Contents

CHAPTER 1

Measures of Atmospheric Composition

Atmospheric chemistry aims to explain the factors controlling the composition of the atmosphere and the implications for life on Earth. The atmosphere is a mixture of gases and also contains suspended liquid and solid particles, called aerosol particles, that grow to form clouds under saturated water vapor conditions. In this chapter we introduce different measures of atmospheric composition (Sections 1.1–1.5), present the phase diagram of water and its implications for cloud formation (Section 1.6), and explain the presence of water in aerosol particles (Section 1.7). Here and elsewhere we use the term species to describe any constituent of interest in the atmosphere, either in the gas or the aerosol phase. We use the term air parcel to describe an idealized volume of air with homogeneous pressure, temperature, and composition.

1.1 Relative concentration

The relative concentration of a species X in the atmosphere is measured as the number of moles of X per mole of air, called the mole fraction and denoted C_X:

$$C_X = \frac{\text{moles of X}}{\text{mole of air}}. \tag{1.1}$$

The mole fraction is a dimensionless quantity but is usually reported in units of mol mol^{-1} (abbreviation for moles per mole) to avoid confusion with the mass fraction (kg kg^{-1}). The mass fraction is rarely used in atmospheric chemistry. A related measure is the mixing ratio, which is the number of moles of X per moles of other species. The difference between mole fraction and mixing ratio is negligible except for the major components of air (Exercise 1.1).

Exercise 1.1 Relate the mixing ratio of a species to its mole fraction.

Answer. Let r_X denote the mixing ratio of X. By definition,

$$r_X = \frac{\text{moles of X}}{\text{mole of air} - \text{moles of X}}.$$

Combine with equation (1.1) to obtain

$$r_X = \frac{C_X}{1 - C_X}.$$

The mixing ratio is larger than the mole fraction by a factor of $1/(1-C_X)$. The difference is important only for species with large C_X. For example, O_2 with a mole fraction $C_{O2} = 0.21$ mol mol^{-1} has a mixing ratio of $r_{O2} = 0.27$ mol mol^{-1}. For a trace species with $C_X << 1$, and making use of the approximation $1/(1-x) \rightarrow 1+x$ as $x \rightarrow 0$, we have

$$r_X \approx C_X(1 + C_X) = C_X + C_X^2.$$

The difference is C_X^2, which is very small for $C_X << 1$.

Mole fractions for gases are sometimes called volume fractions because the volume V occupied by a gas is proportional to the number N of moles following the ideal gas law:

$$pV = NRT \tag{1.2}$$

where p is pressure, $R = 8.314$ J mol^{-1} K^{-1} is the ideal gas constant, and T is absolute temperature. The ideal gas law holds when molecules in a gas are sufficiently separated so that their internal energy is determined solely by temperature and not by interactions with each other. Atmospheric pressures are sufficiently low that the ideal gas law is applicable in all cases.

The mole fraction does not change when the pressure or temperature changes, and that makes it a useful general measure of atmospheric composition. Consider a balloon filled with surface air and allowed to rise in the atmosphere. As the balloon rises, it expands so that the number of moles per unit volume inside the balloon decreases. But the total number of moles in the balloon stays the same, so the mole fractions stay the same.

Table 1-1 lists the mole fractions of the most abundant gases in dry air, excluding water vapor. The gases in Table 1-1 generally have long atmospheric lifetimes and therefore near-uniform mole fractions, except ozone for which a range is given. The most abundant gas in the atmosphere is molecular nitrogen (N_2) with a mole fraction of $C_{N2} = 0.78$ mol mol^{-1}. N_2 accounts for 78% of all molecules in the atmosphere. Next is molecular oxygen (O_2) with $C_{O2} = 0.21$ mol mol^{-1}. N_2 and O_2 together account for 99% of air molecules. Third is argon

Table 1-1. Dry air composition

Gas	Dry air mole fraction (mol mol^{-1})
Nitrogen (N_2)	0.78
Oxygen (O_2)	0.21
Argon (Ar)	0.0093
Water (H_2O)	0
Carbon dioxide (CO_2)	430×10^{-6}
Neon (Ne)	18×10^{-6}
Ozone (O_3)	$(0.01-10)\times10^{-6}$
Helium (He)	5.2×10^{-6}
Methane (CH_4)	1.9×10^{-6}
Krypton (Kr)	1.1×10^{-6}
Hydrogen (H_2)	560×10^{-9}
Nitrous oxide (N_2O)	340×10^{-9}

Note: Listing of the most abundant atmospheric gases, excluding water vapor. Water vapor accounts for 0.40% of total air molecules. Dry air mole fractions are for 2026.

(Ar) with $C_{Ar} = 0.0093$ mol mol^{-1}, slightly less than 1%. Water vapor (H_2O) is the fourth most abundant gas, accounting for 0.40% of air molecules, but its mole fraction is highly variable. It can be as high as 3×10^{-2} mol mol^{-1} in surface air over the tropical oceans but drops to below 5×10^{-6} mol mol^{-1} in the stratosphere. This is why standard tables of atmospheric composition, such as Table 1-1, are given for dry air. If given for total air (that is, including water vapor), mole fractions would fluctuate by a few percentage points simply due to changes in water vapor.

Species other than N_2, O_2, Ar, and H_2O are present in the atmosphere at much lower concentrations and are called trace species. Table 1-1 lists only the most abundant ones. There are many others of interest, including both gases and aerosols, that we will encounter throughout this book. Mole fractions for trace species are commonly expressed using multiplicative factors of micro (μ), nano (n), pico (p), femto (f): 1 μmol mol^{-1} = 1×10^{-6} mol mol^{-1}, 1 nmol mol^{-1} = 1×10^{-9} mol mol^{-1}, 1 pmol mol^{-1} = 1×10^{-12} mol mol^{-1}, 1 fmol mol^{-1} = 1×10^{-15} mol mol^{-1}. Atmospheric chemists often use customary mole fraction units of parts per million (ppm), parts per billion (ppb), parts per trillion (ppt), and parts per quadrillion (ppq). Sometimes volume gets added to the notation for gases (ppmv, ppbv, pptv, ppqv) to clarify that these are mole (or equivalently volume) fractions and not mass fractions,

but the clarification is superfluous for atmospheric chemistry applications and we do not use it.

$$1\ \text{ppm} = 1\times10^{-6}\ \text{mol mol}^{-1} = 1\ \mu\text{mol mol}^{-1}$$
$$1\ \text{ppb} = 1\times10^{-9}\ \text{mol mol}^{-1} = 1\ \text{nmol mol}^{-1}$$
$$1\ \text{ppt} = 1\times10^{-12}\ \text{mol mol}^{-1} = 1\ \text{pmol mol}^{-1}$$
$$1\ \text{ppq} = 1\times10^{-15}\ \text{mol mol}^{-1} = 1\ \text{fmol mol}^{-1}$$

Mole fractions are given for total air unless otherwise indicated. Dry air mole fractions, as given in Table 1-1, are useful for long-lived gases with near-uniform concentrations because the dry air mole fraction is conserved when the water vapor concentration changes but the total air mole fraction is not (Exercise 1.2). The mole fraction is then explicitly stated as being for dry air.

Exercise 1.2 If CO_2 has a dry air mole fraction of 430 ppm, what is its total air mole fraction in surface air over the tropical ocean with $C_{H2O} = 3\times10^{-2}$ mol mol^{-1}?

Answer. One mole of air over the tropical ocean contains $1 - 0.03 = 0.97$ moles of dry air. If the dry air mole fraction of CO_2 is 430 ppm, then the total air mole fraction is $430\times0.97 = 417$ ppm. The total air mole fraction can fluctuate by a few percentage points simply due to changes in water vapor. For this reason, CO_2 mole fractions are generally reported for dry air.

