

# Atmospheric POLLUTION

HISTORY, SCIENCE, AND REGULATION

Mark Z. Jacobson



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## ATMOSPHERIC POLLUTION

*Atmospheric Pollution: History, Science, and Regulation* provides a comprehensive introduction to the history and science of major air pollution issues. It begins with an introduction to the basic atmospheric chemistry and the history of discovery of chemicals in the atmosphere, then moves on to a discussion of the evolution of the earth's atmosphere and the structure and composition of the present-day atmosphere. Subsequently, a comprehensive and accessible discussion of the five major atmospheric pollution topics – urban outdoor air pollution, indoor air pollution, acid deposition, stratospheric ozone reduction, and global climate change – is provided. Each chapter discusses the history and science behind these problems, their consequences, and the effort made through government intervention and regulation to mitigate them. The book contains numerous student examples and problems, more than 200 color illustrations, and is international in scope.

*Atmospheric Pollution: History, Science, and Regulation* forms an ideal introductory textbook on atmospheric pollution for undergraduate and graduate students taking courses in atmospheric chemistry and physics, meteorology, environmental science, earth science, civil and environmental engineering, chemistry, environmental law and politics, and city planning and regulation. It also forms a valuable reference text for researchers and an introduction to the subject for general audiences.

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*To Yvonne and William*

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AND REGULATION**

**Mark Z. Jacobson**

*Stanford University*



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# CONTENTS

<i>Preface</i>	page ix
<i>Acknowledgments</i>	xi
<b>1. BASICS AND HISTORY OF DISCOVERY OF ATMOSPHERIC CHEMICALS</b>	1
<b>1.1. Basic Definitions</b>	2
<b>1.2. History of Discovery of Elements and Compounds of Atmospheric Importance</b>	4
<b>1.3. Chemical Structure and Reactivity</b>	21
<b>1.4. Chemical Reactions and Photoprocesses</b>	24
<b>1.5. Lifetimes of Chemicals</b>	26
<b>1.6. Summary</b>	26
<b>1.7. Problems</b>	26
<b>2. THE SUN, THE EARTH, AND THE EVOLUTION OF THE EARTH'S ATMOSPHERE</b>	29
<b>2.1. The Sun and Its Origin</b>	30
<b>2.2. Spectra of the Radiation of the Sun and the Earth</b>	33
<b>2.3. Primordial Evolution of the Earth and Its Atmosphere</b>	36
<b>2.4. Summary</b>	47
<b>2.5. Problems</b>	48
<b>3. STRUCTURE AND COMPOSITION OF THE PRESENT-DAY ATMOSPHERE</b>	49
<b>3.1. Air Pressure and Density Structure</b>	50
<b>3.2. Processes Affecting Temperature</b>	52
<b>3.3. Temperature Structure of the Atmosphere</b>	54

3.4.	<i>Equation of State</i>	58
3.5.	<i>Composition of the Present-Day Atmosphere</i>	62
3.6.	<i>Characteristics of Selected Gases and Aerosol Particle Components</i>	63
3.7.	<i>Summary</i>	79
3.8.	<i>Problems</i>	79
<b>4.</b>	<b>URBAN AIR POLLUTION</b>	81
4.1.	<i>History and Early Regulation of Urban Air Pollution</i>	82
4.2.	<i>Chemistry of the Background Troposphere</i>	93
4.3.	<i>Chemistry of Photochemical Smog</i>	99
4.4.	<i>Pollutant Removal</i>	111
4.5.	<i>Summary</i>	111
4.6.	<i>Problems</i>	112
<b>5.</b>	<b>AEROSOL PARTICLES IN SMOG AND THE GLOBAL ENVIRONMENT</b>	115
5.1.	<i>Size Distributions</i>	116
5.2.	<i>Sources and Compositions of New Particles</i>	118
5.3.	<i>Processes Affecting Particle Size</i>	128
5.4.	<i>Summary of the Composition of Aerosol Particles</i>	138
5.5.	<i>Aerosol Particle Morphology and Shape</i>	139
5.6.	<i>Health Effects of Aerosol Particles</i>	140
5.7.	<i>Summary</i>	142
5.8.	<i>Problems</i>	142
<b>6.</b>	<b>EFFECTS OF METEOROLOGY ON AIR POLLUTION</b>	145
6.1.	<i>Forces</i>	146
6.2.	<i>Winds</i>	147
6.3.	<i>Global Circulation of the Atmosphere</i>	150
6.4.	<i>Semipermanent Pressure Systems</i>	154
6.5.	<i>Thermal Pressure Systems</i>	155
6.6.	<i>Effects of Large-Scale Pressure Systems on Air Pollution</i>	156
6.7.	<i>Effects of Local Meteorology on Air Pollution</i>	168
6.8.	<i>Summary</i>	175
6.9.	<i>Problems</i>	176
<b>7.</b>	<b>EFFECTS OF POLLUTION ON VISIBILITY, ULTRAVIOLET RADIATION, AND ATMOSPHERIC OPTICS</b>	179
7.1.	<i>Processes Affecting Solar Radiation in the Atmosphere</i>	180
7.2.	<i>Visibility</i>	197
7.3.	<i>Colors in the Atmosphere</i>	202
7.4.	<i>Summary</i>	205
7.5.	<i>Problems</i>	206
7.6.	<i>Project</i>	207



<b>8. INTERNATIONAL REGULATION OF URBAN SMOG SINCE THE 1940s</b>	209
8.1. <i>Regulation in the United States</i>	210
8.2. <i>Pollution Trends and Regulations Outside the United States</i>	225
8.3. <i>Summary</i>	238
8.4. <i>Problems</i>	239
<b>9. INDOOR AIR POLLUTION</b>	241
9.1. <i>Pollutants in Indoor Air and Their Sources</i>	242
9.2. <i>Sick Building Syndrome</i>	251
9.3. <i>Regulation of Indoor Air Pollution</i>	251
9.4. <i>Summary</i>	252
9.5. <i>Problems</i>	252
<b>10. ACID DEPOSITION</b>	253
10.1. <i>Historical Aspects of Acid Deposition</i>	254
10.2. <i>Causes of Acidity</i>	257
10.3. <i>Sulfuric Acid Deposition</i>	260
10.4. <i>Nitric Acid Deposition</i>	263
10.5. <i>Effects of Acid Deposition</i>	263
10.6. <i>Natural and Artificial Neutralization of Lakes and Soils</i>	266
10.7. <i>Recent Regulatory Control of Acid Deposition</i>	270
10.8. <i>Summary</i>	271
10.9. <i>Problems</i>	272
<b>11. GLOBAL STRATOSPHERIC OZONE REDUCTION</b>	273
11.1. <i>Structure of the Present-Day Ozone Layer</i>	274
11.2. <i>Relationship between the Ozone Layer and UV Radiation</i>	277
11.3. <i>Chemistry of the Natural Ozone Layer</i>	278
11.4. <i>Recent Changes to the Ozone Layer</i>	283
11.5. <i>Effects of Chlorine on Global Ozone Reduction</i>	286
11.6. <i>Effects of Bromine on Global Ozone Reduction</i>	293
11.7. <i>Regeneration Rates of Stratospheric Ozone</i>	294
11.8. <i>Antarctic Ozone Depletion</i>	295
11.9. <i>Effects of Enhanced UV-B Radiation on Life and Ecosystems</i>	301
11.10. <i>Regulation of CFCs</i>	303
11.11. <i>Summary</i>	306
11.12. <i>Problems</i>	307
<b>12. THE GREENHOUSE EFFECT AND GLOBAL WARMING</b>	309
12.1. <i>The Temperature on the Earth in the Absence of a Greenhouse Effect</i>	310
12.2. <i>The Greenhouse Effect and Global Warming</i>	316
12.3. <i>Recent and Historical Temperature Trends</i>	323

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<b>12.4. Feedbacks and Other Factors That May Affect Global Temperatures</b>	337
<b>12.5. Possible Consequences of Global Warming</b>	342
<b>12.6. Regulatory Control of Global Warming</b>	345
<b>12.7. Summary</b>	349
<b>12.8. Problems</b>	350
<b>12.9. Essay Questions</b>	351
 <i>Appendix: Conversions and Constants</i>	353
<i>References</i>	355
<i>Photograph Sources</i>	371
<i>Index</i>	377

# PREFACE

Natural air pollution problems on the Earth are as old as the Earth itself. Volcanoes, fumaroles, natural fires, and desert dust have all contributed to natural air pollution. Humans first emitted air pollutants when they burned wood and cleared land (increasing windblown dust). More recently, the burning of coal; chemicals; oil, gasoline, kerosene, diesel, jet and alcohol fuels; natural gas; and waste and the release of chemicals have contributed to several major air pollution problems on a range of spatial scales. These problems include outdoor urban smog, indoor air pollution, acid deposition, Antarctic ozone depletion, global ozone reduction, and global warming.

**Urban smog** is characterized by the outdoor buildup of gases and particles emitted from vehicles, smokestacks, and other human sources, or formed chemically in the air from emitted precursors. Smog affects human and animal health, structures, and vegetation. Urban smog occurs over scales of tens to hundreds of kilometers.

**Indoor air pollution** results from the emission of pollutant gases and particles in enclosed buildings and the transport of pollutants from outdoors into buildings. Indoor air pollutants cause a variety of human health effects. Indoor air pollution occurs over scales of meters to tens of meters.

**Acid deposition** occurs when sulfuric acid, nitric acid, or hydrochloric acid in the air deposits to the ground as a gas or dissolved in rainwater, fogwater, or particles. Acids harm soils, lakes, forests, and structures. In high concentrations, they can harm humans. Acid deposition occurs over scales of meters to thousands of kilometers.

**Antarctic ozone depletion** and **global ozone reduction** are caused, to a large extent, by human-produced chlorine and bromine compounds that are emitted into the air and break down only after they have traveled to the upper atmosphere. Ozone reduction increases the intensity of ultraviolet (UV) radiation from the sun reaching the ground. Intense UV radiation destroys microorganisms on the surface of the Earth and causes skin cancer in humans and animals. Antarctic ozone depletion occurs over a region the size of North America. Global ozone reduction occurs globally.

**Global warming** is the increase in global temperatures, rainfall patterns, and sea level due to human emission of carbon dioxide, methane, nitrous oxide, other gases,

and particulate black carbon. Global warming is a global problem with regional impact.

Air is not owned privately; instead, it is common property (accessible to all individuals). As a result, air has historically been polluted without limit. This is the classic **tragedy of the commons**. The only known mechanism of limiting air pollution, aside from volunteerism, is government intervention. Intervention can take the form of setting up economic markets for the rights to emit pollution, limiting emissions from specific sources, requiring certain emission control technologies, or setting limits on pollutant concentrations and allowing the use of any emission reduction method to meet those limits.

Because government action usually requires consensus that a problem exists, the problem is severe enough to warrant action, and action taken will not have its own set of adverse consequences (usually economic), national governments did not act aggressively to control global air pollution problems until the 1970s and 1980s. For the most part, action was not taken earlier because lawmakers were not always convinced of the severity of air pollution problems. Even when problems were recognized, action was often delayed because industries used their political strength to oppose government intervention. Even today, government intervention is opposed by many industries and politicians out of often-misplaced concern that intervention will cause adverse economic consequences. In many developing countries, intervention is sometimes opposed because of the concern that developed countries are trying to inhibit economic expansion of the less-developed countries. In other cases, pollution is not regulated strictly due to the perceived cost of emission-control technologies and enforcement.

Despite the opposition to government intervention and although work still needs to be done, government intervention has proved effective in mitigating several of the major air pollution problems facing humanity. The problems mitigated but not eliminated include urban air pollution (in some countries), acid deposition (in some countries), and stratospheric ozone reduction. The problem of global climate change has not been controlled to date, and only recently has it been addressed on a global scale.

