# Chapter 12
# Kinetic Theory of Gases: Equipartition of Energy and Ideal Gas Law

## 12.1 Introduction

### Macroscopic Description of Gas

A gas is a system of particles occupying a volume of space that is very large compared to size ($10^{-10}$ m) of any typical atom or molecule. The state of the gas can be described by a few macroscopically measurable quantities that completely determine the system. The volume of the gas in a container can be measured by the size the container. The pressure of a gas can be measured using a pressure gauge. The temperature can be measured with a thermometer. The mass, or number of moles or number of molecules, can measure the quantity of matter.

### Atomistic Description of Gas

A gas consists of a very large number of particles (typically$10^{24}$ or many orders of magnitude more). Each atomic particle can be specified by its position and velocity.

### Macroscopic vs. Atomistic Description

How can we use the laws of mechanics that describe the motions and interactions of individual atomic particles to predict macroscopic properties of the system such as pressure, volume, and temperature? We cannot know exactly where and with what velocities all the particles are moving so we must take averages. In addition, we need quantum mechanical laws to describe how particles interact. In fact, the inability of classical mechanics to predict how the heat capacity of a gas varies with temperature was the first experimental suggestion that a new set of principles (quantum mechanics) operates at the scale of the size of atoms. However, as a starting point we shall use classical mechanics to deduce the ideal gas law, with only a minimum of additional assumptions about the internal energy of a gas.

### Atoms, Moles, and Avogadro’s Number

The atomic mass of one neutral carbon-12 atom is defined to be exactly 12 atomic mass units (12 u). By definition one mole of carbon atoms has mass equal to exactly 12 grams. The results of many experiments have determined that there are $6.022\times10^{23}$ molecules in one mole of carbon 12 atoms. The number of molecules per mole is called the Avogadro constant,

$$N_A = 6.0221415\times10^{23}\cdot\text{mol}^{-1}. \qquad (12.1.1)$$

(For the latest, more precise values of this and other physical constants, see the Particle Data Group’s list at http://pdg.lbl.gov/2006/reviews/consrpp.pdf)

## 12.2 Temperature and Thermal Equilibrium

On a cold winter day, suppose you want to warm up by drinking a cup of tea. You start by filling up a kettle with water from the cold water tap (water heaters tends to add unpleasant contaminants and reduce the oxygen level in the water). You place the kettle on the heating element of the stove and allow the water to boil briefly. You let the water cool down slightly to avoid burning the tea leaves or creating bitter flavors and then pour the water into a pre-heated teapot containing a few teaspoons of tea; the tea leaves steep for a few minutes and then you enjoy your drink.

When the kettle is in contact with the heating element of the stove, energy flows from the heating element to the kettle and then to the water. The conduction of energy is due to the contact between the objects. The random motions of the atoms in the heating element are transferred to the kettle and water via collisions. We can attribute different degrees of "hotness" (based on our experience of inadvertently touching the kettle and the water). Temperature is a measure of the "hotness" of a body. When two objects that are initially at different temperatures are put in contact, the "colder" object heats up while the "hotter" object cools down, until they reach the same temperature, a state we refer to as *thermal equilibrium*. Temperature is that property of a system that determines whether or not a system is in thermal equilibrium with other systems.

Consider two systems A and B that are separated from each other by an adiabatic boundary (*adiabatic = no heat passes through*) that does not allow any thermal contact. Both A and B are placed in thermal contact with a third system C until thermal equilibrium is reached. If the adiabatic boundary is then removed between A and B, no thermal energy will flow between A and B. Thus

> *Two systems in thermal equilibrium with a third system are in thermal equilibrium with each other.*

### Temperature Scales

Any device that measures a thermometric property of an object, for instance the expansion of mercury, is called a *thermometer*. Many different types of thermometers can be constructed, making use of different thermometric properties. Different devices will measure different temperatures.

The gas thermometer measures temperature based on the pressure of a gas at constant volume and is used as the standard thermometer, because the variations between different gases can be greatly reduced when low pressures are used. A schematic device of a gas thermometer is shown in Figure 12.1.

A thermometer needs to have two scale points, for example the height of the column of mercury (the height is a function of the pressure of the gas) when the bulb is placed in thermal equilibrium with ice water and in thermal equilibrium with standard steam.