1.2 Absolute concentration

The absolute concentration of a species X, denoted [X], is the abundance of X per unit volume. It is the relevant measure of atmospheric concentration for calculating reaction rates. Consider a reaction between two species X and Y:

$$\text{X} + \text{Y} \rightarrow \text{products.} \tag{1.3}$$

The reaction rate is determined by the frequency of collisions between X and Y and by the probability that collision will result in reaction. This is expressed by the rate equation

$$-\frac{d[\text{X}]}{dt} = -\frac{d[\text{Y}]}{dt} = k[\text{X}][\text{Y}] \tag{1.4}$$

where the collision frequency is proportional to the product [X][Y] and k is a reaction rate constant that accounts for the probability of a collision resulting in reaction. In our previous example of a balloon rising in the atmosphere, the mole fractions do not change as the balloon expands, but the absolute concentrations decrease and hence the collision frequencies decrease (because the same number of molecules is present in a larger volume). This causes reactions to slow down.

The absolute concentration of a gas is generally expressed as the number density n_X with units of molecules cm^{-3}, representing the number of molecules of X per cm^3 of air:

$$n_X = \frac{\text{number of molecules of X}}{\text{cm}^3 \text{ air}}. \tag{1.5}$$

The number density is related to the mole fraction by

$$n_X = C_X n_a \tag{1.6}$$

where n_a is the number density of air (Exercise 1.3). n_a is related to pressure and temperature by the ideal gas law:

$$n_a = \frac{AN}{V} = \frac{Ap}{RT} \tag{1.7}$$

where $A = 6.022 \times 10^{23}$ molecules mol^{-1} is Avogadro's number. Replacing into the equation:

$$n_X = \frac{Ap}{RT} C_X. \tag{1.8}$$

Unlike the mole fraction, the number density changes as the pressure or temperature changes.

Exercise 1.3 Calculate the number density of air at sea level with pressure of 1013 hPa and temperature of 15°C.

Answer. Apply equation (1.7) to obtain the number density of air n_a. When working with equations including multiple units, it is best to convert all units to the International System (SI) to ensure consistency. Here we have $p = 1.013 \times 10^5$ Pa and $T = 288$ K:

$$n_a = \frac{pA}{RT} = \frac{(1.013 \times 10^5) \times (6.022 \times 10^{23})}{8.314 \times 288}$$
$$= 2.55 \times 10^{25} \text{ molecules m}^{-3} = 2.55 \times 10^{19} \text{ molecules cm}^{-3}.$$

The air density at sea level does not vary much around the world; the sea-level pressure varies by at most 5%, as we will see in Chapter 2, and the temperature rarely deviates by more than 10% from 288 K, so that n_a remains generally within 15% of the value calculated here.

An alternative measure of absolute concentration is the mass concentration μ_X, defined as the mass of species X per unit volume of air:

$$\mu_X = \frac{\text{mass of X}}{\text{unit volume of air}}. \tag{1.9}$$

Typical units for μ_X are $\mu g\ m^{-3}$. Mass concentrations are commonly used for aerosol particles, where the mass is readily measured but the chemical composition may be unknown. Aerosol mass concentrations are typically in the range of 0.1–100 $\mu g\ m^{-3}$.

If the molecular weight M_X ($g\ mol^{-1}$) of X is known, then μ_X can be related to n_X and C_X:

$$\mu_X = \frac{M_X}{A} n_X \tag{1.10}$$

$$\mu_X = \frac{M_X p}{RT} C_X. \tag{1.11}$$

For air itself the mass concentration μ_a is the same as the density, which is the mass per unit volume of pure substance and has standard notation ρ:

$$\rho_a = \frac{M_a}{A} n_a = \frac{M_a p}{RT}. \tag{1.12}$$

The molecular weight of air M_a is the sum of contributions from all its constituents i:

$$M_a = \sum_i C_i M_i. \tag{1.13}$$

It is obtained to good approximation from the contributions of N_2, O_2, and Ar:

$$\begin{aligned} M_a &= C_{N2} M_{N2} + C_{O2} M_{O2} + C_{Ar} M_{Ar} \\ &= (0.78 \times 28) + (0.21 \times 32) + (0.0093 \times 40) \\ &= 29.0\ g\ mol^{-1}. \end{aligned} \tag{1.14}$$

When a cloud forms in an air parcel, condensation of water vapor causes the preexisting aerosol particles to grow considerably. Cloudwater concentrations are generally measured as mass of condensed water per unit volume of air, called liquid water content (LWC) and ice water content (IWC), with units of $g\ m^{-3}$. Because liquid water has density $\rho_{H2O} = 1.00\ g\ cm^{-3}$, cloudwater concentrations can be equivalently expressed in units of m^3 water per m^3 air. Cloudwater concentrations are typically 0.1–1 $g\ m^{-3}$, or equivalently 10^{-7}–10^{-6} m^3 water per m^3 of air. This is ~10^5 higher than typical dry aerosol concentrations because of the massive condensation of water in a cloud.

1.3 Column concentration and optical depth

The column concentration of species X, denoted Ω_X and commonly called the column of X, is the amount of X in the atmosphere above a unit area of Earth's surface. It is generally expressed in units of molecules cm^{-2} for gases and is obtained by integrating the number density over the depth of the atmosphere:

$$\Omega_X = \int_0^\infty n_X(z)\,dz. \tag{1.15}$$

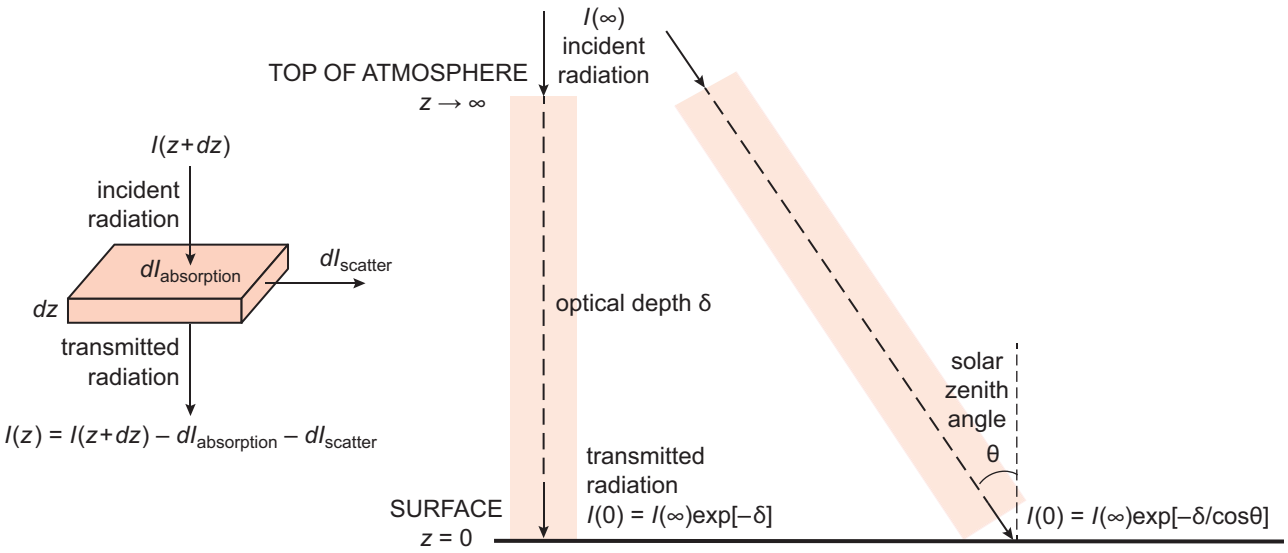


Figure 1-1. Atmospheric propagation of solar radiation of intensity *I*. The left panel illustrates the vertical propagation through a slab of vertical thickness *dz*. The right panel illustrates the propagation through the whole atmosphere for the Sun directly overhead and for the Sun at a solar zenith angle θ. δ is the optical depth of the atmosphere.

