

# **Air Pollution Engineering**

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*.

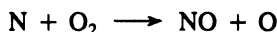
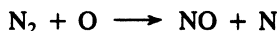
## 1.1 AIR POLLUTANTS

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 (NO<sub>2</sub>) are the two most important nitrogen oxide air pollutants. They are frequently lumped together under the designation NO<sub>x</sub>, although analytical techniques can distinguish clearly between them. Of the two, NO<sub>2</sub> is the more toxic and irritating compound.

Nitric oxide is a principal by-product of combustion processes, arising from the high-temperature reaction between N<sub>2</sub> and O<sub>2</sub> in the combustion air and from the oxidation of organically bound nitrogen in certain fuels such as coal and oil. The oxidation of N<sub>2</sub> by the O<sub>2</sub> in combustion air occurs primarily through the two reactions



known as the Zeldovich mechanism. The first reaction above has a relatively high activation energy, due to the need to break the strong N<sub>2</sub> 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*-NO<sub>x</sub>. 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 NO<sub>x</sub> during combustion. (The remainder is generally converted to N<sub>2</sub>.) Nitric oxide formed in this manner is referred to as *fuel*-NO<sub>x</sub>.

Mobile combustion and fossil-fuel power generation are the two largest anthro-

pogenic sources of  $\text{NO}_x$ . In addition, industrial processes and agricultural operations produce minor quantities. Emissions are generally reported as though the compound being emitted were  $\text{NO}_2$ . 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  $\text{NO}/\text{NO}_2$  being emitted by different sources. Table 1.4 gives  $\text{NO}/\text{NO}_x$  ratios of various types of sources. We see that, although  $\text{NO}$  is the dominant  $\text{NO}_x$  compound emitted by most sources,  $\text{NO}_2$  fractions from sources do vary somewhat with source type. Once emitted,  $\text{NO}$  can be oxidized quite effectively to  $\text{NO}_2$  in the atmosphere through atmospheric reactions, although we will not treat these reactions here. Table 1.5 gives estimated U.S. emissions of  $\text{NO}_x$  in 1976 according to source category. Utility boilers represent about 50% of all stationary source  $\text{NO}_x$  emissions in the United States. As a result, utility boilers have received the greatest attention in past  $\text{NO}_x$  regulatory strategies and are expected to be emphasized in future plans to attain and maintain  $\text{NO}_x$  ambient air quality standards.

### 1.1.2 Sulfur Oxides

Sulfur dioxide ( $\text{SO}_2$ ) 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  $\text{SO}_2$  result almost exclusively from stationary point sources. Estimated annual emissions of  $\text{SO}_2$  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 ( $\text{SO}_3$ ), and sulfuric acid ( $\text{H}_2\text{SO}_4$ ). It is estimated that, by volume, over 90% of the total U.S. sulfur oxide emissions are in the form of  $\text{SO}_2$ , with primary sulfates accounting for the other 10%.

Stationary fuel combustion (primarily utility and industrial) and industrial processes (primarily smelting) are the main  $\text{SO}_2$  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.  $\text{SO}_2$  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 1.1 AIR POLLUTANTS

	Physical properties	Concentration levels <sup>a</sup>	Anthropogenic sources	Natural sources
SO <sub>2</sub>	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 <sup>3</sup> at 293 K)	Global background concentration levels in the range 0.04 to 6 ppb; hourly averaged maximum concentrations in urban areas have occasionally exceeded 1 ppm	Fuel combustion in stationary sources; industrial process emissions; metal and petroleum refining	Atmospheric oxidation of organic sulfides
H <sub>2</sub> S	Colorless, flammable gas; highly toxic; characteristic rotten egg odor	Global background about 3 μg m <sup>-3</sup> ; urban levels have been observed as large as 390 μg m <sup>-3</sup>	Kraft pulp mills; natural gas and petroleum refining; rayon and nylon manufacture; coke ovens	Biological decay processes; volcanoes and geothermal activities
NO	Colorless, odorless gas; nonflammable and slightly soluble in water; toxic	Global background level from 10 to 100 ppt; urban levels have been observed as large as 500 ppb	Combustion	Bacterial action; natural combustion processes; lightning
NO <sub>2</sub>	Reddish-orange-brown gas with sharp, pungent odor; toxic and highly corrosive; absorbs light over much of the visible spectrum	Global background level from 10 to 500 ppt; urban concentrations have reached values exceeding 500 ppb	Combustion	
NH <sub>3</sub>	Colorless gas with pungent odor; detectable at concentrations exceeding 500 ppm; highly soluble in water	Global background level of 1 ppb; urban concentrations in range of 5 ppb	Combustion	Bacterial decomposition of amino acids in organic waste
CO <sub>2</sub>	Colorless, odorless, nontoxic gas moderately soluble in water	Global background concentration has increased from 290 ppm in 1900 to about 345 ppm in 1985	Combustion of fossil fuels	