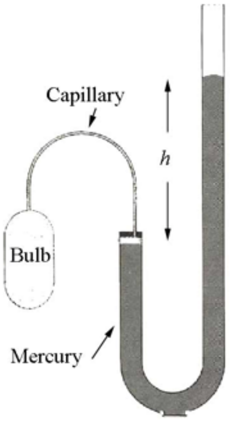

**Figure 12.1** Constant volume gas thermometer.

A linear scale for temperature can be drawn based on the pressure and is given by

$$T = a\,P + T_0 \tag{12.2.1}$$

where $a$ is some constant and $T_0 = 0$ is the temperature when the pressure is zero.

The thermal expansion of mercury was commonly used as the thermometric property because mercury has nearly uniform expansion when compared to gas-thermometer scale. Other materials show slight variation from uniform expansion.

At constant volume, and at ordinary temperatures, the pressure of gases is proportional to the temperature,

$$P \sim T \tag{12.2.2}$$

(note that the above necessitates using $T_0 = 0$).

The gas in the bulb exhibits a linear relationship between temperature and pressure. By this linearity, the ratio of temperatures between any two states of a system is then measured by the ratio of the pressures of those states,

$$\frac{T_1}{T_2} = \frac{P_1}{P_2}\,. \tag{12.2.3}$$

To determine a temperature scale (in order to fix the constant $a$ in Equation (12.2.1)), a standard state must be chosen as a reference point. The standard fixed state for thermometry is the *triple point of water*, the state in which ice, water, and water vapor coexist. This state occurs at only one definite value of temperature and pressure. By convention (1954) the temperature of the triple point of water to assigned to be exactly $273.16\,\mathrm{K}$ on the Kelvin scale, at a water-vapor pressure of $610\,\mathrm{Pa}$. (The SI unit for pressure is the pascal, $1\,\mathrm{Pa} = 1\,\mathrm{N}\cdot\mathrm{m}^{-2}$.)

Fix the constant $a$ as follows: Let $P_{\mathrm{TP}}$ be the value of the pressure $P$ at the triple point in the gas thermometer. Set the constant $a$ according to

$$a = \frac{273.16\ \mathrm{K}}{P_{\mathrm{TP}}} . \tag{12.2.4}$$

Hence the temperature at any value of $P$ is then

$$T(P) = a\,P = \frac{273.16\ \mathrm{K}}{P_{\mathrm{TP}}} P . \tag{12.2.5}$$

Different gases will have different values for the pressure $P$, hence different temperatures $T(P)$. When the pressure in the bulb at the triple point is gradually reduced to near zero, all gases approach the same pressure reading and hence the same temperature. The limit of the temperature $T(P)$ as $P_{\mathrm{TP}} \to 0$ is called the *ideal-gas temperature* and is given by the equation

$$T(P) = \lim_{P_{\mathrm{TP}} \to 0} \frac{273.16\,\mathrm{K}}{P_{\mathrm{TP}}} P . \tag{12.2.6}$$

This definition of temperature is independent of the type of gas used in the gas thermometer. The lowest possible temperatures measured in gas thermometers use ${}^{3}\mathrm{He}$, because this gas becomes a liquid at a lower temperature than any other gas. In this way, temperatures down to $0.5\,\mathrm{K}$ can be measured. We cannot yet define the temperature of absolute zero, $0\,\mathrm{K}$, using this approach.

The commonly used Celsius scale employs the same size for each degree as the Kelvin scale, but the zero point is shifted by $273.15$ degrees so that the triple point of water has a Celsius temperature of $0.01^{\circ}\mathrm{C}$,

$$T\left({}^{\circ}\mathrm{C}\right) = \theta\left(\mathrm{K}\right) - 273.15\,{}^{\circ}\mathrm{C}, \tag{12.2.7}$$

and the freezing point of water at standard atmospheric pressure is $0^{\circ}\mathrm{C}$. The Fahrenheit scale is related to the Celsius scale by

$$T\left({}^{\circ}\mathrm{F}\right) = \frac{9}{5} T\left({}^{\circ}\mathrm{C}\right) + 32^{\circ}\mathrm{F}. \tag{12.2.8}$$

The freezing point of pure water at standard atmospheric pressure occurs at $0^\circ\text{C}$ and $32^\circ\text{F}$. The boiling point of pure water at standard atmospheric pressure is $100^\circ\text{C}$ and $212^\circ\text{F}$.