The purpose of this book is to discuss the history and science of major air pollution problems, the consequences of these problems, and efforts to control these problems through government intervention. Such a study involves the synthesis of chemistry, meteorology, radiative processes, particle processes, cloud physics, soil sciences, microbiology, epidemiology, economics, and law. The field of air pollution is a true interdisciplinary field.

This book is directed at students in the environmental, Earth, and atmospheric sciences. It was designed to be detailed enough to be used as a reference text as well. Chemical symbols and chemical equations are used, but all chemistry required is introduced in Chapter 1 – no previous knowledge of chemistry is needed. The text also describes a handful of physical laws; however, no calculus, geometry, or high math is needed.

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# 1

## **BASICS AND HISTORY OF DISCOVERY OF ATMOSPHERIC CHEMICALS**



**T**he study of air pollution begins with the study of chemicals that make up the air. These chemicals include molecules in the gas, liquid, or solid phases. Because the air contains so many different types of molecules, it is helpful to become familiar with important ones through the history of their discovery. Such a history also gives insight into characteristics of atmospheric chemicals and an understanding of how much our knowledge of air pollution today relies on the scientific achievements of alchemists, chemists, natural scientists, and physicists of the past. This chapter starts with some basic chemistry definitions, then proceeds to examine historical discoveries of chemicals of atmospheric importance. Finally, types of chemical reactions that occur in the atmosphere are identified, and chemical lifetimes are defined.

## 1.1. BASIC DEFINITIONS

**Air** is a mixture of gases and particles, both of which are made of atoms. In this section, atoms, elements, molecules, compounds, gases, and particles are defined.

### 1.1.1. Atoms, Elements, Molecules, and Compounds

In 1913, **Niels Bohr** (1885–1962), a Danish physicist, proposed that an **atom** consists of one or more negatively charged electrons in discrete circular orbits around a positively charged nucleus. Each **electron** carries a charge of  $-1$  and a tiny mass.\* The **nucleus** consists of 1–92 protons and 0–146 neutrons. **Protons** have a net charge of  $+1$  and a mass 1,836 times that of an electron. **Neutrons** have zero net charge and a mass 1,839 times that of an electron. For the net charge of an atom to be zero, the number of electrons must equal the number of protons. Positively charged atoms have fewer electrons than protons. Negatively charged atoms have more electrons than protons. Positively or negatively charged atoms are called **ions**.

The average mass of protons plus neutrons in a nucleus is called the **atomic mass**. Electrons are not included in the atomic mass calculation because the summed mass of electrons in an atom is small in comparison with the summed masses of protons and neutrons. The number of protons in an atomic nucleus is called the **atomic number**.

An **element** is a single atom or a substance composed of several atoms, each with the same atomic number (the same number of protons in its nucleus). Whereas all atoms of an element have a fixed number of protons, not all atoms of the element have the same number of neutrons. Atoms of an element with the same number of protons but a different number of neutrons are **isotopes** of the element. Isotopes of an element have different atomic masses but similar chemical characteristics.

The **periodic table of the elements**, developed in 1869 by Russian chemist **Dmitri Mendeleev** (1834–1907), lists elements in order of increasing atomic number. Table 1.1 identifies the first ten elements of the periodic table and some of their characteristics. The atomic mass of an element in the periodic table is the sum, over all isotopes of the element, of the percentage occurrence in nature of the isotope multiplied by the atomic mass of the isotope.

\*Mass is an absolute property of a material. Mass, multiplied by gravity, equals weight, which is a force. Because gravity varies with location and altitude, weight is a relative property of a material. A person who is nearly “weightless” in space, where gravity is small, has the same mass, whether in space or on the surface of the Earth.

Table 1.1. Characteristics of the First Ten Elements in the Periodic Table

Element	Symbol	Number of Protons (Atomic Number)	Number of Neutrons in Main Isotope	Atomic mass (g mol <sup>-1</sup> )	Number of Electrons
Hydrogen	H	1	0	1.00794	1
Helium	He	2	2	4.00206	2
Lithium	Li	3	4	6.941	3
Beryllium	Be	4	5	9.01218	4
Boron	B	5	6	10.811	5
Carbon	C	6	6	12.011	6
Nitrogen	N	7	7	14.0067	7
Oxygen	O	8	8	15.9994	8
Fluorine	F	9	10	18.9984	9
Neon	Ne	10	10	20.1797	10

The simplest element in the periodic table is **hydrogen** (H), which contains one proton, no neutrons, and one electron. Hydrogen occurs in three natural isotopic forms. The most common (one proton and one electron) is that shown in Fig. 1.1. The other two are **deuterium**, which contains one proton, one neutron, and one electron, and **tritium**, which contains one proton, two neutrons, and one electron. **Helium** (He), also shown in Fig. 1.1, is the second simplest element and contains two protons, two neutrons, and two electrons.

When one atom bonds to another atom of either the same or different atomic number, it forms a molecule. A **molecule** is a group of atoms of like or different elements held together by chemical forces. When a molecule consists of different elements, it is a compound. A **compound** is a substance consisting of atoms of two or more elements in definite proportions that cannot be separated by physical means.

1.1.2. Gases and Particles

Gases are distinguished from particles in two ways. First, a **gas** consists of individual atoms or molecules that are separated, whereas a **particle** consists of aggregates of atoms or molecules bonded together. Thus, a particle is larger than a single gas atom or molecule. Second, whereas particles contain liquids or solids, gases are in their own phase state. Particles may be further segregated into aerosol particles and hydrometeor particles.

An **aerosol** is an ensemble of solid, liquid, or mixed-phase particles suspended in air. An **aerosol particle** is a single liquid, solid, or mixed-phase particle among an ensemble of suspended particles. The term *aerosol* was coined by British physicochemist **Frederick George Donnan** (1870–1956) near the end of World War I (Green and Lane, 1969).

A **hydrometeor** is an ensemble of liquid, solid, or mixed-phase water particles suspended in or falling through the air. A **hydrometeor particle** is a single such particle. Examples of hydrometeor particles are cloud drops, ice crystals, raindrops, snowflakes, and hailstones. The main difference between an aerosol particle and a hydrometeor particle is that the latter contains much more water than the former.

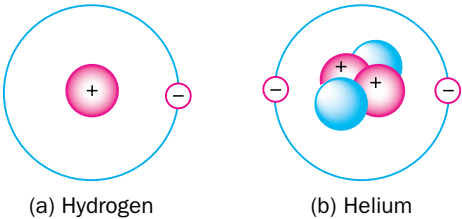


Figure 1.1. Simplified configuration of protons, neutrons, and electrons in (a) a hydrogen atom and (b) a helium atom.



Liquids in aerosol and hydrometeor particles may be pure or may consist of a solution. A **solution** is a homogeneous mixture of substances that can be separated into individual components on a change of state (e.g., freezing). A solution consists of a **solvent**, such as water, and one or more **solutes** dissolved in the solvent. Solids may be mixed throughout a solution, but are not part of the solution. In this text, pure water and solutes dissolved in water are denoted with “(aq)” for **aqueous** (dissolved in water). Gases are denoted with “(g),” and solids are denoted with “(s).”

Gases and aerosol particles may be emitted into the air naturally or anthropogenically or formed chemically in the air. **Anthropogenic emissions** are human-produced emissions, such as from fossil-fuel combustion or industrial burning. Hydrometeor particles generally form from physical processes in the air. **Air pollution** occurs when gases or aerosol particles, emitted anthropogenically, build up in concentration sufficiently high to cause direct or indirect damage to humans, plants, animals, other life forms, ecosystems, structures, or works of art.

## 1.2. HISTORY OF DISCOVERY OF ELEMENTS AND COMPOUNDS OF ATMOSPHERIC IMPORTANCE

In this section, the history of discovery of elements and compounds of atmospheric importance is discussed. Reactive elements that make up most gases are hydrogen (H), carbon (C), nitrogen (N), oxygen (O), fluorine (F), sulfur (S), chlorine (Cl), and bromine (Br). Unreactive elements in the air include helium (He), argon (Ar), krypton (Kr), neon (Ne), and xenon (Xe). Two radioactive elements of importance are polonium (Po) and radon (Rn). Aerosol particles contain the elements present in gases and possibly sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), potassium (K), calcium (Ca), iron (Fe), lead (Pb), or phosphorus (P). Tables 1.2 and 1.3 summarize the dates of discovery of elements and compounds, respectively, of atmospheric importance.

### 1.2.1. Solids and Liquids, Ancient World–1690

In this subsection, solids and liquids discovered from ancient times through the seventeenth century are discussed.

#### 1.2.1.1. Iron

The first elements in the periodic table to be identified were the metals gold (Au), silver (Ag), mercury (Hg), copper (Cu), iron (Fe), tin (Sn), and lead (Pb). Many cultures, including the Egyptians and the Chaldeans, were aware of these metals. Of note were the Chaldeans (612–539 B.C.), who connected them with planets, identifying gold as the sun, silver as the moon, mercury as Mercury, copper as Venus, iron as Mars, tin as Jupiter, and lead as Saturn. Of these six metals, iron and lead are the most important in aerosol particles today. **Iron** (*ferrum* in Latin; *iarn* in Scandinavian) is a dense metal element that is the primary component of the Earth’s core and the fourth most abundant element in the Earth’s crust. It is emitted into the air in soil–dust particles. It is also the particulate element emitted in the greatest abundance from industrial sources today.

#### 1.2.1.2. Lead

**Lead** (*plumbum* in Latin) is a dense bluish-white metal element. Lead was referred to in the Books of *Job* and *Numbers* as “biblicalx.” The Roman Pliny the Elder (23–79 A.D.)

**Table 1.2. Dates of Discovery of Elements of Atmospheric Importance**

Element	Origin of Name or Previous Name	Year Discovered	Discoverer
Iron (Fe)	Named after <i>larn</i>	B.C.	?
Lead (Pb)	Previously <i>biblicalx</i> , <i>plumbum nigrum</i>	B.C.	?
Carbon (C)	Named from <i>carbo</i> , “charcoal”	B.C.	?
Sulfur (S)	Named from <i>sulvere</i> , <i>sulphurium</i> ; previously <i>brimstone</i>	B.C.	?
Phosphorus (P)	Means “light bearer”	1669	Brand (Sweden)
Hydrogen (H)	Means “water producer”	<1520, 1766	Paracelsus (Switzerland), Cavendish (England)
Fluorine (F)	Named from <i>fluere</i> , “flow” or “flux”	1771	Scheele (Sweden)
Nitrogen (N)	Means “nitre maker”	1772	Rutherford (England)
Oxygen (O)	Means “acid maker”	1774, 1772–5	Priestley (England), Scheele (Sweden)
Chlorine (Cl)	Means “green gas”	1774	Scheele (Sweden)
Sodium (Na)	Named from <i>soda</i>	1807	Davy (England)
Potassium (K)	Named from <i>potash</i>	1807	Davy (England)
Calcium (Ca)	Named from <i>calx</i>	1808	Davy (England)
Silicon (Si)	Named from <i>silex</i> , “flint”	1823	Berzelius (Sweden)
Bromine (Br)	Means <i>stench</i>	1826	Balard (France)
Aluminum (Al)	Found in <i>alum</i>	1827	Wöhler (Germany)
Magnesium (Mg)	Named after the city of Magnesia	1830	Bussy (France)
Helium (He)	Named from <i>Helios</i> , Greek sun god	1868	Janssen (France), Lockyer (England)
Argon (Ar)	Named from <i>argos</i> , “lazy”	1894	Rayleigh (England), Ramsay (Scotland)
Krypton (Kr)	Named from <i>kryptos</i> , “concealed”	1898	Ramsey, Travers (Scotland)
Neon (Ne)	Named from <i>neos</i> , “new”	1898	Ramsey, Travers (Scotland)
Xenon (Xe)	Named from <i>xenos</i> , “guest”	1898	Ramsey, Travers (Scotland)
Polonium (Po)	Named after the country of Poland	1898	Curie, Curie (France)
Radon (Rn)	Originally named <i>radium emanation</i>	1900	Dorn (Germany)

called it *plumbum nigrum*. The English word “plumber” describes a person who installs or fixes lead pipes. Beginning in the 1920s, lead was emitted in gasoline. Due to its serious health effects, most countries have since banned leaded gasoline. Lead is also still emitted worldwide during certain industrial processes.