CO	Colorless, odorless, flammable, toxic gas, slightly soluble in water	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	Combustion of fossil fuels	Atmospheric oxidation of methane and other biogenic hydrocarbons
O <sub>3</sub>	Colorless, toxic gas, slightly soluble in water	Global background concentrations range from 20 to 60 ppb; polluted urban levels range from 100 to 500 ppb	No primary sources; formed as a secondary pollutant from atmospheric reactions involving hydrocarbons and oxides of nitrogen	Natural tropospheric chemistry; transport from stratosphere to troposphere
Nonmethane hydrocarbons (see Table 1.2)		Global background concentrations range from 10 to 20 ppb; polluted urban levels range from 500 to 1200 ppb	Incomplete combustion; industrial sources	Vegetation

<sup>a</sup>Two concentration units that are commonly used in reporting atmospheric species abundances are  $\mu\text{g m}^{-3}$  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  $\mu\text{g m}^{-3}$

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

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

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

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

TABLE 1.2 HYDROCARBONS IDENTIFIED IN AMBIENT AIR

Carbon number	Compound	Carbon number	Compound
1	Methane		2,3-Dimethylbutane
2	Ethane		<i>cis</i> -2-Hexene
	Ethylene		<i>trans</i> -2-Hexene
	Acetylene		<i>cis</i> -3-Hexene
			<i>trans</i> -3-Hexene
3	Propane		2-Methyl-1-pentene
	Propylene		4-Methyl-1-pentene
	Propadiene		4-Methyl-2-pentene
	Methylacetylene		Benzene
4	Butane		Cyclohexane
	Isobutane		Methylcyclopentane
	1-Butene	7	2-Methylhexane
	<i>cis</i> -2-Butene		3-Methylhexane
	<i>trans</i> -2-Butene		2,3-Dimethylpentane
	Isobutene		2,4-Dimethylpentane
	1,3-Butadiene		Toluene
5	Pentane	8	2,2,4-Trimethylpentane
	Isopentane		Ethylbenzene
	1-Pentene		<i>o</i> -Xylene
	<i>cis</i> -2-Pentene		<i>m</i> -Xylene
	<i>trans</i> -2-Pentene		<i>p</i> -Xylene
	2-Methyl-1-butene	9	<i>m</i> -Ethyltoluene
	2-Methyl-1,3-butadiene		<i>p</i> -Ethyltoluene
	Cyclopentane		1,2,4-Trimethylbenzene
	Cyclopentene		1,3,5-Trimethylbenzene
	Isoprene	10	<i>sec</i> -Butylbenzene
6	Hexane		$\alpha$ -Pinene
	2-Methylpentane		$\beta$ -Pinene
	3-Methylpentane		3-Carene
	2,2-Dimethylbutane		Limonene

hicles. 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 C<sub>4</sub> to C<sub>9</sub> 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

