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Evolution of the Earth's atmosphere

The composition of the Earth's atmosphere is unique within the solar system. The Earth is situated between Venus and Mars, both of which have atmospheres consisting primarily of CO₂ (an oxidized compound);^{1,a} the outer planets (Jupiter, Saturn, Uranus, Neptune) are dominated by reduced compounds, such as CH₄. By contrast, CO₂ and CH₄ are only minor (although very important) constituents of the Earth's atmosphere. Nitrogen represents ~78% of the molecules in air, and life-sustaining oxygen accounts for ~21%. The presence of so much oxygen is surprising, since it might appear to produce a combustible mixture with many of the other gases in air (e.g., sulfur to form sulfates, nitrogen to form nitrates, hydrogen to form water).

The Earth's atmosphere is certainly not in chemical equilibrium, since the concentrations of N₂, O₂, CH₄, N₂O, and NH₃ are much higher than they would be for perfect equilibrium. Why is this so? A clue is provided by Table 1.1, which lists the five most common elements in the Earth's atmosphere, biosphere, hydrosphere, crust, mantle, and core. Four of the most abundant elements in the atmosphere (nitrogen, oxygen, hydrogen, and carbon) are also among the top five most abundant elements in the biosphere. This suggests that biological processes have played a dominant role in the evolution of the Earth's atmosphere and that they are probably responsible for its present chemical nonequilibrium state. However, as we will see, this has occurred in relatively recent times. In this chapter we will speculate on the development of the Earth's atmosphere since it was first formed some 4.5 billion years ago (4.5 Ga), at which time it probably had no (or very little) atmosphere.

^a Numerical superscripts in the text (1, 2, ... etc.) refer to **Notes** at the end of the chapter.

Table 1.1. *The five most abundant elements (in terms of the number of atoms) in the major chemical reservoirs on Earth (the numbers in parentheses are the masses, in kg, of the reservoirs)^a*

| Atmosphere (5.2×10^{18}) | Biosphere ^b (4.2×10^{15}) | Hydrosphere ^c (2.4×10^{21}) | Crust (2.4×10^{22}) | Mantle (4.0×10^{24}) | Core ^d (1.9×10^{24}) |
|--|--|--|-----------------------------------|------------------------------------|---|
| N | H | H | O | O | Fe |
| O | O | O | Si | Si | Ni |
| H | C | Cl | Al | Mg | C |
| Ar | N | Na | Fe | Fe | S |
| C | Ca | Mg | Mg/Ca | Al | Si |

^a Adapted from P. Brimblecombe, *Air Composition and Chemistry*, Cambridge University Press, Cambridge, 1996, p. 4.

^b Includes plants, animals, and organic matter but not coal or sedimentary carbon.

^c Water in solid and liquid form on or above the Earth's surface.

^d Composition of Earth's core is uncertain.

1.1 The primitive atmosphere

In comparison to the Sun (or the cosmos) the atmosphere of the Earth is deficient in the light volatile elements (e.g., H) and the noble or inert gases (e.g., He, Ne, Ar, Kr, Xe). This suggests that either these elements escaped as the Earth was forming or the Earth formed in such a way as to systematically exclude these gases (e.g., by the agglomeration of solid materials similar to that in meteorites²). In either case, the Earth's atmosphere was probably generated by the degassing of volatile compounds contained within the original solid materials that formed the Earth (a so-called *secondary atmosphere*).

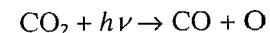
Earlier models of the evolution of the Earth hypothesized that it formed relatively slowly with an initially cold interior that was subsequently heated by radioactive decay. This would have allowed gases to be released by volcanic activity. Until the Earth's core formed, these gases would have been highly reducing (e.g., H₂, CH₄, NH₃), but after the formation of the core they would have been similar to the effluents from current volcanic activity (i.e., H₂O, CO₂, N₂, and small quantities of H₂, CO, and sulfur compounds). More recent models suggest that the Earth's interior was initially hot due to tremendous bombardment (a major impact during this period formed the Moon). In this case, the Earth's core would have formed earlier and

volcanic gases emitted 4.5 Ga ago could have been similar to present emissions (i.e., more oxidized). Also, many of the volatile materials could have been released by the impacts themselves, resulting in an atmosphere of steam during the period that the Earth was accreting material.

