

# CHAPTER 1. MEASURES OF ATMOSPHERIC COMPOSITION

The objective of atmospheric chemistry is to understand the factors that control the concentrations of chemical species in the atmosphere. In this book we will use three principal measures of atmospheric composition: *mixing ratio*, *number density*, and *partial pressure*. As we will see, each measure has its own applications.

## 1.1 MIXING RATIO

The *mixing ratio*  $C_X$  of a gas X (equivalently called the *mole fraction*) is defined as the number of moles of X per mole of air. It is given in units of mol/mol (abbreviation for moles per mole), or equivalently in units of v/v (volume of gas per volume of air) since the volume occupied by an ideal gas is proportional to the number of molecules. Pressures in the atmosphere are sufficiently low that the ideal gas law is always obeyed to within 1%.

The mixing ratio of a gas has the virtue of remaining constant when the air density changes (as happens when the temperature or the pressure changes). Consider a balloon filled with room air and allowed to rise in the atmosphere. As the balloon rises it expands, so that the number of molecules per unit volume inside the balloon decreases; however, the mixing ratios of the different gases in the balloon remain constant. The mixing ratio is therefore a robust measure of atmospheric composition.

Table 1-1 lists the mixing ratios of some major atmospheric gases. The most abundant is molecular nitrogen ( $N_2$ ) with a mixing ratio  $C_{N_2} = 0.78$  mol/mol;  $N_2$  accounts for 78% of all molecules in the atmosphere. Next in abundance are molecular oxygen ( $O_2$ ) with  $C_{O_2} = 0.21$  mol/mol, and argon (Ar) with  $C_{Ar} = 0.0093$  mol/mol. The mixing ratios in Table 1-1 are for dry air, excluding water vapor. Water vapor mixing ratios in the atmosphere are highly variable ( $10^{-6}$ - $10^{-2}$  mol/mol). This variability in water vapor is part of our everyday experience as it affects the ability of sweat to evaporate and the drying rate of clothes on a line.

Gases other than  $N_2$ ,  $O_2$ , Ar, and  $H_2O$  are present in the atmosphere at extremely low concentrations and are called *trace gases*. Despite their low concentrations, these trace gases can be of critical importance for the greenhouse effect, the ozone layer, smog,

and other environmental issues. Mixing ratios of trace gases are commonly given in units of *parts per million volume* (*ppmv* or simply *ppm*), *parts per billion volume* (*ppbv* or *ppb*), or *parts per trillion volume* (*pptv* or *ppt*); 1 ppmv =  $1 \times 10^{-6}$  mol/mol, 1 ppbv =  $1 \times 10^{-9}$  mol/mol, and 1 pptv =  $1 \times 10^{-12}$  mol/mol. For example, the present-day CO<sub>2</sub> concentration is 365 ppmv ( $365 \times 10^{-6}$  mol/mol).

**Table 1-1 Mixing ratios of gases in dry air**

Gas	Mixing ratio (mol/mol)
Nitrogen (N <sub>2</sub> )	0.78
Oxygen (O <sub>2</sub> )	0.21
Argon (Ar)	0.0093
Carbon dioxide (CO <sub>2</sub> )	$365 \times 10^{-6}$
Neon (Ne)	$18 \times 10^{-6}$
Ozone (O <sub>3</sub> )	$0.01\text{-}10 \times 10^{-6}$
Helium (He)	$5.2 \times 10^{-6}$
Methane (CH <sub>4</sub> )	$1.7 \times 10^{-6}$
Krypton (Kr)	$1.1 \times 10^{-6}$
Hydrogen (H <sub>2</sub> )	$500 \times 10^{-9}$
Nitrous oxide (N <sub>2</sub> O)	$320 \times 10^{-9}$

## 1.2 NUMBER DENSITY

The *number density*  $n_X$  of a gas X is defined as the number of molecules of X per unit volume of air. It is expressed commonly in units of molecules cm<sup>-3</sup> (number of molecules of X per cm<sup>3</sup> of air). Number densities are critical for calculating gas-phase reaction rates. Consider the bimolecular gas-phase reaction



The loss rate of X by this reaction is equal to the frequency of collisions between molecules of X and Y multiplied by the probability that a collision will result in chemical reaction. The

collision frequency is proportional to the product of number densities  $n_X n_Y$ . When we write the standard reaction rate expression

$$\frac{d}{dt}[X] = -k[X][Y] \quad (1.1)$$

where  $k$  is a rate constant, the concentrations in brackets must be expressed as number densities. Concentrations of short-lived radicals and other gases which are of interest primarily because of their reactivity are usually expressed as number densities.

