ATMOSPHERIC POLLUTION

HISTORY, SCIENCE, AND REGULATION

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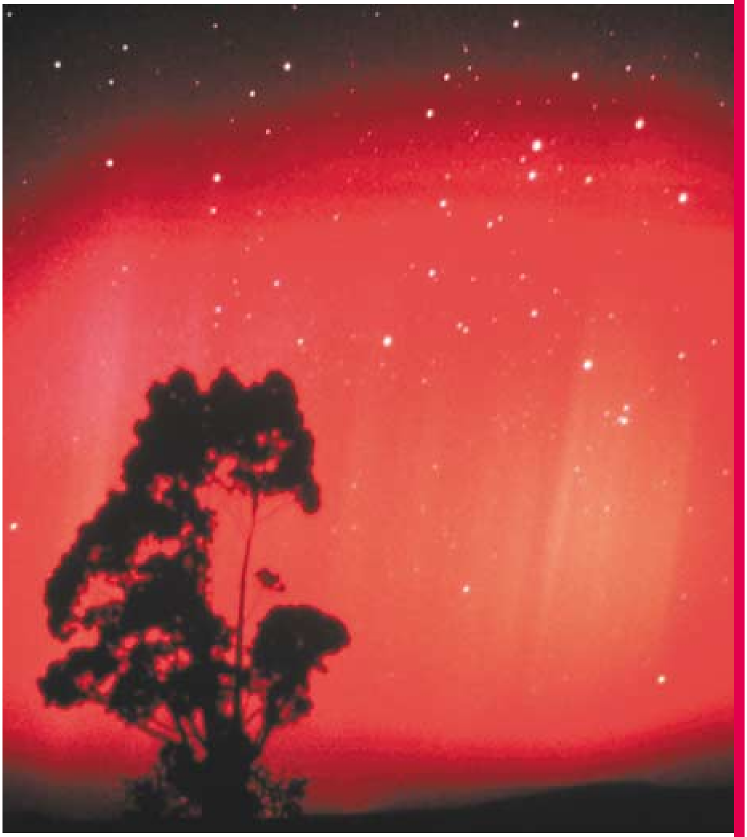


The study of air pollution begins with the study of chemicals that make up the air. These chemicals include molecules in the gas, liquid, or solid phases. Because the air contains so many different types of molecules, it is helpful to become familiar with important ones through the history of their discovery. 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 electrons. 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.

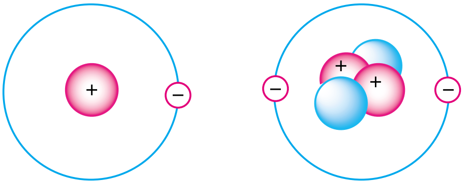
The **periodic table of the elements**, developed in 1869 by Russian chemist **Dmitri Mendeleev** (1834–1907), lists elements in order of increasing atomic number. Table 1.1 identifies the first ten elements of the periodic table and some of their characteristics. The atomic mass of an element in the 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^{-1})	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.



(a) Hydrogen (b) Helium

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

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.

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 *Iarn*	B.C.	?
Lead (Pb)	Previously *biblicalx, plumbum nigrum*	B.C.	?
Carbon (C)	Named from *carbo*, "charcoal"	B.C.	?
Sulfur (S)	Named from *sulvere, sulphurium*; previously *brimstone*	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 *fluere*, "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 *soda*	1807	Davy (England)
Potassium (K)	Named from *potash*	1807	Davy (England)
Calcium (Ca)	Named from *calx*	1808	Davy (England)
Silicon (Si)	Named from *silex*, "flint"	1823	Berzelius (Sweden)
Bromine (Br)	Means *stench*	1826	Balard (France)
Aluminum (Al)	Found in *alum*	1827	Wöhler (Germany)
Magnesium (Mg)	Named after the city of Magnesia	1830	Bussy (France)
Helium (He)	Named from *Helios*, Greek sun god	1868	Janssen (France), Lockyer (England)
Argon (Ar)	Named from *argos*, "lazy"	1894	Rayleigh (England), Ramsay (Scotland)
Krypton (Kr)	Named from *kryptos*, "concealed"	1898	Ramsey, Travers (Scotland)
Neon (Ne)	Named from *neos*, "new"	1898	Ramsey, Travers (Scotland)
Xenon (Xe)	Named from *xenos*, "guest"	1898	Ramsey, Travers (Scotland)
Polonium (Po)	Named after the country of Poland	1898	Curie, Curie (France)
Radon (Rn)	Originally named *radium emanation*	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 [$SO_2(g)$] and aqueous sulfuric acid [$H_2SO_4(aq)$].