Chemical name	Chemical formula	Toxicity <sup>a</sup>	Average concentration <sup>b</sup> (ppt)
<b>Halomethanes</b>			
Methyl chloride	CH <sub>3</sub> Cl	BM	788
Methyl bromide	CH <sub>3</sub> Br	BM	141
Methyl iodide	CH <sub>3</sub> I	SC, BM	2.7
Methylene chloride	CH <sub>2</sub> Cl <sub>2</sub>	BM	978
Chloroform	CHCl <sub>3</sub>	SC, BM	346
Carbon tetrachloride	CCl <sub>4</sub>	SC, NBM	221
<b>Haloethanes and halopropanes</b>			
Ethyl chloride	C <sub>2</sub> H <sub>5</sub> Cl	—	100
1,2-Dichloroethane	CH <sub>2</sub> ClCH <sub>2</sub> Cl	SC, BM	558
1,2-Dibromoethane	CH <sub>2</sub> BrCH <sub>2</sub> Br	SC	32
1,1,1-Trichloroethane	CH <sub>3</sub> CCl <sub>3</sub>	Weak BM	512
1,1,2-Trichloroethane	CH <sub>2</sub> ClCHCl <sub>2</sub>	SC, NBM	29
1,1,2,2-Tetrachloroethane	CHCl <sub>2</sub> CHCl <sub>2</sub>	SC, BM	10
1,2-Dichloropropane	CH <sub>2</sub> ClCHClCH <sub>3</sub>	BM	60
<b>Chloroalkenes</b>			
Vinylidene chloride	CH <sub>2</sub> =CCl <sub>2</sub>	SC, BM	19
Trichloroethylene	CHCl=CCl <sub>2</sub>	SC, BM	143
Tetrachloroethylene	CCl <sub>2</sub> =CCl <sub>2</sub>	SC	401
Allyl chloride	ClCH <sub>2</sub> CH=CH <sub>2</sub>	SC	<5
Hexachloro-1,3-butadiene	Cl <sub>2</sub> C=CCl—CCl=CCl <sub>2</sub>	BM	5
<b>Chloroaromatics</b>			
Monochlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	—	280
α-Chlorotoluene	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	BM	<5
o-Dichlorobenzene	o-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	—	12
m-Dichlorobenzene	m-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	—	6
1,2,4-Trichlorobenzene	1,2,4-C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	—	5
<b>Aromatic hydrocarbon</b>			
Benzene	C <sub>6</sub> H <sub>6</sub>	SC	3,883
<b>Oxygenated and nitrogenated species</b>			
Formaldehyde	HCHO	SC, BM	14,200
Phosgene	COCl <sub>2</sub>	—	<20
Peroxyacetyl nitrate (PAN)	CH <sub>3</sub> COOONO <sub>2</sub>	Phytotoxic	589
Peroxypropionyl nitrate (PPN)	CH <sub>3</sub> CH <sub>2</sub> COOONO <sub>2</sub>	Phytotoxic	103
Acrylonitrile	CH≡CN	SC	—

<sup>a</sup>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.

<sup>b</sup>Average from 2 weeks of measurements in Houston, St. Louis, Denver, and Riverside.

Source: Singh et al. (1981).

**TABLE 1.4** NO/NO<sub>x</sub> RATIOS IN EMISSIONS FROM VARIOUS SOURCE TYPES

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

<sup>a</sup>The lower limit is for idle conditions; the higher for 50 mi/hr (80.5 km h<sup>-1</sup>).

<sup>b</sup>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<sup>-1</sup>); NYCC—7.07 mi/hr (11.4 km h<sup>-1</sup>); CUE—34.79 mi/hr (56.0 km h<sup>-1</sup>). 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<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), and iron oxide (FeO and Fe<sub>2</sub>O<sub>3</sub>). 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<sub>x</sub> EMISSIONS IN THE UNITED STATES IN 1976 (10<sup>6</sup> metric tons/yr, expressed as NO<sub>2</sub>)<sup>a</sup>**

Source category	
Transportation	<b>10.1</b>
Highway vehicles	7.8
Nonhighway vehicles	2.3
Stationary fuel combustion	<b>11.8</b>
Electric utilities	6.6
Industrial	4.5
Residential, commercial, and institutional	0.7
Industrial processes	<b>0.7</b>
Chemicals	0.3
Petroleum refining	0.3
Metals	0
Mineral products	0.1
Oil and gas production and marketing	0 <sup>b</sup>
Industrial organic solvent use	0
Other processes	0
Solid waste disposal	<b>0.1</b>
Miscellaneous	<b>0.3</b>
Forest wildfires and managed burning	0.2
Agricultural burning	0
Coal refuse burning	0.1
Structural fires	0
Miscellaneous organic solvent use	<u>0</u>
	<b>23.0</b>

<sup>a</sup> One metric ton = 10<sup>3</sup> kg.

