

## **PART I**

### **Reactive Systems**

## 1 Introduction to Chemical Kinetics

*Poca favilla gran fiamma seconda.*<sup>1</sup> (A great flame follows a little spark.)  
— Dante Alighieri (1265–1321), *Paradiso*, Canto I, l. 34

In physics, *kinetics* is the study of motion and its causes; it is more commonly known as *dynamics*. Typically it connotes an evolution of the state of a mechanical system as time advances. In chemistry, this notion is slightly modified; for reacting systems, *chemical kinetics* connotes the transformation over time of a system from one chemical state to another. It is less commonly known as *chemical dynamics*. In contrast, the classical definition of *thermodynamics* is the science that deals with heat and work and those properties of matter that relate to heat and work. In most introductory thermodynamics texts, efforts are made to remove most references to time and to consider transformations from one equilibrium state to another. Although a useful construct, this removal of time places limits on theories based solely on equilibrium thermodynamics. For example, thermodynamics is obviously relevant to internal combustion engines; such engines rely on a transformation of chemical energy to thermal energy to mechanical energy. And it is essential that the combustion be completed in a well-defined time for the engine to operate effectively. It thus should be obvious that any prediction of the behavior of an internal combustion engine needs to draw on both equilibrium thermodynamics and time-dependent chemical kinetics. It is this interplay of thermodynamics and dynamics that is the subject of this book.

Our discussion in this and the next five chapters will be confined to systems that are *spatially homogeneous*. That is to say, whereas the systems exist in a finite geometric space, the variables describing the system do not vary with location. They will, however, often vary with time. Spatially homogeneous systems cannot account for the important physical mechanisms of advection and diffusion. These mechanisms are important in a wide variety of combustion systems and will be considered in Chapters 7–12. To summarize, then, our strictly thermodynamic systems will be considered independent of space and time and will typically be described by algebraic equations. Our chemical kinetic systems will draw on thermodynamics and consider evolution in time as described by ordinary differential equations. These ordinary

<sup>1</sup>This verse from *La Divina Commedia* was selected in a spirit of optimism that the poet's better known entreaty from that opus's more topical *Inferno*, "*Lasciate ogne speranza, voi ch'entrate*" (All hope abandon, ye who enter in), Canto III, l. 1, will prove to be irrelevant.

differential equations will have an inhomogeneous forcing function related to chemistry, but there is no forcing due to spatial inhomogeneity. When we introduce advection and diffusion, our system will be modeled by partial differential equations with variation in time and space. For such systems, chemical and spatial inhomogeneities both drive the time evolution.

We begin in this chapter by considering some illustrative examples from gas phase chemical kinetics, the driving physical mechanism in the dynamics and thermodynamics of gas phase combustion. The examples are drawn from realistic physical systems but focus on highly simplified limits that have pedagogical value. In this chapter, our approach is exploratory and motivational. Systematic treatment of the underlying theory is given in later chapters. Because such development requires lengthy exposition, it is useful to have a flavor of the dynamics of thermochemistry for simple problems before embarking in Chapter 2 on a more rigorous path.

In this chapter, we first briefly introduce a gas phase kinetic model for a multi-component continuum mixture and present example mechanisms based on (1) *irreversible* hydrogen-oxygen reactions and then more complicated (2) *reversible* hydrogen-oxygen reactions. Hydrogen-oxygen reactions are posed because (1) they are one of the simplest practical gas phase combustion systems, (2) they have sufficient complexity to illustrate some of the challenges of gas phase combustion modeling, and (3) the model has been well validated against a variety of experiments. From this, we consider a set of problems addressing some of the simplest chemistry possible: *dissociation* of diatomic oxygen into monatomic oxygen and its reverse *recombination* reaction, followed by a slightly more complicated problem of nitric oxide formation. The dynamics of both systems are considered in an isothermal, isochoric environment. We then turn to an even simpler kinetics model that will be a paradigm throughout the book for studying combustion. This simple model asserts transformation of a generic species  $A$  into a generic species  $B$  accompanied by heat release. Dynamics of this model are studied in an adiabatic, isochoric environment, thus introducing what is known as *thermal explosion theory*. Such a theory is useful for predicting the phenomenon of a slowly progressing exothermic reaction that suddenly accelerates to a fast reaction with large heat release. We close the chapter by simple exposition of such a thermal explosion predicted for a realistic hydrogen-air system.