The column concentration is the relevant measure for the attenuation of radiation by the atmosphere. Consider vertically directed solar radiation (Sun at zenith) with intensity *I*, propagating through the atmosphere as illustrated in Figure 1-1 (see Box 1.1 for definition of radiation intensity). As radiation propagates through a horizontal slab of atmosphere of unit horizontal area and vertical thickness *dz,* some of the incident radiation may be absorbed (converted into internal energy of molecules) or scattered (shifted to another direction). The sum of absorption and scattering is called extinction. The radiation that is not absorbed or scattered is said to be transmitted. The probability *dP* that an incident photon will encounter a molecule of X as it propagates downward through the slab is

$$dP = a_X n_X(z) dz \tag{1.16}$$

where a_X (cm^2 molecule^{-1}) is the cross-sectional area of the molecule. The probability that this encounter will result in extinction is called the extinction efficiency, $Q_X = \sigma_X / a_X$, where σ_X (cm^2 molecule^{-1}) is the extinction cross section of X and is the sum of an absorption cross section and a scattering cross section. σ_X is in general a strong function of wavelength. Assuming that X is the only species interfering with radiation, the transmitted intensity through the slab is

$$I(z) = I(z+dz) - I(z) Q_X dP = I(z+dz) - \sigma_X n_X(z) I(z) dz. \tag{1.17}$$

Introducing the differential $dI = I(z+dz) - I(z)$, the equation becomes

$$dI = \sigma_X n_X(z) I(z) dz. \tag{1.18}$$

Box 1.1: Radiation intensity, radiation flux, and actinic flux

Radiation is energy transmitted by electromagnetic waves and quantized as photons. A photon travels in a fixed direction at the speed of light until it is absorbed or scattered. The radiation intensity, also called radiance and denoted I, is defined here as the radiative power (energy per unit time) flowing from a given direction and through a unit surface area perpendicular to that direction. It has units of W m^{-2} sr^{-1}, where steradian (sr) is the unit of solid angle. We apply it in this section to characterize solar radiation propagating in the atmosphere at a solar zenith angle θ (Figure 1-B1).

The radiation flux, denoted F, is defined here as the radiative power flowing from all directions through a unit surface area in a direction normal to that surface. It has units of W m^{-2}. We will apply it in Chapter 6 to the emission of radiation and to the vertical flow of solar and terrestrial radiation. Solar radiation of intensity I and zenith angle θ contributes a vertical flux $F = I\cos\theta$. Isotropic radiation emitted by the Earth's surface with the same intensity I in all directions contributes a flux $F = \pi I$ normal to the surface as obtained by integrating over the hemisphere.

The actinic flux, denoted A, is the total radiation intensity flowing from all directions to a single point. It has units of W m^{-2}. We will apply it in Chapter 7 to calculate photolysis rates as determined by photons impacting a molecule from all directions. For radiation flowing in a single direction, the actinic flux and the intensity are the same: $A = I$. For isotropic radiation, the actinic flux is $A = 4\pi I$ as obtained by integrating the intensity over all solid angles.

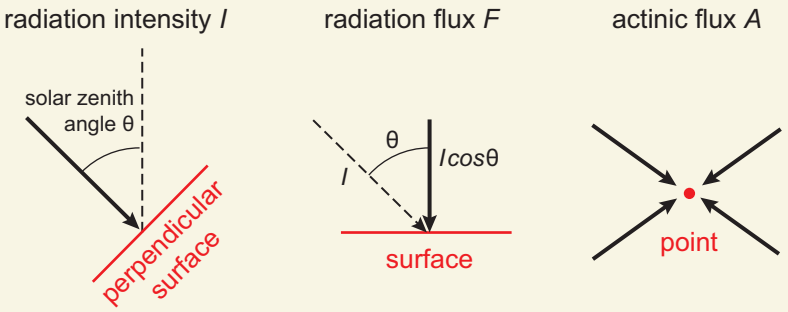


Figure 1-B1. Radiation intensity (also called radiance), radiation flux, and actinic flux.

Integrating by separation of variables from the top of the atmosphere ($z \to \infty$) to the surface ($z = 0$) and assuming that σ_X is uniform with altitude, we obtain

$$I(0) = I(\infty)\exp[-\sigma_X \Omega_X] \tag{1.19}$$

where $I(\infty)$ is the intensity at the top of the atmosphere. The intensity decreases exponentially as it propagates through the atmosphere. The argument of the exponential is called the optical depth of X, denoted δ_X:

$$\delta_X = \sigma_X \Omega_X \tag{1.20}$$

resulting in the compact form

$$I(0) = I(\infty)\exp[-\delta_X]. \tag{1.21}$$

Equation (1.21) is called Beer's law and applies to the propagation of radiation through any absorbing and/or scattering medium.

The Sun is generally not at zenith but at a solar zenith angle θ (Figure 1-1). One then needs to correct for the longer propagation through the atmosphere:

$$I(0) = I(\infty)\exp[-\delta_X/\cos\theta]. \tag{1.22}$$

$\delta_X/\cos(\theta)$ is often called the slant optical depth. Radiation is more attenuated when the sun is low in the sky.

Exercise 1.4

Consider solar UV radiation absorbed by the ozone layer with an optical depth of 2. The ozone column at northern midlatitudes has thinned by 4% since 1970. For a solar zenith angle of 30°, by what fraction has the radiation reaching the Earth's surface increased since 1970?

Answer. The optical depth is proportional to the column and therefore has decreased by $\Delta\delta = 2 \times 0.04 = 0.08$ since 1970. The slant optical depth has decreased by $0.08/\cos(30°) = 0.092$. The resulting UV radiation has increased by $\exp[0.092]$ or 9.6%. Remarkably, the relative increase in radiation is larger than the relative decrease in the ozone column. This is because of the exponential dependence of the attenuation on the optical depth.

The notions of column concentration and optical depth also apply to aerosols and clouds. The aerosol optical depth (AOD), denoted here δ_A, determines the attenuation of solar radiation by the atmospheric aerosol following Beer's law. It is the product of the aerosol mass concentration μ_A (g cm^{-3}) and the extinction cross section σ_A (cm^2 g^{-1}), integrated over the depth of the atmosphere:

$$\delta_A = \int_0^\infty \sigma_A(z)\mu_A(z)dz. \tag{1.23}$$

σ_A depends on the aerosol composition and size distribution, which may vary strongly with altitude. Assuming nevertheless that σ_A is uniform, or can be represented by an effective value, we relate the AOD to the aerosol column concentration Ω_A:

$$\delta_A = \sigma_A\Omega_A. \tag{1.24}$$

Multiple gases may contribute to the attenuation of radiation by the atmosphere at a given wavelength. The corresponding optical depths are additive as can be seen from equation (1.17), where additional species would be represented by additional terms on the

right-hand-side of the equation. The total optical depth δ of the atmosphere at a given wavelength is obtained by summing the contributions of individual gases δ_i and of the aerosol:

$$\delta = \delta_A + \sum_i \delta_i. \tag{1.25}$$

The transmitted solar radiation intensity at the surface for a solar zenith angle θ is then given by

$$I(0) = I(\infty)\exp[-\delta/\cos\theta]. \tag{1.26}$$

The total optical depth δ of the atmosphere at a given wavelength can be inferred experimentally from equation (1.26) by measuring the transmitted solar radiation intensity at the surface and knowing the intensity at the top of the atmosphere. Making this measurement over a range of wavelengths enables determination of the column concentrations of different species.

In the case of a cloudy atmosphere, one defines a cloud optical depth (COD) similarly to the AOD. The COD is much larger than the AOD because cloud formation causes the aerosol particles to swell from their original sizes by uptake of water. Clouds typically have COD > 2 for visible radiation. Most of the incoming solar radiation is then scattered, which explains why the Sun is not visible through the cloud.