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	$CaCO_3(s)$	Calcite, aragonite	Calcspar	B.C.	?
Sodium chloride	$NaCl(s)$	Halite	Common salt	B.C.	?
Potassium nitrate	$KNO_3(s)$	Nitre	Saltpeter, nitrum	B.C.	?
Sulfurous acid	$H_2SO_3(aq)$		Oil of sulfur, acidum volatile	B.C.	?
Sodium carbonate	$Na_2CO_3(s)$	Natrite	Nitrum, nator, nitron, natrum, soda ash, washing soda, salt-cake, calcined soda	B.C.	?
Calcium sulfate dihydrate	$CaSO_4\text{-}2H_2O(s)$	Gypsum	“Plaster”	315 B.C.	Theophrastus (Greece)
Sulfuric acid	$H_2SO_4(aq)$		Oil of vitriol, acidum fixum, vitriolic acid, spirit of alum,spirit of vitriol	<1264	de Beauvais (France)
Ammonium chloride	$NH_4Cl(s)$	Sal ammoniac		<1400	Geber or later author
Molecular hydrogen	$H_2(g)$		Inflammable air	<1520, 1766	Paracelsus (Switzerland), Cavendish (England)
Nitric acid	$HNO_3(aq)$		Spirit of nitre	1585	Libavius (Germany)
Hydrochloric acid	$HCl(aq)$		Spirit of salt	<1640	Sala (Germany)
Carbon dioxide	$CO_2(g)$		Gas silvestre, fixed air	<1648, 1756	Van Helmont (Belgium), Black (Scotland)
Ammonia	$NH_3(g)$		Gas pingue, alkaline acid air	<1648, 1756	Van Helmont (Belgium), Black (Scotland)
Ammonium nitrate	$NH_4NO_3(s)$	Nitrammite	Nitrum flammans, ammonia–nitre, ammoniak–saltpeter	1648	Glauber (Germany)
Sodium sulfate	$Na_2SO_4(s)$	Thenardite	Sal mirabile, Glauber's salt	1648	Glauber (Germany)
Amonium sulfate	$(NH_4)_2SO_4(s)$	Mascagnite	Secret sal ammoniac	<1648	Glauber (Germany)
Potassium sulphate	$K_2SO_4(s)$	Arcanite	Sal polychrestum glaseri, Arcanum duplicatum	1663	Glaser (France)
Calcium nitrate	$Ca(NO_3)_2\text{-}4H_2O(s)$	Nitrocalcite	Baldwin's phosphorus	<1669	Baldwin (Germany)
Magnesium sulfate	$MgSO_4\text{-}7H_2O(s)$	Epsomite	Epsom salt	1695	Grew (England)
Magnesium carbonate	$MgCO_3(s)$	Magnesite	Magnesia alba	c. 1695	?
Nitrogen dioxide	$NO_2(g)$		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	$N_2(g)$		Mephitic air	1772	Rutherford (England)
Nitric oxide	$NO(g)$		Nitrous air	1772	Priestley (England)
Nitrous oxide	$N_2O(g)$		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	$O_2(g)$		Dephlogisticated air	1774, 1772–5	Priestley (England), Scheele (Sweden)
Chlorine gas	$Cl_2(g)$		Dephlogisticated marine (muriatic) acid gas, "green gas"	1774	Scheele (Sweden)
Acetaldehyde	$CH_3CHO(g)$			1774	Scheele (Sweden)
Carbon monoxide	$CO(g)$			1772–1779	Priestley (England)
Sulfur dioxide	$SO_2(g)$		Vitriolic acid air	1774–1779	Priestley (England)
Nitric acid	$HNO_3(g)$			1784	Priestley (England), Cavendish (England)
Hypochlorous acid	$HOCl(g)$			1830	Balard (France)
Ozone	$O_3(g)$		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 [$Na_2CO_3(s)$] 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 [$CaCO_3(s)$] 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** [$CaMg(CO_3)_2(s)$], **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 [$NaCl(s)$], 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 [$KNO_3(s)$] 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** [$H_2SO_3(aq)$] ("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 [$CaSO_4$-$2H_2O(s)$] 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* [$NH_4Cl(s)$, **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.