When the accretionary phase ended and the Earth cooled, the steam could have condensed and rained out to produce the oceans. The atmosphere that was left would likely have been dominated by CO₂, CO, and N₂.³ The partial pressure of CO₂ and CO in the primitive atmosphere could have been ~10 bar,⁴ together with ~1 bar from nitrogen. The Earth continued to be bombarded, even after the main accretionary period, until at least 3.8 Ga ago. If these impacts were cometary in nature, they could have provided CO (by oxidation of organic carbon or by reduction of atmospheric CO₂ by iron-rich impactors) and NO (by shock heating of atmospheric CO₂ and N₂).

1.2 Prebiotic atmosphere and the origins of life

Life on Earth is unlikely to have started (or at least to have survived) during the period of heavy bombardment. However, the fossil record shows that primitive forms of living cells were present no later than 3.5 Ga ago. Laboratory experiments demonstrate that many biologically important organic compounds, including amino acids that are basic to life, can form when a mixture of CH₄, NH₃, H₂, and H₂O is irradiated with ultraviolet (UV) light or sparked by an electric discharge (simulating lightning). However, CH₄ and NH₃ may not have been present 3.5 Ga ago unless the oxidation state of the upper mantle, which affects the chemical composition of volcanic effluents, differed from its present composition. Even if CH₄ and NH₃ were released from volcanoes, they would have been only minor atmospheric constituents because they are quickly photolysed. Thus, the early atmosphere was probably dominated by N₂ and CO₂ (with a concentration perhaps 600 times greater than at present), with trace amounts of H₂, CO, H₂O, O₂, and reduced sulfur gases (i.e., a "weakly reducing" atmosphere). Due to the photodissociation of CO₂



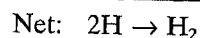
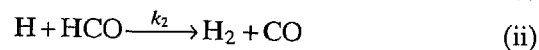
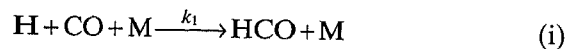
where $h\nu$ represents a photon of frequency ν , followed by



where M represents an inert molecule that can remove some of the energy of the reaction, molecular oxygen would have increased sharply with altitude above ~20 km because of the increased intensity of solar radiation. The concentrations of O₂ at the surface would have been very low (<10⁻¹² present atmospheric levels, PAL) due, in part, to reactions with H₂.

Two key compounds for the formation of life are probably formaldehyde (HCHO) and hydrogen cyanide (HCN), which are needed for the synthesis of sugars and amino acids, respectively. Formaldehyde could have formed by photochemical reactions involving N₂, H₂O, CO₂, H₂, and CO (removal of HCHO from the atmosphere by precipitation would have provided a source of organic carbon for the oceans). Formation of HCN, from N₂ and CO₂, for example, is much more difficult because it requires breaking the strong triple bonds of N₂ and CO. This can occur in lightning discharges, but the N and C atoms are more likely to combine with atomic oxygen than with each other unless [C]/[O] > 1. It is because of this difficulty that theories have been invoked involving the introduction of biological precursor molecules by comets and the origins of life in oceanic hydrothermal vents.

Exercise 1.1. A catalytic cycle that might have contributed to the formation of H₂ from H in the early atmosphere of the Earth is



If this cycle were in steady state, and if the concentrations of CO and M were 1.0 × 10¹² and 2.5 × 10¹⁹ molecule cm⁻³, respectively, and the magnitudes of the rate coefficients *k*₁ and *k*₂ are 1.0 × 10⁻³⁴ cm⁶ s⁻¹ molecule⁻² and 3.0 × 10⁻¹⁰ cm³ s⁻¹ molecule⁻¹, respectively, what would have been the concentration of the radical HCO?