1.4 Aerosol size distribution

Aerosol particles range in size from 1 nm for molecular clusters to more than 10 µm for large dust particles. In clouds, cloud droplets range in size from 1 to 100 µm. Liquid particles are spherical because the spherical shape minimizes the surface area of the particle and hence the surface tension. Size is then measured by the diameter D. Solid particles can be of any shape, but standard practice is to approximate them as spheres, characterized by an equivalent diameter D.

The aerosol size distribution is important to know because it affects aerosol properties. It is a continuous function of D. Particle diameters range over several orders of magnitude, so it is more convenient to describe the size distribution as a function of log D. The number concentration dn of particles in the size range [log D, log $D + d$ log D] is given by

$$dn = n_N d\log D \tag{1.27}$$

where $n_N = dn/d\log D$ is called the number size distribution function. Figure 1-2 shows a typical aerosol size distribution as n_N versus log D. Almost all particles are in the size range 0.01–0.3 µm. There is a bimodal structure that we will explain in Chapter 10. The total number N of particles per unit volume of air is obtained by integrating over all sizes, which means integrating over log D from $-\infty$ to $+\infty$:

$$N = \int_{-\infty}^{+\infty} n_N(\log D) d\log D. \tag{1.28}$$

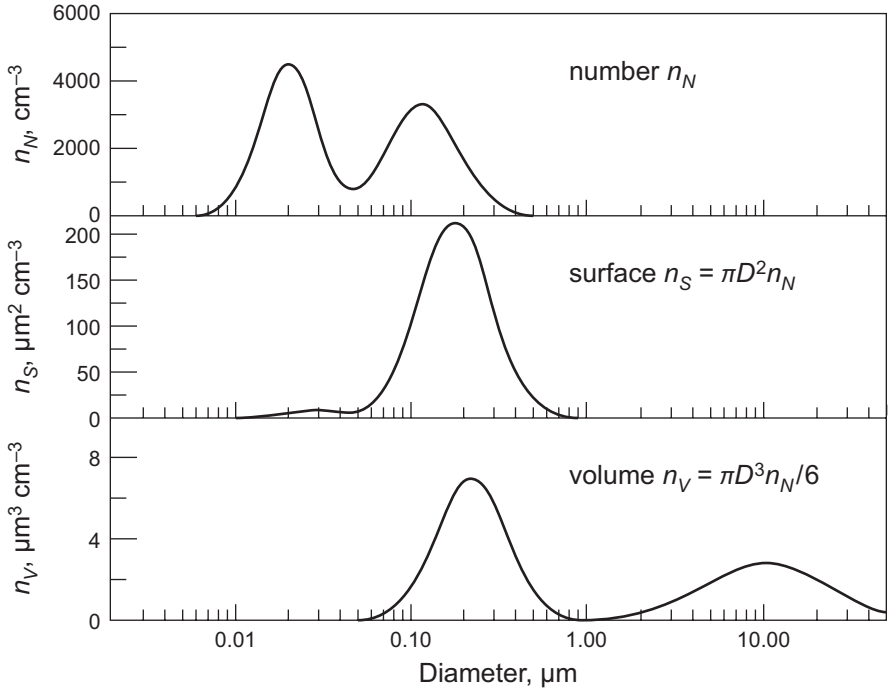


Figure 1-2. Aerosol number, surface, and volume size distribution functions for a typical aerosol population. Note the log scale for the *x*-axis. Adapted from J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics,* Wiley, 2016.

One can also characterize the aerosol size distribution in terms of the surface area or volume of the particles, rather than their number. The surface area concentration of particles in the [log D, log $D + d$ log D] range is

$$\pi D^2 dn = \pi D^2 n_N d \log D = n_S d \log D \tag{1.29}$$

where $n_S = \pi D^2 n_N$ is the surface size distribution function. The volume concentration of particles in the [log D, log $D + d$ log D] range is

$$\frac{\pi D^3}{6} dn = \frac{\pi D^3}{6} n_N d \log D = n_V d \log D \tag{1.30}$$

where $n_V = \pi D^3 n_N/6$ is the volume size distribution function. Total aerosol surface area and volume per unit volume of air are obtained by integrating n_S and n_V over all sizes in the same way as for n_N in equation (1.28).

Figure 1-2 shows large differences between n_N, n_S, and n_V for the same aerosol population. This reflects the weightings of n_S and n_V by D^2 and D^3 over many orders of magnitude. The surface area concentration is dominated by particles in the 0.1–1 μm range, and the volume concentration has an important contribution from particles larger than 1 μm. These different measures of the aerosol size distribution are relevant for different applications. For

example, the number concentration is most relevant for cloud condensation because cloud droplets condense on preexisting particles. The surface area concentration is most relevant for light extinction. The volume concentration is most relevant for health effects.

1.5 Partial pressure

The partial pressure p_X of a gas X in a mixture of gases is the pressure that would be exerted by the molecules of X if all other gases were removed from the mixture. p_X is related to the total pressure p by the mole fraction C_X and this is called Dalton's law:

$$p_X = C_X p. \tag{1.31}$$

p is the atmospheric pressure for our applications. p_X is related to n_X by the ideal gas law:

$$p_X = \frac{RT}{A} n_X. \tag{1.32}$$

The partial pressure describes the collision of molecules of X with surfaces and therefore determines the exchange of molecules between the gas phase and a condensed phase. Concentrations of water vapor and other gases that are of particular interest because of their phase changes are often given as partial pressures.

To understand the physical meaning of partial pressure, consider a pan of liquid water covered by a lid (Figure 1-3). Water molecules continuously escape from the liquid into the gas above, called the head space. The water molecules in the head space exert a water vapor pressure p_{H2O} represented in the figure by collisions with the walls. These collisions eventually return the water vapor molecules to the liquid, so that there is an equilibrium between evaporation and condensation defined by a saturation vapor pressure $p_{H2O,S}$. If we heat the pan, the escape rate of water molecules from the liquid increases, but the residence time of the molecules in the head space stays the same. A new equilibrium between evaporation and condensation is eventually reached in which the concentration of water vapor molecules in the head space has increased. The saturation vapor pressure thus increases as the temperature increases.

Exercise 1.5 Venus has a surface atmospheric pressure of 91 atm and a nitrogen mole fraction $C_{N2} = 3.4 \times 10^{-2}$ mol mol^{-1}. Compare the surface partial pressures of N_2 on Venus and on Earth.

Answer. Apply equation (1.31). On Venus, $p_{N2} = 3.4 \times 10^{-2} \times 91 = 3.1$ atm. On Earth, $p_{N2} = 0.78 \times 1 = 0.78$ atm. Remarkably, the N_2 partial pressures differ by only a factor of 4 between Venus and Earth even though the atmospheric pressure on Venus is 91 times that of Earth. Most of the Venusian atmosphere is CO_2. The factors controlling atmospheric N_2 and the differences between Venus and Earth are examined in Chapter 5.

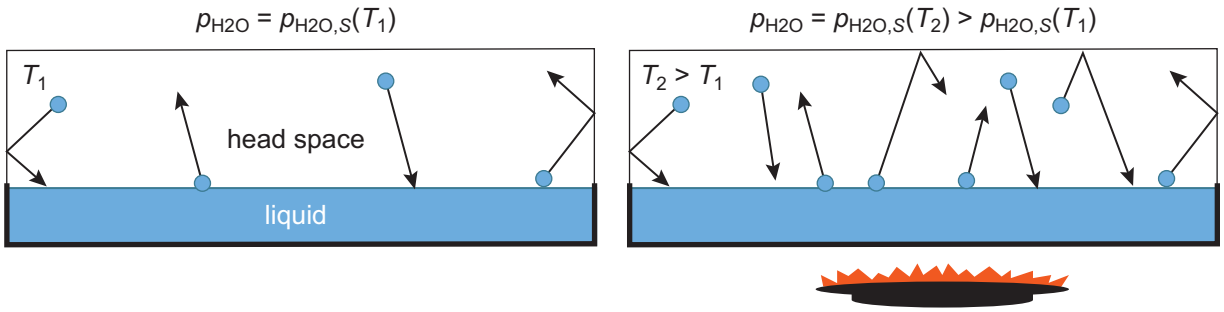


Figure 1-3. Evaporation and condensation of water from a pan covered by a lid. The water partial pressure p_{H2O} in the head space eventually reaches a saturation value $p_{H2O,S}$, where the evaporation flux from the pan (set by the temperature) is balanced by the condensation flux to the surface (set by the water vapor pressure). If the pan is heated (right panel), the evaporation flux increases and the saturation water vapor pressure must therefore increase for the condensation flux to balance the evaporation flux.

