The phenomenon of air pollution involves a sequence of events: the generation of pollutants at and their release from a source; their transport and transformation in and removal from the atmosphere; and their effects on human beings, materials, and ecosystems. Because it is generally either economically infeasible or technically impossible to design processes for absolutely zero emissions of air pollutants, we seek to control the emissions to a level such that effects are either nonexistent or minimized.

We can divide the study of air pollution into three obviously overlapping but somewhat distinct areas:

1. The generation and control of air pollutants at their source. This first area involves everything that occurs before the pollutant is released “up the stack” or “out the tailpipe.”

2. The transport, dispersion, chemical transformation in, and removal of species from the atmosphere. This second area thus includes all the chemical and physical processes that take place between the point of emission and ultimate removal from the atmosphere.

3. The effects of air pollutants on human beings, animals, materials, vegetation, crops, and forest and aquatic ecosystems, including the measurement of gaseous and particulate species.

An air pollution control strategy for a region is a specification of the allowable levels of pollutant emissions from sources. To formulate such a strategy it is necessary to be able to estimate the atmospheric fate of the emissions, and thus the ambient concentrations, so that these concentrations can be compared with those considered to give
rise to adverse effects. The ultimate mix of control actions and devices employed to achieve the allowable levels might then be decided on an economic basis. Therefore, the formulation of an air pollution control strategy for a region involves a critical feedback from area 3 to area 1. Consequently, all three of the areas above are important in air pollution abatement planning.

A comprehensive treatment of each of these three areas is beyond the scope of a single book, however. The present book is devoted to an in-depth analysis of the generation and control of air pollutants at their source, which we refer to as air pollution engineering.

1.1 AIR POLLUTANTS

Table 1.1 summarizes species classified as air pollutants. By and large our focus in this book is on the major combustion-generated compounds, such as the oxides of nitrogen, sulfur dioxide, carbon monoxide, unburned hydrocarbons, and particulate matter. Table 1.2 provides a list of the most prevalent hydrocarbons identified in ambient air, and Table 1.3 lists potentially toxic atmospheric organic species.

1.1.1 Oxides of Nitrogen

Nitric oxide (NO) and nitrogen dioxide (NO₂) are the two most important nitrogen oxide air pollutants. They are frequently lumped together under the designation NOₓ, although analytical techniques can distinguish clearly between them. Of the two, NO₂ is the more toxic and irritating compound.

Nitric oxide is a principal by-product of combustion processes, arising from the high-temperature reaction between N₂ and O₂ in the combustion air and from the oxidation of organically bound nitrogen in certain fuels such as coal and oil. The oxidation of N₂ by the O₂ in combustion air occurs primarily through the two reactions

\[ \text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N} \]

\[ \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} \]

known as the Zeldovich mechanism. The first reaction above has a relatively high activation energy, due to the need to break the strong N₂ bond. Because of the high activation energy, the first reaction is the rate-limiting step for NO production, proceeds at a somewhat slower rate than the combustion of the fuel, and is highly temperature sensitive. Nitric oxide formed via this route is referred to as thermal-NOₓ. The second major mechanism for NO formation in combustion is by the oxidation of organically bound nitrogen in the fuel. For example, number 6 residual fuel oil contains 0.2 to 0.8% by weight bound nitrogen, and coal typically contains 1 to 2%, a portion of which is converted to NOₓ during combustion. (The remainder is generally converted to N₂.) Nitric oxide formed in this manner is referred to as fuel-NOₓ.

Mobile combustion and fossil-fuel power generation are the two largest anthro-
pogenic sources of NOx. In addition, industrial processes and agricultural operations produce minor quantities. Emissions are generally reported as though the compound being emitted were NO2. This method of presentation serves the purpose of allowing ready comparison of different sources and avoids the difficulty in interpretation associated with different ratios of NO/NO2 being emitted by different sources. Table 1.4 gives NO/NOx ratios of various types of sources. We see that, although NO is the dominant NOx compound emitted by most sources, NO2 fractions from sources do vary somewhat with source type. Once emitted, NO can be oxidized quite effectively to NO2 in the atmosphere through atmospheric reactions, although we will not treat these reactions here. Table 1.5 gives estimated U.S. emissions of NOx in 1976 according to source category. Utility boilers represent about 50% of all stationary source NOx emissions in the United States. As a result, utility boilers have received the greatest attention in past NOx regulatory strategies and are expected to be emphasized in future plans to attain and maintain NOx ambient air quality standards.

1.1.2 Sulfur Oxides

Sulfur dioxide (SO2) is formed from the oxidation of sulfur contained in fuel as well as from certain industrial processes that utilize sulfur-containing compounds. Anthropogenic emissions of SO2 result almost exclusively from stationary point sources. Estimated annual emissions of SO2 in the United States in 1978 are given in Table 1.6. A small fraction of sulfur oxides is emitted as primary sulfates, gaseous sulfur trioxide (SO3), and sulfuric acid (H2SO4). It is estimated that, by volume, over 90% of the total U.S. sulfur oxide emissions are in the form of SO2, with primary sulfates accounting for the other 10%.

Stationary fuel combustion (primarily utility and industrial) and industrial processes (primarily smelting) are the main SO2 sources. Stationary fuel combustion includes all boilers, heaters, and furnaces found in utilities, industry, and commercial/institutional and residential establishments. Coal combustion has traditionally been the largest stationary fuel combustion source, although industrial and residential coal use has declined. Increased coal use by electric utilities, however, has offset this decrease. SO2 emissions from electric utilities account for more than half of the U.S. total. A more detailed breakdown of U.S. sulfur oxide emissions in 1978 is given in Table 1.7.

1.1.3 Organic Compounds

Tables 1.2 and 1.3 list a number of airborne organic compounds. Organic air pollutants are sometimes divided according to volatile organic compounds (VOCs) and particulate organic compounds (POCs), although there are some species that will actually be distributed between the gaseous and particulate phases. The emission of unburned or partially burned fuel from combustion processes and escape of organic vapors from industrial operations are the major anthropogenic sources of organic air pollutants.

A major source of airborne organic compounds is the emissions from motor ve-
<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Concentration levels</th>
<th>Anthropogenic sources</th>
<th>Natural sources</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SO$_2$</strong>&lt;br&gt;Colorless gas with irritating, pungent odor; detectable by taste at levels of 0.3 to 1 ppm; highly soluble in water (10.5 g/100 cm$^3$ at 293 K)</td>
<td>Global background concentration levels in the range 0.04 to 6 ppb; hourly averaged maximum concentrations in urban areas have occasionally exceeded 1 ppm</td>
<td>Fuel combustion in stationary sources; industrial process emissions; metal and petroleum refining</td>
<td>Atmospheric oxidation of organic sulfides</td>
</tr>
<tr>
<td><strong>H$_2$S</strong>&lt;br&gt;Colorless, flammable gas; highly toxic; characteristic rotten egg odor</td>
<td>Global background about 3 $\mu g$ m$^{-3}$; urban levels have been observed as large as 390 $\mu g$ m$^{-3}$</td>
<td>Kraft pulp mills; natural gas and petroleum refining; rayon and nylon manufacture; coke ovens</td>
<td>Biological decay processes; volcanoes and geothermal activities</td>
</tr>
<tr>
<td><strong>NO</strong>&lt;br&gt;Colorless, odorless gas; nonflammable and slightly soluble in water; toxic</td>
<td>Global background level from 10 to 100 ppt; urban levels have been observed as large as 500 ppb</td>
<td>Combustion</td>
<td>Bacterial action; natural combustion processes; lightning</td>
</tr>
<tr>
<td><strong>NO$_2$</strong>&lt;br&gt;Reddish-orange-brown gas with sharp, pungent odor; toxic and highly corrosive; absorbs light over much of the visible spectrum</td>
<td>Global background level from 10 to 500 ppt; urban concentrations have reached values exceeding 500 ppb</td>
<td>Combustion</td>
<td></td>
</tr>
<tr>
<td><strong>NH$_3$</strong>&lt;br&gt;Colorless gas with pungent odor; detectable at concentrations exceeding 500 ppm; highly soluble in water</td>
<td>Global background level of 1 ppb; urban concentrations in range of 5 ppb</td>
<td>Combustion</td>
<td>Bacterial decomposition of amino acids in organic waste</td>
</tr>
<tr>
<td><strong>CO$_2$</strong>&lt;br&gt;Colorless, odorless, nontoxic gas moderately soluble in water</td>
<td>Global background concentration has increased from 290 ppm in 1900 to about 345 ppm in 1985</td>
<td>Combustion of fossil fuels</td>
<td></td>
</tr>
<tr>
<td>Nonmethane hydrocarbons (see Table 1.2)</td>
<td>Colorless, odorless, flammable, toxic gas, slightly soluble in water</td>
<td>Global average concentration of 0.09 ppm; concentrations in northern hemisphere are about twice those in southern hemisphere; urban levels in the vicinity of heavily traveled roadways can exceed 100 ppm</td>
<td>Combustion of fossil fuels</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>---------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>CO</td>
<td>Colorless, toxic gas, slightly soluble in water</td>
<td>Global background concentrations range from 20 to 60 ppb; polluted urban levels range from 100 to 500 ppb</td>
<td>No primary sources; formed as a secondary pollutant from atmospheric reactions involving hydrocarbons and oxides of nitrogen</td>
</tr>
</tbody>
</table>

"Two concentration units that are commonly used in reporting atmospheric species abundances are $\mu g \cdot m^{-3}$ and parts per million by volume (ppm). Parts per million by volume is not really a concentration but a dimensionless volume fraction, although it is widely referred to as a "concentration." Parts per million by volume may be expressed as

\[
\text{"concentration" of species } i \text{ in ppm} = \frac{c_i}{c} \times 10^6
\]

where $c_i$ and $c$ are moles/volume of species $i$ and air, respectively, at $p$ and $T$. Given a pollutant mass concentration $m_i$ expressed in $\mu g \cdot m^{-3}$

\[
c_i = \frac{10^{-6} m_i}{M_i}
\]

where $M_i$ is the molecular weight of species $i$ and $c = p/RT$. Thus the "concentration" of a species in ppm is related to that in $\mu g \cdot m^{-3}$ by

\[
\text{"concentration" of species } i \text{ in ppm} = \frac{RT}{p M_i} \times \text{concentration in } \mu g \cdot m^{-3}
\]

Parts per billion by volume (ppb) is just $(c_i/c) \times 10^9$. 


**TABLE 1.2 HYDROCARBONS IDENTIFIED IN AMBIENT AIR**

<table>
<thead>
<tr>
<th>Carbon number</th>
<th>Compound</th>
<th>Carbon number</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane</td>
<td></td>
<td>2,3-Dimethylbutane</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td></td>
<td>cis-2-Hexene</td>
</tr>
<tr>
<td></td>
<td>Ethylene</td>
<td></td>
<td>trans-2-Hexene</td>
</tr>
<tr>
<td></td>
<td>Acetylene</td>
<td></td>
<td>cis-3-Hexene</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>trans-3-Hexene</td>
</tr>
<tr>
<td></td>
<td>Propane</td>
<td>2</td>
<td>2-Methyl-1-pentene</td>
</tr>
<tr>
<td></td>
<td>Propylene</td>
<td></td>
<td>4-Methyl-1-pentene</td>
</tr>
<tr>
<td></td>
<td>Propadiene</td>
<td>3</td>
<td>4-Methyl-2-pentene</td>
</tr>
<tr>
<td></td>
<td>Methylacetylene</td>
<td></td>
<td>Benzene</td>
</tr>
<tr>
<td>4</td>
<td>Butane</td>
<td></td>
<td>Cyclohexane</td>
</tr>
<tr>
<td></td>
<td>Isobutane</td>
<td>7</td>
<td>Methylcyclopentane</td>
</tr>
<tr>
<td></td>
<td>1-Butene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cis-2-Butene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>trans-2-Butene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Isobutene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,3-Butadiene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Pentane</td>
<td>8</td>
<td>2,2,4-Trimethylpentane</td>
</tr>
<tr>
<td></td>
<td>Isopentane</td>
<td></td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td></td>
<td>1-Pentene</td>
<td></td>
<td>o-Xylene</td>
</tr>
<tr>
<td></td>
<td>cis-2-Pentene</td>
<td></td>
<td>m-Xylene</td>
</tr>
<tr>
<td></td>
<td>trans-2-Pentene</td>
<td></td>
<td>p-Xylene</td>
</tr>
<tr>
<td></td>
<td>2-Methyl-1-butene</td>
<td>9</td>
<td>m-Ethyltoluene</td>
</tr>
<tr>
<td></td>
<td>2-Methyl-1,3-buteni</td>
<td></td>
<td>p-Ethyltoluene</td>
</tr>
<tr>
<td></td>
<td>Cyclopentane</td>
<td></td>
<td>1,2,4-Trimethylbenzene</td>
</tr>
<tr>
<td></td>
<td>Cyclohexene</td>
<td></td>
<td>1,3,5-Trimethylbenzene</td>
</tr>
<tr>
<td></td>
<td>Isoprene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Hexane</td>
<td>10</td>
<td>sec-Butylbenzene</td>
</tr>
<tr>
<td></td>
<td>2-Methylpentane</td>
<td></td>
<td>α-Pinene</td>
</tr>
<tr>
<td></td>
<td>3-Methylpentane</td>
<td></td>
<td>β-Pinene</td>
</tr>
<tr>
<td></td>
<td>2,2-Dimethylbutane</td>
<td></td>
<td>3-Carene</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Limonene</td>
</tr>
</tbody>
</table>

Vehicles. Motor vehicle emissions consist of unburned fuel,* in the form of organic compounds; oxides of nitrogen, in the form primarily of nitric oxide; carbon monoxide; and particulate matter. Since motor vehicle emissions vary with driving mode (idle, accelerate, decelerate, cruise), to obtain a single representative emission figure for a vehicle, it is run through a so-called driving cycle in which different driving modes are attained.

*Gasoline is the 313 to 537 K fraction from petroleum distillation and contains approximately 2000 compounds. These include C₄ to C₉ paraffins, olefins, and aromatics. Typical compositions vary from 4% olefins and 48% aromatics to 22% olefins and 20% aromatics. Unleaded fuel has a higher aromatic content than leaded fuel.
### TABLE 1.3 POTENTIALLY HAZARDOUS AIR POLLUTANTS

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Toxicity$^a$</th>
<th>Average concentration$^b$ (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Halomethanes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl chloride</td>
<td>CH₃Cl</td>
<td>BM</td>
<td>788</td>
</tr>
<tr>
<td>Methyl bromide</td>
<td>CH₃Br</td>
<td>BM</td>
<td>141</td>
</tr>
<tr>
<td>Methyl iodide</td>
<td>CH₃I</td>
<td>SC, BM</td>
<td>2.7</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>CH₂Cl₂</td>
<td>BM</td>
<td>978</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl₃</td>
<td>SC, BM</td>
<td>346</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>CCl₄</td>
<td>SC, NBM</td>
<td>221</td>
</tr>
<tr>
<td><strong>Haloethanes and halopropanes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl chloride</td>
<td>C₂H₅Cl</td>
<td>—</td>
<td>100</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>CH₂ClCH₂Cl</td>
<td>SC, BM</td>
<td>558</td>
</tr>
<tr>
<td>1,2-Dibromoethane</td>
<td>CH₂BrCH₂Br</td>
<td>SC</td>
<td>32</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>CH₂CCl₃</td>
<td>Weak BM</td>
<td>512</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>CHCl₂CHCl₂</td>
<td>SC, NBM</td>
<td>29</td>
</tr>
<tr>
<td>1,2-Dichloropropane</td>
<td>CH₂ClCHClCH₃</td>
<td>BM</td>
<td>60</td>
</tr>
<tr>
<td><strong>Chloroalkenes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinylidene chloride</td>
<td>CH₂=CCl₂</td>
<td>SC, BM</td>
<td>19</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>CHCl=CCl₂</td>
<td>SC, BM</td>
<td>143</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>CHCl₂=CCl₂</td>
<td>SC</td>
<td>401</td>
</tr>
<tr>
<td>Allyl chloride</td>
<td>CICH₂CH=CH₂</td>
<td>SC</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Hexachloro-1,3-butadiene</td>
<td>Cl₂C=CCl=CCl=CCl₂</td>
<td>BM</td>
<td>5</td>
</tr>
<tr>
<td><strong>Chloroaromatics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monochlorobenzene</td>
<td>C₆H₅Cl</td>
<td>—</td>
<td>280</td>
</tr>
<tr>
<td>α-Chlorotoluene</td>
<td>C₆H₅CH₂Cl</td>
<td>BM</td>
<td>&lt;5</td>
</tr>
<tr>
<td>o-Dichlorobenzene</td>
<td>o-C₆H₅Cl₂</td>
<td>—</td>
<td>12</td>
</tr>
<tr>
<td>m-Dichlorobenzene</td>
<td>m-C₆H₅Cl₂</td>
<td>—</td>
<td>6</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene</td>
<td>1,2,4-C₆H₅Cl₃</td>
<td>—</td>
<td>5</td>
</tr>
<tr>
<td><strong>Aromatic hydrocarbon</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>SC</td>
<td>3,883</td>
</tr>
<tr>
<td><strong>Oxygenated and nitrogenated species</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>SC, BM</td>
<td>14,200</td>
</tr>
<tr>
<td>Phosgene</td>
<td>COCl₂</td>
<td>—</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Peroxyacetyl nitrate (PAN)</td>
<td>CH₃COOONO₂</td>
<td>Phytotoxic</td>
<td>589</td>
</tr>
<tr>
<td>Peroxypropionyl nitrate (PPN)</td>
<td>CH₃CH₂COOONO₂</td>
<td>Phytotoxic</td>
<td>103</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>CH=CN</td>
<td>SC</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$BM; positive mutagenic activity based on Ames salmonella mutagenicity test (bacterial mutagens); NBM, not found to be mutagenic in the Ames salmonella test (not bacterial mutagens); SC, suspected carcinogens.

