

## 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  $\text{CO}_2$ , 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 bar =  $10^5$  Pa. 1 mb =  $10^2$  Pa = 1 hPa. The pressure at the Earth's surface at the present time (1 atmosphere) is  $\sim 1.013$  bar, or 1,013 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.

We can derive an expression for  $t_{1/2}$  for the case considered earlier by substituting  $[A]_t = [A]_0/2$  and  $t = t_{1/2}$  into Eq. (2.2), which yields

$$t_{1/2} = \frac{2.303 \log 2}{k}$$

Therefore,

$$t_{1/2} = \frac{0.693}{k} \quad (2.3)$$

Note that, in this case,  $t_{1/2}$  is independent of the initial concentration of A.

A first-order chemical reaction in one reactant A is described by Eq. (2.1), where  $k$  is called the *rate coefficient* for the reaction. Because the decay rate per unit mass of a radioactive material (e.g., as measured by the number of clicks per minute of a Geiger counter) is proportional to the number of radioactive atoms present in the remaining sample, its decay is also represented by Eq. (2.1). Radiocarbon dating of organic materials is based on this principle. Carbon-12 (i.e., carbon with a mass number (the number of protons plus the number of neutrons) of 12) is the stable isotope of carbon. Carbon-14 is unstable (i.e., radioactive) with a half-life of 5,700 a. Because carbon-14 is produced by cosmic ray bombardments in the upper atmosphere, the ratio of carbon-14 to carbon-12 in the atmosphere is nearly constant (and is believed to have been so for at least 50,000 a). Carbon-14 is incorporated into atmospheric  $\text{CO}_2$ , which is in turn incorporated, through photosynthesis, into plants. When animals eat plants, the carbon-14 is incorporated into their tissues. While a plant or animal is alive it has a constant intake of carbon compounds, and it maintains a ratio of carbon-14 to carbon-12 that is identical to that of the air. When a plant or animal dies, it no longer ingests carbon compounds, and the ratio of carbon-14 to carbon-12 decreases with time, due to the radioactive decay of carbon-14. Hence, the period that elapsed since a plant or animal or organic material was alive can be deduced by comparing the ratio of carbon-14 to carbon-12 in the material with the corresponding ratio for air.

*Exercise 2.1.* A wooden carving, found on an archaeological site, is subjected to radiocarbon dating. The carbon-14 activity is 12.0 counts per minute per gram of carbon, compared to 15.0 counts per minute per gram of carbon for a living tree. What is the maximum age of the carving?

*Solution.* Since the half-life ( $t_{1/2}$ ) of carbon-14 is 5,700 a, we can substitute this value into Eq. (2.3) to obtain a value for  $k$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5,700} = 1.22 \times 10^{-4} \text{ a}^{-1} = 2.32 \times 10^{-10} \text{ min}^{-1}$$

The amount of radioactive carbon-14 (as measured, say, by a Geiger counter) per gram of carbon in the carving at the time the tree from which it was made died (say, at  $t = 0$ ) is given by Eq. (2.1) as

$$\begin{aligned} [A]_0 &= \frac{(\text{decay rate at } t = 0)}{k} \\ &= \frac{15.0}{2.33 \times 10^{-10}} = 6.44 \times 10^{10} \text{ counts per gram of carbon} \end{aligned}$$

Similarly, at the present time (say,  $t$  years after the tree died), the amount of carbon-14 per gram of carbon in the carving is given by

$$[A]_t = \frac{12.0}{2.33 \times 10^{-10}} = 5.15 \times 10^{10} \text{ counts per gram of carbon}$$

Substituting these values of  $[A]_0$ ,  $[A]_t$ , and  $k$  (in units of  $\text{a}^{-1}$ ) into Eq. (2.2) yields

$$\log(5.15 \times 10^{10}) = \frac{-(1.22 \times 10^{-4})t}{2.303} + \log(6.44 \times 10^{10})$$

or

$$10.71 = -5.3 \times 10^{-5}t + 10.81$$

Therefore,

$$t = 1.89 \times 10^3 \text{ a}$$

Because the carving could not have been made before the tree died, the maximum age of the carving is 1,890 years.

