_2] - k_5[H\bullet] - k_6[H][O_2][X] \tag{4.90}$$

Solving equation (4.90) for [H•] yields

$$[H\bullet] = \frac{2k_1[H_2][O_2]}{k_5 + (k_6[X] - 2k_3)O_2} \tag{4.91}$$

Equation (4.91) is the pseudo-steady-state approximation for the hydrogen atom concentration.

We give several other examples of the use of the pseudo-steady-state approximation in the problems at the end of this chapter. The pseudo-steady-state approximation is very important, so it is important that reader's solve some of these examples themselves to verify that they know how to use the pseudo-steady-state approximation to calculate a rate equation.

4.8.1 Tricks to Simplify the Rate Equation

The one difficulty with the pseudo-steady-state approximation is that the algebra is complicated. I find that students often get lost in the algebra and never get to an answer.

Just to keep track of everything, in the example at the end of Section 4.7, we are trying to get an expression for the hydrogen atom concentration in terms of the concentration of all of the other stable species. The general approach we take is to

1. Set up the differential equation for the species of interest in terms of rate of all of the elementary reactions using equation (4.25) to keep track of the coefficients.
2. Substitute the expression for the rate of each of the elementary reactions using equations from Section 4.3.
3. Set the derivatives of the intermediate concentrations to zero.
4. Eliminate terms in the expression in (1) that contain the concentrations of unstable intermediates other than the species of interest.
5. Solve the resultant expression for the concentration of the species of interest.

For example, if one wanted to calculate the concentration of hydrogen atoms during reaction (4.85), one would start with the expression for change in the concentration of hydrogen atoms:

$$\frac{d[\mathrm{H}\bullet]}{dt} = r_2 - r_3 + r_4 - r_5 - r_6 \tag{4.92}$$

One substitutes in the appropriate rate terms, and sets the derivative of the intermediate concentration to zero.

$$\begin{aligned} 0 \approx \frac{d[\mathrm{H}\bullet]}{dt} &= k_2[\bullet\mathrm{OH}][\mathrm{H}_2] - k_3[\mathrm{H}\bullet][\mathrm{O}_2] \\ &\quad + k_4[\bullet\mathrm{O}][\mathrm{H}_2] - k_5[\mathrm{H}\bullet] - k_6[\mathrm{H}\bullet][\mathrm{O}_2][\mathrm{X}] \end{aligned} \tag{4.93}$$

Next, one would have to determine what terms in this expression need to be eliminated. Notice that the k_3, k_5, and k_6 terms contain [H•]. We are trying to find [H•], so those terms are okay in the expression. In contrast, the k_2 and k_4 terms contain [O•] or [OH•]. These terms need to be eliminated.

The k_2 term contains the hydroxyl concentration, so one can eliminate it by looking at the steady-state approximation for hydroxyls. Setting the derivative in equation (4.88) to zero and solving for $k_2[\mathrm{OH}][\mathrm{H}_2]$ yields

$$k_2[\mathrm{OH}\bullet][\mathrm{H}_2] = 2k_1[\mathrm{H}_2][\mathrm{O}_2] + k_3 - [\mathrm{H}\bullet][\mathrm{O}_2] + k_4[\mathrm{O}:][\mathrm{H}_2] \tag{4.94}$$

Substituting equation (4.94) into equation (4.93) yields

$$0 = 2k_1[\mathrm{H}_2][\mathrm{O}_2] + 2k_4[\mathrm{O}:][\mathrm{H}_2] - k_5[\mathrm{H}\bullet] - k_6[\mathrm{H}\bullet][\mathrm{O}_2][\mathrm{X}] \tag{4.95}$$

Equation (4.95) has only one term to eliminate the k_4 term. The k_4 term contains the concentration of oxygen atoms. One can eliminate the term from the steady-state approximation on oxygen atoms in equation (4.89) by setting the derivative in equation (4.89) equal to zero; then, solving for k_4 [O][H$_2$] yields

$$k_4[\mathrm{O}:][\mathrm{H}_2] = k_3[\mathrm{H}\bullet][\mathrm{O}_2] \tag{4.96}$$

Substituting equation (4.96) into equation (4.95) yields

$$0 = 2k_1[\mathrm{H}_2][\mathrm{O}_2] + 2k_3[\mathrm{H}\bullet][\mathrm{O}_2] - k_5[\mathrm{H}\bullet] - k_6[\mathrm{H}][\mathrm{O}_2][\mathrm{X}] \tag{4.97}$$

Solving equation (4.97) for [H•] yields

$$[\mathrm{H}\bullet] = \frac{2k_1[\mathrm{H}_2][\mathrm{O}_2]}{k_5 + (k_6[\mathrm{X}] - 2k_3)\mathrm{O}_2} \tag{4.98}$$

The point of this exercise is that you need to focus on where you are going when you are simplifying the rate equation. Look at the terms that you need to eliminate, and find a way to eliminate them. It usually works out that other terms cancel as well. The algebra is usually simple unless you have a reaction where two other reactive intermediates collide to form products. In that case, only brute-force algebra works.