#### 1.2.1.3. Sulfur

Elemental **sulfur** (*sulvere* in Sanskrit; *sulphurium* in Latin) is a nonmetallic, pale yellow, crystalline mineral found in volcanic and hot spring deposits, sedimentary beds, and salt domes. Sulfur was known by ancient Egyptian alchemists (Brown, 1913). It was also mentioned by the Greek Dioscorides and by Pliny the Elder in the first century A.D. The word **brimstone** (or “burn-stone,” referring to its combustibility) is an Old English word for sulfur. In the Book of *Genesis*, “brimstone and fire” were said to have rained down on the cities of Sodom and Gomorrah, destroying them. If this event occurred, it may have been due to a volcanic eruption in which various forms of sulfur emanated. Sulfur in the air is primarily in the form of sulfur dioxide gas [SO<sub>2</sub>(g)] and aqueous sulfuric acid [H<sub>2</sub>SO<sub>4</sub>(aq)].

#### 1.2.1.4. Carbon

Elemental **carbon** (*carbo* in Latin, meaning “charcoal”) was well known in the Ancient World, although it is unlikely that alchemists at the time knew that diamonds,

**Table 1.3. Dates of Discovery of Compounds of Atmospheric Importance**

Molecule	Chemical Formula	Mineral Name	Former Name, Alternate Name, or Meaning	Year Discovered	Discoverer
Calcium carbonate	CaCO <sub>3</sub> (s)	Calcite, aragonite	Calcspar	B.C.	?
Sodium chloride	NaCl(s)	Halite	Common salt	B.C.	?
Potassium nitrate	KNO <sub>3</sub> (s)	Nitre	Saltpeter, nitrum	B.C.	?
Sulfurous acid	H <sub>2</sub> SO <sub>3</sub> (aq)		Oil of sulfur, acidum volatile	B.C.	?
Sodium carbonate	Na <sub>2</sub> CO <sub>3</sub> (s)	Natrite	Nitrum, nator, nitron, natrum, soda ash, washing soda, salt-cake, calcined soda	B.C.	?
Calcium sulfate dihydrate	CaSO <sub>4</sub> ·2H <sub>2</sub> O(s)	Gypsum	“Plaster”	315 B.C.	Theophrastus (Greece)
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub> (aq)		Oil of vitriol, acidum fixum, vitriolic acid, spirit of alum, spirit of vitriol	<1264	de Beauvais (France)
Ammonium chloride	NH <sub>4</sub> Cl(s)	Sal ammoniac		<1400	Geber or later author
Molecular hydrogen	H <sub>2</sub> (g)		Inflammable air	<1520, 1766	Paracelsus (Switzerland), Cavendish (England)
Nitric acid	HNO <sub>3</sub> (aq)		Spirit of nitre	1585	Libavius (Germany)
Hydrochloric acid	HCl(aq)		Spirit of salt	<1640	Sala (Germany)
Carbon dioxide	CO <sub>2</sub> (g)		Gas silvestre, fixed air	<1648, 1756	Van Helmont (Belgium), Black (Scotland)
Ammonia	NH <sub>3</sub> (g)		Gas pingue, alkaline acid air	<1648, 1756	Van Helmont (Belgium), Black (Scotland)
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub> (s)	Nitrammite	Nitrum flammans, ammonia–nitre, ammoniak–saltpeter	1648	Glauber (Germany)
Sodium sulfate	Na <sub>2</sub> SO <sub>4</sub> (s)	Thenardite	Sal mirabile, Glauber's salt	1648	Glauber (Germany)
Amonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (s)	Mascagnite	Secret sal ammoniac	<1648	Glauber (Germany)
Potassium sulphate	K <sub>2</sub> SO <sub>4</sub> (s)	Arcanite	Sal polychrestum glaseri, Arcanum duplicatum	1663	Glaser (France)
Calcium nitrate	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(s)	Nitrocalcite	Baldwin's phosphorus	<1669	Baldwin (Germany)
Magnesium sulfate	MgSO <sub>4</sub> ·7H <sub>2</sub> O(s)	Epsomite	Epsom salt	1695	Grew (England)
Magnesium carbonate	MgCO <sub>3</sub> (s)	Magnesite	Magnesia alba	c. 1695	?
Nitrogen dioxide	NO <sub>2</sub> (g)		Nitrous gas, red nitrous vapor	<1714, 1774	Ramazzini (Italy), Priestley (England)

Table 1.3. (continued)

Molecule	Chemical Formula	Mineral Name	Former Name, Alternate Name, or Meaning	Year Discovered	Discoverer
Molecular nitrogen	N <sub>2</sub> (g)		Mephitic air	1772	Rutherford (England)
Nitric oxide	NO(g)		Nitrous air	1772	Priestley (England)
Nitrous oxide	N <sub>2</sub> O(g)		Diminished nitrous air, laughing gas	1772	Priestley (England)
Hydrochloric acid	HCl(g)		Marine acid air, Muriatic gas	1772	Priestley (England)
Hydrofluoric acid	HF(g)		Fluor acid	1773	Scheele (Sweden)
Molecular oxygen	O <sub>2</sub> (g)		Dephlogisticated air	1774, 1772–5	Priestley (England), Scheele (Sweden)
Chlorine gas	Cl <sub>2</sub> (g)		Dephlogisticated marine (muriatic) acid gas, “green gas”	1774	Scheele (Sweden)
Acetaldehyde	CH <sub>3</sub> CHO(g)			1774	Scheele (Sweden)
Carbon monoxide	CO(g)			1772–1779	Priestley (England)
Sulfur dioxide	SO <sub>2</sub> (g)		Vitriolic acid air	1774–1779	Priestley (England)
Nitric acid	HNO <sub>3</sub> (g)			1784	Priestley (England), Cavendish (England)
Hypochlorous acid	HOCl(g)			1830	Balard (France)
Ozone	O <sub>3</sub> (g)		Ozien, “to smell”	1840	Schonbein (Germany)

graphite (plumbago), and charcoal all contained carbon. Carbon in diamonds and graphite is in pure crystalline form. In charcoal, coal, and coke, it takes on a variety of shapes and structures. In the Ancient World, diamonds were valued only for their rarity, not for their beauty, because diamonds were not cut (and thus did not shine) until the fifteenth century. In the Ancient World, graphite was used to make black marks on paper and charcoal was used as a fuel. Today, the emission of elemental carbon (also called *black carbon*) in the form of soot particles exacerbates global warming, visibility, and health problems.

#### 1.2.1.5. Sodium Carbonate (Solid)

**Sodium carbonate** [Na<sub>2</sub>CO<sub>3</sub>(s)] is a crystal mineral first found by the Egyptians in the Lakes of Natron, a group of six lakes to the west of the Nile Delta. The Egyptians called it *nitrum*. Its name was modified to *nator* by the Hebrews, *nitron* by the Greeks, and *natrum* in the fifteenth century. Today, its mineral name is **natrite**. For centuries, it has been used as an ingredient in soaps. Some chemical industry names for it have been **washing soda**, **soda ash**, and **salt cake**. The manufacture of sodium carbonate for use in soaps caused acid deposition problems in England and France in the nineteenth century (Chapter 10). In the air, sodium carbonate is present in soil-dust particles.

#### 1.2.1.6. Calcium Carbonate (Solid)

**Calcium carbonate** [ $\text{CaCO}_3(\text{s})$ ] is a crystal present in pure form in the minerals **calcite** and **aragonite** and in mixed form in limestone, marble, chalk, and shells and skeletons of invertebrates. **Limestone** is sedimentary rock containing calcite or **dolomite** [ $\text{CaMg}(\text{CO}_3)_2(\text{s})$ ], **marble** is recrystallized limestone, and **chalk** is fine-grained rock made of skeletons of microorganisms. In the ancient world, chalk was used for writing. In the air, calcium carbonate is a component of soil-dust particles. The name *calcite* originates from the word “calcspar,” itself derived from the Greek word for limestone, *khálix*.

#### 1.2.1.7. Sodium Chloride (Solid)

**Sodium chloride** [ $\text{NaCl}(\text{s})$ ], a crystal mineral formed from the evaporation of ocean water, was well-known in the ancient world. It was found mixed with earthy material and mentioned in the Old Testament to “lose its savor” on its exposure. Today, its mineral name is **halite**, from the Greek word *hals* (“salt”). In the air, sodium chloride is present in sea-spray particles.

#### 1.2.1.8. Potassium Nitrate (Solid)

**Potassium nitrate** [ $\text{KNO}_3(\text{s})$ ] is a crystal mineral also called **saltpeter** (“salt of rock”) because it was often found as a saltlike crust on rocks. Saltpeter was an ingredient of Greek fires. In the fifteenth century, it was called *nitrum* (the same early name as sodium carbonate). Today, its mineral name is **nitre**. Potassium nitrate forms chemically in soil-dust and sea-spray particles and may be the most abundant nitrogen-containing solid in the air.

#### 1.2.1.9. Sulfurous Acid (Aqueous)

Ancient Egyptian alchemists obtained **sulfurous acid** [ $\text{H}_2\text{SO}_3(\text{aq})$ ] (“oil of sulfur”) by combusting elemental sulfur in the presence of water. Such burning was also carried out in Homer’s time for the purpose of fumigation. Sulfurous acid’s use in bleaching wool is mentioned by Pliny the Elder. In the air, sulfurous acid, a precursor to acid deposition, forms when sulfur dioxide gas dissolves in water-containing particles.

#### 1.2.1.10. Calcium Sulfate Dihydrate (Solid)

**Calcium sulfate dihydrate** [ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$ ] is a crystal mineral, more commonly known as **gypsum** (*gypsos*, “plaster” in Greek). Gypsum was first referred to in 315 B.C. by the Greek botanist and alchemist, **Theophrastus** (371–286 B.C.), born in Lesbos, who wrote 10 books on botany, stones, metals, and minerals. Gypsum is a naturally occurring mineral that appears worldwide in soils and aerosol particles. It forms chemically when aqueous sulfuric acid reacts with the mineral calcite. When aerosol particles containing sulfuric acid deposit onto marble statues (which contain calcite), a gypsum crust also forms. Gypsum soil beds are mined to produce plaster of paris, obtained by heating pure gypsum and adding water. **Plaster of paris** was named such because early Parisians found gypsum in the clays and muds of the Paris basin and used the gypsum to make plaster and cement. Gypsum is possibly the most common sulfur-containing solid in the atmosphere.

#### 1.2.1.11. Ammonium Chloride (Solid)

**Geber** (or Abu Abdallah Jaber ben-Hayyam al-Kufi, Fig. 1.2) was an Arabian alchemist who lived about 750–800 A.D. Although the writings attributed to him may

have been forged in the thirteenth century, it is clear that Geber or the writer was aware of *sal ammoniac* [ $\text{NH}_4\text{Cl}(\text{s})$ , **ammonium chloride**], a mineral crystal obtained from the Libyan desert near the temple of Jupiter Ammon (the ultimate source of the name for the gas, **ammonia**). Ammonium chloride can form when ammonia gas enters sea-spray particles, which contain chlorine. It may be the most abundant ammonium-containing solid in the air.