## 2.2 Residence time and renewal time

Chemicals are injected continually into the atmosphere from natural and anthropogenic sources, and they are also produced by chemical reactions in the air. Yet the overall chemical composition of the atmosphere does not change greatly over relatively short periods of time (although, as we shall see, there are important exceptions). This is because there are sinks that remove trace chemicals from the atmosphere at about the same rate as the chemicals are injected into (and/or produced within)

the atmosphere, so that most chemicals in air exist in roughly steady-state conditions.

An important parameter related to a chemical under steady-state conditions is its *residence time*, or *lifetime*, ( $\tau$ ) in the atmosphere, which is defined as

$$\tau = \frac{M}{F} \quad (2.4)$$

where  $M$  is the amount of the chemical in the atmosphere and  $F$  the *efflux* (i.e., rate of removal plus rate of destruction) of the chemical from the atmosphere. If  $M$  and  $F$  change with time

$$\tau_t = \frac{M_t}{F_t} \quad (2.5)$$

where the subscript  $t$  indicates the value at time  $t$ . We can define, in an analogous way, the residence time in terms of the *influx* (i.e., rate of input plus rate of production) of a chemical to the atmosphere.

A useful analogy here is a tank of water, which can represent the atmosphere. Suppose the tank is full of water and is overflowing at its top due to water being pumped into the bottom of the tank at a rate  $F$ . Then the rate of removal of water from the tank is  $F$ . If we assume that the water entering the bottom of the tank steadily displaces the water above it by pushing it upwards without any mixing, the time spent by each small element of water that enters the bottom of the tank before it overflows at the top is  $M/F$ , where  $M$  is the volume of the tank (this is the reason for defining residence time as  $M/F$  in Eq. (2.4)). In this case, when no mixing occurs in the reservoir, the residence time of the water is the same as the *renewal time* ( $T$ ), which is defined as the *time required to completely displace the original water from the tank*. That is,

$$\tau = T \quad (\text{for no mixing}) \quad (2.6)$$

Consider now a more realistic situation in which mixing takes place between the material that is injected into the atmosphere and the material already residing in it. For simplicity, we still consider the mixing to be complete and thorough (i.e., *perfect mixing*). The tank analogy is again helpful. Suppose that at time zero the tank is full of dirty water, and at this time clean water starts to be pumped into the bottom of the tank. Since the mixing is perfect, the rate of removal of dirty water from the top of the tank will be proportional to the fraction of the water in the

tank that is dirty. Therefore, if  $W$  is the amount of dirty water in the tank at time  $t$ ,

$$-\frac{dW}{dt} = kW \quad (2.7)$$

where  $k$  is a constant of proportionality. Since Eqs. (2.7) and (2.1) have the same form, the half-life of the dirty water is given by Eq. (2.3). Also, from Eqs. (2.4) and (2.7) we have for the dirty water

$$\tau = \frac{M}{F} = \frac{W}{(-dW/dt)} = \frac{1}{k} \quad (2.8)$$

Combining Eqs. (2.3) and (2.8), we obtain the following relationship between the half-life ( $t_{1/2}$ ) and the residence time ( $\tau$ )

$$t_{1/2} = 0.693 \tau \quad (\text{for perfect mixing}) \quad (2.9)$$

In the case of perfect mixing, the renewal time ( $T$ ) is strictly infinitely long because some molecules of dirty water will always be present in the tank. However, we can obtain an idea of the "effective" value of  $T$  for perfect mixing as follows. From the definition of the half-life ( $t_{1/2}$ ), we know that after  $t_{1/2}$  minutes one half of the dirty water will be left in the tank, and after  $2t_{1/2}$  minutes  $(1/2)(1/2) = (1/2)^2$  of the dirty water will be left in the tank, and so on. Therefore, after  $6t_{1/2}$  minutes,  $(1/2)^6 = (1/64)$  of the dirty water will be left in the tank. If we (arbitrarily) decide that  $1/64$  is a sufficiently small fraction that most of the dirty water can be considered to have been displaced, then, for a chemical that is perfectly mixed in the atmosphere and for which the efflux is given by a first-order Reaction (Eq. 2.7), we have the following relationships between the effective renewal time ( $T$ ), the half-life ( $t_{1/2}$ ) and the residence time ( $\tau$ )

$$T = 6t_{1/2} = 4 \tau \quad (\text{for perfect mixing}) \quad (2.10)$$

In practice, of course, the atmosphere falls somewhere between the cases of no mixing and perfect mixing.