$^b$Average from 2 weeks of measurements in Houston, St. Louis, Denver, and Riverside.

*Source:* Singh et al. (1981).
TABLE 1.4 NO/NO\textsubscript{x} RATIOS IN EMISSIONS FROM VARIOUS SOURCE TYPES

<table>
<thead>
<tr>
<th>Source type</th>
<th>NO/NO\textsubscript{x}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial boilers</td>
<td></td>
</tr>
<tr>
<td>Natural gas</td>
<td>0.90-1.0</td>
</tr>
<tr>
<td>Coal</td>
<td>0.95-1.0</td>
</tr>
<tr>
<td>No. 6 fuel oil</td>
<td>0.96-1.0</td>
</tr>
<tr>
<td>Motor vehicle</td>
<td></td>
</tr>
<tr>
<td>Internal combustion engine</td>
<td>0.99-1.0</td>
</tr>
<tr>
<td>Diesel-powered car</td>
<td>0.77-1.0\textsuperscript{a}</td>
</tr>
<tr>
<td>Diesel-powered truck and bus</td>
<td>0.73-0.98</td>
</tr>
<tr>
<td>Uncontrolled tail gas from nitric acid plant</td>
<td>~0.50</td>
</tr>
<tr>
<td>Petroleum refinery heater: natural gas</td>
<td>0.93-1.0</td>
</tr>
<tr>
<td>Gas turbine electrical generator: No. 2 fuel oil</td>
<td>0.55-1.0\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The lower limit is for idle conditions; the higher for 50 mi/hr (80.5 km h\textsuperscript{-1}).

\textsuperscript{b}The lower limit is for no load; the higher for full load.

Source: U.S. Environmental Protection Agency (1982a).

for prescribed periods. The driving cycle is carried out in the laboratory on a device called a dynamometer that offers the same resistance to the engine as actual road driving.

Three different driving cycles have been employed in emissions testing: the Federal Test Procedure (FTP), a cycle reflecting a mix of low and high speeds; the New York City Cycle (NYCC), a low-speed cycle to represent city driving; and the Crowded Urban Expressway (CUE) cycle, representative of high-speed driving. The average cycle speeds of the three cycles are: FTP—19.56 mi/hr (31.5 km h\textsuperscript{-1}); NYCC—7.07 mi/hr (11.4 km h\textsuperscript{-1}); CUE—34.79 mi/hr (56.0 km h\textsuperscript{-1}). Emissions of all pollutants are generally larger for the lower-speed cycles.

1.1.4 Particulate Matter

Particulate matter refers to everything emitted in the form of a condensed (liquid or solid) phase. Table 1.7 gives the total estimated U.S. particulate matter emissions in 1978, and Table 1.8 presents a summary of the chemical characteristics of uncontrolled particulate emissions from typical air pollution sources.

In utility and industrial use, coal and, to a lesser extent, oil combustion contribute most of the particulate (and sulfur oxides) emissions. Coal is a slow-burning fuel with a relatively high ash (incombustible inorganic) content. Coal combustion particles consist primarily of carbon, silica (SiO\textsubscript{2}), alumina (Al\textsubscript{2}O\textsubscript{3}), and iron oxide (FeO and Fe\textsubscript{2}O\textsubscript{3}). In contrast to coal, oil is a fast-burning, low-ash fuel. The low ash content results in formation of less particulate matter, but the sizes of particles formed in oil combustion are generally smaller than those of particles from coal combustion. Oil combustion particulate matter contains cadmium, cobalt, copper, nickel, and vanadium.
### TABLE 1.5 ESTIMATED ANTHROPOGENIC NO\textsubscript{x} EMISSIONS IN THE UNITED STATES IN 1976
(10\textsuperscript{6} metric tons/yr, expressed as NO\textsubscript{2})\textsuperscript{a}

<table>
<thead>
<tr>
<th>Source category</th>
<th>Emissions (10\textsuperscript{6} metric tons/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transportation</td>
<td>10.1</td>
</tr>
<tr>
<td>Highway vehicles</td>
<td>7.8</td>
</tr>
<tr>
<td>Nonhighway vehicles</td>
<td>2.3</td>
</tr>
<tr>
<td>Stationary fuel combustion</td>
<td>11.8</td>
</tr>
<tr>
<td>Electric utilities</td>
<td>6.6</td>
</tr>
<tr>
<td>Industrial</td>
<td>4.5</td>
</tr>
<tr>
<td>Residential, commercial, and institutional</td>
<td>0.7</td>
</tr>
<tr>
<td>Industrial processes</td>
<td>0.7</td>
</tr>
<tr>
<td>Chemicals</td>
<td>0.3</td>
</tr>
<tr>
<td>Petroleum refining</td>
<td>0.3</td>
</tr>
<tr>
<td>Metals</td>
<td>0</td>
</tr>
<tr>
<td>Mineral products</td>
<td>0.1</td>
</tr>
<tr>
<td>Oil and gas production and marketing</td>
<td>0\textsuperscript{b}</td>
</tr>
<tr>
<td>Industrial organic solvent use</td>
<td>0</td>
</tr>
<tr>
<td>Other processes</td>
<td>0</td>
</tr>
<tr>
<td>Solid waste disposal</td>
<td>0.1</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>0.3</td>
</tr>
<tr>
<td>Forest wildfires and managed burning</td>
<td>0.2</td>
</tr>
<tr>
<td>Agricultural burning</td>
<td>0</td>
</tr>
<tr>
<td>Coal refuse burning</td>
<td>0.1</td>
</tr>
<tr>
<td>Structural fires</td>
<td>0</td>
</tr>
<tr>
<td>Miscellaneous organic solvent use</td>
<td>0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>23.0</strong></td>
</tr>
</tbody>
</table>

\textsuperscript{a}One metric ton = 10\textsuperscript{3} kg.

\textsuperscript{b}A zero entry indicates emissions of less than 50,000 metric tons/yr.

**Source:** U.S. Environmental Protection Agency (1982a).

### TABLE 1.6 ESTIMATED ANTHROPOGENIC SO\textsubscript{2} EMISSIONS IN THE UNITED STATES IN 1978
(10\textsuperscript{6} metric tons/yr)

<table>
<thead>
<tr>
<th>Source category</th>
<th>Emissions (10\textsuperscript{6} metric tons/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stationary fuel combustion</td>
<td>22.1</td>
</tr>
<tr>
<td>Industrial processes</td>
<td>4.1</td>
</tr>
<tr>
<td>Transportation</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>27.0</strong></td>
</tr>
</tbody>
</table>

**Source:** U.S. Environmental Protection Agency (1982b).
TABLE 1.7  ESTIMATED ANTHROPOGENIC SULFUR OXIDE AND PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES IN THE UNITED STATES IN 1978 (10^3 metric tons/yr)

<table>
<thead>
<tr>
<th>Source category</th>
<th>Sulfur oxides</th>
<th>Particulate matter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel combustion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Utility</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>15,900</td>
<td>2,350</td>
</tr>
<tr>
<td>Oil</td>
<td>1,720</td>
<td>140</td>
</tr>
<tr>
<td>Gas</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Industrial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>1,890</td>
<td>700</td>
</tr>
<tr>
<td>Oil</td>
<td>1,150</td>
<td>90</td>
</tr>
<tr>
<td>Gas</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>Other fuelsa</td>
<td>150</td>
<td>280</td>
</tr>
<tr>
<td>Commercial/institutional</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Oil</td>
<td>900</td>
<td>60</td>
</tr>
<tr>
<td>Gas</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Residential</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>Oil</td>
<td>260</td>
<td>20</td>
</tr>
<tr>
<td>Gas</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>Industrial processes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron and steel</td>
<td>110</td>
<td>830</td>
</tr>
<tr>
<td>Primary smelting</td>
<td>1,960</td>
<td>480</td>
</tr>
<tr>
<td>Iron foundries</td>
<td>0</td>
<td>140</td>
</tr>
<tr>
<td>Other</td>
<td>0</td>
<td>120</td>
</tr>
<tr>
<td>Mineral products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement</td>
<td>670</td>
<td>780</td>
</tr>
<tr>
<td>Asphalt</td>
<td>0</td>
<td>150</td>
</tr>
<tr>
<td>Lime</td>
<td>0</td>
<td>150</td>
</tr>
<tr>
<td>Crushed rock</td>
<td>0</td>
<td>1,340</td>
</tr>
<tr>
<td>Other</td>
<td>30</td>
<td>910</td>
</tr>
<tr>
<td>Petroleum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refining</td>
<td>900</td>
<td>70</td>
</tr>
<tr>
<td>Natural gas production</td>
<td>140</td>
<td>0</td>
</tr>
<tr>
<td>Chemical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>220</td>
<td>0</td>
</tr>
<tr>
<td>Other</td>
<td>0</td>
<td>190</td>
</tr>
<tr>
<td>Other</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grain processing</td>
<td>0</td>
<td>730</td>
</tr>
<tr>
<td>Pulp and paper</td>
<td>80</td>
<td>240</td>
</tr>
<tr>
<td>Other</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Solid waste disposal</td>
<td>0</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td><strong>26,180</strong></td>
<td><strong>10,460</strong></td>
</tr>
</tbody>
</table>

*Primarily wood/bark waste.

Major industrial process sources of particulate matter include the metals, mineral products, petroleum, and chemicals industries. Iron and steel and primary smelting operations are the most significant emission sources in the metals industry. The iron and steel industry involves coke, iron, and steel production, each of which is a source of particulate emissions. The primary metals industry includes the smelting of copper, lead, and zinc, along with aluminum production. Sulfur in unprocessed ores is converted to \( \text{SO}_2 \) during smelting, with a relatively small portion emitted as particulate sulfate and sulfuric acid. Emissions from the mineral products industry result from the production of portland cement, asphalt, crushed rock, lime, glass, gypsum, brick, fiberglass, phosphate rock, and potash. The particles emitted from crushing, screening, conveying, grinding, and loading operations tend to be larger than 15 \( \mu \text{m} \).

### 1.2 AIR POLLUTION LEGISLATION IN THE UNITED STATES

The 1970 Clean Air Act Amendments* was a major piece of legislation that in many respects first put teeth into air pollution control in the United States. A major goal of the Act was to achieve clean air by 1975. The Act required the Environmental Protection Agency (EPA) to establish National Ambient Air Quality Standards (NAAQS)—both primary standards (to protect public health) and secondary standards (to protect public welfare). The Act also required states to submit State Implementation Plans (SIPs) for attaining and maintaining the national primary standards within three years.

Automobile emissions were arbitrarily set at a 90% reduction from the 1970 (for CO and hydrocarbons) or 1971 (for \( \text{NO}_x \)) model year emissions to be achieved by 1975 (or 1976 for \( \text{NO}_x \)). Since there was no proven way to achieve these goals when the law was enacted, the industry was in effect forced to develop new technology to meet the standards by a certain deadline. This has been called "technology-forcing legislation." Emissions standards were to be written by the EPA for certain new industrial plants. These New Source Performance Standards (NSPS) represented national standards that were to be implemented and enforced by each state.

The Clean Air Act Amendments of 1977 incorporated a number of modifications and additions to the 1970 Act, although it retained the basic philosophy of federal management with state implementation. In this Act, the EPA was required to review and update, as necessary, air quality criteria and regulations as of January 1, 1980 and at five-year intervals thereafter. A new aspect was included for "prevention of significant deterioration" (PSD) of air quality in regions cleaner than the NAAQS. Prior to the 1977 Amendments it was theoretically possible to locate air pollution sources in such regions and pollute clean air up to the limits of the ambient standards. However, the Act defined class 1 (pristine) areas, class 2 (almost all other areas), and class 3 (industrialized) areas. Under the PSD provisions, the ambient concentrations of pollutants will be

*The original Clean Air Act was passed in 1963.
<table>
<thead>
<tr>
<th>Source category</th>
<th>Particle size (weight % less than stated size)</th>
<th>Chemical composition</th>
<th>Trace elements (less than 1% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 µm</td>
<td>2.5 µm</td>
<td>1.0 µm</td>
</tr>
<tr>
<td>Fuel combustion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Utility</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>15-90</td>
<td>5-70</td>
<td>1-15</td>
</tr>
<tr>
<td>Oil</td>
<td>95</td>
<td>70-95</td>
<td>5-20</td>
</tr>
<tr>
<td>Industrial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commercial/institutional/residential</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial processes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron and steel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35-99</td>
<td>30-95</td>
<td></td>
</tr>
<tr>
<td>Source: U.S. Environmental Protection Agency (1982b).</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
allowed to rise very little in class 1 areas, by specified amounts in class 2 areas, and by larger amounts in class 3 areas.

The 1977 Amendments also addressed the issue of nonattainment areas: those areas of the country that were already in violation of one or more of the NAAQS. The law appeared to prohibit any more emissions whatsoever and thus seemed as if it would prevent any further growth in industry or commerce in these areas. However, subsequent interpretations by EPA led to a policy known as emissions offset that allowed a new source to be constructed in a nonattainment area provided that its emissions were offset by simultaneous reductions in emissions from existing sources.

Emissions standards for automobiles were delayed, and the standard for NO\textsubscript{x} was permanently relaxed from the original goals of the 1970 Act. CO and hydrocarbon standards were set at a 90\% reduction from the 1970 model year to 3.4 g/mi for CO and 0.41 g/mi for hydrocarbons to be achieved by the 1981 model year. The required NO\textsubscript{x} reduction was relaxed to 1 g/mi by the 1982 model year, representing a reduction from about 5.5 g/mi in 1970. Standards were also proposed for heavy-duty vehicles such as trucks and buses.

Two types of air pollution standards emerged from the legislation. The first type is ambient air quality standards, those that deal with concentrations of pollutants in the outdoor atmosphere. The second type is source performance standards, those that apply to emissions of pollutants from specific sources. Ambient air quality standards are always expressed in concentrations such as micrograms per cubic meter or parts per million; whereas source performance standards are written in terms of mass emissions per unit of time or unit of production, such as grams per minute or kilograms of pollutant per ton of product.

Table 1.9 presents the current National Ambient Air Quality Standards. Some states, such as California, have set their own standards, some of which are stricter than those listed in the table. New Source Performance Standards (NSPS) are expressed as mass emission rates for specific pollutants from specific sources. These standards are

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Averaging time</th>
<th>Primary standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur dioxide</td>
<td>Annual average</td>
<td>80 μg m\textsuperscript{-3}</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>365 μg m\textsuperscript{-3}</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>Annual average</td>
<td>100 μg m\textsuperscript{-3}</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>8 h</td>
<td>10 mg m\textsuperscript{-3}</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
<td>40 mg m\textsuperscript{-3}</td>
</tr>
<tr>
<td>Ozone</td>
<td>1 h</td>
<td>0.12 ppm (235 μg m\textsuperscript{-3})</td>
</tr>
<tr>
<td>Particulate matter (PM\textsubscript{10})\textsuperscript{a}</td>
<td>Annual geometric mean</td>
<td>50 μg m\textsuperscript{-3}</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>150 μg m\textsuperscript{-3}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}See the text.

generally derived from field tests at a number of industrial plants. A separate category of standards for emissions from point sources has been created for hazardous air pollutants, such as beryllium, mercury, vinyl chloride, benzene, and asbestos.

The particulate matter entry in Table 1.9 requires some explanation. After a periodic review of the National Ambient Air Quality Standards and a revision of the Health and Welfare Criteria as required in the 1977 Clean Air Act Amendments, the EPA proposed in 1987 the following relative to the particulate matter standard:

1. That total suspended particulate matter (TSP) as an indicator for particulate matter be replaced for both the primary standards, that is, the annual geometric mean and the 24-hour average, by a new indicator that includes only those particles with an aerodynamic diameter smaller than or equal to a nominal 10 \( \mu \text{m} \) \((\text{PM} \_{10})\)
2. That the level of the 24-hour primary standard be 150 \( \mu \text{g} \text{ m}^{-3} \) and the deterministic form of the standard be replaced with a statistical form that permits one expected exceedance of the standard level per year
3. That the level of the annual primary standard be 50 \( \mu \text{g} \text{ m}^{-3} \), expressed as an expected annual arithmetic mean

EPA also proposed in the Federal Register to revise its regulations governing State Implementation Plans to account for revisions to the NAAQS for TSP and \( \text{PM} \_{10} \). Under the Act, each state must adopt and submit an SIP that provides for attainment and maintenance of the new or revised standards within nine months after the promulgation of an NAAQS. The revision authorizes the EPA Administrator to extend the deadline for up to 18 months as necessary.