## 12.3 Internal Energy of Gas

The internal energy of a gas is defined to be the total energy of the gas when the center of mass of the gas is at rest. The internal energy consists of the kinetic energy, $K$, of the center-of-mass motions of the molecules; the potential energy associated with the intermolecular interactions, $U_{\text{inter}}$; and the potential energy associated with the intramolecular interactions, $U_{\text{intra}}$;

$$E_{\text{internal}} = K + U_{\text{inter}} + U_{\text{intra}} . \tag{12.3.1}$$

Generally, the intermolecular force associated with the potential energy is repulsive for small $r$ and attractive for large $r$, where $r$ is the separation between molecules. At low temperatures, when the average kinetic energy is small, the molecules can form bound states with negative energy $E_{\text{internal}} < 0$ and condense into liquids or solids. The intermolecular forces act like restoring forces about an equilibrium distance between atoms, a distance at which the potential energy is a minimum. For energies near the potential minimum, the atoms vibrate like springs. For larger (but still negative) energies, the atoms still vibrate but no longer like springs and with larger amplitudes, undergoing thermal expansion. At higher temperatures, due to larger average kinetic energies, the internal energy becomes positive, $E_{\text{internal}} > 0$. In this case, molecules have enough energy to escape intermolecular forces and become a gas.

### Degrees of Freedom

Each individual gas molecule can translate in any spatial direction. In addition, the individual atoms can rotate about any axis. Multi-atomic gas molecules may undergo rotational motions associated with the structure of the molecule. Additionally, there may be intermolecular vibrational motion between nearby gas particles, and vibrational motion arising from intramolecular forces between atoms that form the molecules. Further, there may be more contributions to the internal energy due to the internal structure of the individual atoms. Any type of motion that contributes a quadratic in some generalized coordinate to the internal energy is called a *degree of freedom*. Examples include position, $(1/2)\,kx^2$, speed, $(1/2)\,mv^2$, or angular velocity for rotational motion, $(1/2)\,I\omega^2$ where $I$ is a *moment of inertia*, discussed in Chapter 13. A single atom can have three translational degrees of freedom and three rotational degrees of freedom, as well as internal degrees of freedom associated with its atomic structure.

According to our classical theory of the gas, all of these modes (translational, rotational, vibrational) should be equally occupied at all temperatures but in fact they are not. This important deviation from classical physics was historically the first instance where a more detailed model of the atom was seen to be needed to describe correctly the experimental observations.

Not all of the three rotational degrees of freedom contribute to the energy at all temperatures. As an example, a nitrogen molecule, $\mathrm{N}_2$, has three translational degrees of freedom but only two rotational degrees of freedom at temperatures lower than the temperature at which the diatomic molecule would dissociate. Diatomic nitrogen also has an intramolecular degree of freedom that does not contribute to the internal energy at room temperatures. As discussed in Section 12.6, $\mathrm{N}_2$ constitutes most ($\sim 78\%$) of the earth's atmosphere.

### Equipartition of Energy

We shall make our first assumption about how the internal energy distributes itself among $N$ gas molecules, as follows:

*Each independent degree of freedom has an equal amount of energy equal to* $(1/2)kT$,

where the constant $k$ is called the *Boltzmann constant* and is equal to

$$k = 1.3806505 \times 10^{-23}\ \mathrm{J \cdot K^{-1}} .$$

The total internal energy of the ideal gas is then

$$E_{\text{internal}} = N(\#\ \text{of degrees of freedom})\,\frac{1}{2}kT . \qquad (12.3.2)$$

This equal division of the energy is called the *equipartition of the energy***.** (12.3.3)

The Boltzmann constant is an arbitrary constant and fixes a choice of temperature scale. Its value is chosen such that the temperature scale in Equation (12.3.2) closely agrees with the temperature scales discussed in Section 12.2.

### 12.3.1 Example: Diatomic nitrogen gas

What is the internal energy of the diatomic $\mathrm{N}_2$ gas?

**Answer:** As discussed above, at high temperatures, but low enough for nitrogen to form diatomic molecules, there are six degrees of freedom, so

$$E_{\text{internal}} = N(\#\ \text{of degrees of freedom})\frac{1}{2}kT = 3N\,kT . \qquad (12.3.4)$$

At room temperature, the internal energy is due to only the five degrees of freedom associated with the three translational and two rotational degrees of freedom,

$$E_{\text{internal}} = N\frac{5}{2}kT\,. \tag{12.3.5}$$

## 12.4 Ideal Gas

Consider a gas consisting of a large number of molecules inside a rigid container. We shall assume that the volume occupied by the molecules is small compared to the volume occupied by the gas, that is, the volume of the container (dilute gas assumption). We also assume that the molecules move randomly and satisfy Newton's Laws of Motion. The gas molecules collide with each other and the walls of the container. We shall assume that all the collisions are instantaneous and any energy converted to potential energy during the collision is recoverable as kinetic energy after the collision is finished. Thus the collisions are elastic and have the effect of altering the direction of the velocities of the molecules but not their speeds. We also assume that the intermolecular interactions contribute negligibly to the internal energy.