<sup>b</sup> 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<sub>2</sub> EMISSIONS IN THE UNITED STATES IN 1978 (10<sup>6</sup> metric tons/yr)**

Source category	
Stationary fuel combustion	22.1
Industrial processes	4.1
Transportation	<u>0.8</u>
	<b>27.0</b>

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<sup>3</sup> metric tons/yr)

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

<sup>a</sup>Primarily wood/bark waste.

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

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 SO<sub>2</sub> 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 μm.

## 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 NO<sub>x</sub>) model year emissions to be achieved by 1975 (or 1976 for NO<sub>x</sub>). 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 1.8 CHARACTERISTICS OF UNCONTROLLED PARTICULATE EMISSIONS

Source category	Particle size (weight % less than stated size)			Chemical composition	
	15 $\mu\text{m}$	2.5 $\mu\text{m}$	1.0 $\mu\text{m}$	Major elements and compounds	Trace elements (less than 1% by weight)
<b>Fuel combustion</b>					
<b>Utility</b>					
Coal	15-90	5-70	1-15	Al, Ca, Fe, Si, sulfates, organics	As, B, Ba, Be, Cd, Cl, Co, Cr, Cu, F, Hg, K, Mg, Mn, Na, Ni, P, Pb, S, Se, Ti, V, Zn, Zr
Oil	95	70-95	5-20	Al, Ca, Fe, Mg, Na, sulfates, organics	As, Ba, Br, Co, Cr, Cu, K, Mn, Mo, Ni, Pb, Se, Sr, Ti, V
<b>Industrial</b>					
Oil	—	—	65-95	Al, Fe, Mg, Si, sulfates, organics	As, Ba, Ca, Cd, Co, Cr, Cu, Hg, K, Mo, Ni, Pb, Se, Sr, Ti, V, Zn
Gas	—	—	100	Cl, Na, sulfates, organics	—
<b>Commercial/institutional/residential</b>					
Oil	—	—	—	Al, Ca, Mg, Zn, sulfates	As, Ba, Cd, Cr, Cu, Hg, K, Ni, Pb, Sb, C
Gas	—	—	100	Cl, Na, sulfates, organics	—
<b>Industrial processes</b>					
<b>Metals</b>					
Iron and steel	—	35-99	30-95	Al, C, Ca, Cr, Fe, K, Mg, Mn, Pb, Si, Zn, sulfates, organics	Ag, As, Br, Cd, Cs, Cu, F, I, Mo, Ni, Rb, Se, Sn, Sr, V, Zr

Primary aluminum	90	75	35-45	Al, C, Ca, F, Fe, Na	—
Primary copper	—	20-95	70	Cu, Pb, S, Zn	Ag, Al, As, Cd, Hg, Sb, Se, Si, Te
Primary lead	—	80	—	Pb, Zn	As, Cd, Se, Te
Primary zinc	—	90-98	—	Cd, Fe, Pb, S, Zn	Cu, Hg, Mn, Sn
Iron foundries	70-95	65-90	65	—	—
Mineral products					
Cement	80	30	5-30	Al, C, Ca, Cl, K, Mg, Na, Si, carbonates, sulfates	Ag, Ba, Cd, Cr, Cu, F, Fe, Mn, Mo, Ni, Pb, Rb, Se, Ti, Zn
Asphalt	10-15	1-2	<½	Al, C, Ca, Fe, K, Mg, Si, sulfates	Ag, As, Ba, Cr, Ti
Lime	—	25-50	5	Ca, Fe, Mg, Se, Si, carbonates	—
Gypsum	—	—	20	Al, C, Ca, Mg, Na, sulfates	As, Ba, Br, Cd, Cl, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Se, Sr, Y, Zn
Crushed rock	—	—	1-2	Ca, Si, P	Ba, Cu, Fe, K, Mn, Sr
Petroleum	—	—	50-90	Asphalt, coke dust, sulfuric acid mist, fly ash, soot	—
Chemicals					
Sulfuric acid	—	40-95	10-55	Sulfuric acid mist	—
Others					
Grain processing	15	1	0	Organics	—
Pulp and paper	90-95	70-80	—	Ca, Mg, Na, carbonates, sulfates	—
Solid-waste disposal incinerators	45	35	—	—	—