Another important application of number densities is to measure the absorption or scattering of a light beam by an optically active gas. The degree of absorption or scattering depends on the number of molecules of gas along the path of the beam and therefore on the number density of the gas. Consider in Figure 1-1 the atmosphere as extending from the Earth's surface ( $z = 0$ ) up to a certain top ( $z = z_T$ ) above which number densities are assumed negligibly small (the meaning of  $z_T$  will become clearer in Chapter 2). Consider in this atmosphere an optically active gas X. A slab of unit horizontal surface area and vertical thickness  $dz$  contains  $n_X dz$  molecules of X. The integral over the depth of the atmosphere defines the *atmospheric column* of X as

$$Column = \int_0^{z_T} n_X dz . \quad (1.2)$$

This atmospheric column determines the total efficiency with which the gas absorbs or scatters light passing through the atmosphere. For example, the efficiency with which the ozone layer prevents harmful solar UV radiation from reaching the Earth's surface is determined by the atmospheric column of ozone (problem 1. 3).

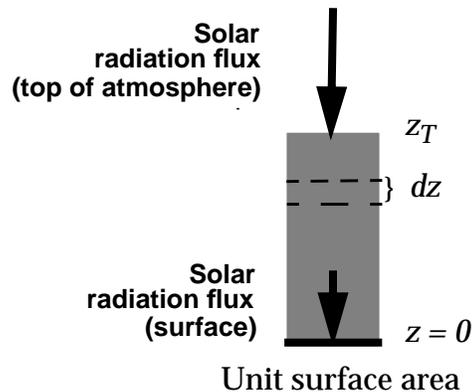


Figure 1-1 Absorption of radiation by an atmospheric column of gas.

The number density and the mixing ratio of a gas are related by the number density of air  $n_a$  (molecules of air per  $\text{cm}^3$  of air):

$$n_X = C_X n_a \quad (1.3)$$

The number density of air is in turn related to the atmospheric pressure  $P$  by the ideal gas law. Consider a volume  $V$  of atmosphere at pressure  $P$  and temperature  $T$  containing  $N$  moles of air. The ideal gas law gives

$$PV = NRT \quad (1.4)$$

where  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$  is the gas constant. The number density of air is related to  $N$  and  $V$  by

$$n_a = \frac{A_v N}{V} \quad (1.5)$$

where  $A_v = 6.023 \times 10^{23} \text{ molecules mol}^{-1}$  is Avogadro's number. Substituting equation (1.5) into (1.4) we obtain:

$$n_a = \frac{A_v P}{RT} \quad (1.6)$$

and hence

$$n_X = \frac{A_v P}{RT} C_X \quad (1.7)$$

We see from (1.7) that  $n_X$  is not conserved when  $P$  or  $T$  changes.

A related measure of concentration is the *mass concentration*  $\rho_X$ , representing the mass of X per unit volume of air (we will also use  $\rho_X$  to denote the *mass density* of a body, i.e., its mass per unit volume; the proper definition should be clear from the context).  $\rho_X$  and  $n_X$  are related by the molecular weight  $M_X$  ( $\text{kg mol}^{-1}$ ) of the gas:

$$\rho_X = \frac{n_X M_X}{A_v} \quad (1.8)$$

The mean molecular weight of air  $M_a$  is obtained by averaging the contributions from all its constituents  $i$ :

$$M_a = \sum_i C_i M_i \quad (1.9)$$

and can be approximated (for dry air) from the molecular weights of  $N_2$ ,  $O_2$ , and Ar:

$$\begin{aligned} M_a &= C_{N_2}M_{N_2} + C_{O_2}M_{O_2} + C_{Ar}M_{Ar} \\ &= (0.78 \cdot 28 \times 10^{-3}) + (0.21 \cdot 32 \times 10^{-3}) + (0.01 \cdot 40 \times 10^{-3}) \quad (1.10) \\ &= 28.96 \times 10^{-3} \text{ kg mol}^{-1} \end{aligned}$$

