Chapter 10

100 Years of Progress in Gas-Phase Atmospheric Chemistry Research

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ABSTRACT

Remarkable progress has occurred over the last 100 years in our understanding of atmospheric chemical composition, stratospheric and tropospheric chemistry, urban air pollution, acid rain, and the formation of airborne particles from gas-phase chemistry. Much of this progress was associated with the developing understanding of the formation and role of ozone and of the oxides of nitrogen, NO and NO₂, in the stratosphere and troposphere. The chemistry of the stratosphere, emerging from the pioneering work of Chapman in 1931, was followed by the discovery of catalytic ozone cycles, ozone destruction by chlorofluorocarbons, and the polar ozone holes, work honored by the 1995 Nobel Prize in Chemistry awarded to Crutzen, Rowland, and Molina. Foundations for the modern understanding of tropospheric chemistry were laid in the 1950s and 1960s, stimulated by the eye-stinging smog in Los Angeles. The importance of the hydroxyl (OH) radical and its relationship to the oxides of nitrogen (NO and NO₂) emerged. The chemical processes leading to acid rain were elucidated. The atmosphere contains an immense number of gas-phase organic compounds, a result of emissions from plants and animals, natural and anthropogenic combustion processes, emissions from oceans, and from the atmospheric oxidation of organics emitted into the atmosphere. Organic atmospheric particulate matter arises largely as gas-phase organic compounds undergo oxidation to yield low-volatility products that condense into the particle phase. A hundred years ago, quantitative theories of chemical reaction rates were nonexistent. Today, comprehensive computer codes are available for performing detailed calculations of chemical reaction rates and mechanisms for atmospheric reactions. Understanding the future role of atmospheric chemistry in climate change and, in turn, the impact of climate change on atmospheric chemistry, will be critical to developing effective policies to protect the planet.

1. Introduction

Any historical account of a field as broad and deep as atmospheric chemistry must, by necessity, be selective. In a short account, such as this one, many important individuals, concepts, and discoveries must be omitted from discussion, despite their importance. Moreover, a selective account, such as this one gives the impression that progress was made by following a singular path. This impression could not be further from the truth! Progress

in atmospheric chemistry proceeds by a process more akin to diffusion—an apparently random walk of scientific discovery, where blind alleys and false steps abound. Further, every discovery has been by researchers bathed in the rich mélange of shared scientific knowledge, conjecture, and theory derived not just from atmospheric chemistry, but from all scientific fields. In the following, we describe only a few of the countless paths, but we trust that this account conveys a sense of the excitement of discovery that drives the whole enterprise.

We start with a historical overview of research into atmospheric chemical composition, urban air pollution,

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and acid rain. We then progress through 100 years of stratospheric and tropospheric chemistry research highlighting progress made toward a chemical understanding of stratospheric ozone depletion, urban air quality, and atmospheric particle formation. We discuss the progress and emerging promise of theoretical treatments of gas-phase atmospheric chemistry; the impacts of atmospheric chemistry on climate change and vice versa. Finally, we attempt to peer into the future and offer our subjective view of what the next 100 years of gas-phase atmospheric chemistry might bring.

2. Atmospheric composition and detection

As chemists, the initial questions that come to mind when we think of the atmosphere include: What is its chemical composition? Why does it have that composition? Is the composition changing and what are the ramifications for human welfare?

The ancient Greeks believed that air together with earth, water, and fire were the four elements from which all material things were composed. We have come a long way in our understanding of atmospheric phenomena since the ancient Greeks. Scientific investigation of the chemical composition of the atmosphere is interlinked with the emergence of chemistry as a distinct scientific discipline in the eighteenth and nineteenth centuries. We describe the history of the evolution of comprehension of the chemical composition of the atmosphere, discussing gases in the approximate chronological order in which they were discovered in the atmosphere, leading to the current understanding of composition given in [Table 10-1](#).

a. Water vapor

Apart from its obvious presence in precipitation, water vapor was the first atmospheric vapor to be identified and was recognized by Aristotle (c. 384–322 BC) in his treatise *Meteorologica* ([Möller 2008](#)). The first measurement of water vapor content in air is attributed to Nicholas de Cusa (1401–64), who used a mass balance to measure the change in weight of a sample of wool exposed to humid air. Leonardo da Vinci (1452–1519) described a hygrometer operating on the same principle but using cotton as absorbant ([Walker 2012](#)). Various other devices were invented in the 1500s–1700s based on observing the change in weight or length of hygroscopic materials (string, hair, inorganic crystals) to provide estimates of humidity.

John Dalton (1766–1844) provided the first accurate absolute determination of atmospheric water vapor content in 1802 ([Dalton 1802](#)). In the laboratory, Dalton used a mercury manometer to carefully measure the

TABLE 10-1. Average composition of dry air ([Seinfeld and Pandis 2016](#)).

Gas	Parts per million by volume (ppmv)
N ₂	781 000
O ₂	209 000
Ar	9340
CO ₂ ^a	406
Ne	18
He	5.2
CH ₄ ^b	1.85
H ₂	0.58
N ₂ O ^c	0.33
CO	0.1
O ₃ (troposphere)	0.01–0.10
O ₃ (stratosphere)	0.5–10.0
Non-methane hydrocarbons	0.005–0.02
Halocarbons	0.001
Nitrogen oxides (NO _x)	0.000 01–0.2

^a [Dlugokencky and Tans \(2018\)](#).

^b [Dlugokencky \(2018\)](#).

^c [NOAA \(2018\)](#).

vapor pressure of water as a function of temperature. In the field, he filled a cup with cold spring water and poured the water into a clear glass tumbler, noting the temperature of the water in the glass and whether dew formed on the outside of the glass. He then poured the water back into the cup, dried the glass, and poured the water back into the glass. This process was repeated with the water warming slightly during each iteration as it gained heat from the environment, the temperature of the water the first time that no condensation was observed was recorded as the dewpoint. Dalton then compared the dewpoint with results from his laboratory experiments, reasoning, according to what we would now refer to as Dalton's law of partial pressures, that the partial pressure of water vapor in air at the dewpoint would be the same as the absolute vapor pressure measured in the laboratory at the same temperature ([Dalton 1802, 1805](#); [Lawrence 2005](#); [Oliver and Oliver 2003](#)).

During the 1800s the wet-and-dry-bulb thermometer method was developed to determine atmospheric humidity ([Gatley 2004](#)). The method uses two thermometers, one dry and one covered by an absorbent material such as muslin or cotton kept wet using distilled water. Evaporation of water from the wet-bulb keeps its temperature below that of the dry-bulb thermometer. The lower the humidity, the greater the difference between the wet- and dry-bulb temperatures. Using the wet- and dry-bulb temperatures, the dewpoint and water vapor pressure could be determined from tables listing dewpoints and water vapor pressures for given dry-bulb and wet-bulb readings ([Marvin 1900](#)). This method was cumbersome. Willis Carrier (1876–1950) made a significant advance in 1904 by

providing a convenient calibration chart that allowed relative humidity and absolute water vapor content to be read off by simply locating the intersection of the wet- and dry-bulb temperatures (Gatley 2004). Carrier is perhaps better known as the inventor of modern air conditioning and as the founder of the Carrier Corporation. The wet-and-dry-bulb thermometer method is a convenient method to measure humidity and has been widely used over the past 100 years. Beginning approximately in the 1960s with the advent of modern electronics, techniques based on measuring changes in capacitance or resistance of materials when exposed to humid air or changes in the thermal conductivity of air have been developed to measure humidity.

Satellite measurements of atmospheric water content started in the 1970s. Atmospheric water vapor concentrations are now routinely monitored from satellite observations using infrared sounders and microwave radiometers. The global coverage provided by satellite observations, which started in about 1980, has enabled the detection of an increase in atmospheric vapor content that is consistent with the observed global average temperature increase and the Clausius–Clapeyron relation: about $7\% \text{ } ^\circ\text{C}^{-1}$ (Chung et al. 2014; Held and Soden 2006; IPCC 2013; Soden et al. 2005). The observed increase in global atmospheric temperature of approximately 1°C from the start of the instrumental temperature record in the 1880s to the present (NASA 2018) implies an increase of atmospheric water vapor content of approximately 7% since the 1880s. As discussed later in this chapter, the increase in atmospheric water vapor content has important ramifications for radiative forcing of climate change and for hydroxyl radical formation from reaction of $\text{O}(^1\text{D})$ atoms with gas-phase H_2O .

b. Carbon dioxide

In 1640, the Flemish chemist Jan Baptist van Helmont (1580–1644) was the first to use the word “gas” (from the Greek word for chaos) and to document that there are gases in the atmosphere that have properties distinct from those of air. He recognized that the same gas (carbon dioxide) was liberated by burning charcoal and by fermentation and that this gas did not support combustion or animal life. Joseph Black (1728–99) is credited with discovering carbon dioxide in 1754 after noticing the generation of a gas upon heating of calcium carbonate. This gas, which he called “fixed air” (carbon dioxide), was denser than air and did not support combustion or animal life. Black showed that bubbling air through limewater resulted in the precipitation of calcium carbonate and deduced that carbon dioxide was a component of air (Black 1756).

Brown and Escombe (1905) described an accurate quantitative method for measuring CO_2 concentrations in ambient air. They passed air through a solution of caustic sodium hydroxide and quantified the resulting sodium carbonate using a double titration method (Brown and Escombe 1900; Hart 1887). Using this approach, the CO_2 concentration in air in the North Atlantic region at the turn of the twentieth century was determined to be 274 ± 5 ppmv (Callendar 1938). In 1958, the International Geophysical Year, Charles David Keeling (1928–2005) started his iconic series of measurements of atmospheric CO_2 concentrations at the Mauna Loa Observatory in Hawaii and at the South Pole by exploiting the strong infrared (IR) absorption of CO_2 . The instrument used by Keeling had a non-dispersive IR source and measured the absorption of IR radiation traversing a cell through which samples of air, or calibrated gas mixtures containing CO_2 , were flowed. The greater the CO_2 concentration in the cell, the greater the absorption of an IR beam that was measured using a detector placed after the sample cell. The detector consisted of a cell filled with CO_2 in argon and equipped with a microphone. The IR beam was mechanically chopped at 20 Hz, and the strength of the photoacoustic signal from the microphone was proportional to the intensity of the IR beam. The instrument had sufficient accuracy, approximately ± 0.2 ppmv (Smith 1953; Pales and Keeling 1965), to discern the natural annual cycle of atmospheric CO_2 concentrations caused by seasonal photosynthetic activity (Keeling 1960). More importantly perhaps, Keeling was able to observe a global increase in atmospheric CO_2 concentration resulting from fossil fuel combustion and, to a lesser extent, from deforestation. The ongoing plot of increasing CO_2 concentrations as measured at the Mauna Loa Observatory is now known as the “Keeling Curve.”

In addition to the IR absorption technique, Keeling used liquid nitrogen to condense CO_2 from air, which allowed quantification using a gas manometer and isotopic analysis of CO_2 using mass spectrometry (Keeling 1958). This method has been used to analyze the ^{13}C , ^{14}C , and ^{18}O isotopic content and the evolution of atmospheric CO_2 . Modern isotope ratio mass spectrometry techniques have remarkable precision enabling the $^{13}\text{C}/^{12}\text{C}$ isotope ratio in atmospheric CO_2 to be measured to better than 1 part in 10^5 (Ferretti et al. 2000). Comparison of atmospheric CO_2 isotopic signatures with those of known sources and sinks provides a powerful tool to understand the cycling of CO_2 through the atmosphere. Emissions of CO_2 from fossil fuel combustion have $^{13}\text{C}/^{12}\text{C}$ isotopic ratios that are smaller than those in atmospheric CO_2 , and the $^{13}\text{C}/^{12}\text{C}$ isotopic ratio

in atmospheric CO₂ is being diluted by emissions from fossil fuel use (IPCC 2007).

Measurements of CO₂ in bubbles of ancient air trapped in ice in Antarctica and Greenland have demonstrated that there has been a substantial increase in levels of atmospheric CO₂ since the Industrial Revolution. The 1750 globally averaged abundance of atmospheric CO₂ based on measurements of air extracted from ice cores is 278 ± 2 ppmv (Etheridge et al. 1996). At the end of 2017 the global average CO₂ concentration was 406 ppmv and increasing at a rate of $2\text{--}3$ ppmv yr⁻¹ (Dlugokencky and Tans 2018) as the result of fossil fuel use and deforestation.

Beginning in the 2000s, atmospheric carbon dioxide concentrations have been measured by satellite observations based upon IR absorption. The first satellite measurements of CO₂ were provided using the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY), which was launched into orbit in 2002 by the European Space Agency (Buchwitz et al. 2005; Kuze et al. 2009). The first satellite specifically designed for CO₂ measurements was the *Greenhouse Gases Observing Satellite* (GOSAT) launched in 2009 by the Japanese Aerospace Exploration Agency (Kuze et al. 2009, 2016). Following the unsuccessful launch of the Orbiting Carbon Observatory (OCO) in 2009, the OCO-2 was placed into orbit by NASA in 2014 (Eldering et al. 2017a) and became the second satellite in orbit specifically designed for CO₂ measurements. GOSAT and OCO-2 provide essentially global coverage of CO₂ concentrations with a precision of approximately 0.3% (Kuze et al. 2016). Comparison of satellite OCO-2 data with measurements from the ground-based Total Carbon Column Observing Network indicate absolute median differences of less than 0.4 ppmv and root-mean-square differences of less than 1.5 ppmv (Wunch et al. 2017). The wealth of precise spatially and temporally resolved data for atmospheric CO₂ concentrations from GOSAT and OCO-2 (Eldering et al. 2017b) is transforming our understanding of the sources, sinks, and trends in atmospheric CO₂.

c. Oxygen

Oxygen was discovered independently by Carl Scheele (1742–86) in 1772 and by Joseph Priestly (1733–1804) in 1774. Priestly is given priority as he was the first to publish his discovery. Priestly focused sunlight on mercury oxide (HgO) in a glass tube and observed the production of a gas that had unique properties, including that it was better than air at supporting combustion and respiration. Antoine Lavoisier (1743–94) demonstrated that heating mercury in air led to a volume decrease and formation of mercury oxide and that the process could be reversed by decomposing the mercury oxide.

Lavoisier concluded in 1783 that air consists of approximately 4 parts of an inert gas and 1 part oxygen (Hartley 1947; Toulmin 1957) and laid the foundation for the modern theory of combustion and respiration.

Cavendish in 1781 was the first to provide an accurate measurement of the O₂ concentration in air of 20.84% oxygen (Ramsay 1915). Responding to concerns that human activities might be substantially depleting atmospheric O₂, Machta and Hughes (1970) measured the O₂ concentration in clean air between 50°N and 60°S in 1967–70 to be $20.946\% \pm 0.006\%$ and noted this was statistically indistinguishable from all reliable measurements since 1910.

In the late 1980s Ralph Keeling developed a novel and extremely sensitive method for determining changes in O₂ concentration from changes in the relative refractivity of dried air between two emission lines of ¹⁹⁸Hg at 2537.269 and 4359.562 Å using dual-wavelength interferometry (Keeling 1988). Keeling and coworkers have used this technique to measure a small but discernable decrease in atmospheric O₂ concentration since the 1980s (Manning and Keeling 2006). The atmospheric levels of O₂ declined by approximately 80 ppmv over the 20-yr period 1992–2012. This decrease represents a mere 0.04% of the atmospheric abundance of O₂ and is not of any direct concern, but it is important in providing independent evidence that the increase in CO₂ levels is caused by an oxidation process rather than by, for example, volcanic emissions (IPCC 2013). The observed trend of decreased global atmospheric O₂ concentrations and the lower O₂ levels in the Northern Hemisphere than in the Southern Hemisphere are consistent with expectations from fossil fuel combustion (IPCC 2013).

In contrast to nitrogen, oxygen is a reactive gas of great importance in atmospheric chemistry and indeed in life itself. Atmospheric oxygen is produced by photosynthesis and is consumed by respiration and by combustion. Atmospheric oxygen levels are determined by biological and geochemical processes. Annual production of oxygen via photosynthesis is approximately 4×10^{14} kg, the atmosphere contains approximately 1.2×10^{18} kg of O₂ and hence oxygen cycles through the atmosphere on a time scale of approximately 3000 years (Wayne 2000). On a geological time scale this is a short response time, and atmospheric O₂ concentrations have varied widely over geologic time (Lane 2002).

d. Nitrogen

Daniel Rutherford (1749–1819) is credited with discovering nitrogen in 1772 (Weeks 1934). Rutherford noted that taking air and removing oxygen (by either burning a candle, or confining an unfortunate mouse until it suffocated) and carbon dioxide (by using caustic

alkali) left behind a very large portion of the air. The residual gas had properties similar to carbon dioxide, in that it did not support animal life or combustion, but it was a distinctly different gas (Weeks 1934). Henry Cavendish (1731–1810) was the first to quantify the level of nitrogen in air. Cavendish used nitric oxide in the presence of water to remove oxygen, and potash to remove carbon dioxide. In a careful set of experiments conducted in 1781, Cavendish showed that there was no discernable difference in the composition of air sampled in London, in a nearby village, and in air measured on 60 different days in London with different meteorological conditions (fine, overcast, raining). Cavendish reported the composition of the air from which carbon dioxide had been removed as 79.16% nitrogen and 20.84% oxygen by volume (Ramsay 1915); close to the currently accepted values of 78.1% nitrogen and 20.1% oxygen.

Atmospheric nitrogen is slowly cycled through the biosphere. Human activity dominates the global nitrogen cycle with removal rates for the Haber–Bosch process, cultivation-enhanced biological fixation, and NO_x formation from fuel combustion of approximately 125, 60, and 30 Tg N yr^{-1} , respectively, compared to approximately 60 Tg N yr^{-1} for natural biological fixation on land (IPCC 2013). Denitrifying bacteria return nitrogen to the atmosphere in the form of N_2 and N_2O . The total nitrogen flux is dwarfed by 3.9×10^9 Tg of N_2 in the atmosphere (Wayne 2000). The atmospheric concentration of N_2 is believed to have not varied significantly over the past approximately 3 billion years (Wordsworth 2016). With its strong $\text{N}\equiv\text{N}$ triple bond, molecular nitrogen is a relatively inert and, from the atmospheric chemistry viewpoint, an uninteresting gas.

e. Ozone (O_3)

A historical perspective of atmospheric ozone has been provided recently by Calvert et al. (2015), which we draw upon here. Christian Friedrich Schönbein (1799–1868) noticed that the odor at the positive electrode during the electrolysis of water was similar to that produced from lightning. He reported that the odor could be contained indefinitely in a glass bottle but was destroyed on contact with finely ground charcoal, and he suggested the odor was attributable to a new compound (Schönbein 1840). The formation of ozone by passing an electric arc through pure oxygen showed that ozone was an allotrope of oxygen. Jacques-Louis Soret (1827–90) took ozone– O_2 mixtures and exposed equal volumes to heating, or to natural oils (turpentine or cinnamon oil). The increase in volume on heating was half of the decrease in volume from exposure to oil. Soret reasoned that heating led to decomposition of ozone into molecular oxygen, reaction with oil removed the ozone, and

hence that the density of ozone was 1.5 times that of O_2 , and thus the molecular formula of ozone was O_3 (Soret 1863).