#### 1.2.1.12. Sulfuric Acid (Aqueous)

**Vincent de Beauvais** (1190–1264), a French philosopher, mentions the solvent power of the liquid acid distilled from the natural crystal, potassium alum [ $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(\text{s})$ ]. The acid was probably dissolved **sulfuric acid** [ $\text{H}_2\text{SO}_4(\text{aq})$ ], and de Beauvais may have been the first to record its observation. In 1585, **Andreas Libavius** (1540–1616; Fig. 1.3), a German chemist who wrote one of the first noteworthy chemical textbooks, found that sulfuric acid could also be extracted from “green vitriol” (ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$ , a blue-green natural crystal) and obtained by burning elemental sulfur with saltpeter [ $\text{KNO}_3(\text{s})$ ] in the presence of liquid water. Sulfuric acid is present in aerosol particles and responsible for most acid deposition problems today.

#### 1.2.1.13. Nitric Acid (Aqueous)

Libavius also reacted elemental sulfur with dissolved **nitric acid** [ $\text{HNO}_3(\text{aq})$ ], indicating that dissolved nitric acid was known during his time. It was most likely formed from the reaction of  $\text{H}_2\text{SO}_4(\text{aq})$  with  $\text{KNO}_3(\text{s})$ . Today, nitric acid is an abundant component of aerosol particles.

#### 1.2.1.14. Hydrochloric Acid (Aqueous)

**Angelus Sala** (1575–1640), a German physician, produced ammonium chloride [ $\text{NH}_4\text{Cl}(\text{s})$ ] by treating **ammonium carbonate** [ $(\text{NH}_4)_2\text{CO}_3(\text{s})$ ] with dissolved **hydrochloric acid** [ $\text{HCl}(\text{aq})$ ]. This may be the first recorded use of  $\text{HCl}(\text{aq})$ . Hydrochloric acid was probably obtained by reacting common salt [ $\text{NaCl}(\text{s})$ ] with sulfuric acid [ $\text{H}_2\text{SO}_4(\text{aq})$ ]. Hydrochloric acid is an abundant component of sea-spray particles.

#### 1.2.1.15. Sodium Sulfate Decahydrate, Ammonium Nitrate, and Ammonium Sulfate (Solids)

**Johann Rudolf Glauber** (1604–1688; Fig. 1.4), a German chemist, discovered what is now called **Glauber's salt** [ $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(\text{s})$ , **sodium sulphate decahydrate**]. He called it *sal mirabile* and referred to it as a universal medicine. Glauber was also aware of the mineral **ammonium nitrate** [ $\text{NH}_4\text{NO}_3(\text{s})$ ], which he called *nitrum*



Figure 1.2. Geber (c. 750–800).



Figure 1.3. Andreas Libavius (1540–1616).



*flammans*, and the mineral **ammonium sulfate**  $[(\text{NH}_4)_2\text{SO}_4(\text{s})]$ , which he called *secret sal ammoniac*. In his book, *Miraculum Mundi*, he provided a recipe for producing ammonium sulfate and stated that it may have previously been used by two alchemists, Paracelsus and Van Helmont. Ammonium sulfate is also a natural sublimation product

of the fumaroles of Mount Vesuvius and Mount Etna. Mascagni first described the natural occurrence of this salt; therefore, its mineral name today is **mascagnite**. Without the hydrated water, sodium sulfate is a mineral called **thenardite**, named after Baron Louis Jacques Thenard (1777–1857), who found it in Espartinas salt lake, near Madrid, Spain. Ammonium nitrate is not a common naturally occurring mineral in soil, although it was found to exist in Nicojack Cavern, Tennessee. Its mineral name is **nitrammite**, named after its composition. All three salts form chemically within aerosol particles.



**Figure 1.4.** Johann Rudolf Glauber (1604–1688).

**nitrate**  $[\text{Ca}(\text{NO}_3)_2(\text{s})]$ , which is phosphorescent in the dark. Because of its appearance, he named the substance *phosphorus*, meaning “light-bearer.” It is now known as **Baldwin’s phosphorus** because it differs from elemental phosphorus. Elemental **phosphorus** (P), a nonmetallic substance that also glows in the dark, was discovered in Germany in 1669 by **Hennig Brand** (?–c.1692) of Sweden by distilling a mixture of sand and evaporated urine. The extraction of phosphorus was replicated by Johann Kunckel (1630–1750) of Germany, who knew both Baldwin and Brand, and called phosphorus the “**phosphorus of Brand**.” Kunckel published a treatise on phosphorus in 1678. Calcium nitrate forms chemically in aerosol particles. Phosphorous is a component of the Earth’s crust and of soil-dust particles.

#### 1.2.1.18. Magnesium Sulfate (Solid)

In 1695, **Nehemiah Grew**, a London physician, evaporated water from the mineral spring at Epsom to obtain the crystal, **magnesium sulfate**  $[\text{MgSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})]$ , which was subsequently called **Epsom salt**. Magnesium sulfate can be found in the air as a constituent of soil-dust and sea-spray particles.

#### 1.2.1.16. Potassium Sulfate (Solid)

In 1663, **Christopher Glaser** (1615–1673), a French apothecary to Louis XIV, combined sulfur with melted saltpeter  $[\text{KNO}_3(\text{s})]$  to form the crystal **potassium sulfate**  $[\text{K}_2\text{SO}_4(\text{s})]$ , which he named *sal polychrestum glaseri*. Its present mineral name is **arcanite**, from the Latin words *arcanum duplicatum*, an early alchemist name for the salt. Arcanite is a chemically produced component of aerosol particles.

#### 1.2.1.17. Calcium Nitrate (Solid)

In 1675, **Christopher Baldwin** (1600–1682) wrote a book in which he discussed a preparation of chalk [made primarily of calcite,  $\text{CaCO}_3(\text{s})$ ] with nitric acid  $[\text{HNO}_3(\text{aq})]$ , to produce the crystal **calcium**

### 1.2.2. Studies of Gases in the Air, 1450–1790

Gases were more difficult to observe and isolate than were liquids or solids, so the study of gases began only after many liquids and solids had been investigated. In this subsection, the history of discovery of gases from the fifteenth through eighteenth centuries is discussed.

#### 1.2.2.1. Water Vapor

Although water vapor was known in the ancient world, changes in its abundance were not detected until the fifteenth century. In 1450, **Nicolas Cryfts** suggested that changes in atmospheric water vapor could be measured with a **hygroscope**, which could be constructed of dried wool placed on a scale. A change in weight of the wool over time would represent a change in the water-vapor content of the air. Capitalizing on Cryfts notes, **Leonardo da Vinci** (1452–1519) built such a hygroscope. Wood and seaweed were later used in place of wool. In the seventeenth century, gut, string, cord, and hair were also used to measure changes in water vapor because the lengths of these materials would change on their absorption of water from the air.

#### 1.2.2.2. Molecular Hydrogen (Gas)

**Paracelsus** (1493–1541; Fig. 1.5), an alchemist born near Zurich, may have been the first to observe what is now known as **hydrogen gas** or **molecular hydrogen** [ $\text{H}_2(\text{g})$ ]. He found that when sulfuric acid was poured over certain metals, it gave off an inflammable vapor. In 1766, Henry Cavendish found the same result, but isolated the vapor's properties and is more well-known for the discovery of molecular hydrogen. Molecular hydrogen is a well-mixed gas in today's lower atmosphere.

#### 1.2.2.3. Ammonia and Carbon Dioxide (Gases)

**John Baptist Van Helmont** (1577–1644), born in Belgium, introduced the term **gas** into the chemical vocabulary. He produced what he called *gas silvestre* (“gas that is wild and dwells in out-of-the-way places”) by fermenting alcoholic liquor, burning charcoal, and acidifying marble and chalk. The gas he discovered in all three cases, but did not know at the time, was **carbon dioxide** [ $\text{CO}_2(\text{g})$ ]. Another gas he produced was an inflammable vapor evolved from dung. He called this gas *gas pingue*, which was probably impure **ammonia** [ $\text{NH}_3(\text{g})$ ]. Today, carbon dioxide is thought to be the main cause of global warming. Ammonia, produced naturally and anthropogenically, dissolves and reacts in aerosol particles.

#### 1.2.2.4. Fire-Air

In 1676, **John Mayow** (1643–1679; Fig. 1.6), an English physician, found that air appeared to contain two components, one that allowed fire to burn and animals to breathe (which Mayow called *nitro-aereo*, or “**fire-air**”), and another that did not.



Figure 1.5. Paracelsus (1493–1541).



When he placed a lighted candle and a small animal in a closed vessel, the lighted candle went out before the animal died. When he placed only the animal in the vessel, the animal took twice as long to die. Thus, Mayow showed that air was diminished by combustion and breathing. Fire–air later turned out to be **molecular oxygen** [ $\text{O}_2(\text{g})$ ].



**Figure 1.6.** John Mayow (1643–1679).

#### 1.2.2.5. Phlogisticated Air

In 1669, **Johann Joachim Becher** (1635–1682), a German physician, took a step backward in the understanding of the composition of air when he wrote *Physica Subterranea*. In this book, he stated that every combustible material contains different amounts of *terra mercurialis* (“fluid or mercurial earth,” thought to be mercury), *terra lapidia* (“strong or vitrifiable earth,” thought to be salt), and *terra pinguis* (“fatty earth,” thought to be sulfur). During combustion, *terra pinguis* was thought to be expelled to the air. The principle that every combustible material releases its “source” of combustion was not new, but it was more specific than were previous theories.

One of Becher’s followers was **Georg Ernst Stahl** (1660–1734). In 1702, Stahl published *Specimen Becherianum*, in which he restated that every material contains a special combustible substance that escapes to the air when the material is burned. Stahl called the combustible substance, previously named *terra pinguis* by Becher, **phlogiston** after the Greek word *phlogizein*, “to set on fire.” Stahl felt that *phlogiston* disappeared either as fire or

as **soot**, which he felt was the purest form of *phlogiston*. Becher’s and Stahl’s theories of *terra pinguis* and *phlogiston* turned out to be incorrect because combustion occurs when oxygen from the air combines with a substance on heating, and the resulting oxide of the substance is released as a gas, not when a material alone in a substance is released on heating.

Interestingly, in *Specimen Becherianum*, Stahl was the first to point out that sulfurous acid is more volatile (evaporates more readily) than is sulfuric acid. He called the former *acidum volatile* and the latter *acidum fixum*. He also noted that sulfuric acid is the stronger acid.

#### 1.2.2.6. Carbon Dioxide Again – Fixed Air

In 1756, **Joseph Black** (1728–1799; Fig. 1.7), a Scottish physician and chemist, performed an experiment in which he heated **magnesium carbonate** [ $\text{MgCO}_3(\text{s})$ ], called *magnesia alba* (“white magnesia”) at the time. On heating,  $\text{MgCO}_3(\text{s})$  lost weight, producing a heavy gas that neither sustained a flame nor supported life. When the gas was exposed to quicklime [ $\text{CaO}(\text{s})$ , calcium oxide], a white-gray crystal, the weight was reabsorbed. Black called the gas “**fixed air**” because of its ability to attach or “fix” to compounds exposed to it. The fixed air turned out to be **carbon dioxide** [ $\text{CO}_2(\text{g})$ ], and when it was reabsorbed on exposure to  $\text{CaO}(\text{s})$ , it was really forming calcium carbonate [ $\text{CaCO}_3(\text{s})$ ]. Fixed air was renamed to carbon dioxide in 1781 by

the French chemist, **Antoine Laurent Lavoisier** (1743–1794). What Black did not recognize was that fixed air, or  $\text{CO}_2(\text{g})$ , had previously been discovered by Van Helmont more than a century earlier. In 1756, Black also isolated ammonia gas [ $\text{NH}_3(\text{g})$ ], previously observed by Van Helmont and later called **alkaline acid air** by Joseph Priestley. Black is separately known for making the first systematic study of a chemical reaction and developing the concepts of latent heat and specific heat.

