Thermal Physics of the Atmosphere

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Thermal Physics
of the Atmosphere
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Preface

This book grew out of the notes for a masters level course in atmospheric physics at the Department of Meteorology at the University of Reading. The course and the book have evolved in parallel with the desire to provide a more explicit and straightforward link between classical thermodynamics, as taught in university physics departments, and thermal physics, as presented in the atmospheric science literature.

In this book we cover the key thermal physics aspects of atmospheric science from a mainstream thermodynamics point of view. It could be argued that there is no such thing as mainstream thermodynamics. Indeed, not many branches of physics invite such heated debates as thermodynamics. Here we ignore those often metaphysical debates and build on classical techniques of thermodynamics as described in many excellent texts. In particular, the text by C. J. Adkins\(^1\) has influenced my view on thermodynamics and its imprint can be found throughout this book.

Atmospheric science is characterized by the inclusion of gravity and vertical structure, the importance of phase transitions in mixtures of air and water, the peculiar physics of droplet formation, the transfer of radiation through deep, inhomogeneous layers of atmosphere, and the lack of thermodynamic equilibrium in the atmosphere as a whole. This pushes the subject well beyond the traditional boundaries of thermodynamics. Hence the use of the words ‘thermal physics’ in the title, with a nod to the classical text by Kittel and Kroemer\(^2\).

The book is aimed at graduate, or advanced undergraduate level students. Students must be thoroughly at ease with the use of calculus, in particular partial differentiation, and, in the case of Chapter 10, vector calculus and fluid mechanics. There are two introductory chapters on ideal gases and the laws of thermodynamics but they do not present a comprehensive discussion of the fundamental laws of thermodynamics. There are many excellent textbooks available that cover these subjects in more detail.

The first five chapters contain the fundamentals of atmospheric thermal physics, presented largely as a linear narrative. The final five chapters may be


viewed as individual applications, although in each of them additional physics is introduced. Black arrows are used to indicate key equations throughout.

In our case, this text provides the background material for a one trimester masters-level course, but it contains more material than could be covered in such a period. Just by historical precedent, we normally exclude sections 2.4–2.6, 3.4, 3.7, 4.5, 4.6, 5.4, 7.4, 9.7–9.9, and Chapters 8 and 10. The problems at the end of each chapter often invite extensions and elaborations on theoretical ideas in the main text. The problems can be open-ended and may require numerical solution. In our own tutorials we add many hands-on exercises to help students get to grips with the basics and get a feeling for the typical values and ranges of variables.

The depth of the subject of atmospheric thermal physics is only revealed when we start to discover the many links that it provides between apparently distant fields of enquiry. To this end, the book contains a selection of subjects that goes beyond the traditional utilitarian set that is normally associated with atmospheric science. I hope that the reader looks kindly on this, perhaps occasionally flawed, attempt to convey this deep beauty.

I received substantial help through discussions, proofreading, and course development from Suzanne Gray, David Grimes, Giles Harrison, Keith Shine, and Remi Tailléux. Many students and colleagues have contributed by asking questions and suggesting improvements in the material. I thank all of them.

M. AMBAUM
Reading, September 2009
Useful data

**Universal constants:**

- Boltzmann constant \( k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} \)
- Avogadro number \( N_A = 6.022 \times 10^{23} \)
- Universal gas constant \( R^* = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \)
- Planck constant \( h = 6.626 \times 10^{-34} \text{ J s} \)
- Speed of light \( c = 2.998 \times 10^8 \text{ m s}^{-1} \)
- Stefan–Boltzmann constant \( \sigma = 5.670 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \)
- Permittivity of vacuum \( \epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1} \)
- Elementary charge \( e = 1.602 \times 10^{-19} \text{ C} \)

**Dry air properties:**

- Effective molar mass \( \mu_d = 29.0 \text{ g mol}^{-1} \)
- Specific gas constant \( R, R_d = 287 \text{ J kg}^{-1} \text{ K}^{-1} \)
- Specific heat at constant pressure \( c_p, c_{pd} = 1004 \text{ J kg}^{-1} \text{ K}^{-1} \)