Table 1.10 gives some selected New Source Performance Standards. The uncontrolled emission rates for a variety of processes can be estimated from the data available in the EPA publication generally referred to as AP-42, "Compilation of Air Pollutant Emission Factors" (U.S. Environmental Protection Agency, 1977).

### 1.3 ATMOSPHERIC CONCENTRATION UNITS

We note from Table 1.8 that two concentration units that are commonly used in reporting atmospheric species abundance are \( \mu \text{g} \text{ m}^{-3} \) and parts per million by volume (ppm). Parts per million by volume is just

\[
\frac{c_i}{c} \times 10^6
\]

where \( c_i \) and \( c \) are moles per volume of species \( i \) and air, respectively, at pressure \( p \) and temperature \( T \). Note that in spite of the widespread reference to it as a concentration, parts per million by volume is not really a concentration but a dimensionless volume fraction.
### TABLE 1.10 SOME NEW SOURCE PERFORMANCE STANDARDS (NSPS)

<table>
<thead>
<tr>
<th>Source Description</th>
<th>Mass Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam electric power plants</td>
<td></td>
</tr>
<tr>
<td>Particulate matter</td>
<td>13 g/10⁶ kJ</td>
</tr>
<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>86 g/10⁶ kJ</td>
</tr>
<tr>
<td>Gaseous fuel</td>
<td>130 g/10⁶ kJ</td>
</tr>
<tr>
<td>Liquid fuel</td>
<td>260 g/10⁶ kJ</td>
</tr>
<tr>
<td>Coal</td>
<td>86 g/10⁶ kJ</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>At least 70% removal depending on conditions</td>
</tr>
<tr>
<td>Gas or liquid fuel</td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>0.18 g/dscm&lt;sup&gt;a&lt;/sup&gt; corrected to 12% CO&lt;sub&gt;2&lt;/sub&gt; (3-hr average)</td>
</tr>
<tr>
<td>Solid waste incinerators: particulate matter</td>
<td>0.65 g/kg sludge input (dry basis)</td>
</tr>
<tr>
<td>Sewage sludge incinerators: particulate matter</td>
<td>50 mg/dscm&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Iron and steel plants: particulate matter</td>
<td>50 mg/dscm&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Primary copper smelters</td>
<td>0.065% by volume</td>
</tr>
</tbody>
</table>

<sup>a</sup>Dry standard cubic meter.


---

Given a pollutant mass concentration \( m_i \) expressed in \( \mu g m^{-3} \),

\[
c_i = \frac{10^{-6} m_i}{M_i}
\]

where \( M_i \) is the molecular weight of species \( i \) and \( c = p/RT \). Thus

\[
\text{concentration of species } i \text{ in ppm} = \frac{RT}{pM_i} \times \text{concentration in } \mu g \ m^{-3}
\]

If \( T \) is in kelvin and \( p \) in pascal, then (see Table 1.15 for the value of the gas law constant \( R \))

\[
\text{concentration of species } i \text{ in ppm} = \frac{8.314T}{pM_i} \times \text{concentration in } \mu g \ m^{-3}
\]

**Example 1.1 Conversion between Parts per Million and Micrograms per Cubic Meter**

Confirm the relation between ppm and \( \mu g m^{-3} \) for ozone given in Table 1.9 at \( T = 298 \) K and \( p = 1 \) atm \( (1.0133 \times 10^5 \) Pa\)

\[
\text{concentration in } \mu g \ m^{-3} = \frac{pM_i}{8.314T} \times \text{concentration in ppm}
\]

\[
= \frac{(1.0133 \times 10^5)(48)}{8.314(298)} \times 0.12
\]

\[
= 235.6 \mu g m^{-3}
\]
Appendix A

Chemical Kinetics

The 24-hour SO$_2$ NAAQS is $365 \mu g m^{-3}$. Convert this to ppm at the same temperature and pressure.

$$\text{concentration in ppm} = \frac{(8.314)(298)}{(1.0133 \times 10^5)(64)} \times 365$$

$$= 0.139 \text{ ppm}$$

1.4 THE APPENDICES TO THIS CHAPTER

Analysis of the generation and control of air pollutants at the source, air pollution engineering, requires a basis of thermodynamics, fluid mechanics, heat and mass transfer, and chemical kinetics. This chapter concludes with five appendices, the first four of which provide some basic material on chemical kinetics, heat and mass transfer, probability, and turbulence that will be called upon in later chapters. Appendix E presents the units that will be used throughout the book.

APPENDIX A CHEMICAL KINETICS

Chemical kinetics is concerned with the mechanisms and rates of chemical reactions. A single chemical reaction among $S$ species, $A_1, A_2, \ldots, A_S$, can be written as

$$\sum_{i=1}^{S} \nu_i A_i = 0$$

(A.1)

where the stoichiometric coefficient $\nu_i$ is positive (by convention) for the products and negative for the reactants. For example, the reaction

$$\nu_1 A_1 + \nu_2 A_2 \rightarrow \nu_3 A_3 + \nu_4 A_4$$

is written in the form of (A.1) as

$$\nu_3 A_3 + \nu_4 A_4 - \nu_1 A_1 - \nu_2 A_2 = 0$$

If there are $R$ chemical reactions, we denote them by

$$\sum_{i=1}^{S} \nu_{ij} A_i = 0 \quad j = 1, 2, \ldots, R$$

(A.2)

where $\nu_{ij}$ is the stoichiometric coefficient of species $i$ in reaction $j$.

Let $R_i$ be the rate of generation of species $i$ by chemical reaction (g-moles $i$ m$^{-3}$ s$^{-1}$), and let $r_j$ be the rate of reaction $j$ (g-mol m$^{-3}$ s$^{-1}$). Then in a closed system,

$$\frac{dc_i}{dt} = R_i = \sum_{j=1}^{R} \nu_{ij} r_j \quad i = 1, 2, \ldots, S$$

(A.3)
which also implies that

\[
\frac{(R_l) \text{ due to reaction } j}{(R_i) \text{ due to reaction } i} = \frac{v_{ij}}{v_{ij}} \quad i, l = 1, 2, \ldots, S; \quad j = 1, 2, \ldots, R \quad (A.4)
\]

We now define the extents of the \( R \) reactions, \( \xi_1, \ldots, \xi_R \), by

\[
c_i - c_{io} = \sum_{j=1}^{R} v_{ij} \xi_j \quad i = 1, 2, \ldots, S \quad (A.5)
\]

so that the extents satisfy

\[
\frac{d\xi_j}{dt} = r_j(\xi_1, \ldots, \xi_R) \quad j = 1, 2, \ldots, R; \quad \xi_j(0) = 0 \quad (A.6)
\]

Consider the gas-phase chemical reaction

\[
A + B \xrightarrow{k} C
\]

occurring in a closed reactor, the volume of which \( V(t) \) can change with time. The intrinsic reaction rate is \( kc_A c_B \). Let us examine the rate of change of the concentrations in the system. The molar concentration of species \( A \) at any time \( t \) is \( c_A = n_A/V \), and the rate of change of the number of moles of species \( A \) is

\[
\frac{d}{dt} (c_A V) = V k c_A c_B \quad (A.7)
\]

or

\[
\frac{d c_A}{dt} = k c_A c_B - \frac{c_A}{V} \frac{dV}{dt} \quad (A.8)
\]

Thus we see that in a system with volume change, the concentration of a reacting species changes due to the volume change as well as to the reaction itself. It is desirable to be able to express the rate of change of the concentration in a way that depends only on the chemical reaction occurring. In a closed system the total mass \( m \) is unchanging, so a concentration based on the total mass in the system rather than on the total volume would seem to satisfy our desires. Let \( \rho \) be the overall mass density of the system, equal to \( m/V \). Let us replace \( V \) by \( m/\rho \) in (A.7):

\[
\frac{d}{dt} \left( \frac{c_A m}{\rho} \right) = \frac{m}{\rho} k c_A c_B \quad (A.9)
\]

Since \( m \) is constant, it can be canceled from both sides, giving

\[
\rho \frac{d}{dt} \left( \frac{c_A}{\rho} \right) = k c_A c_B \quad (A.10)
\]

Thus, for a system where volume is changing in time, a quantity that reflects only the concentration change due to chemical reaction is
We will frequently use this form of writing the rate of a combustion reaction to isolate the effects of chemistry from those due to expansions, heating and cooling.

**Example 1.2 Extent of Reaction**

Consider the two reactions

\[ \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2 \]
\[ \text{NO}_2 + \text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2 \]

We let \( A_1 = \text{O}_2 \), \( A_2 = \text{NO} \), \( A_3 = \text{NO}_2 \), and \( A_4 = \text{N}_2\text{O}_4 \). Assume that at \( t = 0 \) only \( \text{N}_2\text{O}_4 \) is present. The stoichiometric coefficients are \( \nu_{31} = 2 \), \( \nu_{41} = -1 \), \( \nu_{32} = 2 \), \( \nu_{12} = 1 \), and \( \nu_{32} = -2 \). We introduce the extents of reaction, according to (A.5),

\[ c_1 = \xi_2 \]
\[ c_2 = 2 \xi_2 \]
\[ c_3 = 2 \xi_1 - 2 \xi_2 \]
\[ c_4 - c_{40} = -\xi_1 \]

For a closed, uniform system at constant volume,

\[ \frac{dc_i}{dt} = \sum_{j=1}^{2} \nu_{ij} r_j \quad i = 1, 2, 3, 4 \]

which can be written in terms of the extents of the two reactions,

\[ \frac{d\xi_1}{dt} = r_1(\xi_1, \xi_2) \quad \frac{d\xi_2}{dt} = r_2(\xi_1, \xi_2) \]

Theory provides expressions for the reaction rates \( r_j \) as functions of concentrations and temperature, including certain parameters such as the frequency factor and the activation energy. A reaction as written above is an elementary reaction if it proceeds at the molecular level as written. Sometimes a reaction does not proceed microscopically as written but consists of a sequence of elementary reactions. For example, the photolysis reaction

\[ \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \]

consists of the sequence of elementary reactions,

\[ \text{Br}_2 + h\nu \rightarrow 2\text{Br} \]
\[ \text{Br} + \text{H}_2 \leftrightarrow \text{HBr} + \text{H} \]
\[ \text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br} \]
\[ \text{Br} + \text{Br} \rightarrow \text{Br}_2 \]
The sequence of elementary reactions is called the *mechanism* of the reaction. Aside from the fundamental interest of understanding the chemistry on a molecular level, a reaction mechanism allows us to derive an expression for the reaction rate.

The number of molecules participating in an elementary reaction is its *molecularity*. Customarily, there are monomolecular and bimolecular reactions. Truly monomolecular reactions consist only of photolysis, such as \( \text{Br}_2 + hv \) above, radioactive decay, or a spontaneous transition from a higher to a lower electronic state. Frequently, reactions written as monomolecular, such as isomerizations, are in fact bimolecular because the energy necessary to cause the reaction is provided by collision of the molecule with a background species. Such a background species that acts only as a reaction chaperone is usually designated \( M \). There are no true termolecular reactions in the sense that three molecules collide simultaneously; one written as \( A + B + C \rightarrow \) is most likely the result of two bimolecular steps,

\[
A + B \rightarrow AB \quad AB + C \rightarrow 
\]

**Example 1.3 Independence of Reactions**

Given a chemical reaction mechanism, there is the possibility that two reactions are multiples of each other or that one reaction is a linear combination of two others. Such a reaction tells us nothing more in a stoichiometric sense than the reactions on which it is dependent, since any changes in composition it predicts could equally well be accounted for by the other reactions.

For small numbers of reactions we can frequently determine if they are linearly independent by inspection, observing whether any reaction can be reproduced by adding or subtracting other reactions. In general, however, there is a systematic approach to determining the independence of a set of reactions (Aris, 1965).

Consider the set of reactions

\[
\begin{align*}
H_2 + O_2 & \rightarrow 2OH \\
OH + H_2 & \rightarrow H_2O + H \\
H + O_2 & \rightarrow OH + O \\
OH + H & \rightarrow H_2 + O
\end{align*}
\]

If we define

\[
\begin{align*}
A_1 &= H_2 \\
A_2 &= O_2 \\
A_3 &= H_2O \\
A_4 &= O \\
A_5 &= OH \\
A_6 &= H
\end{align*}
\]

the reactions may be written as

\[
\begin{align*}
-A_1 -A_2 +2A_5 &= 0 \\
-A_1 +A_3 -A_5 +A_6 &= 0 \\
-A_2 +A_4 +A_5 -A_6 &= 0 \\
A_1 +A_4 -A_5 -A_6 &= 0
\end{align*}
\]
To test for independence, form a matrix of the stoichiometric coefficients with $\nu_{ij}$ in the $j$th row and the $i$th column, that is,

$$
\begin{bmatrix}
-1 & -1 & 0 & 0 & 2 & 0 \\
-1 & 0 & 1 & 0 & -1 & 1 \\
0 & -1 & 0 & 1 & 1 & -1 \\
1 & 0 & 0 & 1 & -1 & -1 \\
\end{bmatrix}
$$

Now take the first row with a nonzero element in the first column (in this case it is the first row) and divide that row by the leading element. This will yield a new row of

$$1 \left( \frac{\nu_{2j}}{\nu_{1j}} \right) \frac{\nu_{3j}}{\nu_{1j}} \cdots \frac{\nu_{5j}}{\nu_{1j}}$$

where $j$ is the number of the row used. This new row may be used to make all the other elements in the first column zero by subtracting $\nu_{1k}$ times the new row from the corresponding element of the $k$th row,

$$0 \left( \frac{\nu_{2k}}{\nu_{1k}} - \frac{\nu_{2j}}{\nu_{1j}} \right) \cdots \left( \frac{\nu_{5k}}{\nu_{1k}} - \frac{\nu_{5j}}{\nu_{1j}} \right)$$

The matrix for the present example becomes

$$\begin{bmatrix}
1 & 1 & 0 & 0 & -2 & 0 \\
0 & 1 & 1 & 0 & -3 & 1 \\
0 & -1 & 0 & 1 & 1 & -1 \\
0 & -1 & 0 & 1 & 1 & -1 \\
\end{bmatrix}
$$

The next step is to ignore the first row and first column and repeat this matrix reduction process for the reduced matrix containing $R - 1$ rows. This yields

$$\begin{bmatrix}
1 & 1 & 0 & 0 & -2 & 0 \\
0 & 1 & 1 & 0 & -3 & 1 \\
0 & 0 & 1 & 1 & -2 & 0 \\
0 & 0 & 1 & 1 & -2 & 0 \\
\end{bmatrix}
$$

This reduction process is continued until we have 1's as far as possible down the diagonal and 0's in all elements in rows below the last 1 on the diagonal. Continuing, we find

$$\begin{bmatrix}
1 & 1 & 0 & 0 & -2 & 0 \\
0 & 1 & 1 & 0 & -3 & 1 \\
0 & 0 & 1 & 1 & -2 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
$$

At this point we have three rows with 1's on the diagonal and only 0's in the final row. The number of independent reactions is the number of 1's with only zeros to their left. Alternatively it is the number of reactions minus the number of rows that are entirely zero. In this case, then, only three of the four reactions are linearly independent. The pro-
procedure does not tell us which reactions are dependent, but inspection of the set reveals that reaction 3 is the sum of reactions 1 and 4. Thus we need to replace any one of reactions 1, 3, or 4 with another reaction and repeat the test. For example, reaction 4 could be replaced with

\[ \text{O}_2 \rightarrow 2\text{O} \]

which will be found to be independent.

A.1 Reaction Rates

Gas molecules can react only when they come close enough to one another for direct energy exchange that can lead to bond breaking. For the di- or triatomic molecules that are important in the latter phases of combustion chemistry, the centers of the two molecules must approach within a few angstroms. From elementary kinetic theory, the frequency of collisions per unit volume of gas of molecules of type \( i \) of mass \( m_i \) with molecules of type \( j \) of mass \( m_j \) is (Benson, 1960)

\[ Z_{ij} = \left( \frac{8k_B T}{\pi m_{ij}} \right)^{1/2} \pi \sigma_{ij}^2 N_i N_j \quad \text{m}^{-3} \text{s}^{-1} \]  

where \( N_i \) is the number concentration of species \( i \) (m\(^{-3}\)), \( (8k_B T/\pi m_{ij})^{1/2} \) is the root-mean-square relative speed of the \( i \) and \( j \) molecules, \( k_B \) is the Boltzmann constant (1.38 \( \times \) 10\(^{-23} \) J molecule\(^{-1}\) K\(^{-1}\)), \( m_{ij} = m_i m_j/(m_i + m_j) \) is the reduced mass, and \( \pi \sigma_{ij}^2 \) is the cross-sectional area in which interaction can occur.

The characteristic time during which molecules in thermal motion in a gas are close enough to interact is brief, on the order of \( 10^{-12} \) to \( 10^{-13} \) s. At ambient temperature and pressure the mean time between molecular collisions can be shown from (A.11) to be the order of \( 10^{-9} \) s. Thus collisions are short in duration compared to the time between collisions.