### 1.1 A Gas Phase Kinetic Model

Let us consider the reaction of  $N$  molecular chemical species composed of  $L$  elements via  $J$  chemical reactions. Let us assume that the gas is an ideal mixture of ideal gases that satisfies Dalton's<sup>2</sup> law of partial pressures (see Sec. 2.3). Full discussion of the entire model encompasses most of Chapters 2–5. The reaction will be considered to be driven by *molecular collisions*. We will not model individual collisions but instead attempt to capture their collective effect.

An example of a model of such a reaction is listed in Table 1.1. There we find an  $N = 9$  species,  $J = 37$  step irreversible reaction mechanism for an  $L = 3$  hydrogen-oxygen mixture from Maas and Warnatz (1988), with corrected  $f_{\text{H}_2}$  from Maas and Pope (1992). The symbol  $M$  represents an arbitrary *third body* and is an inert participant in the reaction, such as argon, a noble gas that cannot react chemically. Third bodies  $M$  are not restricted to noble gases. In some reactions, certain molecules

<sup>2</sup>John Dalton (1766–1844), English chemist.

## 1.1 A Gas Phase Kinetic Model

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Table 1.1. *Nine-Species, Thirty-Seven-Step Irreversible Reaction Mechanism for a Hydrogen-Oxygen Mixture*

$j$	Reaction	$a_j$	$\beta_j$	$\bar{E}_j$
1	$\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{O}$	$2.00 \times 10^{14}$	0.00	70.30
2	$\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H}$	$1.46 \times 10^{13}$	0.00	2.08
3	$\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$	$5.06 \times 10^4$	2.67	26.30
4	$\text{OH} + \text{H} \rightarrow \text{H}_2 + \text{O}$	$2.24 \times 10^4$	2.67	18.40
5	$\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$	$1.00 \times 10^8$	1.60	13.80
6	$\text{H}_2\text{O} + \text{H} \rightarrow \text{H}_2 + \text{OH}$	$4.45 \times 10^8$	1.60	77.13
7	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$1.50 \times 10^9$	1.14	0.42
8	$\text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{OH}$	$1.51 \times 10^{10}$	1.14	71.64
9	$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	$1.80 \times 10^{18}$	-1.00	0.00
10	$\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$	$6.99 \times 10^{18}$	-1.00	436.08
11	$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	$2.20 \times 10^{22}$	-2.00	0.00
12	$\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{OH} + \text{M}$	$3.80 \times 10^{23}$	-2.00	499.41
13	$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$2.90 \times 10^{17}$	-1.00	0.00
14	$\text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M}$	$6.81 \times 10^{18}$	-1.00	496.41
15	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$2.30 \times 10^{18}$	-0.80	0.00
16	$\text{HO}_2 + \text{M} \rightarrow \text{H} + \text{O}_2 + \text{M}$	$3.26 \times 10^{18}$	-0.80	195.88
17	$\text{HO}_2 + \text{H} \rightarrow \text{OH} + \text{OH}$	$1.50 \times 10^{14}$	0.00	4.20
18	$\text{OH} + \text{OH} \rightarrow \text{HO}_2 + \text{H}$	$1.33 \times 10^{13}$	0.00	168.30
19	$\text{HO}_2 + \text{H} \rightarrow \text{H}_2 + \text{O}_2$	$2.50 \times 10^{13}$	0.00	2.90
20	$\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{H}$	$6.84 \times 10^{13}$	0.00	243.10
21	$\text{HO}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{O}$	$3.00 \times 10^{13}$	0.00	720
22	$\text{H}_2\text{O} + \text{O} \rightarrow \text{HO}_2 + \text{H}$	$2.67 \times 10^{13}$	0.00	242.52
23	$\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$	$1.80 \times 10^{13}$	0.00	-1.70
24	$\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{O}$	$2.18 \times 10^{13}$	0.00	230.61
25	$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	$6.00 \times 10^{13}$	0.00	0.00
26	$\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{OH}$	$7.31 \times 10^{14}$	0.00	303.53
27	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$2.50 \times 10^{11}$	0.00	-5.20
28	$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	$3.25 \times 10^{22}$	-2.00	0.00
29	$\text{H}_2\text{O}_2 + \text{M} \rightarrow \text{OH} + \text{OH} + \text{M}$	$2.10 \times 10^{24}$	-2.00	206.80
30	$\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2 + \text{HO}_2$	$1.70 \times 10^{12}$	0.00	15.70
31	$\text{H}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{H}$	$1.15 \times 10^{12}$	0.00	80.88
32	$\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{OH}$	$1.00 \times 10^{13}$	0.00	15.00
33	$\text{H}_2\text{O} + \text{OH} \rightarrow \text{H}_2\text{O}_2 + \text{H}$	$2.67 \times 10^{12}$	0.00	307.51
34	$\text{H}_2\text{O}_2 + \text{O} \rightarrow \text{OH} + \text{HO}_2$	$2.80 \times 10^{13}$	0.00	26.80
35	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}$	$8.40 \times 10^{12}$	0.00	84.09
36	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$5.40 \times 10^{12}$	0.00	4.20
37	$\text{H}_2\text{O} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{OH}$	$1.63 \times 10^{13}$	0.00	132.71