**Water properties** (temperature dependent properties determined at 0°C):

- Molar mass \( \mu_v = 18.015 \text{ g mol}^{-1} \)
- Specific gas constant \( R_v = 461.5 \text{ J kg}^{-1} \text{ K}^{-1} \)
- Specific heat at constant pressure (vapour) \( c_{pv} = 1859 \text{ J kg}^{-1} \text{ K}^{-1} \)
- Specific heat at constant pressure (liquid) \( c_{pl} = 4218 \text{ J kg}^{-1} \text{ K}^{-1} \)
- Specific heat at constant pressure (solid) \( c_{ps} = 2050 \text{ J kg}^{-1} \text{ K}^{-1} \)
- Enthalpy of vaporization \( L = 2.501 \times 10^6 \text{ J kg}^{-1} \)
- Enthalpy of fusion \( L_f = 0.334 \times 10^6 \text{ J kg}^{-1} \)
- Enthalpy of sublimation \( L + L_f = 2.835 \times 10^6 \text{ J kg}^{-1} \)
- Surface tension \( \gamma = 75.6 \times 10^{-3} \text{ N m}^{-1} \)

**Other useful data:**

- Standard pressure \( = 101325 \text{ Pa} \)
- Standard temperature \( = 15^\circ \text{ C} = 288.15 \text{ K} \)
- Acceleration of gravity (Earth surface) \( g_0 = 9.81 \text{ m s}^{-2} \)
- Earth: mean radius \( R_E = 6.371 \times 10^6 \text{ m} \)
- Earth: mean orbital radius \( r_E = 149.5 \times 10^9 \text{ m} \)
- Earth: orbital eccentricity \( e = 0.0167 \)
- Sun: radius \( R_S = 696 \times 10^6 \text{ m} \)
1

Ideal gases

In this chapter we introduce the concept of an ideal gas, a gas of non-interacting molecules. An ideal gas is an accurate model of dilute gases such as the atmosphere.

We further introduce the notion of macroscopic variables, amongst them such familiar ones as temperature or pressure. These macroscopic variables must be related to some property of the microscopic state of the molecules that make up the substance. For example, for the systems we consider here, temperature is related to the mean kinetic energy of the molecules. The linking of the macroscopic and microscopic worlds is the subject of statistical mechanics. In this chapter we give an elementary application of it to ideal gases.

1.1 THERMODYNAMIC VARIABLES

Consider a volume of gas. A useful mental picture is that of a gas in a closed cylinder with a piston, similar to the driving cylinder of a steam engine, see Figure 1.1. In this way we can control certain properties of the gas, such as its volume or temperature, and perform experiments on it. Such experiments are normally thought experiments, although in principle they can be performed in the laboratory.

At the macroscopic level, the gas has some familiar properties:

- volume \( V \) (units: \( \text{m}^3 \))
- mass \( M \) (units: \( \text{kg} \))
- density \( \rho = M/V \) (units: \( \text{kg m}^{-3} \))
- temperature \( T \) (units: K, Kelvin)
- pressure \( p \) (units: \( \text{Pa} = \text{N m}^{-2} \), Pascal).

The gas is made up of molecules with individual mass \( M_1 \), so the total mass of gas is

\[
M = NM_1,
\]

(1.1)
with $N$ the number of molecules. The number of molecules $N$ is often expressed as a multiple of the Avogadro number $N_A$,

$$N_A = 6.022 \times 10^{23}. \tag{1.2}$$

The Avogadro number is defined as the number of molecules in 12 g of carbon-12. The number of molecules is then defined as a multiple $n$ of $N_A$

$$N = nN_A, \tag{1.3}$$

where $n$ is the number of moles. With this definition of the mol, the mass of the gas can be written as

$$M = n \mu \tag{1.4}$$

with $\mu = N_A M_1$ the molar mass. So the molar mass of carbon-12 is by definition precisely 12 g mol$^{-1}$.