The key thing to remember when simplifying rate expressions are

- Write down the differential equations in terms of the rates and then substitute in the rate equations.
- Keep track of what terms you want to eliminate, and eliminate them.

The solutions are normally straightforward and the methods work when you keep track of where you are going.

4.9 RATE-DETERMINING STEPS

The pseudo-steady-state approximation is the key approximation that people use to derive rate equations. Consequently, this approximation is very important. There are a series of other approximations that are occasionally used. I do not think they are important. Still, I wanted to mention them so that you know what people are doing when they use another approximation.

One key simplification occurs if one can assume that one step, called the **rate-determining step** or **rate-limiting step**, is much slower than all of the other steps in the mechanism. The objective of this section is to work out the details. One can skip this section without loss of continuity.

Let us start by considering a simple reaction mechanism where the idea of a rate-determining step might be important. Consider a reaction where molecule A collides with a collision partner to yield an unstable excited species, A‡. Then the excited species reacts to form a product B:

$$\begin{aligned} \mathrm{A} + \mathrm{X} &\underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{A}^{\ddagger} + \mathrm{X} \\ \mathrm{A}^{\ddagger} &\xrightarrow{3} \mathrm{B} \end{aligned} \tag{4.99}$$

The rate of formation of B, r_B is given by

$$r_B = k_3[A^{\ddagger}] \tag{4.100}$$

where $[A^{\ddagger}]$ is the concentration of excited A molecules and k_3 is the rate constant for reaction 3. One can derive an equation for $[A^{\ddagger}]$ using the pseudo-steady-state approximation:

$$r_A^{\ddagger} = k_1[A][X] - k_2[A^{\ddagger}][X] - k_3[A^{\ddagger}] \approx 0 \tag{4.101}$$

where $r_A^{\ddagger}$ is the rate of formation of excited A molecules; [A], $[A^{\ddagger}]$, and [X] are respectively the concentrations of A molecules, excited A molecules, and collision partners; and, k_1, k_2, and k_3 are the rate constants for reactions 1, 2, and 3, respectively. Solving equation (4.101) for $[A^{\ddagger}]$ and then substituting that into equation (4.100) yields

$$r_B = \frac{k_3 k_1[A][X]}{k_2[X] + k_3} \tag{4.102}$$

Now consider the case where $k_2[X] \gg k_3$ so that reaction 3 is much slower than the rest. In that limit, equation (4.102) simplifies to

$$r_B = \frac{k_3 k_1}{k_2}[A] \tag{4.103}$$

This is a key result because it shows that the reaction looks first order when $k_2[X] \gg k_3$.

Next, we will show that one could have gotten to equation (4.103) more simply. When $k_2[X] \gg k_3$, reactions 1 and 2 are just about in equilibrium. At equilibrium, the ratio of the concentration of excited A molecules to total A molecules is given by the equilibrium constant $K_{1,2}$:

$$\frac{[A^{\ddagger}]}{[A]} = K_{1,2} = \frac{k_1}{k_2} \tag{4.104}$$

In equation (4.104), we noted that the equilibrium constant for a reaction is given by the ratio of the equilibrium constants for a reaction, as noted in Section 4.3. Substituting equation (4.104) into equation (4.100) yields

$$r_B = \frac{k_3 k_1}{k_2}[A] \tag{4.105}$$

Notice that equations (4.103) and (4.105) are identical. Therefore, in the limit that $k_2[X] \gg k_3$, one can calculate an accurate rate equation by assuming that reactions 1 and 2 are in equilibrium.

One can generalize this process to any reaction. The idea is to assume that one step, called the **rate-determining step** or **rate-limiting step**, is much slower than the rest of the steps in the mechanism. One can show that if one step is extremely slow, then all of the steps before the slow step can be assumed to be in equilibrium with the reactants, and all of the steps after the rate-determining step can be considered to be in equilibrium with the products. If so, one can often derive a suitable rate equation for the reaction using somewhat less algebra than in the case where none of the steps are slow.