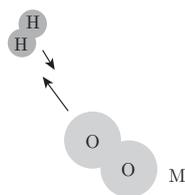
Note: Units of  $a_j$  are  $(\text{mol}/\text{cm}^3)^{(1-\nu'_{M,j} - \sum_{i=1}^N \nu'_{ij})} / \text{s}/K^{\beta_j}$ . The parameter  $\beta_j$  is dimensionless. Units of  $\bar{E}_j$  are kJ/mol. Third-body collision efficiencies with M are  $f_{\text{H}_2} = 1.00$ ,  $f_{\text{O}_2} = 0.35$ , and  $f_{\text{H}_2\text{O}} = 6.5$ .

that could react do not; their presence. However, is necessary for the collision-based reaction to occur. The adjective “third” is traditional but not always accurate. For instance, in Reaction 13 of Table 1.1,  $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$ , there are three bodies colliding, O, O, and M. But in Reaction 14 of Table 1.1,  $\text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M}$ , there are two bodies colliding,  $\text{O}_2$  and M. So for Reaction 14 of Table 1.1, M is better called a second body; however, such usage is uncommon.

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## Introduction to Chemical Kinetics

before collision  
(with  $M=O_2$ )



after collision  
(with  $M=O_2$ )

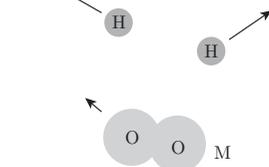


Figure 1.1. Sketch of a chain-initiation reaction following molecular collision. Here,  $M$  is  $O_2$ .



We need not worry yet about  $f_{H_2}$ ,  $f_{O_2}$ , or  $f_{H_2O}$ . These are known as *collision efficiency coefficients*. They account for the fact that some collisions are different than others and allow for fine-tuning of the model to better match experimental data. Other mechanisms, not shown here, additionally include adjustments in the rate coefficients due to pressure. Details are given by Kee et al. (2003, Chapter 9), and many others. This model of so-called *detailed chemical kinetics* can accurately describe the dynamics of the formation of the dominant product,  $H_2O$ , from dominant reactants,  $H_2$  and  $O_2$ . The study of detailed chemical kinetics began in the early twentieth century; contributions of Bodenstein,<sup>3</sup> Semenov,<sup>4</sup> and Hinshelwood<sup>5</sup> were seminal (e.g., Semenov, 1935).