In addition to gases, the atmosphere also contains solid or liquid particles suspended in the gaseous medium. These particles represent the atmospheric *aerosol*; "aerosol" is a general term describing a dispersed condensed phase suspended in a gas. Atmospheric aerosol particles are typically between 0.01 and 10  $\mu\text{m}$  in diameter (smaller particles grow rapidly by condensation while larger particles fall out rapidly under their own weight). General measures of aerosol abundances are the *number concentration* (number of particles per unit volume of air) and the *mass concentration* (mass of particles per unit volume of air). A full characterization of the atmospheric aerosol requires additional information on the size distribution and composition of the particles.

**Exercise 1-1** Calculate the number densities of air and  $\text{CO}_2$  at sea level for  $P = 1013 \text{ hPa}$ ,  $T = 0^\circ\text{C}$ .

*Answer:* Apply (1.6) to obtain the number density of air  $n_a$ . Use International System (SI) units at all times in numerical calculations to ensure consistency:

$$n_a = \frac{A_v P}{RT} = \frac{(6.023 \times 10^{23}) \cdot (1.013 \times 10^5)}{8.31 \cdot 273} = 2.69 \times 10^{25} \text{ molecules m}^{-3}$$

After you obtain the result for  $n_a$  in SI units, you can convert it to the more commonly used unit of molecules  $\text{cm}^{-3}$ :  $n_a = 2.69 \times 10^{19} \text{ molecules cm}^{-3}$ . The air density at sea level does not vary much around the world; the sea-level pressure varies by at most 5%, and the temperature rarely departs by more than 15% from 273 K, so that  $n_a$  remains within 25% of the value calculated here.

The number density of  $\text{CO}_2$  is derived from the mixing ratio  $C_{\text{CO}_2} = 365 \text{ ppmv}$ :

$$n_{\text{CO}_2} = C_{\text{CO}_2} n_a = 365 \times 10^{-6} \times 2.69 \times 10^{25} = 9.8 \times 10^{21} \text{ molecules m}^{-3}$$

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**Exercise 1-2** In surface air over the tropical oceans the mixing ratio of water vapor can be as high as 0.03 mol/mol. What is the molecular weight of this moist air?

*Answer.* The molecular weight  $M_a$  of moist air is given by

$$M_a = (1 - C_{H_2O})M_{a,dry} + C_{H_2O}M_{H_2O}$$

where  $M_{a,dry} = 28.96 \times 10^{-3} \text{ kg mol}^{-1}$  is the molecular weight of dry air derived in (1.10), and  $M_{H_2O} = 18 \times 10^{-3} \text{ kg mol}^{-1}$ . For  $C_{H_2O} = 0.03 \text{ mol/mol}$  we obtain  $M_a = 28.63 \times 10^{-3} \text{ kg mol}^{-1}$ . A mole of moist air is lighter than a mole of dry air.

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### 1.3 PARTIAL PRESSURE

The *partial pressure*  $P_X$  of a gas X in a mixture of gases of total pressure  $P$  is defined as the pressure that would be exerted by the molecules of X if all the other gases were removed from the mixture. Dalton's law states that  $P_X$  is related to  $P$  by the mixing ratio  $C_X$ :

$$P_X = C_X P \quad (1.11)$$

For our applications,  $P$  is the total atmospheric pressure. Similarly to (1.6), we use the ideal gas law to relate  $P_X$  to  $n_X$ :

$$P_X = \frac{n_X}{A_v} RT \quad (1.12)$$

The partial pressure of a gas measures the frequency of collisions of gas molecules with surfaces and therefore determines the exchange rate of molecules between the gas phase and a coexistent condensed phase. Concentrations of water vapor and other gases that are of most interest because of their phase changes are often given as partial pressures.