Solution. The rate of formation of HCO by Reaction (i) is *k*₁[H][CO][M], where the square brackets indicate concentrations in molecules per cm³. The rate of destruction of HCO by Reaction (ii) is *k*₂[H][HCO]. At steady state, the rate of formation of HCO must equal its rate of destruction. Therefore,

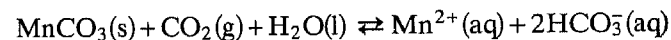
$$k_1 [\text{H}][\text{CO}][\text{M}] = k_2 [\text{H}][\text{HCO}]$$

or

$$\begin{aligned} [\text{HCO}] &= \frac{k_1}{k_2} [\text{CO}][\text{M}] \\ &= \frac{1.0 \times 10^{-34}}{3.0 \times 10^{-10}} (1.0 \times 10^{12}) (2.5 \times 10^{19}) \\ &\approx 8.3 \times 10^6 \text{ molecule cm}^{-3} \end{aligned}$$

Well-founded astrophysical theory leads us to believe that the temperature of the Sun has increased since its birth to the present time. Thus, 4.6 Ga ago the Sun was probably 25% to 30% weaker than it is now (the so-called faint young Sun). If the early atmosphere had a chemical composition similar to the present, its equilibrium surface temperature with respect to the faint young Sun would have been below 0°C until about 2 Ga ago. However, the formation of sedimentary rocks ~3.8 Ga ago, and the development of life which started more than 3.5 Ga ago, indicate that liquid water was present at these early times. Since CO₂ is a “greenhouse” gas (i.e., it reduces the loss of longwave radiation to space from the Earth's surface), its presence in high concentrations in the Earth's early atmosphere could have maintained the temperature of the Earth above freezing some ~3.5 to 3.8 Ga ago even with a faint young Sun.

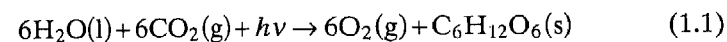
Cooling of the Earth might have triggered a negative feedback involving CO₂ and the chemical weathering of rocks. For example, in addition to the CaCO₃ reservoir, dissolved CO₂ reacts with rhodochrosite (MnCO₃(s)),⁵



But with decreasing temperature, this and other similar sinks for CO₂ decrease, thereby allowing atmospheric CO₂ concentrations to increase.

1.3 Rise of oxygen and ozone

The advent of biological activity on Earth led the way to rapid increases in atmospheric molecular oxygen through photosynthesis. In photosynthesis by green plants, light energy is used to convert H₂O and CO₂ into O₂ and energy-rich organic compounds called carbohydrates (e.g., glucose, C₆H₁₂O₆), which are stored in the plants



Exercise 1.2. What change in the oxidation number of the carbon atom is produced by Reaction (1.1)?

Solution. Since the oxidation number of each oxygen atom in CO_2 is -2 , the oxidation number of the C atom is $+4$. In $\text{C}_6\text{H}_{12}\text{O}_6$ the oxidation numbers of the H and O are $+1$ and -2 , respectively. Therefore, the oxidation number of the C atom in $\text{C}_6\text{H}_{12}\text{O}_6$ is 0 . Hence, Reaction (1.1) decreases the oxidation number of the C atom from $+4$ to zero; that is, the carbon is reduced. (Note that the reverse of Reaction (1.1) will oxidize the C atom, since its oxidation number will rise from zero to $+4$.)

The geologic record shows that atmospheric O_2 first reached appreciable concentrations ~ 2 Ga ago. The combined atmosphere-ocean system appears to have gone through three main stages. In the first stage, almost the entire system was a reducing environment. In the next stage the atmosphere and the surface of the ocean presented an oxidizing environment, although the deep ocean was still reducing. In the third (and current) stage, the entire system is oxidizing with abundant free molecular oxygen (O_2).