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

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  $\text{NO}_x$  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  $\text{NO}_x$  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 1.9 NATIONAL AMBIENT AIR QUALITY STANDARDS (PRIMARY)**

Pollutant	Averaging time	Primary standard
Sulfur dioxide	Annual average	80 $\mu\text{g m}^{-3}$
	24 h	365 $\mu\text{g m}^{-3}$
Nitrogen dioxide	Annual average	100 $\mu\text{g m}^{-3}$
Carbon monoxide	8 h	10 $\text{mg m}^{-3}$
	1 h	40 $\text{mg m}^{-3}$
Ozone	1 h	0.12 ppm (235 $\mu\text{g m}^{-3}$ )
Particulate matter ( $\text{PM}_{10}$ ) <sup>a</sup>	Annual geometric mean	50 $\mu\text{g m}^{-3}$
	24 h	150 $\mu\text{g m}^{-3}$

<sup>a</sup>See the text.

Source: 40 CFR (Code of Federal Regulations) 50, 1982.

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  $150\ \mu\text{g m}^{-3}$  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  $50\ \mu\text{g m}^{-3}$ , 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  $\mu\text{g m}^{-3}$  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)

Steam electric power plants	
Particulate matter	13 g/10 <sup>6</sup> kJ
NO <sub>x</sub>	
Gaseous fuel	86 g/10 <sup>6</sup> kJ
Liquid fuel	130 g/10 <sup>6</sup> kJ
Coal	260 g/10 <sup>6</sup> kJ
SO <sub>2</sub>	
Gas or liquid fuel	86 g/10 <sup>6</sup> kJ
Coal	At least 70% removal depending on conditions
Solid waste incinerators: particulate matter	0.18 g/dscm <sup>a</sup> corrected to 12% CO <sub>2</sub> (3-hr average)
Sewage sludge incinerators: particulate matter	0.65 g/kg sludge input (dry basis)
Iron and steel plants: particulate matter	50 mg/dscm <sup>a</sup>
Primary copper smelters	
Particulate matter	50 mg/dscm <sup>a</sup>
SO <sub>2</sub>	0.065% by volume

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

Source: 40 CFR (Code of Federal Regulations) 60, 1982.

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

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

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

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

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

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

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

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

$$\begin{aligned} \text{concentration in } \mu\text{g m}^{-3} &= \frac{pM_i}{8.314T} \times \text{concentration in ppm} \\ &= \frac{(1.0133 \times 10^5)(48)}{8.314(298)} \times 0.12 \\ &= 235.6 \mu\text{g m}^{-3} \end{aligned}$$



The 24-hour SO<sub>2</sub> NAAQS is 365 μg m<sup>-3</sup>. Convert this to ppm at the same temperature and pressure.

$$\begin{aligned}\text{concentration in ppm} &= \frac{(8.314)(298)}{(1.0133 \times 10^5)(64)} \times 365 \\ &= 0.139 \text{ ppm}\end{aligned}$$

## 1.4 THE APPENDICES TO THIS CHAPTER

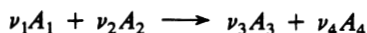
Analysis of the generation and control of air pollutants at the source, air pollution engineering, requires a basis of thermodynamics, fluid mechanics, heat and mass transfer, and chemical kinetics. This chapter concludes with five appendices, the first four of which provide some basic material on chemical 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,  $A_1, A_2, \dots, A_S$ , can be written as

$$\sum_{i=1}^S \nu_i A_i = 0 \quad (\text{A.1})$$

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



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

$$\sum_{i=1}^S \nu_{ij} A_i = 0 \quad j = 1, 2, \dots, R \quad (\text{A.2})$$

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<sup>-3</sup> s<sup>-1</sup>), and let  $r_j$  be the rate of reaction  $j$  (g-mol m<sup>-3</sup> s<sup>-1</sup>). Then in a closed system,

$$\frac{dc_i}{dt} = R_i = \sum_{j=1}^R \nu_{ij} r_j \quad i = 1, 2, \dots, S \quad (\text{A.3})$$

which also implies that

$$\frac{(R_i) \text{ due to reaction } j}{(R_l) \text{ due to reaction } j} = \frac{\nu_{ij}}{\nu_{lj}} \quad i, l = 1, 2, \dots, S; \quad j = 1, 2, \dots, R \quad (\text{A.4})$$