Schönbein suggested that ozone was present in the atmosphere. He showed that starch-iodide paper exposed to air developed the characteristic brown color because of the formation of iodine and used this to develop a semiquantitative determination of ozone concentration (Rubin 2001):

Schönbein recognized the potential for physiological effects of ozone and conducted some of the first experiments in the area. Exposure to ozone irritates mucous membranes, and it was showed that breathing ozone (at high concentrations!) is fatal to mice and rabbits (Schönbein 1851). The availability of commercial kits using the Schönbein paper method and interest in ozone led to widespread measurements of ozone in ambient air in Europe, Asia, Africa, and the Americas by the late 1800s. Schönbein paper is still used in schools today as a student experiment to detect ozone. Unfortunately, because of sensitivities to humidity, wind speed, and duration of exposure, the historical measurements of ozone using Schönbein paper are not of quantitative value (Kley et al. 1988).

Alfred Cornu studied the ultraviolet solar spectrum and observed that the intensity of radiation reaching the surface drops off rapidly below approximately 300 nm (Cornu 1879) and hypothesized that the cutoff was due to the presence of an absorbing species in the atmosphere. Hartley measured the ozone UV absorption spectrum, compared this with the solar spectrum cutoff, and concluded that attenuation of UV by the atmosphere was attributable to the presence of ozone mainly located in the upper atmosphere (Hartley 1881). Fabry and Buisson (1913) made precise measurements of the cutoff in the solar spectrum and calculated that the total amount of ozone in the atmosphere (the column density) corresponded to a layer approximately 5 mm thick (presumably at standard temperature and pressure, but not specified); modern measurements show it is typically 3–4 mm thick. Fowler and Strutt (1917) demonstrated the presence of absorption bands in the solar spectrum near the cutoff just below 300 nm that matched those from ozone. Strutt (1918) was unable to observe absorption bands of ozone when making observations of a light source 4 miles across a valley and confirmed that the majority of ozone was present at high altitudes, not near the ground.

In the 1920s Dobson invented a spectrometer to measure the total column (amount of ozone in a path

directly overhead) and the altitude profile of ozone (Dobson and Harrison 1926; Dobson et al. 1927). The Dobson spectrometer compares the relative intensity of solar flux at pairs of UV wavelengths. From the ratios of transmitted intensity of the pairs of UV wavelengths and knowledge of the UV spectrum of ozone, the amount of ozone in the path (the column density) can be calculated. Ozone column densities are expressed in Dobson units; one Dobson unit (DU) corresponds to a layer of ozone that at standard temperature and pressure (STP) is 0.01 mm thick (i.e., 100 Dobson units = 1 mm of ozone at STP = 2.69×10^{18} molecules cm^{-2}). Thus, atmospheric ozone thicknesses of 3–4 mm correspond to 300–400 DU. Dobson spectrometers have proven to be remarkably robust and have provided accurate measurements of ozone since the 1920s. Dobson spectrometers are still used in ground-based observing stations. A Dobson spectrometer was the instrument used in the 1980s to detect what is now known as the Antarctic ozone hole (Farman et al. 1985), which is discussed in section 5 of this chapter.

Surface (0–2 km) ozone measurements started in the 1870s and have employed Schönbein paper, wet-chemical KI methods, and UV absorption. As mentioned above, the historical Schönbein paper measurements are not considered to provide useful quantitative information (Kley et al. 1988; Calvert et al. 2015; Galbally et al. 2017). By far the most extensive early set of ozone measurements were conducted using wet-chemical potassium iodide (KI) methods at the Montsouris Observatory in Paris 1876–1910 (Albert-Lévy 1877). The technique was well documented and has been replicated and found to agree with modern UV absorption instruments within 2% when measuring ozone in N_2/O_2 mixtures (Volz and Kley 1988). Volz and Kley (1988) analyzed the Montsouris data and concluded that surface ozone levels in central Europe were approximately 10 ppbv in 1876–1910. This value is much lower than currently measured surface ozone levels, which are typically in the range 25–45 ppbv and has led to concern that background ozone levels had more than doubled by the end of the twentieth century (IPCC 2013). However, wet-chemical KI methods suffer from chemical interferences by air pollutants common in urban areas. In particular, SO_2 causes a negative interference. To account for SO_2 interference, Volz and Kley (1988) applied a correction of 2–5 ppbv based on differences in ozone readings when the wind was blowing from the city compared to other directions. Recently, it has been argued that the corrections for SO_2 interference were grossly underestimated in light of modern estimates of coal consumption and measurements of sulfate in precipitation in the Paris area, hence suggesting that the Montsouris dataset does not provide a reliable basis for

assessing regional ozone concentrations (Calvert et al. 2015; Galbally et al. 2017).

Galbally et al. (2017) reviewed the historical data for surface ozone measurements over the period 1896–1975. Screening the data for those obtained using techniques traceable to modern instruments, with sampling that minimizes vertical gradients, and in locations likely to be free of chemical interferences, a total of 58 datasets were identified. No evidence was observed in this limited dataset for a trend in surface ozone over the period 1896–1975 and a best estimate median of 23 ± 6 ppbv was derived for surface (0–2 km) ozone during this period.

However, from 1975 to approximately 2000 there is clear evidence from surface, ozone sonde, and satellite measurements for an increase in background tropospheric ozone levels in the Northern Hemisphere (Logan et al. 2012; Oltmans et al. 2013; Parrish et al. 2012; Cooper et al. 2014; Monks et al. 2015). Logan et al. (2012) analyzed ozone measurements from sondes, aircraft, and alpine sites to assess changes in ozone levels in Europe over the period 1979–2009. They found that ozone increased by 6.6–10 ppbv in 1978–1989 and by 2.5–4.5 ppbv in the 1990s, and it then decreased by 4 ppbv in the 2000s in the summer. There were no significant trends observed in seasons other than in summer. Parrish et al. (2012) analyzed the ozone trend at mid-latitude background stations in the Northern Hemisphere in North America, Europe, and Asia. They found that prior to 2000 the average increase in ozone at all sites was approximately $1\% \text{ yr}^{-1}$ relative to the concentrations in 2000. At most sites, particularly in Europe, the rate of increase slowed after 2000 such that ozone levels are decreasing at some sites in some seasons, particularly in summer. Oltmans et al. (2013) examined changes in tropospheric ozone over the period 1970–2010. At midlatitudes in the Northern Hemisphere there was a significant increase in ozone concentrations from 1970 to 2000 followed by little, or no, growth in 2000–10. Oltmans et al. (2013) attributed the change in trend to controls of ozone precursors. Modeling studies suggest an approximately 30% increase in global tropospheric ozone burden from 1850 to 2000 with the majority of this additional ozone being found in the Northern Hemisphere extra tropics, reflecting the industrial emissions of ozone precursors in this region (Young et al. 2013).

Satellite measurements of ozone began in the 1970s with vertical profiles and total ozone columns measured using backscattered solar UV. Information from satellite Solar Backscatter UV (SBUV), Total Ozone Mapping Spectrometer (TOMS), Global Ozone Monitoring Experiment (GOME), SCIAMACHY, and the Ozone Mapping Instrument (OMI) have been merged together

with ground-based measurements to form a rich record of total ozone column densities since the 1970s. Compared to the 1970s, the total-column ozone declined over most of the globe in the 1980s and early 1990s (by approximately 3%–4% averaged over 60°S–60°N). Over 2000–13, there is evidence for a small recovery in ozone levels (approximately 1%–2% averaged over 60°S–60°N) since the 1990s (Ajavon et al. 2014).

The decline in the 1980s and early 1990s reflects the adverse impact of chlorofluorocarbons (CFCs) and other ozone-depleting substances on stratospheric ozone as discussed later in this chapter. The stabilization in the 1990s and recent evidence for a recovery reflects the decrease in atmospheric levels of ozone-depleting substances and the stratospheric cooling effect of increased levels of CO₂, which has slowed down the stratospheric ozone-depleting chemistry (Ajavon et al. 2014). Declines in stratospheric ozone over the Antarctic have been severe, with an approximately 25% decrease of total-column ozone at 60°–90°S in the 1980s and 1990s (Chipperfield et al. 2017). Fortunately, there has been a marked change in this trend with a stabilization of Antarctic stratospheric ozone around 2000 and evidence for a modest recovery over the past decade (Chipperfield et al. 2017).

f. Argon and the noble gases

The story of the discovery of argon provides an interesting example of the scientific method in action and includes careful observations, hypothesis development, engagement with the technical community, extension of previous work by others, teamwork, and perseverance (Giunta 1998). The first evidence for the existence of argon appears in the 1785 description by Cavendish of his “experiments on air.” Cavendish passed a spark through samples of nitrogen mixed with excess oxygen. The spark converted nitrogen into nitrogen oxides, which he removed using potash. Passing the spark through the mixtures until there was no further decrease in volume and then removing the excess oxygen left a small bubble of gas that Cavendish estimated as no more than 1/120 of the volume of the original nitrogen (Cavendish 1785). Cavendish was limited by the relatively crude technology available in his day, and his interest was in quantifying the main atmospheric components. Having established that nitrogen and oxygen account for at least approximately 99% of air, and lacking suitable means to investigate the small bubble of residual gas, he turned his considerable experimental skills and scientific curiosity to other matters.

Rayleigh (1842–1919) noticed and reported a small, but distinct, anomaly in the density of nitrogen prepared from air using two different methods (Rayleigh 1892).

The methods differed in the means used to remove O₂ from the air sample. In the first method oxygen was removed by passing air over red hot copper, in the second method oxygen was removed by passing a mixture of air and ammonia through a red hot copper tube:

Nitrogen samples obtained by the second method were approximately 1/1000 part less dense than samples obtained by the first method. Likely sources of impurities were investigated and ruled out. Rayleigh was puzzled by the results and suggested that a possible explanation might be that nitrogen might exist in a slightly different (dissociated) state in the two samples (Rayleigh 1892). In latter work, Rayleigh showed that samples of “chemical nitrogen” prepared from nitric acid, nitrous acid, urea, or ammonium nitrate were approximately 0.5% less dense than samples of “atmospheric nitrogen” prepared by removing O₂ from air by reacting with either copper or iron (Rayleigh 1893). Working with the chemist William Ramsay, Rayleigh repeated the experiments of Cavendish taking advantage of technology that had improved enormously during the intervening century, not least of which being a reliable public supply of electricity. Ramsay and Rayleigh were able to isolate sufficient quantities of a new gas to quantify its unique properties. They named the new gas argon, after the Greek word for “lazy” or “inactive,” and showed that it was denser than nitrogen. Its presence at approximately 1% explained why “atmospheric nitrogen” had a greater density than “chemical nitrogen” (Rayleigh and Ramsay 1895). The measured ratio of specific heat capacities at constant pressure and constant volume of 1.61 was indistinguishable within the experimental uncertainties from the value of 1.67 expected for a monatomic gas. Thus Rayleigh and Ramsay showed that argon was an unreactive monatomic gas and recognized it as a member of a new group of elements in the periodic table; the noble gases.

Using fractional distillation of air, Ramsay and Travers discovered and quantified the other noble gases, helium, neon, krypton, and xenon in air (Ramsay and Travers 1900, and as read to Royal Society in June 1898). In 1904 Rayleigh received the Nobel Prize in Physics for “his investigations of the densities of the most important gases and for his discovery of argon in connection with these studies” and Ramsay received the Nobel Prize in Chemistry “in recognition of his services in the discovery of the inert gaseous elements in air, and his determination of their place in the periodic system.” The noble gases are unreactive, essentially insoluble in water, and with the

exception of helium, their atmospheric abundance reflects the cumulative outgassing from the lithosphere over the lifetime of the planet. Helium is sufficiently light that a significant fraction of the helium atoms in the highest regions of atmosphere have velocities sufficient ($>10\text{ km s}^{-1}$) to escape into space. The atmospheric lifetime of helium with respect to loss into space of approximately 3×10^6 years is long compared to human time scales, but it is quite short compared to geological time scales (Wayne 2000).

g. Methane (CH_4)

The emission of “marsh gas” into the atmosphere as the result of enteric fermentation in cattle and microbial anaerobic decomposition of organic matter in wetlands and swamps has been known for centuries. However, it was only in the 1770s that marsh gas was identified as methane by Alessandro Volta and only in the last century has its presence as a trace component in the global atmosphere been firmly established. Methane was first detected in the atmosphere in 1948 from its characteristic IR absorption features in the solar spectrum around $3.3\text{--}3.5\text{ }\mu\text{m}$ ($2900\text{--}3000\text{ cm}^{-1}$) recorded in Columbus, Ohio (Migeotte 1948a,b). Rinsland et al. (1985) analyzed solar spectra recorded at the Jungfraujoch Observatory in Switzerland in 1951 and at the Kitt Peak Observatory in Arizona in 1981. Tropospheric methane concentrations of 1.14 ± 0.08 and 1.58 ± 0.09 ppmv determined in 1951 and 1981, respectively, equate to an annual increase of $1.1 \pm 0.2\%$ from 1951 to 1981.

Analytical chemistry was revolutionized by the 1952 invention of gas chromatography (GC) and subsequent development in the late 1950s of sensitive and robust detection systems, such as flame ionization detectors (FID) and electron capture detectors (ECD) (Bartle and Myers 2002). In the 1960s and 1970s GC–FID methods were developed that enabled accurate measurement of methane concentrations in air samples (Rasmussen and Khalil 1981; Blake et al. 1982; Stephens 1985). The new GC–FID instruments were accurate, robust, low-cost, and relatively easy to automate. Essentially continuous measurements of atmospheric methane at key sampling locations were initiated together with campaigns where samples of air from remote locations were collected by opening evacuated flasks and brought back to the laboratory for analysis. By the end of the 1980s it was well established that atmospheric methane levels were increasing at a rate of approximately $1\%\text{--}2\% \text{ yr}^{-1}$ (Blake and Rowland 1988; Steele et al. 1987). These measurements are continuing with internationally agreed measurement protocols as part of the World Meteorological Organization’s Global Atmospheric Watch Programme (Dlugokencky et al. 2005).

The global average atmospheric methane concentration in 2017 was approximately 1.85 ppmv (Dlugokencky 2018), which is about a factor of 2.5 times the pre-industrial level of 0.7 ppmv established from ice core measurements (Etheridge et al. 1998).

Satellite measurements of methane were first made in 1996–97 using the IMG thermal infrared instrument, in 2003–12 by solar backscatter measurements from the SCIAMACHY mission, from 2009 to the present using GOSAT, and will be available from the Tropospheric Monitoring Instrument (TROPOMI) launched in October 2017 (Jacob et al. 2016). Measurements from the TROPOMI instrument are expected to provide near global coverage on a daily basis with a resolution of $7\text{ km} \times 7\text{ km}$ and vastly increase the data available for atmospheric methane. Satellite-based instruments are available that can achieve spatial resolution with a footprint as small as $50\text{ m} \times 50\text{ m}$, which will be useful for investigation of point source emissions (Jacob et al. 2016). As for other atmospheric chemical components, satellite observations combined with inverse modeling are a powerful and rapidly advancing means for understanding sources and sinks for atmospheric methane.

h. Nitrous oxide (N_2O)

Evidence of N_2O in the atmosphere was first reported in 1939 from its characteristic IR absorption features at 7.77 and $8.57\text{ }\mu\text{m}$ in solar spectra recorded at Lowell Observatory in Flagstaff, Arizona (Adel 1939, 1941). Analyses of the spectra indicate a level of approximately 300 ppbv in 1940 (Roscoe and Clemitshaw 1997).

Beginning in the late 1970s a series of measurements of atmospheric N_2O levels have been made in remote monitoring sites using GC–ECD techniques. The measurements provide an essentially continuous dataset starting in 1977 and show that the global background N_2O concentration has increased from approximately 300 ppbv in 1977 to 330 ppbv at the end of 2017; a 10% increase in 40 years (NOAA 2018) mainly as a result of increasing intensification of agriculture (IPCC 2013). The preindustrial level in 1750 derived from ice core measurements was 270 ± 7 ppbv (Prather et al. 2012). In addition to GC–ECD measurements made at a network of global monitoring sites, N_2O is now also monitored using satellite observations of its characteristic IR absorption (Ricaud et al. 2009; Lambert et al. 2007).

i. CFCs and related halogenated organic compounds

CFCs are a group of chemicals that are inexpensive to produce, nonflammable, and nontoxic and were commercialized in the 1920s and 1930s as refrigerants. By the 1960s and 1970s CFCs were in widespread and growing use as refrigerants, aerosol propellants, and foam-blowing agents.

CFCs are present in the atmosphere as a result of emissions associated with these uses particularly during the 1960s–80s. James Lovelock invented the ECD, which combined with GC provides exquisitely sensitive detection of halogen-containing compounds in atmospheric samples (Lovelock 1958, 1961). This new analytical technique allowed CFCs to be detected in the atmosphere starting in the early 1970s when accumulation of CFC-11 (CCl_3F) in the global atmosphere was reported (Lovelock et al. 1973). These measurements led to the realization of the threat that CFCs pose to stratospheric ozone (Molina and Rowland 1974) and to international agreements to limit the emissions of CFCs and other ozone-depleting substances. The Advanced Global Atmospheric Gases Experiment (AGAGE; <https://agage.mit.edu/research>), a global network of GC-ECD instruments, has been providing essentially continuous measurements of atmospheric concentrations of CFCs and halogenated organics at levels down to parts per trillion (pptv) since the late 1970s (Prinn et al. 2000).

j. NO_x

Nitrogen monoxide (NO), more commonly referred to as nitric oxide, and nitrogen dioxide (NO_2) in the sunlit atmosphere are interconverted on a time scale of minutes and it is convenient to use the term “ NO_x ” to refer to the sum of these species ($\text{NO}_x = \text{NO} + \text{NO}_2$). The collective name for the total reactive oxidized species in the atmosphere is NO_y ($\text{NO}_y = \text{NO}_x + \text{HNO}_3 + \text{HONO} + \text{N}_2\text{O}_5 + \text{PAN} + \text{organic nitrates}$). As discussed below, NO_x plays an important role in ozone formation in the troposphere and ozone loss in the stratosphere. Accurate measurements of NO_x emissions and ambient concentrations are required to understand atmospheric ozone chemistry. NO_2 has adverse health impacts, ambient air quality standards have been developed for NO_2 , and measurement methods are needed to assess local air quality against these standards.

NO is usually measured by detecting chemiluminescence from the electronically excited NO_2 product of the reaction of NO and ozone:

This technique was developed in the early 1970s (Fontijn et al. 1970; Niki et al. 1971; Stedman et al. 1972) in the research laboratories of Aerochem and the Ford Motor Company. Chemiluminescence instruments are selective, sensitive, and robust and in widespread use to measure emissions and atmospheric concentrations of NO.