The earliest life forms probably developed in aqueous environments, far enough below the surface to be protected from the Sun's lethal UV radiation but close enough to the surface to have access to visible solar radiation needed for photosynthesis. There is also speculation that life might have originated in hydrothermal systems in the deep ocean, where bacteria do not rely on photosynthesis.

By means of processes to be discussed in Section 10.1, the buildup of oxygen in the atmosphere led to the formation of the ozone layer in the upper atmosphere, which filters out UV radiation from the Sun. With the development of the ozone layer, less and less UV radiation reached the Earth's surface. In this increasingly favorable environment, plant life was able to spread to the uppermost layers of the ocean, thereby gaining access to increasing amounts of visible radiation, an essential ingredient in the photosynthesis Reaction (1.1). More oxygen – less UV radiation – more access to visible radiation – more abundant plant life – still more oxygen production: through this bootstrap process, life may have slowly but inexorably worked its way upward toward the surface until it finally emerged onto land some 400 million years ago.

1.4 Oxygen and carbon budgets

For every molecule of oxygen produced in Reaction (1.1), one atom of carbon is incorporated into an organic compound. Most of these carbon

Table 1.2. Estimate of inventory of carbon near the Earth's surface (units are gigatons (10^{15} g) of carbon)

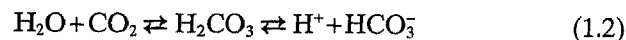
| | |
|-------------------------------------|------------|
| Biosphere: | |
| Marine | 2–5 |
| Terrestrial (land, plants) | 600 |
| Atmosphere (as CO_2) | 750 |
| Ocean (as dissolved CO_2) | 38,000 |
| Fossil fuels | 8,000 |
| Shales | 8,000,000 |
| Carbonate rocks | 65,000,000 |

atoms are oxidized in respiration or in the decay of organic matter, which is the reverse of Reaction (1.1). However, for every few tens of thousands of molecular carbons formed by photosynthesis, one escapes oxidation by being buried or “fossilized.” Most of the Earth's unoxidized carbon is contained in shales, and smaller amounts are stored in more concentrated forms in fossil fuels (coal, oil, and natural gas). The relatively “short-term” storage of organic carbon in the biosphere represents a minute fraction of the total storage. More quantitative information on the relative amounts of carbon stored in various forms is given in Table 1.2.

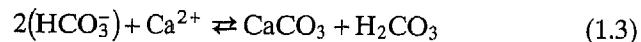
The burning of fossil fuels undoes the work of photosynthesis by oxidizing that which was reduced. At the present rate of fuel consumption, humans burn in one year what it took photosynthesis $\sim 1,000$ years to produce! This rate of consumption seems less alarming when one bears in mind that photosynthesis has been at work for hundreds of millions of years. One can take further comfort from the fact that the bulk of the organic carbon in the Earth's crust is stored in a form that is far too dilute for humans to exploit.

Of the net amount of oxygen that has been produced by plant life during the Earth's history (i.e., production by photosynthesis minus consumption by respiration and the decay of organic matter), only about 10% is presently stored in the atmosphere. Most of the oxygen has found its way into oxides (such as Fe_2O_3) and biogenically precipitated carbonate compounds (CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$) in the Earth's crust. The biological formation of carbonate compounds is of particular interest since it is the major sink for the vast amounts of CO_2 that have been released in volcanic activity.

Carbonates are formed by means of ion exchange reactions that take place within certain marine organisms, the most important being the one-celled foraminifera. The dissolved CO_2 forms a weak solution of carbonic acid (H_2CO_3)

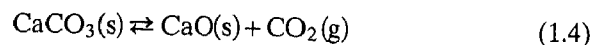


It has been suggested that a sequence of reactions then follows, the net result of which is



The CaCO_3 enters into the shells of animals, which fall to the sea floor and are eventually compressed into limestone in the Earth's crust. The hydrogen ions released in Reaction (1.2) react with metallic oxides in the Earth's crust, from which they steal an oxygen atom to form another water molecule. The stolen oxygen atom is eventually replaced by one from the atmosphere. Thus, oxygen is removed from the atmosphere during the formation of carbonates, and it is given back to the atmosphere when carbonates dissolve. It has been proposed that foraminifera and other carbonate-producing sea species, by virtue of their role as mediators in the process of carbonate formation, regulate the amount of oxygen present in the atmosphere, which has been remarkably constant over the past few million years.