The temperature can be defined as ‘that property which can be measured with a thermometer’. This definition sounds circular but it can be shown to be a perfectly valid definition. The SI unit$^3$ for temperature is the Kelvin (K). Temperature is often denoted in degrees Celsius, °C with $T(\degree C) = T(K) - 273.15$, or in degrees Fahrenheit, °F with $T(\degree F) = 1.8T(\degree C) + 32$, see Figure 1.2. Temperature can never be lower than 0 K, or absolute zero; the temperature in Kelvin is also called the absolute temperature.

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$^3$SI stands for Système International d’Unités, the internationally agreed system of units for physical quantities.
1.1 THERMODYNAMIC VARIABLES

Figure 1.3 illustrates the typical mean temperatures encountered through the depth of the Earth’s atmosphere. This figure uses the logarithm of pressure as a vertical coordinate because this is approximately proportional to the geometric height in the atmosphere.

Pressure is the force a gas exerts on its bounding walls per unit area. This does not mean that gas only has a pressure defined at the bounding walls: the internal pressure of a gas can in principle be measured by inserting some probe and measuring the force per unit area on the probe. There are several units of pressure in use, each with its specific area of application. The SI unit for pressure is the Pascal (Pa) which is equivalent to one Newton per square metre. In atmospheric applications we normally use the hectoPascal (hPa; by definition, 1 hPa = 100 Pa) or millibar (mbar; with 1 mbar = 1 hPa).

Pressure and temperature do not correspond to a property of individual molecules. They are bulk properties that can only be defined as a statistical property of a large number of molecules. This will be discussed in the next section.

There are several other macroscopic variables that can be used to describe the state of a simple gas; these are known as thermodynamic variables. If we know all the relevant thermodynamic variables, we know the full thermodynamic state of the gas. All these variables are interrelated and it turns out that for a simple substance (a substance with a fixed composition, such as dry air) we only need two thermodynamic variables to describe the whole thermodynamic state.\(^4\)

For more complex systems we need more variables. For example, in a mixture of varying composition we need to know the concentrations of the constituents. Moist air is such a mixture. The number of water molecules in the air is highly variable and these variations need to be taken into account. For sea water, on the other hand, we need to know the salinity – the quantity of dissolved salts – because it has important consequences for the density. Finally, for cloud drops we need to know the surface area as well as the amount of dissolved solute, both of which have profound consequences for the thermodynamics of the drops.

Thermodynamic variables are either:

- **extensive**, proportional to the mass of the system
- **intensive**, independent of the mass of the system.

Volume and mass are extensive variables, temperature and density are intensive variables. For most variables it is obvious whether they are extensive or intensive.

\(^4\)The number \(\mathcal{N}\) of thermodynamic variables required to define the state of any system is given by the Gibbs’ phase rule,

\[ \mathcal{N} = 2 + C - P, \]

with \(C\) the number of independent constituents and \(P\) the number of coexisting phases (gas, liquid, solid) in the system.
Going up in altitude, the temperature first decreases (troposphere), increases (stratosphere), and then decreases (mesosphere). The mesosphere ends at about 90 km altitude, above which the temperature starts to increase again (thermosphere). These atmospheric layers are separated by the tropopause, stratopause, and mesopause, respectively. The temperature increase in the stratosphere is due to the photo-dissociation of ozone, which
Extensive variables can be divided by the mass of the system to become intensive; such new variables are then called specific variables. Specific and extensive variables are usually denoted by the same letter, but with the specific variable written in lower case and its extensive equivalent in upper. For example, the volume $V$ of a system divided by the mass $M$ of the system becomes the specific volume $v$ with $v = V/M$. Note that

$$v = 1/\rho,$$  \hspace{1cm} (1.5)

where $\rho$ is the density. Later we will come across other extensive variables. For example, the entropy $S$ of a system is an extensive variable, so we can define $s = S/M$ as the specific entropy. Although temperature $T$ is an intensive variable it is normally denoted by an upper case letter, a convention we adopt here as well.