Whereas the collision of two molecules is a necessary condition for reaction, sufficient energy must be available to break chemical bonds. Theory indicates that the fraction of collisions involving energy greater than a required energy \( E \) is given by exp \( (-E/k_B T) \). In this form \( E \) has units of energy per molecule. More commonly, \( E \) is expressed in terms of energy per mole, and we use exp \( (-E/RT) \), where \( R \) is the universal gas constant (see Table 1.15). The rate of reaction is expressed in a form that accounts for both the frequency of collisions and the fraction that exceed the required energy,

\[ r = A(T) \exp \left( -\frac{E}{RT} \right) c_i c_j \]  

The preexponential factor \( A(T) \) may depend on temperature since the translational kinetic energy and internal degrees of freedom of the molecules influence the probability of reaction in any collision event. The rate of reaction is usually written as \( r = kc_i c_j \).
where the parameter $k$ is called the rate constant,

$$k = A(T) \exp\left(-\frac{E}{RT}\right)$$  \hspace{1cm} (A.13)

If $A(T)$ is independent of $T$, we have the Arrhenius form, $k = A \exp\left(-\frac{E}{RT}\right)$.

The parameter $E$ appearing in (A.13) is the activation energy. Figure 1.1 illustrates the energetics of an exchange reaction of the type

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

The difference in the energies of the initial and final states is the heat of reaction $\Delta h_r$. The peak in the energy along the reaction coordinate is associated with the formation of an activated complex $AB^+$, a short-lived intermediate through which the reactants must pass if the encounter is to lead to reaction. By estimating the structure of this transition state the activation energy $E$ may be estimated (Benson, 1960), although the most reliable estimates of $E$ are obtained by correlating rates measured at different temperatures to the Arrhenius form of $k$.

Most elementary reactions can be considered to be reversible,

$$A + B \rightleftharpoons \frac{k_f}{k_b} C + D$$

The time rate of change of one of the reactants or products due to this one reaction is

$$\rho \frac{d([D]/\rho)}{dt} = k_f[A][B] - k_b[C][D]$$

where the brackets represent an alternative notation for the species concentration (i.e., $[A] = c_A$) and where we have used the moles per unit mass, $[D]/\rho$, in anticipation of combustion kinetics.

![Figure 1.1 Energetics of an exchange reaction $A + B \rightarrow C + D$.](image-url)
At chemical equilibrium

\[ 0 = k_f[A][B] - k_b[C][D] \]  \hspace{1cm} (A.14)

or, rearranging,

\[ \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} \]  \hspace{1cm} (A.15)

The right-hand side is equal to the equilibrium constant expressed in terms of concentrations, \( K_c \). Thus we see that the ratio of the forward and reverse rate constants of a reaction is equal to the equilibrium constant, \( k_f(T)/k_b(T) = K_c(T) \). This principle of detailed balancing is very important in the study of chemical kinetics since it allows one of the two rates to be calculated from the other rate and the equilibrium constant. Often, direct measurements of rate constants are available for only one reaction direction. When measurements are available for both reactions, detailed balancing provides a check on the consistency of the two rates.

**A.2 The Pseudo-Steady-State Approximation**

Many chemical reactions, including those occurring in combustion processes, involve very reactive intermediate species such as free radicals, which, due to their very high reactivity, are consumed virtually as rapidly as they are formed and consequently exist at very low concentrations. The pseudo-steady-state approximation (PSSA) is a fundamental way of dealing with such reactive intermediates when deriving the overall rate of a chemical reaction mechanism.

It is perhaps easiest to explain the PSSA by way of a simple example. Consider the unimolecular reaction \( A \rightarrow B + C \) whose elementary steps consist of the activation of \( A \) by collision with a background molecule \( M \) to produce an energetic \( A \) molecule denoted by \( A^* \), followed by decomposition of \( A^* \) to give \( B + C \),

\[ A + M \overset{1_f}{\underset{1_b}{\rightleftharpoons}} A^* + M \]

\[ A^* \overset{2}{\rightarrow} B + C \]

Note that \( A^* \) may return to \( A \) by collision and transfer of its excess energy to an \( M \). The rate equations for this mechanism are

\[ \frac{d[A]}{dt} = -k_{1_f}[A][M] + k_{1_b}[A^*][M] \]  \hspace{1cm} (A.16)

\[ \frac{d[A^*]}{dt} = k_{1_f}[A][M] - k_{1_b}[A^*][M] - k_2[A^*] \]  \hspace{1cm} (A.17)

The reactive intermediate in this mechanism is \( A^* \). The PSSA states that the rate of generation of \( A^* \) is equal to its rate of disappearance; physically, what this means is that
Appendix A Chemical Kinetics

25

$A^*$ is so reactive, as soon as an $A^*$ molecule is formed, that it reacts by one of its two paths. Thus the PSSA gives

$$k_{1f}[A][M] - k_{1b}[A^*][M] - k_2[A^*] = 0 \quad (A.18)$$

From this we find the concentration of $A^*$ in terms of the concentrations of the stable molecules $A$ and $M$,

$$[A^*] = \frac{k_{1f}[A][M]}{k_{1b}[M] + k_2} \quad (A.19)$$

This expression can then be used in (A.16) to give

$$\frac{d[A]}{dt} = -\frac{k_{1f}k_2[M][A]}{k_{1b}[M] + k_2} \quad (A.20)$$

We see that the single overall reaction $A \rightarrow B + C$ with a rate given by (A.20) is not elementary because of the dependence on $M$. If the background species $M$ is in such excess that its concentration is effectively constant, the overall rate can be expressed as $d[A]/dt = -k[A]$, where $k = k_{1f}k_2[M]/(k_{1b}[M] + k_2)$ is a constant. If $k_{1b}[M] \gg k_2$, then $d[A]/dt = -k[A]$, with $k = k_{1f}k_2/k_{1b}$. On the other hand, if $k_{1b}[M] \ll k_2$, then $d[A]/dt = -k_{1f}[M][A]$.

One comment is in order. The PSSA is based on the presumption that the rates of formation and disappearance of a reactive intermediate are equal. A consequence of this statement is that $d[A^*]/dt = 0$ from (A.17). If this is interpreted to mean that $[A^*]$ does not change with time, this interpretation is incorrect. $[A^*]$ is at steady state with respect to $[A]$ and $[M]$. We can, in fact, compute $d[A^*]/dt$. It is

$$\frac{d[A^*]}{dt} = \frac{d}{dt} \left[ \frac{k_{1f}[A][M]}{k_{1b}[M] + k_2} \right] \quad (A.21)$$

which, if $[M]$ is constant, is

$$\frac{d[A^*]}{dt} = -\frac{k_{1f}^2k_2[M]^2[A]}{(k_{1b}[M] + k_2)^2} \quad (A.22)$$

The key point is that (A.19) is valid only after a short initial time interval needed for the rates of formation and disappearance of $A^*$ to equilibrate. After that time $[A^*]$ adjusts slowly on the time scale associated with changes in $[A]$ so as to maintain that balance. That slow adjustment is given by (A.22).

Example 1.4 Analysis of Bimolecular Reactions

When two molecules collide and form a single molecule,

$$A + B \xrightleftharpoons[k_{-2}]{k_{2a}} AB^*$$

the initial collision produces an activated complex that has sufficient energy to overcome an energy barrier and decompose. The lifetime of the activated complex is short, on the
order of the vibrational period of the complex (e.g., $10^{-12}$ to $10^{-13}$ s). Unless another molecule collides with the activated complex within this period and removes some of this excess energy, that is,

$$AB^* + M \xrightarrow{k_{-s}} AB + M$$

the activated complex will decay back to $A$ and $B$. At ambient temperature and pressure the frequency of collisions of background molecules (e.g., air) with the complex is of the order of $10^9$ s$^{-1}$. Thus only one $AB^*$ complex out of $10^3$ to $10^4$ formed can produce a stable molecule. The actual number may be lower and may depend on the type of third body $M$ involved.

The rate of formation of the stable product, $AB$, is

$$\frac{d[AB]}{dt} = k_{+s}[AB^*][M] - k_{-s}[AB][M]$$

The PSSA can be applied to $[AB^*]$, giving

$$[AB^*] = \frac{k_{+a}[A][B] + k_{-s}[AB][M]}{k_{-a} + k_{+s}[M]}$$

Substituting into the rate equation and grouping terms, we find that

$$\frac{d[AB]}{dt} = \frac{k_{+a}k_{+s}[A][B][M]}{k_{-a} + k_{+s}[M]} - \frac{k_{-a}k_{-s}[AB][M]}{k_{-a} + k_{+s}[M]}$$

At low pressure, $[M] = p/RT$ is small, so $k_{-a} \gg k_{+s}[M]$ and

$$\frac{d[AB]}{dt} = \frac{k_{+a}k_{+s}[A][B][M]}{k_{-a}} - \frac{k_{-a}k_{-s}[AB][M]}{k_{+s}}$$

In the high-pressure limit, $k_{-a} \ll k_{+s}[M]$ and

$$\frac{d[AB]}{dt} = \frac{k_{+s}[A][B]}{k_{+a}} - \frac{k_{-a}k_{-s}[AB]}{k_{+s}}$$

We see that in the low-pressure limit the forward reaction appears from the rate expression to be a termolecular reaction, whereas the reverse reaction is bimolecular. On the other hand, in the high-pressure limit, because of the high concentration of $M$, the collisional stabilization of the activated complex is very efficient and the forward reaction appears to be bimolecular, whereas the reverse reaction appears to be unimolecular.

### A.3 Hydrocarbon Pyrolysis Kinetics

As a prelude to our analysis of combustion kinetics it will be useful to consider the thermal decomposition or pyrolysis of hydrocarbons. It is generally accepted that the pyrolysis of hydrocarbons occurs by a free-radical mechanism. Free radicals are entities that contain one unpaired electron. They are often molecular fragments formed by the rupture of normal covalent bonds in which each fragment retains possession of its contributing electron. Examples of free radicals are the methyl radical, $\text{CH}_3^\cdot$, the ethyl radical $\text{CH}_2\text{CH}_2^\cdot$, and the chlorine atom, Cl.
Let us consider the mechanism for the pyrolysis of ethane. The process is initiated by the thermal breakdown of the ethane molecule into two methyl radicals:

\[
C_2H_6 + M \rightarrow \text{CH}_3\cdot + M
\]

The alternative \( C_2H_6 \rightarrow C_2H_5\cdot + H\cdot \) has a much higher activation energy than reaction 1 and thus can be neglected. This initiation reaction is followed by the chain propagation steps:

\[
\begin{align*}
\text{CH}_3\cdot + C_2H_6 & \rightarrow \text{CH}_4 + C_2H_5\cdot \\
C_2H_5\cdot + M & \rightarrow C_2H_4 + H\cdot + M \\
H\cdot + C_2H_6 & \rightarrow H_2 + C_2H_5\cdot
\end{align*}
\]

These reactions are called chain propagation reactions since free radicals are continuously propagated by the reactions. Although some radicals are destroyed, others are generated in equal numbers. The termination reactions involve the combination of two free radicals to form a stable molecule or molecules:

\[
\begin{align*}
2H\cdot & \rightarrow H_2 \\
H\cdot + C_2H_5\cdot & \rightarrow C_2H_6 \\
H\cdot + C_2H_5\cdot & \rightarrow C_2H_4 + H_2 \\
H\cdot + \text{CH}_3\cdot & \rightarrow \text{CH}_4 \\
\text{CH}_3\cdot + C_2H_5\cdot & \rightarrow \text{C}_3H_8 \\
2C_2H_5\cdot & \rightarrow \text{C}_4H_{10}
\end{align*}
\]

Note that if the termination reactions did not occur, it theoretically would be necessary for only one molecule of \( C_2H_6 \) to decompose by reaction 1 in order for complete conversion of \( C_2H_6 \) to \( C_2H_4 \) to occur. All the rest of the \( C_2H_6 \) would react via reaction 2 and the chain sequence of reactions 3 and 4. If, on the other hand, hydrogen atoms are terminated by any of reactions 5 to 7 as soon as they are generated by reaction 3 and before they can react by reaction 4, each molecule of \( C_2H_6 \) that decomposes by reaction 1 can generate (via \( \text{CH}_3\cdot \)) at most two molecules of \( C_2H_4 \). Under these conditions the chain sequence of reactions 3 and 4 is completely suppressed. Actually, an intermediate situation will exist in which propagation and termination reactions compete for radicals. The average number of times that the chain sequence is repeated before a chain-propagating radical is terminated is called the chain length of the reaction.

For hydrocarbons larger than ethane the initial bond rupture may occur at any
C—C bond; for example, \( n \)-pentane may decompose by

\[
\begin{align*}
\text{C}_5\text{H}_{12} & \rightarrow \text{CH}_3' + \text{C}_4\text{H}_9' \\
& \rightarrow \text{C}_2\text{H}_5' + \text{C}_3\text{H}_7'.
\end{align*}
\]

It is generally assumed that the activation energy of the initiation step is approximately equal to the bond energy of the bonds being broken. The reverse radical recombination reactions then have zero activation energy.

The rate at which hydrogen abstraction reactions of types 2 and 4 proceed depends on the location of the hydrogen atom on the carbon chain backbone. A primary carbon atom forms a normal covalent bond with one other carbon; a secondary C atom with two other C atoms; a tertiary with three other C atoms. Consider 2-dimethyl,4-methyl pentane:

\[
\begin{align*}
\text{H}_3\text{C} & \text{C}^1 \text{H}_3 \\
\text{H} & \text{C}^2 \text{C}^3 \text{C}^1 \text{H}_3
\end{align*}
\]

where \( \text{C}^1 \) are primary carbons, \( \text{C}^2 \) is a secondary carbon, \( \text{C}^3 \) is a tertiary carbon, and \( \text{C}^4 \) is a quaternary carbon. The rate of H-atom abstraction from such a molecule generally proceeds in the order \( \text{C}^3 > \text{C}^2 > \text{C}^1 \), with an approximate difference in activation energy of about 2 kcal (8374 J; see Table 1.15 for conversion factor) between each carbon, that is, \( E_3 - E_2 \approx E_2 - E_1 \approx 2000 \text{ cal/g-mol} \) (8374 J/g-mol).

Let us now analyze the mechanism for ethane pyrolysis. In doing so, we want to determine which of the termination reactions are most important. To decide which is the dominant termination reaction, we have to consider the relative concentration of the free radicals, the relative rate constants, and the need for a third body. Since recombination reactions can be assumed to have zero activation energy, the frequency factor determines the rate constant. Theory predicts that the frequency factor is lower the larger the molecules. Thus the frequency factor for \( \text{C}_2\text{H}_5' + \text{C}_2\text{H}_5' \) is lower than that for \( \text{C}_2\text{H}_5' + \text{CH}_3' \), and so on. On the other hand, recombination reactions such as \( \text{H}'+ \text{H}' \), \( \text{H}'+ \text{CH}_3' \), and \( \text{H}'+ \text{C}_2\text{H}_5' \) require a third body, so in spite of their higher frequency factor, their rate is considerably lower than those of the larger radicals. Finally, and most important for this case, the concentration of ethyl radicals is much higher than those of \( \text{H}' \) and \( \text{CH}_3' \).

We can estimate the relative concentrations of free radicals using their PSSA equations, neglecting the contributions from initiation and termination reactions. Neglecting the initiation and termination reactions is valid if the chain length of the reaction is sufficiently long. For example, the PSSA applied to \( \text{C}_2\text{H}_5' \) under these conditions is

\[
-k_3[M][\text{C}_2\text{H}_5'] + k_4[H'][\text{C}_2\text{H}_6] \approx 0
\]

from which we obtain

\[
\frac{[H']}{[\text{C}_2\text{H}_5']} = \frac{k_3[M]}{k_4[\text{C}_2\text{H}_6]}
\]
The ratio is \( << 1 \) since \( k_3[M] << k_4[C_2H_6] \). Thus we can consider reaction 10 to be the sole termination reaction.

To derive a rate equation for the overall process, we apply the PSSA to \([H^\cdot], [CH_3^\cdot], \) and \([C_2H_5^\cdot] \):

\[
0 = k_3[C_2H_5^\cdot][M] - k_4[H^\cdot][C_2H_6]
\]
\[
0 = 2k_1[C_2H_6][M] - k_2[CH_3^\cdot][C_2H_6]
\]
\[
0 = k_2[CH_3^\cdot][C_2H_6] - k_3[C_2H_5^\cdot][M] + k_4[H^\cdot][C_2H_6] - 2k_{10}[C_2H_5^\cdot]^2
\]

We obtain

\[
[C_2H_5^\cdot] = \left( \frac{k_1[M]}{k_{10}} \right)^{1/2} [C_2H_6]^{1/2}
\]
\[
[CH_3^\cdot] = \frac{2k_1[M]}{k_2}
\]
\[
[H^\cdot] = \frac{k_3[M]}{k_4} \left( \frac{k_1[M]}{k_{10}} \right)^{1/2} [C_2H_6]^{-1/2}
\]

The overall rate of disappearance of ethane is

\[
\frac{d[C_2H_6]}{dt} = -3k_1[M][C_2H_6] - k_4 \left( \frac{k_1[M]}{k_{10}} \right)^{1/2} [C_2H_6]^{1/2}
\]

If we neglect the contribution from initiation (assuming long chains), we have

\[
\frac{d[C_2H_6]}{dt} = -k_4 \left( \frac{k_1[M]}{k_{10}} \right)^{1/2} [C_2H_6]^{1/2}
\]

and the overall reaction has order \( \frac{1}{2} \).

If, instead of reaction 10, we had specified the principal termination reaction to be reaction 9, the overall reaction can be shown to have order 1.