The widespread occurrence of marine limestone deposits suggests that ion exchange reactions in sea water have played an important role in the removal of CO_2 from the Earth's atmosphere. Therefore, the dominance of CO_2 in the present Martian atmosphere may be due, in part at least, to the absence of liquid water on the surface. In contrast to the situation on Mars, the massive CO_2 atmosphere of Venus may be a consequence of the high surface temperatures on that planet. At such temperatures there should exist an approximate state of equilibrium between the amount of CO_2 in the atmosphere and the carbonate deposits in rocks on the surface, as expressed by the reaction



The concentration of CO_2 in the Earth's atmosphere has been rising steadily since the early part of this century (Fig. 1.1), which suggests that the rate of removal of CO_2 from the Earth's atmosphere is not large enough to keep pace with the ever-increasing rate of input due to the burning of fossil fuels. However, the present rate of increase in atmo-

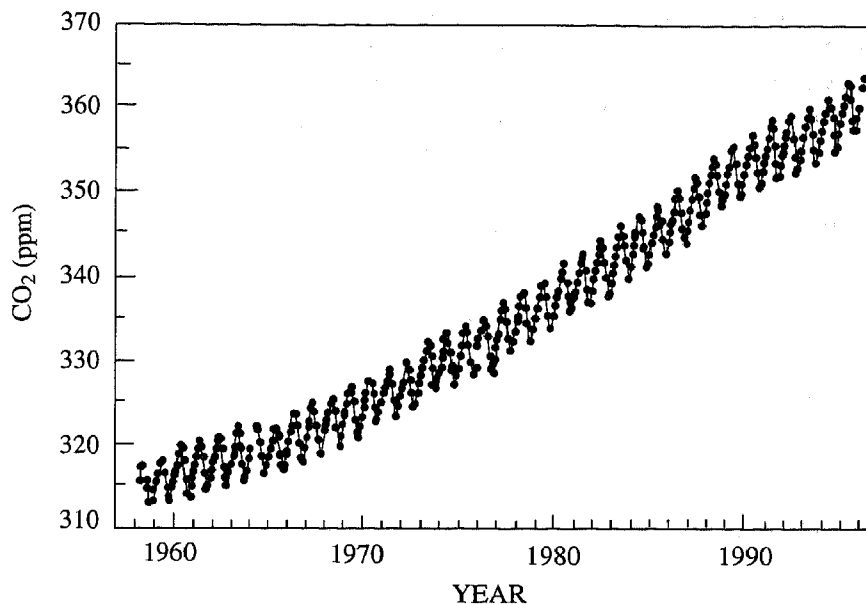


Figure 1.1. Concentration of atmospheric CO_2 at Mauna Loa Observatory, Hawaii, for the period 1958–1996. Data prior to May 1974 are from the Scripps Institute of Oceanography, and data since May 1974 are from the National Oceanic and Atmospheric Administration.

spheric CO_2 is only about half the rate at which CO_2 is being added to the atmosphere by the burning of fossil fuels. This implies that about half of the CO_2 added by fossil fuel burning is going into the oceans, forests, or other sinks.

1.5 Some other atmospheric constituents

By means of ion exchange reactions analogous to Reaction (1.3) and fixation by soil microorganisms, a small fraction of the nitrogen released into the atmosphere has entered into nitrates in the Earth's crust. However, because of the chemical inertness of nitrogen and its low solubility in water (1/70th that of CO_2), most of the nitrogen released by volcanoes has remained in the atmosphere. Because of the nearly complete removal from the Earth's atmosphere of water vapor (to form liquid water in the oceans and hydrated crystalline rocks) and CO_2 by the processes described earlier, nitrogen has become the dominant gaseous constituent of the Earth's atmosphere.