For example, consider a reversible reaction:

$$A + B \underset{-1}{\overset{1}{\rightleftarrows}} C + D \underset{-2}{\overset{2}{\rightleftarrows}} E + F \underset{-3}{\overset{3}{\rightleftarrows}} G + H \underset{-4}{\overset{4}{\rightleftarrows}} I + J \underset{-5}{\overset{5}{\rightleftarrows}} L + M \tag{4.106}$$

One can write, r_A, the rate formation of the reactant A by

$$r_A = r_{-1} - r_1 \tag{4.107}$$

where r_1 and r_{-1} are the rates of reactions 1 and −1, respectively. The steady-state approximation on C shows

$$\frac{d[C]}{dt} = r_1 - r_{-1} - r_2 + r_{-2} \approx 0 \tag{4.108}$$

where r_1, r_{-1}, r_2, and r_{-2} are respectively the rates of reaction 1, −1, 2, and −2. Similarly, the steady-state approximation on E shows

$$\frac{d[E]}{dt} = r_2 - r_{-2} - r_3 + r_{-3} \approx 0 \tag{4.109}$$

where r_2, r_{-2}, r_3, and r_{-3} are the rates of reaction 2, −2, 3 and −3, respectively. Adding equations (4.107)–(4.109) yields

$$r_A = r_{-3} - r_3 \tag{4.110}$$

Substituting the expressions for r_3 and r_{-3} into equation (4.110) yields

$$r_A = k_{-3}[G][H] - k_3[E][F] \tag{4.111}$$

Equation (4.110) is a key result. It says that if one has a reaction consisting of several steps, then at steady state, the net rates of each of the steps are equal. Consequently, one can calculate the rate of reaction by considering the net rate of reaction at any point during the reaction sequence.

Now, let's assume that reaction 3 and −3 are much slower than the rest. Then it will be permissible to assume that the concentrations of E and F are in equilibrium with the reactants. The analysis in Section 4.4 shows:

$$[E][F] = \frac{k_1 k_2}{k_{-1} k_{-2}}[A][B] \tag{4.112}$$

Similarly, the concentration of G and H will be in equilibrium with the products:

$$\frac{[L][M]}{[G][H]} = \frac{k_4 k_5}{k_{-4} k_{-5}} \tag{4.113}$$

Substituting equation (4.112) and (4.113) into equation (4.111) yields

$$r_A = \frac{k_{-3} k_{-4} k_{-5}}{k_4 k_5}[L][M] - \frac{k_1 k_2 k_3}{k_{-1} k_{-2}}[A][B] \tag{4.114}$$

Equation (4.114) is the equivalent of the pseudo-steady-state approximation when k_3 and k_{-3} are small.

In my experience, there is not that much simplification in assuming that one of the steps in a mechanism is at equilibrium, and one often misses some key information. Therefore, there is some uncertainty in using the idea of a rate-determining step to derive a rate equation.

Still, the idea of a rate-determining step is a useful construct to understand reactions. Typically, there is one step in a reaction mechanism, called the *rate-determining* step, which is much slower than the other reactions in the mechanism. This slow step is the bottleneck. Anything one can do to eliminate the bottleneck will greatly enhance the rate of reaction.

4.10 TESTING THE ACCURACY OF THE PSEUDO-STEADY-STATE APPROXIMATION

Next, I want to change topics and consider when the pseudo-steady-state approximation is accurate. In practice, this approximation is used to calculate rate equations for a wide range of reactions. It usually works but unfortunately, there are a few exceptions. The exceptions come in systems that can explode, or in systems with other unusual behavior, such as oscillations. These are rare examples, but there are still a few cases where the pseudo-steady-state approximation does not work.

The fact that the pseudo-steady-state approximation may not work is pretty significant. For example, let's assume that you are trying to determine the kinetics for a reaction that has never been studied before. In principle, you can derive a mechanism and then use the pseudo-steady-state approximation to derive a rate equation. The difficulty, though, is that at that point you will not know whether the pseudo-steady-state approximation is accurate. As a result, you will not know whether to believe the results derived using the pseudo-steady-state approximation.

In this section, we will discuss how one can determine whether the pseudo-steady-state approximation is accurate for a given reaction network. Let's start with the case discussed in Section 4.4:

$$A + H^+ \underset{2}{\overset{1}{\rightleftarrows}} I \xrightarrow{3} P + H_2 \tag{4.115}$$

Figure 4.4 compares the intermediate concentration calculated via the pseudo-steady-state approximation [equation (4.62)] to the concentration calculated via the exact result [equation (4.54)] for several values of the rate constants. Notice that in the exact case ($k_2 = 5.7 \times 10^6$/minute), the pseudo-steady-state approximation works extremely well, and in fact, this approximation is still accurate when k_2 is reduced by a factor of 10^5. Significant deviations are seen only when k_2 is reduced to about 1.