1.6 Phase diagram of water and cloud formation

Cloud formation takes place when the water vapor pressure p_{H2O} exceeds the saturation value $p_{H2O,S}$. This can happen when air cools, since we saw in Section 1.5 that the saturation water vapor pressure $p_{H2O,S}$ is an increasing function of temperature. But are there other variables besides temperature determining the saturation water vapor pressure? To answer this question, we turn to the phase rule.

The phase rule quantifies the number n of independent variables (equivalently called degrees of freedom) that determine the equilibrium of a system of c chemical species distributed between a number q of different phases. It is given by

$$n = c + 2 - q. \tag{1.33}$$

See Box 1.2 for a derivation. In the case of the equilibrium of liquid water with its vapor, there is only one relevant species ($c = 1$) and two phases ($q = 2$), therefore $n = 1$. This means that the equilibrium condition between the two phases is determined by a single independent variable. At a given temperature T, there is only one saturation vapor pressure $p_{H2O,S}(T)$ for which liquid and gas are in equilibrium. The dependence of $p_{H2O,S}$ on T is given by the Clausius–Clapeyron equation:

$$p_{H2O,S}(T) = p_{H2O,S}(T_o)\exp\left[-\frac{L}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \tag{1.34}$$

where L is the specific heat of vaporization (J mol^{-1}) and T_o is a reference temperature. For $T_o = 273$ K, we have $p_{H2O,S}(T_o) = 6.11$ hPa. Constant values $L/R = 5410$ K for liquid-gas equilibrium and $L/R = 6140$ K for ice-gas equilibrium can be used over the range of atmospheric temperatures.

Figure 1-4 gives the phase diagram for water. Phase diagrams describe the conditions determining the equilibrium of a system between different phases. They can become complicated

Box 1.2: Derivation of the phase rule

Consider an equilibrium system of c chemical species distributed among q phases. Let C_{ij} represent the mole fraction of species i in phase j. To describe the composition of the system, we need to know C_{ij} for each species in each phase, a total of cq variables. To complete the thermodynamic description of the system, we also need to know the temperature and the total pressure, adding up to $cq+2$ variables. Not all these variables are independent, however. The sum of mole fractions in each phase j must equal unity:

$$\sum_i C_{ij} = 1. \tag{B1.1}$$

With q phases, we have q equations of type (B1.1) that reduce the number of independent variables from $cq+2$ to $cq+2-q$. In addition, the equilibrium of each species i between a pair of phases j and k is defined by an equilibrium constant K_{ijk}:

$$K_{ijk} = \frac{C_{ij}}{C_{ik}} \tag{B1.2}$$

which yields a set of $q-1$ independent equations for each species i. For c species, there are $c(q-1)$ equations of type (B1.2) that correspondingly reduce the number of independent variables. The final number n of independent variables defining the equilibrium state of the system is given by

$$n = cq+2-q-c(q-1) = c+2-q. \tag{B1.3}$$

$n=c+2-q$ is known as the phase rule. For a number c of species distributed among a number q of phases in equilibrium, the phase rule gives the number n of independent variables that determine the equilibrium state of the system.

when several species are involved, as we will see in Chapter 8 with a two-species phase diagram. The simple phase diagram for water is a useful introduction. The diagram is a 2-D representation of the (p_{H2O}, T) domain, which according to the phase rule defines the phase(s) of water at equilibrium. In general, a single phase is present at equilibrium, which means two degrees of freedom according to the phase rule. A pair of values (p_{H2O}, T) corresponding to any point in Figure 1-4 uniquely defines the phase of water present at equilibrium. For the gas phase to be present in equilibrium with a condensed phase, we need to have $p_{H2O} = p_{H2O,S}(T)$ as given by the Clausius–Clapeyron equation. This means that we have only one degree of freedom; if T is chosen, then $p_{H2O,S}$ is imposed and vice versa. This is represented by lines in Figure 1-4 (there is also a vertical line at 0°C representing equilibrium between liquid water and ice). Equilibrium between the three phases of gas, liquid, and ice ($q=3$) has zero degrees of freedom ($n=0$) and is called the triple point. It is uniquely specified as the point in the diagram where the lines intersect ($T=0$°C, $p_{H2O}=6.11$ hPa).

Also shown in Figure 1-4 is a thin line below 0°C that represents the metastable equilibrium between water vapor and liquid water. A metastable equilibrium is a condition where the system is stable but is not in its lowest energy state. Below 0°C, the lowest energy state of condensed water is ice. However, conversion of liquid water to ice does not actually happen

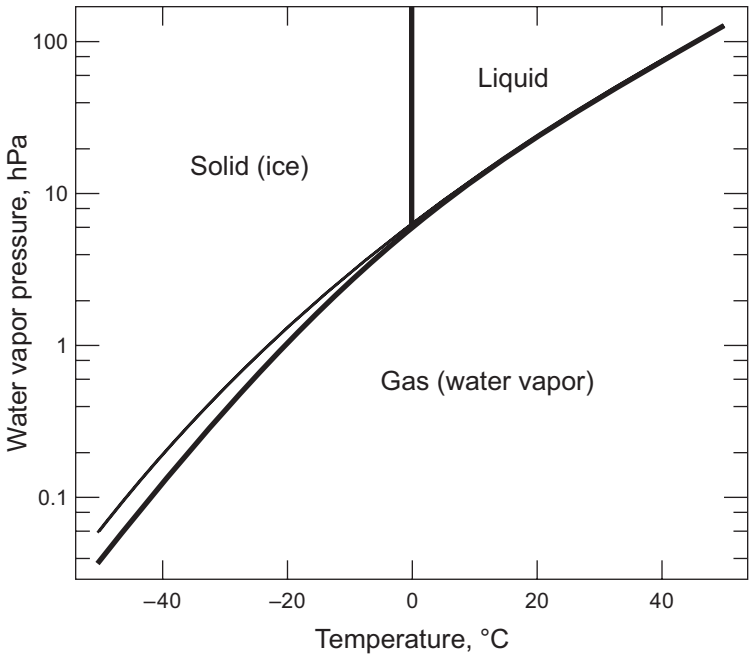


Figure 1-4. Phase diagram for water. The thin line is the saturation vapor pressure above supercooled liquid water. Note the log scale for the *y*-axis.

until temperatures much colder than 0°C unless there is a preexisting solid surface for ice crystals to form. Without a preexisting surface, the surface tension for the formation of an ice-liquid interface is an energy barrier that hinders ice formation. The way to understand surface tension is that, although bulk ice molecules below 0°C have a lower free energy than liquid water molecules, the ice molecules at the ice-liquid interface are not as tightly bound with the bulk and are therefore at a higher energy level. Producing this interface requires energy and this is what surface tension describes. Aerosol particles in a cloud provide surfaces for condensation of liquid water, but these surfaces are generally not suited for formation of ice crystals. Cloud droplets may therefore remain in a supercooled liquid state down to temperatures as low as –40°C. A familiar manifestation of this is the rime forming on objects in fog at subfreezing temperatures. The supercooled liquid fog droplets freeze instantly when brought in contact with surfaces.