Let us elaborate on the partial pressure of water  $P_{H_2O}$ , commonly called the *water vapor pressure*. To understand the physical meaning of  $P_{H_2O}$ , consider a pan of liquid water exposed to the atmosphere (Figure 1-2a).

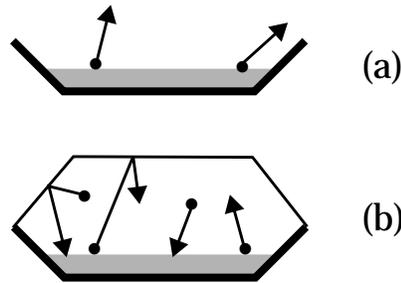


Figure 1-2 Evaporation of water from a pan

The  $\text{H}_2\text{O}$  molecules in the liquid are in constant motion. As a result of this motion,  $\text{H}_2\text{O}$  molecules at the surface of the pan evaporate to the atmosphere. If we let this evaporation take place for a long enough time, the pan will dry out. Let us place a lid on top of the pan to prevent the  $\text{H}_2\text{O}$  molecules from escaping (Figure 1-2b). The  $\text{H}_2\text{O}$  molecules escaping from the pan bounce on the lid and must now eventually return to the pan; a steady state is achieved when the rate at which molecules evaporate from the pan equals the rate at which water vapor molecules return to the pan by collision with the liquid water surface. The collision rate is determined by the water vapor pressure  $P_{\text{H}_2\text{O}}$  in the head space. Equilibrium between the liquid phase and the gas phase is achieved when a *saturation vapor pressure*  $P_{\text{H}_2\text{O},\text{SAT}}$  is reached in the head space. If we increase the temperature of the water in the pan, the energy of the molecules at the surface increases and hence the rate of evaporation increases. A higher collision rate of water vapor molecules with the surface is then needed to maintain equilibrium. Therefore,  $P_{\text{H}_2\text{O},\text{SAT}}$  increases as the temperature increases.

Cloud formation in the atmosphere takes place when  $P_{\text{H}_2\text{O}} \geq P_{\text{H}_2\text{O},\text{SAT}}$ , and it is therefore important to understand how  $P_{\text{H}_2\text{O},\text{SAT}}$  depends on environmental variables. From the phase rule, the number  $n$  of independent variables determining the equilibrium of  $c$  chemical components between a number  $p$  of different phases is given by

$$n = c + 2 - p \quad (1.13)$$

In the case of the equilibrium of liquid water with its vapor there is only one component and two phases. Thus the equilibrium is determined by one single independent variable; at a given temperature  $T$ , there is only one saturation vapor pressure  $P_{\text{H}_2\text{O},\text{SAT}}(T)$  for which liquid and gas are in equilibrium. The

dependence of  $P_{H_2O,SAT}$  on  $T$  is shown in Figure 1-3. Also shown on the Figure are the lines for the gas-ice and liquid-ice equilibria, providing a complete *phase diagram* for water. There is a significant kinetic barrier to ice formation in the atmosphere because of the paucity of aerosol surfaces that may serve as templates for condensation of ice crystals. As a result, cloud liquid water readily *supercools* (remains liquid) down to temperatures of about 250 K, and the corresponding curve is included in Figure 1-3.