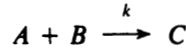
We now define the *extents* of the  $R$  reactions,  $\xi_1, \dots, \xi_R$ , by

$$c_i - c_{io} = \sum_{j=1}^R \nu_{ij} \xi_j \quad i = 1, 2, \dots, S \quad (\text{A.5})$$

so that the extents satisfy

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

Consider the gas-phase chemical reaction



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

$$\frac{d}{dt}(c_A V) = -Vkc_A c_B \quad (\text{A.7})$$

or

$$\frac{dc_A}{dt} = -kc_A c_B - \frac{c_A}{V} \frac{dV}{dt} \quad (\text{A.8})$$

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):

$$\frac{d}{dt} \left( \frac{c_A m}{\rho} \right) = -\frac{m}{\rho} kc_A c_B \quad (\text{A.9})$$

Since  $m$  is constant, it can be canceled from both sides, giving

$$\rho \frac{d}{dt} \left( \frac{c_A}{\rho} \right) = -kc_A c_B \quad (\text{A.10})$$

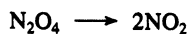
Thus, for a system where volume is changing in time, a quantity that reflects only the concentration change due to chemical reaction is

$$\rho \frac{d}{dt} \left( \frac{c_i}{\rho} \right)$$

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



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  $\nu_{31} = 2$ ,  $\nu_{41} = -1$ ,  $\nu_{22} = 2$ ,  $\nu_{12} = 1$ , and  $\nu_{32} = -2$ . We introduce the extents of reaction, according to (A.5),

$$c_1 = \xi_2$$

$$c_2 = 2\xi_2$$

$$c_3 = 2\xi_1 - 2\xi_2$$

$$c_4 - c_{40} = -\xi_1$$

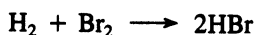
For a closed, uniform system at constant volume,

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

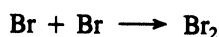
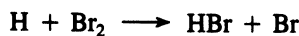
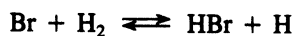
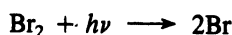
which can be written in terms of the extents of the two reactions,

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

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

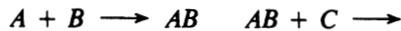


consists of the sequence of elementary reactions,



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  $\text{Br}_2 + h\nu$  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,

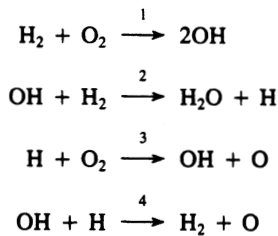


### Example 1.3 Independence of Reactions

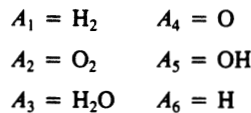
Given a chemical reaction mechanism, there is the possibility that two reactions are multiples of each other or that one reaction is a linear combination of two others. Such a reaction tells us nothing more in a stoichiometric sense than the reactions on which it is dependent, since any changes in composition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



If we define



the reactions may be written as

$$\begin{array}{ccccccc} -A_1 & -A_2 & & +2A_5 & & & = 0 \\ -A_1 & & +A_3 & & -A_5 & +A_6 & = 0 \\ & -A_2 & & +A_4 & +A_5 & -A_6 & = 0 \\ A_1 & & & +A_4 & -A_5 & -A_6 & = 0 \end{array}$$

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

$$1 \quad \frac{\nu_{2j}}{\nu_{1j}} \quad \frac{\nu_{3j}}{\nu_{1j}} \quad \dots \quad \frac{\nu_{sj}}{\nu_{1j}}$$

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,

$$0 \left( \nu_{2k} - \nu_{1k} \frac{\nu_{2j}}{\nu_{1j}} \right) \dots \left( \nu_{sk} - \nu_{1k} \frac{\nu_{sj}}{\nu_{1j}} \right)$$

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

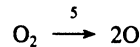
$$\begin{bmatrix} 1 & 1 & 0 & 0 & -2 & 0 \\ 0 & 1 & 1 & 0 & -3 & 1 \\ 0 & 0 & 1 & 1 & -2 & 0 \\ 0 & 0 & 1 & 1 & -2 & 0 \end{bmatrix}$$