**APPENDIX B MASS AND HEAT TRANSFER**

Virtually every process that we will study in this book involves heat and/or mass transfer. The rates of combustion reactions depend on the rates of mixing of fuel and air, on the rate of removal of energy in the combustion equipment, and in the case of the burning of solid particles or liquid drops, on heat and mass transfer between the particle and the surrounding gas. Several of the most important processes for removal of gaseous pollutants from effluent streams involve contacting of the waste gas stream with a liquid or solid sorbent. In such a process the vapor species must diffuse to the gas–liquid or gas–solid interface, cross the interface, and, in the case of a liquid, diffuse into the bulk of the liquid.
B.1 Basic Equations of Convective Diffusion

Whereas we assume that most readers will have some familiarity with heat transfer, this may not be the case with mass transfer. Thus in this section we develop the basic equations of mass transfer that will be used subsequently in the book and present some essential material on heat transfer.

Consider a binary mixture of species $A$ and $B$. The mass flux of $A$ (kg m$^{-2}$ s$^{-1}$) at any point in a fluid is $n_A = \rho_A u_A$, where $\rho_A$ is the density of species $A$ (kg m$^{-3}$) and $u_A$ is the average velocity of species $A$ molecules at that point (m s$^{-1}$). If species $A$ is being generated by chemical reaction at a rate $\bar{r}_A$ (kg m$^{-3}$ s$^{-1}$), a balance on species $A$ over an incremental volume of the fluid produces the differential equation of continuity of component $A$ in a binary mixture of $A$ and $B$,

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot n_A = \bar{r}_A \tag{B.1}$$

The same equation in molar units is

$$\frac{\partial c_A}{\partial t} + \nabla \cdot N_A = r_A \tag{B.2}$$

where $N_A$ is the molar flux of $A$ (g-mol m$^{-2}$ s$^{-1}$), equal to $c_A u_A$, $c_A$ is the molar concentration of $A$ (g-mol m$^{-3}$), and $r_A$ is the molar rate of generation of $A$ (negative if $A$ is being consumed).

To obtain equations strictly in terms of $\rho_A$ or $c_A$ we need to relate the fluxes $n_A$ and $N_A$ to these quantities. The fundamental relation describing mass transfer by molecular diffusion in a binary mixture is Fick’s law, expressed in mass and molar units as

$$n_A = \frac{\rho_A \rho}{\rho} (n_A + n_B) - \rho D_{AB} \nabla \frac{\rho_A}{\rho} \tag{B.3}$$

$$N_A = x_A (N_A + N_B) - c D_{AB} \nabla x_A \tag{B.4}$$

Notice that the flux of species $A$ in a binary mixture at a point is the sum of two contributions. Let us examine the first terms on the right-hand sides of (B.3) and (B.4). The sum $n_A + n_B = \rho u$, the product of the total density of the mixture and the mass average velocity (i.e., the total mass flux at that point). The quantity $\rho_A / \rho$ is the mass fraction of species $A$, so the first term on the right-hand side of (B.3) is the fraction of the total mass flux of the fluid that is $A$. Similarly, $N_A + N_B = c u^*$, where $c$ is the total molar concentration of the mixture, and $u^*$ is the molar average velocity, $u^* = x_A u_A + (1 - x_A) u_B$. Thus the first terms on the right-hand sides of (B.3) and (B.4) are the contributions to the fluxes from convection. In sum, then, the flux of species $A$ (or $B$) may arise from bulk flow of the mixture and/or molecular diffusion.

Substituting (B.3) and (B.4) in (B.1) and (B.2), respectively, we obtain the binary convective diffusion equations,

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A u) = \nabla \cdot \rho D_{AB} \nabla \frac{\rho_A}{\rho} + \bar{r}_A \tag{B.5}$$
Either of these equations describes the concentration profiles in a binary diffusing system. They are valid for systems with variable total density (\( \rho \) or \( c \)) and variable diffusivity \( D_{AB} \).

If \( \rho \) and \( D_{AB} \) can be assumed to be constant, we can employ the overall continuity equation, \( \nabla \cdot \mathbf{u} = 0 \), and then divide (B.5) by \( M_A \) to obtain

\[
\frac{\partial c_A}{\partial t} + \mathbf{u} \cdot \nabla c_A = D_{AB} \nabla^2 c_A + r_A
\]  

(B.7)

### B.2 Steady-State Mass Transfer to or from a Sphere in an Infinite Fluid

In both combustion and aerosol applications we will be interested in mass transfer to or from a sphere in an infinite fluid. We assume that the gas phase is a binary mixture of a diffusing species \( A \) in a background gas \( B \) (e.g., air). We wish to determine the steady-state concentration profile of \( A \) around the sphere and the mass flux. Although we can in principle solve the steady-state form of (B.7), difficulties arise in specifying the velocity \( \mathbf{u} \). It is easier to begin with a balance on species \( A \) over a thin shell between radii \( r \) and \( r + \Delta r \) in the gas. If \( A \) is not reacting in the gas, such a balance gives

\[
(4\pi r^2 N_A)_r - (4\pi (r^2 N_A)_r + \Delta r) = 0
\]  

(B.8)

which, upon dividing by \( \Delta r \) and letting \( \Delta r \to 0 \), becomes

\[
\frac{d}{dr} (4\pi r^2 N_A) = 0
\]  

(B.9)

or

\[
4\pi r^2 N_A = \text{constant}
\]  

(B.10)

If species \( B \) is not transferring between the gas and the sphere, then \( N_B = 0 \) everywhere. Thus (B.4) becomes

\[
N_{Ar} = -\frac{cD_{AB}}{1 - x_A} \frac{dx_A}{dr}
\]  

(B.11)

Combining (B.10) and (B.11) and calling the constant \(-C_1\) gives

\[
4\pi r^2 \frac{cD_{AB}}{1 - x_A} \frac{dx_A}{dr} = C_1
\]  

(B.12)

Integrating (B.12) gives

\[
-4\pi cD_{AB} \ln (1 - x_A) = -\frac{C_1}{r} + C_2
\]  

(B.13)
One boundary condition is that \( x_A = x_{A\infty} \) as \( r \to \infty \), from which we find

\[
C_2 = -4\pi c D_{AB} \ln (1 - x_{A\infty}) \tag{B.14}
\]

The other boundary condition is that the mole fraction of \( A \) just above the surface of the sphere is \( x_{A0} \) (i.e., \( x_A = x_{A0} \) at \( r = R \)). Applying this condition gives

\[
C_1 = 4\pi R c D_{AB} \ln \frac{1 - x_{A0}}{1 - x_{A\infty}} \tag{B.15}
\]

and thus, from (B.13),

\[
\ln \frac{1 - x_A}{1 - x_{A\infty}} = \frac{R}{r} \ln \frac{1 - x_{A0}}{1 - x_{A\infty}} \tag{B.16}
\]

or

\[
\frac{1 - x_A}{1 - x_{A\infty}} = \left( \frac{1 - x_{A0}}{1 - x_{A\infty}} \right)^{R/r} \tag{B.17}
\]

Let us compute the flux of species \( A \) at the surface of the sphere. Since \(-4\pi R^2 N_{AR} = C_1\), we have

\[
N_{AR} = -\frac{c D_{AB}}{R} \ln \frac{1 - x_{A0}}{1 - x_{A\infty}} \tag{B.18}
\]

Note that if \( x_{A0} < x_{A\infty} \), \( N_{AR} < 0 \) and the flux of \( A \) is toward the sphere; and that if \( x_{A0} > x_{A\infty} \), \( N_{AR} > 0 \) and the flux of \( A \) is away from the sphere.

The mass average velocity at any point is related to the fluxes of \( A \) and \( B \) by \( n_A + n_B = \rho u \). Since \( n_B = 0 \) everywhere, \( n_A = \rho u_r \). At constant \( T \) and \( \rho \), \( \rho \) is constant, so

\[
u_r = \frac{N_{AR} M_A}{\rho} = -\frac{M_A R}{\rho} c D_{AB} \ln \frac{1 - x_{A0}}{1 - x_{A\infty}} \tag{B.19}
\]

If \( x_{A0} < x_{A\infty} \), \( u_r < 0 \) and the net flux is toward the particle, and vice versa. We note that \( u_r \) satisfies the overall continuity equation for a fluid at constant density,

\[
\frac{d}{dr} (r^2 u_r) = 0
\]

A frequently used approximation to the foregoing development is that the mole fraction of \( A \) is so small (i.e., \( x_A \ll 1 \)) that the flux (B.11) may be approximated by the pure diffusive contribution

\[
N_{Ar} = -c D_{AB} \frac{dx_A}{dr} \tag{B.20}
\]
From
\[ 4\pi r^2 cD_{AB} \frac{dx_A}{dr} = C_1 \]
integrating and using the two boundary conditions gives
\[ \frac{x_A - x_{A,\infty}}{x_{A_0} - x_{A,\infty}} = \frac{R}{r} \]  \hspace{1cm} (B.21)
with the flux at the sphere surface
\[ N_{Ar} = \frac{cD_{AB}}{R} (x_{A_0} - x_{A,\infty}) \]  \hspace{1cm} (B.22)
We can compute the rate of change of the size of the sphere due to the flux of \( A \). If the molar density of the sphere is \( c_s \), then
\[ -4\pi R^2 N_{Ar} = c_s \frac{d}{dt} \left( \frac{4}{3} \pi R^3 \right) \]  \hspace{1cm} (B.23)
or
\[ -c_s \frac{dR}{dt} = N_{Ar} \]  \hspace{1cm} (B.24)
Inherent in this result, if we use (B.18) or (B.22) for \( N_{Ar} \), is the assumption that even though the size of the sphere is changing due to mass transfer of \( A \) between the sphere and the ambient gas, the size change occurs slowly enough that the flux of \( A \) can be computed from its steady-state value. In other words, the characteristic time to achieve the steady-state concentration profile of \( A \) in the gas is short compared to the characteristic time for the particle to grow or shrink. We will return to this point shortly.

### B.3 Heat Transfer

The equation for conservation of energy for a pure fluid, neglecting viscous dissipation, is (Bird et al., 1960, Table 10.4-1)
\[ \rho \bar{c}_p \left( \frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) = k \nabla^2 T + \frac{\partial}{\partial t} \left( \frac{1}{\rho} \right) \frac{\partial \ln (1/\rho)}{\partial T} \left( \frac{\partial p}{\partial t} + \mathbf{u} \cdot \nabla p \right) \]  \hspace{1cm} (B.25)
where \( \bar{c}_p \) is the heat capacity at constant pressure per unit mass and \( k \) is the thermal conductivity. At constant pressure the second term on the right-hand side of (B.25) vanishes.

Let us continue with our spherical example. At steady state and constant pressure, the temperature distribution around the sphere satisfies
\[ \rho \bar{c}_p u_r \frac{dT}{dr} = k \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dT}{dr} \right) \]  \hspace{1cm} (B.26)
The left-hand side of (B.26) is the contribution from the bulk, convective motion of the fluid, and the right-hand side represents that from conduction.

We can determine the temperature profile by solving (B.26) with \( u_r \) from (B.19)

\[-\rho \overline{c}_p \frac{M_A R}{r^2} c D_{AB} \left( \ln \frac{1 - x_{A0}}{1 - x_{A\infty}} \right) \frac{dT}{dr} = k \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dT}{dr} \right)\]

Letting \( \beta = \overline{c}_p M_A R c D_{AB} \ln \left[ \frac{(1 - x_{A0})}{(1 - x_{A\infty})} \right] / k \), this equation becomes

\[-\beta \frac{dT}{dr} = \frac{d}{dr} \left( r^2 \frac{dT}{dr} \right)\]

To solve this equation, we let \( y = dT/dr \), giving

\[\frac{d}{dr} \left( r^2 y \right) = -\beta y\]

which, upon integration, becomes

\[r^2 y = D_1 e^{\beta/r}\]

or

\[r^2 \frac{dT}{dr} = D_1 e^{\beta/r}\]

Integrating again gives

\[T = -D_1 \left( \frac{1}{\beta} e^{\beta/r} \right) + D_2\]

The two constants of integration are determined from the boundary conditions \( T = T_\infty \) as \( r \to \infty \) and \( T = T_0 \) at \( r = R \). The final result is

\[\frac{T - T_\infty}{T_0 - T_\infty} = \frac{1 - e^{\beta/r}}{1 - e^{\beta/R}}\]  

(B.27)

The heat flow at the surface of the sphere is

\[4\pi R^2 \left[ \rho \overline{c}_p u_r T - k \frac{dT}{dr} \right]_{r = R}\]  

(B.28)

In the case in which we can neglect the velocity \( u_r \), which corresponds to assuming a very dilute system [e.g., (B.20)], the original shell energy balance gives

\[\frac{d}{dr} \left( 4\pi r^2 q_r \right) = 0\]  

(B.29)

which, with the use of Fourier’s law, \( q_r = -k \partial T / \partial r \), gives (B.26) with \( u_r = 0 \). Solving that equation, namely
subject to $T = T_\infty$ as $r \to \infty$ and $T = T_0$ at $r = R$ produces the steady-state temperature profile,

$$\frac{T - T_\infty}{T_0 - T_\infty} = \frac{R}{r} \quad (B.31)$$

by direct analogy to (B.21). The heat flux at the sphere's surface is just

$$q_R = \frac{k}{R} (T_0 - T_\infty) \quad (B.32)$$

Clearly, if $T_0 > T_\infty$, $q_R > 0$, and vice versa.

Let us say that the transfer of species $A$ to or from the sphere is accompanied by heat generation or consumption in the particle, such as if species $A$ is condensing or evaporating. Let $\Delta h$ be the enthalpy change per mole of $A$. Then if the steady-state heat flux to or from the sphere is that due to the heat consumed or generated by species $A$, and if the concentration of $A$ is sufficiently small that the convective contribution to the heat flux at the sphere surface can be neglected,

$$-4\pi R^2 N_A \Delta h = 4\pi R^2 q_R \quad (B.33)$$

### B.4 Characteristic Times

We have just been obtaining expressions for steady-state profiles of mole fraction and temperature around a sphere in an infinite fluid. If conditions are changing in time, the appropriate unsteady-state equations are needed. In such a case it will always be necessary to evaluate first the characteristic times of the processes occurring to see if phenomena are taking place on vastly different time scales. For example, we noted above that if the characteristic time to achieve a steady-state profile is very short compared to other times in the system, steady-state profiles may be assumed to exist at any instant of time.

For a spherical particle of radius $R$, the characteristic times for relaxation of the temperature and concentration profiles in the gas phase to their steady-state values are

$$\tau_h = \frac{R^2}{\alpha} \quad (B.34)$$

$$\tau_m = \frac{R^2}{D_{AB}} \quad (B.35)$$

where $\alpha = k/\rho c_p$, the thermal diffusivity. The characteristic time for heat conduction within the sphere is

$$\tau_{hp} = \frac{R^2}{\alpha_p} \quad (B.36)$$
TABLE 1.11 CHARACTERISTIC TIMES FOR HEAT AND
MASS TRANSFER INVOLVING A SPHERICAL PARTICLE
IN AIR*

<table>
<thead>
<tr>
<th>Material</th>
<th>$\tau_{hp} = \frac{\alpha}{\alpha_p}$</th>
<th>$\tau_m = \frac{\alpha}{D_{AB}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organics</td>
<td>200</td>
<td>2-4</td>
</tr>
<tr>
<td>Water</td>
<td>90</td>
<td>0.86</td>
</tr>
<tr>
<td>Metals</td>
<td>5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

* $\tau_h = R^2/\alpha$, heat conduction in gas phase; $\tau_m = R^2/D_{AB}$, diffusion in gas phase; $\tau_{hp} = R^2/\alpha_p$, heat conduction in particle.

where $\alpha_p = k_p/\rho_p c_p$. Table 1.11 compares the characteristic times for spherical particles having the properties of organics, water, and metals. We see that the characteristic time for equilibration of the temperature profile in the particle is generally considerably longer than that for the gas phase. The characteristic times for relaxation of the temperature and concentration profiles in the gas phase are the same order of magnitude. The large value of $\tau_{hp}/\tau_h$ suggests that any heat released at the particle’s surface is conducted primarily outward. As combustion, for example, begins, the particle surface temperature rises until the rate of outward heat conduction balances the rate of heat release. The formation of the external temperature and vapor concentration profiles occurs simultaneously on approximately the same time scales. Consequently, the steady-state fluxes of energy and mass may be related by a steady-state energy balance, such as in (B.33), to determine the surface temperature during the combustion of the particle.

Although we do not yet introduce characteristic times for the rate of change of the particle size, due, for example, to consumption by combustion reactions or growth by vapor condensation, we will see later that such times are generally considerably longer than those for heat and mass transfer in the vapor phase. Thus the gas-phase temperature and concentration profiles may be assumed to be in a pseudo-steady state at any instant of time.

APPENDIX C ELEMENTS OF PROBABILITY THEORY

For processes that occur under turbulent flow conditions it is impossible to predict the exact values of variables at any time or location; consequently, it is necessary to analyze such situations within the language of random variables. The main process of interest to us in this book that falls in this category is turbulent combustion.

