Chemical Kinetics

A. INTRODUCTION

Flames will propagate through only those chemical mixtures that are capable of reacting quickly enough to be considered explosive. Indeed, the expression "explosive" essentially specifies very rapid reaction. From the standpoint of combustion, the interest in chemical kinetic phenomena has generally focused on the conditions under which chemical systems undergo explosive reaction. Recently, however, great interest has developed in the rates and mechanisms of steady (non-explosive) chemical reactions, since most of the known complex pollutants form in zones of steady, usually lower-temperature, reactions during, and even after, the combustion process.

These essential features of chemical kinetics, which occur frequently in combustion phenomena, are reviewed in this chapter. For a more detailed understanding of any of these aspects and a thorough coverage of the subject, refer to any of the books on chemical kinetics, such as those listed in Refs. [1, 1a].

B. RATES OF REACTIONS AND THEIR TEMPERATURE DEPENDENCE

All chemical reactions, whether of the hydrolysis, acid-base, or combustion type, take place at a definite rate and depend on the conditions of the system.
The most important of these conditions are the concentration of the reactants, the temperature, radiation effects, and the presence of a catalyst or inhibitor. The rate of the reaction may be expressed in terms of the concentration of any of the reacting substances or of any reaction product; i.e., the rate may be expressed as the rate of decrease of the concentration of a reactant or the rate of increase of a reaction product.

A stoichiometric relation describing a one-step chemical reaction of arbitrary complexity can be represented by the equation [2, 3]

\[ \sum_{j=1}^{n} v_j' (M_j) = \sum_{j=1}^{n} v_j'' (M_j) \]  

where \( v_j' \) is the stoichiometric coefficient of the reactants, \( v_j'' \) is the stoichiometric coefficient of the products, \( M \) is an arbitrary specification of all chemical species, and \( n \) is the total number of species involved. If a species represented by \( M_j \) does not occur as a reactant or product, its \( v_j \) equals zero. Consider, as an example, the recombination of \( H \) atoms in the presence of \( H \) atoms, i.e., the reaction

\[ H + H + H \rightarrow H_2 + H \]

\( n = 2, \quad M_1 = H, \quad M_2 = H_2; \quad v_1' = 3, \quad v_1'' = 1, \quad v_2' = 0, \quad v_2'' = 1 \)

The reason for following this complex notation will become apparent shortly. The law of mass action, which is confirmed experimentally, states that the rate of disappearance of a chemical species \( i \), defined as \( RR_i \), is proportional to the product of the concentrations of the reacting chemical species, where each concentration is raised to a power equal to the corresponding stoichiometric coefficient; i.e.,

\[ RR_i \sim \prod_{j=1}^{n} (M_j)^{v_j'}, \quad RR_i = k \prod_{j=1}^{n} (M_j)^{v_j'} \]  

where \( k \) is the proportionality constant called the specific reaction rate coefficient. In Eq. (2) \( \sum v_j' \) is also given the symbol \( n \), which is called the overall order of the reaction; \( v_j' \) itself would be the order of the reaction with respect to species \( j \). In an actual reacting system, the rate of change of the concentration of a given species \( i \) is given by

\[ \frac{d(M_i)}{dt} = [v_i'' - v_i'] RR = [v_i'' - v_i'] k \prod_{j=1}^{n} (M_j)^{v_j'} \]  

since \( v_i' \) moles of \( M_i \) are formed for every \( v_i' \) moles of \( M_i \) consumed. For the previous example, then, \( d(H)/dt = -2k(H)^2 \). The use of this complex representation prevents error in sign and eliminates confusion when stoichiometric coefficients are different from 1.
In many systems $M_j$ can be formed not only from a single-step reaction such as that represented by Eq. (3), but also from many different such steps, leading to a rather complex formulation of the overall rate. However, for a single-step reaction such as Eq. (3), $\Sigma \nu_j$ not only represents the overall order of the reaction, but also the molecularity, which is defined as the number of molecules that interact in the reaction step. Generally the molecularity of most reactions of interest will be 2 or 3. For a complex reaction scheme the concept of molecularity is not appropriate and the overall order can take various values including fractional ones.

1. The Arrhenius Rate Expression

In most chemical reactions the rates are dominated by collisions of two species that may have the capability to react. Thus, most simple reactions are second-order. Other reactions are dominated by a loose bond-breaking step and thus are first-order. Most of these latter type reactions fall in the class of decomposition processes. Isomerization reactions are also found to be first-order. According to Lindemann’s theory [1, 4] of first-order processes, first-order reactions occur as a result of a two-step process. This point will be discussed in a subsequent section.

An arbitrary second-order reaction may be written as

$$A + B \to C + D$$

(4)

where a real example would be the reaction of oxygen atoms with nitrogen molecules

$$O + N_2 \to NO + N$$

For the arbitrary reaction (4), the rate expression takes the form

$$-RR = \frac{d(A)}{dt} = -\frac{d(C)}{dt} = -\frac{d(0)}{dt}$$

(5)

The convention used throughout this book is that parentheses around a chemical symbol signify the concentration of that species in moles or mass per cubic centimeter. Specifying the reaction in this manner does not infer that every collision of the reactants A and B would lead to products or cause the disappearance of either reactant. Arrhenius [5] put forth a simple theory that accounts for this fact and gives a temperature dependence of $k$. According to Arrhenius, only molecules that possess energy greater than a certain amount, $E$, will react. Molecules acquire the additional energy necessary from collisions induced by the thermal condition that exists. These high-energy activated molecules lead to products. Arrhenius’
postulate may be written as

$$RR = Z_{AB} \exp(-E/RT)$$

(6)

where $Z_{AB}$ is the gas kinetic collision frequency and $\exp(-E/RT)$ is the Boltzmann factor. Kinetic theory shows that the Boltzmann factor gives the fraction of all collisions that have an energy greater than $E$.