NO_2 can be measured after conversion to NO by passage over a heated molybdenum surface or via photolysis using UV lamp (Ridley et al. 1988). NO is unaffected by

such converters, and the concentration of NO_2 in a sample containing NO and NO_2 can be inferred from the difference between readings when samples are passed through, or bypass, the converter. Care must be exercised to account for interferences from nitrogen-containing compounds other than NO_2 that can be reduced to NO by the converter (Kleffmann et al. 2013). Additional techniques that have been developed to measure NO_2 include laser-induced fluorescence, cavity-ring down spectroscopy, differential optical absorption spectroscopy, and wet-chemical methods including reaction with luminol and the Saltzman reaction (Saltzman 1954). Conversion to NO and detection via chemiluminescence is the approved regulatory method for measuring atmospheric NO_2 concentrations in the United States. Satellite measurements of NO_2 using its characteristic absorption at 425–450 nm started in the 1990s (Bovensmann et al. 1999; Burrows et al. 1999) and now provide essentially global coverage of NO_2 total columns.

3. Urban air pollution

From the dawn of civilization, human settlements have been associated with high levels of population density, economic activity, fuel use and associated emissions, and air pollution—both indoor and outdoor. Urban air pollution in antiquity is well documented (Heidorn 1978; Brimblecombe 1995; Makra 2015). Seneca in AD 61 commented “as soon as I escaped from the oppressive atmosphere of the city [Rome], and from that awful odor of reeking kitchens which, when in use, pour forth a ruinous mess of steam and soot, I perceived at once that my health was mended” (Heidorn 1978; Makra 2015). “Sulfurous smog” began to appear in the thirteenth century, as coal came into widespread use in the cities of Britain and Europe. Owing to the smell from burning high-sulfur British bituminous coal, Edward I of England banned the burning of coal in 1306 on pain of death. John Evelyn (1620–1706) published in 1661 the pamphlet, *Fumifugium, or The inconveniencie of the aer and smoak of London dissipated together with some remedies humbly proposed by J.E. esq. to His Sacred Majestie, and to the Parliament now assembled*. As one of the earliest known writings on air pollution, it is broken down into three parts that explain the problem, propose a solution, and describe a way of improvement upon the air in London. In a letter addressed to Charles II, Evelyn discussed problems with the capital’s air pollution dating back to medieval times. He wrote in *Fumifugium*: “It is this horrid Smoake which obscures our Church and makes our palaces look old, which fouls our Cloth and corrupts the Waters, so the very Rain, and refreshing Dews, which fall in the several Seasons, precipitate to impure vapour, which, with its black and

tenacious quality, spots and contaminates whatever is exposed to it.” By the late 1600s, “great stinking fogs” occurred in London, with associated increases in death rates (Brimblecombe 2017). In 1905, the term “smog” was coined to describe the combination of smoke and fog (Wayne 2000).

The first major air pollution episode in the United States occurred in 1948. Between 28 and 30 October 1948, an atmospheric inversion settled over the southwestern Pennsylvania river town of Donora. Located on the western bank of the Monongahela River, 37 miles south of Pittsburgh, Donora was home to U.S. Steel Corporation’s Zinc Works and its American Steel and Wire plant. Extraordinarily high levels of SO_2 , sulfates, and fluorides built up in the air of the valley over the three days. By the time the rain cleared the air on 30 October, 20 people had died and thousands of others were sickened (Snyder 1994). Four years later, on 5 December 1952, a mixture of dense fog and sooty black coal smoke descended upon London. By 7 December, visibility fell to 1 ft. Roads were littered with abandoned cars. When wind finally dispersed the mixture of 9 December, the four-day episode had resulted in at least 4000 deaths, nearly 3 times the normal toll during such a period. Total deaths could have been as high as 13 500 if those through March are counted (Bell and Davis 2001). The “London Killer Fog,” as it is now known, stands as one of the deadliest environmental episodes in recorded history (Stone 2002).

“Acid rain” (better termed “acid deposition”) bears some similarity to London smog. Like London smog, acid rain results from sulfur dioxide (SO_2) as a primary pollutant, together with photochemical oxidation to convert the SO_2 to sulfuric acid (H_2SO_4). Acid deposition is harmful to aquatic environments, and there is evidence that it may also be harmful to some types of vegetation (Cape 1993).

At about the same time as the episodes in Donora and London, a new type of air pollution, so-called photochemical smog, emerged in Los Angeles. As distinguished from the sulfurous mixture in London, “Los Angeles smog” tends to occur on sunny days with relatively low humidity. Los Angeles smog was first noticed during World War II, and injuries to crops grown in Los Angeles County were noted as early as 1944 (Finlayson-Pitts and Pitts 2000). This type of oxidizing air pollution, characterized by high ozone concentrations, results from sunlight acting on primary emissions of hydrocarbons and oxides of nitrogen. Photochemical smog is now prevalent in virtually every urban area worldwide; prominent examples include Mexico City, Beijing, Lagos, Bangkok, Karachi, New Delhi, and Sao Paulo. Tropospheric air pollution is so pervasive that great regions are affected, as material is transported around the world by global winds. Indeed, it is

difficult to find regions of Earth where its impact cannot be detected.

4. Acid rain

The phenomenon of acid rain appears to have been recognized at least three centuries ago. In 1692 Robert Boyle published *A General History of the Air*, recognizing the presence of sulfur compounds and acids in air and rain. Boyle referred to them as “nitrous or salino-sulfurous spirits.” In 1853, Robert Angus Smith, an English chemist, published a report on the chemistry of rain in and around the city of Manchester, “discovering” the phenomenon. Smith published *Air and Rain: The Beginnings of Chemical Climatology* in 1872, introducing the term “acid rain.” Little attention was paid to acid rain for almost a century thereafter. In 1961, Svante Odén, a Swedish chemist, established a Scandinavian network to monitor surface water chemistry. On the basis of his measurements, Odén showed that acid rain was a large-scale regional phenomenon in much of Europe with well-defined source and sink regions, that precipitation and surface waters were becoming more acidic, and that there were marked seasonal trends in the deposition of major ions and acidity. Odén also hypothesized long-term ecological effects of acid rain, including decline of fish populations, leaching of toxic metals from soils into surface waters, and decreased forest growth.

The major foundations for our present understanding of acid rain and its effects were laid by Eville Gorham. Born in 1925, Gorham is a Canadian–American scientist who is generally credited with discovering the role of acid rain in lake acidification. On the basis of his research in England and Canada, Gorham showed as early as 1955 that much of the acidity of precipitation near industrial regions can be attributed to combustion emissions, that progressive acidification of surface waters can be traced to precipitation, and that the acidity in soils receiving acid precipitation results primarily from sulfuric acid. Scandinavian and European studies, including the Norwegian Interdisciplinary Research Programme “Acid Precipitation–Effects on Forest and Fish,” and the study by the European Organization for Economic Cooperation and Development, elucidated the effects of acid rain on fish and forests and long-distance transport of pollutants in Europe.

Concern about acid rain in North America developed first in Canada and later in the United States, with the true scope of the problem not being fully appreciated until the 1970s. Acid rain in the U.S. eastern states was clearly identified in North America in the mid-1960s as resulting from emissions from Midwest coal-fired power

plants. Acid rain leached calcium from soils and affected lakes in areas like the Adirondack Mountains of New York, leaving low-pH waters within which fish could not survive. In 1970, the U.S. Congress imposed acid emission regulations through the Clean Air Act. In 1978, the United States and Canada established a Bilateral Research Consultation Group on the Long Range Transport of Pollutants and in 1980 signed a memorandum of intent to develop bilateral agreements on transboundary air pollution, including acid deposition. Both countries instituted long-term programs for the chemical analysis of precipitation. The National Acid Precipitation Assessment Program (NAPAP) served from 1980 to 1990 as the umbrella of one of the most comprehensive acid rain studies (U.S. NAPAP 1991). By the 2000s, sulfate and nitrate in precipitation in the eastern United States had decreased by 40%. Brimblecombe (1977), Wisniewski and Kinsman (1982), and Cowling (1982) provide historical perspectives associated with the discovery of and attempts to deal with acid rain.

The nature of acid deposition depends on the interaction between gas-phase and liquid-phase chemistry, on airborne transport and removal, and competition between dry and wet deposition. The gas/particulate/aqueous forms of sulfuric and nitric acids are the major contributors to acid deposition in polluted areas; hydrochloric acid and organic acids (mainly formic and acetic) make smaller contributions. Atmospheric bases, mainly NH_3 and Ca^{2+} , and other crustal elements play as important a role as do the acids, neutralizing to various extents the atmospheric acidity (Li et al. 2016). The net acidity is the overall result of the acid and base contributions.

Sulfur dioxide is converted to sulfate by reactions in gas, aerosol, and aqueous phases. The aqueous-phase pathway is estimated to be responsible for more than half of the ambient atmospheric sulfate concentrations, with the remainder produced by the gas-phase oxidation of SO_2 by OH (“OH” is the hydroxyl free radical, sometimes written as “HO”) (U.S. NAPAP 1991). These results are in agreement with calculations suggesting that gas-phase daytime SO_2 oxidation rates are $\sim 1\%–5\% \text{ h}^{-1}$, while a representative in-cloud oxidation rate is $\sim 10\% \text{ min}^{-1}$ for 1 ppbv of H_2O_2 .

The low amount of liquid water associated with aerosol particles (volume fraction 10^{-10} in an air mass, compared to clouds, for which the volume fraction is on the order of 10^{-7}) precludes significant aqueous-phase conversion of SO_2 in such particles. These particles can contribute to sulfate formation only for very high relative humidity (90% or higher) and in areas close to emissions of NH_3 or alkaline dust. Gas-phase production of HNO_3 by reaction of OH with NO_2 is approximately 10 times faster than the OH reaction with SO_2 . The peak daytime conversion rate of NO_2 to HNO_3

in the gas phase is $\sim 10\%–50\% \text{ h}^{-1}$. A second pathway for formation of nitrate is the reaction sequence:

This reaction pathway operates only at night, as during the daytime NO_3 photolyzes rapidly. The NO_3 radical formed during the nighttime also reacts with unsaturated organic compounds, producing organic nitrates. Aqueous-phase production of nitrate by NO and NO_2 reactions is negligible under most conditions, including reactions of NO_2 with O_2 , O_3 , H_2O_2 , and H_2O . This leaves the gas-phase $\text{NO}_2 + \text{OH}$ reaction as the dominant daytime nitrate production pathway and the heterogeneous reaction (10-8) of gas-phase N_2O with liquid water surfaces as the main nighttime production pathway.

NO and NO_2 have low solubility in water. Virtually no NO_x is removed from fresh plumes. HNO_3 formed by gas-phase oxidation of NO_2 is very soluble in water and the principal source of nitrate in precipitation. Since the secondary products are much more easily scavenged than NO_x , scavenging increases with plume dilution and oxidation. About one-third of the anthropogenic NO_x emissions in the United States are estimated to be removed by wet deposition. The distinct seasonal character of sulfur wet deposition is absent in the case of nitrogen wet deposition. This is because HNO_3 has a strong affinity for ice as well as liquid water, its formation has no direct dependence on hydrogen peroxide, which peaks in summer, and nitrate can be formed in low winter sunlight.

The U.S. National Science Foundation established 26 Long Term Ecological Research (LTER) sites across the United States and around the world in ecosystems from deserts to coral reefs to coastal estuaries. One of these sites is at Hubbard Brook, New Hampshire, where the effects of acid rain on forest growth and on soil and stream chemistry continue to be studied. Long-term biogeochemical measurements at Hubbard Brook have documented a decline in calcium levels in soils and plants over the past 40 years as calcium is leached from the soil. It has been discovered that higher CO_2 levels are affecting water quality of forested watersheds in much the same manner as acid rain.

5. Chemistry of the stratosphere

a. Early days: Ozone

Less than two decades before the American Meteorology Society was founded, Léon Philippe Teisserenc

de Bort (1902) and Richard Assmann (1902) independently reported that, instead of continuing to decrease at higher altitudes, the temperature of the ambient atmosphere (measured using instrumented hydrogen balloons) reaches a minimum and then begins to rise again at still higher altitudes. De Bort went on to coin the terms “troposphere” and “stratosphere,” and recognized that the two atmospheric regions must differ in their dynamics. It was not yet known that they also differ chemically, but that was about to change.

Ozone in the atmosphere had been an important topic since 1881, when Hartley discovered that ozone strongly absorbs ultraviolet light and argued that atmospheric ozone is responsible for limiting the observed solar spectrum at wavelengths shorter than around 295 nm (Hartley 1881). Some decades later, Fabry and Buisson measured the absorption coefficient of ozone as a function of wavelength (Fabry and Buisson 1913). They used the potassium iodide wet-chemistry method to measure ozone concentrations and a double spectrograph and photographic photometry (Brönnimann et al. 2003) to measure relative light intensity as a function of wavelength in what is now called the Hartley band. From these measurements and the Beer–Lambert law, they obtained absorption coefficients and confirmed Hartley’s suggestion that atmospheric ozone is responsible for blocking ultraviolet sunlight at short wavelengths. Subsequently, they also reported the first quantitative measurement of the total-column abundance of atmospheric ozone (Fabry and Buisson 1921).

In the early 1920s, Gordon M. B. Dobson and coworkers at Oxford University began an ambitious program of measuring the solar spectrum and atmospheric ozone absorption (Dobson 1923; Dobson and Harrison 1926; Dobson et al. 1927). Their apparatus consisted at first of just a filter and later of a quartz prism single-spectrograph and filter combination, which they had developed.

Dobson’s plan for ozone studies included establishment of a European network of stations for monitoring atmospheric ozone. In 1926, Dobson sent a calibrated spectrometer to F. W. Paul Götz for monitoring atmospheric ozone at Lichtklimatisches Observatorium, Arosa, Switzerland (Dütsch 1992). Götz had begun monitoring atmospheric ozone at Arosa in 1921, but by a lower-resolution filter technique. When the instrument arrived from Dobson in 1926, he began using it for his systematic measurements of the ozone column, and this date marks the beginning of the longest record of total-column ozone in the world.

In 1929, Götz noticed that the ratio of the atmospheric transmittance at two neighboring wavelengths passes through a minimum—the slope of the line reverses—as a function of solar zenith angle (the “umkehr effect”; in German, *umkehr* means “reversal”). With the development

by Dobson of a new quartz prism double-monochromator equipped with a photoelectric detector (Brönnimann et al. 2003), Götz, Dobson, and A. R. Meetham jointly developed an improved “umkehr method,” which utilized clear-air scattering of ultraviolet sunlight at selected pairs of wavelengths (e.g., 305.5 and 325.4 nm) chosen to be relatively close together such that the solar flux entering the atmosphere is similar but at wavelengths where there is a large difference in the absorption by ozone (Götz et al. 1933, 1934). The intensity ratio automatically corrects for solar intensity variations due to haze and other effects. The improved technique enabled better measurements of the vertical profile, which showed that most atmospheric ozone resides in the stratosphere. This finding was confirmed by E. Regener and V. Regener (Regener and Regener 1934), who performed “the first balloon sounding of ozone” (Warneck 1988).

Subsequent incremental developments of ozone monitoring instruments based on Dobson’s designs resulted in improved observations (Brönnimann et al. 2003). In the 1940s, Dobson replaced the photoelectric cell with a commercially available photomultiplier tube, which enabled measurement of wavelength pairs at shorter wavelengths and with higher sensitivity. According to Brönnimann, development of the Dobson instrument had reached its peak at around the time of the International Geophysical Year (1957–58) when a global ozone monitoring network was organized, including installation of a Dobson instrument at Halley Bay Station, Antarctica. The station was established by the British Antarctic Survey in January 1956 and the Dobson spectrometer began operation in September of the same year.

By 1973, about 100 Dobson spectrometers had been distributed over the globe, and the climatology of atmospheric ozone had been reasonably well established (Dütsch 1974). The total ozone column and vertical profile were found to depend on both latitude and season of the year, as illustrated in Fig. 10-1. At high latitudes, the base of the ozone layer was found at lower altitudes, coinciding with the tropopause, as shown in Fig. 10-2. Seasonally, the ozone concentration generally varied with insolation as expected, but the detailed variations could only be explained by invoking meridional atmospheric circulation. Vertical profiles obtained using the umkehr method were obtained routinely, but in situ chemical measurements from sounding balloons and rockets were found to provide better vertical resolution and greater accuracy (Dütsch 1974), thus obtaining data at higher altitudes (Brasseur and Solomon 1986).

b. Chapman mechanism

In the early 1930s, the Dobson spectrometer and umkehr method were the state of the art. The ozone

FIG. 10-1. Average total ozone column as a function of month and latitude in the Northern Hemisphere [from Brasseur and Solomon (1986, p. 210, Fig. 5.5), reprinted by permission from Springer Nature; attributed to Dobson (1968), © Oxford University Press, reproduced with permission of the licensor through PLSclear].

vertical profiles reported by Götz et al. in 1933 and 1934 were found to be in good qualitative agreement with theoretical predictions published just a few years earlier by Sydney Chapman (1930a,b). Chapman, then at Imperial College London, presented a carefully reasoned analysis that took into account everything then known about the photochemical kinetics of oxygen and ozone. He argued that in sunlight ozone is produced and destroyed continuously by rapid reactions that maintain a quasi-steady-state concentration. Ozone formation is ultimately the result of the ultraviolet photolysis of molecular oxygen.

The chemical mechanism proposed by Chapman (commonly called the “Chapman mechanism”) can be summarized with five elementary reactions:

In these equations, $h\nu$ represents a photon of light and M is a collider gas molecule, which can collisionally deactivate a vibrationally excited intermediate that would otherwise dissociate immediately. In the atmosphere, N_2 , O_2 , and Ar are the most abundant collider

FIG. 10-2. Average vertical profile of ozone as a function of altitude [from Brasseur and Solomon (1986, p. 212, Fig. 5.7), reprinted by permission from Springer Nature; attributed to Hering and Borden (1965) and Krueger (1973)].

gases. The reactions involving M are treated mathematically as third order and the reactions involving $h\nu_1$ and $h\nu_3$ are treated as first order with a rate coefficient that depends parametrically on light intensity. The two most reactive species in this scheme are O_3 and O atoms, which are rapidly interconverted and together constitute the “odd oxygen” chemical family (i.e., $\text{O}_x = \text{O} + \text{O}_3$) (Chapman 1942). In mathematical equations describing the reaction kinetics for this system, the concentrations (i.e., number densities) of ozone, O atoms, and odd oxygen are conventionally designated with square brackets enclosing the name of each chemical species, that is, $[\text{O}_3]$, $[\text{O}]$, and $[\text{O}_x]$, respectively.

In the early 1930s, photochemical kinetics data on the reactions constituting the Chapman mechanism were fragmentary, at best. From a modern vantage point, it is now known that the rate constant for reaction (10-13) (Tsang and Hampson 1986) is much too slow for the reaction to be important anywhere in the terrestrial atmosphere, but the other four reactions are fast enough (Ammann et al. 2013; Burkholder et al. 2015) to be

included in every modern stratospheric chemistry model. Reaction (10-9), which produces two O_x molecules, depends on light intensity, which is strongly attenuated at lower altitudes. Reaction (10-12) destroys two O_x molecules, while reactions (10-10) and (10-11) do not produce or destroy O_x , but simply control the relative concentrations of O_3 and O atoms. Reactions (10-9) and (10-11) involve absorption of sunlight energy, which is released as chemical energy and ultimately as heat, thus warming the stratosphere.

