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978-0-521-77800-8 - Introduction to Atmospheric Chemistry: A Companion Text to Basic Physical Chemistry for the Atmospheric Sciences

Peter V. Hobbs

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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 CO_2 (an oxidized compound);^{1,a} the outer planets (Jupiter, Saturn, Uranus, Neptune) are dominated by reduced compounds, such as CH_4 . By contrast, CO_2 and CH_4 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 N_2 , O_2 , CH_4 , N_2O , and NH_3 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.

^dComposition of Earth's core is uncertain.

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[More information](#)*Prebiotic atmosphere and the origins of life*

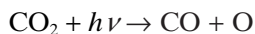
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volcanic gases emitted 4.5 Ga ago could have been similar to present emissions (i.e., more oxidized). Also, many of the volatile materials could have been released by the impacts themselves, resulting in an atmosphere of steam during the period that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



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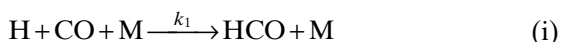
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where M represents an inert molecule that can remove some of the energy of the reaction, molecular oxygen would have increased sharply with altitude above ~20 km because of the increased intensity of solar radiation. The concentrations of O₂ at the 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 1.0×10^{12} and 2.5×10^{19} 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 $k_1[\text{H}][\text{CO}][\text{M}]$, where the square brackets indicate concentrations in molecules per cm³. The rate of destruction of HCO by Reaction (ii) is $k_2[\text{H}][\text{HCO}]$. At steady state, the rate of formation of HCO must equal its rate of destruction. Therefore,

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

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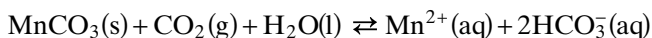
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or

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

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.

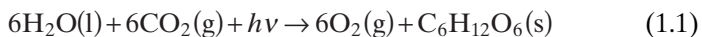
Cooling of the Earth might have triggered a negative feedback involving CO₂ and the chemical weathering of rocks. For example, in addition to the CaCO₃ reservoir, dissolved CO₂ reacts with rhodochrosite (MnCO₃(s)),⁵



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



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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 ~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 Fe₂O₃) and biogenically precipitated carbonate compounds (CaCO₃ and CaMg(CO₃)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 CO₂ that have been released in volcanic activity.

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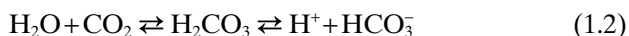
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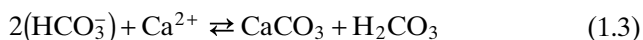
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Carbonates are formed by means of ion exchange reactions that take place within certain marine organisms, the most important being the one-celled foraminifera. The dissolved CO_2 forms a weak solution of carbonic acid (H_2CO_3)

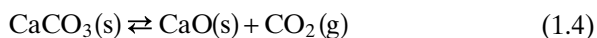


It has been suggested that a sequence of reactions then follows, the net result of which is



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-

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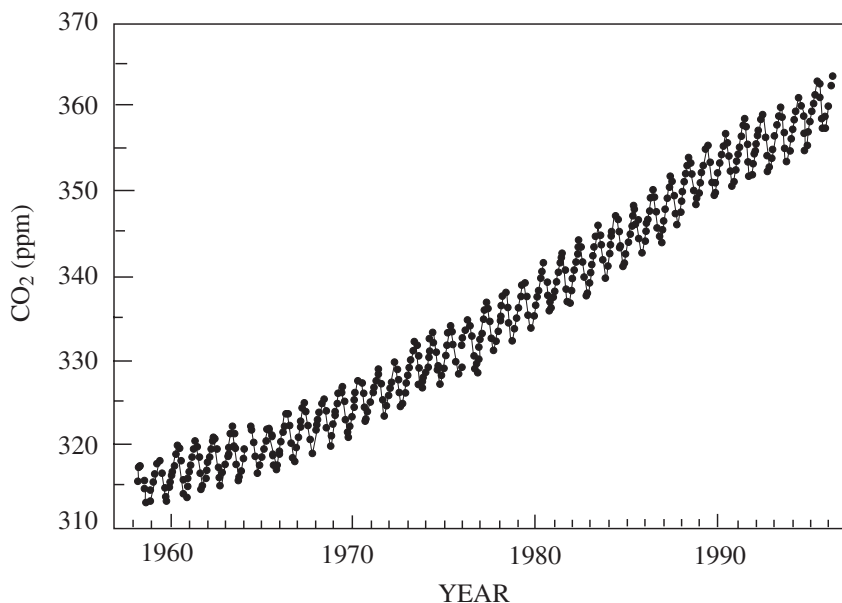


Figure 1.1. Concentration of atmospheric CO₂ at Mauna Loa Observatory, Hawaii, for the period 1958–1996. Data prior to May 1974 are from the Scripps Institution of Oceanography, and data since May 1974 are from the National Oceanic and Atmospheric Administration.

spheric CO₂ is only about half the rate at which CO₂ is being added to the atmosphere by the burning of fossil fuels. This implies that about half of the CO₂ 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 CO₂), 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 CO₂ by the processes described earlier, nitrogen has become the dominant gaseous constituent of the Earth's atmosphere.

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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