Notice that at the point where the pseudo-steady-state approximation fails, the intermediate concentration is already a few percent of the reactant concentration. This is a general finding. The pseudo-steady-state approximation is essentially exact when the intermediate concentration is much smaller than the reactant and product concentrations. One can, however, start to see deviations when the intermediate concentration begins to be significant compared to the reactant (or product) concentration. Later in this chapter, we will note that there are some cases where the pseudo-steady-state approximation works even though the intermediate concentrations are significant. However, the key point to remember now is that the pseudo-steady-state approximation always works when the intermediate concentrations are much less than the reactant or product concentrations.

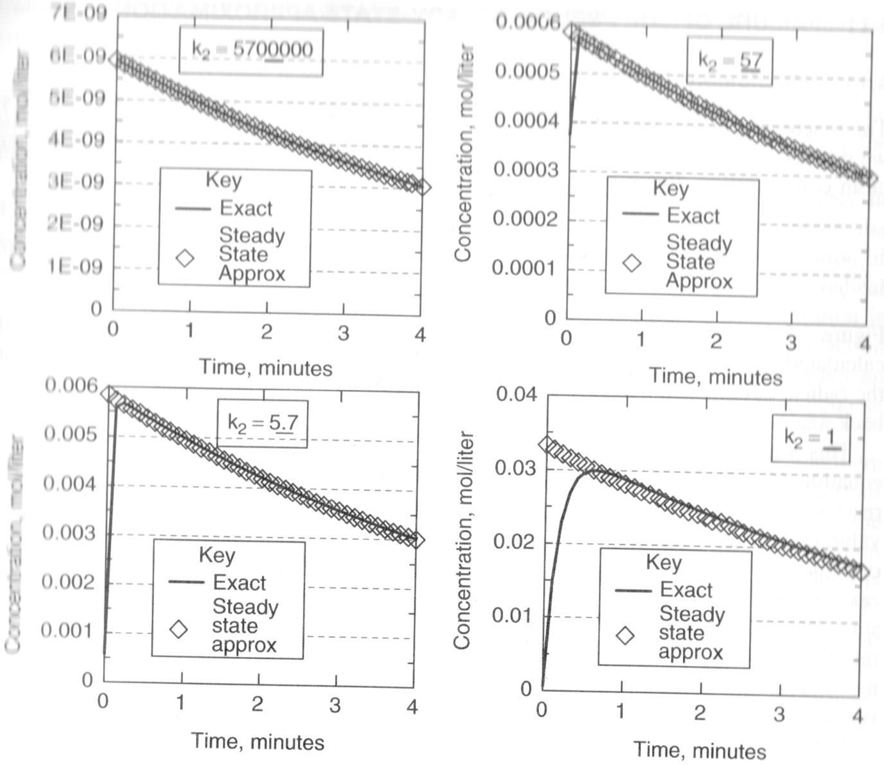

Figure 4.4 A comparison of the intermediate concentration calculated via the steady-state approximation to the concentration calculated via the exact result: equations (4.54) to (4.57) with $k_6 = 0.2$, $k_3 = 5k_2$, and various values of k_2.

Physically, when we set the net rate of formation of the intermediate to zero, we are saying that the amount of the intermediate that we are forming is negligible. That is a good approximation if the intermediate concentration is tiny so that the amount we are forming is negligible. However, it is a bad approximation if we form a nonnegligible amount of impurity.

One can use the idea that the concentration of the intermediates is negligible to check whether the pseudo-steady-state approximation works for a specific example. The idea is to use the pseudo-steady-state approximation to calculate the concentrations of all of the intermediates and see whether the concentration of any of the intermediates is significant compared to the reactants or products.

For example, there are two intermediates in reaction (4.67): [H] and [Br]. One can estimate the intermediate concentrations from equation (4.80) and (4.82). Rate constants are given in Westley (1980). When we plug numbers into equations (4.80) and (4.82), we find that at 300 K the intermediate concentrations are a factor of 10^{-8} lower than the reactant concentrations. The intermediate concentrations are low, which implies that the steady-state approximation will work.

4.11 FAILURE OF THE PSEUDO-STEADY-STATE APPROXIMATION

4.11.1 Explosions

The reaction between hydrogen and oxygen [reaction (4.84)] is different. In Section 4.7, we derived an expression for the pseudo-steady-state approximation to [H], the hydrogen atom concentration. Rearranging the expression yields

$$[\mathrm{H}] = \frac{2k_1[\mathrm{H}_2][\mathrm{O}_2]}{k_5 + k_6[\mathrm{X}][\mathrm{O}_2] - 2k_3[\mathrm{O}_2]} \tag{4.116}$$

Figure 4.5 is a plot of the radical concentration as a function of the oxygen pressure calculated from equation (4.116) for some typical values of the parameters. Notice that the radical concentration goes first to infinity and then to negative infinity and then comes back again.