The heating of the stratosphere by ozone absorbing sunlight was anticipated by Lindemann and Dobson (1923), but Chapman developed the idea much further (Chapman 1931). Chapman noted that the intensity of sunlight decreases as it penetrates through the atmosphere, and the concentration of O_2 increases at lower altitudes. Because the vertical gradients of the sunlight intensity and the O_2 concentration have opposite signs, the volume rate of light absorption peaks in a layer at an intermediate altitude. Since photolysis of O_2 produces O atoms, it is apparent that O_x is produced in a layer. This model of a “Chapman layer” gives a semiquantitative account of atmospheric energy deposition and production of reactive chemical species.

The Chapman mechanism, the Chapman layer model, and the poorly known rate coefficients of the era provided a reasonable description of ozone in the stratosphere, especially when atmospheric transport was also invoked, but to make further progress required accurate laboratory measurements of the chemical reaction rate constants. In the 1960s and 1970s, revolutionary new laboratory techniques began to be developed for sensitively detecting reactive gas-phase atoms and free radicals, which enabled better rate constant measurements and more stringent tests of the Chapman models. In particular, Benson and Axworthy (Benson and Axworthy 1957, 1965) performed careful measurements of the rate constants for reactions (10-10) and (10-12), which ultimately showed that reaction (10-12), taken alone, is not fast enough to explain the observed concentration of stratospheric ozone (Schiff 1969) (Crutzen 1970, 1974): the Chapman mechanism with modern rate coefficients overestimates the atmospheric ozone concentration by at least a factor of 2. This discrepancy is displayed in Fig. 10-3, which compares an observed ozone vertical profile to profiles predicted by the Chapman mechanism. Something else, besides reactive O atoms, must be depleting stratospheric ozone.

c. Catalytic cycles

Ozone is the most abundant minor reactive constituent in the atmosphere and was of great interest, but evidence for the presence of other reactive atoms and free radicals was accumulating. Meinel (1950) identified OH free

FIG. 10-3. Stratospheric ozone concentrations observed over Panama (9°N) and predicted by the Chapman mechanism [from Seinfeld and Pandis (2016, p. 129, Fig. 5.5)].

radicals as responsible for an emission line at 656 nm observed in the night glow. This motivated Bates and Nicolet (1950) to analyze the chemical reactions that might produce and destroy OH . In their analysis, Bates and Nicolet identified several reactions that can catalyze ozone depletion, including the following *catalytic cycles*, which have been confirmed to be important in the stratosphere:

HO_x cycle 1

HO_x cycle 2

In both of these cycles, the catalyst is regenerated and two O_x molecules are destroyed during each repetition.

Bates and Nicolet addressed the reactions involving these so-called odd hydrogen species ($HO_x = H + OH + HO_2$) in the context of the mesosphere and thermosphere, where

they assumed that HO_x derives from short wavelength UV photolysis of H_2O . At lower altitudes where short wavelength UV does not penetrate, however, the H_2O photolysis rate is too slow to be important. Instead, HO_x is formed in the stratosphere by reaction of electronically excited $\text{O}(^1\text{D})$ atoms with H_2O and other hydrogen-containing trace species, as discovered by McGrath and Norrish (1960). The stratospheric $\text{O}(^1\text{D})$ atoms are produced mostly by photolysis of O_3 , followed by the reaction with H_2O to produce OH free radicals:

Starting in the 1950s, much new information on the abundances of species in the stratosphere (and above) was obtained from in situ sounding balloons and rockets (Ehhalt 1974). More recently, satellite measurements have played an increasingly important role in monitoring atmospheric ozone and many other species (Ackerman et al. 2019). Much of the work on atmospheric composition published up to the mid-1980s is summarized in the monograph by Brasseur and Solomon (1986). Later findings are summarized in reports on the state of the stratosphere, such as the reports on the “Scientific Assessment of Ozone Depletion,” which appear every four years and can be found on the World Meteorological Organization website (www.wmo.int), as well as in the reports published by the Intergovernmental Panel on Climate Change (<http://www.ipcc.ch/>). It is beyond the scope of the present work to review this huge body of material, but it suffices to say that many chemical families are important in the stratosphere. The odd nitrogen chemical family ($\text{NO}_x = \text{NO} + \text{NO}_2$) is one of the most important.

David Bates and Paul Hays (Bates and Hays 1967) showed that biogenic N_2O produced at Earth’s surface is transported to the stratosphere, where it is photodissociated by ultraviolet sunlight and also reacts with $\text{O}(^1\text{D})$ (most of which comes from photolysis of atmospheric O_3) to produce nitric oxide, in addition to diatomic nitrogen and oxygen:

Nitric oxide reacts with ozone as the first step in an important catalytic cycle, which, along with others, was fully elucidated by Paul Crutzen (Crutzen 1970, 1971) and by Harold Johnston (Johnston 1971):

This catalytic cycle regenerates the NO_x catalyst and destroys two O_x molecules in each repetition; its rate is governed by the concentration of NO_x , the catalyst. For his work on understanding atmospheric catalytic cycles, Paul Crutzen shared the 1995 Nobel Prize in Chemistry with two other atmospheric researchers, as discussed below.

A catalytic cycle can repetitively destroy O_x , but the number of repetitions (the “chain length”) is limited by “termination” reactions that consume the catalyst. In the atmosphere, “termination” is not permanent, however, since the termination products can often react on a longer time scale with other species or be photolyzed by sunlight, resulting in slow regeneration of the catalyst. In this case, the termination product is called a “reservoir species,” since it stores the catalyst for a period of time in a nonreactive form before releasing it again. An important example of a reservoir species is gas-phase nitric acid (HONO_2), which is the product of a reaction between members of the HO_x and NO_x families:

(The set of parentheses surrounding “+M” indicates that the rate law for this reaction is second order with a rate coefficient that depends parametrically on total concentration of air.) The NO_x catalyst can be regenerated by photolysis of HONO_2 and by reaction with OH free radicals:

Reaction (10-23) illustrates only one of the ways that two chemical families can be coupled, but there are many others. For example, reaction (10-27) is particularly important, because it converts a less reactive species (HO_2) and one that only weakly absorbs sunlight (NO) into a more reactive species (OH) and one that absorbs sunlight readily (NO_2):

Thus, the atmospheric catalytic cycles are embedded in a complex chemical mechanism that includes multiple chemical families, which are extensively coupled, and numerous reservoir species.

In his work, Harold Johnston pointed out that a fleet of Supersonic Transport (SST) aircraft, which fly in the stratosphere, would emit NO_x in their exhaust, resulting in the catalytic depletion of stratospheric ozone (Johnston 1971). As a result of this scientific analysis, the U.S. Congress declined to provide funding subsidies to support manufacturing a fleet of American SSTs, effectively terminating the program. The economic impact of the SST controversy highlighted the need for a better understanding of stratospheric chemistry, which motivated an increase in government research support around the world. In 1973 and 1974, international symposia were held in Kyoto, Japan (Schiff 1974), and near Washington, D.C. (Benson et al. 1975), to bring together the scientists who were advancing stratospheric chemistry.

At the Kyoto Symposium, Richard Stolarski and Ralph Cicerone (Stolarski and Cicerone 1974) reported that the ClO_x chemical family ($\text{ClO}_x = \text{Cl} + \text{ClO}$) could catalyze depletion of stratospheric ozone, just like the NO_x chemical family. They were concerned about ozone in the stratosphere, because chlorine is injected into the stratosphere by solid fuel rocket exhaust, in addition to natural sources, such as volcanic eruptions. The Stolarski and Cicerone catalytic cycle is similar to those for the other chemical families:

As in the other catalytic cycles, the rate of O_x destruction depends on the concentration of the catalyst (ClO_x). The total available chlorine is defined as the sum of ClO_x and the chlorine reservoir species, chlorine nitrate (ClONO_2) and hydrochloric acid (HCl). These reservoir species are formed via reactions (10-30) and (10-31), respectively, and destroyed (releasing ClO_x) via reactions (10-32) and (10-33), respectively:

In the lower stratosphere, where temperatures are low, almost all of the total available chlorine is “stored” in these reservoirs, but in the upper stratosphere, where temperatures and UV intensities are higher, much less ClO_x is stored in inert form and the ClO_x cycle [reactions (10-28) and (10-29)] is more important.

The identification of the ClO_x cycle by Stolarski and Cicerone fell on fertile ground, because Mario Molina and Sherry Rowland (University of California, Irvine) were at that time thinking deeply about the atmospheric fate of man-made CFCs, which were widely used commercially as solvents, refrigerants, and propellants for pressurized aerosol cans. CFCs are inexpensive, colorless, odorless, nonflammable, good solvents, and non-toxic, which explains their widespread use. Lovelock et al. (1973) showed by direct atmospheric sampling that CFCs were accumulating in the environment, which suggested that they had no environmental sinks (loss processes, such as reaction and dissolution in natural waters). Molina and Rowland studied this problem and concluded that although CFCs are essentially inert in the troposphere and do not dissolve significantly in Earth surface waters, they can be destroyed by ultraviolet photolysis. Thus they argued that CFCs undergo slow transport into the stratosphere, where they are photolyzed by short wavelength ultraviolet sunlight (Molina and Rowland 1974). This proposal was soon confirmed by Lovelock (1974), who reported vertical profiles of CFCs, which have relatively high concentrations in the troposphere and decreasing concentrations at altitudes above the tropopause (e.g., see Fig. 10-4). In addition to addressing the fate of CFCs, Molina and Rowland also pointed out that chlorine atoms from CFC photolysis would deplete ozone catalytically via the ClO_x catalytic cycle identified earlier by Stolarski and Cicerone. In recognition of their analysis of the fate of CFCs and their prediction that stratospheric ozone would be depleted as a result, Molina and Rowland shared the 1995 Nobel Prize in Chemistry with Paul Crutzen, who had previously elucidated the general role of catalytic atmospheric cycles.

d. The Great Ozone Debate

The publication by Molina and Rowland in 1974 marked the beginning of what many called the “ozone war” between scientific groups who accumulated evidence suggesting that CFCs could lead to significant stratospheric ozone depletion and groups who argued that the scientific evidence was not persuasive. If CFC manufacturing had to be curtailed to save the environment, the economic impacts would be immense. An anecdotal account of “the ozone war” was published in a book of the same title (Dotto and Schiff 1978), written by Lydia Dotto, a science writer, and Harold Schiff, an atmospheric scientist. The book was published in 1978, but the Great Ozone Debate continued until the mid-1980s, when the discovery of the polar stratospheric ozone hole settled the issue.

The ozone debate was motivated in large part by a health concern: the incidence of skin cancer in humans is

FIG. 10-4. Vertical profile of CF_2Cl_2 measured by various investigators [from Brasseur and Solomon (1986, p. 272, Fig. 5.52), reprinted by permission from Springer Nature].

correlated with ultraviolet sunlight exposure, which, in turn, is limited by the stratospheric ozone layer. Support for this argument is the correlation between the incidence of melanoma and latitude, as shown in Fig. 10-5, with higher sunlight intensity and greater time spent outdoors combining to give greater exposure and higher cancer incidence for populations at lower latitudes.

Development of satellites to monitor global ozone was motivated specifically because of the Great Ozone Debate. The TOMS instrument, which was first launched in 1978, utilizes SBUV imaging to create ozone maps by monitoring the fraction of ultraviolet sunlight at selected wavelengths that is absorbed by atmospheric ozone as the incident sunlight passes down through the atmosphere and is scattered back up through the atmosphere again to the satellite instrument (Ackerman et al. 2019).

During the period of the Great Ozone Debate, much progress was made in understanding the stratosphere. Laboratory studies of elementary reactions produced many reaction rate constants of high accuracy, laboratory studies of spectroscopy and photolysis quantum yields added considerable new knowledge, and detailed chemical reaction models were developed. Progress can be traced by reference to the reports issued by two expert panels that were established in 1977 to critically evaluate photochemical and rate data published in the burgeoning scientific literature (see section 7).

An important component of laboratory studies was the development of new analytical techniques for sensitively detecting reactive atoms, free radicals, and other trace chemical species that participate in atmospheric chemical cycles. Some of these new techniques were adapted for atmospheric observations, leading to important advances. For laboratory gas-phase reaction rate studies, two “direct” experimental approaches were heavily exploited, starting around 1950. The first of those methods, flash photolysis (Norrish and Porter 1949), utilizes high intensity light from a pulsed flash lamp to photolyze a precursor on a short time scale, producing a highly reactive intermediate whose reaction is then followed on a longer time scale. When they became available, pulsed lasers were used in place of the flash lamps. In early experiments, the concentration of the reactive intermediate was followed by using time-resolved absorption spectroscopy. Later, the atomic resonance absorption method was adopted (Michael and Weston 1966; Myerson et al. 1965), followed by atomic resonance fluorescence (Braun and Lenzi 1967; Clyne and Cruse 1972). Subsequently, the versatile laser-induced fluorescence (LIF) method (Tango et al. 1968) and various laser pump-probe techniques have supplanted the earlier optical detection techniques. Mass spectrometry coupled to a flow tube reactor has also been used to great effect.

In addition to the “direct” detection techniques, relative rate methods are heavily exploited for measuring reaction rate constants with reaction rates determined by comparison with the known rate of a reference reaction. With the advent of commercial Fourier transform infrared (FTIR) spectrometers in the late 1960s, sensitive, specific detection of reactants and products became possible, enabling the measurement of many atmospheric reaction rates. Some of the leading researchers in this area included James N. Pitts, Roger Atkinson, and others at the University of California, Riverside, and Hiromi Niki, at the Ford Scientific Research Laboratory. Tunable diode laser absorption spectrometry (TDLAS) was also developed for atmospheric sampling during this period (Schiff et al. 1994).

Along with new measurement techniques, computational methods were developed for accurately solving the set of coupled ordinary differential equations (ODEs) that describe a coupled reaction mechanism. Atmospheric reaction modeling is highly challenging. In part, the challenge comes from the wide range of atmospheric conditions and the size and complexity of the chemical mechanisms. In addition, a fundamental numerical problem had to be overcome. Because the time constants of the individual chemical reactions in a chemical mechanism typically span orders of magnitude, the corresponding coupled set of ODEs is described as

FIG. 10-5. Incidence of death due to skin melanoma among white males in the United States, displayed as a function of latitude [from Wayne (2000, p. 203, Fig. 4.19), attributed to Rowland (1982), further attributed to Scotto et al. (1975)].

“stiff” and cannot be solved accurately by using traditional finite difference methods. Instead, new methods were needed for solving stiff ODEs (Gear 1971; Hindmarsh 1974). The discovery of these algorithms revolutionized the solution of kinetics ODEs and enabled major advances in accurately modeling atmospheric reaction systems.

Practical theoretical treatments of pressure-dependent atmospheric reactions were developed and applied during this period. The treatments were ultimately based on the Rice, Ramsperger, Kassel, Marcus (RRKM) theory (Marcus 1952a,b,c), which has proven to be an exceptionally powerful tool. Dwight Tardy and Seymour Rabinovitch (Tardy and Rabinovitch 1966) showed how RRKM theory could be couched in master equation techniques to obtain results that were more accurate. Jürgen Troe developed a set of semiempirical equations for efficiently describing results from RRKM theory and master equation treatments (Troe 1977a,b). Master equation simulations (based on RRKM theory) and Troe’s equations are today in wide use for analyzing and summarizing atmospheric rate data in critical evaluations (Ammann et al. 2013; Burkholder et al. 2015) and other compilations (Jenkin et al. 2003; Saunders et al. 2003). Roger Patrick and David Golden (Patrick and Golden 1983) applied RRKM theory to a collection of pressure-dependent

stratospheric reactions and Patrick et al. (1984) employed a master equation simulation of the $\text{HO}_2 + \text{HO}_2$ recombination reaction.

The rate constants measured in laboratories enabled critical tests of the hypothesis that CFCs transported to the stratosphere could result in depletion of stratospheric ozone. Critical rate parameters were combined with atmospheric transport models to obtain atmospheric chemical models that could be used to understand stratospheric chemistry and for comparisons with observations. The models generally predicted that stratospheric ozone was being depleted by a few percent. In comparison, however, the “noise” (random errors) in atmospheric ozone abundance data was at least that large, preventing definitive conclusions from being reached. Because the theoretical models contained many parameters, each with an associated uncertainty, the possible accumulation of uncertainty also prevented definitive conclusions. Although regulation of CFCs, was advocated by many, it was resisted by those who were concerned about the economic impacts and cited the scientific uncertainties as justification for delaying regulatory action. The ozone war appeared to be approaching a stalemate.

During this period, governments provided strong support for atmospheric research. Measurement techniques

FIG. 10-6. Vertical profiles of ClO free radicals measured by Menzies (1979) and Anderson (1980) [from Brasseur and Solomon (1986, p. 279, Fig. 5.55), reprinted by permission from Springer Nature].

that had been developed and tested in the laboratory were translated to atmospheric measurements. Instruments based on those techniques were carried aloft by high-altitude balloons and rockets to sample the upper atmosphere. Atmospheric observations were performed by many researchers, as summarized elsewhere (Brasseur and Solomon 1986).

An example of how laboratory methods were translated to field measurements is provided by the activities of James G. Anderson. Anderson earned his Ph.D. under the direction of Charles A. Barth (University of Colorado), who was well known for his research on the upper atmosphere and the development of spaceborne instrumentation. As a postdoctoral research associate in the early 1970s, Anderson worked with Fred Kaufmann and Thomas M. Donahue. Kaufman was an expert on the use of laboratory flow systems for measuring gas-phase reaction rate constants, and Donahue was an expert in rocket and satellite measurements of Earth and planetary atmospheres. Anderson and Kaufman used the flow tube resonance fluorescence technique to measure rates of reaction involving OH free radicals (Margitan et al. 1975) and the atomic fluorescence technique to measure rates of reaction involving Cl atoms (Zahniser et al. 1976). Anderson designed and constructed an aerodynamic “flow-through” instrument equipped with resonance fluorescence detection for in situ measurements of atmospheric free radicals and atoms. Air flowed through the instrument (much like a laboratory flow tube) while the module was descending by parachute after being dropped from a balloon or rocket. Anderson used this instrument to make the first ever

measurement of the absolute concentration of stratospheric O atoms (Anderson 1975). He carried out similar experiments to measure the absolute stratospheric concentration of OH free radicals (Anderson 1976) and, because of the excitement generated by Molina and Rowland (1974), he measured ClO free radicals in the stratosphere (Anderson et al. 1977, 1980). He has continued both laboratory and field measurements (Anderson 2016).