### Monatomic Gas Internal Energy

An ideal monatomic gas atom has no internal structure, so we treat it as point particle. There are no possible rotational degrees of freedom or internal degrees of freedom; the ideal gas has only three degrees of freedom, and the internal energy of the ideal gas is

$$E_{\text{internal}} = N\frac{3}{2}kT\,. \tag{12.4.1}$$

Equation (12.4.1) is called the *thermal equation of state* of a monatomic ideal gas. The average kinetic energy of each ideal gas atom is then

$$\frac{1}{2}m\left(v^2\right)_{\text{ave}} = \frac{3}{2}kT \tag{12.4.2}$$

where $\left(v^2\right)_{\text{ave}}$ is the average of the square of the speeds. The temperature of this ideal gas is proportional to the average kinetic of the ideal gas molecule. It is an incorrect inference to say that temperature is defined as the mean kinetic energy of gas. At low temperatures or non-dilute densities, the kinetic energy is no longer proportional to the temperature. For some gases, the kinetic energy depends on number density and a more complicated dependence on temperature than that given in Equation (12.4.2).[1]

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[1] Ralph Baierlein, The meaning of Temperature, The Physics Teacher, Feb 1990, pp. 94-96.

## 12.5 Pressure of an Ideal Gas

Consider an ideal gas consisting of a large number $N$ of molecules inside a container of volume $V$ and pressure $P$. The gas molecules collide elastically with each other and the walls of the container. The pressure that the gas exerts on the container is due to the elastic collisions of the gas molecules with the walls of the container. We shall now use only the principles of conservation of energy and momentum to model collisions between the gas molecules and the walls of the container in order to determine the pressure of the gas in terms of the volume $V$, particle number $N$ and Kelvin temperature $T$.

We shall begin by considering the collision of one molecule with one of the walls of the container, oriented with a unit normal vector pointing out of the container in the positive $\hat{\mathbf{i}}$-direction (Figure 12.2). Suppose the molecule has mass $m$ and is moving with velocity $\vec{\mathbf{v}} = v_x\,\hat{\mathbf{i}} + v_y\,\hat{\mathbf{j}} + v_z\,\hat{\mathbf{k}}$. Since the collision with the wall is elastic, the $y$-and $z$-components of the velocity of the molecule do not change and the $x$-component of the velocity changes direction (Figure 12.2).

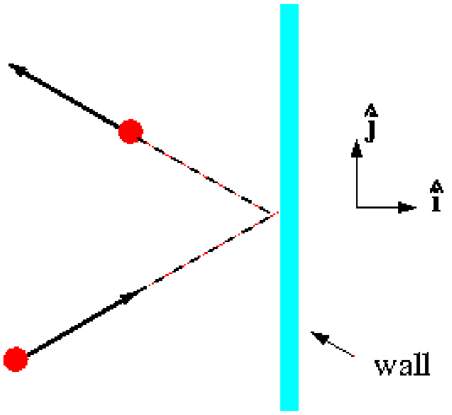


**Figure 12.2** Collision of a gas molecule with a wall of a container

The impulse that the wall delivers to the molecule is given by

$$\vec{\mathbf{F}}_{\text{molecule, wall}}\,\Delta t = \Delta\vec{\mathbf{p}} = -2mv_x\,\hat{\mathbf{i}}\,. \qquad (12.5.1)$$

We now consider the effect of the collisions of a large number of molecules with random motion. For our purposes, “random” will be taken to mean that any direction of motion is possible, and the distribution of velocity components is the same for each direction.

How many of the molecules will collide within a given area $A$ of the wall normal to the $x$-direction in some fixed time interval $\Delta t$? On average half the molecules have a positive $+x$-component of velocity. Therefore half the molecules contained inside a cylindrical volume of cross sectional area $A$ and length $v_x \Delta t$ will strike the wall within a given area $A$ during the time interval $\Delta t$ (note that in Figure 12.2 and Equation (12.5.1) $v_x > 0$). In Figure 12.3 each gas molecule is depicted with a speed equal to the magnitude of the $x$-component of the velocity. (Note that only the magnitude of the $x$-component of the average velocity matters because the same number of particles will enter and leave from the sides of the cylindrical body during the time interval $\Delta t$.) The mass density of gas molecules is $\rho$.