Although the overall reaction may be described by a so-called *global kinetics* model such as  $2H_2 + O_2 \rightarrow 2H_2O$ , the global kinetics mechanism does not accurately reflect the actual intermediate steps of reaction. The global mechanism suggests that two diatomic hydrogen molecules need to collide with a diatomic oxygen molecule to form two water molecules. This in fact does not happen. Instead, reaction of a mixture of  $H_2$  and  $O_2$  may commence with a *chain-initiation reaction*, such as Reaction 10 in Table 1.1:



in which the fuel  $H_2$  collides with *any* molecule to form the two *free radicals*  $H$  and  $H$ . We sketch a single collision for Reaction 10 in Fig. 1.1. Relative to the somewhat stable species  $H_2$ , the free radical species  $H$  is highly reactive. Chain-initiation reactions are often endothermic, as it takes some energy to break the bonds of either  $H_2$  or  $O_2$ . This and other chain-initiation reactions provide radicals for various *chain-branching reactions*, such as Reaction 1 in Table 1.1:



Here, there is one free radical  $H$  among the reactants and two free radicals,  $OH$  and  $O$ , among the products. Also possible are *chain-propagation reactions*, such as Reaction 5 in Table 1.1:



<sup>3</sup>Max Ernst August Bodenstein (1871–1942), German physical chemist.

<sup>4</sup>Nikolai Nikolaevich Semenov (1896–1986), Soviet physicist, chemist; 1956 Nobel laureate in Chemistry; often spelled “Semenoff.”

<sup>5</sup>Sir Cyril Norman Hinshelwood (1897–1967), English physical chemist; 1956 Nobel laureate in Chemistry.

## 1.1 A Gas Phase Kinetic Model

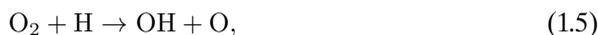
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Such reactions, relative to chain-initiation reactions, are often nearly thermally neutral. Moreover, there is no net change in the number of free radicals. Here, one free radical OH is among the reactants and one free radical H is among the products. When enough free radicals accumulate, exothermic *chain-termination reactions* begin to occur to form the dominant final product. For example, collision of two free radical molecules of OH occurs in Reaction 7 of Table 1.1 to form the product H<sub>2</sub>O:



It is the chain-termination steps in which significant heat release usually occurs, temperature rises are often observed, and the number of free radicals is reduced.

The one-sided arrows indicate that each individual reaction is considered to be irreversible. For nearly each reaction, a separate reverse reaction is listed; thus, pairs of irreversible reactions can in some sense be considered to model reversible reactions. For example, Reaction 1 in Table 1.1 is the reverse of Reaction 2:



Each of the elementary reactions is described by a set of parameters. For the  $j$ th reaction, we have the *collision frequency coefficient*  $a_j$ , the *temperature-dependency exponent*  $\beta_j$ , and the *activation energy*  $\bar{E}_j$ . These are explained in short order. Each individual reaction is not in fact modeling a single collision. Instead, it is modeling the cumulative effect of a large number of collisions of the reactants.

Table 1.2. *Nine-Species, Nineteen-Step Reversible Reaction Mechanism for a Hydrogen-Oxygen Mixture*

$j$	Reaction	$a_j$	$\beta_j$	$\bar{E}_j$
1	$\text{H}_2 + \text{O}_2 \rightleftharpoons \text{OH} + \text{OH}$	$1.70 \times 10^{13}$	0.00	47780
2	$\text{OH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}$	$1.17 \times 10^9$	1.30	3626
3	$\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$	$5.13 \times 10^{16}$	-0.82	16507
4	$\text{O} + \text{H}_2 \rightleftharpoons \text{OH} + \text{H}$	$1.80 \times 10^{10}$	1.00	8826
5	$\text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2 + \text{M}$	$2.10 \times 10^{18}$	-1.00	0
6	$\text{H} + \text{O}_2 + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{O}_2$	$6.70 \times 10^{19}$	-1.42	0
7	$\text{H} + \text{O}_2 + \text{N}_2 \rightleftharpoons \text{HO}_2 + \text{N}_2$	$6.70 \times 10^{19}$	-1.42	0
8	$\text{OH} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$	$5.00 \times 10^{13}$	0.00	1000
9	$\text{H} + \text{HO}_2 \rightleftharpoons \text{OH} + \text{OH}$	$2.50 \times 10^{14}$	0.00	1900
10	$\text{O} + \text{HO}_2 \rightleftharpoons \text{O}_2 + \text{OH}$	$4.80 \times 10^{13}$	0.00	1000
11	$\text{OH} + \text{OH} \rightleftharpoons \text{O} + \text{H}_2\text{O}$	$6.00 \times 10^8$	1.30	0
12	$\text{H}_2 + \text{M} \rightleftharpoons \text{H} + \text{H} + \text{M}$	$2.23 \times 10^{12}$	0.50	92600
13	$\text{O}_2 + \text{M} \rightleftharpoons \text{O} + \text{O} + \text{M}$	$1.85 \times 10^{11}$	0.50	95560
14	$\text{H} + \text{OH} + \text{M} \rightleftharpoons \text{H}_2\text{O} + \text{M}$	$7.50 \times 10^{23}$	-2.60	0
15	$\text{H} + \text{HO}_2 \rightleftharpoons \text{H}_2 + \text{O}_2$	$2.50 \times 10^{13}$	0.00	700
16	$\text{HO}_2 + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{O}_2$	$2.00 \times 10^{12}$	0.00	0
17	$\text{H}_2\text{O}_2 + \text{M} \rightleftharpoons \text{OH} + \text{OH} + \text{M}$	$1.30 \times 10^{17}$	0.00	45500
18	$\text{H}_2\text{O}_2 + \text{H} \rightleftharpoons \text{HO}_2 + \text{H}_2$	$1.60 \times 10^{12}$	0.00	3800
19	$\text{H}_2\text{O}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{HO}_2$	$1.00 \times 10^{13}$	0.00	1800