C.1 The Concept of a Random Variable

Think of a laboratory experiment the result of which is unknown until the experiment has been completed, as opposed to an experiment the result of which can be predicted precisely knowing all the conditions beforehand (of course, in the latter case we probably
would not want to perform the experiment in the first place if we knew what the outcome would be). Fortunately (or maybe unfortunately), we usually do not know the result of an experiment until it is finished. Let us call the result of such an experiment an event. There may be a discrete number or a continuous spectrum of possible events, or outcomes, but the most we might be able to say about which event will result from a particular trial is the probability of observing each possible event.

We have now introduced a concept, probability, that we must define in order to be more precise about the outcomes of our experiment. Let us write Prob \( \{ X \} = P(X) \) to signify the probability that an event \( X \) occurs. Even though \( X \) denotes an outcome rather than a number, \( P(X) \) is a number (i.e., the probability that \( X \) occurs). Now, how do we define probability? We can only define probability on the basis of our physical reasoning about the process the outcome of which may be \( X \). Nevertheless, we can set down some general rules to help us determine the outcome probabilities for a particular process.

Intuitively, we would say that the probability of a certain event is 1, while the probability of an event that cannot occur is zero. Also, if there are two mutually exclusive events \( X_1 \) and \( X_2 \), the probability of obtaining either \( X_1 \) or \( X_2 \) is the sum of the individual probabilities, \( P(X_1) \) and \( P(X_2) \). We can state the following axioms of probability theory formally:

1. \( P(X) \geq 0 \) (probability is nonnegative).
2. If \( X \) is certain, \( P(X) = 1 \).
3. If two events \( X_1 \) and \( X_2 \) are mutually exclusive,
   \[ \text{Prob} \{ X_1 \text{ or } X_2 \} = P(X_1) + P(X_2) \]

Consider for a moment the roll of a single die. Each of the outcomes corresponds to a number, the number being one of the integers 1, 2, \ldots, 6. We can let \( X \) denote the number that will result from the roll of the die; that is, \( X \) is a random variable that can assume the integer values 1, 2, \ldots, 6. If we throw the die \( n \) times and the value \( j \) occurs \( n_j \) times, it seems reasonable to define the probability of outcome \( j \) as

\[ \text{Prob} \{ X = j \} = P(X = j) = \lim_{n \to \infty} \frac{n_j}{n} \]

The random variable, which we have denoted by \( X \), is a symbol for the outcome of the event in which we are interested. In the die example, the random variable \( X \) assumes discrete values, the integers from 1 to 6. However, \( X \) can also denote the instantaneous value of a continuous variable, say the concentration in a flame at a given location and time. Even if the outcome of an event has no obvious numerical value, we can assign numerical values to the random variable \( X \) corresponding to the possible outcomes. For example, in the tossing of a coin, we can let \( X = 1 \) denote a head and \( X = 2 \) denote a tail.

It is customary to denote random variables by capital letters and to denote the values they may assume by the corresponding lowercase letters. Therefore, \( x \) denotes
one of the values that $X$ may assume. In the case of a throw of the die we could have written $P(X = x)$, where $x$ assumes the values 1 to 6.

The random variable $X$ is called a **discrete random variable** if it may assume a finite or a denumerably infinite set of values, denoted as $x_j, j = 1, 2, \ldots, N$. The probability that $X$ assumes the value $x_j$ is denoted by $p(j)$. $p(j)$ is called the **probability mass function** of the random variable $X$, because the values of $X$ may be thought of as being confined to the mass points $x_1, \ldots, x_N$. The probability mass function $p(j)$ has the following properties:

$$0 \leq p(j) \leq 1$$

$$\sum_{j=1}^{N} p(j) = 1$$

If $X$ is a **continuous random variable**, we define the **probability density function** $p(x)$ such that

$$p(x) \, dx = \text{Prob} \{ x < X \leq x + dx \}$$

where $p(x) \, dx$ may be thought of as the fraction of the total mass of $X$ that lies in the range $x$ to $x + dx$; that is, $p(x)$ is the **density** of $X$ in this region. The probability density function has the following properties:

$$0 \leq p(x) \leq 1$$

$$\int_{-\infty}^{\infty} p(x) \, dx = 1$$

We stress that $p(x)$ itself is not a probability; rather, $p(x) \, dx$ is a probability. Whatever the units of the random variable, the probability mass or density function is measured in (units)$^{-1}$.

We shall now introduce the **distribution function**. Consider the probability that a random variable $X$ will not exceed a given value $x$. Clearly, this probability is a function of the threshold value $x$. We call this function the distribution function and denote it by $F(x)$. For a discrete random variable $F(x_j)$ or $F(j)$ is the probability that $X \leq x_j$, where $x_1 < \cdots < x_N$. In terms of the probability mass function

$$F(j) = \sum_{i=1}^{j} p(i)$$

(C.1)

Let us return to the die-throwing experiment. For $x_1 = 1, p(1) = \frac{1}{6}$, so $F(1)$, the probability that $X \leq 1$ (clearly, $X$ cannot be less than 1, but only exactly equal to 1), is $\frac{1}{6}$. At $x = 1$, $F(j)$ jumps from 0 to $\frac{1}{6}$, just as at $x = 2$, $F(j)$ jumps from $\frac{1}{6}$ to $\frac{1}{3}$. Finally, $F(6) = 1$, since no numbers higher than 6 can be obtained. Thus the distribution function for a discrete random variable is a staircase function of discrete jumps.

For a continuous random variable, $F(x)$ is related to the probability density function by
A distribution function $F(x)$ has the following general properties:

1. $0 \leq F(x) \leq 1$.
2. $\lim_{x \to -\infty} F(x) = 0$ and $\lim_{x \to \infty} F(x) = 1$.
3. As $x$ increases, $F(x)$ must not decrease.
4. $\text{Prob} \{x_1 < X \leq x_2\} = F(x_2) - F(x_1)$.

Properties 1 and 2 follow since $F(x)$ is itself a probability and since the value of $X$ must lie somewhere on the $x$-axis. Clearly, as $x$ increases, the probability that $X \leq x$ must not decrease, since new intervals are continually being added to $x$. If these new intervals have probability zero, then $F(x)$ must at least remain constant. Property 4 follows from axiom 3, namely that

$$\text{Prob} \{X \leq x_2\} = \text{Prob} \{X \leq x_1\} + \text{Prob} \{x_1 < X \leq x_2\}$$

For a continuous random variable, this becomes

$$F(x_2) - F(x_1) = \int_{x_1}^{x_2} p(x) \, dx \quad (C.3)$$

At point $x$ where the derivative of $F(x)$ exists, the derivative is equal to the density $p(x)$ at that point:

$$p(x) = \frac{dF(x)}{dx} \quad (C.4)$$

In Figure 1.2 we illustrate probability mass and density functions and their associated distribution functions. We also show the region corresponding to the probability that $x_1 < X \leq x_2$.

### C.2 Properties of Random Variables

We shall now consider special properties of random variables, namely, their expectations. The expected value of the random variable $X$ is denoted by $E(X)$ and is also called the mean of $X$. The expected value is computed by

$$E(X) = \begin{cases} 
\sum_{j=1}^{N} x_j p(j) & \text{(discrete)} \\
\int_{-\infty}^{\infty} xp(x) \, dx & \text{(continuous)}
\end{cases} \quad (C.5)$$
The expected value of a function of $X, f(X)$, is found from

$$E[f(X)] = \begin{cases} \sum_{j=1}^{N} f(x_j) p(j) & \text{(discrete)} \\ \int_{-\infty}^{\infty} f(x) p(x) \, dx & \text{(continuous)} \end{cases} \quad (C.7)$$

**Example 1.5 The Poisson Distribution**

Let the discrete random variable $X$ assume the values $j = 0, 1, 2, \ldots$ with probability mass function (the Poisson distribution)

$$p(j) = \frac{\lambda^j}{j!} e^{-\lambda} \quad \lambda > 0$$
Appendix C  Elements of Probability Theory

Compute the expected value of $X$ using (C.5):

$$E(X) = \sum_{j=0}^{\infty} \frac{\lambda^j}{j!} e^{-\lambda} = \lambda e^{-\lambda} \sum_{j=1}^{\infty} \frac{\lambda^{j-1}}{(j-1)!}$$

$$= \lambda e^{-\lambda} \sum_{k=0}^{\infty} \frac{\lambda^k}{k!} = \lambda e^{-\lambda} = \lambda$$

**Example 1.6 The Binomial Distribution**

Let the discrete random variable $X$ assume the values $j = 0, 1, 2, \ldots, N$ with probability mass function (the binomial distribution)

$$p(j) = \frac{N!}{j!(N-j)!} p^j (1-p)^{N-j} \quad 0 < p < 1$$

Compute the expected value of $X$.

$$E(X) = \sum_{j=0}^{N} \frac{N!}{j!(N-j)!} p^j (1-p)^{N-j}$$

$$= \sum_{j=1}^{N} \frac{N!}{j!(N-j)!} p^j (1-p)^{N-j}$$

$$= Np \sum_{j=1}^{N} \frac{(N-1)!}{(j-1)! (N-j)!} p^{j-1} (1-p)^{N-j}$$

$$= Np \sum_{j=0}^{N-1} \frac{(N-1)!}{j! (N-1-j)!} p^j (1-p)^{N-1-j}$$

$$= Np \left[ p + (1-p) \right]^{N-1} = Np$$

The general expectations of probability distributions are the *moments* of the distribution, of which the mean is a special case. We shall define the expectation $E(X')$ as the $r$th noncentral moment of $X$. We shall use the notation $\mu_r'$ for this moment. Thus for discrete and continuous random variables,

$$\mu_r' = \sum_{j=0}^{N} x_j' p(j) \quad (C.9)$$

$$= \int_{-\infty}^{\infty} x' p(x) \, dx \quad (C.10)$$

By definition, $\mu_0' = 1$, and $\mu_r'$ is the mean of $X$. We shall define the expectation $E[(X - \mu_r')]$ as the $r$th central moment of $X$, that is, the $r$th moment about the mean $\mu_r'$. Thus, denoting the central moments by $\mu_r$,

$$\mu_r = \sum_{j=0}^{N} (x_j - \mu_r') p(j) \quad (C.11)$$

$$= \int_{-\infty}^{\infty} (x - \mu_r') p(x) \, dx \quad (C.12)$$
From the definition of the central moments, \( \mu_0 = 1 \) and \( \mu_1 = 0 \). The second central moment \( \mu_2 \) is called the variance of the distribution and is often denoted by \( \sigma^2 \). \( \mu_3 \) is a measure of the skewness of the distribution about the mean, and \( \mu_3 = 0 \) if the distribution is symmetric. \( \mu_4 \) is a measure of the distortion from a normal (Gaussian) distribution resulting in a low center and high ends of the distribution or a high center and low ends, that is, a measure of the flatness of the distribution.

The two most important moments of a distribution are the mean \( \mu_1 \) and the variance \( \mu_2 \). The nonnegative square root of the variance, usually denoted \( \sigma \), is called the standard deviation of the distribution. The standard deviation \( \sigma \) has the same units as the random variable \( X \) and is often used as a measure of the dispersion of a distribution about its mean value.

Two other parameters often used to characterize distributions are the coefficient of variation \( \nu \), defined as the ratio of the standard deviation to the expected value,

\[
\nu = \frac{\sigma}{\mu_1} \tag{C.13}
\]

and the coefficient of skewness \( \gamma \), given by

\[
\gamma = \frac{\mu_3}{\sigma^3} \tag{C.14}
\]

The coefficient of skewness \( \gamma \) measures the extent to which a distribution departs from a symmetric distribution [one for which \( F(a-x) = 1 - F(a+x) = \text{Prob}\{X = a+x\} \)]. In a symmetric distribution all the central moments of odd order equal zero. Thus each central moment of odd order serves as a measure of asymmetry of the distribution. The coefficient of skewness expresses the third central moment relative to the standard deviation. \( \gamma \) may be positive or negative, giving rise to what is called positive or negative asymmetry.

### C.3 Common Probability Distributions

We shall now present several of the more common discrete and continuous probability distributions that arise in the analysis of physical system. The distributions are summarized in Tables 1.12 and 1.13.

**Example 1.7 The Binomial Distribution**

Let us derive the mean and variance of the binomial distribution shown in Table 1.12. We can describe a sequence of \( n \) Bernoulli trials in terms of \( n \) independent random variables \( X_1, X_2, \ldots, X_n \), where \( X_i = 1 \) if the \( i \)th trial is successful and \( X_i = 0 \) if unsuccessful. Each variable \( X_i \) has the probability mass function

\[
\text{Prob}\{X_i = 1\} = p(1) = p
\]
\[
\text{Prob}\{X_i = 0\} = p(0) = q = 1 - p
\]
TABLE 1.12 SOME COMMON PROBABILITY MASS FUNCTIONS

<table>
<thead>
<tr>
<th>Name</th>
<th>Probability mass function</th>
<th>Moments</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binomial</td>
<td>[ p(m) = \binom{n}{m} p^m q^{n-m}, \quad m = 0, 1 \ldots, n ]</td>
<td>[ \mu'_1 = np ]</td>
<td>[ \mu'_1 = npq + n^2p^2 ]</td>
</tr>
<tr>
<td></td>
<td>[ \mu'_2 = npq ]</td>
<td>[ \mu_2 = npq ]</td>
<td>[ \mu_2 = npq ]</td>
</tr>
<tr>
<td>Poisson</td>
<td>[ p(j) = \frac{\lambda^j e^{-\lambda}}{j!}, \quad \lambda &gt; 0, \quad j = 0, 1, 2, \ldots ]</td>
<td>[ \mu'_1 = \lambda ]</td>
<td>[ \mu'_1 = \lambda(\lambda + 1) ]</td>
</tr>
<tr>
<td></td>
<td>[ \mu'_2 = \lambda ]</td>
<td>[ \mu_2 = \lambda ]</td>
<td>[ \mu_2 = \lambda ]</td>
</tr>
</tbody>
</table>

The binomial distribution arises when an event has two possible outcomes, the probability of the first outcome (success) being \( p \) and the second (failure) being \( q = 1 - p \), and the event is repeated \( n \) times. \( p(m) \) represents the probability that in \( n \) trials there will be \( m \) successes. Each event is assumed independent of the others, and the probability of success and failure are the same for every trial. An experiment of this type is called a sequence of Bernoulli trials.

Consider random events occurring in time, such as radioactive disintegrations or incoming telephone calls to an exchange. Each event is represented by a point on the time axis, and we are interested in the probability that we shall discover exactly \( j \) points in an interval of fixed length if the average rate of occurrence of points in that interval is \( \lambda \). Events occur independently, obtained as the limit of the binomial distribution as \( n \) becomes large with \( np = \lambda \).
<table>
<thead>
<tr>
<th>Name</th>
<th>Probability density function</th>
<th>Moments</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform</td>
<td>( p(x) = \frac{1}{b - a}, \ a \leq x \leq b )</td>
<td>( \mu_r = \frac{b^{r+1} - a^{r+1}}{(r+1)(b-a)} )</td>
<td>( X ) has a uniform likelihood of being found anywhere on the segment of the real line between ( x = a ) and ( x = b ). The simplest case of a continuous random variable.</td>
</tr>
<tr>
<td></td>
<td>0, ( x &lt; a, x &gt; b )</td>
<td>( \mu_2 = (b - a)^2/12 )</td>
<td></td>
</tr>
<tr>
<td>Normal (Gaussian)</td>
<td>( p(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{1}{2} \left(\frac{x - \mu}{\sigma}\right)^2\right] ), ( -\infty &lt; x &lt; \infty )</td>
<td>( \mu_4 = (b - a)^4/80 )</td>
<td>The distribution approached by the sum of a large number of independent random variables under most conditions, and usually describing experimental errors. Approached as the limit of the binomial and Poisson distributions.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \mu_2 = \sigma^2 + \mu^2 )</td>
<td></td>
</tr>
<tr>
<td>Exponential</td>
<td>( p(x) = ae^{-ax}, x \geq 0 )</td>
<td>( \mu_r = \frac{r!}{a^r} )</td>
<td>Consider events occurring randomly in time, such as radioactive disintegration or incoming telephone calls to an exchange. Each event is represented by a point on the time axis, and we are interested in the density function for ( X ), the time elapsed between occurrences, where the</td>
</tr>
</tbody>
</table>
events occur at an average rate of $a$ per time. Let $p(x)\,dx$ = probability that the time elapsed between two events is between $x$ and $x+dx$. This distribution also describes the residence time density of a particle in an ideally mixed vessel.

Consider the sum $Z$ of $n$ independent random variables, $Z = X_1 + X_2 + \cdots + X_n$, each exponentially distributed with average rate $a$. Then $p_n(z)$, the distribution of $Z$, is given by the gamma distribution. For example, $Z$ can represent the residence time of a particle in a series of $n$ ideally mixed vessels.