Other research groups were also interested in direct atmospheric monitoring, especially measurement of species related to catalytic ozone depletion, and they developed additional advanced instrumentation for field measurements. Robert Menzies at JPL used balloon observations of the solar spectrum to detect the characteristic infrared bands of ClO radicals (Menzies 1979). The ClO concentrations that he deduced were in reasonable agreement with those of Anderson et al. as shown in Fig. 10-6. Later, Waters et al. developed a balloon-borne limb-sounding microwave spectrometer, which could measure stratospheric species that possess a permanent dipole moment (e.g., O₃ and ClO radicals) (Waters et al. 1981). Limb-sounding instruments operate by viewing the atmosphere just above the horizon (the “limb”), thus observing absorption and/or emission over a long atmospheric path. The viewing angle above the horizon is related to altitude, enabling the determination of vertical concentration profiles.

More recently, satellite-borne instruments have provided much data on stratospheric composition. The *Dynamics Explorer 2* satellite carried a limb-sounding instrument that utilized a Fabry–Pérot interferometer to isolate single emission lines of specific stratospheric

species (Hays et al. 1981). Instruments on the *Upper Atmosphere Research Satellite* (UARS; launched in 1991), included, among others, the High Resolution Doppler Imager for measuring high-altitude winds (Hays et al. 1993) and instruments for measuring stratospheric chemical concentrations: the Microwave Limb Sounder (Waters et al. 1993), the Cryogenic Limb Array Etalon Spectrometer (Roche et al. 1993), and the Halogen Occultation Experiment (Russell et al. 1993). The chemical instruments aboard UARS produced the first global mapping of stratospheric ClO free radicals and several reservoir species (Schoeberl et al. 1994). But, of course, those data were not available in the 1980s.

The 1980s opened a new chapter in stratospheric chemistry. The Great Ozone Debate had reached a near stalemate, although incremental scientific advances continued to be made. Much had been learned about ozone climatology and measurements were continuing at observatories around the world, a century after Hartley first noted the presence of ozone in the atmosphere. Much of the motivation for the ozone measurements was to accumulate longer time histories and to reduce the “noise” in the ozone observations, so that the predicted small anthropogenic perturbations (Cicerone et al. 1983; Prather et al. 1984) might be detected.

By the early 1980s, it was generally felt in the atmospheric chemistry community that stratospheric ozone was broadly understood and only the details remained to be worked out (see, e.g., Turco 1985). Odd oxygen was produced by photolysis of O_2 at wavelengths shorter than 242 nm and its loss was controlled by gas-phase catalytic cycles involving several chemical families: O_x , HO_x , NO_x , ClO_x , and BrO_x . Although questions remained about the reaction rate constants, quantum yields, lifetimes of reservoir species, etc., it was expected that these details could be addressed by better laboratory and observational data and, in principle, an accurate theoretical model of stratospheric chemistry could be constructed with perhaps several dozen chemical species and several hundred elementary reactions. It was believed that reactions on surfaces were not likely to be important, except perhaps for explaining the role of sulfate aerosols in the Junge layer (Junge et al. 1961; Turco 1985; Warneck 1988).

e. A hole in the theory

The Halley Bay Station of the British Antarctic Survey had been regularly gathering ozone data from October through March (when the sun was high enough) since 1957. During the period from 1957 to 1973, the ozone column density was about the same in every annual cycle in the months of October (austral spring) and March (austral autumn), but that pattern began to change in

FIG. 10-7. October mean O_3 column density (DU; lines with error bars) and Southern Hemisphere freons (F11 and F12, pptv: filled and open circles, respectively) [from Farman et al. (1985, Fig. 2a), reprinted by permission from Springer Nature].

1974, when the October measurements (originally $\sim 320 \pm 30$ DU) began to decline markedly, while those in March remained more or less unchanged. By October 1984, the October column density had dropped by more than a third (Fig. 10-7), which was a far greater decrease than the predicted anthropogenic perturbation of a few percent. Farman, Gardiner, and Shanklin published their findings in May 1985 (Farman et al. 1985), sending shock waves throughout the atmospheric science community.

Something important was missing from current understanding of stratospheric ozone. The stratospheric ozone hole, in which $\sim 40\%$ of the column ozone was depleted in only ~ 3 weeks during austral spring, was a complete surprise. The atmospheric science community responded by launching expeditions to the Antarctic in search of an explanation.

Anderson (1995) gives a good account of the logical sequence as the ozone hole puzzle was solved. The first expedition, the National Ozone Experiment (NOZE I, funded by NSF), took place in 1986. Ozone balloon sondes found that ozone was essentially completely absent in some layers in the lower stratosphere by the beginning of October 1986 (Hofmann 1988); an example from 1993 is shown in Fig. 10-8. Ground-based microwave spectrometry measurements found that stratospheric ClO free radical concentrations were elevated (de Zafra et al. 1987). A ground-based UV-visible spectrometer showed that OClO and NO_2 concentrations were higher than normal and lower than normal,

FIG. 10-8. Ozone vertical profiles at over the Antarctic in 1992 and 1993 (from Hofmann et al. 1994).

respectively (Mount et al. 1987; Solomon et al. 1987). A ground-based infrared spectrometer detected perturbed concentrations of HCl and ClONO₂, the ClO_x stratospheric reservoir species (Farmer et al. 1987). All of these observations were associated with a meteorological feature called the polar vortex, and most of them implicated chlorine chemistry unambiguously, but did not reveal the mechanism that was responsible.

There was no shortage of suggested chemical mechanisms. The Stolarski–Cicerone (Stolarski and Cicerone 1974) ClO_x cycle [reactions (10-28) and (10-29)] was already known, but to provide the O atoms necessary to complete the cycle would require ultraviolet sunlight, which is not abundant at high latitudes during austral spring. At least three alternative cycles that do not require ultraviolet light were proposed during 1986 and 1987.

Solomon cycle (Solomon et al. 1986):

McElroy cycle (McElroy et al. 1986):

Molina cycle (Molina and Molina 1987):

To support their suggestion, Molina and Molina measured the absorption spectrum of ClOOC(Cl) and showed that it has a wing extending into the near UV and visible regions of the spectrum.

The proposed cycles were plausible, but they did not address what happened to the reservoir species and there were questions about whether any of the cycles is fast enough to explain the rapid depletion of ozone

during austral spring. To address these questions, laboratory measurements of the key reaction steps were undertaken, resulting in considerable new laboratory data for use in atmospheric models. These results were reviewed critically by the NASA and the International Union of Pure and Applied Chemistry (IUPAC) panels of experts that were mentioned above. Also during this period, following a suggestion by Solomon et al. (Solomon et al. 1986), several groups began to investigate the possible role of heterogeneous reactions in polar stratospheric clouds (PSCs), which can be visually observed from the ground at high latitudes.

PSCs form only under the extremely cold conditions found in the polar lower stratosphere. The stratosphere is extremely dry, with typical H₂O mixing ratios of <10 ppmv, thus clouds composed of pure of water ice can occur only rarely, when the temperature is low enough. However, about 10–20 ppmv of gas-phase nitric acid is also present in the stratosphere and nitric acid di- and trihydrates have very low vapor pressures. Thus PSCs are found in well-defined layers, where the temperature is cold enough, and they usually consist largely of hydrated nitric acid particles (Kolb et al. 1995; Toon et al. 1989).

Independently, Molina et al. (1987) and Tolbert et al. (1987) reported laboratory evidence for fast reactions of the ClO_x reservoir species on surfaces, suggesting that these reactions on PSC surfaces are the key to explaining the atmospheric observations. The reactions take place in the dark at cold temperatures, releasing gas-phase products (Cl₂ and HOCl) that can be photolyzed by visible light to produce ClO_x species:

The first of these reactions had been suggested previously by Solomon et al. (1986). Several groups then embarked on laboratory studies of heterogeneous processes and the physical and chemical properties of PSCs. Many of those studies are discussed in a review by Kolb et al. (1995) and recent data have been reviewed by the NASA Panel on Data Evaluation (Burkholder et al. 2015) and the IUPAC Task Group on Atmospheric Chemistry Data Evaluation (Crowley et al. 2010).

Concurrently with the laboratory studies, a second field campaign, the Airborne Antarctic Ozone Expedition (AAOE), was organized for the purpose of making in situ measurements of the chemical composition in the polar vortex. For the AAOE, Anderson and coworkers developed an instrument to be carried by the high-altitude ER-2 aircraft, which is operated by NASA

(Brune et al. 1989). The instrument is basically an aerodynamically designed flow tube equipped with a chlorine atomic fluorescence detector. To measure the ambient concentration of ClO free radicals, an excess concentration of nitric oxide is added to the airflow upstream of the detector: nitric oxide reacts rapidly with ClO, producing free Cl atoms, which are then measured with the detector. After appropriate calibration, the atmospheric concentration of ClO radicals is obtained. Instruments operating on the same principles were later used to detect BrO free radicals and ClOOCl; the latter was detected by using electrical heating to thermally dissociate it upstream of the nitric oxide inlet, followed by detection of the free chlorine atoms (Stimpfle et al. 2004).

The AAOE mission, which took place in August and September 1987, was noteworthy because it settled the Great Ozone Debate by showing unequivocally that chlorine is involved in stratospheric ozone depletion (Anderson 1995; Anderson et al. 1991). Anderson (1995) points out that the AAOE mission demonstrated that the chemically perturbed region in the polar vortex is dynamically isolated: chemical exchange with its surroundings can take place, but only slowly (Schoeberl and Hartmann 1991). Because the AAOE mission investigated the polar stratosphere over the entire period when ozone was being depleted, it confirmed the earlier finding of the NOZE I mission that ClO free radical concentrations are perturbed. In fact, they were found to be elevated by a factor of ~500 and during the formation of the hole they were anticorrelated with O₃ (Anderson et al. 1991), as shown in Fig. 10-9. This was the “smoking gun” that essentially settled the Great Ozone Debate, which had raged for more than a decade (Anderson et al. 1991). The third finding of the AAOE mission was enabled by measuring concentrations of multiple chemical species and by the availability of high quality laboratory rate coefficients (Sander et al. 1995) that had been gathered by that time (Anderson 1995). The mission results were analyzed to determine the relative importance of the several mechanisms proposed for depleting stratospheric O₃ (see discussion above). The analysis revealed that the Molina mechanism is the most important, but that the mechanisms proposed by Solomon et al. (Solomon et al. 1986), by McElroy et al. (McElroy et al. 1986), and by Stolarski and Cicerone (Stolarski and Cicerone 1974) also contribute significantly to both stratospheric ozone depletion and ozone hole formation (Anderson et al. 1991, Anderson 1995).

As a result of the NOZE I, AAOE, and subsequent missions that have investigated the polar stratosphere in both the Arctic and the Antarctic, a clear understanding has emerged of how human activities lead to ozone depletion (Anderson 1995; Anderson et al. 1991; Fahey

FIG. 10-9. Anticorrelation between O_3 (pptv) and ClO free radical (ppbv) at the edge of the polar vortex on 16 September 1987 (from Anderson et al. 1989).

and Ravishankara 1999; Webster et al. 1994). The first step is emission of chlorine-containing compounds (e.g., CFCs) that are essentially inert in the troposphere, where they accumulate because transport above the tropopause is very slow. Once in the lower stratosphere, however, these compounds photolyze, releasing chlorine to produce ClO_x . However, formation of chlorine reservoir species from ClO_x is rapid in the lower stratosphere, tying up almost all of the total available chlorine. The small amount of remaining ClO_x depletes ozone catalytically, but the process is slow (a few percent per year). This is the situation for most of the stratosphere, most of the time. In the polar regions, however, the stratosphere cools by emitting infrared radiation during late fall and winter, resulting in subsidence of the air mass and condensation of PSC particles consisting mostly of nitric acid and water in a molar ratio of 1:3. The surfaces of the PSCs are catalytic for reactions (10-45) and (10-46), which convert the chlorine reservoir species to compounds that photolyze efficiently in visible light, which becomes available in late winter and early spring. Photolysis then releases ClO_x back into the gas phase, where it catalytically depletes ozone. Since more than 99% of the total available chlorine was stored in the reservoir species, and since most of the reservoir species react on the PSC surfaces, the ClO_x concentration in early spring increases to ~ 500 times greater than normal, and the ozone destruction rate increases accordingly, depleting ozone and producing the polar stratospheric ozone holes in just a few weeks. As the season progresses, the atmosphere warms up again, the

PSCs evaporate, the ozone holes dissipate, and the atmosphere returns to “normal.”

With the realization that the emission of anthropogenic CFCs provided the vehicle to convey chlorine into the stratosphere, an international agreement was reached to take measures to protect the ozone layer. The Montreal Protocol on Substances that Deplete the Ozone Layer was signed on 16 September 1987 in Montreal, Canada. Since then, it has been endorsed by nearly 200 countries and amended regularly to reflect improved scientific knowledge and the realities of implementation. The treaty has led to the replacement of CFCs with less impactful compounds. Stratospheric total available chlorine (the sum of ClO_x and the chlorine reservoir species) is trending downward (Anderson et al. 2000; Froidevaux et al. 2006; Rinsland et al. 2003; Strahan and Douglass 2018) and is expected to return to the 1980 level in a few decades (Douglass et al. 2014). The ozone layer and the ozone hole are showing signs of recovery (Ajavon et al. 2014, Fahey et al. 2019). Beyond its scientific achievements, the Montreal Protocol has been exceptionally successful in demonstrating that effective international agreements on environmental issues can be reached. Its success suggests that international agreements on other scientific issues (e.g., climate change) can also be successful.

Interest in stratospheric composition (Douglass et al. 2017) and the ozone holes (Wohltmann et al. 2017) continues. Direct observations of the stratosphere are being conducted to test theoretical models and identify gaps in understanding (Li et al. 2017; Santee et al. 2010, 2008). New platforms, such as unmanned autonomous aircraft and long-duration pressurized balloons (Jones 2004), are becoming more prominent. There is still much to learn about stratospheric chemistry.

6. Tropospheric chemistry

a. Early studies of photochemical smog

Foundations for the modern understanding of tropospheric photochemistry were laid following the Second World War in the 1950s and 1960s. Los Angeles experienced severe air pollution episodes in the 1940s with visibility reduced to just a few city blocks. It was recognized that the type of urban air pollution in Los Angeles was chemically different from that experienced elsewhere (see section 3). Los Angeles smog is highly oxidizing; in the 1940s and 1950s it was known to contain ozone but the contributions of other oxidants, such as NO_2 and H_2O_2 , were unclear (Renzetti 1956). Blacet in 1952 recognized that the photolysis of NO_2 could be an important source of ozone in polluted urban air (Blacet 1952). Haagen-Smit conducted experiments demonstrating photochemical formation of ozone and other oxidants and aerosols (see section 7a) from

reactions of nitrogen oxides and hydrocarbons in sunlight and investigated their human and ecological health impacts (Haagen-Smit 1952; Haagen-Smit et al. 1953). The air pollution in Los Angeles is the result of photochemistry and was called “photochemical smog” (Rogers 1958). A growing body of data in the 1950s showed that volatile organic compound (VOC) and NO_x emissions from the fleet of automobiles in California made an important contribution to smog formation. This led to regulations in California to limit VOC and NO_x emissions from vehicles and other sources starting in the 1960s and spreading to the rest of the world in the following decades.

Haagen-Smit and coworkers were limited by the rather primitive analytical methods that were available at that time and measured the concentration of ozone from the cracking of rubber exposed to the gas mixtures. Nitrogen oxides in ambient air were measured in the 1950s using wet-chemical methods that were cumbersome and subject to interferences (Thomas et al. 1956). Total oxidants were measured using potassium iodide solution, and were found to correlate with eye irritation, visibility effects, and crop damage. Stephens and coworkers used a long pathlength IR spectrometer to identify the formation of peroxyacetylnitrate [CH₃C(O)O₂NO₂; PAN] in smog (Stephens et al. 1956; Stephens 1964). PAN and homologous peroxyacetyl nitrates [RC(O)O₂NO₂] were found to be toxic to plants and responsible for the eye irritation associated with smog (Stephens 1964).

Leighton (1961) reviewed the existing state of knowledge of the photochemistry of air pollution noting the importance of chain reactions involving oxygen atoms, ozone, and organic radicals. In the 1950s and 1960s the first gas-phase kinetic studies of the key radical reactions thought to be involved in photochemical smog formation were conducted and chemical mechanisms started to be developed. It was realized that photolysis of NO₂ occurs on a time scale of a few minutes in the sunlit troposphere and gives NO and an oxygen atom that combines with O₂ within a few microseconds to give ozone. It was also realized that the rapid reaction of NO with O₃ precluded the simultaneous existence of high concentrations of both NO and ozone in the same air parcel:

Assuming a photostationary steady state for NO₂ gives

$$d[\text{NO}_2]/dt = k_{21}[\text{NO}][\text{O}_3] - j[\text{NO}_2] = 0,$$

where k_{21} is the rate coefficient for reaction (10-21), and j is the rate of photolysis of NO₂. Rearrangement leads

to an expression for the ozone concentration that is known as the Leighton relationship:

$$[\text{O}_3] = j[\text{NO}_2]/k_{21}[\text{NO}].$$

This expression provides a useful approximation of the relationship between [O₃], [NO₂], and [NO] in the daytime in urban areas although deviations exist (Finlayson-Pitts and Pitts 2000).

b. The importance of hydroxyl radicals

Interest in the 1950s and 1960s focused on O atoms, which, following their production by photolysis of NO₂, were believed to be the key species driving the formation of photochemical smog (Leighton 1961; Altshuller and Bufalini 1971). In the late 1960s concern was raised that carbon monoxide emissions from vehicles might accumulate in the atmosphere. Weinstock (1969) noted that the rate of natural production of ¹⁴C via cosmic rays colliding with nitrogen in the atmosphere was known, that ¹⁴C atoms are converted into ¹⁴CO, which is then oxidized into ¹⁴CO₂, and that the amount of ¹⁴CO in the atmosphere was known. Dividing the ¹⁴CO atmospheric burden by its production rate gave an estimate of 0.1 years for the atmospheric lifetime of CO and the conclusion that it would not accumulate in the atmosphere. By analogy to the fate of CO in the stratosphere (Bates and Witherspoon 1952), Weinstock proposed that reaction with OH radicals was responsible for tropospheric loss of CO:

In a seminal paper in 1971, Levy identified the source of OH radicals required to explain the observed lifetime of CO. His analysis was based on information that was already known, but he put the pieces together and solved the puzzle. Levy noted that photolysis of ozone produces electronically excited oxygen atoms, O(¹D), and that while the majority of O(¹D) atoms are collisionally deactivated to ground state O(³P) atoms, a small fraction react with water vapor to produce OH radicals:

Levy further noted that OH radicals react with CO, O₃, and CH₄ to give HO₂ and CH₃O₂ radicals, which he recognized then react with NO to regenerate OH radicals and start the cycle again. McConnell et al. (1971)

FIG. 10-10. Photochemical reaction model showing the importance of OH radicals [from Levy (1971, Fig. 1), reprinted with permission from AAAS].

confirmed the importance of these reactions in the atmospheric chemistry of methane and CO. The photochemical mechanism proposed by Levy is reproduced in Fig. 10-10 and is the foundation of the modern understanding of tropospheric photochemistry.