This weird behavior occurs because there is a negative term in the denominator of equation (4.116). That term increases as the concentration of molecular oxygen in the reactor increases. When the denominator of equation (4.116) decreases, the calculated value of the hydrogen atom concentration increases. If one plugs in the rate constants, one finds that at temperatures above 450 K, the denominator of equation (4.116) goes to zero at moderate oxygen concentrations. Consequently, according to the pseudo-steady-state approximation, under some conditions, the radical concentration should approach infinity. One can even get to the situation where the denominator is negative, which means that according to the pseudo-steady-state approximation, the radical concentration is negative.

What is going on is that the pseudo-steady-state approximation fails in cases where the hydrogen atom concentration is comparable to or larger than the H_2 concentration, or when the calculated concentrations are negative. Physically, it is impossible for the hydrogen atom concentration to be negative. Large hydrogen atom concentrations are impossible as well since the only hydrogen source is the H_2 initially fed into the reactor. Consequently, the hydrogen atom concentration can never exceed twice the initial H_2 concentration.

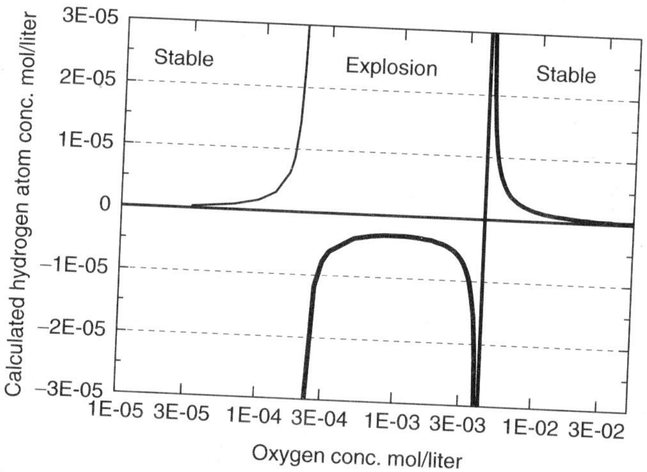

Figure 4.5 A plot of the hydrogen atom concentration calculated from equation (4.116) as a function of the oxygen concentration.

The pseudo-steady-state approximation fails whenever the intermediate concentration is comparable to the H_2 concentration, which one can test by plugging numbers into equation (4.116). The weird behavior in Figure 4.5 is associated with the failure of the steady-state approximation.

That does not imply that the pseudo-steady-state approximation was useless in this example. If one runs the hydrogen/oxygen reaction under conditions where the denominator in equation (4.116) is small or negative, one finds that the concentration of radicals does increase rapidly when one loads the reactants into the reactor. The radical concentration does not actually increase to infinity; instead the radical concentration is finite. However, there is a rapid production of radicals, which means that the reaction rate gets to be very large. One calls a rapid increase in the radical concentration an **explosion**. You already know that a hydrogen/oxygen mixture can explode. Now you can see mathematically how the explosion happens.

If one actually runs the hydrogen/oxygen reaction experimentally, one finds that there is some complex behavior because the rate of the reactions with the walls [i.e., reactions 5 and 7 in equation (4.85)] depends on the rate at which molecules diffuse through the gas mixture. One can also find circumstances where the heat generated during a reaction heats up the reaction mixture leading to an explosion. However, the thing to remember is that an explosion happens when the concentration of reactive intermediates grows quickly during the course of the reaction. Once you start to build up radicals, the radicals are so reactive that the reaction rate quickly grows toward a large value. In the $H_2 + O_2$ case, one observes an upper and lower explosion limit. The lower explosion occurs because, as you raise the oxygen pressure, the $-k_3[O_2]$ term in the denominator of equation (4.116) grows until the denominator becomes zero. The upper explosion limit occurs because at high pressure, the $k_6[X][O_2]$ term becomes important, and so the denominator becomes positive again. One can also get a thermal explosion, where the heat generated by the reaction raises the temperature, which, in turn, raises the radical concentration.

There are many other examples where the pseudo-steady-state approximation fails. For example, OH and HO_2 radicals are stable in the upper atmosphere, so one cannot apply the pseudo-steady-state approximation to them. The pseudo-steady-state approximation works only when the intermediate concentrations are much smaller than the reactant and product concentrations. The pseudo-steady-state approximation does not work well in cases where the intermediate concentrations are comparable to the reactant concentrations. In those cases, one can solve the rate equations numerically as described in Section 4.5. The pseudo-steady-state approximation is quite useful, but it does not work all the time.