We have ignored internal variations in the volume of gas or material under consideration. For example, we assume there is no internal macroscopic motion of the gas, which would be associated with pressure variations and internal kinetic energy. Clearly this is not the case for the atmosphere as a whole. The pressure and density vary enormously through the atmosphere, usually most dramatically in the vertical: at 10 km height the pressure is about a quarter of its surface value. Indeed, such variations are the source of all atmospheric motion.

We assume that we can define the intensive thermodynamic variables locally and that they have their usual equilibrium thermodynamic relations. We then say that the gas is in local thermodynamic equilibrium. Local thermodynamic equilibrium is valid if there is a large separation between the spatial and temporal scales of macroscopic variations and those of microscopic variations. The spatial scale of macroscopic variations needs to be much larger than the mean free path of molecules, the mean distance a molecule travels between collisions with other molecules. The temporal scale of macroscopic variations needs to be much larger than the mean time between molecular collisions. Near the Earth’s surface the mean free path in the atmosphere is

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**Figure 1.3 (continued)** absorbs the solar energy in the UV part of the spectrum (wavelengths shorter than about 320 nm). Indeed, the ozone itself is formed by photodissociation of molecular oxygen, which occurs at wavelengths shorter than 240 nm. The maximum ozone concentration (‘the ozone-layer’) is at about 25 km altitude.

It is of note that the temperature in the troposphere is at its maximum in the tropics, while in the stratosphere it is at a maximum in the summer hemisphere and a minimum in the winter hemisphere. This latitudinal temperature gradient is reversed in the mesosphere. Note also that the tropopause is coldest and highest in the tropics.

The thermosphere (outside this plot) is heated by absorption of UV radiation and subsequent ionization of the molecular constituents, thus forming the ionosphere. At these altitudes the density is so low that energy does not get thermalized effectively and local thermodynamic equilibrium is not fully attained. The thermosphere gives way to space in the exosphere.
about 0.1 μm (about 30 times the average molecular distance) with typical molecular velocities of several hundreds of metres per second, so local thermodynamic equilibrium is satisfied. It turns out that above about 100 km height, local thermodynamic equilibrium breaks down.

A small volume of gas in the atmosphere, for which the internal motion can be ignored and which has well-defined density, temperature, and so on, is called an air parcel. Because an air parcel is, by definition, in local thermodynamic equilibrium, its thermodynamic variables satisfy all the relationships that are found in equilibrium systems. At the level of an air parcel we need not worry about non-equilibrium effects.

### 1.2 MICROSCOPIC VIEWPOINT

From the microscopic viewpoint, temperature is defined as the average kinetic energy of the molecules,

\[
\frac{3}{2} k_B T = \left\langle \frac{1}{2} M \nu_x^2 \right\rangle + \left\langle \frac{1}{2} M \nu_y^2 \right\rangle + \left\langle \frac{1}{2} M \nu_z^2 \right\rangle,
\]

with \((\nu_x, \nu_y, \nu_z)\) the three-dimensional vector velocity of the molecule. The brackets \(\langle \ldots \rangle\) denote the average, a time average for a single molecule, the average over all molecules, or the average over an ensemble of gases in the same macroscopic state. A key assumption of statistical mechanics is that all these averages lead to the same result. The constant \(k_B\) is the Boltzmann constant,

\[
k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}. \tag{1.7}
\]

In statistical physics as well as macroscopic thermodynamics, energy is the fundamental quantity. Temperature is a derived quantity which has been given its own units because it is measured with a thermometer. The Boltzmann constant is merely a proportionality constant between energy and absolute temperature. The fundamental point is that statistical mechanics can be formulated such that the microscopic definition of temperature in terms of the mean kinetic energy of the molecules corresponds to the thermodynamic definition of temperature.