In the 1960s and 1970s revolutionary new experimental techniques were developed to study radical reactions relevant to tropospheric chemistry; these included flash photolysis, discharge flow, laser-induced fluorescence, long pathlength FTIR spectroscopy, and smog chamber techniques discussed in section 5e. In the 1980s, laboratory studies of OH reaction kinetics (Atkinson 1989) combined with modeling studies of tropospheric chemistry (Logan et al. 1981) had shown that OH radicals were responsible for initiating the atmospheric oxidation of most organic and inorganic compounds emitted into the atmosphere. Methyl chloroform, CH_3CCl_3 , emissions result from human activities, are well documented, and can be used to estimate average tropospheric OH levels (Lovelock 1977). Observed CH_3CCl_3 atmospheric concentrations, emissions estimates, and kinetic data for reaction with OH radicals were used to deduce that the global average tropospheric concentration of OH radicals was approximately 10^6 cm^{-3} (Prinn et al. 1992). Direct measurement of hydroxyl radicals in the troposphere is extremely

challenging because of their low concentration (sub pptv) and high reactivity. Laser-induced fluorescence and chemical ionization mass spectroscopy techniques to measure ambient OH concentrations were developed in the 1980s and 1990s and refined in the 2000s. While such measurements are still far from routine, they are now regular components of atmospheric chemistry field campaigns. Tropospheric hydroxyl radical concentrations vary with location, season, time of day, cloudiness, and presence of sources (e.g., ozone) and sinks (e.g., reactive hydrocarbons) and typically range from near zero during nighttime to maxima of approximately 10^7 cm^{-3} during daytime (Stone et al. 2012).

c. Tropospheric ozone

Until Levy's paper in 1971, it was believed that the main source of background tropospheric ozone was transfer from the stratosphere (Junge 1962) in tropospheric folding events. In the 1970s it became recognized that OH-initiated oxidation of methane and other organic compounds in the presence of NO_x was a large source of ozone in the troposphere (Crutzen 1973; Chameides and Walker 1973). Photochemistry accounts for the formation of approximately 4500 Tg of ozone per year in the troposphere, which is approximately an order of magnitude greater than the annual flux of approximately 500 Tg from the stratosphere

FIG. 10-11. Mechanism of reaction of ozone with alkenes [from Taatjes (2017, Fig. 1), reproduced with permission of *Annu. Rev.* in the format journal/magazine via Copyright Clearance Center, attributed to Taatjes et al. (2014), reproduced with permission of Royal Society of Chemistry in the format journal/magazine via Copyright Clearance Center].

(Royal Society 2008; Wild 2007). In addition to its central role in tropospheric chemistry, ground level ozone has important impacts on human and ecosystem health. The large effort expended over the past 100 years to measure tropospheric ozone levels and trends is described in section 2e.

Realization of the importance of ozone in urban air pollution and in the troposphere led to studies of the kinetics and mechanisms of gas-phase reactions of ozone with organic compounds (Cadle and Schadt 1952; Criegee 1957). By the 1980s there was a large kinetic database for the reactions of ozone with organic compounds. It was established that ozone reactions with saturated hydrocarbons, oxygenated organic compounds, and aromatic compounds were slow and not of atmospheric significance. However, the presence of an unsaturated bond results in a dramatic increase in reactivity (Atkinson and Carter 1984). As discussed in section 7, reaction with ozone is an important atmospheric loss for unsaturated organic compounds such as isoprene, terpenes, and sesquiterpenes that are emitted in large quantities by plants. Reactions of ozone with biogenics are an important source of atmospheric aerosols (see section 7).

Rudolph Criegee (1902–75) proposed that the ozonolysis of alkenes proceeds via formation of a primary ozonide that decomposes to give a carbonyl compound and a carbonyl oxide (Criegee 1957). The carbonyl oxide has both diradical and zwitterion characteristics and is known as a Criegee radical, Criegee zwitterion, or Criegee

intermediate. The simplest Criegee intermediate is CH_2OO . The mechanism of reaction of ozone with alkenes is shown in Fig. 10-11 (Taatjes 2017); the reaction is highly exothermic and produces excited Criegee intermediates, which may isomerize, decompose, or undergo collisional stabilization. Stabilized Criegee intermediates react with important atmospheric constituents such as SO_2 , NO_2 , water vapor, and inorganic (HNO_3 and HCl) and organic acids. The kinetics and mechanisms of gas-phase atmospherically relevant reactions have been studied using indirect methods since the 1970s (Cox and Penkett 1971), but Criegee intermediates were only recently detected and measured directly in laboratory experiments (Welz et al. 2012). Criegee intermediates exist in syn- and anticonformers with important differences in reactivities of different conformers. Reactions involving Criegee intermediates are important in the atmospheric oxidation of SO_2 , the gas-phase production of organic acids (Leather et al. 2012), and the formation of OH radicals (Taatjes et al. 2014; Taatjes 2017). With the recent availability of new laboratory techniques, Criegee intermediate chemistry is one of the most active areas of gas-phase atmospheric chemistry research and we expect many exciting developments will be forthcoming.

d. Nitrate radicals

As discussed in section 4, nitrate radicals (NO_3) are formed by the reaction of NO_2 with ozone and are in equilibrium with N_2O_5 :

Leighton was the first to recognize the potential importance of reactions of NO_3 radicals with species other than nitrogen oxides in polluted urban air (Leighton 1961; Wayne et al. 1991). Studies of the kinetics of reactions of NO_3 radicals with aldehydes and olefins beginning in the 1970s (Morris and Niki 1974; Japar and Niki 1975), together with spectroscopic observations of high concentrations of NO_3 radicals in polluted air (Platt et al. 1980), showed that reaction with NO_3 radicals is an important loss process for organic compounds in the nighttime atmosphere. NO_3 radicals have a lifetime of only ~ 4 s with respect to photolysis for an overhead sun (Calvert et al. 2015) and this depresses NO_3 radical concentrations to low levels during the daytime. NO_3 radicals react rapidly with NO. At nighttime in the absence of photolysis and when NO concentrations drop to low levels (usually because of rapid reaction with ozone) the concentration of NO_3 radicals can rise to 100 pptv, $2.5 \times 10^9 \text{ cm}^{-3}$, in polluted air (Seinfeld and Pandis 2016). As discussed in section 4, formation of N_2O_5 followed by hydrolysis is an important mechanism for conversion of NO_x into HNO_3 . Reaction of NO_3 radicals with unsaturated organic compounds such as isoprene is an important source of organic nitrates (Wayne et al. 1991; Seinfeld and Pandis 2016).

e. Halogen atom chemistry

The discovery in the late-1980s of reactions on ice surfaces converting inactive forms of chlorine into active forms in the Antarctic ozone hole (see section 5e) led to the question of whether such processes could occur in the troposphere. Schroeder and Urone showed that the reaction of $\text{NO}_2/\text{N}_2\text{O}_4$ (at the NO_2 concentrations used there is significant presence of the dimer N_2O_4) with NaCl particles produces NOCl, which can photolyze to give Cl atoms (Schroeder and Urone 1974). Finlayson-Pitts and coworkers showed that under tropospheric conditions reaction of N_2O_5 with NaCl particles gives ClNO_2 , which photolyzes rapidly to give Cl atoms (Finlayson-Pitts et al. 1989):

The reaction of hypochlorous acid (HOCl) with NaCl produces molecular chlorine, which is photolyzed to give chlorine atoms:

Significant concentrations of Cl_2 (Pszenny et al. 1993) and ClNO_2 have been observed in the troposphere (Thornton et al. 2010). Over the past decade it has become clear that chlorine atom chemistry can be important locally and regionally in the troposphere. Chlorine atoms react rapidly with most organic compounds. The impact of chlorine chemistry in the troposphere is not fully defined and remains an area of current research.

Large losses of ozone at polar sunrise in March and April in the lower (0–2 km) Arctic atmosphere (Barrie et al. 1988) have been explained by autocatalytic reactions involving Br atoms and BrO radicals liberated from solvated bromide ions in sea salt aerosols and/or snow and ice (Vogt et al. 1996). High concentrations of Br_2 and BrCl are observed in the Arctic at polar sunrise (Foster et al. 2001). This process is sometimes referred to as the “bromine explosion”:

Halogen chemistry associated with bromine- and iodine-containing compounds emitted from open-ocean sources is responsible for significant ozone loss in the tropical marine boundary layer (Carpenter 2003; Read et al. 2008). The importance of halogen chemistry (primarily bromine and iodine) for tropospheric ozone on a global basis has been investigated by Saiz-Lopez et al. (2012). Emissions of CHBr_3 , CH_2Br_2 , CH_2BrCl , CHBr_2Cl , and CHBrCl_2 , CH_2I_2 , CH_2IBr and CH_2ICl when included in a global atmospheric chemistry model reduce the annually averaged tropical tropospheric ozone column by $\sim 10\%$. Compared to chlorine atoms, bromine atoms are much less reactive and iodine atoms are essentially unreactive toward organic compounds. The impact of tropospheric bromine and chlorine atom chemistry is largely confined to ozone destruction (Calvert et al. 2015).

f. Critical evaluations and model development

Approximately 100 years ago Sidney Chapman developed a five-reaction model that, using the kinetic data available at the time, provided a semiquantitative explanation for the stratospheric ozone layer, as described in section 5b of this chapter. The invention of electronic computers and relentless pace of Moore’s law

FIG. 10-12. Atmospheric organic carbon number spectrum.

has enabled the development of sophisticated numerical models of stratospheric and tropospheric atmospheric chemistry. At their most detailed, these models now contain thousands of chemical reactions. Models are used by regulatory agencies to develop policies and regulations to limit atmospheric pollution and its impacts. The economic ramifications of results from the models can be substantial, and it is important that models are updated with the latest atmospheric science. Models are used to integrate and test our knowledge of atmospheric chemistry and highlight important gaps in our knowledge.

Critically evaluated data for the rates and mechanisms of gas-phase reactions are needed as inputs for the models. Evaluations compiled by individuals and groups of experts are available in the literature. As discussed in section 5d, the longest standing efforts are those of the IUPAC and NASA data evaluation panels that have been in existence for 40 years (Cox 2012). The NASA panel concentrates mostly on reaction rate constants and photochemical parameters important in stratospheric and upper tropospheric chemistry, while the IUPAC panel covers both stratospheric and tropospheric reactions. Evaluated data for approximately 1000 gas-phase reactions relevant to tropospheric

chemistry are available online (<https://jpldataeval.jpl.nasa.gov/> and <http://iupac.pole-ether.fr/>).

7. Chemistry of atmospheric organic particle formation

The nature of fine particles (aerosols) in the atmosphere is discussed, especially in regard to their role in cloud physics in this monograph (Kreidenweis et al. 2019). Atmospheric aerosols comprise literally a kitchen sink of compounds, arising from direct emissions of particles as well as from condensation of vapor species onto preexisting particles. Earth's atmosphere contains an immense number of gas-phase organic compounds. Their presence is a result of emissions from plants and animals (biogenic compounds), natural and anthropogenic combustion processes, emissions from oceans, and from the atmospheric oxidation of organics emitted into the atmosphere (Fig. 10-12). Atmospheric organic compounds span an enormous range of chemical structures and physico-chemical properties; these include molecular size, atomic composition, degree of oxidation, presence of functional groups, and vapor pressure (volatility). This chemical complexity and diversity lead to significant challenges in detecting, quantifying, and

characterizing the array of organic compounds present in the atmosphere. Description of any individual compound involves, at a minimum, the numbers of C, O, and H atoms (or more if heteroatoms such as N or S are involved). A molecular taxonomy has evolved in which an individual species is characterized by its carbon number (n_C), oxygen number (n_O), elemental ratios (H:C and O:C), and volatility (vapor pressure). Earlier in this chapter the exquisite complexity of the gas-phase chemistry of the stratosphere and troposphere has been discussed.

The composition of tropospheric particles can now be measured routinely with an array of instruments. Nonetheless, these measurements are carried out routinely only in some areas of the world and only at the surface. Also, most instrumentation, whether on the ground or on an aircraft, focuses on submicrometer particles (and generally of aerodynamic diameter < 700 nm). The restricted nature of these measurements has implications for obtaining global aerosol mass budgets. A convenient distinction in overall particle mass composition is between inorganic and organic constituents. Worldwide, airborne particle composition is roughly 50% organic in nature, and in many locations as much as 80% organic.

Organic atmospheric particulate matter can be emitted directly into the atmosphere, primarily from combustion sources, but the majority of organic aerosol reaches the condensed phase via a pathway in which VOCs undergo gas-phase oxidation in the atmosphere to yield low-volatility oxidation products that condense into the aerosol phase. Particulate organic material that reaches the condensed phase via this pathway is termed secondary organic aerosol (SOA). Substantial efforts have been made to estimate the global atmospheric burden of SOA, but its global burden is difficult to constrain because of the varied pathways by which organics reach the particle phase and also because many of its sources are natural, so they are more difficult to inventory than single-point sources, like power plants. Moreover, the natural sources have high variability and depend strongly on conditions like temperature, light intensity, soil moisture and wind, plant growth cycles, etc.

The overall nature of the conversion of atmospheric VOCs to the particle phase is well understood. Reaction of VOCs with atmospheric oxidants such as OH, O₃, and NO₃ can lead to the formation of so-called semivolatile organic compounds (SVOCs), which can condense into the particle phase or continue to undergo further gas-phase oxidation to become low-volatility organic compounds (LVOCs) that partition into the particle phase even more strongly (Kroll and Seinfeld 2008; Hallquist

et al. 2009; Donahue et al. 2012a; Seinfeld and Pandis 2016; Donahue et al. 2019). Once organics partition into the particle phase, they can be further transformed chemically into dimers, oligomers, and other higher-molecular-mass compounds (Kalberer et al. 2004; Gao et al. 2004; Ervens et al. 2011; McNeill 2015). Some portion of the particle-phase LVOCs can be transformed back to (semi)volatile compounds or CO/CO₂ by fragmentation reactions triggered by OH or other oxidants at the particle surface or in the particle itself (Kroll and Seinfeld 2008; Jimenez et al. 2009).

When a VOC undergoes atmospheric oxidation to produce organic aerosol, the ratio of the mass of organic aerosol produced to the mass of the parent VOC reacted is termed the SOA yield. The SOA yield is a convenient quantity to measure the relative aerosol-forming capability of VOC-oxidant combinations. The SOA yield depends in a complex manner on the involvement of other atmospheric species that influence the oxidation pathway, especially the level of oxides of nitrogen (NO and NO₂). Study of the chemistry and physics accompanying the transformation of volatile organic compounds into low-volatility species, with the consequent production and growth of aerosols, occupies a major area of atmospheric chemistry research. Such studies are frequently carried out in large laboratory reactors; so-called smog chambers (Schwantes et al. 2017).

a. Atmospheric oxidation of volatile organic compounds to produce low-volatility species

The first notion that the atmospheric oxidation of volatile organic compounds may lead to condensed organic material can be found in the classic paper of Haagen-Smit titled “Chemistry and physiology of Los Angeles smog” (Haagen-Smit 1952). Haagen-Smit observed that “it has been noticed in the fumigation experiments that the vapor-phase oxidation of olefins is always accompanied by aerosol formation,” and “these effects are especially noticeable with ring compounds having a double bond in the ring, such as cyclohexene, indene, and dicyclopentadiene. In these cases, the opening of the ring will yield practically nonvolatile oxidation products. Because of the introduction of several polar groups, the volatility decreases so radically that aerosol formation is inevitable.” Following Haagen-Smit’s landmark paper, in two classic papers in 1960, entitled “Blue hazes in the atmosphere” (Went 1960a) and “Organic matter in the atmosphere, and its possible relation to petroleum formation” (Went 1960b), F.W. Went noted, “when we are in the countryside far away from cities, a blue haze is still present, usually much bluer than industrial smokes and hazes.” After ruling out smoke, dust, water vapor, and fog as the

source of the blue hazes, Went concluded that the blue hazes must consist of minute, submicroscopic particles. When airborne particles are smaller than the wavelength of light, they scatter blue wavelengths more strongly than red wavelengths. This is called Rayleigh scattering. For particles larger than the wavelength of light the scattering is more intense, not very dependent on incident light wavelength, and hence produces a whiter haze. This is known as Mie scattering. We now know that in forested regions trees are copious emitters of monoterpenes, like α - and β -pinene, the oxidation of which produces nanometer-sized particles that scatter light and give a blue haze.

Referring to the observations of Haagen-Smit published eight years earlier, Went noted that when low concentrations of terpenes are injected into an ozone-bearing atmosphere, a blue haze develops. He estimated a global emission rate to the atmosphere of 1.75×10^8 tons of terpene-like hydrocarbons or slightly oxygenated hydrocarbons. He suggested that ultraviolet or visible light in the presence of nitrogen oxides will cause the formation of peroxides and ozonides and noted that the more dilute the organic vapor, the deeper blue is the haze formed and the longer it takes to form. Going back to observations of Tyndall in 1869, Went suggested that such particles eventually grow to a size of about $1 \mu\text{m}$. Went noted that Leonardo da Vinci actually described the blue haze centuries before, although without knowledge of organic chemistry, da Vinci attributed the presence of such hazes to the exhalation of moisture from plants.

Atmospheric gas-phase oxidation of VOCs is initiated largely by reaction with the OH radical, ozone (O_3), and the nitrate radical (NO_3). Oxidation of VOCs mostly leads to volatile products, but, as noted above, a fraction of such reactions can produce species of sufficiently low vapor pressure such that their preferred state is to be in a condensed phase. The vapor pressure of a species, determined largely by its polarity and molecular size, is the prime determinant of the extent to which the species will reside in the particle phase. An important determinant of the vapor pressure of a species is the presence of functional groups on the molecule. The oxidant (OH, O_3 , NO_3) that initiates the atmospheric degradation of a VOC plays a major role in determining the distribution of its oxidation products and therefore their volatility.

Reactions of OH, O_3 , and NO_3 with VOCs lead to the creation of functional groups on the molecule; these include hydroxy (CHOH), carbonyl ($\text{C}=\text{O}$), aldehydic (CHO), nitrooxy (CHONO_2), hydroperoxy (CHOOH), carboxyl [$\text{C}(\text{O})\text{OH}$], and ester [$\text{C}(\text{O})\text{OR}$], or to decomposition of the original VOC. The presence of functional groups leads to molecules that are more polar and less volatile than the parent VOC and thus have a greater

tendency to condense into the particle phase. Once in the particle phase, these compounds can undergo additional chemistry, such as isomerization, dehydration, and dimerization (reactions that link two organic compounds through chemical bonds to form larger compounds), that lead to particle-phase compounds of even lower volatility. Early experiments, carried out in smog chambers, investigating secondary organic aerosol formation from hydrocarbon oxidation, were reported by O'Brien et al. (1975a,b), Kamens et al. (1981, 1982), Leone et al. (1985), Stern et al. (1987), and Pandis et al. (1991).