#### 1.2.2.7. Molecular Hydrogen

##### Again – Inflammable Air

In 1766, **Henry Cavendish** (1731–1810; Fig. 1.8), an English chemist and physicist, followed up Black's work by producing a gas he called "**inflammable air**." This gas was obtained by diluting either sulfuric acid [ $\text{H}_2\text{SO}_4(\text{aq})$ ] or hydrochloric acid [ $\text{HCl}(\text{aq})$ ] with water and pouring the resulting solution on a metal, such as iron, zinc, or tin. This experiment was similar to that of Paracelsus, who also observed an inflammable vapor. Cavendish thought "inflammable air" was *phlogiston*, but this turned out to be incorrect. Nevertheless, Cavendish isolated the properties of the gas. In 1783, he found that exploding a mixture of the gas with air produced water. Subsequently, Lavoisier called the gas **hydrogen**, the "water producer." More specifically, the gas was **molecular hydrogen** [ $\text{H}_2(\text{g})$ ].

In other experiments, Cavendish exposed marble, which contains  $\text{CaCO}_3(\text{s})$ , to hydrochloric acid [ $\text{HCl}(\text{aq})$ ] to produce  $\text{CO}_2(\text{g})$ , as Van Helmont had done earlier. Cavendish took the further step of measuring the properties of  $\text{CO}_2(\text{g})$ . Cavendish is also known for studying the weights of gases and the density of the Earth. In 1783, after oxygen had been discovered, Cavendish calculated that air contained 20.83 percent oxygen by volume, close to the more accurate measurement today of 20.95 percent.

#### 1.2.2.8. Molecular Nitrogen (Gas) – Mephitic Air

In 1772, **Daniel Rutherford** (1749–1819; Fig. 1.9) performed an experiment by which he allowed an animal to breathe the air in an enclosed space until the animal died [removing the molecular oxygen,  $\text{O}_2(\text{g})$ , which had not been discovered yet]. He then exposed the remaining air to the crystal **caustic potash** [ $\text{KOH}(\text{s})$ , potassium hydroxide or pot ashes], obtained by burning wood in a large iron pot.  $\text{CO}_2(\text{g})$  in the remaining air reacted with caustic potash, forming **pearl ash** or **potash** [ $\text{K}_2\text{CO}_3(\text{s})$ , potassium carbonate]. The residue after  $\text{CO}_2(\text{g})$  was removed could

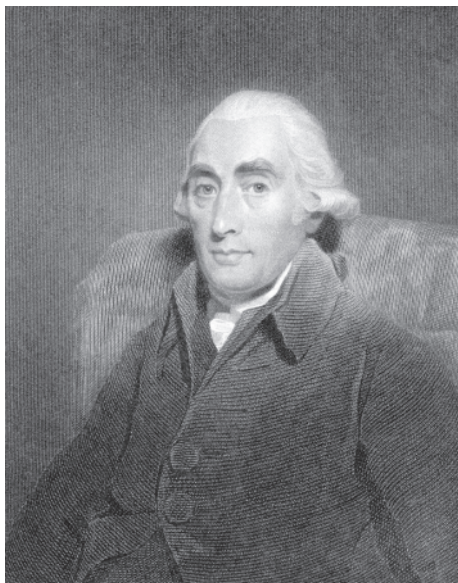
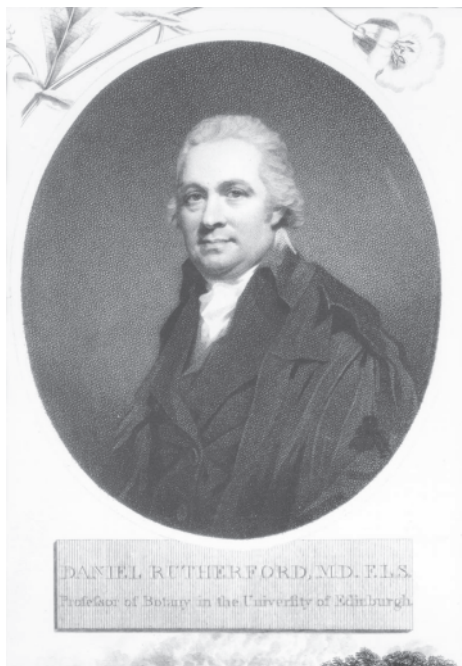


Figure 1.7. Joseph Black (1728–1799).



Figure 1.8. Henry Cavendish (1731–1810).

not sustain life; thus, Rutherford called it “**mephitic** [poisonous or foul-smelling] **air**.” Mephitic air is now known as **molecular nitrogen** gas [ $\text{N}_2(\text{g})$ ], which makes up nearly 80 percent of air by volume. The name **nitrogen**, the “nitre maker,” was given by **Jean-Antoine Chaptal** (1756–1832), a French industrial chemist, because nitrogen was found to be a constituent of the crystal nitre [ $\text{KNO}_3(\text{s})$ ].

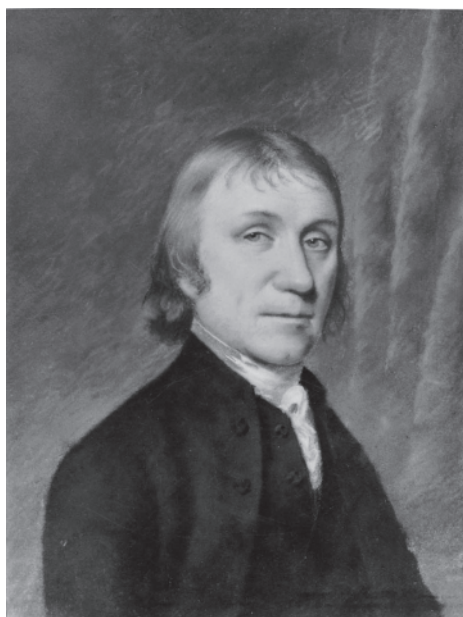


**Figure 1.9.** Daniel Rutherford (1749–1819).

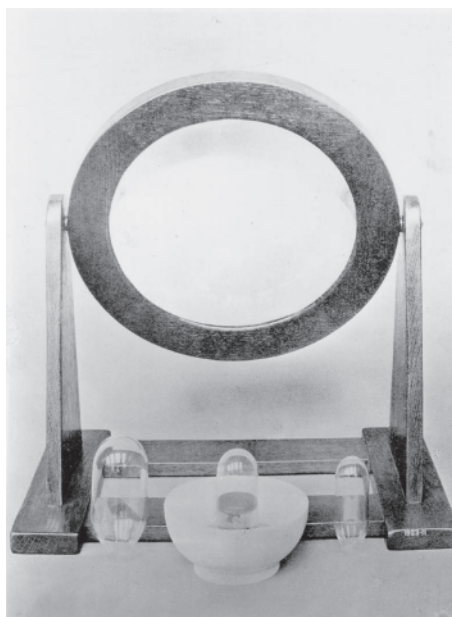
#### 1.2.2.9. Molecular Oxygen (Gas) – Dephlogisticated Air

**Molecular oxygen** gas [ $\text{O}_2(\text{g})$ ] was discovered independently by two chemists, on August 1, 1774, by **Joseph Priestley** (1733–1804; Fig. 1.10) and sometime between 1772 and 1775 by **Karl Wilhelm Scheele** (1742–1786; Fig. 1.11), a Swedish chemist. Although both chemists discovered oxygen near the same time, Priestley announced his discovery in 1774, and Scheele published his discovery in 1777.

To obtain oxygen, Priestley burned the element mercury ( $\text{Hg}$ ), a silvery-white liquid metal, in air to form bright red mercuric oxide [ $\text{HgO}(\text{s})$ ], a powder. He then heated the mercuric oxide in a container from which all air had been removed. Burning mercuric oxide in a vacuum released oxygen so that the only gas in the container was molecular oxygen. Due to the container's high oxygen content, flammable material burned more readily in the container than in regular air.



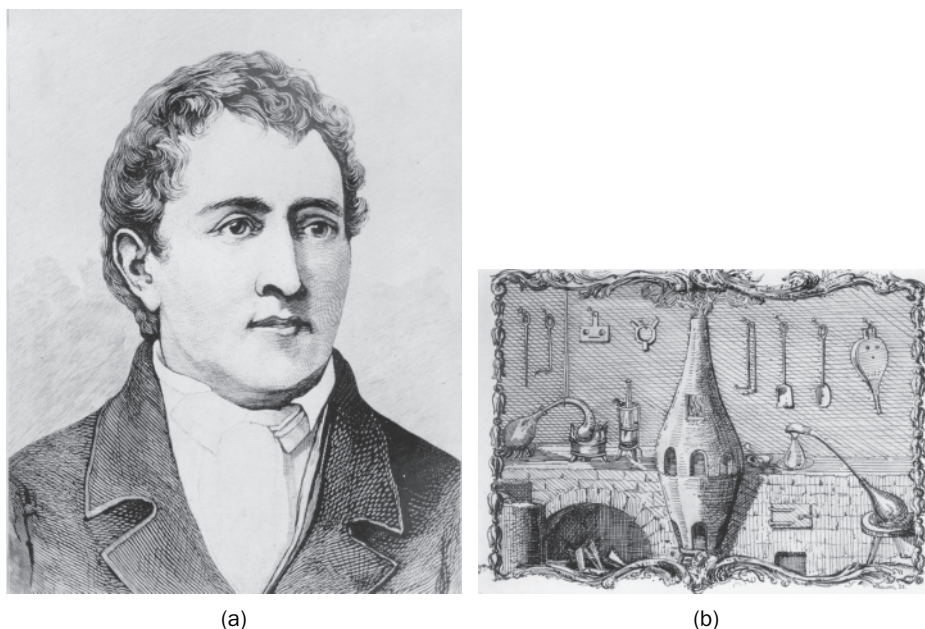
(a)



(b)

**Figure 1.10.** (a) Joseph Priestley (1733–1804). (b) Reconstruction of Priestley's oxygen apparatus.





**Figure 1.11.** (a) Karl Wilhelm Scheele (1742–1786). (b) Scheele's laboratory, with oven in the center.

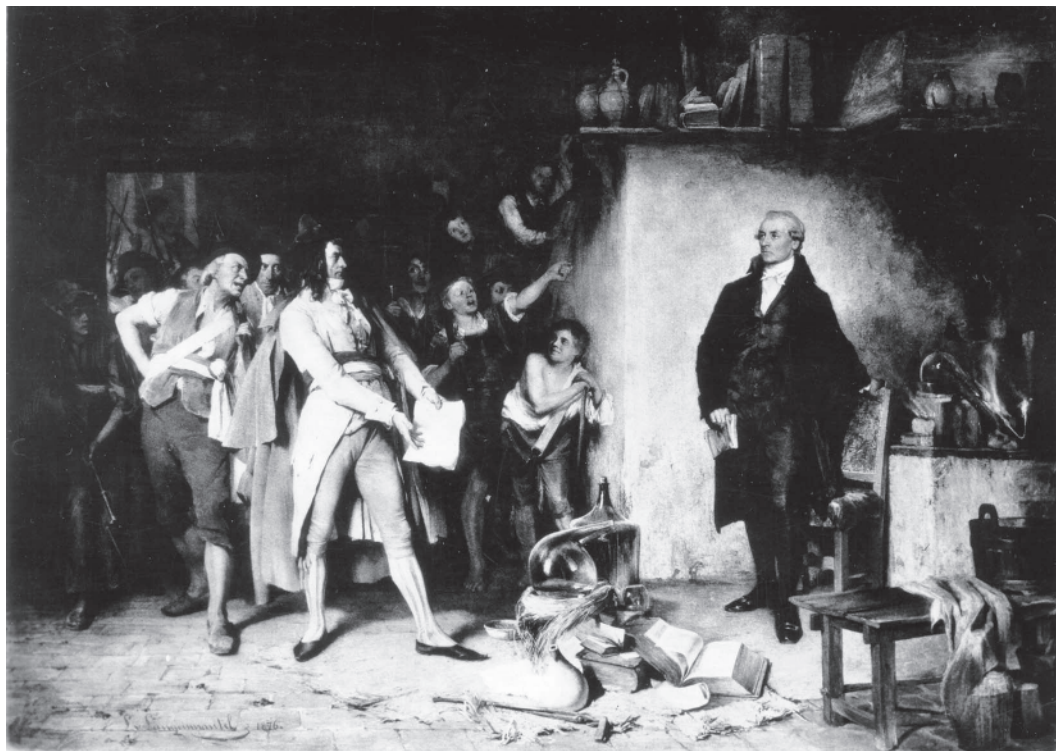
Priestley called the new gas “**dephlogisticated air**” because he incorrectly believed that burning occurred so brightly because the gas contained no *phlogiston*. He thought that, on the burning of a substance, the substance emitted *phlogiston* into the gas, causing the flame to die out eventually.