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-

cedure 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



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)

$$Z_{ij} = \left( \frac{8k_B T}{\pi m_{ij}} \right)^{1/2} \pi \sigma_{ij}^2 N_i N_j \quad \text{m}^{-3} \text{ s}^{-1} \quad (\text{A.11})$$

where  $N_i$  is the number concentration of species  $i$  ( $\text{m}^{-3}$ ),  $(8k_B T/\pi m_{ij})^{1/2}$  is the root-mean-square relative speed of the  $i$  and  $j$  molecules,  $k_B$  is the Boltzmann constant ( $1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$ ),  $m_{ij} = m_i m_j / (m_i + m_j)$  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,

$$r = A(T) \exp\left(-\frac{E}{RT}\right) c_i c_j \quad (\text{A.12})$$

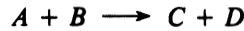
The preexponential factor  $A(T)$  may depend on temperature since the translational kinetic energy and internal degrees of freedom of the molecules influence the probability of reaction in any collision event. The rate of reaction is usually written as  $r = kc_i c_j$ ,

where the parameter  $k$  is called the *rate constant*,

$$k = A(T) \exp\left(-\frac{E}{RT}\right) \quad (\text{A.13})$$

If  $A(T)$  is independent of  $T$ , we have the *Arrhenius form*,  $k = A \exp(-E/RT)$ .

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



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  $AB^\ddagger$ , 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,



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.

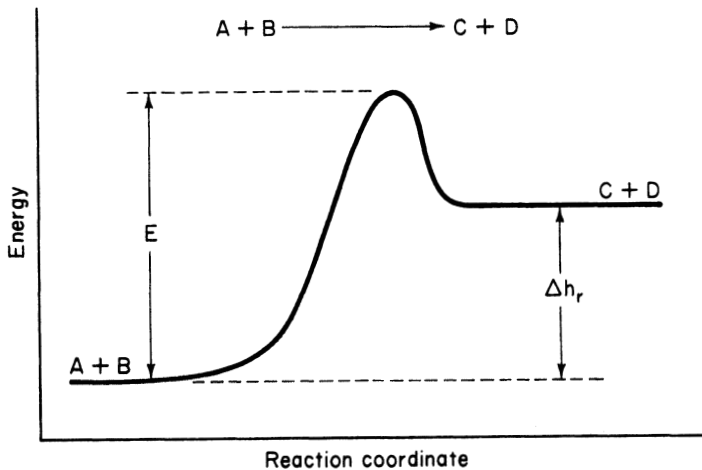


Figure 1.1 Energetics of an exchange reaction  $A + B \rightarrow C + D$ .

At chemical equilibrium

$$0 = k_f[A]_e[B]_e - k_b[C]_e[D]_e \quad (\text{A.14})$$

or, rearranging,

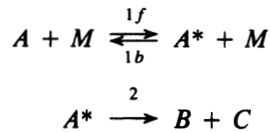
$$\frac{k_f}{k_b} = \frac{[C]_e[D]_e}{[A]_e[B]_e} \quad (\text{A.15})$$

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  $B + C$ ,



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

$$\frac{d[A]}{dt} = -k_{1f}[A][M] + k_{1b}[A^*][M] \quad (\text{A.16})$$

$$\frac{d[A^*]}{dt} = k_{1f}[A][M] - k_{1b}[A^*][M] - k_2[A^*] \quad (\text{A.17})$$

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



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

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

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

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

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

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

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

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

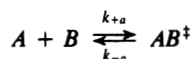
which, if  $[M]$  is constant, is

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

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).

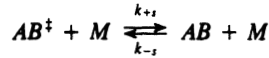
#### Example 1.4 Analysis of Bimolecular Reactions

When two molecules collide and form a single molecule,



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,



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  $10^9 \text{ s}^{-1}$ . Thus only one  $AB^\ddagger$  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

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

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

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

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

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

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

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

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

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

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  $\text{CH}_3\text{CH}_2\cdot$ , and the chlorine atom,  $\text{Cl}\cdot$ .