The energy term in the Boltzmann factor may be considered as the size of the barrier along a potential energy surface for a system of reactants going to products, as shown schematically in Fig. 1. The state of the reacting species at this activated energy can be regarded as some intermediate complex that leads to the products. This energy is referred to as the activation energy of the reaction and is generally given the symbol $E_A$. In Fig. 1, this energy is given the symbol $E_A$, to distinguish it from the condition in which the product species can revert to reactants by a backward reaction. The activation energy of this backward reaction is represented by $E_D$ and is obviously much larger than $E_f$ for the forward step.

Figure 1 shows an exothermic condition for reactants going to products. The relationship between the activation energy and the heat of reaction has been developed [1a]. Generally, the more exothermic a reaction is, the smaller the activation energy. In complex systems, the energy release from one such reaction can sustain other, endothermic reactions, such as that represented in Fig. 1 for products reverting back to reactants. For example, once the reaction is initiated, acetylene will decompose to the elements in a monopropellant rocket in a sustained fashion because the energy release of the decomposition process is greater than the activation energy of the process. In contrast a calculation of the decomposition of benzene shows the process to be exothermic, but the activation energy of the benzene decomposition process is so large that it will not sustain monopropellant decomposition. For this reason, acetylene is considered an unstable species and benzene a stable one.

Considering again Eq. (6) and referring to $E$ as an activation energy, attention is focused on the collision rate $Z_{AB}$, which from simple kinetic theory can be

\[ FIGURE 1 \] Energy as a function of a reaction coordinate for a reacting system.
represented by

\[ Z_{AB} = (A)(B)\sigma_{AB}^2 \left[ 8\pi k_B T / \mu \right]^{1/2} \]  

(7)

where \( \sigma_{AB} \) is the hard sphere collision diameter, \( k_B \) the Boltzmann constant, \( \mu \) is the reduced mass \( [m_A m_B / (m_A + m_B)] \), and \( m \) is the mass of the species. \( Z_{AB} \) may be written in the form

\[ Z_{AB} = Z'_{AB}(A)(B) \]  

(7')

where \( Z'_{AB} = \sigma_{AB}^2 \left[ 8\pi k_B T / \mu \right]^{1/2} \). Thus, the Arrhenius form for the rate is

\[ RR = Z'_{AB}(A)(B) \exp(-E/RT) \]

When one compares this to the reaction rate written from the law of mass action [Eq. (2)], one finds that

\[ k = Z'_{AB} \exp(-E/RT) = Z''_{AB} T^{1/2} \exp(-E/RT) \]  

(8)

Thus, the important conclusion is that the specific reaction rate constant \( k \) is dependent on temperature alone and is independent of concentration. Actually, when complex molecules are reacting, not every collision has the proper steric orientation for the specific reaction to take place. To include the steric probability, one writes \( k \) as

\[ k = Z''_{AB} T^{1/2} \left[ \exp(-E/RT) \right] \phi \]  

(9)

where \( \phi \) is a steric factor, which can be a very small number at-times. Most generally, however, the Arrhenius form of the reaction rate constant is written as

\[ k = \text{const} \ T^{1/2} \exp(-E/RT) = A \exp(-E/RT) \]  

(10)

where the constant \( A \) takes into account the steric factor and the terms in the collision frequency other than the concentrations and is referred to as the kinetic pre-exponential \( A \) factor. The factor \( A \) as represented in Eq. (10) has a very mild \( T^{1/2} \) temperature dependence that is generally ignored when plotting data. The form of Eq. (10) holds well for many reactions, showing an increase in \( k \) with \( T \) that permits convenient straight-line correlations of data on \( \ln k \) versus \( 1/T \) plots. Data that correlate as a straight line on a \( \ln k \) versus \( 1/T \) plot are said to follow Arrhenius kinetics, and plots of the logarithm of rates or rate constants as a function of \( 1/T \) are referred to as Arrhenius plots. The slopes of lines on these plots are equal to \( -E/R \); thus the activation energy may be determined readily (see Fig. 2). Low activation energy processes proceed faster than high activation energy processes at low temperatures and are much less temperature-sensitive. At high temperatures, high activation energy reactions can prevail because of this temperature sensitivity.
2. Transition State and Recombination Rate Theories

There are two classes of reactions for which Eq. (10) is not suitable. Recombination reactions and low activation energy free-radical reactions in which the temperature dependence in the pre-exponential term assumes more importance. In this low-activation, free-radical case the approach known as absolute or transition state theory of reaction rates gives a more appropriate correlation of reaction rate data with temperature. In this theory the reactants are assumed to be in equilibrium with an activated complex. One of the vibrational modes in the complex is considered loose and permits the complex to dissociate to products. Figure 1 is again an appropriate representation, where the reactants are in equilibrium with an activated complex, which is shown by the curve peak along the extent of the reaction coordinate. When the equilibrium constant for this situation is written in terms of partition functions and if the frequency of the loose vibration is allowed to approach zero, a rate constant can be derived in the following fashion.