It may be confusing that the phase diagram of water assumes water vapor to always be present as a nonzero p_{H2O} even though water vapor may not be a stable phase. Consider a situation where the pair of values (p_{H2O}, T) falls in the upper part of the diagram where liquid or ice is the stable phase. Water vapor will condense to form the stable phase, and as it does p_{H2O} will decrease. Eventually, the Clausius–Clapeyron line will be reached at which point no further net condensation will occur. Some water vapor is therefore always present at equiibrium.

Surface air is generally subsaturated, meaning that $p_{H2O} < p_{H2O,S}$ (when surface air is saturated, we have fog). This drives evaporation from the surface to the atmosphere. As air rises

in the atmosphere, it cools until it reaches the Clausius–Clapeyron line in the phase diagram. At that point a cloud forms. The cloud may eventually warm or mix with dry air and dissipate (90% of clouds dissipate), or it may grow and eventually produce precipitation. Precipitation returns water to the surface, closing the atmospheric water cycle.

Water vapor concentrations in weather reports are generally given as relative humidity (RH) or dew point (T_d). RH is the ratio of the water vapor pressure to the saturation vapor pressure at the local temperature, expressed as a percentage:

$$\mathrm{RH} = 100 \times \frac{p_{\mathrm{H2O}}}{p_{\mathrm{H2O},S}(T)}. \tag{1.35}$$

RH measures how far an air parcel is from saturation and thus how rapidly net evaporation from a wet surface can take place. At RH = 100%, we have $p_{\mathrm{H2O}} = p_{\mathrm{H2O},S}$ and there is no net evaporation; this is the situation shown in Figure 1-3. At RH = 50%, $p_{\mathrm{H2O}} = p_{\mathrm{H2O},S}/2$; for every two molecules leaving the surface there is only one returning, so rapid evaporation can take place. For a fixed p_{H2O}, RH increases with decreasing temperature following the Clausius–Clapeyron equation, eventually leading to cloud formation.

The dew point T_d is the temperature to which air of a given p_{H2O} needs to be cooled to be saturated with respect to liquid water:

$$p_{\mathrm{H2O}} = p_{\mathrm{H2O},S}(T_d). \tag{1.36}$$

It measures the potential for an air parcel to form a cloud by cooling. It also measures the ability of the human body, with a fixed temperature of 37°C, to cool by evaporation of sweat. At low temperatures one may report instead the frost point, defined as the temperature at which the air would be saturated with respect to ice.

Exercise 1.6 For an atmosphere with $p_{\mathrm{H2O}} = 10$ hPa and $T = 20$°C, what is the stable phase of water? What is the relative humidity? What is the dew point? Read the information from Figure 1-4.

Answer. From Figure 1-4 we see that the point ($p_{\mathrm{H2O}} = 10$ hPa, $T = 20$°C) lies in the domain where water vapor is the stable phase of water. By drawing a vertical line from the point up to the Clausius–Clapeyron equilibrium line, we find that the saturation vapor pressure is $p_{\mathrm{H2O},S} = 23$ hPa. The relative humidity is therefore $(10/23) \times 100 = 43\%$. By drawing a horizontal line from the point left to the intersection with the Clausius–Clapeyron line, we find a dew point $T_d = 7$°C.

1.7 Aerosol water and visibility

Aerosol particles often contain water even at RH < 100%. To understand this, consider our previous experiment of a pan of liquid water covered by a lid (Figure 1-3) and replace the pure liquid water with an A-H_2O solution, where A is a solute (Figure 1-5). Let x_{H2O} and x_{A} represent the mole fractions of H_2O and A in the solution. The sum of mole fractions must

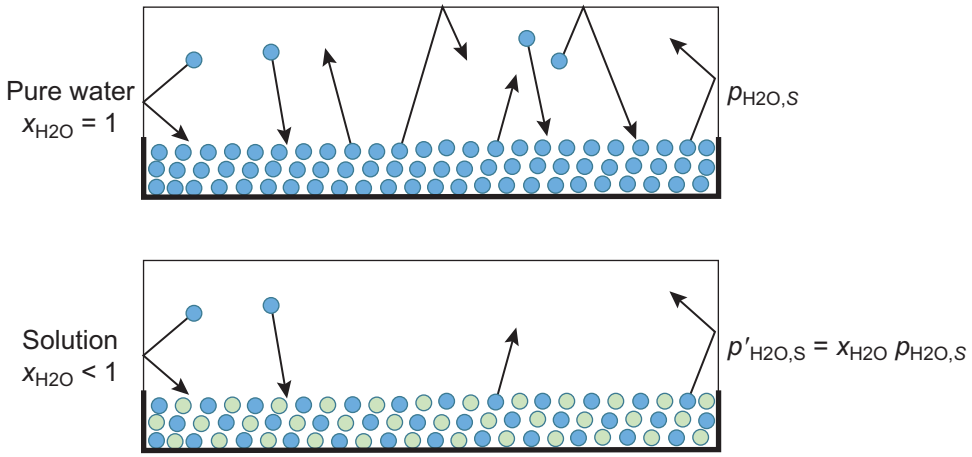


Figure 1-5. Saturation water vapor pressure over pure water (top) and over a water solution (bottom). Solute molecules are in green.

add up to 1, so $x_{H2O} + x_A = 1$. Water molecules occupy only a fraction x_{H2O} of the surface, therefore the evaporation rate from the pan is only a fraction x_{H2O} of what it would be for pure water. Once the H_2O molecules are in the head space, however, they return to the surface at the same rate as in the pure water case. As a result, the saturation water vapor pressure $p'_{H2O,S}$ over the solution is only a fraction x_{H2O} of the value $p_{H2O,S}$ over pure water:

$$p'_{H2O,S} = x_{H2O}\, p_{H2O,S}. \tag{1.37}$$

This is called Raoult's law. It applies to an ideal solution, where the properties of the water molecules are unaffected by the solute. This is an appropriate assumption for dilute solutions, but here we use it more broadly as an approximation.

Equation (1.37) implies that an aerosol particle can be in equilibrium as an aqueous solution at RH < 100% if it has a water mole fraction:

$$x_{H2O} = \frac{RH}{100}. \tag{1.38}$$

This requires that the aerosol component be able to dissolve in water to form an aqueous solution. Consider a solid aerosol compound with molecular composition A_aB_b dissolving in water following

$$A_aB_b(s) \rightleftarrows aA(aq) + bB(aq) \tag{1.39}$$

where (s) denotes the solid phase and (aq) denotes the aqueous phase. The solubility product constant K_s places an upper limit on the dissolved mole fractions:

$$x_A^a x_B^b \le K_s. \tag{1.40}$$

But this also needs to accommodate the H_2O mole fraction x_{H2O} set by equation (1.38), as well as the closure requirement that the sum of mole fractions adds up to 1:

$$\sum_i x_i = 1 \tag{1.41}$$

where the sum is over all the components of the solution. The closure requirement typically imposes an RH limit below which the solute cannot dissolve and the particle stays dry. We may therefore expect an aerosol particle to be dry at low RH and aqueous at high RH.

Consider as an example the uptake of water by a sea salt aerosol, assumed here to be pure NaCl. Dissolution of NaCl requires

$$x_{\mathrm{Na+}} x_{\mathrm{Cl-}} \leq K_s \tag{1.42}$$

with additional equations

$$x_{\mathrm{Na+}} + x_{\mathrm{Cl-}} + x_{\mathrm{H2O}} = 1 \tag{1.43}$$

$$x_{\mathrm{Na+}} = x_{\mathrm{Cl-}}. \tag{1.44}$$

Combining equations (1.42)–(1.44) with equation (1.38), we find that a sea salt aerosol is aqueous only if

$$\mathrm{RH} \geq 100(1 - 2\sqrt{K_s}) \tag{1.45}$$

which corresponds to a threshold relative humidity of 75%. This threshold is called the deliquescence point. At lower RH the sea salt aerosol is expected to be dry, although it may be in a metastable aqueous state.