Note: Units of  $a_j$  are  $(\text{mol}/\text{cm}^3)^{(1-\nu'_{M,j}-\sum_{i=1}^N \nu'_{ij})} / \text{s}/\text{K}^{\beta_j}$ . The parameter  $\beta_j$  is dimensionless. Units of  $\bar{E}_j$  are cal/mol. Third-body collision efficiencies with M are  $f_5(\text{H}_2\text{O}) = 21$ ,  $f_5(\text{H}_2) = 3.3$ ,  $f_{12}(\text{H}_2\text{O}) = 6$ ,  $f_{12}(\text{H}) = 2$ ,  $f_{12}(\text{H}_2) = 3$ , and  $f_{14}(\text{H}_2\text{O}) = 20$ .

It is perhaps more common to describe chemical kinetics systems as being composed of reversible reactions. Such reactions are usually denoted by two-sided arrows. One such system for hydrogen-oxygen combustion is reported by Powers and Paolucci (2005), and is listed in Table 1.2. While more compact than the model of Table 1.1, reversible reactions pose more mathematical complexity. As such we delay their study until we have given examples of irreversible kinetic systems.

### 1.2 Isothermal, Isochoric Kinetics

For simplicity, we first focus attention on cases in which the temperature  $T$  and volume  $V$  are both constant. Such conditions are known as *isothermal* and *isochoric*, respectively. The volume contains a mixture of  $N$  reacting species each with a number  $n_i$  of moles. We restrict attention here to *closed* systems. Such systems do not exchange mass with their environment and thus have constant total mass  $m$ . The system is allowed to exchange energy with its surroundings. For typically exothermic combustion reactions, energy exchange is necessary to maintain a constant temperature. A sketch of this configuration is given in Fig. 1.2. We define the *molar concentration*  $\bar{\rho}_i$  of species  $i$  as the number of moles,  $n_i$ , per volume:

$$\bar{\rho}_i = n_i/V, \quad i = 1, \dots, N. \quad (1.7)$$

It has units of mol/cm<sup>3</sup>. We might also call this the *molar density*. Our notation for molar concentration,  $\bar{\rho}_i$ , is nonstandard. In general, we will take the “bar” notation to indicate a property on molar basis; equivalent properties without the bar will indicate the property to be on a mass basis. For example, the mass density of species  $i$  will be denoted  $\rho_i$  and have units of g/cm<sup>3</sup>. More commonly, most properties with a bar will be per unit mol; their equivalent without a bar will be per unit mass. For example, the *molar specific internal energy* of species  $i$ ,  $\bar{e}_i$ , may have units of erg/mol; the *mass specific internal energy*  $e_i$  would have units erg/g. Quantities on a mol basis are related to those on a mass basis by appropriately scaling by the *molecular mass*,  $M_i$ , the mass in g of a mol of species  $i$ . To convert from molar density to mass density for species  $i$ , we have