The concentration of the activated complex may be calculated by statistical thermodynamics in terms of the reactant concentrations and an equilibrium constant [1, 6]. If the reaction scheme is written as

\[
A + BC \rightleftharpoons (ABC)^\# \rightarrow AB + C
\]  

(11)

the equilibrium constant with respect to the reactants may be written as

\[
K_n = \frac{(ABC)^\#}{(A)(BC)}
\]  

(12)

where the symbol \# refers to the activated complex. As discussed in Chapter 1, since \( K_n \) is expressed in terms of concentration, it is pressure-dependent. Statistical
thermodynamics relates equilibrium constants to partition functions; thus for the case in question, one finds [6]

\[ K_y = \frac{(Q_T)^y}{(Q_T)_A(T)_{BC}} \exp \left( -\frac{E}{RT} \right) \]  

(13)

where \( Q_T \) is the total partition function of each species in the reaction. \( Q_T \) can be considered separable into vibrational, rotational, and translation partition functions.

However, one of the terms in the vibrational partition function part of \( Q^y \) is different in character from the rest because it corresponds to a very loose vibration that allows the complex to dissociate into products. The complete vibrational partition function is written as

\[ Q_{\text{vib}} = \prod_i \left[ 1 - \exp(-h\nu_i/k_BT) \right]^{-1} \]  

(14)

where \( h \) is Planck’s constant and \( \nu_i \) is the vibrational frequency of the \( i \)th mode. For the loose vibration, one term of the complete vibrational partition function can be separated and its value employed when \( \nu \) tends to zero,

\[ \lim_{\nu \to 0} \left[ 1 - \exp(-h\nu/k_BT) \right]^{-1} = (k_BT/h\nu) \]  

(15)

Thus

\[ \{ (ABC)^y / [(A)(BC)] \} = \{ [(Q_{T-1})^y (k_BT/h\nu)] / [(Q_T)_A(T)_{BC}] \} \times \exp(-E/RT) \]  

(16)

which rearranges to

\[ \nu(ABC)^y = \{ [(A)(BC)(k_BT/h)(Q_{T-1})^y] / [(Q_T)_A(T)_{BC}] \} \times \exp(-E/RT) \]  

(17)

where \( (Q_{T-1})^y \) is the partition function of the activated complex evaluated for all vibrational frequencies except the loose one. The term \( \nu(ABC)^y \) on the left-hand side of Eq. (17) is the frequency of the activated complex in the degree of freedom corresponding to its decomposition mode and is therefore the frequency of decomposition. Thus,

\[ k = (k_BT/h) \frac{(Q_{T-1})^y}{(Q_T)_A(T)_{BC}} \exp(-E_A/RT) \]  

(18)

is the expression for the specific reaction rate as derived from transition state theory.

If species \( A \) is only a diatomic molecule, the reaction scheme can be represented by

\[ A \rightleftharpoons A^y \rightarrow \text{products} \]  

(19)
Thus \((Q_{T-1})^\theta\) goes to 1. There is only one bond in \(A\), so

\[ Q_{\text{vib}, A} = \left[1 - \exp(-\hbar \nu_A/k_B T)\right]^{-1} \]

(20)

Then

\[ k = (k_B T/h) \left[1 - \exp(-\hbar \nu_A/k_B T)\right] \exp(-E/RT) \]

(21)

If \(\nu_A\) of the stable molecule is large, which it normally is in decomposition systems, then the term in square brackets goes to 1 and

\[ k = (k_B T/h) \exp(-E/RT) \]

(22)

Note that the term \((k_B T/h)\) gives a general order of the pre-exponential term for these dissociation processes.

Although the rate constant will increase monotonically with \(T\) for Arrhenius' collision theory, examination of Eqs. (18) and (22) reveals that a nonmonotonic trend can be found [7] for the low activation energy processes represented by transition state theory. Thus, data that show curvature on an Arrhenius plot probably represent a reacting system in which an intermediate complex forms and in which the activation energy is low. As the results from Problem 1 of this chapter reveal, the term \((k_B T/h)\) and the Arrhenius pre-exponential term given by Eq. (7') are approximately the same and/or about 10^{14} \(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) at 1000 K. This agreement is true when there is little entropy change between the reactants and the transition state and is nearly true for most cases. Thus one should generally expect pre-exponential values to fall in a range near 10^{12} to 10^{14} \(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\). When quantities far different from this range are reported, one should conclude that the representative expression is an empirical fit to some experimental data over a limited temperature range. The earliest representation of an important combustion reaction that showed curvature on an Arrhenius plot was for the CO + OH reaction by the author's group [7], which, by application of transition state theory, correlated a wide temperature range of experimental data. Since then, consideration of transition state theory has been given to many other reactions important to combustion [8].

The use of transition state theory as a convenient expression of rate data is obviously complex owing to the presence of the temperature-dependent partition functions. Most researchers working in the area of chemical kinetic modeling have found it necessary to adopt a uniform means of expressing the temperature variation of rate data and consequently have adopted a modified Arrhenius form

\[ k = AT^n \exp(-E/RT) \]

(23)

where the power of \(T\) accounts for all the pre-exponential temperature-dependent terms in Eqs. (10), (18), and (22). Since most elementary binary reactions exhibit Arrhenius behavior over modest ranges of temperature, the temperature dependence can usually be incorporated with sufficient accuracy into the exponential
alone; thus, for most data \( n = 0 \) is adequate, as will be noted for the extensive listing in the appendixes. However, for the large temperature ranges found in combustion, "non-Arrhenius" behavior of rate constants tends to be the rule rather than the exception, particularly for processes that have a small energy barrier. It should be noted that for these processes the pre-exponential factor that contains the ratio of partition functions (which are weak functions of temperature compared to an exponential) corresponds roughly to a \( T^n \) dependence with \( n \) in the \( \pm 1-2 \) range [9]. Indeed the values of \( n \) for the rate data expressions reported in the appendixes fall within this range. Generally the values of \( n \) listed apply only over a limited range of temperatures and they may be evaluated by the techniques of thermochemical kinetics [10].