Elemental ratios of compounds are measured by instruments either directly via molecular ions or from bulk average composition determined by fragment ions (Isaacman-VanWertz et al. 2017). From such ratios, the average oxidation state of carbon atoms in an organic compound (OS_C) can be estimated (Kroll et al. 2011). The oxidation state of a compound can be estimated, assuming that all nitrogen in the compound is present as organic nitrates, as

$$\text{OS}_\text{C} = 2(\text{O/C}) - (\text{H/C}) - 5(\text{N/C}).$$

In the absence of nitrogen in the compound, the oxidation state is

$$\text{OS}_\text{C} = 2(\text{O/C}) - (\text{H/C}).$$

The maximum carbon oxidation state is +4 (for CO_2). The average carbon oxidation state of atmospheric organic aerosol lies between approximately -2 and $+1$. An increase in the O/C ratio of an oxidized molecule can arise either from addition of oxygen or loss of carbon atoms (Heald et al. 2010). The addition of oxygen atoms is generally a result of functionalization, whereas the loss of carbon is generally the result of fragmentation. Atmospheric oxidation can increase the volatility of organics by cleavage of carbon-carbon bonds or decrease volatility by addition of polar functional groups (Jimenez et al. 2009; Kroll et al. 2011; Donahue et al. 2012a,b).

In the present context, functionalization reactions produce molecules with the same number of carbon atoms as the parent compound but a larger number of oxygen-containing functional groups. Fragmentation reactions lead to C-C bond scission and the formation of two smaller molecules. When C-C bond scission reactions occur on the pathway to forming secondary organic aerosol, such systems tend to exhibit smaller yields of organic aerosol than if functionalization is predominant. Fragmentation tends to lead to organic aerosol with a higher O:C ratio than in the absence of fragmentation, because smaller molecules require more oxygen atoms to achieve a sufficiently low vapor pressure to be in the aerosol phase.

The production of extremely low-volatility organic compounds (ELVOCs) results from either multigeneration reactions, wherein functional groups are added in consecutive reaction steps, or from rapid addition of several functional groups in virtually a single step. It has recently been recognized that autoxidation is an effective mechanism for atmospheric oxidation of organic molecules (Crounse et al. 2013; Praske et al. 2018). In autoxidation, peroxy radicals (RO_2) produced after initial reaction of a VOC with an oxidant (e.g., OH or O_3) undergo a unimolecular isomerization reaction to produce an alkyl radical and a hydroperoxide functional group. The alkyl radical can react rapidly with O_2 again to regenerate an RO_2 radical. This process is a pathway by which functional groups (especially hydroperoxide groups) can be rapidly added to the molecule. As a result of their exceptionally low volatility, these products condense essentially irreversibly into the particle phase.

The extent to which a gas-phase organic compound in the atmosphere will reside in the particle phase can be measured largely by its vapor pressure. Organic compounds in the atmosphere with vapor pressures in the range from 10^{-5} to 10^{-11} atm (1 atm = 1013.25 hPa) are found distributed between the gas and particle phases, whereas those with vapor pressure less than about 10^{-11} atm are found largely in the particle phase. ELVOCs are responsible for the early stages of particle nucleation and growth in the atmosphere; these compounds have also been designated as highly oxygenated molecules (HOMs) (Ehn et al. 2012; 2014; Trostl et al. 2016).

Once in the atmosphere, gas-phase organic compounds can undergo continued oxidation, primarily by OH. A typical ambient daytime OH concentration is $\sim 2 \times 10^6$ molecules cm^{-3} . For a typical organic–OH reaction rate constant of $\sim 3 \times 10^{-11}$ cm^3 molecule $^{-1}$ s $^{-1}$, the chemical lifetime of a gas-phase organic molecule in the atmosphere is ~ 5 h. The typical time scales for the other pathways of organic molecule removal from the atmosphere, wet and dry deposition, are from days to weeks. Thus, an organic compound in the atmosphere can undergo several generations of gas-phase reaction prior to ultimate removal by wet or dry deposition. A consequence of that pathway is conversion to secondary organic aerosol.

Another important pathway for the production of atmospheric secondary organic aerosol is via absorption of vapors into cloud water followed by aqueous-phase chemistry. Then, as cloud water evaporates, the organic material remains as organic-containing particles (Sorooshian et al. 2007; Ervens et al. 2011, 2014; Tan et al. 2012; Woo et al. 2013; McNeill et al. 2014; McNeill 2015, 2017).

b. Atmospheric chemistry of biogenic compounds

Volatile organic compounds emitted from vegetation significantly impact tropospheric chemistry. About

1000 Tg of volatile organic compounds are emitted annually from plants, about 50% of which is isoprene, (2-methyl-1,3-butadiene, C_5H_8), about 15% monoterpenes ($\text{C}_{10}\text{H}_{16}$ compounds), and about 3% sesquiterpenes ($\text{C}_{15}\text{H}_{24}$ compounds). By contrast, anthropogenic combustion and use of fossil fuels leads to emissions of about 127 Tg yr $^{-1}$ (estimated range 98–158 Tg yr $^{-1}$) (Glasius and Goldstein 2016).

Isoprene, with an estimated global emission rate of 500 TgC yr $^{-1}$, is the single most abundant source of non-methane organic carbon to the atmosphere (Guenther et al. 2006, 2012). As a five carbon conjugated diene, isoprene reacts rapidly with OH, O_3 , and NO_3 , such that, despite its large emission flux, it is present only at moderate mixing ratios in the atmosphere (0–10 ppbv). Under typical daytime conditions, isoprene has a lifetime of about 1–2 h. The hydroxyl radical is the dominant reactive sink of isoprene ($\tau_{\text{OH}} = 1.25$ h at $[\text{OH}] = 2 \times 10^6$ molecules cm^{-3}), followed by O_3 ($\tau_{\text{O}_3} = 17$ h at $[\text{O}_3] = 50$ ppbv), and the nitrate radical ($\tau_{\text{NO}_3} = 16$ h at $[\text{NO}_3] = 1$ pptv). Because isoprene emissions peak in the daytime and NO_3 radical concentrations peak in nighttime, reaction with O_3 is generally a larger sink for isoprene than is NO_3 .

As a result of the large flux and rapid rate of oxidation of isoprene, its chemistry and that of its oxidation products are of substantial importance to tropospheric chemistry. With its complex oxidation mechanism, isoprene exerts control of the oxidative capacity of the troposphere in the regions where its emissions are prevalent. In such regions, isoprene chemistry significantly affects tropospheric ozone production via perturbation of the NO_x ($\text{NO} + \text{NO}_2$) and HO_x ($\text{OH} + \text{HO}_2$) cycles. Subsequent reactions of its oxidation products can either reduce or increase the oxidative potential of the atmosphere depending on the relative abundance of NO_x and HO_x . Isoprene may indeed play a major role in controlling OH and O_3 on a large scale through its oxidation cascade and the products generated therein.

Owing to its two double bonds, the atmospheric mechanism of isoprene oxidation, by OH, O_3 , and NO_3 , is extraordinarily complex (Wennberg et al. 2018). The main daytime oxidation of isoprene is initiated by reaction with OH. Addition of OH to either of the two double bonds of isoprene produces a hydroxyalkyl radical of isoprene, which then reacts with molecular oxygen to form an organic peroxy radical, commonly denoted as ISOPO_2 . The four sites for OH addition combined with allylic resonance in the initially formed hydroxy alkyl radicals leads to the formation of six chemically distinct peroxy radicals; four α -hydroxy peroxy radicals and two β -hydroxy peroxy radicals. The fate of the ISOPO_2 radical depends largely on the

FIG. 10-13. Biogenic terpenes and sesquiterpenes.

prevailing NO_x level. In high NO_x environments, reaction with NO forms an alkoxy radical, which likely fragments to form highly volatile products, including methacrolein (MACR) and methyl vinyl ketone (MVK), and/or isomerizes to form hydroxycarbonyl isomers. When NO_x levels are sufficiently low, isoprene oxidation proceeds primarily by a pathway in which the ISOPO_2 radical reacts with the hydroperoxyl radical (HO_2), leading to formation of a family of isoprene hydroxyl hydroperoxides (denoted ISOPOOH) (Paulot et al. 2009a,b; Bates et al. 2014) in molar yields exceeding 70%. ISOPOOH reacts further by OH addition and isomerization to form isoprene epoxydiols (IEPOX) in molar yields exceeding 75% (Paulot et al. 2009a,b). In pristine regions where the lifetime of the ISOPO_2 radical is sufficiently long, unimolecular isomerization reactions produce hydroperoxyaldehydes (HPALDs).

A number of recent studies have identified what appear to be the major SOA formation pathways from isoprene, and the factors controlling SOA formation, for example, particle acidity and RH (Surratt et al. 2006, 2007, 2008, 2010; Gaston et al. 2014). Condensed-phase chemistry in the acidic particles induces transformation into lower volatility and/or higher solubility products such as organosulfates, 2-methyltetrols, and oligomers. The discovery of significant IEPOX production from ISOPOOH provided a direct explanation of the presence of C_5 -tetrols first identified in ambient aerosols in the Amazon (Claeys et al. 2004). The importance of IEPOX-generated SOA has been confirmed in a variety of field measurements (Xu et al. 2015a,b; Budisulistiorini et al.

2015). Such measurements show that IEPOX-SOA components make up a substantial fraction of total organic aerosol mass in the southeastern United States and the Amazon (Isaacman-VanWertz et al. 2016). The oxidation chemistry of isoprene (and monoterpenes) exhibits particularly complex dependencies on the NO_x level (Kroll et al. 2006; Ng et al. 2007; Xu et al. 2014). The $\text{RO}_2 + \text{NO}_2$ pathway can potentially lead to substantial SOA formation through further oxidation of peroxy methacroyl nitrate (MPAN) (Chan et al. 2010; Lin et al. 2013; Nguyen et al. 2015). Moreover, organic nitrate functional groups formed via a branch of the $\text{RO}_2 + \text{NO}$ reaction have been observed to be a significant fraction of atmospheric SOA (Brown et al. 2009, 2013; Beaver et al. 2012; Fry et al. 2013; Lin et al. 2015; Xu et al. 2015a,b; Lee et al. 2016; Ng et al. 2017).

Finally, monoterpenes (biogenic molecules with formula $\text{C}_{10}\text{H}_{16}$) (Fig. 10-13) are also important precursors of SOA in forested regions of the globe. Predicted global SOA formation from monoterpenes is not at present well constrained; estimates vary from 14 to 246 Tg yr^{-1} (Pye et al. 2010; Spracklen et al. 2011).

c. Gas-particle partitioning

Partitioning of organic oxidation products between the gas and particle phases is fundamental to the formation of secondary organic aerosol (Seinfeld and Pandis 2016). The process is controlled both by the volatility of the species and the concentration of aerosol into which the species condenses. The volatility of a given compound is customarily represented by its

effective saturation mass concentration C_i^* (expressed in units of $\mu\text{g m}^{-3}$):

$$C_i^* = M_i P_i \gamma_i / RT,$$

where M_i is the molecular weight of the species, P_i is its saturation vapor pressure, and γ_i is its activity coefficient in the condensed phase, R is the gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is temperature (K). It is often assumed, for lack of information to the contrary, that the aerosol-phase activity coefficient γ_i is unity. The C_i^* can be interpreted as the gas-phase mass concentration (units of $\mu\text{g m}^{-3}$) at which the compound resides half in the gas phase and half in the particle phase.

The C_i^* depends primarily on the length of the carbon backbone and the number and type of functional groups present and somewhat less importantly on the specific structure of the molecule. For example, the addition of a ketone to a hydrocarbon backbone leads to a decrease in vapor pressure by a factor of ~ 10 – 20 , an alcohol by a factor of ~ 160 , and the addition of a carboxylic acid by essentially the product of these two factors.

The extent to which a particular compound exists in the gas or particle phases is measured by its effective saturation mass concentration C_i^* , and a number of volatility categories can be delineated:

Extremely low-volatility organic compounds (ELVOCs), with volatility bins 10^{-4} and $10^{-5} \mu\text{g m}^{-3}$. These compounds immediately condense into the particle phase.

Low-volatility organic compounds (LVOCs), with volatility bins 10^{-3} , 10^{-2} , and $10^{-1} \mu\text{g m}^{-3}$: These compounds reside in the particle phase at typical atmospheric particle concentration levels.

Semivolatility organic compounds (SVOCs), with volatility bins 1, 10, and $100 \mu\text{g m}^{-3}$: The corresponding compounds exist in both the gas and particle phases under typical ambient conditions.

Intermediate-volatility organic compounds (IVOCs), with volatility bins 10^3 , 10^4 , 10^5 , and $10^6 \mu\text{g m}^{-3}$: These compounds exist in the gas phase in the atmosphere but, upon oxidation, can be readily converted to condensable compounds leading to secondary organic aerosol particles. IVOCs are a group of compounds with saturation concentrations roughly in the range of C_{12} – C_{22} *n*-alkanes.

Volatile organic compounds (VOCs), with $C^* > 10^6 \mu\text{g m}^{-3}$: Most of the emissions of gas-phase organics fall in this traditional category.

d. Yield of secondary organic aerosol particles

The first model that was developed to describe the process of SOA formation was based on the assumption that gas-phase oxidation of a VOC leads to a series of

products, each with a constant yield that is equal to the moles of product molecule i formed per mole of VOC reacted (Odum et al. 1996). A fraction of each oxidation product F_i was considered to condense into an absorbing organic particle phase to form SOA, and it was assumed that each product rapidly achieves thermodynamic equilibrium between the gas and particle phases. It was presumed that atmospheric aerosols consist of liquid particles, for which gas-particle equilibrium is attained in seconds to minutes.

The gas-particle equilibrium of an individual organic compound can be described in terms of a gas-particle partitioning coefficient K_i , given by

$$K_i = [\text{OC}_i]_p / [\text{OC}_i]_g C_p = RT / M \gamma_i P_i,$$

where $[\text{OC}_i]_p / [\text{OC}_i]_g$ is the ratio of the concentrations of the compound in the gas and particle phases (moles m^{-3} of air), C_p is the mass concentration of the absorbing particle phase (kg m^{-3} of air), M the mean molecular mass of the absorbing organic particle phase (kg mol^{-1}), and P_i the subcooled liquid vapor pressure of the condensing species. The particle-phase fraction of compound i , F_i , is then given by

$$F_i = [\text{OC}]_p / ([\text{OC}]_g + [\text{OC}]_p) \\ = (1 + 1/K_i C_p)^{-1}.$$

The SOA yield is expressed in terms of the mass of oxidation products and VOC reacted because the mass of SOA is the quantity measured, but also because the SOA composition is generally too complex to identify the moles of each product formed. Figure 10-14 shows the gas-particle partitioning distribution for a series of oxidation products of O_3 + α -pinene.

Within the last decade, strong evidence has emerged that certain organic aerosols can achieve the state of amorphous glasses in which diffusion of condensing molecules is highly restricted [see the extensive review of Shrivastava et al. (2017)]. In this case, uptake of the condensing species into the entire particle cannot be considered to occur rapidly, and the process of accommodation into the particle will depend on particle surface area, molecular accommodation coefficient of the condensing molecule, and diffusion coefficient of the species in the particle itself. As well, the formation of particle-phase products can be limited by reaction or diffusion in the particle itself, as rate coefficients for dimer formation are relatively low ($< 10 \text{ M}^{-1} \text{ s}^{-1}$) and large molecules tend to diffuse slowly (Pfrang et al. 2011; Abramson et al. 2013; Shiraiwa et al. 2013). Clear experimental evidence now exists that shows the

FIG. 10-14. Gas-particle partitioning of O_3 oxidation products of α -pinene. Total absorbing organic aerosol mass = $50 \mu\text{g m}^{-3}$ is assumed (1 torr = 0.001 315 79 atm).

differences in aerosol growth rates depending on the nature of the molecular uptake process (Shiraiwa et al. 2017; Zaveri et al. 2018). Most observations are in the relatively warm boundary layer, and the phase of particles in the much cooler free troposphere is unclear.

e. Atmospheric evolution of organic aerosols

Once formed, secondary organic aerosol “ages” in the atmosphere, owing to continued uptake of low-volatility vapors and subsequent particle-phase chemistry. Shiraiwa et al. (2014) showed that the evolution of secondary organic aerosol in the atmosphere can be represented in a so-called molecular corridor that encapsulates SOA formation and aging in terms of volatility, molar mass, O:C ratio, and phase state. Figure 10-15 shows an ensemble of molecular corridors with a total of 909 identified oxidation products from seven different SOA precursors. The corridors are constrained by two boundary lines corresponding to the volatility of n -alkanes $\text{C}_n\text{H}_{2n+2}$ and sugar alcohols $\text{C}_n\text{H}_{2n+2}\text{O}_n$. These lines encapsulate the regular dependence of volatility on the molar mass of organic compounds; the different slopes of 14 g mol^{-1} for $\text{C}_n\text{H}_{2n+2}$ and 30 g mol^{-1} for $\text{C}_n\text{H}_{2n+2}\text{O}_n$ reflect the stronger decrease of volatility with increasing molar mass for polar compounds. Early generation gas-phase oxidation products of alkanes, as well as dimers or

oligomers with low O:C ratio (LOC), tend to fall into a molecular corridor close to the $\text{C}_n\text{H}_{2n+2}$ line, which is designated as the LOC corridor (blue shaded area). Aqueous-phase reaction and autoxidation products with high O:C ratio (HOC), on the other hand, tend to fall into a corridor near the $\text{C}_n\text{H}_{2n+2}\text{O}_n$ line, which is designated as HOC corridor (red shaded area). The area in between is characterized by intermediate O:C ratios and accordingly designated as IOC corridor. Small precursor VOCs, such as glyoxal, methylglyoxal, and isoprene (C_2 – C_5), evolve through the HOC corridor, and terpenes, such as α -pinene and limonene (C_{10}), evolve through the IOC corridor. Long-chain alkanes, such as dodecane and cyclododecane (C_{12}), evolve through the LOC corridor.

Characteristic reaction pathways and relevant kinetic regimes are also shown in Fig. 10-15. SOA precursor VOCs with high volatility and low molar mass are located in the upper-left corner of the molecular corridor ensemble. As illustrated in the insert in Fig. 10-15, single-step functionalization usually leads to a small increase in molar mass, corresponding to one order of decrease in volatility, while dimerization and oligomerization tend to decrease volatility by several orders of magnitude (e.g., three to four orders of magnitude for long-chain alkane and terpene SOA). Fragmentation, on the other hand, can lead to a substantial decrease of

FIG. 10-15. Molecular corridors of SOA oxidation products. Volatility, as measured by species saturation concentration, as a function of molar mass (molecular weight). Volatility decreases as molecular weight increases. The slope of the line defining the corridor is steeper for molecules with higher O:C ratio and polarity because of stronger hydrogen bonding and larger enthalpy of evaporation. The C_i^* is related to C_i^o by $C_i^* = \gamma_i C_i^o$ [from Shiraiwa et al. (2014, Fig. D2), CC BY 3.0 (<https://creativecommons.org/licenses/by/3.0/>)].

molar mass and increase in volatility (Yee et al. 2012); simple gas-phase oxidation products are confined to the upper-left area in the 2D space. Particle-phase dimerization and oligomerization, leading to the formation of compounds with low volatility and high molar mass, lie in the lower-right area in the 2D space.

f. Chemical characterization of the spectrum of atmospheric organic carbon

SVOCs, defined as compounds with effective saturation mass concentrations C^* between 0.1 and $10 \mu\text{g m}^{-3}$, are major precursors to anthropogenic atmospheric SOA. Only recently, with the advent of new mass spectrometric techniques, has it become possible to separate and identify the vast number of individual organic species that make up SVOCs, what was

traditionally known as the *unresolved complex mixture* (UCM) (Lewis et al. 2000; Chan et al. 2013; Isaacman-VanWertz et al. 2017; Worton et al. 2017). The UCM had been presumed to comprise a large number of linear, branched, and/or cyclic alkanes. Formation of SOA from oxidation of the varied components of the UCM is known to depend strongly on the number of rings and alkyl branches in alkanes (Ziemann 2011; Yee et al. 2013).