$$\rho_i = \bar{\rho}_i M_i. \quad (1.8)$$

To convert specific internal energy from a molar to mass basis, we have

$$e_i = \bar{e}_i/M_i. \quad (1.9)$$

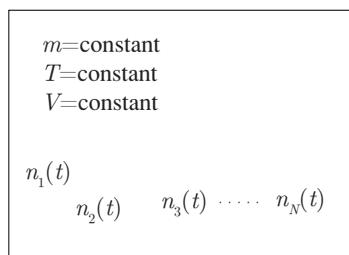


Figure 1.2. Configuration for closed, isothermal, isochoric, spatially homogeneous reaction of  $N$  species.

## 1.2 Isothermal, Isochoric Kinetics

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A more common notation for molar concentration, which we generally avoid, is given by square brackets, for example,  $\bar{\rho}_{\text{O}_2} = [\text{O}_2]$ . Our notation makes obvious the symmetries between molar and mass concentrations in a variety of relations to be discussed in Chapter 2.

### 1.2.1 O-O<sub>2</sub> Dissociation

One of the simplest physical examples is provided by the dissociation of O<sub>2</sub> into its atomic component O, accompanied by a recombination of O into O<sub>2</sub>. A good fundamental treatment of elementary reactions of this type is given by Vincenti and Kruger (1965), in their detailed monograph.

#### Pair of Irreversible Reactions

We begin by assuming that the dissociation and recombination process is described by a pair of irreversible reactions from Table 1.1. To begin, let us focus for now only on reactions  $j = 13$  and  $j = 14$  from Table 1.1 in the limiting case in which  $T$  and  $V$  are constant.

**MATHEMATICAL MODEL.** The two reactions are



with

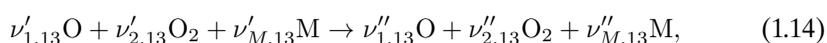
$$a_{13} = 2.90 \times 10^{17} \left( \frac{\text{mol}}{\text{cm}^3} \right)^{-2} \frac{\text{K}}{\text{s}}, \quad \beta_{13} = -1.00, \quad \bar{\mathcal{E}}_{13} = 0 \frac{\text{kJ}}{\text{mol}}, \quad (1.12)$$

$$a_{14} = 6.81 \times 10^{18} \left( \frac{\text{mol}}{\text{cm}^3} \right)^{-1} \frac{\text{K}}{\text{s}}, \quad \beta_{14} = -1.00, \quad \bar{\mathcal{E}}_{14} = 496.41 \frac{\text{kJ}}{\text{mol}}. \quad (1.13)$$

Also, we have the collision efficiency for O<sub>2</sub> as  $f_{\text{O}_2} = 0.35$ . For O, we take by default that  $f_{\text{O}} = 1$ . We envision Reaction 13 as one in which two O atoms and a third body (either O or O<sub>2</sub>) collide simultaneously. Two of the O atoms combine to form a single O<sub>2</sub> molecule, and the third body remains as it was. Similarly, in Reaction 14, an O<sub>2</sub> molecule collides with a “third” body (in reality, a second body), either O<sub>2</sub> or O. The collision is of sufficient strength to induce the O<sub>2</sub> to dissociate into two O atoms. Again, the “third” body remains as it was. We sketch a single collision with  $\text{M} = \text{O}_2$  for Reaction 14 in Fig. 1.3.

The irreversible nature of the reaction is indicated by the one-sided arrow. Although they participate in the overall hydrogen oxidation problem, these two reactions are in fact self-contained and can thus be considered in isolation. So, let us just consider that we have only oxygen in our volume with  $N = 2$  species, O and O<sub>2</sub>,  $J = 2$  reactions (those being 13 and 14), and  $L = 1$  element, that being O. We will take  $i = 1$  to correspond to O and  $i = 2$  to correspond to O<sub>2</sub>.