In the atmosphere, the very stable gas nitrogen has a residence time of ~1 to 10 million years, whereas oxygen has a residence time of ~3,000 to 10,000 a. The very reactive species sulfur dioxide and water, on the other hand, have residence times in the atmosphere of only a few days and ten days, respectively. Of course, residence times may be determined by physical removal processes (e.g., scavenging by precipitation) as well as chemical processes. The residence times of some gases in the atmosphere are given in Table 2.1.

Table 2.1. Residence times of some atmospheric gases<sup>a</sup>  
(in many cases only very rough estimates are possible)

Gas	Residence Time
Nitrogen (N <sub>2</sub> )	1.6 × 10 <sup>7</sup> a
Helium (He)	10 <sup>6</sup> a
Oxygen (O <sub>2</sub> )	3,000–10,000 a
Carbon dioxide (CO <sub>2</sub> )	3–4 a
Nitrous oxide (N <sub>2</sub> O)	150 a
Methane (CH <sub>4</sub> )	9 a
CFC-12 (CF <sub>2</sub> Cl <sub>2</sub> )	>80 a
CFC-11 (CFCl <sub>3</sub> )	~80 a
Hydrogen (H <sub>2</sub> )	4–8 a
Methyl chloride (CH <sub>3</sub> Cl)	2–3 a
Carbonyl sulfide (COS)	~2 a
Ozone (O <sub>3</sub> )	100 days
Carbon disulfide (CS <sub>2</sub> )	40 days
Carbon monoxide (CO)	~60 days
Water vapor <sup>b</sup>	~10 days
Formaldehyde (CH <sub>2</sub> O)	5–10 days
Sulfur dioxide (SO <sub>2</sub> )	1 day
Ammonia + Ammonium (NH <sub>3</sub> + NH <sub>4</sub> <sup>+</sup> )	2–10 days
Nitrogen dioxide (NO <sub>2</sub> )	0.5–2 days
Nitrogen oxide (NO)	0.5–2 days
Hydrogen chloride (HCl)	4 days
Hydrogen sulfide (H <sub>2</sub> S)	1–5 days
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	1 day
Dimethyl sulfide (CH <sub>3</sub> SCH <sub>3</sub> )	0.7 days

<sup>a</sup>The residence time (or lifetime) is defined as the amount of the chemical in the atmosphere divided by the rate at which the chemical is removed from the atmosphere. This time scale characterizes the rate of adjustment of the atmospheric concentration of the chemical if the emission rate is changed suddenly.

<sup>b</sup>The residence time of liquid water in clouds is ~6 h.

**Exercise 2.2.** Ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) comprise 1 × 10<sup>-8</sup>, 3 × 10<sup>-5</sup>, and 7 × 10<sup>-5</sup>% by mass of the Earth's atmosphere, respectively. If the effluxes of these chemicals from the atmosphere are 5 × 10<sup>10</sup>, 1 × 10<sup>10</sup>, and 4 × 10<sup>11</sup> kg a<sup>-1</sup>, respectively, what are the residence times of NH<sub>3</sub>, N<sub>2</sub>O, and CH<sub>4</sub> in the atmosphere? (Mass of the Earth's atmosphere = 5 × 10<sup>18</sup> kg.)

**Solution.** From Eq. (2.4) the residence time is given by

$$\tau = \frac{M}{F}$$

where  $M$  is the quantity of chemical in the atmosphere, and  $F$  the efflux. For NH<sub>3</sub>,

$$M = \frac{1 \times 10^{-8}}{100} (5 \times 10^{18}) \text{ kg}$$

and  $F = 5 \times 10^{10} \text{ kg a}^{-1}$ , therefore,  $\tau_{\text{NH}_3} = 0.01 \text{ a} = 4 \text{ days}$ . For N<sub>2</sub>O,

$$M = \frac{(3 \times 10^{-5})}{100} \times (5 \times 10^{18}) \text{ kg}$$

and  $F = 1 \times 10^{10} \text{ kg a}^{-1}$ , therefore,  $\tau_{\text{N}_2\text{O}} = 150 \text{ a}$ . For CH<sub>4</sub>,

$$M = \frac{(7 \times 10^{-5})(5 \times 10^{18})}{100} \text{ kg}$$

and  $F = 4 \times 10^{11} \text{ kg a}^{-1}$ , therefore,  $\tau_{\text{CH}_4} = 9 \text{ a}$ .