The units for the reaction rate constant \( k \) when the reaction is of order \( n \) (different from the \( n \) power of \( T \)) will be \( [(\text{conc})^{-1} \times \text{(time)}]^{-1} \). Thus, for a first-order reaction the units of \( k \) are in reciprocal seconds (s\(^{-1}\)), and for a second-order reaction process the units are in moles per cubic centimeter per second (mol cm\(^{-3}\) s\(^{-1}\)).

Radical recombination is another class of reactions in which the Arrhenius expression will not hold. When simple radicals recombine to form a product, the energy liberated in the process is sufficiently great to cause the product to decompose into the original radicals. Ordinarily, a third body is necessary to remove this energy to complete the recombination. If the molecule formed in a recombination process has a large number of internal (generally vibrational) degrees of freedom, it can redistribute the energy of formation among these degrees, so a third body is not necessary. In some cases the recombination process can be stabilized if the formed molecule dissipates some energy radiatively (chemiluminescence) or collides with a surface and dissipates energy in this manner.

If one follows the approach of Landau and Teller [11], who in dealing with vibrational relaxation developed an expression by averaging a transition probability based on the relative molecular velocity over the Maxwellian distribution, one can obtain the following expression for the recombination rate constant [6]:

\[
k \sim \exp(C/T)^{1/3}
\]  

(24)

where \( C \) is a positive constant that depends on the physical properties of the species of concern [6]. Thus, for radical recombination, the reaction rate constant decreases mildly with the temperature, as one would intuitively expect. In dealing with the recombination of radicals in nozzle flow, one should keep this mild temperature dependence in mind. Recall the example of H atom recombination given earlier. If one writes \( M \) as any (or all) third body in the system, the equation takes the form

\[
H + H + M \rightarrow H_2 + M
\]  

(25)
The rate of formation of H₂ is third-order and given by
\[ \frac{d(H_2)}{dt} = k(H)^3(M) \]  
(25a)

Thus, in expanding dissociated gases through a nozzle, the velocity increases and the temperature and pressure decrease. The rate constant for this process thus increases, but only slightly. The pressure affects the concentrations and since the reaction is third-order, it enters the rate as a cubed term. In all, then, the rate of recombination in the high-velocity expanding region decreases owing to the pressure term. The point to be made is that third-body recombination reactions are mostly pressure-sensitive, generally favored at higher pressure, and rarely occur at very low pressures.

C. SIMULTANEOUS INTERDEPENDENT REACTIONS

In complex reacting systems, such as those in combustion processes, a simple one-step rate expression will not suffice. Generally, one finds simultaneous, interdependent reactions or chain reactions.

The most frequently occurring simultaneous, interdependent reaction mechanism is the case in which the product, as its concentration is increased, begins to dissociate into the reactants. The classical example is the hydrogen–iodine reaction:
\[ H_2 + I_2 \xrightleftharpoons[k_b]{k_f} 2HI \]  
(26)

The rate of formation of HI is then affected by two rate constants, \( k_f \) and \( k_b \), and is written as
\[ \frac{d(HI)}{dt} = 2k_f(H_2)(I_2) - 2k_b(HI)^2 \]  
(27)

in which the numerical value 2 should be noted. At equilibrium, the rate of formation of HI is zero, and one finds that
\[ 2k_f(H_2)_{eq}(I_2)_{eq} - 2k_b(HI)_{eq}^2 = 0 \]  
(28)

where the subscript eq designates the equilibrium concentrations. Thus,
\[ \frac{k_f}{k_b} = \frac{(HI)_{eq}^2}{(H_2)_{eq}(I_2)_{eq}} \equiv K_c \]  
(29)

i.e., the forward and backward rate constants are related to the equilibrium constant \( K_c \) based on concentrations \( (K_c) \). The equilibrium constants are calculated from basic thermodynamic principles as discussed in Section 1.8, and the relationship \( (k_f/k_b) = K_c \) holds for any reacting system. The calculation of the equilibrium
constant is much more accurate than experimental measurements of specific reaction rate constants. Thus, given a measurement of a specific reaction rate constant, the reverse rate constant is determined from the relationship $K_c = (k_f / k_b)$. For the particular reaction in Eq. (29), $K_c$ is not pressure-dependent as there is a concentration squared in both the numerator and denominator. Indeed, $K_c$ equals $(k_f / k_b) = K_p$ only when the concentration powers cancel.

With this equilibrium consideration the rate expression for the formation of HI becomes

$$\frac{d[(HI)]}{dt} = 2k_f(H_2)(I_2) - 2\frac{k_f}{K_c}(HI)^2$$

which shows there is only one independent rate constant in the problem.

D. CHAIN REACTIONS

In most instances, two reacting molecules do not react directly as $H_2$ and $I_2$ do; rather one molecule dissociates first to form radicals. These radicals then initiate a chain of steps. Interestingly, this procedure occurs in the reaction of $H_2$ with another halogen, $Br_2$. Experimentally, Bodenstein [12] found that the rate of formation of HBr obeys the expression

$$\frac{d[HBr]}{dt} = \frac{k'_{exp}(H_2)(Br_2)^{1/2}}{1 + k'_{exp}[(HBr)/(Br_2)]}$$

This expression shows that HBr is inhibiting to its own formation.