Masses of linear, branched, and cyclic alkanes for carbon numbers between 20 and 25 at Los Angeles and Bakersfield, California, on 30 May 2010 and 23 June 2010, respectively, are shown in Fig. 10-16. Compounds in the C_{21} – C_{24} volatility range coexist in both the gas and particle phases. Despite their coexistence between the gas and aerosol phases, this class of hydrocarbons is sufficiently volatile that gas-phase reactions with OH

FIG. 10-16. Masses of linear, branched, and cyclic alkanes with carbon numbers between 20 and 25 measured in the atmospheres of (a),(b) Los Angeles and (c),(d) Bakersfield, CA, on 30 May 2010 and 23 Jun 2010, respectively. Branched acyclic alkanes are more abundant relative to linear alkanes in Bakersfield than Los Angeles. Branched isomers are reported only for acyclic alkanes. Branched isomers that contain x alkyl branches are denoted as B x isomers. B0 refers to the linear alkane, B1 refers to the alkane with one alkyl branch, etc. (from Chan et al. 2013, Fig. 3).

are still dominant at the ambient levels shown in Fig. 10-16. A major source of hydrocarbons in the Los Angeles basin atmosphere is motor vehicles (Gentner et al. 2017), whereas hydrocarbons in the more rural Bakersfield atmosphere reflect a broader range of sources. For example, the high concentration of odd-numbered alkanes (C₂₃ and C₂₅) in Bakersfield suggests the presence of plant wax as a major source.

Oxidation of semivolatile alkanes has been proposed as a major source of urban SOA formation. The tendency for alkanes to form SOA depends on both the carbon number of the alkane and its structure. For linear alkanes in the range of C₂₁–C₂₄, fragmentation is not expected to occur upon reaction with OH, whereas branched alkane isomers are more likely to fragment upon OH oxidation (Ziemann 2011). If the carbon chain remains intact as functional groups are added, the volatility of the molecule decreases, leading to an increased tendency to form SOA. Emission rates of branched alkanes from typical urban sources tend to be higher than those of linear alkanes, and, in addition, despite the tendency for increased fragmentation during oxidation, branched alkanes undergo oxidation by OH more rapidly. The structural dependence of SOA formation arises largely as a consequence of the fate of the alkoxy radicals (RO) formed in the reaction RO₂ + NO → NO₂ + RO (Atkinson 2007). As an alkoxy radical

becomes more branched, the rate at which it decomposes to carbonyls and alkyl radicals increases versus that of isomerization. The competing factors of molecular structure, rapidity of oxidation, and prevalence in emissions must be considered to explain alkane-derived SOA levels.

g. The global nonmethane reactive organic carbon budget

Reactive organic carbon (ROC) can be considered as the sum of atmospheric nonmethane volatile organic compounds (NMVOCs) and organic aerosol (OA) (Heald et al. 2008). Primary organic aerosol (POA) is emitted directly from sources, and SOA is formed when NMVOCs are oxidized to form low-volatility products that condense to form aerosol. Budgets of reactive organic carbon in the troposphere have traditionally been characterized by large uncertainties (Goldstein and Galbally 2007; Hallquist et al. 2009). A 2014 intercomparison of global tropospheric models reported median primary emissions of OA of 56 (range 34–144) Tg yr⁻¹ and of secondary OA also of 56 (range 16–121) Tg SOA yr⁻¹ (Tsigaridis et al. 2014).

Safieddine et al. (2017) used the global chemical transport model GEOS-Chem v9-02 to develop a ROC global budget. In the model, SOA formation is treated from biogenic (isoprene, monoterpenes, and sesquiterpenes) and aromatic

FIG. 10-17. Chemical speciation of global ROC in 2010 as predicted by the global atmospheric chemical transport model GEOS-Chem. (a) Annual mean global distribution of the ROC column concentrations. (b) Global annual mean ROC burden (Tg C) by chemical class. (c) Annual mean surface level total OH reactivity. (d) Annual mean surface OH reactivity by chemical class, calculated by multiplying the mean concentration of reactive species at the surface with their respective OH reaction rate constant. The plus sign indicates that the category includes the reaction products of the precursor (from Safieddine et al. 2017, Fig. 1).

(benzene, toluene, and xylene) compounds (Pye et al. 2010). Safieddine et al. (2017) estimate an overall uncertainty of 15% in the tropospheric burden of reactive organic carbon. Figure 10-17 shows the predicted chemical speciation of global reactive organic carbon in this budget. The leading contributors to ROC are the longer-lived alkanes, alkenes, and aromatics, ketones, and acids. OA is predicted to be 5% of the total burden. Figure 10-17 also shows the predicted total gas-phase OH reactivity (the inverse of OH lifetime) near Earth's surface, calculated as $\Sigma[X_i]k_{\text{OH}+X_i}$, where $[X_i]$ is the concentration of each of the species reacting with OH. High-emission regions, such as the tropics, East Asia, and the southeastern United States, exhibit the highest OH reactivities ($\sim 5\text{--}50 \text{ s}^{-1}$); OH reactivity values over the ocean are as low as 5 s^{-1} , and those in the free troposphere are $0.2\text{--}2 \text{ s}^{-1}$. Over central Africa and Amazonia, biogenic compounds dominate the total OH reactivity. Direct emissions of ROC and oxidation of CH_4 are estimated as 1350 TgC yr^{-1} , including direct ROC emissions = 935 TgC yr^{-1} , of which 29 TgC yr^{-1} is primary organic aerosol (OA). The annual mean flux from ROC to CO/CO_2 is estimated as 885 TgC yr^{-1} . The production of CO_2 by atmospheric chemistry is approximately an order of

magnitude less than the emissions associated with fossil fuel combustion (8750 TgC of CO_2 in 2016; International Energy Agency 2018).

The estimated global ROC balance of Safieddine et al. (2017) does not include sources of IVOCs that are precursors to SOA; available studies suggest that IVOCs could constitute a source of $\sim 50\text{--}200 \text{ Tg yr}^{-1}$ (Hodzic et al. 2016). The ROC balance also does not include sources of in-cloud SOA formation, estimates of which range from 20 to 30 Tg yr^{-1} (McNeill 2015). In summary, the estimated global annual mean ROC burden of 16 TgC is dominated by long-lived species, such as ketones, acids, alkanes, alkenes, and aromatic hydrocarbons. Future work will undoubtedly continue to refine and sharpen the total reactive organic carbon budget in the atmosphere.

8. Chemical theory and atmospheric chemistry

A hundred years ago, the concept of elementary chemical reactions and their connection with rate equations had been established, but useful quantitative theories of chemical reaction rates were nonexistent. This situation changed decisively with the development

of quantum physics and statistical mechanics in the mid-1920s (De Broglie 1925; Schrödinger 1926). Before that, the classical theory of nonreactive bimolecular collisions provided some guidance, but was not sufficient for making accurate interpretations. Part of the problem was that binary collision theory cannot, by itself, account for the approximately exponential dependence of reaction rates on temperature, which was quantified in 1889 by Svante Arrhenius (also known for his 1896 estimate of the magnitude of global warming due to CO₂, founding the discipline of Physical Chemistry, and winning the 1903 Nobel Prize for Chemistry). From developments in statistical mechanics, it was surmised that the reaction temperature dependence originated from the need for surmounting an energy barrier and the tendency of thermal systems to maintain a Boltzmann energy distribution, which contains an exponential factor (Kassel 1932; Tolman 1938).

The situation was somewhat improved in the late 1930s with formulation of the Transition State Theory (TST) of chemical reaction rates by Eugene Wigner (Wigner 1938), who later won the 1963 Nobel Prize in Physics for his fundamental theoretical work on nuclear reaction theory. Henry Eyring and coworkers are well known for further development of TST, which they energetically promoted as an “Absolute Rate Theory” that is capable of describing many phenomena (Glasstone et al. 1941). Although input data of high accuracy were not available in those days, TST could systematically describe various types of elementary reactions and enabled semiempirical estimates within a thermochemical framework, as was shown by Sydney Benson and his colleagues, starting in the mid-1950s (Benson 1976). In roughly the same period, Rudy Marcus (who later won the 1992 Nobel Prize in Chemistry for his work on electron transfer reactions) formulated a statistical dynamical theory (Marcus 1952a,b,c) now known as RRKM theory, where the initials acknowledge the contributions by Rice, Ramsperger, Kassel, and Marcus (Forst 2003). RRKM theory describes important atmospheric reactions, such as recombination and unimolecular dissociation, in which chemical reaction and collisional energy transfer are occurring simultaneously. More advanced theories utilize what are termed “master equations” (Forst 2003), which are currently regarded as the standard treatment for this category of reactions. Many of these methods are discussed in a recent review (Vereecken et al. 2015).

Computer codes are available for performing calculations using all of the theories mentioned in the preceding paragraph. Some of the free codes for master equation calculations include the following: ChemRate (Bedanov et al. 1995; Knyazev and Tsang 2000; Tsang

et al. 1996; <http://kinetics.nist.gov/ChemRate/>), VariFlex (Klippenstein et al. 1999), MultiWell (Barker 2001; Barker et al. 2017), Master Equation Solver for Multi-Energy Well Reactions (MESMER; Glowacki et al. 2012), and Multi-Species Multi-Channel (MSMC; Duong et al. 2015; <https://sites.google.com/site/msmccode/>). For simple reactions that do not require a master equation treatment, conventional TST rate constants that include quantum mechanical tunneling through a reaction barrier is often sufficient, and most of the codes listed in the preceding sentence offer that capability. Polyrate (Zheng et al. 2017), which is based on years of development by Don Truhlar and his colleagues at the University of Minnesota (Truhlar et al. 1985; Fernandez-Ramos et al. 2007), is the code that perhaps has been most fully tested for computing rate constants with conventional TST.

All of the kinetics theories mentioned in the preceding paragraph can be used for making useful predictions when accurate input data are available. In many cases, experimental data are available for reactants and products, but such data are not available for transition states, since they cannot be observed directly. Data for transition states are only available from empirical estimation and from theoretical calculations. In recent decades, quantum chemical computer codes have become available and computing power has increased to the point that parameters for reactants, products, and transition states can be computed with useful accuracy from near-first principles. These codes are extremely useful for gathering insights into chemical mechanisms, as well as for computing molecular properties (Vereecken et al. 2015). Most of the codes have been developed commercially, but a few are available as free software. Each code has strengths and weaknesses, and a comprehensive review is far beyond the scope of this chapter. (One recent list of quantum chemistry codes can be found here: https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software.)

Conventional TST is derived from classical mechanics and does not include quantum effects, such as vibrational zero point energies and quantum mechanical tunneling through potential barriers. Codes such as Polyrate apply sophisticated correction factors for these and other missing features to achieve high accuracy in computing rate constants (Zheng et al. 2017). In the 1970s, William H. Miller at Berkeley derived Semi-Classical TST (SCTST), in which the missing quantum effects are included intrinsically (Miller 1977; Miller et al. 1990), thus avoiding the need for correction factors. SCTST also allows for coupling among all of the internal degrees of freedom, a feature that is missing from the usual versions of conventional TST. Experience with SCTST is not yet very extensive, but in tests

carried out so far (Nguyen et al. 2017), it has proved to be highly accurate. When applied to atmospheric reactions (Nguyen et al. 2010, 2011, 2012; Weston et al. 2013), the predicted SCTST rate constants are as accurate as the best experimental data over very wide temperature ranges, when high accuracy quantum chemistry methods are used to supply the required input data.

For more than two decades, quantum chemistry and theoretical kinetics methods have been used to investigate atmospheric reaction systems. In the early days, quantum chemistry methods and computing power had not advanced sufficiently for making accurate predictions, but they were useful for elucidating reaction mechanisms and for providing some of the input data (e.g., vibrational and rotational constants) needed for chemical kinetics modeling [e.g., see Fermann et al. (1997), Sander et al. (1995), and Zhu and Lin (2001, 2002, 2003)]. Over time, capabilities have improved to the point where it is now becoming possible to make quantitative predictions of useful accuracy for reactions involving small chemical species (e.g., 5–10 atoms) and this capability is growing (Vereecken and Francisco 2012). Recent examples are presented in the extensive review by Vereecken et al. (Vereecken et al. 2015). Vereecken et al. also point out that theoretical methods beyond TST (e.g., classical trajectory, molecular dynamics, and quantum scattering calculations) are expected to play increasing roles in the future, although they have not yet contributed very much to understanding gas-phase atmospheric reactions. Considering the huge numbers of chemical species and chemical reactions involved, we anticipate that eventually most chemical data needed for motivating atmospheric chemistry models will be generated by computer calculations, and experimental studies will be limited to performing tests and validation.

9. Atmospheric chemistry and climate change

Atmospheric chemistry contributes to climate change, and a changing climate influences atmospheric chemistry. Climate change has already led to increased water vapor concentrations (see section 2a), affecting both tropospheric OH and O₃ concentrations. Because O₃ itself is a greenhouse gas, any chemically induced changes in O₃ will feed back to alter the climate (Isaksen et al. 2009; Prather and Holmes 2013). Given the importance of H₂O, CH₄, CO, NO, and O₃ to tropospheric OH abundance, if climate change affects the levels of these species, a change in climate would have the potential to alter global OH levels. Reactions between OH and CO and CH₄ cycle OH within the HO_x family (OH + HO₂) and affect the prevailing OH/HO₂ ratio.

The dominant nonlinear chemical feedback in the atmosphere involves CH₄. Increased CH₄, with its oxidation by OH, leads to additional CO formation. The CH₄ itself and the CO formed act to suppress OH, the major sink for CH₄. As a result, the lifetime for removal of additional CH₄ lengthens from about 8–10 years to about 12 years (Voulgarakis et al. 2013; Kirschke et al. 2013). A reduction of OH increases the lifetimes of other trace gases that are themselves removed by OH. CH₄ released from the surface becomes well mixed in the troposphere, a portion of which is transported to the stratosphere, where it becomes entwined in the stratospheric chemistry that controls O₃ abundance. CH₄ reacts with Cl atoms to produce HCl, a reservoir species that sequesters active chlorine, slowing down the ClO_x catalytic cycles, and thus increasing O₃. At the same time, oxidation of this CH₄ increases stratospheric H₂O vapor. In addition, changes to stratospheric H₂O and O₃ have radiative forcing impacts.

Cardelino and Chameides (1990) recognized the increased challenge that climate change poses to meeting ambient air quality goals for ozone in urban areas. In addition to impacts on meteorology, humidity, and biogenic VOC emissions, increased temperature affects the rates of key reactions associated with photochemical production of ozone. Increased temperature leads to an increase in the dissociation of peroxyacetyl nitrate, CH₃C(O)OONO₂ (PAN). PAN is an important reservoir for both radicals and NO_x in polluted air (Stephens 1969; Sillman et al. 1990). The rate of PAN thermal decomposition increases exponentially with temperature, and in a warmer climate, PAN decomposition will release more radicals and NO_x accelerating photochemical reactions in urban air masses. The rates of the reactions of OH with saturated VOCs that drive ozone formation generally increase with temperature, while the rate of the reaction of OH with NO₂ decreases with increasing temperature. The reaction of OH with NO₂ generates HNO₃, which is an important radical and NO_x sink, and slows down the sequence of reactions leading to ozone formation. The combined impacts of climate change on meteorology (increased frequency of periods of stagnant air), increased humidity [increased fraction of O(¹D) atoms that react with H₂O to give OH], increased biogenic VOC emissions, and increased photochemical activity will make achievement of ambient air quality standards more challenging (Steiner et al. 2006; Murazaki and Hess 2006; Jing et al. 2017).

Observations of surface ozone levels suggest that background ozone levels have increased appreciably over the last century at midlatitudes in the Northern Hemisphere, but there have been no appreciable changes elsewhere (Staehelin et al. 1994; Parrish et al.

2012; Galbally et al. 2017). Tropospheric ozone is a potent greenhouse gas; in terms of radiative forcing of climate change its contribution is the third most significant behind carbon dioxide and methane (IPCC 2013). Increased tropospheric ozone levels have contributed a radiative forcing of $0.3\text{--}0.5\text{ W m}^{-2}$ (Shindell et al. 2006; IPCC 2007; Søvde et al. 2011; Skeie et al. 2011) and 0.3°C of the approximately 0.5°C warming from 1890 to 1990 (Shindell et al. 2006). Decreased stratospheric ozone resulting from human activities, primarily emissions of chlorine- and bromine-containing compounds, has led to a small negative radiative forcing of approximately -0.05 W m^{-2} (IPCC 2007) since the Industrial Revolution.

It seems inevitable that climate change will have a major impact on human society over the next 100 years. Understanding the future role of atmospheric chemistry in climate change and, in turn, the impact of climate change on atmospheric chemistry will be critical to developing effective policies to protect our global environment.

10. Conclusions and the next 100 years

Progress in gas-phase atmospheric chemistry research over the past 100 years has made a major contribution to human welfare. The development of a scientific understanding of local air pollution and stratospheric ozone depletion has enabled the formulation of effective policies to protect human and ecosystem health. It is hard to overstate the benefits of the Montreal Protocol in preserving the ozone layer that shields us from solar UV radiation. While challenges remain, dramatic progress has been made in urban air quality in developed nations over the past 100 years.

One hundred years ago, other than the major gases, little was known about the minor constituents of Earth's atmosphere. The presence of particles in the air was recognized, but virtually nothing was known about their sources and composition. With the emergence and subsequent characterization of air pollution, the exquisite tapestry of the atmosphere's trace constituents began to be revealed, and major phenomena, such as urban smogs in London and Los Angeles, and stratospheric ozone depletion by chlorofluorocarbons, spurred the blossoming of a major research establishment in atmospheric chemistry. With the advent of ever more powerful instrumentation in the laboratory, in the field, and spaceborne, coupled with advances in chemical theory and mechanism development, we are well on our way to a comprehensive understanding of gas- and particle-phase atmospheric chemistry in both the troposphere and stratosphere.

The future of atmospheric chemistry research is being driven largely by the need to understand the

implications of climate change on the coupling of chemistry and climate and by effects of trace airborne species, especially particulate matter, on human health. New platforms for atmospheric composition measurements are emerging, such as widely distributed field instrumentation, remotely piloted drones, and pressurized balloons, as well as new laboratory instruments with heretofore unimagined accuracy and specificity. The next 100 years will no doubt provide striking advances in our chemical understanding of Earth's atmosphere.

There is much work to be done in this fascinating, and still relatively young, field of atmospheric chemistry. Many important discoveries are waiting to be uncovered.

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