Figure 1.2. Geber (c. 750–800).

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 [$KAl(SO_4)_2$-$12H_2O(s)$]. The acid was probably dissolved **sulfuric acid** [$H_2SO_4(aq)$], 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, $FeSO_4$-$7H_2O(s)$, a blue-green natural crystal) and obtained by burning elemental sulfur with saltpeter [$KNO_3(s)$] 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** [$HNO_3(aq)$], indicating that dissolved nitric acid was known during his time. It was most likely formed from the reaction of $H_2SO_4(aq)$ with $KNO_3(s)$. 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 [$NH_4Cl(s)$] by treating **ammonium carbonate** [$(NH_4)_2CO_3(s)$] with dissolved **hydrochloric acid** [$HCl(aq)$]. This may be the first recorded use of HCl(aq). Hydrochloric acid was probably obtained by reacting common salt [$NaCl(s)$] with sulfuric acid [$H_2SO_4(aq)$]. Hydrochloric acid is an abundant component of sea-spray particles.

Figure 1.3. Andreas Libavius (1540–1616).

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** [Na_2SO_4-$10H_2O(s)$, **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** [$NH_4NO_3(s)$], which he called *nitrum* *flammans*, and the mineral **ammonium sulfate** [$(NH_4)_2SO_4(s)$], 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).

1.2.1.16. Potassium Sulfate (Solid)

In 1663, **Christopher Glaser** (1615–1673), a French apothecary to Louis XIV, combined sulfur with melted saltpeter [$KNO_3(s)$] to form the crystal **potassium sulfate** [$K_2SO_4(s)$], 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, $CaCO_3(s)$] with nitric acid [$HNO_3(aq)$], to produce the crystal **calcium nitrate** [$Ca(NO_3)_2(s)$], 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** [$MgSO_4\text{-}7H_2O(s)$], which was subsequently called **Epsom salt**. Magnesium sulfate can be found in the air as a constituent of soil-dust and sea-spray particles.

1.2.2. 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** [H_2(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** [CO_2(g)]. Another gas he produced was an inflammable vapor evolved from dung. He called this gas *gas pingue*, which was probably impure **ammonia** [NH_3(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.

Figure 1.5. Paracelsus (1493–1541).

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.

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** [$O_2(g)$].

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** [$MgCO_3(s)$], called *magnesia alba* ("white magnesia") at the time. On heating, $MgCO_3(s)$ lost weight, producing a heavy gas that neither sustained a flame nor supported life. When the gas was exposed to quicklime [$CaO(s)$, 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** [$CO_2(g)$], and when it was reabsorbed on exposure to $CaO(s)$, it was really forming calcium carbonate [$CaCO_3(s)$]. 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 $CO_2(g)$, had previously been discovered by Van Helmont more than a century earlier. In 1756, Black also isolated ammonia gas [$NH_3(g)$], 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.

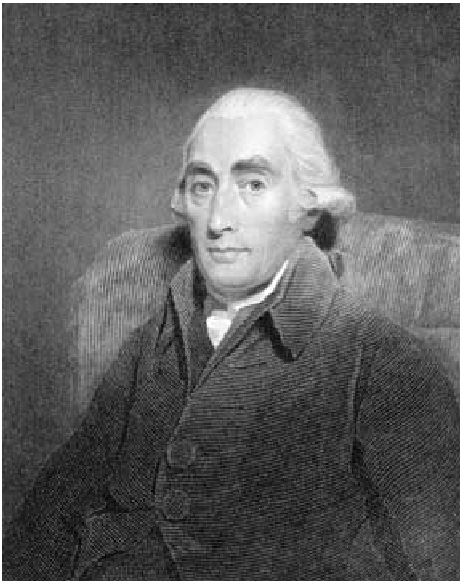


Figure 1.7. Joseph Black (1728–1799).

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 [$H_2SO_4(aq)$] or hydrochloric acid [$HCl(aq)$] 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** [$H_2(g)$].