Bodenstein explained this result by suggesting that the $H_2$–$Br_2$ reaction was chain in character and initiated by a radical ($Br^-$) formed by the thermal dissociation of $Br_2$. He proposed the following steps:

1. $M + Br_2 \xrightleftharpoons{k_1} 2Br^- + M$ \hspace{1cm} \text{(chain initiating step)}
2. $Br^- + H_2 \xrightarrow{k_2} HBr + H^-$
3. $H^- + Br_2 \xrightarrow{k_4} HBr + Br^-$ \hspace{1cm} \text{(chain carrying or propagating steps)}
4. $H^- + HBr \xrightarrow{k_4} H_2 + Br^-$
5. $M + 2Br^- \xrightarrow{k_5} Br_2 + M$ \hspace{1cm} \text{(chain terminating step)}

The Br$_2$ bond energy is approximately 189 kJ/mol and the H$_2$ is approximately 427 kJ/mol. Consequently, over all the temperatures but the very highest, Br$_2$ dissociation will be the initiating step. These dissociation steps follow Arrhenius kinetics and form a plot similar to that shown in Fig. 2. In Fig. 3 two Arrhenius plots are shown, one for a high activation step and another for a low activation energy step. One can readily observe that for low temperature, the smaller $E_A$ step prevails.
Perhaps the most important of the various chain types is the chain step that is necessary to achieve nonthermal explosions. This chain step, called chain branching, is one in which two radicals are created for each radical consumed. Two typical chain branching steps that occur in the $\text{H}_2-\text{O}_2$ reaction system are

$$\text{H}^- + \text{O}_2 \rightarrow \cdot\text{OH} + \cdot\text{O}^-$$

$$\cdot\text{O}^- + \text{H}_2 \rightarrow \cdot\text{OH} + \text{H}^-$$

where the dot next to or over a species is the convention for designating a radical. Such branching will usually occur when the monoradical (such as $\text{H}^-$) formed by breaking a single bond reacts with a species containing a double bond type structure (such as that in $\text{O}_2$) or when a biradical (such as $\cdot\text{O}^-$) formed by breaking a double bond reacts with a saturated molecule (such as $\text{H}_2$ or $\text{RH}$ where $\text{R}$ is any organic radical). For an extensive discussion of chain reactions, refer to the monograph by Dainton [13].

As shown in the $\text{H}_2-\text{Br}_2$ example, radicals are produced by dissociation of a reactant in the initiation process. These types of dissociation reactions are highly endothermic and therefore quite slow. The activation energy of these processes would be in the range of 160–460 kJ/mol. Propagation reactions similar to reactions (2)–(4) in the $\text{H}_2-\text{Br}_2$ example are important because they determine the rate at which the chain continues. For most propagation reactions of importance in combustion, activation energies normally lie between 0 and 40 kJ/mol. Obviously, branching chain steps are a special case of propagating steps and, as mentioned, these are the steps that lead to explosion. Branching steps need not necessarily occur rapidly because of the multiplication effect; thus, their activation energies
may be higher than those of the linear propagation reactions with which they compete [14].

Termination occurs when two radicals recombine; they need not be similar to those shown in the H₂–Br₂ case. Termination can also occur when a radical reacts with a molecule to give either a molecular species or a radical of lower activity that cannot propagate a chain. Since recombination processes are exothermic, the energy developed must be removed by another source, as discussed previously. The source can be another gaseous molecule M₂ as shown in the example, or a wall. For the gaseous case, a termolecular or third-order reaction is required; consequently, these reactions are slower than other types except at high pressures.

In writing chain mechanisms note that backward reactions are often written as an individual step; that is, reaction (4) of the H₂–Br₂ scheme is the backward step of reaction (2). The inverse of reaction (3) proceeds very slowly; it is therefore not important in the system and is usually omitted for the H₂–Br₂ example.

From the five chain steps written for the H₂–Br₂ reaction, one can write an expression for the HBr formation rate:

\[
\frac{d\text{(HBr)}}{dt} = k_2(\text{Br}) \text{(H₂)} + k_3(\text{H}) \text{(Br₂)} - k_4(\text{H})(\text{HBr})
\]

(32)

In experimental systems, it is usually very difficult to measure the concentration of the radicals that are important intermediates. However, one would like to be able to relate the radical concentrations to other known or measurable quantities. It is possible to achieve this objective by the so-called steady-state approximation for the reaction's radical intermediates. The assumption is that the radicals form and react very rapidly so that the radical concentration changes only very slightly with time, thereby approximating a steady-state concentration. Thus, one writes the equations for the rate of change of the radical concentration, then sets them equal to zero. For the H₂–Br₂ system, then, one has for (H) and (Br)

\[
\frac{d(\text{H})}{dt} = k_2(\text{Br})(\text{H₂}) - k_3(\text{H})(\text{Br₂}) - k_4(\text{H})(\text{HBr}) \equiv 0
\]

(33)

\[
\frac{d(\text{Br})}{dt} = 2k_1(\text{Br₂}) - k_2(\text{Br})(\text{H₂}) + k_3(\text{H})(\text{Br₂})
\]

\[+ k_4(\text{H})(\text{HBr}) - 2k_5(\text{Br})^2 \equiv 0
\]