Figure 1-6 shows the implications for the growth of an NaCl aerosol particle as a function of RH. At low RH the particle is dry. When the RH rises to reach the deliquescence point, the particle transitions abruptly from dry to aqueous and swells, as water now accounts for 75% of the molar content. As the RH continues to increase, the particle continues to grow. If from there the RH decreases below the deliquescence point, the particle may remain aqueous in metastable equilibrium due to surface tension limitations in forming the solid phase, in the same way that a cloud remains liquid at temperatures below 0°C. The particle may eventually dry out if the RH is pushed low enough and this is called efflorescence.

The RH-dependent uptake of water by aerosol particles has important implications for visibility because particles swollen by uptake of water scatter light over a larger cross section. Visibility is defined by the ability to detect the contrast in light between an object and its background. Particles in the line of sight of the object scatter light emitted by the object away from the observer, and surrounding particles scatter stray background light into the line of sight (Figure 1-7). Both types of scattering reduce visibility by decreasing the contrast between the object and its background. High RH may in this manner decrease visibility down to a few kilometers; this is the familiar phenomenon known as haze. A common misconception is that the decrease of visibility under hazy conditions is due to water vapor, but in fact water vapor is transparent at visible wavelengths. The decrease of visibility is due to particles swollen by uptake of water at high RH. This means that the decrease of visibility is more severe under polluted conditions where aerosol concentrations are high.

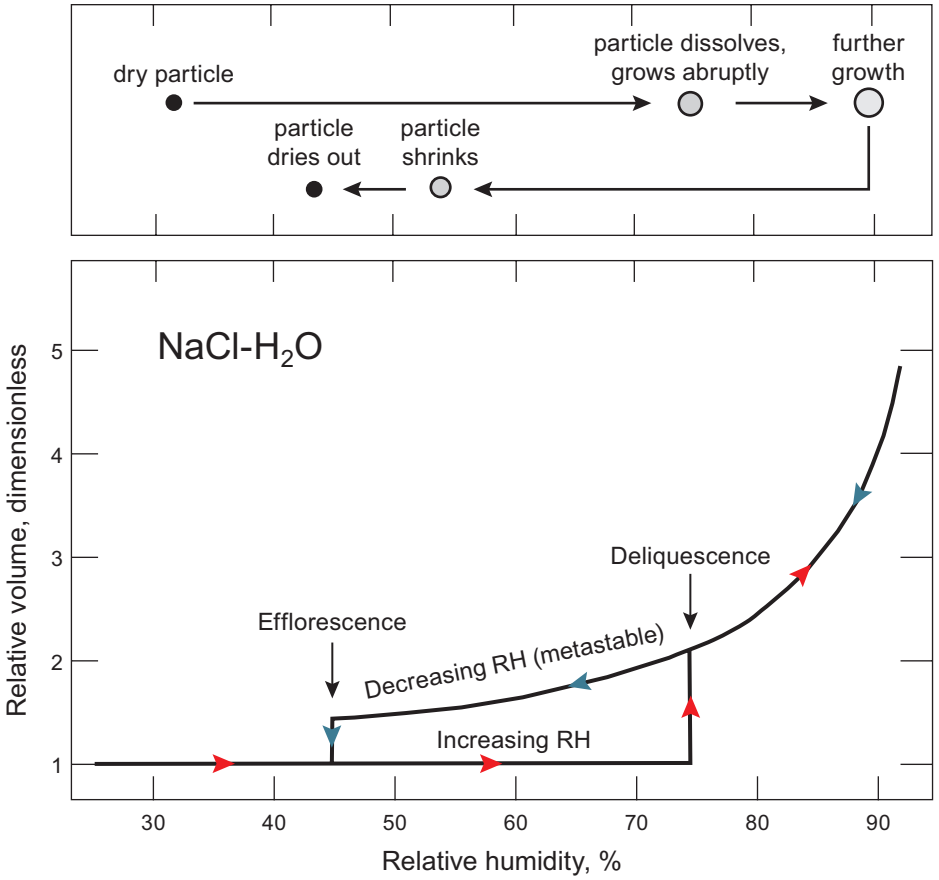


Figure 1-6. Growth of an NaCl aerosol particle by uptake of water as a function of relative humidity (RH). The red arrows track a path of increasing RH; the blue arrows track a path of decreasing RH. The growth curve features a hysteresis where an initially wet particle will remain wet in a metastable state below the deliquescence point and until the efflorescence point.

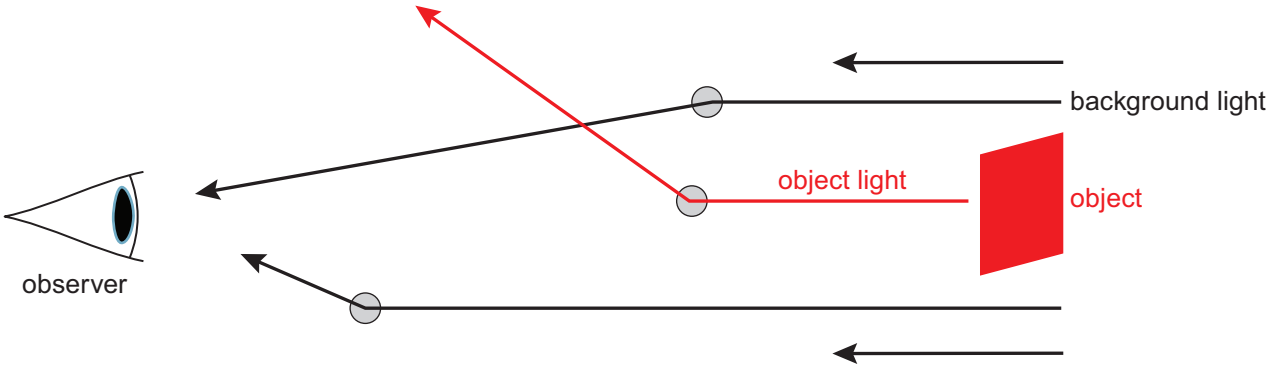


Figure 1-7. Decrease of visibility by aerosol particles. The particles decrease the ability of an observer to see an object by scattering light from the object out of the line of sight and by scattering background stray light into the line of sight.

Exercise 1.7 Visibility reduction by aerosol particles varies roughly as the cross-sectional area of the particles. What is the fractional increase in the cross-sectional area of water-soluble aerosol particles when RH increases from 90% to 95%? Assume that solute and water have the same molar volumes.

Answer. At 90% RH the particles are 90% molar water; at 95% RH they are 95% molar water. So at 90% RH the particles are nine molar parts water for one part solute; at 95% they are nineteen parts water for one part solute. Assuming the same molar volumes for solute and water, the volume of the particles doubles when RH rises from 90% to 95%. Since liquid particles are spherical (diameter D), the particle volume increases as D^3 and the cross-sectional area as D^2. So the cross-sectional area increases by a factor of $2^{2/3}$, or 59%, when the volume doubles. A small change of RH under hazy conditions has a big effect on visibility.

QUESTIONS AND PROBLEMS, CHAPTER 1

1.1 Questions

1. Molecular oxygen (O_2) has a constant mole fraction in the atmosphere. How would you expect its number density in surface air to vary between day and night? How would you expect its partial pressure in surface air to vary between day and night?

2. Is humid air lighter or heavier than dry air?

3. Give a rough order of magnitude for the number of molecules in an aerosol particle of 0.1 μm diameter.

4. Air quality standards place an upper limit on the acceptable mass concentration of $PM_{2.5}$ (particulate matter smaller than 2.5 μm diameter). For the aerosol size distribution in Figure 1-2, and if all particles have the same density, roughly what fraction of total aerosol mass is $PM_{2.5}$?

5. In an atmosphere with a fixed mole fraction of water vapor, what two processes can cause an increase in relative humidity?