4.11.2 Oscillations

There is one major class of reactions where the pseudo-steady-state approximation fails dismally: systems where oscillations in rate are observed. We briefly mentioned oscillating reactions in Chapter 2. The classic example is a modified Belousov–Zhabotinskii (BZ) reaction:

$$\mathrm{HOOCCH_2COOH + HBrO_3} \xrightarrow{\mathrm{Fe}^{3+}} \text{products} \tag{4.117}$$

If you run reaction (4.117) in a beaker with phenanthroline to complex the iron, the color of the mixture oscillates from red to blue. This makes a great demonstration during class. In a batch reactor, the oscillations eventually stop because one runs out of reactants.

However, one can also run the reaction in a flow reactor if one continuously feeds reactants into the flow reactor, the oscillations can be sustained forever (see Figure 4.6).

Clearly, if the reaction rate oscillates, the pseudo-steady-state approximation is not going to work.

Unfortunately, the BZ reaction is very complicated, so it does not make a good example for the discussion here. Therefore, I would like to instead consider a simpler example: the oxidation of a molecule called *nicotinamide adenine dineuclotide hydride* (NADH), shown in Figure 4.7. The oxidation reaction can be written

$$\mathrm{NADH} + \mathrm{H}^+ + \tfrac{1}{2}\mathrm{O}_2 \longrightarrow \mathrm{NAD}^+ + \mathrm{H_2O} \qquad (4.118)$$

The oxidation is catalyzed by an enzyme called *peroxidase*. Reaction (4.118) is one of the key steps in the energy cycle of cells. It is also used to produce cell walls in plants.

Benson and Scheeline (1996) examined the chemistry in detail using the mechanism in Figure 4.6. They find that the key reactions are

$$\mathrm{NADH} + \mathrm{O}_2 + \mathrm{H}^+ \xrightarrow{1} \mathrm{NAD}^+ + \mathrm{H_2O_2} \qquad (4.119)$$

$$\mathrm{Per}^{3+} + \mathrm{H_2O_2} + 2\mathrm{H}^+ \xrightarrow{2} \mathrm{Per}^{5+} + 2\mathrm{H_2O} \qquad (4.120)$$

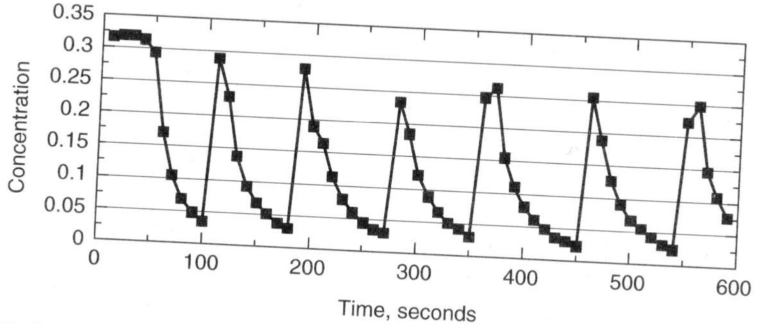

Figure 4.6 Rate oscillations during reaction (4.117). (Unpublished data of G. E. Poisson, D. A. Tuchmann, and R. I. Masel).

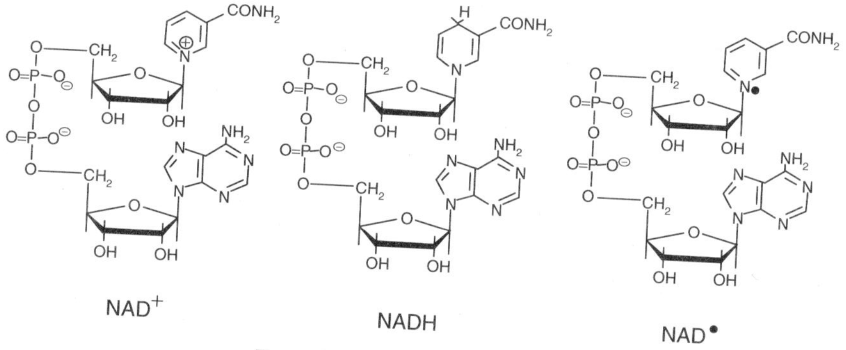

Figure 4.7 NAD$^+$, NADH and NAD$^•$.