(34)

Writing these two equations equal to zero does not imply that equilibrium conditions exist, as was the case for Eq. (28). It is also important to realize that the steady-state approximation does not imply that the rate of change of the radical concentration is necessarily zero, but rather that the rate terms for the expressions of radical formation and disappearance are much greater than the radical concentration rate term. That is, the sum of the positive terms and the sum of the negative terms on the right-hand side of the equality in Eqs. (33) and (34) are, in absolute magnitude, very much greater than the term on the left of these equalities [3].
Thus in the $\text{H}_2$–$\text{Br}_2$ experiment it is assumed that steady-state concentrations of radicals are approached and the concentrations for H and Br are found to be

$$\frac{\text{Br}}{k_1/k_3} = (k_{1}/k_3)^{1/2}(\text{Br}_2)^{1/2}$$

$$\frac{\text{H}}{k_2} = k_2(k_1/k_3)^{1/2}(\text{H}_2)(\text{Br}_2)^{1/2}$$

By substituting these values in the rate expression for the formation of HBr [Eq. (32)], one obtains

$$\frac{d(\text{HBr})}{dt} = \frac{2k_2(k_1/k_3)^{1/2}(\text{H}_2)(\text{Br}_2)^{1/2}}{1 + [k_4(\text{HBr})/k_3(\text{Br}_2)]]}$$

which is the exact form found experimentally [Eq. (31)]. Thus,

$$k'_{\exp} = 2k_2(k_1/k_3)^{1/2}, \quad k''_{\exp} = k_4/k_3$$

Consequently, it is seen, from the measurement of the overall reaction rate and the steady-state approximation, that values of the rate constants of the intermediate radical reactions can be determined without any measurement of radical concentrations. Values $k'_{\exp}$ and $k''_{\exp}$ evolve from the experimental measurements and the form of Eq. (31). Since $(k_4/k_3)$ is the inverse of the equilibrium constant for $\text{Br}_2$ dissociation and this value is known from thermodynamics, $k_2$ can be found from $k'_{\exp}$. The value of $k_4$ is found from $k_2$ and the equilibrium constant that represents reactions (2) and (4), as written in the $\text{H}_2$–$\text{Br}_2$ reaction scheme. From the experimental value of $k''_{\exp}$ and the calculated value of $k_4$, the value $k_3$ can be determined.

The steady-state approximation, found to be successful in application to this straight-chain process, can be applied to many other straight-chain processes, chain reactions with low degrees of branching, and other types of nonchain systems. Because the rates of the propagating steps greatly exceed those of the initiation and termination steps in most, if not practically all, of the straight-chain systems, the approximation always works well. However, the use of the approximation in the initiation or termination phase of a chain system, during which the radical concentrations are rapidly increasing or decreasing, can lead to substantial errors.

E. PSEUDO–FIRST-ORDER REACTIONS AND THE "FALL-OFF" RANGE

As mentioned earlier, practically all reactions are initiated by bimolecular collisions; however, certain bimolecular reactions exhibit first-order kinetics. Whether a reaction is first- or second-order is particularly important in combustion because of the presence of large radicals that decompose into a stable species and a smaller radical (primarily the hydrogen atom). A prominent combustion example
is the decay of a paraffinic radical to an olefin and a H atom. The order of such reactions, and hence the appropriate rate constant expression, can change with the pressure. Thus, the rate expression developed from one pressure and temperature range may not be applicable to another range. This question of order was first addressed by Lindemann [4], who proposed that first-order processes occur as a result of a two-step reaction sequence in which the reacting molecule is activated by collisional processes, after which the activated species decomposes to products. Similarly, the activated molecule could be deactivated by another collision before it decomposes. If A is considered the reactant molecule and M its nonreacting collision partner, the Lindemann scheme can be represented as follows:

\[
A + M \xrightleftharpoons[{k_b}]{k_1} A^* + M
\]  (38)

\[
A^* \xrightarrow{k_p} \text{products}
\]  (39)

The rate of decay of species A is given by

\[
\frac{d(A)}{dt} = -k_l(A)(M) + k_p(A^*)(M)
\]  (40)

and the rate of change of the activated species A* is given by

\[
\frac{d(A^*)}{dt} = k_l(A)(M) - k_b(A^*)(M) - k_p(A^*) \approx 0
\]  (41)

Applying the steady-state assumption to the activated species equation gives

\[
(A^*) = \frac{k_l(A)(M)}{k_b(M) + k_p}
\]  (42)

Substituting this value of (A*) into Eq. (40), one obtains

\[
-\frac{1}{(A)} \frac{d(A)}{dt} = \frac{k_lk_p(M)}{k_b(M) + k_p} = k_{\text{diss}}
\]  (43)

where \(k_{\text{diss}}\) is a function of the rate constants and the collision partner concentration—that is, a direct function of the total pressure if the effectiveness of all collision partners is considered the same. Owing to size, complexity, and the possibility of resonance energy exchange, the effectiveness of a collision partner (third body) can vary. Normally, collision effectiveness is not a concern, but for some reactions specific molecules may play an important role [15].