Scheele independently isolated molecular oxygen in at least three ways: heating manganic oxide [ $\text{Mn}_2\text{O}_3(\text{s})$ ] (a black powder), heating red mercuric oxide [ $\text{HgO}(\text{s})$ ], and heating a mixture of nitric acid [ $\text{HNO}_3(\text{aq})$ ] and potassium nitrate [ $\text{KNO}_3(\text{s})$ ].

At the end of 1774, Priestley went to Paris to explain his method of preparing dephlogisticated air to Lavoisier, who subsequently experimented with the gas for 12 years and revised its name to **oxygen**, the “acid maker,” because he believed (incorrectly) that all acids contained oxygen. Almost all oxygen in the air is in the form of **molecular oxygen** [ $\text{O}_2(\text{g})$ ].

Subsequently, Lavoisier formalized the oxygen theory of combustion and proved the law of conservation of mass, which states that, in a chemical reaction, mass is conserved. For example, when sulfur, phosphorus, carbon, or another solid is burned, its gas-plus solid-phase mass increases by an amount equal to the loss in mass of oxygen from the air. Lavoisier used the fact that oxygen combines with a solid to form an oxide of the solid that is released to the air during combustion to disprove the theory of *phlogiston*, which was premised on the belief that only material in the original solid was released on combustion. Lavoisier similarly showed that rusting is a mass-conserving process by which oxygen from the air combines with a solid to form an oxide of the solid.

In 1775–6, Lavoisier found that diamonds contain pure carbon and produce carbon dioxide when heated. In 1781, he renamed Black's fixed air to carbon dioxide and determined its elemental composition. Lavoisier also devised the first chemical system of nomenclature and specified that matter exists in three states – gas, liquid, and solid. He found that gases could be reduced to liquids or solids by cooling the air. Lavoisier is said to be the founder of modern chemistry.



**Figure 1.12.** “The Arrest of Lavoisier,” (1876) by L. Langenmantel. Courtesy of the Edgar Fahs Smith Collection, University of Pennsylvania Library.

Unfortunately, Lavoisier was arrested during the French Revolution (Fig. 1.12) because he was a member of an unpopular political group, the *Ferme Générale*. On May 8, 1794, after a trial of less than a day, he and 27 others were guillotined and his body was thrown into a common grave.

Ironically, Priestley was attacked for his staunch defense of the principles of the French Revolution. On July 14, 1791, he lost his house, library, and laboratory in Birmingham, England, to a fire set by a mob angry at his public support of the revolution (Fig. 1.13). Priestley ultimately fled to the United States, where he lived until 1804.

#### **1.2.2.10. Additional Discoveries by Priestley**

During his career, Priestley discovered several additional gases relevant to air pollution. Between 1767 and 1773, while working at Mill Hill Chapel, in Leeds, Yorkshire, he isolated **nitric oxide** [ $\text{NO(g)}$ , “nitrous air”], **nitrogen dioxide** [ $\text{NO}_2\text{(g)}$ , “red nitrous vapor”], **nitrous oxide** [ $\text{N}_2\text{O(g)}$ , “diminished nitrous air”], and **hydrochloric acid** gas [ $\text{HCl(g)}$ , “marine acid air”]. Nitrogen dioxide may have been observed earlier by **Bernardo Ramazzini** (1633–1714), an Italian medical doctor and early pioneer in industrial medicine. Priestley also discovered **carbon monoxide** [ $\text{CO(g)}$ ], and **sulfur dioxide** [ $\text{SO}_2\text{(g)}$ , “vitriolic acid air”]. He formed gas-phase **nitric acid** [ $\text{HNO}_3\text{(g)}$ ], although Cavendish uncovered its composition. Priestley is also known for inventing the eraser and carbonated water (soda pop) and for being the first to observe photosynthesis.



**Figure 1.13.** The destruction of Priestley's house, library, and laboratory, Fair Hill, Birmingham, 1791. Courtesy of the Edgar Fahs Smith Collection, University of Pennsylvania Library.

Today,  $\text{NO}(\text{g})$ ,  $\text{NO}_2(\text{g})$ , and  $\text{CO}(\text{g})$  are emitted during fossil-fuel combustion and biomass burning and are components of urban smog.  $\text{N}_2\text{O}(\text{g})$  is produced from microbial metabolism, fossil-fuel combustion, and biomass burning.  $\text{HCl}(\text{g})$  is emitted by volcanos, evaporates from sea-spray particles, and is a product of chlorine reactions in the upper atmosphere.  $\text{SO}_2(\text{g})$  is emitted by volcanos, coal-fired power plants, and vehicles.  $\text{NO}_2(\text{g})$  and  $\text{SO}_2(\text{g})$  are precursors of acid deposition.

#### 1.2.2.11. Hydrofluoric Acid (Gas)

A meticulous artist at his craft, Scheele also discovered **hydrofluoric acid** gas [ $\text{HF}(\text{g})$ ] in 1773. Scheele named  $\text{HF}(\text{g})$  “fluor acid” after the crystal mineral **fluorspar** [ $\text{CaF}_2(\text{s})$ , fluorite], which contains it. The name *fluorspar* was coined in 1529 by Georgius Agricola from the Latin and French word *fluere*, which means “flow” or “flux,” because feldspar appeared to flow. Elemental **fluorine** (F) was isolated from  $\text{HF}(\text{g})$  only in 1886 by French chemist **Henri Moissan** (1852–1907). Prior to that time, at least two chemists died from toxic exposure trying to isolate F from  $\text{HF}(\text{g})$ . Moissan won a Nobel Prize for isolating fluorine and inventing the electric arc furnace. Today,  $\text{HF}(\text{g})$  is a product of chemical reactions in the upper atmosphere involving anthropogenically emitted fluorine compounds.



#### 1.2.2.12. Chlorine (Gas)

In 1774, Scheele discovered **chlorine gas** [ $\text{Cl}_2(\text{g})$ ], and thus the element chlorine (Cl), by reacting dissolved hydrochloric acid [ $\text{HCl}(\text{aq})$ ] with pyrolusite [ $\text{MnO}_2(\text{s})$ ]. Chlorine gas is a dense, odorous, greenish-yellow, corrosive, toxic gas. He called it *dephlogisticated marine acid gas*. Lavoisier changed the name to *oxymuriatic acid* because he incorrectly thought it contained oxygen and chlorine. The name was eventually changed to *chlorine*, the “green gas,” in 1810 by Sir Humphry Davy, who showed that chlorine was an element and did not contain oxygen. Today,  $\text{Cl}_2(\text{g})$  is a product of chemical reactions, primarily in the upper atmosphere.

### 1.2.3. Discoveries after 1790

After 1790, the pace at which gas, liquid, and solid chemicals were discovered increased. In the following subsections, more chemicals of atmospheric importance are discussed.

#### 1.2.3.1. Elemental Potassium, Sodium, Calcium, and Chlorine

In 1807–8, **Sir Humphry Davy** (1778–1829; Fig. 1.14), who, along with Priestley, is the most well-known British chemist, developed electrolysis, which led to the discovery of the elements **potassium** (K), **sodium** (Na), **calcium** (Ca), and **barium** (Ba).



**Figure 1.14.** Sir Humphry Davy (1778–1829).

**Electrolysis** is the passage of an electric current through a solution to break down a compound or cause a reaction. Potassium was isolated by electrolysis from **caustic potash** [potassium hydroxide,  $\text{KOH}(\text{s})$ ]. Potassium is the seventh-most abundant element in the Earth's crust and is emitted into the air in soil-dust and sea-spray particles. Sodium was isolated by electrolysis from **caustic soda** [sodium hydroxide,  $\text{NaOH}(\text{s})$ ]. The name *sodium* derives from the Italian word *soda*, a term applied to all alkalis in the Middle Ages. Sodium is the sixth-most abundant element in the Earth's crust and is emitted in soil-dust and sea-spray particles. Calcium was isolated by electrolysis from quicklime [ $\text{CaO}(\text{s})$ ]. The name *calcium* was derived from the word *calx*, the name the Romans used for lime. Calcium is the fifth-most abundant element in the Earth's crust and is emitted in soil-dust and sea-spray particles.

In 1810, Davy also named the element **chlorine**, previously called *oxymuriatic acid*. He proved that chlorine was an element and that muriatic gas [ $\text{HCl}(\text{g})$ , hydrochloric acid gas] contains chlorine and hydrogen, but no oxygen. He similarly proved that hydrofluoric acid gas [ $\text{HF}(\text{g})$ ] contains no oxygen. Both proofs contradicted Lavoisier's theory that all acids contained oxygen.

#### 1.2.3.2. Elemental Silicon and Chemical Symbols

A contemporary of Davy, **Jöns Jakob Berzelius** (1779–1848; Fig. 1.15) of Sweden discovered the elements **silicon** (Si) in 1823, selenium (Se) in 1817, and

thorium (Th) in 1828. He also spent 10 years determining the atomic or molecular weights of more than 2,000 elements and compounds, publishing the results in 1818 and 1826. Berzelius isolated *silicon*, a name derived from the Latin word *silex*, meaning “flint,” by fusing iron, carbon, and the crystal **quartz** [ $\text{SiO}_2(\text{s})$ ]. Silicon is the second-most abundant element in the Earth’s crust, after oxygen, and is present in soil-dust particles.

Berzelius’s most noticeable achievement was to invent a system of chemical symbols and notation. For elements, he used the first one or two letters of the element’s Latin or Greek name. For example, oxygen was denoted with an O, hydrogen with an H, mercury with Hg (hydrargyrum), and lead with Pb (plumbum). For compounds with more than one atom of an element, he identified the number of atoms of the element with a subscript. For example, he identified water with  $\text{H}_2\text{O}$ .

#### 1.2.3.3. Elemental Bromine and Hypochlorous Acid (Gas)

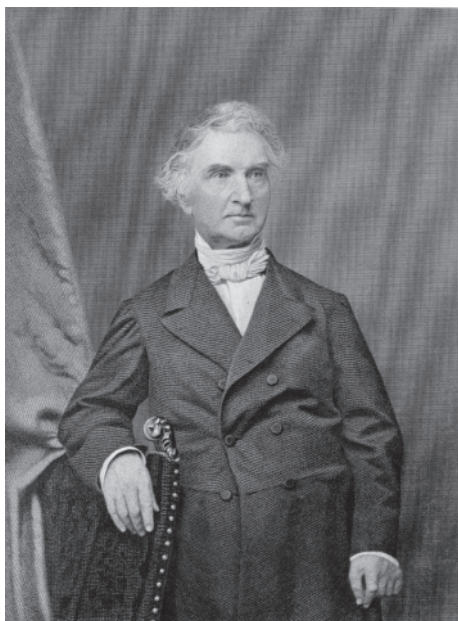
In 1826, **Antoine-Jérôme Balard** (1802–1876), a French apothecary, accidentally discovered the element **bromine** (Br) after analyzing the “bittern” (saline liquor) that remained after common salt had crystallized out of concentrated water in a salt marsh near the Mediterranean sea. *Bromine* means “stench” in Greek. It is a heavy, reddish-brown liquid that evaporates at room temperature to a red gas that irritates the throat and eyes and has a strong smell. It is the only nonmetallic element that can be in the liquid phase at room temperature. Balard is also known for his discovery of **hypochlorous acid** gas [ $\text{HOCl}(\text{g})$ ]. Bromine and hypochlorous acid contribute to ozone destruction in the upper atmosphere today.