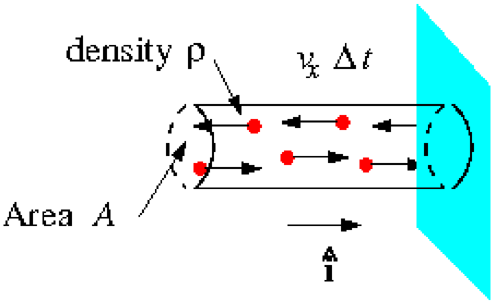


**Figure 12.3** Half the particles inside the cylinder that will hit the wall in a time interval $\Delta t$

The total mass of the molecules with positive $+x$-component of velocity contained in the cylinder is

$$m^{\text{total}} = \frac{\rho}{2} A v_x \Delta t \,. \tag{12.5.2}$$

Each one of these particles that strike the wall will change its $x$-component of the momentum by a factor $\Delta \vec{\mathbf{p}} = -2 m v_x \,\hat{\mathbf{i}}$ due to the collision. The total impulse that the wall exerts on the molecules in the tube is then

$$\begin{aligned} \vec{\mathbf{F}}_{\text{gas, wall}} \Delta t &= \Delta \vec{\mathbf{p}}^{\text{total}} = -2 m^{\text{total}} v_x \,\hat{\mathbf{i}} \\ &= -2\left(\frac{\rho}{2} A v_x \Delta t\right) v_x \,\hat{\mathbf{i}} = -\rho A v_x^2 \,\Delta t \,\hat{\mathbf{i}}. \end{aligned} \tag{12.5.3}$$

Therefore the force of the wall on the molecules is independent of the time interval $\Delta t$ and is given by

$$\vec{\mathbf{F}}_{\text{gas, wall}} = -\rho A v_x^2 \,\hat{\mathbf{i}} \,. \tag{12.5.4}$$

By Newton's Third Law, the force of the gas molecules on the wall is then

$$\vec{\mathbf{F}}_{\text{wall, gas}} = \rho A v_x^2 \,\hat{\mathbf{i}} . \qquad (12.5.5)$$

The pressure that the gas exerts on the wall is the magnitude of this force divided by the cross sectional area of the cylindrical tube,

$$P = \frac{\left|\vec{\mathbf{F}}_{\text{wall, gas}}\right|}{A} = \rho v_x^2 . \qquad (12.5.6)$$

At this point, we have to make the argument that the total pressure will be the same as that above, Equation (12.5.6), with the square of the $x$-component of the velocity replaced by the average of the square of the $x$-component of the velocity, $\left(v_x^2\right)_{\text{ave}}$. While this is not difficult to show, the derivation will not be part of these notes. The essential part of this derivation would be to describe "that contribution to the pressure due to the molecules with $x$-component of velocity $v_x$" and a similar contribution to the mass density.

From symmetry, the average square of the $x$-, $y$- and $z$-components of the velocity of the molecules are equal,

$$\left(v_x^2\right)_{\text{ave}} = \left(v_y^2\right)_{\text{ave}} = \left(v_z^2\right)_{\text{ave}} . \qquad (12.5.7)$$

Therefore the average square $\left(v^2\right)_{\text{ave}}$ of the velocity is equal to the sum of the average of the squares of the components,

$$\left(v^2\right)_{\text{ave}} = \left(v_x^2\right)_{\text{ave}} + \left(v_y^2\right)_{\text{ave}} + \left(v_z^2\right)_{\text{ave}} = 3\left(v_x^2\right)_{\text{ave}} . \qquad (12.5.8)$$

The square root of $\left(v^2\right)_{\text{ave}}$ is called the *root-mean-square* ("rms") speed of the molecules. Thus the pressure of the gas is given by

$$P = \frac{1}{3}\rho\left(v^2\right)_{\text{ave}} . \qquad (12.5.9)$$

The density of the gas is the total mass of the gas divided by the volume $V$ of the container, $\rho = M^{\text{total}}/V$. The total mass of the gas is equal to the product of the number of gas molecules and the mass of each individual gas molecule, $M^{\text{total}} = N\,m$. Thus the pressure is

$$P = \frac{1}{3}\rho\left(v^2\right)_{\text{ave}} = \frac{1}{3}\left(\frac{M^{\text{total}}}{V}\right)\left(v^2\right)_{\text{ave}} = \frac{1}{3}\left(\frac{N\,m}{V}\right)\left(v^2\right)_{\text{ave}} . \qquad (12.5.10)$$