At high pressures, \(k_b(M) \gg k_p\) and

\[
k_{\text{diss, oc}} \equiv \frac{k_lk_p}{k_b} = K k_p
\]  (44)
where \( k_{\text{diss,\infty}} \) becomes the high-pressure-limit rate constant and \( K \) is the equilibrium constant \((k_f/k_b)\). Thus at high pressures the decomposition process becomes overall first-order. At low pressure, \( k_b(M) \ll k_p \) as the concentrations drop and

\[
k_{\text{diss,0}} = k_f(M)
\]  

(45)

where \( k_{\text{diss,0}} \) is the low-pressure-limit rate constant. The process is then second-order by Eq. (43), simplifying to \(-d(A)/dt = k_f(M)A\). Note the presence of the concentration \((A)\) in the manner in which Eq. (43) is written.

Many systems fall in a region of pressures (and temperatures) between the high- and low-pressure limits. This region is called the “fall-off range,” and its importance to combustion problems has been very adequately discussed by Troe [16]. The question, then, is how to treat rate processes in the fall-off range. Troe proposed that the fall-off range between the two limiting rate constants be represented using a dimensionless pressure scale

\[
\left( \frac{k_{\text{diss,0}}}{k_{\text{diss,\infty}}} \right) = \frac{k_b(M)}{k_p}
\]  

(46)

in which one must realize that the units of \( k_b \) and \( k_p \) are different so that the right-hand side of Eq. (46) is dimensionless. Substituting Eq. (44) into Eq. (43), one obtains

\[
\frac{k_{\text{diss}}}{k_{\text{diss,\infty}}} = \frac{k_b(M)}{k_b(M) + k_p} = \frac{k_b(M)/k_p}{[k_b(M)/k_p] + 1}
\]  

(47)

or, from Eq. (46),

\[
\frac{k_{\text{diss}}}{k_{\text{diss,\infty}}} = \frac{k_{\text{diss,0}}}{k_{\text{diss,\infty}}}/\left( 1 + \frac{k_{\text{diss,0}}}{k_{\text{diss,\infty}}} \right)
\]  

(48)

For a pressure (or concentration) in the center of the fall-off range, \( \left( k_{\text{diss,0}}/k_{\text{diss,\infty}} \right) = 1 \) and

\[
k_{\text{diss}} = 0.5k_{\text{diss,\infty}}
\]  

(49)

Since it is possible to write the products designated in Eq. (39) as two species that could recombine, it is apparent that recombination reactions can exhibit pressure sensitivity; so an expression for the recombination rate constant similar to Eq. (48) can be developed [16].

The preceding discussion stresses the importance of properly handling rate expressions for thermal decomposition of polyatomic molecules, a condition that prevails in many hydrocarbon oxidation processes. For a detailed discussion on evaluation of low- and high-pressure rate constants, again refer to Ref. [16].

Another example in which a pseudo-first-order condition can arise in evaluating experimental data is the case in which one of the reactants (generally the oxidizer in a combustion system) is in large excess. Consider the arbitrary process

\[ A + B \rightarrow D \]  

(50)
where (B) \gg (A). The rate expression is

\[
\frac{d(A)}{dt} = -\frac{d(D)}{dt} = -k(A)(B)
\]  \hspace{1cm} (51)

Since (B) \gg (A), the concentration of B does not change appreciably and \(k(B)\) would appear as a constant. Then Eq. (51) becomes

\[
\frac{d(A)}{dt} = -\frac{d(D)}{dt} = -k'(A)
\]  \hspace{1cm} (52)

where \(k' = k(B)\). Equation (52) could represent experimental data because there is little dependence on variations in the concentration of the excess component B. The reaction, of course, appears overall first-order. One should keep in mind, however, that \(k'\) contains a concentration and is pressure-dependent. This pseudo-first-order concept arises in many practical combustion systems that are very fuel-lean; i.e., \(O_2\) is present in large excess.

F. THE PARTIAL EQUILIBRIUM ASSUMPTION

As will be discussed in the following chapter, most combustion systems entail oxidation mechanisms with numerous individual reaction steps. Under certain circumstances a group of reactions will proceed rapidly and reach a quasi-equilibrium state. Concurrently, one or more reactions may proceed slowly. If the rate or rate constant of this slow reaction is to be determined and if the reaction contains a species difficult to measure, it is possible through a partial equilibrium assumption to express the unknown concentrations in terms of other measurable quantities. Thus, the partial equilibrium assumption is very much like the steady-state approximation discussed earlier. The difference is that in the steady-state approximation one is concerned with a particular species and in the partial equilibrium assumption one is concerned with particular reactions. Essentially then, partial equilibrium comes about when forward and backward rates are very large and the contribution that a particular species makes to a given slow reaction of concern can be compensated for by very small differences in the forward and backward rates of those reactions in partial equilibrium.

A specific example can illustrate the use of the partial equilibrium assumption. Consider, for instance, a complex reacting hydrocarbon in an oxidizing medium. By the measurement of the CO and CO\(_2\) concentrations, one wants to obtain an estimate of the rate constant of the reaction

\[
CO + OH \rightarrow CO_2 + H
\]  \hspace{1cm} (53)

The rate expression is

\[
\frac{d(CO_2)}{dt} = -\frac{d(CO)}{dt} = k(CO)(OH)
\]  \hspace{1cm} (54)
Then the question is how to estimate the rate constant $k$ without a measurement of the OH concentration. If we assume that equilibrium exists between the H$_2$–O$_2$ chain species, one can develop the following equilibrium reactions of formation from the complete reaction scheme:

$$\frac{1}{2}H_2 + \frac{1}{2}O_2 \rightleftharpoons OH, \quad H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$$

$$K_{C,H,O}^2 = \frac{(OH)_{eq}^2}{(H_2)_{eq}(O_2)_{eq}}, \quad K_{C,H,O} = \frac{(H_2O)_{eq}}{(H_2)_{eq}(O_2)_{eq}}^{1/2}$$