The factor 3/2 in the microscopic definition of temperature reflects a classic result in the mechanics of systems with many components, namely that each degree of freedom contains, on average, the same energy. A degree of freedom is an independent variable in which the system can vary. A single molecule carries three translational degrees of freedom: motion in the \(x\), \(y\), and \(z\)-directions. There can also be internal degrees of freedom corresponding to rotations and vibrations of the molecule. The equipartition theorem states that each accessible degree of freedom\(^5\) carries on average the same energy,

\(^5\)Not all available degrees are necessarily accessible. Quantization of energy levels implies that there is a minimum energy required to excite any degree of freedom.
and this energy equals $k_B T/2$. Adding the average kinetic energies in the three spatial directions then gives the result of Eq. 1.6.

Pressure is the result of many collisions of individual molecules against the walls of a vessel or a probe. If a molecule approaches the wall with a velocity $\mathcal{U}$ and elastically collides with the wall, then the molecule’s momentum in the direction of the wall changes by $2M_1 \mathcal{U}$, from $M_1 \mathcal{U}$ to $-M_1 \mathcal{U}$. This momentum is transferred to the wall. By Newton’s laws, the amount of momentum transferred per unit time is the force on the wall, see Figure 1.4. For an interior point we can define the local pressure as the momentum flux density through some imaginary surface in the interior of the fluid.

So how many molecules collide with the wall? Let the number density of molecules, that is the number of molecules per unit volume, be denoted with $\tilde{n}$. We can now write the number density of molecules with $x$-velocities between $\mathcal{U}$ and $\mathcal{U} + d\mathcal{U}$ as $\tilde{n}_x$, which is related to the total number density $\tilde{n}$ by

$$\tilde{n} = \int \tilde{n}_x \, d\mathcal{U}. \tag{1.8}$$

Over a time $\delta t$, those molecules with positive velocity between $\mathcal{U}$ and $\mathcal{U} + d\mathcal{U}$ that are located within a distance $\mathcal{U} / \delta t$ of the wall will collide with the wall. Therefore, the number of such molecules that have collided with the wall will be $\tilde{n}_x / \mathcal{U} \, \delta t \, A$, with $A$ the area of the wall. To get the momentum transfer per unit time, simply multiply this number by the momentum transfer per molecule, $2M_1 \mathcal{U}$, and divide by the time taken, $\delta t$. This is the force $F_\mathcal{U}$ exerted on the wall by molecules with positive velocities between $\mathcal{U}$ and $\mathcal{U} + d\mathcal{U}$.

$$F_\mathcal{U} = 2\tilde{n}_x M_1 \mathcal{U}^2 A. \tag{1.9}$$

To find the total pressure we need to divide by $A$ and integrate the force over all positive velocities, that is to say those $\mathcal{U} > 0$, because molecules with negative velocities will not collide with the wall and thus will not contribute.
to the pressure,

\[ p = \int_{\mathcal{U}>0} 2\hat{n}_{\mathcal{U}} M_1 \mathcal{U}^2 \, d\mathcal{U}. \]  

(1.10)

By symmetry, there will be an equal number of molecules with positive and negative \( \mathcal{U} \). We can therefore integrate over all velocities \( \mathcal{U} \), positive and negative, and divide the result by two. The expression for the pressure then becomes

\[ p = \hat{n} \langle M_1 \mathcal{U}^2 \rangle, \]  

(1.11)

with \( \hat{n} \) the total number density. The equipartition theorem states that \( \langle M_1 \mathcal{U}^2 \rangle = k_B T \) so that the pressure satisfies

\[ pV = Nk_B T, \]  

(1.12)

where we have substituted \( \hat{n} = N/V \). This is the ideal gas law.

By writing the total number of molecules \( N \) as \( nN_A \), the ideal gas law can be written

\[ pV = nR^* T, \]  

(1.13)

where \( R^* \) is called the universal gas constant,

\[ R^* = N_A k_B = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}. \]  

(1.14)

Before the microscopic definitions of temperature and pressure were known, it was already hypothesized by Avogadro (and later confirmed to be true) that the constant \( R^* \) is the same for all types of gases.