In other experiments, Cavendish exposed marble, which contains $CaCO_3(s)$, to hydrochloric acid [$HCl(aq)$] to produce $CO_2(g)$, as Van Helmont had done earlier. Cavendish, took the further step of measuring the properties of $CO_2(g)$. 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.

Figure 1.8. Henry Cavendish (1731–1810).

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, $O_2(g)$, which had not been discovered yet]. He then exposed the remaining air to the crystal **caustic potash** [$KOH(s)$, potassium hydroxide or pot ashes], obtained by burning wood in a large iron pot. $CO_2(g)$ in the remaining air reacted with caustic potash, forming **pearl ash** or **potash** [$K_2CO_2(s)$, potassium carbonate]. The residue after $CO_2(g)$ was removed could not sustain life; thus, Rutherford called it "**mephitic** [poisonous or foul-smelling] **air**." Mephitic air is now known as **molecular nitrogen** gas [$N_2(g)$], 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 [$KNO_3(s)$].

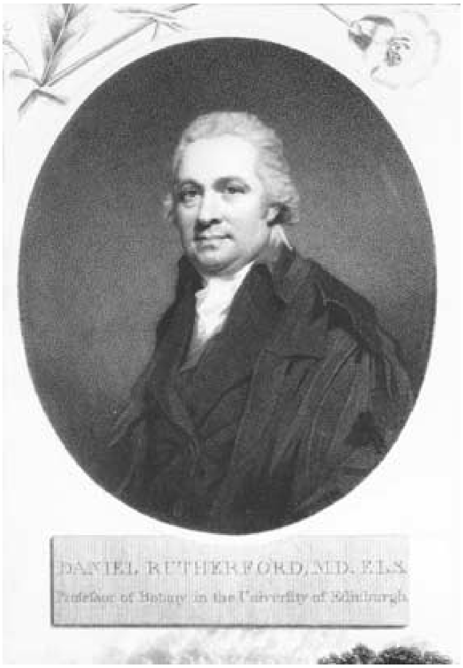
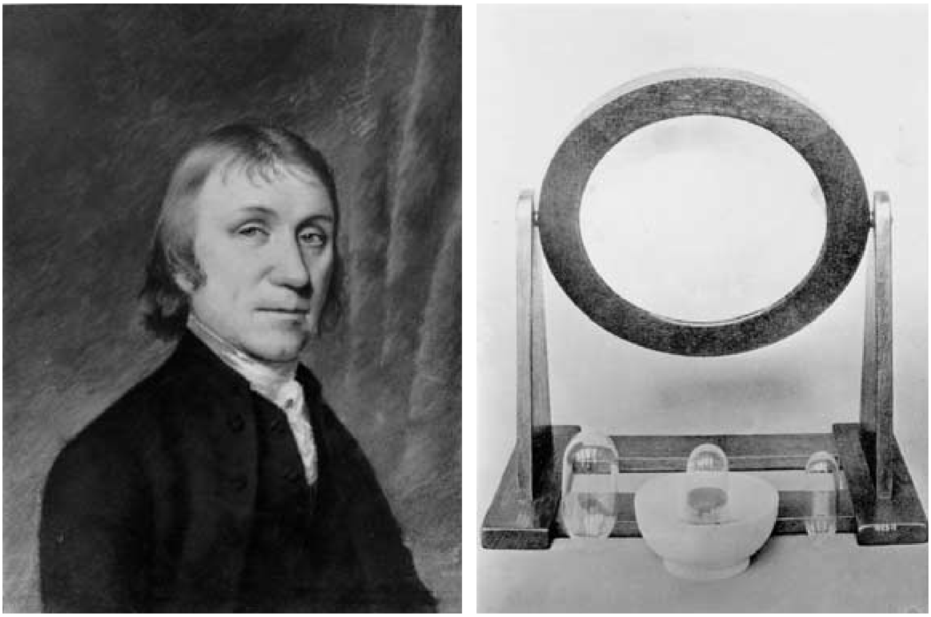


Figure 1.9. Daniel Rutherford (1749–1819).

1.2.2.9. Molecular Oxygen (Gas) – Dephlogisticated Air

Molecular oxygen gas [$O_2(g)$] 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 (Hg), a silvery-white liquid metal, in air to form bright red mercuric oxide [$HgO(s)$], 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.