#### 1.2.3.4. Organic Chemistry

**Baron Justus von Liebig** (1803–1873; Fig. 1.16) is considered the founder of organic and agricultural chemistry. Not only did he discover numerous organics and identify their properties, but he also introduced a systematic method of determining the empirical composition of organics, discovered several organic radicals, and isolated the atmospheric versus soil sources of plant nutrients, including carbon dioxide, water, and ammonia. He suggested that mineral fertilizers should be added to plants when their soils become depleted in nutrients.



**Figure 1.15.** Jöns Jakob Berzelius (1779–1848).



**Figure 1.16.** Baron Justus von Liebig (1803–1873).



#### 1.2.3.5. Elemental Magnesium

**Magnesium** (Mg) is the eighth-most abundant element in the Earth's crust. It is present in soil-dust and sea-spray particles. Although Sir Humphry Davy isolated an impure form of magnesium in 1808, it was not until 1828 that French chemist **Antoine-Alexandre-Brutus Bussy** isolated it in a pure state by reacting magnesium chloride with metallic potassium. Magnesium is named from **magnesia** [MgO(s), magnesium oxide], the crystal that contains it. Magnesia is named after the ancient city of Magnesia in Thessaly, a region of east-central Greece. The Greeks mined magnesia as an ingredient in the **philosopher's stone**, an elixir and a mineral that was believed to have the ability to convert metal into gold.

#### 1.2.3.6. Elemental Aluminum

In 1761, chemist Louis Bernard Guyton de Morveau (1737–1816) named the base in potassium alum [ $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(\text{s})$ ] **alumine**. In 1807, Davy proposed the name **aluminium** for the metal although it had yet to be isolated. An impure form of aluminum was isolated by Oersted in 1825, but it was not until 1827 that an associate of Liebig, **Friedrich Wöhler** (1800–1882), a German chemist, isolated a pure form of the metal and renamed it **aluminum**. Aluminum is the most abundant metal in the Earth's crust. Pure aluminum is silvery-white. Aluminum is present in soil-dust particles.



**Figure 1.17.** Christian Friedrich Schönbein (1799–1868).

#### 1.2.3.7. Ozone (Gas)

In 1839, one of the most important trace gases in the air, **ozone** [ $\text{O}_3(\text{g})$ ], was discovered by German chemist **Christian Friedrich Schönbein** (1799–1868; Fig. 1.17). Schönbein named ozone after the Greek word, *ozien*, which means “to smell,” because ozone has a pungent, sweet smell. Schönbein was also known for his discovery of gun-cotton in 1846. This compound is produced by reaction of either nitric acid or nitric plus sulfuric acid with a carbonaceous compound. Gun-cotton was the first of a group of “nitro-compound” explosives invented.

#### 1.2.3.8. Noble Gases

The air contains several inert noble gases in trace quantities, including helium (He), argon (Ar), neon (Ne), krypton (Kr), and xenon (Xe). All were discovered between 1868 and 1898. In 1868, **Pierre**

**Janssen** (1824–1907), a French astronomer, observed a yellow line in the spectrum of the sun's chromosphere. Because no known element on Earth could account for this line, he thought it was due to an element unique to the sun. **Joseph Norman Lockyer** (1836–1920), an English astronomer, confirmed Janssen's findings, and named the new element **helium** (He), after *Helios*, the Greek god of the sun. The element was not discovered on Earth until 1895, when **Sir William Ramsay** (1852–1916), a Scottish chemist, found it in the mineral **clevite**. Swedish chemists Per Theodor Cleve (after whom *clevite* is named) and Nils Abraham Langlet found helium in the mineral at

about the same time. Helium is the most abundant element in the universe next to hydrogen. On Earth, helium is emitted to the air following the decay of radioactive minerals.

In 1894, **Lord Baron Rayleigh**, an English physicist born John William Strutt (1842–1919), found that nitrogen gas from the air was 0.5 percent heavier than was that prepared chemically. He and Sir Ramsay found that the difference was due to an additional gas that they called **argon** (Ar), after the Greek word *argos*, meaning “lazy” in reference to the inert qualities of the gas. The two shared a Nobel Prize for their discovery. Argon forms from the radioactive decay of potassium (K). In his 1898 book *War of the Worlds*, H. G. Wells wrote that Martians used “toxic brown argon gas” to attack London, but were subdued by the common cold. Argon is neither brown nor poisonous at typical atmospheric concentrations. It is colorless and odorless as a gas and liquid. Sir Ramsay, together with M. W. Travers, went on to discover the elements **neon** (Ne), **krypton** (Kr), and **xenon** (Xe), all in 1898. All three are named after Greek words: *neos* (“new”), *kryptos* (“concealed”), and *xenos* (“guest”), respectively. The source of krypton and xenon is the radioactive decay of elements in the Earth’s crust, and the source of neon is volcanic outgassing.

#### 1.2.3.9. Radioactive Gases

In the twentieth century, two radioactive elements of atmospheric importance, **polonium** (Po) and **radon** (Rn), were discovered. These elements are carcinogenic and are found in the air of many homes overlying uranium-rich soils. In 1898, French chemists **Pierre** (1859–1906) and **Marie Curie** (1867–1934; Fig. 1.18) discovered polonium, which was named after Marie Curie’s native country, Poland. In 1903, Pierre and Marie Curie, along with French physicist **Antoine Henri Becquerel** (1852–1908), won a Nobel Prize for their fundamental research on radioactivity. In 1911, Marie Curie won a second prize for her discoveries of polonium and **radium** (Ra), a radon precursor. Radon, itself, was discovered in 1900 by German physicist **Friedrich Ernst Dorn** (1848–1916), who called it **radium emanation** because it is a product of radioactive decay of radium. The name *radium* is from the Latin word *radius*, meaning “ray.” Ramsay and Gray, who isolated radon and determined its density, changed its name to **niton** in 1908. In 1923, niton was renamed radon.



Figure 1.18. Marie Curie (1867–1934).

### 1.3. CHEMICAL STRUCTURE AND REACTIVITY

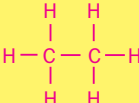
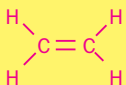
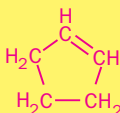
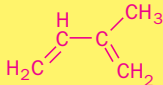
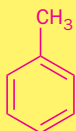
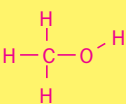

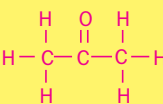
In this section, the structure and reactivity of a few compounds identified in earlier sections are discussed. Table 1.4 shows the chemical structure of selected compounds. Single, double, and triple lines between atoms denote single, double, and

Table 1.4. Structures of Some Common Compounds			
Compound Name	Structure Showing Bonds and Free Electrons	Formula with Free Electrons	Formula without Free Electrons
Molecular oxygen	$O=O$	$O_2(g)$	$O_2(g)$
Molecular nitrogen	$N \equiv N$	$N_2(g)$	$N_2(g)$
Ozone	$\begin{array}{c} O^+ \\ / \quad \backslash \\ -O \quad O \end{array}$	$O_3(g)$	$O_3(g)$
Hydroxyl radical	$\begin{array}{c} \bullet \\   \\ O-H \end{array}$	$\dot{O}H(g)$	$OH(g)$
Water vapor	$\begin{array}{c} H \\ / \quad \backslash \\ O \quad H \\   \quad   \\ H \quad H \end{array}$	$H_2O(g)$	$H_2O(g)$
Nitric oxide	$\begin{array}{c} \bullet \\   \\ N=O \end{array}$	$\dot{N}O(g)$	$NO(g)$
Nitrogen dioxide	$\begin{array}{c} \bullet \quad + \\   \quad \backslash \\ -O \quad N \quad O \end{array}$	$\dot{N}O_2(g)$	$NO_2(g)$
Sulfur dioxide	$\begin{array}{c} S \\ // \quad \backslash \\ O \quad O \end{array}$	$SO_2(g)$	$SO_2(g)$
Carbon monoxide	$\begin{array}{c} - \quad C \equiv O^+ \end{array}$	$CO(g)$	$CO(g)$
Carbon dioxide	$O=C=O$	$CO_2(g)$	$CO_2(g)$
Methane	$\begin{array}{c} H \\   \\ H-C-H \\   \\ H \end{array}$	$CH_4(g)$	$CH_4(g)$
Sulfate ion	$\begin{array}{c} O \\    \\ O=S-O^- \\   \\ O^- \end{array}$	$SO_4^{2-}$	$SO_4^{2-}$

triple bonds, respectively. For some compounds [OH(g), NO(g), NO<sub>2</sub>(g)], a single dot is shown adjacent to an atom. A single dot indicates that the atom has a free electron. Compounds with a free electron are called **free radicals** and are highly reactive. Some nonfree radicals that have a single bond [e.g., O<sub>3</sub>(g)] are also reactive because single bonds are readily broken. Compounds with triple bonds [N<sub>2</sub>(g), CO(g)] are not so reactive because triple bonds are difficult to break. **Noble elements** (He, Ar, Ne, Kr, Xe) have no free electrons and no potential to form bonds with other elements; thus, they are chemically unreactive (inert).

For some compounds in Table 1.4 [NO<sub>2</sub>(g), O<sub>3</sub>(g), CO(g)], positive and negative charges are shown. Such a charge distribution arises when one atom transfers charge to another atom during molecular formation. During NO<sub>2</sub>(g) formation, for example, a net negative charge is transferred to an oxygen atom from the nitrogen atom, resulting in the charge distribution shown. Compounds with both positive and negative charges have zero net charge and are not ions, but the positive (negative) end of the compound is likely to attract negative (positive) charges from other compounds, enhancing the reactivity of the compound. For SO<sub>4</sub><sup>2-</sup>, a net negative charge is shown, indicating that it is an ion.

**Table 1.5. Structures of Some Common Organic Compounds Found in Air**

Alkane	Alkene	Cycloalkene	Hemiterpene
Ethane $C_2H_6(g)$ 	Ethene $C_2H_4(g)$ 	Cyclopentene $C_5H_8(g)$ 	Isoprene $C_5H_8(g)$ 
Aromatic	Alcohol	Aldehyde	Ketone
Toluene $C_6H_5CH_3(g)$ 	Methanol $CH_3OH(g)$ 	Formaldehyde $HCHO(g)$ 	Acetone $CH_3COCH_3(g)$ 

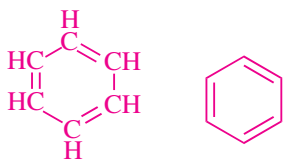
When oxygen combines with an element or compound during a chemical reaction, the process is called **oxidation**, and the resulting substance is said to be **oxidized**. The substances  $O_2(g)$ ,  $O_3(g)$ ,  $OH(g)$ ,  $H_2O(g)$ ,  $NO(g)$ ,  $NO_2(g)$ ,  $SO_2(g)$ ,  $CO(g)$ , and  $CO_2(g)$  are oxidized. When oxygen is removed from a substance during a reaction, the process is called **reduction**, and the resulting element or compound is said to be **reduced**. The substances  $H_2(g)$ ,  $N_2(g)$ ,  $NH_3(g)$ , and  $CH_4(g)$  are reduced.