Sulfur and its compounds H_2S and SO_2 , which are released into the Earth's atmosphere by volcanic emissions, are quickly oxidized to SO_3 , which dissolves in cloud droplets to form a dilute solution of H_2SO_4 . After being scavenged from the atmosphere by precipitation particles, the sulfate ions combine with metal ions to form sulfates within the Earth's crust. Sulfur dioxide may also react with NH_3 in the presence of liquid water and an oxidant to produce ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$.

1.6 The Gaia hypothesis

As we have seen in Section 1.3, the biosphere is responsible for the buildup and maintenance of oxygen in the Earth's atmosphere and for the present nonequilibrium state of the atmosphere. In the *Gaia* ("mother Earth") hypothesis, the influence of the biosphere on the atmosphere is seen as "purposeful." The biosphere and atmosphere are viewed as an ecosystem, in which the chemical composition and climate of the Earth are maintained in optimum states (for the biosphere) by the metabolism and evolutionary development of the biota. This might be achieved through a rich web of positive and negative feedbacks. For example, we saw in Section 1.4 that carbonate-producing sea species might regulate the amount of oxygen in the atmosphere.

Like many stimulating viewpoints, the Gaia hypothesis is controversial. The Darwinian theory, whereby biota adapt to the environment imposed on them, is the more commonly held view, although, as discussed earlier, the atmosphere has been completely reformulated by biological activity.

1.7 Summary

The Earth's primitive atmosphere was probably formed by the accretion of extraterrestrial volatile materials and by outgassing of the Earth's interior. As accretion diminished and the Earth evolved, the steamy atmosphere condensed to form oceans, leaving an atmosphere dominated by CO_2 (~1 to 10 bar), CO and N_2 (~1 bar). Despite a faint young Sun, the initially high concentration of CO_2 maintained surface temperatures on Earth above 0°C by means of the greenhouse effect (see Section 4.7). The weakly reducing primitive atmosphere was favorable for the emergence of biota. Photosynthesis then increased oxygen concentrations, which, in turn, allowed ozone formation in the upper atmosphere by photochemical reactions. The shielding of the Earth's surface

from dangerous solar UV radiation by ozone in the upper atmosphere permitted life to evolve onto land. At the same time, the concentrations of CO_2 (and other greenhouse gases) declined, thereby compensating for an increasingly bright Sun. The relatively stable climate of the Earth over the past 3.5 Ga, during which time the mean surface temperature has remained in the range of -5 to 50°C , is probably due to the negative feedback between surface temperature, atmospheric CO_2 , and the weathering rates of rocks.

The likely general trends of O_2 , O_3 , and CO_2 since the Earth's atmosphere first formed are shown in Figure 1.2.