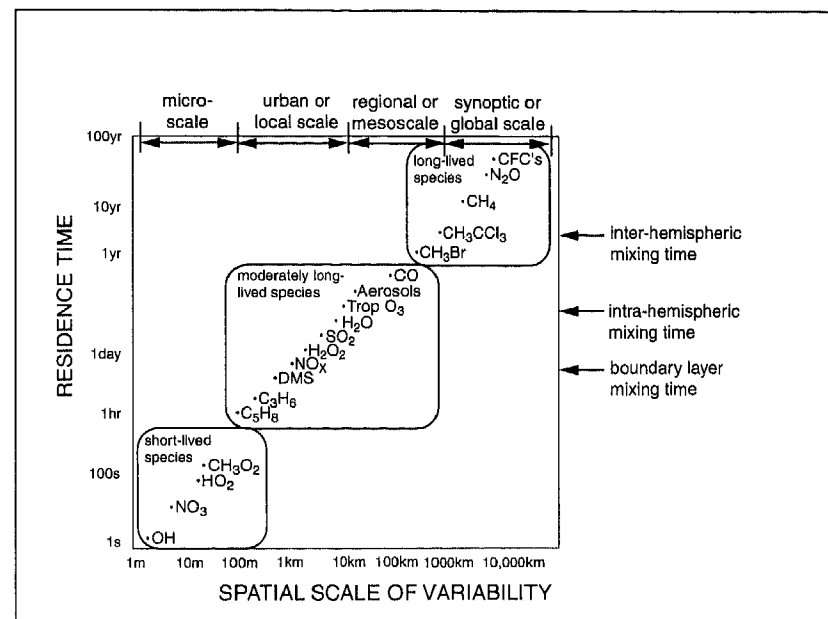


Figure 2.1. Spatial and temporal scales of variability for some atmospheric constituents. The temporal scale is represented by residence time. [Adapted with permission from *The Atmospheric Sciences Entering the Twenty-First Century*. Copyright © 1998 by the National Academy of Sciences. Courtesy of the National Academy Press.]

### 2.3 Spatial and temporal scales of variability

If a chemical species has a very short (or very long) residence time in the atmosphere, significant variations in the concentration of the species will generally occur over very short (or very large) spatial scales (Fig. 2.1). Species with short residence times will be present in high concentrations close to localized sources, and in low concentrations far removed from their sources.

#### Exercises

See Exercise 1(g) and Exercises 6–9 in Appendix I.

## 3

### Present chemical composition of the atmosphere

#### 3.1 Units for chemical abundance

Before discussing the chemical composition of the atmosphere, we need to describe the various units that can be used for expressing the amounts (or abundances) of chemicals in the atmosphere.

The most common unit for expressing the abundance of gases in air is *mixing ratio by volume*, that is, the fraction of the volume of the air occupied by a gas. Depending on the magnitude of the mixing ratio, the most convenient units can be *percent by volume*, *parts per million by volume* (ppmv), *parts per billion by volume* (ppbv), or *parts per trillion by volume* (pptv), where, 1 ppmv = 1 unit of volume per  $10^6$  units (or  $10^{-6}$ ), 1 ppbv = 1 unit of volume per  $10^9$  units (or  $10^{-9}$ ), and 1 pptv = 1 unit of volume per  $10^{12}$  units (or  $10^{-12}$ ). Note that we use the American definitions of billion ( $10^9$ ) and trillion ( $10^{12}$ ). It is very convenient to express the abundance of a gas as a mixing ratio by volume, because, from the gas equation, we know that the volumes occupied by different gases at the same temperature and pressure are proportional to the numbers of molecules of the gases. For example, if the mixing ratio of  $N_2O$  in air is 330 ppbv, we know that the fraction of the total number of molecules in air that are  $N_2O$  (that is the *mole fraction* of  $NO_2$ ) is  $330 \times 10^{-9}$ , or, for every  $10^9$  molecules in the air 330 are  $N_2O$ . Also, the partial pressure exerted by a gas in a mixture is proportional to the mole fraction of the gas. Therefore, at the surface of the Earth, where the total pressure of air is 1 atm,  $N_2O$  with a mixing ratio of 330 ppbv would exert a partial pressure of  $330 \times 10^{-9}$  atm.

*Problem 3.1.* If the mixing ratio of  $CO_2$  in the atmosphere is 354 ppmv, how many  $CO_2$  molecules are there in  $1 \text{ m}^3$  of air at 1 atm and  $0^\circ\text{C}$ ?