We recast the mechanism as



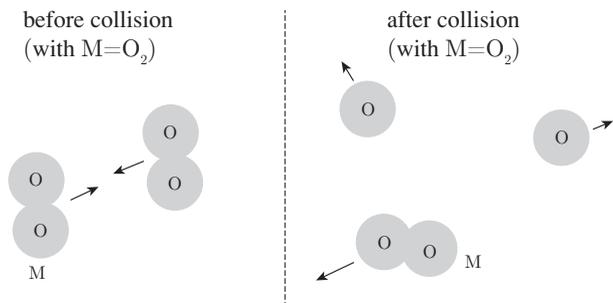


Figure 1.3. Sketch of dissociation of  $O_2$  following molecular collision with an inert participant  $M$ , here  $O_2$ .

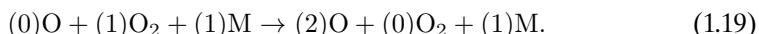
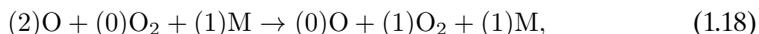


with the forward stoichiometric coefficients,  $\nu'_{ij}$ , and the reverse stoichiometric coefficients,  $\nu''_{ij}$ , taking the values

$$\nu'_{1,13} = 2, \nu'_{2,13} = 0, \nu'_{M,13} = 1, \nu''_{1,13} = 0, \nu''_{2,13} = 1, \nu''_{M,13} = 1, \quad (1.16)$$

$$\nu'_{1,14} = 0, \nu'_{2,14} = 1, \nu'_{M,14} = 1, \nu''_{1,14} = 2, \nu''_{2,14} = 0, \nu''_{M,14} = 1, \quad (1.17)$$

so that the mechanism is



As can be seen from Table 1.1, the units of  $a_j$  are unusual. There is no settled set of units within the combustion community. For the most part, we make the common choice of cgs-based units (centimeter-gram-second), most often used in chemistry; occasionally, we use MKS-based units (meter-kilogram-second), most often used in physics and engineering. For reaction  $j = 13$ , we find the exponent for the  $(\text{mol}/\text{cm}^3)$  portion of the units for  $a_{13}$  to be

$$1 - \nu'_{M,j} - \sum_{i=1}^N \nu'_{ij} = 1 - \nu'_{M,13} - (\nu'_{1,13} + \nu'_{2,13}) = 1 - 1 - (2 + 0) = -2. \quad (1.20)$$

Thus, the units of  $a_{13}$  are  $(\text{mol}/\text{cm}^3)^{-2}/\text{s}/\text{K}^{-1}$ . Similarly, for reaction  $j = 14$ , we find the exponent for the  $(\text{mol}/\text{cm}^3)$  portion of the units for  $a_{14}$  to be

$$1 - \nu'_{M,j} - \sum_{i=1}^N \nu'_{ij} = 1 - \nu'_{M,14} - (\nu'_{1,14} + \nu'_{2,14}) = 1 - 1 - (0 + 1) = -1. \quad (1.21)$$

Recall that in the cgs system,  $1 \text{ erg} = 1 \text{ dyne cm} = 10^{-7} \text{ J} = 10^{-10} \text{ kJ}$ . Recall also that the cgs unit of force is the dyne and that  $1 \text{ dyne} = 1 \text{ g cm}/\text{s}^2 = 10^{-5} \text{ N}$ . So, for cgs, we have

$$\bar{\mathcal{E}}_{13} = 0 \frac{\text{erg}}{\text{mol}}, \quad \bar{\mathcal{E}}_{14} = 496.41 \frac{\text{kJ}}{\text{mol}} \left( 10^{10} \frac{\text{erg}}{\text{kJ}} \right) = 4.9641 \times 10^{12} \frac{\text{erg}}{\text{mol}}. \quad (1.22)$$

We next introduce a common model for chemical dynamics of spatially homogeneous systems. We thus consider dependency only on time  $t$ , and not on space, because of neglect of modeling advection or diffusion. The standard model for spatially homogeneous chemical kinetics, which is generalized and discussed in more detail in Chapters 4 and 5, induces the following two ordinary differential equations