$$\mathrm{Per}^{5+} + \mathrm{NADH} \xrightarrow{3} \mathrm{Per}^{4+} + \mathrm{NAD}\bullet + \mathrm{H}^+ \qquad (4.121)$$

$$\mathrm{Per}^{4+} + \mathrm{NADH} \xrightarrow{4} \mathrm{Per}^{3+} + \mathrm{NAD}\bullet + \mathrm{H}^+ \qquad (4.122)$$

$$\mathrm{NAD}\bullet + \mathrm{O}_2 \xrightarrow{5} \mathrm{NAD}^+ + \mathrm{O_2}^-\bullet \qquad (4.123)$$

$$\mathrm{Per}^{3+} + \mathrm{O_2}^-\bullet + 4\mathrm{H}^+ \xrightarrow{6} \mathrm{Per}^{6+} + 2\mathrm{H_2O} \qquad (4.124)$$

$$2\mathrm{O_2}^-\bullet + 2\mathrm{H}^+ \xrightarrow{7} \mathrm{H_2O_2} + \mathrm{O}_2 \qquad (4.125)$$

$$\mathrm{Per}^{6+} + \mathrm{NAD}\bullet \xrightarrow{8} \mathrm{Per}^{5+} + \mathrm{NAD}^+ \qquad (4.126)$$

$$\mathrm{NADH_R} \xrightarrow{9} \mathrm{NADH} \qquad (4.127)$$

$$\mathrm{NADH} \xrightarrow{10} \mathrm{NADH_R} \qquad (4.128)$$

$$\mathrm{O}_{2(g)} \longrightarrow \mathrm{O}_{2(aq)} \qquad (4.129)$$

$$\mathrm{O}_{2(aq)} \longrightarrow \mathrm{O}_{2(g)} \qquad (4.130)$$

$$2\mathrm{NAD}\bullet \xrightarrow{11} (\mathrm{NAD})_2 \qquad (4.131)$$

where NAD• is the NAD radical shown in Figure 4.7; Per^{3+}, Per^{4+}, Per^{5+}, and Per^{6+} are the different oxidation states of the peroxidase enzyme; and $\mathrm{NADH_R}$ is a different isomer of NADH.

Figure 4.8 shows a pictorial representation of the mechanism. The mechanism contains a classic catalytic cycle with five important isomers of horseradish peroxidase, and two forms of O_2 (i.e., O_2 and $\mathrm{O_2}^-$ with different properties.

The NAD radicals are classic unstable intermediates. As a result, one would expect their concentrations to be low. However, the radicals can form dimers. The dimers are stable and can accumulate in the system. Consequently, one cannot use the steady-state approximation to calculate the dimer concentration.

What one needs to do, instead, is to follow the procedures in Section 4.4 and set up the differential equations for all of the species in the system. For example, one would say that the concentration of NAD radicals follows

$$\frac{d[\mathrm{NAD}\bullet]}{dt} = k_3[\mathrm{NADH}][\mathrm{Per}^{5+}] + k_4[\mathrm{NAD}\bullet][\mathrm{Per}^{4+}] - k_5[\mathrm{NAD}\bullet][\mathrm{O}_2] - k_8[\mathrm{NAD}^+][\mathrm{Per}^{6+}] - k_{11}[\mathrm{NAD}\bullet]^2 \qquad (4.132)$$

Benson and Scheeline (1996) list the other differential equations to describe the behavior of the species produced during NADH oxidation.

One can numerically integrate these differential equations to calculate the behavior of the system using a modification of the computer program at the end of Example 4.B.6.C. Benson and Scheeline did so, and the key result is shown in Figure 4.9. Notice that the concentrations of many species oscillate with time. Therefore, the system never reaches steady state.

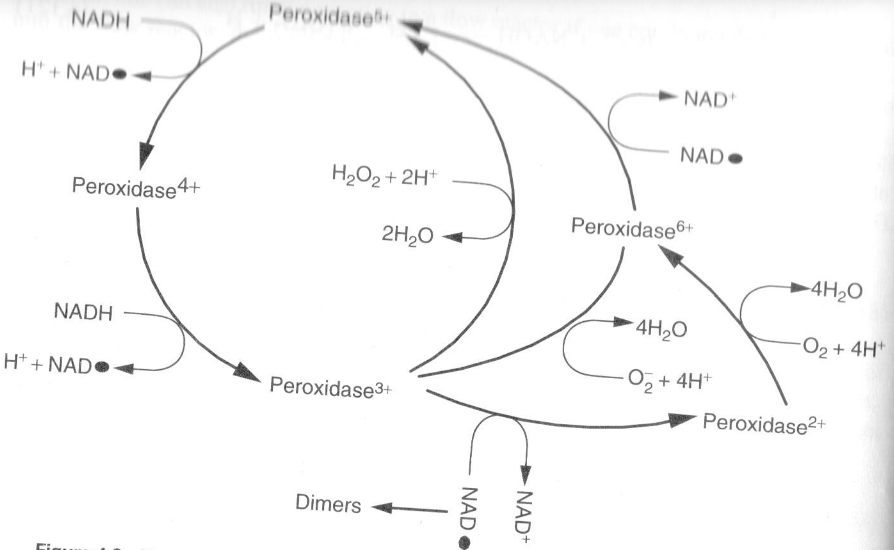

Figure 4.8 The mechanism of NADH oxidation as suggested by Benson and Scheeline (1996).