Table 1.4 shows structures of inorganic compounds and methane, an organic compound. Table 1.5 shows structures of additional organic compounds. **Inorganic compounds** are compounds that contain any element, including hydrogen (H) or carbon (C), but not both H and C. **Organic compounds** are compounds that contain both H and C, but may also contain other elements. Methane is the simplest organic compound.

Organic compounds that contain only H and C are **hydrocarbons**. Hydrocarbons include alkanes, cycloalkanes, alkenes, cycloalkenes, alkynes, aromatics, and terpenes. Examples of some of these groups are given in Table 1.5. **Alkanes** (paraffins) are open-chain (noncyclical) hydrocarbons with a single bond between each pair of carbon atoms and have the molecular formula  $C_nH_{2n+2}$ . **Cycloalkanes** (not shown) are like alkanes, but with a cyclical structure. **Alkenes** (olefins) are open-chain hydrocarbons with a double bond between one pair of carbon atoms and have the molecular formula  $C_nH_{2n}$ . **Cycloalkenes** are similar to alkenes, but with a cyclical structure. **Alkynes** (acetylenes, not shown) are open-chain hydrocarbons with a triple bond between at least one pair of carbon atoms. **Terpenes** are a class of naturally occurring hydrocarbons that include hemiterpenes ( $C_5H_8$ ) **monoterpenes** ( $C_{10}H_{16}$ ), **sesquiterpenes** ( $C_{15}H_{24}$ ), **diterpenes** ( $C_{20}H_{32}$ ), and so on. **Aromatic hydrocarbons** are hydrocarbons with a benzene ring and possibly other carbon and hydrogen atoms attached to the ring. Two representations of a benzene ring are shown in Fig. 1.19.

Aromatics are so named because the first aromatics isolated were obtained from substances that had a pleasant fragrance, or *aroma*. Around 1868, Austrian chemist

**Joseph Loschmidt** (1821–1895) found that such aromatic compounds could be obtained by replacing one or more hydrogen atoms on a benzene ring with another atom or group. The name *aromatic* was subsequently applied to any compound that had a benzene ring in its structure. Loschmidt was the first to explain the structure of benzene, toluene, and ozone. He is also the first to quantify accurately Avogadro's number (Section 3.4).



**Figure 1.19.** Two representations of a benzene ring.

When methane, a fairly unreactive hydrocarbon, is excluded from the list of hydrocarbons, the remaining hydrocarbons are called **nonmethane hydrocarbons (NMHCs)**. When oxygenated functional groups, such as aldehydes, ketones, alcohols, acids, and nitrates, are added to hydrocarbons, the resulting compounds are called **oxygenated hydrocarbons**. In Table 1.5, the alcohol, aldehyde, and ketone are oxygenated hydrocarbons. Nonmethane

hydrocarbons and oxygenated hydrocarbons are **reactive organic gases (ROGs)**. **Total organic gas (TOG)** is the sum of ROGs and methane. **Volatile organic compounds (VOCs)** are organic compounds with relatively low boiling points that, therefore, readily evaporate. Although all VOCs are not necessarily ROGs, these terms are often interchanged. Finally, aldehydes and ketones are called **carbonyls**. The sum of nonmethane hydrocarbons and carbonyls is **nonmethane organic carbon (NMOC)**.

## 1.4. CHEMICAL REACTIONS AND PHOTOPROCESSES

Many of the pollution problems today are exacerbated by atmospheric chemical reactions. Reactions are initiated by sunlight, lightning, changes in temperature, or molecular collisions. In this section, chemical reactions are briefly discussed.

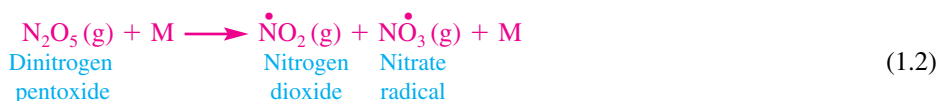
Gas-phase chemical reactions are conveniently divided into *photolysis reactions* (also called *photoprocesses*, *photodissociation reactions*, or *photolytic reactions*) and *chemical kinetic reactions*. Photolysis reactions are **unimolecular** (involving one reactant) and are initiated when solar radiation strikes a molecule and breaks it into two or more products. An example of a **photolysis reaction** is



where  $h\nu$  implies a photon of solar radiation and  $\lambda$  is the wavelength of the radiation (defined in Chapter 2).

Chemical kinetic reactions are usually **bimolecular** (involving two reactants). Types of kinetic reactions include thermal decomposition, isomerization, and standard collision reactions. Thermal decomposition and isomerization reactions occur when a reactant molecule collides with an air molecule. The kinetic energy of the collision elevates the reactant to an energy state high enough that it can thermally decompose or isomerize. **Thermal decomposition** occurs when the excited reactant dissociates into two or more products. **Isomerization** occurs when the excited reactant changes chemical structure, but not composition or molecular weight.

An example of a bimolecular **thermal decomposition reaction** is

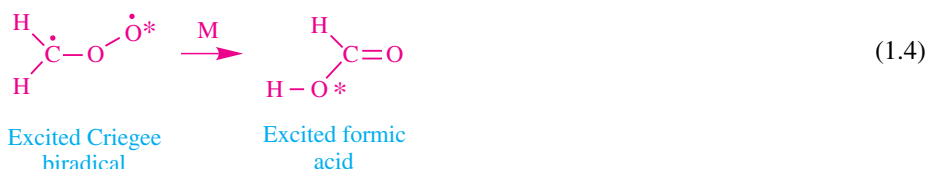


where M is the molecule that provides the collisional energy. M can be any molecule. Because molecular oxygen [O<sub>2</sub>(g)] and nitrogen [N<sub>2</sub>(g)] together make up more than 99 percent of the gas molecules in the air today, M is most likely to be O<sub>2</sub>(g) or N<sub>2</sub>(g).

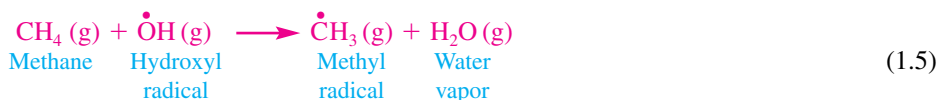
Because M in Reaction 1.2 does not change concentration, the reaction can also be written as



Thermal decomposition reactions are temperature dependent. At high temperatures, they proceed faster than at low temperatures. Isomerization reactions are similar to Reaction 1.3, except that an isomerization reaction has one product, which is another form of the reactant. An example of an isomerization reaction is

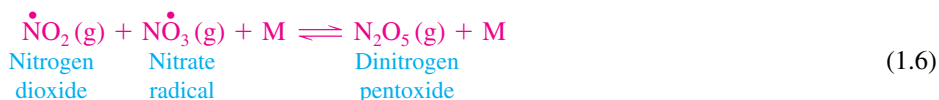


The bimolecular **collision reaction** is the most common type of kinetic reaction and may occur between any two chemically active reactants that collide. A prototypical collision reaction is



In some cases, bimolecular reactions result in **collision complexes** that ultimately break into products. Such reactions have the form  $A + B \rightleftharpoons AB^* \rightarrow D + F$ , where  $AB^*$  is a molecule that has weak bonds and is relatively unstable, and the double arrow indicates that the reaction is **reversible**.

**Termolecular** (involving three reactants) collision reactions are rare because the probability that three trace gases collide simultaneously and change form is not large. For descriptive purposes, however, pairs of reactions, can be written as termolecular **combination reactions**. For example, the combination of the bimolecular kinetic reaction  $\text{NO}_2(\text{g}) + \text{NO}_3(\text{g}) \rightleftharpoons \text{N}_2\text{O}_5(\text{g})^*$  with the isomerization reaction  $\text{N}_2\text{O}_5(\text{g})^* + \text{M} \rightleftharpoons \text{N}_2\text{O}_5(\text{g}) + \text{M}$  gives



In this case, M is any molecule, whose purpose is to carry away energy released during the reaction. The purpose of M in Reaction 1.6 differs from its purpose in Reaction 1.2,



where it provided collisional energy for the reaction. In both cases, M is usually either  $\text{N}_2(\text{g})$  or  $\text{O}_2(\text{g})$ . Reactions 1.2 and 1.6 are pressure dependent because the concentration of M is proportional to the air pressure. Because M in Reaction 1.6 does not change concentration, Reaction 1.6 can also be written as



## 1.5. LIFETIMES OF CHEMICALS

Some gases are important because their concentrations are high, suggesting that these gases do not degrade quickly. Others are important because they react quickly to form one or more products that are harmful or otherwise important. Gases that do not react away quickly include  $\text{N}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ , and  $\text{CO}_2(\text{g})$ . Some that do react away quickly (but may also reform quickly) include  $\text{OH}(\text{g})$ ,  $\text{NO}(\text{g})$ ,  $\text{NO}_2(\text{g})$ , and  $\text{O}_3(\text{g})$ , most of which are free radicals. The time required for the concentration of a gas to decrease to  $1/e$  its original concentration as a result of chemical reaction is called an ***e*-folding lifetime**. This parameter is similar to the **half-lifetime**, which is the time required for a gas concentration to decrease to one-half its original concentration. Throughout this text, these terms are used to evaluate the importance of different chemicals.

## 1.6. SUMMARY

In this chapter, atoms, molecules, elements, and compounds were defined and a history of the discovery of elements and compounds of atmospheric importance was given. Only a few elements, including carbon, sulfur, and certain metals, and a few solid compounds, including calcite, halite, and nitre, were known in ancient times. An acceleration of the discovery of elements and compounds, particularly of gases, occurred near the end of the eighteenth century. Several types of chemical reactions occur in the air, including photolysis, kinetic, thermal decomposition, isomerization, and combination reactions. The rate of reaction depends on the reactivity and concentration of molecules. The chemical *e*-folding lifetime of a substance is the time required for its concentration to decrease to  $1/e$  its original value and gives an indication of the reactivity of the substance. Molecules with free electrons are called *free radicals* and are highly reactive.

## 1.7. PROBLEMS

- 1.1. What are the main differences between gases and aerosol particles?
- 1.2. What compound might you expect to form on the surface of a statue made of marble or limestone (both of which contain calcite – calcium carbonate) if aqueous sulfuric acid deposits onto the statue?
- 1.3. Describe one experiment you could devise to isolate molecular oxygen.

- 1.4. What was the fundamental flaw with the theory of phlogiston?
- 1.5. Why did Lavoisier name oxygen as he did? Was his definition correct? Why or why not?
- 1.6. Is a termolecular combination reaction the result of the collision of three molecules simultaneously? Why or why not?
- 1.7. If the chemical  $t$ -folding lifetimes of the harmless substances A, B, and C are 1 hour, 1 week, and 1 year, respectively, and all three substances produce harmful products when they break down, which substance would you prefer to eliminate from urban air first? Why?
- 1.8. Match each person below with a surrogate name or description of a chemical s/he discovered.

(a) Priestly	(1) "gas that is wild and dwells in out-of-the-way places"
(b) Schönbein	(2) "Poland"
(c) M. Curie	(3) "foul-smelling air"
(d) Baldwin	(4) "stench"
(e) Theophrastus	(5) "plaster"
(f) Paracelsus	(6) "water maker"
(g) Van Helmont	(7) "lazy gas"
(h) Balard	(8) "acid maker"
(i) Rayleigh	(9) "light bearer"
(j) D. Rutherford	(10) "to smell"





# 2

## **THE SUN, THE EARTH, AND THE EVOLUTION OF THE EARTH'S ATMOSPHERE**