## 1.2 Isothermal, Isochoric Kinetics

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for the temporal evolution of O and O<sub>2</sub> molar concentrations:

$$\frac{d\bar{\rho}_O}{dt} = -2 \underbrace{a_{13} T^{\beta_{13}} \exp\left(\frac{-\bar{\mathcal{E}}_{13}}{\bar{R}T}\right)}_{r_{13}} \bar{\rho}_O \bar{\rho}_O \bar{\rho}_M + 2 \underbrace{a_{14} T^{\beta_{14}} \exp\left(\frac{-\bar{\mathcal{E}}_{14}}{\bar{R}T}\right)}_{r_{14}} \bar{\rho}_{O_2} \bar{\rho}_M, \quad (1.23)$$

$$\frac{d\bar{\rho}_{O_2}}{dt} = \underbrace{a_{13} T^{\beta_{13}} \exp\left(\frac{-\bar{\mathcal{E}}_{13}}{\bar{R}T}\right)}_{r_{13}} \bar{\rho}_O \bar{\rho}_O \bar{\rho}_M - \underbrace{a_{14} T^{\beta_{14}} \exp\left(\frac{-\bar{\mathcal{E}}_{14}}{\bar{R}T}\right)}_{r_{14}} \bar{\rho}_{O_2} \bar{\rho}_M. \quad (1.24)$$

Detailed exposition is given in Sec. 5.1. Equation (1.24) has its analog in the forward reaction of Eq. (5.13). The symbol  $\bar{R}$  is the universal gas constant, for which

$$\bar{R} = 8.314 \frac{\text{J}}{\text{mol K}} \left( \frac{10^7 \text{ erg}}{\text{J}} \right) = 8.314 \times 10^7 \frac{\text{erg}}{\text{mol K}}. \quad (1.25)$$

Because the universal gas constant is on a per unit mol basis, we give it a “bar.” We also use the common notation of a temperature-dependent portion of the dynamics of reaction  $j$ ,  $k_j(T)$ , as we write the equivalent of the upcoming Eq. (5.17):

$$k_j(T) = a_j T^{\beta_j} \exp\left(\frac{-\bar{\mathcal{E}}_j}{\bar{R}T}\right), \quad j = 1, \dots, J. \quad (1.26)$$

Sometimes  $k_j(T)$  is known as the *reaction rate coefficient* for reaction  $j$ . The actual *reaction rates* for Reactions 13 and 14,  $r_{13}$  and  $r_{14}$ , are

$$r_{13} = k_{13} \bar{\rho}_O \bar{\rho}_O \bar{\rho}_M, \quad r_{14} = k_{14} \bar{\rho}_{O_2} \bar{\rho}_M. \quad (1.27)$$

See Eq. (5.14) for a more general form. The reaction rates are proportional to the product of the molar concentrations and thus can be inferred to be related to the probability of molecular collisions. For example, if there is no O, there is no chance of a collision to induce Reaction 13, so the rate is zero.

The system of equations (1.23)–(1.24) can be written as

$$\frac{d\bar{\rho}_O}{dt} = -2r_{13} + 2r_{14}, \quad \frac{d\bar{\rho}_{O_2}}{dt} = r_{13} - r_{14}. \quad (1.28)$$

More simply, using Gibbs’s<sup>6</sup> boldfaced notation for vectors and matrices,<sup>7</sup> Eqs. (1.28) can be written in the form of the upcoming Eq. (5.344):

$$\frac{d\bar{\rho}}{dt} = \boldsymbol{\nu} \cdot \mathbf{r}. \quad (1.29)$$

Here, we have taken

$$\bar{\rho} = \begin{pmatrix} \bar{\rho}_O \\ \bar{\rho}_{O_2} \end{pmatrix}, \quad \boldsymbol{\nu} = \begin{pmatrix} -2 & 2 \\ 1 & -1 \end{pmatrix}, \quad \mathbf{r} = \begin{pmatrix} r_{13} \\ r_{14} \end{pmatrix}. \quad (1.30)$$

<sup>6</sup>Josiah Willard Gibbs (1839–1903), American mechanical engineer.

<sup>7</sup>One must recognize that these vectors and matrices are not associated with any ordinary physical geometry; they can be thought of as residing within a geometry whose coordinates are defined by thermochemical variables. This unusual space is often of dimension greater than three.