Now we note that $\left(v^2\right)_{\text{ave}}$ represents three translational degrees of freedom, each of which has an energy $\left(1/2\right)kT$ , so that

$$\frac{1}{3}m\left(v^2\right)_{\text{ave}} = \frac{2}{3}\left(\frac{1}{2}m\left(v^2\right)_{\text{ave}}\right) = \frac{2}{3}\left(\frac{3}{2}kT\right) = kT . \qquad (12.5.11)$$

Thus, Equation (12.5.10) can be re-expressed as

$$PV = N\,kT . \qquad (12.5.12)$$

Equation (12.5.12) is known as the *ideal gas equation of state* also known as the *Perfect Gas Law* or *Ideal Gas Law*.

The total number of molecules in the gas $N = n_{\text{m}}\,N_A$ where $n_{\text{m}}$ is the number of moles and $N_A$ is Avogadro's constant (the number of molecules in a mole; see Section 13.1.). The ideal gas law becomes

$$PV = n_{\text{m}}N_A\,kT . \qquad (12.5.13)$$

The *universal gas constant* is $R = k\,N_A = 8.31\,\text{J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$. The ideal gas law can be re-expressed as

$$PV = n_{\text{m}}\,RT . \qquad (12.5.14)$$

Although we started with atomistic description of the collisions of individual gas molecules satisfying the principles of conservation of energy and momentum, we ended up with a relationship between the macroscopic variables pressure, volume, and temperature that are measurable properties of the system.

One important consequence of the Ideal Gas Law is that equal volumes of different ideal gases at the same temperature and pressure must contain the same number of molecules,

$$N = \frac{1}{k}\frac{PV}{T} . \qquad (12.5.15)$$

When gases combine in chemical reactions at constant temperature and pressure, the numbers of each type of gas molecule combine in simple integral proportions. This implies that the volumes of the gases must always be in simple integral proportions.

Avogadro used this last observation about gas reactions to define one mole of a gas as a unit for large numbers of particles and specified that one mole contains $6.02\times10^{23}\text{ molecules}$.

## 12.6 Atmospheric Pressure

The atmosphere is a very complex dynamic interaction between many different species of atoms and molecules. The average percentage compositions of the eleven most abundant gases in the atmosphere up to an altitude of 25 km are shown in Table 1.

**Table 1:** Average composition of the atmosphere up to an altitude of 25 km.

| **Gas Name** | **Chemical Formula** | **Percent Volume** |
|---|---|---|
| Nitrogen | $N_2$ | 78.08% |
| Oxygen | $O_2$ | 20.95% |
| *Water | $H_2O$ | 0 to 4% |
| Argon | Ar | 0.93% |
| *Carbon Dioxide | $CO_2$ | 0.0360% |
| Neon | Ne | 0.0018% |
| Helium | He | 0.0005% |
| *Methane | $CH_4$ | 0.00017% |
| Hydrogen | $H_2$ | 0.00005% |
| *Nitrous Oxide | $N_2O$ | 0.00003% |
| *Ozone | $O_3$ | 0.000004% |

* variable gases

In the atmosphere, nitrogen forms a diatomic molecule with molar mass $M_{\mathrm{N_2}} = 28.0\text{ g}\cdot\text{mole}^{-1}$ and oxygen also forms a diatomic molecule $\mathrm{O_2}$ with molar mass $M_{\mathrm{O_2}} = 32.0\text{ g}\cdot\text{mole}^{-1}$. Since these two gases combine to form 99% of the atmosphere, the average molar mass of the atmosphere is

$$(0.78)\left(28.0\text{ g}\cdot\text{mole}^{-1}\right)+(0.21)\left(32.0\text{ g}\cdot\text{mole}^{-1}\right)=M_{\text{atm}}=28.6\text{ g}\cdot\text{mole}^{-1}. \quad (12.6.1).$$

The density $\rho$ of the atmosphere as a function of molar mass $M_{\text{atm}}$, the volume $V$, and number of moles $n_{\text{m}}$ contained in the volume is given by

$$\rho=\frac{M^{\text{total}}}{V}=\frac{n_{\text{m}}\,M_{\text{molar}}}{V}. \qquad (12.6.2)$$

How does the pressure of the atmosphere vary a function of height above the surface of the earth? In Figure 12.5, the height above sea level in kilometers is plotted against the pressure. (Also plotted on the graph as a function of height is the density in kilograms per cubic meter.)