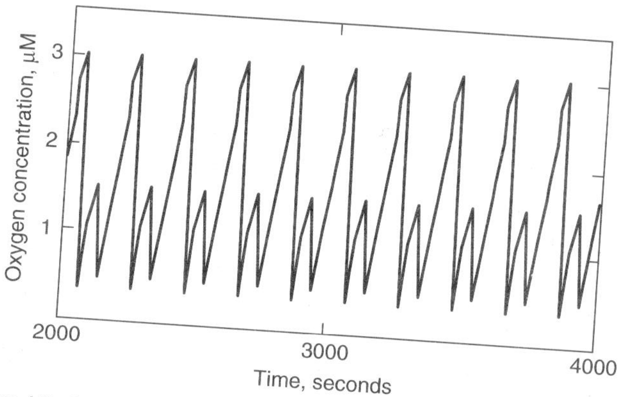

Figure 4.9 Solution of the differential equations of Bensen and Scheeline (1996).

There are many other systems that oscillate. Generally, one can determine whether a given reaction shows oscillations by numerically integrating the rate equations for all of the species in the system. If the system can oscillate, then one will observe oscillations in the numerical solutions. One can also do analysis on the differential equations for each of the species to see when oscillations can occur. The details are beyond the scope of this book. See Gray and Scott (1990) for more information.

The key point to remember is that the steady-state approximation fails when the concentrations of the reactive intermediates become significant. One must integrate the rate equations for the system in cases where the steady-state approximation fails. In such a case, one can get unusual behavior, including, possibly, oscillations or explosions.

4.12 USING THE PSEUDO-STEADY-STATE APPROXIMATION TO INFER MECHANISMS

In Sections 4.6 and 4.10, we discussed cases where the mechanism of a reaction was known and showed how one can use the pseudo-steady-state approximation to derive a rate equation for the reaction. I have to tell you that in practice I have rarely used the pseudo-steady-state approximation in that way. It is usually hard to determine the mechanism of a reaction from experiments. Kinetic measurements are much easier. Consequently, if all that one could do with the pseudo-steady-state approximation were to calculate something that is easy to measure, namely, a rate equation, from something that is hard to measure, namely, a mechanism, the pseudo-steady-state approximation would not be very useful.

In Chapter 5, we will show that one can often predict mechanisms of reactions from first principles. In that case, the pseudo-steady-state approximation is useful. However, in a more general case, one will not know the mechanism very well. In that case, one can apply the pseudo-steady-state approximation in reverse and use kinetic measurements to infer something about the mechanism of a reaction.

Generally, I find that it is best to try to infer the rate law and the mechanism simultaneously. The general procedure is to first do some kinetic measurements. You need to know if the reaction is closer to first-order or second-order in each reactant or something in between. Once you have some kinetic information, you

1. Guess at a mechanism.
2. Use the pseudo-steady-state approximation to derive a rate equation for that mechanism.
3. Take rate data.
4. See if the rate data fits the mechanism. Generally, once you have a mechanism, you need to take more rate data to verify that the rate equation fits the kinetic data.
5. Modify the proposed mechanism and iterate.

Unfortunately, there is a lot of black art in trying to find a mechanism. For years, people mainly guessed, using their best judgment, and then iterated. Such a procedure allows you to fit kinetic data. However, often more than one mechanism will fit the data. Consequently, it is incorrect to assume that just because a mechanism fits the rate data, the mechanism is correct. On the other hand, if the rate equation does not fit the data, the mechanism is incorrect. Consequently, one can use the pseudo-steady-state approximation to eliminate proposed mechanisms.

Let's solve an equation to show how one can use these ideas to fit rate data. Assume that you were trying to determine the mechanism of the following reaction:

$$H_2 + Br_2 \Longrightarrow 2HBr \tag{4.133}$$

As a first guess, let's assume that you could write the rate equation for the reaction as follows:

$$r_{HBr} = k_{HBr}[Br_2]^n[H_2]^m \tag{4.134}$$

where r_{HBr} is the rate of HBr formation; $[H_2]$ and $[Br_2]$ are the concentrations of hydrogen and bromine in the reactor; and, k_{HBr}, m and n are constants. Now the question is how to fit the constants k_{HBr}, m, and n.

Well, the procedures in Chapter 3 give you a clue. For example, one could use the swamping method. You could load Br_2 and a large excess of hydrogen into a glass vessel,