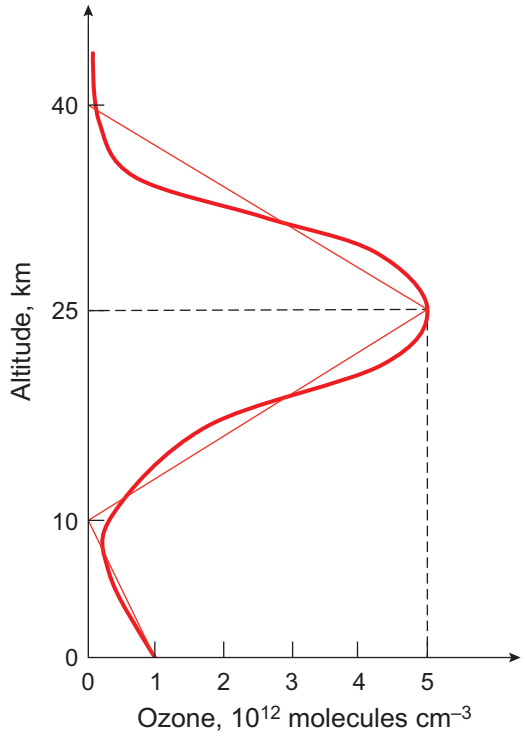
6. At a given temperature below freezing, and for a given total amount of water in an air parcel, will a cloud contain more condensed water if it is liquid or if it is ice?

7. We derived from the phase rule that the gas-liquid equilibrium of water has only one degree of freedom ($c=1$ and $q=2$ imply $n=1$), explaining why the saturation water vapor pressure depends only on temperature T. However, the actual atmosphere contains many chemical species other than water. Consider the H_2O-N_2-O_2 system; here we have $c=3$, and therefore gas-liquid equilibrium for water implies $n=3$ (three degrees of freedom). Is this inconsistent with the statement that the saturation water vapor pressure depends only on T?

8. At a given temperature, how does evaporation of water from the ocean depend on ocean salinity?

1.2 The ozone layer

The ozone layer peaks at about 25 km altitude in the stratosphere and protects the surface from UV radiation. But ozone in surface air is toxic, and the US air quality standard as of 2026 required that surface ozone not exceed 70 ppb. The figure below shows a typical vertical profile of ozone number density as the thick solid line. Read values off that figure for what follows.



1. Calculate the mole fraction of ozone at the peak of the ozone layer ($z = 25$ km; $p = 35$ hPa; $T = 220$ K). Would it exceed the US air quality standard if found in surface air? (It's good that the ozone layer is up in the stratosphere and not at the surface!)

2. Calculate the mole fraction of ozone in surface air ($z = 0$ km; $p = 1000$ hPa; $T = 300$ K). Is it in compliance with the US air quality standard? Notice that the relative decrease in the ozone mole fraction between 25 km and the surface is considerably larger than the relative decrease in number density. Why is this?

3. The ozone column determines the efficiency with which the ozone layer prevents solar UV radiation from reaching the Earth's surface. Estimate the ozone column by approximating the profile with the piecewise linear function shown as the thin solid line. You should find a value of 8.0×10^{18} molecules cm^{-2}.

4. Consider harmful UV radiation for which ozone has an absorption cross section of $\sigma_{O3} = 5 \times 10^{-19}$ cm^2 molecule^{-1}. For a solar zenith angle of 30°, show that 99% of this radiation is absorbed by the ozone layer before it reaches the ground.

5. To illustrate how thin the ozone layer is, imagine that all the ozone in the atmospheric column was brought to sea level as a layer of pure ozone gas under standard conditions of temperature and pressure (1000 hPa, 273 K). Calculate the thickness of this layer. You should find a value of 3.0 mm.

1.3 Gravitational settling of particles

The gravitational settling velocity v (cm s^{-1}) of an aerosol particle is proportional to the square of its diameter, D: $v = kD^2$, where k is a constant. Assuming that all particles have the same density ρ, derive an expression for the total aerosol gravitational settling flux F (kg m^{-2} s^{-1}) as a function of the number size distribution function n_N. From Figure 1-2, roughly which size range of particles contributes most to the gravitational settling flux?

1.4 Phase partitioning of water in a cloud

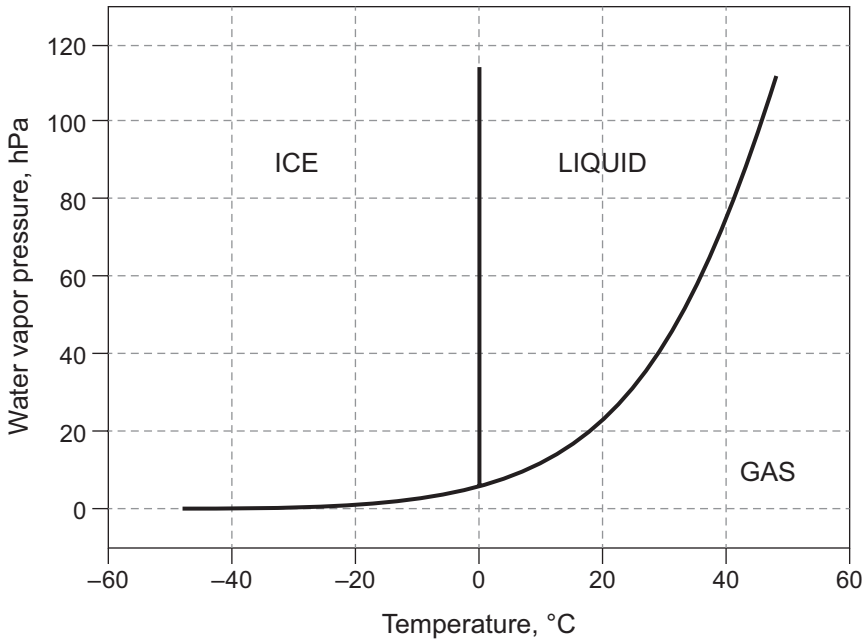
What is the mass concentration of water vapor (g H_2O per m^3 of air) in a liquid water cloud at a temperature of 273 K? Cloud liquid water contents are usually in the range of 0.1–1 g m^{-3}. Is most of the water in the cloud present as vapor or as liquid?

1.5 Seeing your breath

On cold days you can see your breath—let's understand why, using the phase diagram of water. The figure below shows the phase diagram with water vapor pressure on a linear scale, unlike in Figure 1-4 where it is on a log scale. Your breath is at 37°C and 100% RH when it leaves your mouth (make this point A on the diagram). It mixes with outside air of a certain temperature and RH (make this point B on the diagram). Let f be the fraction of outside air mixed into your breath plume, gradually increasing from $f = 0$ at your mouth (point A) to $f = 1$ when the plume has totally dissipated (point B). We have in the plume

$$T = fT_B + (1-f)T_A$$
$$p_{H2O} = fp_{H2O,B} + (1-f)p_{H2O,A}$$

where T is temperature and p_{H2O} is water vapor pressure. Show on the phase diagram the range of values for point B that would lead to cloud formation in the breath plume. Explain why it is important to use the phase diagram in linear scale (as opposed to log scale) for this analysis. Briefly discuss your result in terms of the atmospheric conditions conducive to seeing your breath.



1.6 Dew point during heat waves

Consider a severe heat wave with a midday temperature of 40°C and 50% RH, dropping at night to 30°C and 80% RH. Use equation (1.34) or a lookup table for the temperature dependence of the saturation water vapor pressure.

1. Calculate the dew points at midday and at night. Explain why the dew point varies less between day and night than the RH.

2. The human body is at a relatively constant temperature of 37°C. Explain why the dew point is a more relevant metric than RH in determining our ability to cool off by evaporating sweat.

3. Consider now a 2°C increase in the heat wave temperature, keeping RH the same. By how much does the dew point change? Does cooling by evaporating sweat become more difficult?

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