(55)

Solving the two latter expressions for $(OH)_{eq}$ and eliminating $(H_2)_{eq}$, one obtains

$$(OH)_{eq} = (H_2O)^{1/2}(O_2)^{1/4} [K_{C,H,O}^2/K_{C,H,O}]^{1/2}$$

(56)

and the rate expression becomes

$$\frac{d(CO_2)}{dt} = -\frac{d(CO)}{dt} = k [K_{C,H,O}^2/K_{C,H,O}]^{1/2} (CO)(H_2O)^{1/2}(O_2)^{1/4}$$

(57)

Thus, one observes that the rate expression can be written in terms of readily measurable stable species. One must, however, exercise care in applying this assumption. Equilibria do not always exist among the H$_2$–O$_2$ reactions in a hydrocarbon combustion system—indeed, there is a question if equilibrium exists during CO oxidation in a hydrocarbon system. Nevertheless, it is interesting to note the availability of experimental evidence that shows the rate of formation of CO$_2$ to be (1/4)-order with respect to O$_2$, (1/2)-order with respect to water, and first-order with respect to CO [17, 18]. The partial equilibrium assumption is more appropriately applied to NO formation in flames, as will be discussed in Chapter 8.

G. PRESSURE EFFECT IN FRACTIONAL CONVERSION

In combustion problems, one is interested in the rate of energy conversion or utilization. Thus it is more convenient to deal with the fractional change of a particular substance rather than the absolute concentration. If $(M)$ is used to denote the concentrations in a chemical reacting system of arbitrary order $n$, the rate expression is

$$\frac{d(M)}{dt} = -k(M)^n$$

(58)

Since $(M)$ is a concentration, it may be written in terms of the total density $\rho$ and the mole or mass fraction $\varepsilon$; i.e.,

$$(M) = \rho\varepsilon$$

(59)
It follows that at constant temperature

$$\rho \frac{d\epsilon}{dt} = -k(\rho \epsilon)^n$$  \hspace{1cm} (60)

$$\frac{d\epsilon}{dt} = -k\epsilon^n \rho^{n-1}$$  \hspace{1cm} (61)

For a constant-temperature system, $\rho \sim P$ and

$$\frac{d\epsilon}{dt} \sim P^{n-1}$$  \hspace{1cm} (62)

That is, the fractional change is proportional to the pressure raised to the reaction order $-1$.

PROBLEMS

1. For a temperature of 1000 K, calculate the pre-exponential factor in the specific reaction rate constant for (a) any simple bimolecular reaction and (b) any simple unimolecular decomposition reaction following transition state theory.

2. The decomposition of acetaldehyde is found to be overall first-order with respect to the acetaldehyde and to have an overall activation energy of 60 kcal/mol. Assume the following hypothetical sequence to be the chain decomposition mechanism of acetaldehyde:

   (1) $\text{CH}_2\text{CHO} \xrightarrow{k_1} 0.5\text{CH}_3\text{CO} + 0.5\text{CH}_3 + 0.5\text{CO} + 0.5\text{H}_2$
   (2) $\text{CH}_3\text{CO} \xrightarrow{k_2} \text{CH}_3 + \text{CO}$
   (3) $\text{CH}_3 + \text{CH}_3\text{CHO} \xrightarrow{k_3} \text{CH}_4 + \text{CH}_3\text{CO}$
   (4) $\text{CH}_3 + \text{CH}_3\text{CO} \xrightarrow{k_4}$ minor products

   For these conditions,

   (a) List the type of chain reaction and the molecularity of each of the four reactions.
   (b) Show that these reaction steps would predict an overall reaction order of 1 with respect to the acetaldehyde
   (c) Estimate the activation energy of reaction (2), if $E_1 = 80$, $E_3 = 10$, and $E_4 = 5$ kcal/mol.

   Hint: $E_1$ is much larger than $E_2$, $E_3$, and $E_4$.

3. Assume that the steady state of (Br) is formally equivalent to partial equilibrium for the bromine radical chain-initiating step and recalculate the form of Eq. (37) on this basis.

4. Many early investigators interested in determining the rate of decomposition of ozone performed their experiments in mixtures of ozone and oxygen. Their
observations led them to write the following rate expression:

\[ \frac{d(O_3)}{dt} = k_{exp} \left[ \frac{(O_3)^2}{(O_2)} \right] \]

The overall thermodynamic equation for ozone conversion to oxygen is

\[ 2O_3 \rightarrow 3O_2 \]

The inhibiting effect of the oxygen led many to expect that the decomposition followed the chain mechanism

\[ M + O_3 \rightarrow_{k_1} O_2 + O + M \]
\[ M + O + O_2 \rightarrow_{k_2} O_3 + M \]
\[ O + O_3 \rightarrow_{k_3} 2O_2 \]

(a) If the chain mechanisms postulated were correct and if \( k_2 \) and \( k_3 \) were nearly equal, would the initial mixture concentration of oxygen have been much less than or much greater than that of ozone?

(b) What is the effective overall order of the experimental result under these conditions?

(c) Given that \( k_{exp} \) was determined as a function of temperature, which of the three elementary rate constants is determined? Why?

(d) What type of additional experiment should be performed in order to determine all the elementary rate constants?

REFERENCES


5. Arrhenius, S., Phys. Chem. 4, 226 (1889).