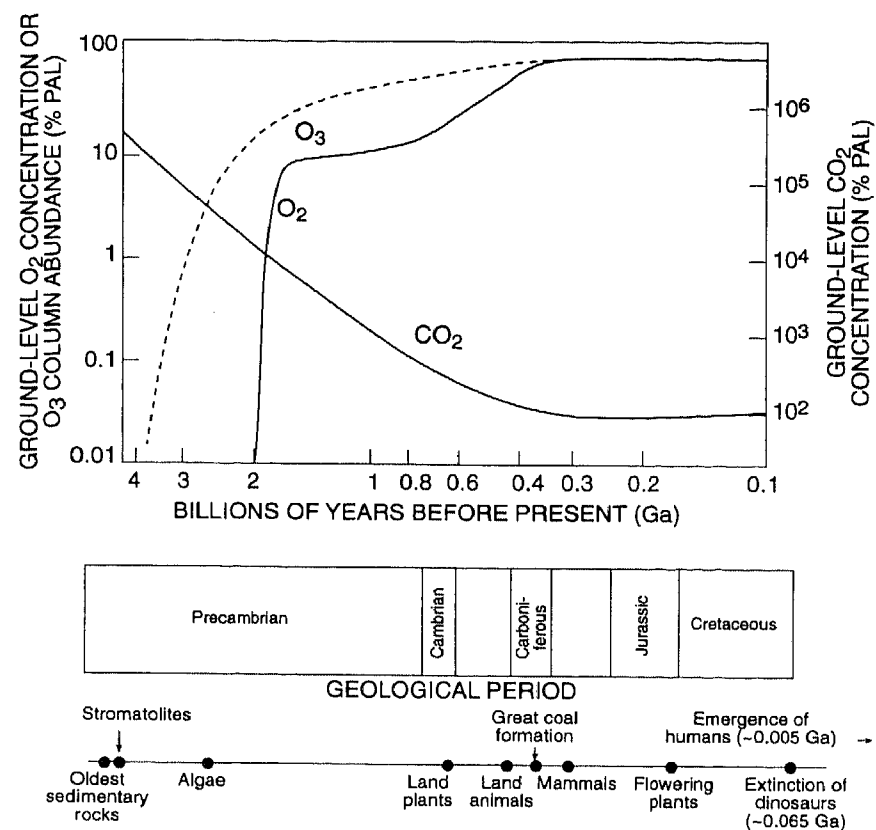


Figure 1.2. Schematic diagram showing predictions of the evolution of oxygen, ozone and carbon dioxide to present atmospheric levels (PAL). [After R. P. Wayne, *Chemistry of Atmospheres*, Oxford University Press, p. 404 (1991) by permission of Oxford University Press; and, J. F. Kasting, personal communication (1999).]

Exercises

See Exercises 1(a)–(f), and Exercises 2–5 in Appendix I.

Notes

- 1 A list of chemical symbols is given in Appendix III.
- 2 Such material probably included small amounts of volatile substances (i.e., materials capable of existing in gaseous form within the range of temperatures found on the surface of the Earth). For example, water could have been present as ice or in chemical combination with other solid substances.
- 3 Carbon-containing compounds are second only to water as the most abundant volatiles on the Earth's surface. However, most carbon on Earth is "tied up" in carbonate rocks. The amount of carbon in the Earth's crust is $\sim 10^{20}$ kg; if all of this were present in the atmosphere as CO_2 , the pressure at the Earth's surface would be 60 to 80 times greater than present atmospheric levels (as it is in the atmosphere of Venus).
- 4 $1 \text{ bar} = 10^5 \text{ Pa}$. $1 \text{ mb} = 10^2 \text{ Pa} = 1 \text{ hPa}$. The pressure at the Earth's surface at the present time (1 atmosphere) is $\sim 1.013 \text{ bar}$, or $1,013 \text{ hPa}$.
- 5 When we wish to emphasize the phase of a chemical species, we will use parenthetical insertions: *g* for gas, *l* for liquid, *s* for solid, and *aq* for aqueous.

2

Half-life, residence time, and renewal time of chemicals in the atmosphere

In atmospheric chemistry it is important to have some idea and some measure of the characteristic times that various chemicals spend in the atmosphere. In this chapter we discuss several ways of doing this. We also discuss a connection between the residence time of a chemical in the atmosphere and its spatial variability.

2.1 Half-life

Let us start by considering a chemical A, which is depleted at a rate that is proportional to its concentration $[A]$ at time t ; that is,

$$-\frac{d[A]}{dt} = k[A] \quad (2.1)$$

where k is a constant. Then,

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

where $[A]_0$ and $[A]_t$ are the initial concentrations of A and the concentration of A at time t , respectively. Hence,

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

or, converting to base-10 logarithms (indicated by "log"),

$$\log[A]_t = -\frac{kt}{2.303} + \log[A]_0 \quad (2.2)$$

The *half-life* ($t_{1/2}$) of a chemical in the atmosphere is defined as the time required for its concentration decrease to half of its initial value.