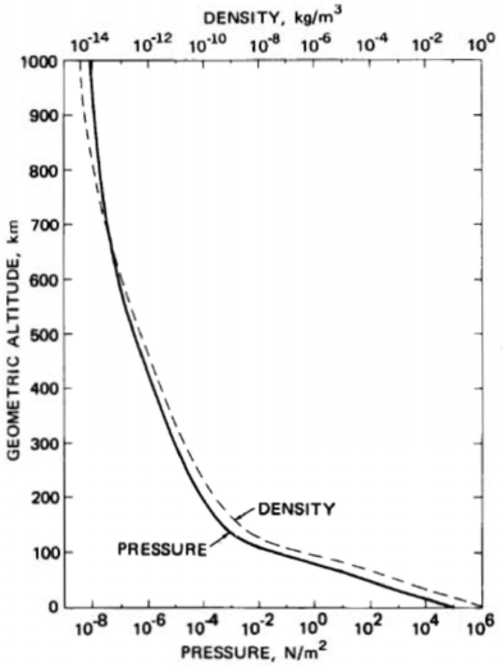


**Figure 12.5** Total pressure and density as a function of geometric altitude

### Isothermal Ideal Gas Atmosphere

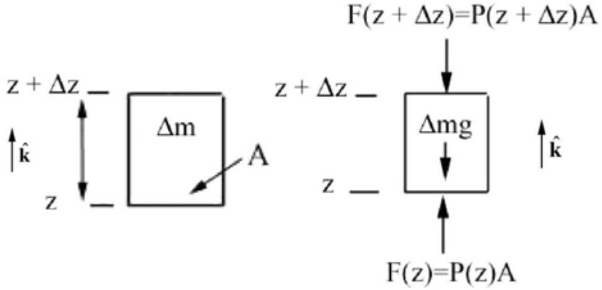
We model the atmosphere as an ideal gas in static equilibrium at constant temperature $T = 250\ \mathrm{K}$. The pressure at the surface of the earth is $P_0 = 1.02 \times 10^5\ \mathrm{Pa}$. The pressure of an ideal gas, using the ideal gas equation of state (Equation (12.5.14)) can be expressed in terms of the pressure $P$, the universal gas constant $R$, molar mass of the atmosphere $M_{\mathrm{atm}}$, and the temperature $T$.

$$P = n_{\mathrm{m}} R \frac{T}{V} = \frac{M^{\mathrm{total}}}{V} \frac{RT}{M_{\mathrm{atm}}} = \rho \frac{RT}{M_{\mathrm{atm}}} . \qquad (12.6.3)$$

Thus the equation of state for the density of the gas can be expressed as

$$\rho = \frac{M_{\mathrm{atm}}}{RT} P . \qquad (12.6.4)$$

We use Newton's Second Law determine the condition on the forces that are acting on a small cylindrical volume of atmosphere (Figure 12.6a) in static equilibrium of cross section area $A$ located between the heights $z$ and $z + \Delta z$.



**Figures 12.6a** (left), Mass element of atmosphere, and
**Figure 12.6b** (right), Force diagram for the mass element

The mass contained in this element is the product of the density $\rho$ and the volume element $\Delta V = A\Delta z$,

$$\Delta m = \rho \Delta V = \rho A \Delta z\,. \tag{12.6.5}$$

The force due to the pressure on the top of the cylinder points downward and is equal to $\vec{\mathbf{F}}(z+\Delta z) = P(z+\Delta z)\,A\left(-\hat{\mathbf{k}}\right)$ where $\hat{\mathbf{k}}$ is the unit vector directed upward. The force due to the pressure on the bottom of the cylinder is directed upward and is equal to $\vec{\mathbf{F}}(z) = P(z)\,A\,\hat{\mathbf{k}}$. The pressure on the top $P(z+\Delta z)$ and bottom $P(z)$ of this element are not equal but differ by an amount $\Delta P = P(z+\Delta z) - P(z)$. The force diagram for this element is shown in the Figure 12.6b.