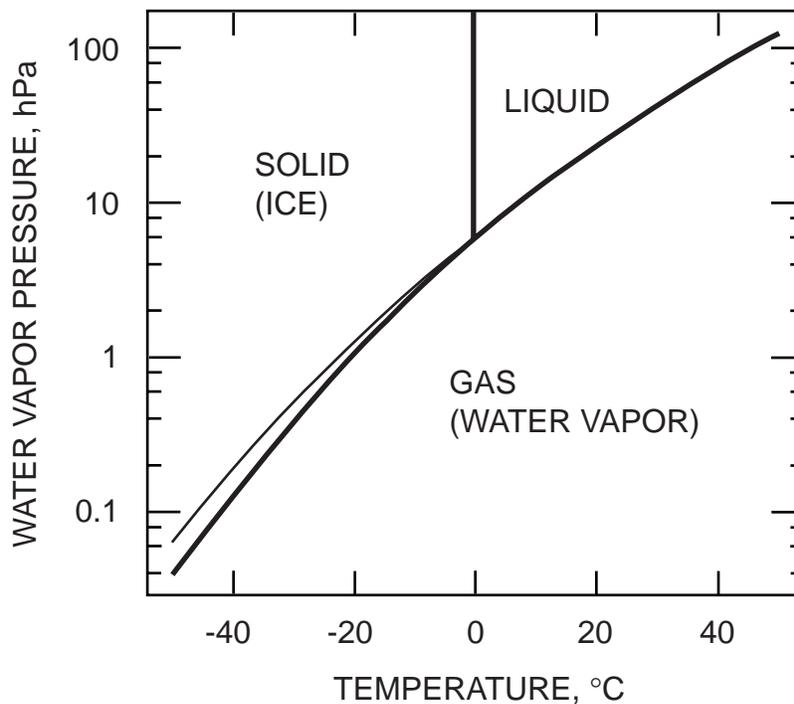
In weather reports, atmospheric water vapor concentrations are frequently reported as the relative humidity (RH) or the dew point ( $T_d$ ). The relative humidity is defined as:

$$RH(\%) = 100 \cdot \frac{P_{H_2O}}{P_{H_2O,SAT}(T)} \quad (1.14)$$

so that cloud formation takes place when  $RH \geq 100\%$ . The dew point is defined as the temperature at which the air parcel would be saturated with respect to liquid water:

$$P_{H_2O} = P_{H_2O,SAT}(T_d) \quad (1.15)$$

At temperatures below freezing, one may also report the *frost point*  $T_f$  corresponding to saturation with respect to ice.



**Figure 1-3** Phase diagram for water. The thin line is the saturation vapor pressure above supercooled liquid water.

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**Exercise 1-3** How many independent variables determine the liquid-vapor equilibrium of the H<sub>2</sub>O-NaCl system? What do you conclude regarding the ability of sea salt aerosol particles in the atmosphere to take up water?

*Answer.* There are two components in this system: H<sub>2</sub>O and NaCl. Liquid-vapor equilibrium involves two phases: the H<sub>2</sub>O-NaCl liquid solution and the gas phase. Application of the phase rule gives the number of independent variables defining the equilibrium of the system:

$$n = c + 2 - p = 2 + 2 - 2 = 2$$

Because  $n = 2$ , temperature alone does not define the saturation water vapor pressure above a H<sub>2</sub>O-NaCl solution. The composition of the solution (i.e., the mole fraction of NaCl) is another independent variable. The presence of NaCl molecules on the surface of the solution slows down the evaporation of water because there are fewer H<sub>2</sub>O molecules in contact with the gas phase (Figure 1-2). Therefore, NaCl-H<sub>2</sub>O solutions exist at equilibrium in the atmosphere at relative humidities less than 100%; the saturation water vapor pressure over a NaCl-H<sub>2</sub>O solution decreases as the NaCl mole fraction increases. In this manner, sea salt aerosol particles injected to the atmosphere by wave action start to take up water at relative humidities as low as 75% (not at lower relative humidities, because the solubility constant of NaCl in H<sub>2</sub>O places an upper limit on the mole fraction of NaCl in a NaCl-H<sub>2</sub>O solution). The same lowering of water vapor pressure applies for other types of aerosol particles soluble in water. The resulting swelling of particles by uptake of water at high humidities reduces visibility, producing the phenomenon known as *haze*.

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*Further reading:*

**Levine, I.N., *Physical Chemistry*, 4th ed., McGraw-Hill, New York, 1995.** Phase rule, phase diagrams.