Consider the probability that exactly $n$ events will occur in a time interval $x$ if the time between individual events is exponentially distributed. In terms of the gamma distribution, if $Z_n$ is the total time taken for $n$ events to occur, then $Z_n > x$ and $Z_{n+1} \leq x$. The probability that exactly $n$ events have occurred in time $x$ is $F_{Z_n}(x) - F_{Z_{n+1}}(x)$, where $F_Z(x)$ is the distribution function for the gamma density. Then $p_n(x)$ for the Poisson distribution is $p_n(x) = F_{Z_n}(x) - F_{Z_{n+1}}(x)$. 

\begin{align*}
\text{Gamma} \\
\quad p_n(z) &= \frac{a^n z^{n-1} e^{-az}}{(n-1)!}, \\
\quad z \geq 0 \\
\mu_1 &= \frac{n}{a} \\
\mu_2 &= \frac{n(n+1)}{a^2} \\
\mu_3 &= \frac{n}{a^3} \\
\mu_4 &= \frac{n(n+1)}{a^4} \\
\mu_5 &= \frac{n(n+1)(n+2)}{a^5} \\
\mu_6 &= \frac{n(n+1)(n+2)(n+3)}{a^6}
\end{align*}

\begin{align*}
\text{Poisson} \\
\quad p_n(x) &= \frac{(ax)^n}{n!} e^{-ax}, \\
\quad x \geq 0 \\
\mu_1 &= ax \\
\mu_2 &= (ax)^2 + ax \\
\mu_3 &= (ax)^3 + 3(ax)^2 + ax \\
\mu_4 &= (ax)^4 + 6(ax)^3 + ax \\
\mu_5 &= (ax)^5 + 10(ax)^4 + ax \\
\mu_6 &= (ax)^6 + 15(ax)^5 + ax
\end{align*}
The total number of successes in \( n \) trials is simply the sum of the \( X_i \)s,
\[
Z = X_1 + X_2 + \cdots + X_n
\]
since \( X_i = 0 \) if the \( i \)th trial is a failure.

We can determine the mean and variance of the number of successes \( Z \). The mean of \( Z \) is simply the sum of the means, which are all identical to that of \( X_1 \):
\[
E(Z) = nE(X_i)
\]

Since the \( X_i \)s are independent, the variance of \( Z \) is the sum of the individual variances which are all equal to that of \( X_1 \). Since \( E(X_i) = 0 \cdot q + 1 \cdot p = p \),
\[
E(Z) = np
\]

Also, \( E[(X_i - p)^2] = p^2q + q^2p = pq \). Thus
\[
E[(Z - np)^2] = npq
\]

We are often interested in obtaining the probability density of a random variable \( Y \) which is some given function of a random variable \( X \) that has a known probability density \( p_X(x) \). Let us say that we want to compute
\[
Y = f(X) \tag{C.15}
\]
The unknown density is written as \( p_Y(y) \). If \( X \) changes its value by \( dx \) and the corresponding change in \( Y \) is \( dy \), the probability of finding \( X \) between \( x \) and \( x + dx \) is the same as observing \( Y \) between the corresponding \( y \) and \( y + dy \). Therefore,
\[
p_X(x) \, dx = p_Y(y) \, dy \tag{C.16}
\]
which really should be written as
\[
p_X(x) \, |dx| = p_Y(y) \, |dy| \tag{C.17}
\]
since the probabilities are equal to the magnitudes of the areas under \( dx \) and \( dy \). Thus
\[
p_Y(y) = \frac{p_X(x)}{|dy/dx|} = \frac{p_X(x)}{|df/dx|} \tag{C.18}
\]
Since \( p_Y(y) \) is a function of \( y \), the right-hand side of (C.18) must be expressed in terms of \( y \). Assuming that (C.15) can be inverted, we can express \( x \) in terms of \( y \) by \( x = f^{-1}(y) \) in (C.18).

**APPENDIX D TURBULENT MIXING**

Mixing plays an important role in combustion. The fuel and air must be brought into rapid and intimate contact for the combustion reactions to occur. Since most combustion systems are operated in the turbulent mode, to understand the role of mixing in combustion, we must devote some attention to turbulent mixing. Turbulence cannot maintain itself without a source of energy, and we will find that energy must be supplied to achieve the high mixing rates desired in combustion systems.
D.1 Scales of Turbulence

Turbulence can be viewed as a flow characterized by chaotic, random motions on length scales that vary from those of the container in which the flow exists down to scales at which the viscosity of the fluid prevents the generation of even smaller scales by dissipating small-scale energy into heat. The largest scales, or eddies, are responsible for most of the transport of momentum and species. A classic picture of turbulence, due to Kolmogorov, is one in which the energy is transferred from larger eddies to smaller ones, where it is ultimately dissipated. Since the small-scale motions have correspondingly small time scales, it can be assumed that these motions are statistically independent of the relatively large scale, slower motions. In such a case, the nature of the small-scale motion should depend only on the rate at which it is supplied with energy by the large-scale motion and on the viscosity of the fluid. Since the small-scale motions adjust rapidly to changes in this cascade of energy, the instantaneous rate of dissipation is equal to the rate of energy supplied from the large-scale motion.

If the properties of the small-scale eddies are independent of those of the large scale, these properties can be dependent only on viscosity (since dissipation depends on viscosity) and the rate of energy transfer $\epsilon (\text{cm}^2 \text{s}^{-3})$ into the small eddies. This is Kolmogorov's first hypothesis. Between the large energy-containing eddies and the small dissipation eddies there is a region of eddies containing little energy and dissipating little energy whose properties must depend solely on $\epsilon$. This region is called the inertial subrange and constitutes Kolmogorov's second hypothesis.

In the smallest eddies, the parameters governing the small-scale motion are the dissipation rate per unit mass $\epsilon (\text{cm}^2 \text{s}^{-3})$ and the kinematic viscosity $\nu (\text{cm}^2 \text{s}^{-1})$. With these two parameters, one can define characteristic length, time, and velocity scales as follows:

$$\eta = \left( \frac{\nu^3}{\epsilon} \right)^{1/4} \quad \tau = \left( \frac{\nu}{\epsilon} \right)^{1/2} \quad \nu = \left( \nu \epsilon \right)^{1/4}$$

These scales are referred to as the Kolmogorov microscales of length, time, and velocity. Note that the Reynolds number formed from $\eta$ and $\nu$, $\eta \nu / \nu = 1$, indicating that the small-scale motion is indeed viscous and that the rate of dissipation $\epsilon$ adjusts itself to the energy supply through adjustment of the length and velocity scales.

The largest scale of turbulent motion, $L$, corresponds approximately to the length scale of the container (e.g., the diameter of a pipe in turbulent pipe flow). The rate of generation of energy in the large-scale motion, and hence the rate of dissipation by the small-scale motion, $\epsilon$, can be estimated as the product of the kinetic energy per unit mass of the large-scale turbulence, proportional to $u^2$, and the rate of transfer of that energy, $u/L$ (i.e., $u^3/L$), where $u$ is a characteristic large-scale velocity. Thus $\epsilon \sim u^3/L$. This estimate implies that the large-scale eddies lose a significant fraction of their kinetic energy, $u^2/2$, within one “turnover” time $L/u$. The Reynolds number of the turbulent flow is $\text{Re} = uL/\nu$. On this basis, with $\epsilon \sim u^3/L$, we have that

$$\frac{\eta}{L} \sim \text{Re}^{-3/4} \quad \frac{\tau u}{L} \sim \text{Re}^{-1/2} \quad \frac{\nu}{u} \sim \text{Re}^{-1/4}$$
and since \( Re \gg 1 \), we see that the length, time, and velocity scales of the smallest eddies are very much smaller than those of the largest eddies, and that the separation increases as the Reynolds number increases.

### D.2 Statistical Properties of Turbulence

Turbulence is *stationary* if all its statistical properties are independent of time. The variables themselves, such as the velocity components, are indeed functions of time, but if the turbulence is stationary, their statistical properties, such as the mean, are independent of time. Turbulence is *homogeneous* if all statistical properties are independent of location in the field. Turbulence is *isotropic* if all statistical properties are independent of the orientation of the coordinate axes. Kolmogorov's hypothesis was that the small-scale eddies are isotropic.

The velocity component in direction \( i \) at location \( x \), \( u_i(x, t) \), is a random function of time \( t \). The mean of such a random function is computed in theory by an ensemble average in which the function is averaged over an infinite ensemble of identical experiments. Unfortunately, in the real world we cannot repeat an experiment indefinitely to obtain an ensemble average. In some cases we can replace the ensemble average with a time average over a single experiment, for example,

\[
\bar{u}_i(x) = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0+T} u_i(x, t) \, dt
\]  

A direct correspondence between the ensemble average, denoted by \( \langle u_i(x, t) \rangle \), and \( \bar{u}_i(x) \), exists only when \( u_i \) is a stationary function, because then \( \langle u_i \rangle \) is independent of \( t \) and \( \bar{u}_i \) is independent of \( t_0 \).

It is common practice to decompose a turbulent quantity such as the velocity component \( u_i \) into its mean \( \bar{u}_i \), and a random component, \( u'_i \). The mean kinetic energy per unit mass is then \( \frac{1}{2} (\bar{u}_1^2 + \bar{u}_2^2 + \bar{u}_3^2) = \frac{1}{2} (\bar{u}_1^2 + \bar{u}_2^2 + \bar{u}_3^2) + \frac{1}{2} (u'_1^2 + u'_2^2 + u'_3^2) \). The *intensity* of turbulence, say in direction \( i \), is defined by \( \frac{(u'_i)^{1/2}}{\bar{u}_i} \), a measure of the size of the fluctuations relative to the mean velocity component at the same location.

The properties \( \bar{u}_i \) and \( u_i^{1/2} \) are based on a single velocity component at a single location and time. If we want to describe the time evolution of a random function like \( u_i(x, t) \) at point \( x \), we can define the Eulerian autocorrelation, \( \bar{u}_i(x, t) \ u_i(x, t + \tau) \), between the values of \( u_i \) at point \( x \) at times \( t \) and \( t + \tau \). Because we are generally interested in stationary turbulence, this correlation does not depend on the time origin \( t \), only on the time separation \( \tau \). We thus define the Eulerian temporal velocity autocorrelation coefficient by

\[
R_{ii}(\tau) = \frac{\bar{u}_i(x, t) \ u_i(x, t + \tau)}{u_i^2} \tag{D.3}
\]

where \( R_{ii}(0) = 1 \). Based on \( R_{ii}(\tau) \) we can define the Eulerian integral time scale \( T_E \) by

\[
T_E = \max_i \int_0^\infty R_{ii}(\tau) \, d\tau \tag{D.4}
\]
$T_E$ is a measure of the length of time over which the velocity at a point is correlated with itself.

In a similar vein, we can define the autocorrelation $\overline{u_i(x, t) u_i(x + r, t)}$ between the values of $u_i$ at time $t$ separated by a distance $r$, the corresponding spatial velocity autocorrelation coefficient,

$$S_{ii}(r) = \frac{\overline{u_i(x, t) u_i(x + r, t)}}{u_i^2}$$  \hspace{1cm} (D.5)

in homogeneous turbulence and the integral length scale (for scalar separation $r$)

$$L = \max_i \int_0^{\infty} S_{ii}(r) \, dr$$  \hspace{1cm} (D.6)

### D.3 The Microscale

These velocity autocorrelation coefficients have the general shape shown in Figure 1.3. Note that the integral time or length scale, the value of the integral, can be represented as shown. Also, the curvature of the autocorrelation coefficient at the origin can be used to define a characteristic time or length scale $\lambda$ by, for example (Tennekes and Lumley, 1972),

$$\left(\frac{d^2 R}{d\tau^2}\right)_{\tau=0} = -\frac{2}{\lambda^2}$$  \hspace{1cm} (D.7)

Expanding $R(\tau)$ in a Taylor series about the origin, we can write for small $\tau$,

$$R(\tau) \approx 1 - \frac{\tau^2}{\lambda^2}$$  \hspace{1cm} (D.8)

This scale, called the *microscale*, is thus the intercept of the parabola that matches $R(\tau)$.

*Figure 1.3* Velocity autocorrelation coefficients showing the integral time scale $T_E$ and the Taylor microscale $\lambda$. 

---

The text discusses the concept of turbulence mixing, focusing on the integral time scale $T_E$ and the microscale, which are key measures in understanding the dynamics of turbulent flows. The equations provided capture the autocorrelation of velocity fluctuations and how they relate to the integral length scale. The graphical representation further illustrates these concepts, showing how velocity autocorrelation coefficients vary with distance and time.
at the origin. Since \( u_i(t) \) is stationary, we can write

\[
0 = \frac{d^2}{dt^2} \overline{u_i^2} = 2u_i \frac{d^2 u_i}{dt^2} + 2 \overline{(du_i/dt)^2} \tag{D.9}
\]

Using (D.7)-(D.9), we find that

\[
\overline{(du_i/dt)^2} = \frac{2u_i^2}{\lambda^2} \tag{D.10}
\]

a relation that will turn out to be useful shortly.

Let us return to the discussion of the large and small scales of motion. The dissipation of energy at the small-scale end of the spectrum depends on several terms like \( (\partial u_i/\partial x_j)^2 \), most of which cannot be measured conveniently. Since the small-scale motions tend to be isotropic, it can be shown that the dissipation rate \( \epsilon \) in isotropic turbulence is given by (Hinze, 1959)

\[
\epsilon = 15\nu \overline{(\partial u_1/\partial x_1)^2} \tag{D.11}
\]

The coefficient 15 arises because of summing a number of terms like \( (\partial u_i/\partial x_j)^2 \). By analogy to (D.10) we define a length scale \( \lambda \) by (omitting the factor of 2)

\[
\overline{(\partial u_1/\partial x_1)^2} = \frac{u_i^2}{\lambda^2} \tag{D.12}
\]

The length scale in (D.12) is called the Taylor microscale in honor of G. I. Taylor who first defined (D.12). Note that in isotropic turbulence \( u_1^2 = u_2^2 = u_3^2 \). Thus, from (D.11) and (D.12),

\[
\epsilon = \frac{15\nu u_i^2}{\lambda^2} \tag{D.13}
\]

is a convenient estimate of \( \epsilon \).

A relation between \( \lambda \) and \( L \), the macroscopic length scale of the system, can be obtained if we equate the rate of production of turbulent energy by shear to the rate of viscous dissipation (Tennekes and Lumley, 1972),

\[
\frac{\overline{Au_1^3}}{L} = \frac{15\nu u_i^2}{\lambda^2} \tag{D.14}
\]

where \( A \) is an undetermined constant order of 1. The ratio \( \lambda/L \) is then

\[
\frac{\lambda}{L} = \left( \frac{15}{A} \right)^{1/2} \left( \frac{\overline{u_1^2}^{1/2} L}{\nu} \right)^{-1/2}
\]

\[
= \left( \frac{15}{A} \right)^{1/2} \text{Re}^{-1/2} \tag{D.15}
\]
Appendix D  Turbulent Mixing

Since $\text{Re} \gg 1$, the Taylor microscale $\lambda$ is always much smaller than the macroscopic length scale $L$ of the flow.

The Taylor microscale is not the smallest length scale in turbulence; that is the Kolmogorov microscale $\eta$. The Taylor microscale does not represent the eddy sizes at which dissipation effects dominate, which is $\eta$. Rather, $\lambda$ is defined on the basis of the characteristic length scale of the velocity gradients.

D.4 Chemical Reactions

Of primary interest to us is the assessment of chemical reaction rates when the reactants are embedded in a turbulent fluid and are inhomogeneously mixed. For a second-order reaction at constant temperature, if the chemical reaction rate is slow compared with the molecular diffusion rate (which determines how quickly local inhomogeneities are smoothed out), no effect of inhomogeneous mixing is observed and the reaction rate is that predicted on the basis of the spatial average concentrations. On the other hand, if the chemical reaction rate is fast compared with the molecular diffusion rate, the rate of reaction is limited by the rate at which the reactants can be brought together by molecular diffusion. Combustion reactions fall within the latter category.

We now derive the basic equations for predicting the mean concentrations of two reacting species, call them $A$ and $B$, in a turbulent flow. For a second-order isothermal reaction with rate constant $k$, the local, instantaneous rates of consumption of $A$ and $B$ are

$$\frac{\partial c_A}{\partial t} = -k c_A c_B$$  \hspace{1cm} (D.16)

$$\frac{\partial c_B}{\partial t} = -k c_A c_B$$  \hspace{1cm} (D.17)

If we let $c_A = \bar{c}_A + c'_A$ and $c_B = \bar{c}_B + c'_B$, and then substitute into (D.16) and (D.17) and average, we obtain the mean rates of consumption as

$$\frac{\partial \bar{c}_A}{\partial t} = -k(\bar{c}_A \bar{c}_B + c'_A c'_B)$$  \hspace{1cm} (D.18)

$$\frac{\partial \bar{c}_B}{\partial t} = -k(\bar{c}_A \bar{c}_B + c'_A c'_B)$$  \hspace{1cm} (D.19)

We see that the local mean rate of disappearance of $A$ and $B$ is $-k \bar{c}_A \bar{c}_B$ only if $\bar{c}_A \bar{c}_B \gg c'_A c'_B$ for the particular conditions in question. Let us see if we can determine the conditions for this approximation to hold. To do so we need to examine the continuity equation that governs the mean of the product of the concentration fluctuations of $A$ and $B$, $c'_A c'_B$. Although the general equation governing $c'_A c'_B$ is rather complicated, we can consider the behavior of $c'_A c'_B$ in the absence of any appreciably large gradients. In that case the contributions to the local rate of change of the correlation $c'_A c'_B$ arise only from
the chemical reaction and molecular diffusion (Donaldson and Hilst, 1972),
\[
\frac{\partial c_A' c_B'}{\partial t} = \left( \frac{\partial c_A' c_B'}{\partial t} \right)_{\text{chem}} - 2D \left( \frac{\partial c_A'}{\partial x_i} \frac{\partial c_B'}{\partial x_i} \right)
\] (D.20)

where we have assumed for simplicity that both \(A\) and \(B\) have molecular diffusivity \(D\). The first term on the right-hand side of (D.20) represents the generation of the correlation \(c_A' c_B'\) by the chemical reaction, and the second term is the decay of the correlation by the action of molecular diffusion.