Another form of the ideal gas law follows by dividing by the mass \( M = n\mu \) of the gas to find

\[ \rho v = RT, \text{ or } p = \rho RT, \]  

(1.15)

where \( R \) is the so-called specific gas constant,

\[ R = R^*/\mu. \]  

(1.16)

This is the form of the ideal gas law that is normally used in atmospheric science. Confusingly, the convention is to use a capital \( R \) for the specific gas constant even though it is a specific quantity. Note also that in most general physics literature the letter \( R \) stands for the universal gas constant; it should be clear from the context which is meant. This is one of those instances where the convention used in atmospheric science literature is not particularly helpful. Furthermore, the ideal gas law in the form of Eq. 1.13 is more general and more useful.
The ideal gas law encompasses:

- **Boyle’s law**: at constant temperature, the product of pressure and volume is constant

- **Gay-Lussac’s law**: at constant volume, the pressure of a gas is proportional to its temperature.

Figure 1.5 illustrates these laws in diagrams. These laws were originally determined experimentally. They are only strictly valid for ideal gases.

In deriving the ideal gas law, we have not considered subtleties such as inelastic collisions, where energy transfer between the gas and the wall occurs, or the consideration that the wall is not a mathematical flat plane but made up of molecules. These complications do not alter the basic result.

We have also not considered interactions between the molecules and interactions at a distance between the molecules and the wall. This does make a difference and it defines the difference between real gases and ideal gases. Ideal gases are made up of non-interacting molecules, vanishingly small molecules that are unaware of the presence of any other molecules.

We assume that molecules in an ideal gas do not interact with each other and also that the molecules are in thermal equilibrium. Strictly speaking these assumptions are inconsistent, as a gas can only achieve thermal equilibrium through many collisions between the molecules. The colliding molecules distribute the energy amongst all the accessible degrees of freedom and thus achieve equipartition. This process of energy distribution is called thermalization. A gas is in local thermodynamic equilibrium if all the available energy is thermalized. If collisions are rare, energy cannot be thermalized effectively and the gas cannot achieve local thermodynamic equilibrium. This occurs at high altitudes in the atmosphere (higher than, say, 100 km) where the energy input from radiation is not thermalized due to the low number of collisions.

The ideal gas law is an example of an equation of state. Real gases are not ideal and will therefore have a different relationship between pressure, density and temperature. For example, the equation of state for real gases is
more accurately described by \textit{van der Waals’ equation},

\[
    \left(p + a \left(\frac{n}{V}\right)^2\right) (V - nb) = nR^* T, \tag{1.17}
\]

with $a$ and $b$ constants that depend on the particular gas. The term $-nb$ represents the reduction in available volume due to the finite effective size of the molecules. The term $a(n/V)^2$ is related to the average interaction energy between molecules (which is why the term is quadratic in the number density) and it contributes as an effective pressure; the relation between pressure and energy density will be explained in Section 2.2, and a derivation of van der Waals’ equation will be presented in Section 3.4. Van der Waals’ equation is more accurate for gases at high densities, and approximately describes such important processes as phase transitions.

Densities of gases in the atmosphere are such that the ideal gas law gives essentially the same results as van der Waals’ equation, so we stick to the much simpler ideal gas law. Indeed, for low densities van der Waals’ equation reduces to the ideal gas law,

\[
    \text{Eq. 1.17} \rightarrow pV = nR^* T \quad \text{if } n/V \rightarrow 0. \tag{1.18}
\]

Conversely, for large pressures,

\[
    \text{Eq. 1.17} \rightarrow V = nb \quad \text{if } p \rightarrow \infty. \tag{1.19}
\]

So the high pressure, incompressible liquid is also a limiting case of van der Waals’ equation.

In general, an equation of state is some relationship between the variables of the system,

\[
    f(p, N, V, T, a_1, a_2, a_3, \ldots) = 0, \tag{1.20}
\]

where $a_1, a_2 \ldots$ represent any other variables that influence the state of the system, such as humidity in air, or salinity in water. The equation of state is dependent on the precise nature of the system and results derived using an equation of state are therefore only valid for that particular system. We will see that many of the results in this book are derived without reference to an equation of state and will therefore be valid for any substance.