To derive the second term on the right-hand side of (D.20), begin with the species conservation equations, (B.7), expressed here as (assuming \(D_A = D_B = D\))
\[
\frac{\partial c_A}{\partial t} + u_i \frac{\partial c_A}{\partial x_i} = D \frac{\partial^2 c_A}{\partial x_i \partial x_i}
\]
(D.21a)
\[
\frac{\partial c_B}{\partial t} + u_i \frac{\partial c_B}{\partial x_i} = D \frac{\partial^2 c_B}{\partial x_i \partial x_i}
\]
(D.21b)

where \(u_i \partial c / \partial x_i\) is a shorthand notation for \(u \cdot \nabla c\) and \(\partial^2 c / \partial x_i \partial x_i\) for \(\nabla^2 c\). Thus the repeated index \(i\) denotes the summation over the three components of the term. If the concentration field is homogeneous, the spatial gradient of any mean quantity is zero. Using \(c_A = \bar{c}_A + c_A'\) and \(c_B = \bar{c}_B + c_B'\) in (D.21) yields
\[
\frac{\partial}{\partial t} (\bar{c}_A + c_A') + u_i \frac{\partial}{\partial x_i} (\bar{c}_A + c_A') = D \frac{\partial^2}{\partial x_i \partial x_i} (\bar{c}_A + c_A')
\]
(D.22a)
\[
\frac{\partial}{\partial t} (\bar{c}_B + c_B') + u_i \frac{\partial}{\partial x_i} (\bar{c}_B + c_B') = D \frac{\partial^2}{\partial x_i \partial x_i} (\bar{c}_B + c_B')
\]
(D.22b)

Multiply (D.22a) by \(c_B'\) and (D.22b) by \(c_A'\) and add the resulting equations,
\[
c_B' \frac{\partial}{\partial t} (\bar{c}_A + c_A') + c_A' \frac{\partial}{\partial t} (\bar{c}_B + c_B') + u_i c_B' \frac{\partial}{\partial x_i} (\bar{c}_A + c_A') + u_i c_A' \frac{\partial}{\partial x_i} (\bar{c}_B + c_B')
\]
\[
= D c_B' \frac{\partial^2}{\partial x_i \partial x_i} (\bar{c}_A + c_A') + D c_A' \frac{\partial^2}{\partial x_i \partial x_i} (\bar{c}_B + c_B')
\]
(D.23)

Now take the mean of this equation. Note that the means of \(c_A'\) and \(c_B'\), by themselves, are by definition zero. The terms in (D.23) become, upon averaging,
\[
\frac{\partial}{\partial t} (\bar{c}_A + c_A') + c_A' \frac{\partial}{\partial x_i} (\bar{c}_B + c_B') = \frac{\partial}{\partial t} c_A' c_B'
\]
\[
u \frac{\partial}{\partial x_i} (\bar{c}_A + c_A') = \nu \frac{\partial}{\partial x_i} (\bar{c}_B + c_B') = 0
\]
\[
D c_B' \frac{\partial^2}{\partial x_i \partial x_i} (\bar{c}_A + c_A') + D c_A' \frac{\partial^2}{\partial x_i \partial x_i} (\bar{c}_B + c_B') = -2D \frac{\partial c_A'}{\partial x_i} \frac{\partial c_B'}{\partial x_i}
\]
Thus (D.23) reduces to
\[ \frac{\partial}{\partial t} c'_A c'_B = -2D \frac{\partial c'_A}{\partial x_i} \frac{\partial c'_B}{\partial x_i} \] (D.24)

By analogy to (D.10), we can represent the right-hand side of (D.24) by means of a microscale \( \lambda_c \) (Corrsin, 1957)
\[ \frac{\partial c'_A}{\partial x_i} \frac{\partial c'_B}{\partial x_i} = \frac{c'_A c'_B}{\lambda_c^2} \] (D.25)

where the additional factor of 3 results from the summation over the 3 coordinate components. Thus the characteristic time for the destruction of the correlation \( c'_A c'_B \) by molecular diffusion is
\[ \tau_d = \frac{\lambda_c^2}{12D} \] (D.26)

The effect of the first term on the right-hand side of (D.20) can be seen by examining the local equation governing \( \overline{c_A c_B} \) due only to chemistry.
\[ \frac{\partial}{\partial t} (\overline{c_A c_B}) = -k(\overline{c_A} + \overline{c_B})(\overline{c_A c_B} + c'_A c'_B) \] (D.27)

From this equation we see that the effect of the chemical reaction is to drive \( \overline{c_A c_B} \) to the negative of \( c'_A c'_B \), or vice versa, with a characteristic time
\[ \tau_c = \frac{1}{k(\overline{c_A} + \overline{c_B})} \] (D.28)

Equation (D.27) states that the reaction between \( A \) and \( B \) will always stop (i.e., \( \overline{c_A c_B} + c'_A c'_B = 0 \)) short of the exhaustion of \( A \) or \( B \) unless \( A \) and \( B \) are perfectly mixed in the turbulent field. The reason for this is that in the absence of diffusion, if \( A \) and \( B \) are not perfectly mixed to start with, there is no mechanism to replenish the reactants once they have been consumed in a local volume element.

From (D.25) if the concentration microscale \( \lambda_c \) is small enough and the reaction rate is slow enough, the dissipation term in (D.20) will dominate and \( c'_A c'_B \approx 0 \). Physically, this means that molecular diffusion is rapid enough to keep \( A \) and \( B \) well mixed locally. On the other hand, if \( \lambda_c \) is large and the reaction rate is fast, the generation of \( c'_A c'_B \) by the chemistry will be dominant and \( c'_A c'_B \) will tend toward \(-\overline{c_A c_B}\), indicating that the two species are poorly mixed. In this case the overall rate of reaction in the flow is governed not by the rate of reaction but by the rate at which \( A \) and \( B \) are brought together locally by molecular diffusion.

For gases at sufficiently high Reynolds number, the concentration microscale \( \lambda_c \) is related to the Taylor microscale by (Corrsin, 1957)
\[ \frac{\lambda_c}{\lambda} \approx 2 \frac{D}{\nu} \] (D.29)
Using (D.26) and (D.29), the decay time for concentration fluctuations is related to the Taylor microscale by

\[ \tau_d \approx \frac{\lambda^2}{6\nu} \]  

(\text{D.30})

**APPENDIX E UNITS**

The units used in this book are largely those of the International System of Units (SI). The SI system of units consists of a set of basic units, prefixes to extend the range of values that can be handled conveniently with the units, and a set of derived units. All the derived units can be expressed in terms of the basic units, although each derived unit has its own symbol that can be used for conciseness. The prefixes can be used with either the basic units or the derived units.

**TABLE 1.14 DERIVED SI UNITS**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Name of unit</th>
<th>Unit symbol or abbreviation</th>
<th>Relation to basic units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>hertz</td>
<td>Hz</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>Angular velocity</td>
<td>radian per second</td>
<td>N</td>
<td>rad s⁻¹</td>
</tr>
<tr>
<td>Force</td>
<td>newton</td>
<td>N m⁻¹</td>
<td>kg m s⁻²</td>
</tr>
<tr>
<td>Surface tension</td>
<td>newton per meter</td>
<td>N m⁻¹</td>
<td>kg s⁻²</td>
</tr>
<tr>
<td>Pressure</td>
<td>pascal, newton per square meter</td>
<td>Pa, N m⁻²</td>
<td>kg m⁻¹ s⁻²</td>
</tr>
<tr>
<td>Viscosity</td>
<td>newton-second per square meter</td>
<td>N s m⁻²</td>
<td>kg m⁻¹ s⁻¹</td>
</tr>
<tr>
<td>Kinematic viscosity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusivity</td>
<td>meter squared per second</td>
<td>m² s⁻¹</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>Thermal diffusivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td>joule</td>
<td>J</td>
<td>kg m² s⁻²</td>
</tr>
<tr>
<td>Power</td>
<td>watt, joule per second</td>
<td>W, J s⁻¹</td>
<td>kg m² s⁻³</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>joule per kilogram degree</td>
<td>J kg⁻¹ K⁻¹</td>
<td>m² s⁻² K⁻¹</td>
</tr>
<tr>
<td>Gas constant</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enthalpy per unit mass</td>
<td>joules per kilogram</td>
<td>J kg⁻¹</td>
<td>m² s⁻²</td>
</tr>
<tr>
<td>Entropy per unit mass</td>
<td>joules per kilogram degree</td>
<td>J kg⁻¹ K⁻¹</td>
<td>m² s⁻² K⁻¹</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>joules per meter second degree</td>
<td>J m⁻¹ s⁻¹ K⁻¹</td>
<td>kg m⁻³ s⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Mass transfer coefficient</td>
<td>meter per second</td>
<td>m s⁻¹</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>Electric charge</td>
<td>coulomb</td>
<td>C</td>
<td>A s</td>
</tr>
<tr>
<td>Electromotive force</td>
<td>volt</td>
<td>V</td>
<td>kg m² A⁻¹ s⁻³</td>
</tr>
<tr>
<td>Electric field strength</td>
<td>volt per meter</td>
<td>V m⁻¹</td>
<td>kg m A⁻¹ s⁻³</td>
</tr>
<tr>
<td>Electric resistance</td>
<td>ohm</td>
<td>Ω</td>
<td>kg m² A⁻² s⁻²</td>
</tr>
<tr>
<td>Electric conductivity</td>
<td>ampere per volt meter</td>
<td>A V⁻¹ m⁻¹</td>
<td>A² s³ kg⁻¹ m⁻³</td>
</tr>
<tr>
<td>Electric capacitance</td>
<td>farad</td>
<td>F</td>
<td>A² s⁴ kg⁻¹ m⁻²</td>
</tr>
</tbody>
</table>
### TABLE 1.15 CONVERSION FACTORS TO SI UNITS

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Conversion factors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Length</strong></td>
<td></td>
</tr>
<tr>
<td>$10^{-6} \frac{m}{\mu m}$</td>
<td>$10^{-10} \frac{m}{\AA}$</td>
</tr>
<tr>
<td>$0.4536 \frac{kg}{lbm}$</td>
<td>$0.3048 \frac{m}{ft}$</td>
</tr>
<tr>
<td><strong>Time</strong></td>
<td></td>
</tr>
<tr>
<td>$3600 \frac{s}{h}$</td>
<td>$86,400 \frac{s}{day}$</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td></td>
</tr>
<tr>
<td>$0.5555 \frac{K}{^\circ R}$</td>
<td>$0.5555 \frac{K}{^\circ F}$</td>
</tr>
<tr>
<td>$1.0 \frac{K}{^\circ C}$</td>
<td></td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td></td>
</tr>
<tr>
<td>$3.785 \times 10^{-3} \frac{m^3}{gal (U.S.)}$</td>
<td></td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td></td>
</tr>
<tr>
<td>$10^3 \frac{kg \ m^{-3}}{g \ cm^{-3}}$</td>
<td></td>
</tr>
<tr>
<td><strong>Force</strong></td>
<td></td>
</tr>
<tr>
<td>$10^{-5} \frac{N}{dyn}$</td>
<td>$10^5 \frac{Pa}{bar}$</td>
</tr>
<tr>
<td>$1.0133 \times 10^5 \frac{Pa}{std \ atm}$</td>
<td>$133.3 \frac{Pa}{mmHg}$</td>
</tr>
<tr>
<td><strong>Energy</strong></td>
<td></td>
</tr>
<tr>
<td>$4.187 \frac{J}{cal}$</td>
<td>$4187 \frac{J}{kcal}$</td>
</tr>
<tr>
<td>$10^7 \frac{J}{erg}$</td>
<td>$1055 \frac{J}{Btu}$</td>
</tr>
<tr>
<td>$3.6 \times 10^6 \frac{J}{kWh}$</td>
<td></td>
</tr>
<tr>
<td>$2.685 \times 10^6 \frac{J}{hp \ h}$</td>
<td></td>
</tr>
<tr>
<td><strong>Power</strong></td>
<td></td>
</tr>
<tr>
<td>$4.187 \frac{W}{cal \ s^{-1}}$</td>
<td>$10^7 \frac{W}{erg \ s^{-1}}$</td>
</tr>
<tr>
<td>$745.8 \frac{W}{hp}$</td>
<td>$0.293 \frac{W}{Btu \ h^{-1}}$</td>
</tr>
<tr>
<td><strong>Specific energy</strong> (energy per unit mass)</td>
<td>$4187 \frac{J}{kg^{-1}}$</td>
</tr>
<tr>
<td>$4.187 \times 10^6 \frac{J \ kg^{-1}}{kcal \ g^{-1}}$</td>
<td></td>
</tr>
<tr>
<td>$2326 \frac{J \ kg^{-1}}{Btu \ lbm^{-1}}$</td>
<td></td>
</tr>
<tr>
<td>**Specific heat and gas constant$^a$</td>
<td>$4187 \frac{J \ kg^{-1} \ K^{-1}}{cal \ g^{-1} \ ^\circ C^{-1}}$</td>
</tr>
<tr>
<td><strong>Thermal conductivity</strong></td>
<td>$418.7 \frac{W \ m^{-1} \ K^{-1}}{cal \ s^{-1} \ cm^{-1} \ ^\circ C^{-1}}$</td>
</tr>
</tbody>
</table>

$^a$ Temperature difference

$^b$ Universal gas constant

\[ R = 8.314 \times 10^3 \ J \ kg^{-1} \ mol^{-1} \ K^{-1} \]

\[ = 1.987 \ cal \ g^{-1} \ mol^{-1} \ K^{-1} \]

\[ = 82.05 \ cm^{-1} \ atm \ g^{-1} \ mol^{-1} \ K^{-1} \]

\[ = 8.314 \ Pa \ m^3 \ g^{-1} \ mol^{-1} \ K^{-1} \]
The basic SI units are:

- **Length:** meter \( m \)
- **Mass:** kilogram \( kg \)
- **Time:** second \( s \)
- **Electric current:** ampere \( A \)
- **Temperature:** kelvin \( K \)

Some of the standard prefixes are:

- \( 10^{-12} : \) pico \( p \)
- \( 10^{-9} : \) nano \( n \)
- \( 10^{-6} : \) micro \( \mu \)
- \( 10^{-3} : \) milli \( m \)
- \( 10^{-2} : \) centi \( c \)
- \( 10^3 : \) kilo \( k \)
- \( 10^6 : \) mega \( M \)
- \( 10^9 : \) giga \( G \)
- \( 10^{12} : \) tera \( T \)

The symbol for the prefix is attached to the symbol for the unit. For example, \( 10^{-6} m = 1 \mu m \). This particular unit, the micrometer, is often referred to simply as a micron.

From time to time it will be more convenient to employ the centimeter \( (cm) \) as the basic unit of length and the gram \( (g) \) as the basic unit of mass. For example, mass density is usually expressed in terms of \( g \) \( cm^{-3} \). The derived units that are used in this book are listed in Table 1.14, and Table 1.15 lists several common conversion factors.

### PROBLEMS

1.1. The 1-hour NAAQS for carbon monoxide is 40 mg \( m^{-3} \). Convert this to ppm at standard temperature and pressure.

1.2. A solid-waste incinerator emits particulate matter at the NSPS rate of 0.18 g/dscm. The incinerator burns 50 metric tons per day \((1 \text{ metric ton} = 10^3 \text{ kg})\) and exhausts gases at a ratio of 20 kg of gases per kilogram of feed at atmospheric pressure and 453 K. Assume that the average molecular weight of the emitted gases is 30 and that they contain 12% CO\(_2\) and 10% H\(_2\)O. What is the daily emission rate of particulate matter?

1.3. Consider the following sequence for the thermal decomposition of the hydrocarbon molecule \( M_1 \):\[
M_1 \rightarrow 2R_1 \quad (E = 80)
\]
If the chains (reactions 2 and 3) are long and $k_1$ is relatively small, show that the overall rate of disappearance of $M_1$ is approximately

$$\frac{d[M_1]}{dt} = -\left(\frac{k_1k_2k_3}{k_4}\right)^{1/2}[M_1]$$

and that the overall activation energy is 62.5.

1.4. For the reaction mechanism of Problem 1.3, show that the overall order of the reaction depends on the termination reaction as indicated in the following table.

<table>
<thead>
<tr>
<th>Termination reaction</th>
<th>Overall order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_2 + R_2$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td>$R_1 + R_2$</td>
<td>1</td>
</tr>
<tr>
<td>$R_1 + R_i$</td>
<td>$\frac{3}{3}$</td>
</tr>
</tbody>
</table>

1.5. If the random variable $X$ obeys the normal distribution

$$p_X(x) = \frac{1}{\sqrt{2\pi} \sigma} e^{-(x-\mu)^2/2\sigma^2}$$

determine $p_Y(y)$ if $Y = X^2$.

REFERENCES


Singh, H. B., Salas, L. J., Smith, A., Stiles, R., and Shigeishi, H. "Atmospheric Measure-