\subsection*{1.3 Ideal Gas Mixtures}

Ideal gases are defined as gases where the molecules themselves have negligible volume and have negligible interactions with each other. So if we mix several ideal gases at the same temperature in a single volume they do not
‘feel’ each other’s presence. This means that each constituent gas contributes independently to the pressure. The contribution of each constituent to the total pressure is called the partial pressure. So \( n_i \) mols of constituent \( i \) will have a partial pressure \( p_i \) equal to:

\[
p_i = \frac{n_i R^* T}{V}.
\]

(1.21)

The fact that these partial pressures independently make up the total pressure of the mixture is called Dalton’s law:

\[
p = \sum_i p_i.
\]

(1.22)

Dalton’s law is only true for ideal gases. For real gases, partial pressures cannot be easily defined.

From Dalton’s law it follows that

\[
p = \sum_i \frac{n_i R^* T}{V} = \sum_i \frac{M}{V} \frac{n_i \mu_i}{M \mu_i} R^* T = \rho RT,
\]

where

\[
R = \frac{R^*}{\mu_e},
\]

(1.24)

with the effective molar mass \( \mu_e \) of the mixture defined as

\[
\frac{1}{\mu_e} = \sum_i \frac{c_i}{\mu_i},
\]

(1.25)

and \( c_i = n_i \mu_i / M \) the mass fraction of constituent \( i \) – that is, the fraction constituent \( i \) contributes to the total mass. Another way of interpreting this result is that the specific gas constant \( R \) of the mixture is the weighted mean of the specific gas constant of the pure constituents \( R_i = R^* / \mu_i \), that is,

\[
R = \sum_i c_i R_i.
\]

(1.26)

Table 1.1 lists the main constituents of air. The dry air constituents are well mixed and long-lived which means that the bulk composition of dry air is fixed throughout the atmosphere up to very high altitudes. There is a long-term upward trend in CO\(_2\) concentration over time due to human activity but this has only a minor effect on the ideal gas properties of dry air, see Figure 1.6. However, the CO\(_2\) trend does have a profound effect on the radiative properties of the air and it is the main agent of human-induced climate change.
### Table 1.1 Main constituents of air.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Molar mass, $\mu$ (g mol$^{-1}$)</th>
<th>Mass fraction, $c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$</td>
<td>28.02</td>
<td>0.755</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>32.00</td>
<td>0.231</td>
</tr>
<tr>
<td>Ar</td>
<td>39.93</td>
<td>0.013</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>44.01</td>
<td>$\sim 0.0006$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>18.02</td>
<td>0 to $\sim 0.03$</td>
</tr>
</tbody>
</table>

Using the numbers in Table 1.1 it is straightforward to verify that the effective molar mass $\mu_d$ for dry air is

$$\mu_d = 29.0 \text{ g mol}^{-1}$$

(1.27)

and the specific gas constant $R$ for dry air is

$$R = 287 \text{ J kg}^{-1} \text{ K}^{-1}.$$  \hspace{1cm} (1.28)

This value of $R$ can be used in the ideal gas law, Eq. 1.15, which then relates the pressure, density, and temperature for dry air. Figure 1.7 is a nomogram expressing this relation graphically.

Now we can also calculate the effect of water vapour on the ideal gas law. The amount of water vapour in the air can be quantified by its mass fraction $c$. For dry air, this fraction is zero, but as the air becomes more humid, the fraction increases.

![Figure 1.6](image-url) Mass fraction (left axis, in parts per million) and molar mixing ratio (right axis, in parts per million) of CO$_2$ as measured at Mauna Loa Observatory, Hawaii. Inset: mean annual cycle of CO$_2$, scales as main graph. This annual cycle is dominated by vegetation growth and resulting CO$_2$ capture in the Northern Hemisphere summer. Data from Tans, P. P. *Trends in Atmospheric Carbon Dioxide - Mauna Loa*. Available from: www.esrl.noaa.gov/gmd/ccgg/trends/. See also Keeling, C. D. et al. (1976) *Tellus* 28, 538–551.