Since the atmosphere is in static equilibrium in our model, the sum of the forces on the volume element are zero,

$$\vec{\mathbf{F}}^{\text{total}} = \Delta m\ \vec{\mathbf{a}} = \vec{\mathbf{0}}\,. \tag{12.6.6}$$

Thus the condition for static equilibrium of forces in the $z$ -direction is

$$-P(z+\Delta z)A + P(z)A - \Delta m\,g = 0\,. \tag{12.6.7}$$

The change is pressure is then given by

$$\Delta P A = -\Delta m\,g\,. \tag{12.6.8}$$

Using Equation (12.6.5) for the mass $\Delta m$, substitute into Equation (12.6.8) yielding

$$\Delta P\,A = -\rho A \Delta z\,g = -\frac{M_{\text{atm}} g}{RT} A \Delta z\,P\,. \tag{12.6.9}$$

The derivative of the pressure as a function of height is then linearly proportional to the pressure,

$$\frac{dP}{dz} = \lim_{\Delta z \to 0} \frac{\Delta P}{\Delta z} = -\frac{M_{\text{atm}}\, g}{RT} P \,. \tag{12.6.10}$$

This is a separable differential equation; separating the variables,

$$\frac{dP}{P} = -\frac{M_{\text{atm}}\, g}{RT} dz \,. \tag{12.6.11}$$

Integrate this result to find

$$\int_{P_0}^{P(z)} \frac{dP}{P} = \ln \frac{P(z)}{P_0} = -\int_0^z \frac{M_{\text{atm}} g}{RT} dz = -\frac{M_{\text{atm}} g}{RT} z \,. \tag{12.6.12}$$

Exponentiate $\ln(P(z)/P_0)$ in Equation (12.6.12) to find the pressure $P(z)$ in the atmosphere as a function of height $z$ above the surface of the earth,

$$P(z) = P_0 \exp\left( -\frac{M_{\text{atm}} g}{RT} z \right). \tag{12.6.13}$$

**Example**: What is the ratio of the pressure at $z = 9.0\ \text{km}$ to the pressure at the surface of the earth?

$$\begin{aligned} \frac{P(9.0\ \text{km})}{P_0} &= \exp\left( -\frac{\left(28.6 \times 10^{-3}\ \text{kg} \cdot \text{mole}^{-1}\right)\left(9.8\ \text{m} \cdot \text{s}^{-2}\right)}{\left(8.31\ \text{J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}\right)(250\ \text{K})} \left(9.0 \times 10^{3}\ \text{m}\right) \right) \\ &= 0.30. \end{aligned} \tag{12.6.14}$$

Several assumptions about the atmosphere were introduced in this model.

Uniform Temperature Assumption:

Isothermal atmosphere. The temperature actually varies according to the specific region of the atmosphere. A plot of temperature as a function of height is shown in Figure 12.7.

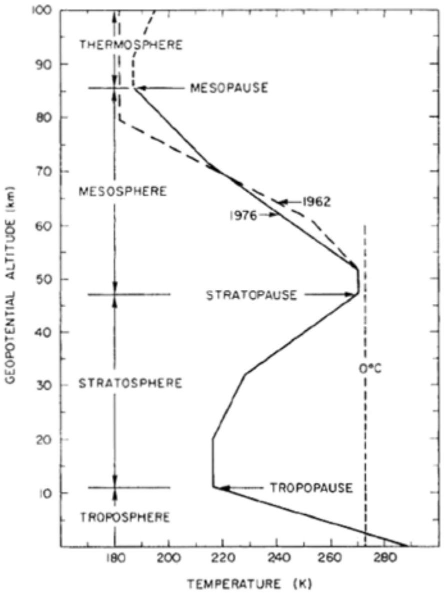


**Figure 12.7** Temperature-height profile for U.S. Standard Atmosphere

1. Troposphere: the temperature decreases with altitude; the earth is the main heat source (absorption of infrared (IR) radiation by trace gases and clouds, and convection/conduction).

2. Stratosphere: the temperature increases with altitude; absorption of ultraviolet (UV) radiation from the sun by ozone.

3. Mesosphere: the temperature decreases with altitude; the atmosphere and earth below the mesosphere are the main source of IR that is absorbed by the ozone.

4. Thermosphere: the sun heats the thermosphere by the absorption of X-rays and UV by oxygen. Temperatures range from 500 K to 2000 K depending on solar activity.

Uniform Mixing Assumption:

The lower atmosphere is dominated by turbulent mixing which is independent of the molecular mass. Near 100 km, both diffusion and turbulent mixing occur. The upper atmosphere composition is due to diffusion. So the ratio of mixing of gases changes and the mean molar mass decreases as a function of height. Only the lightest gases are present at higher levels. The variable components like water vapor and ozone will also affect the absorption of solar radiation and IR heat from the earth. The graph of height vs. mean molecular weight is shown in Figure 12.8. The number density of individual species and the total number density are plotted in Figure 12.9.

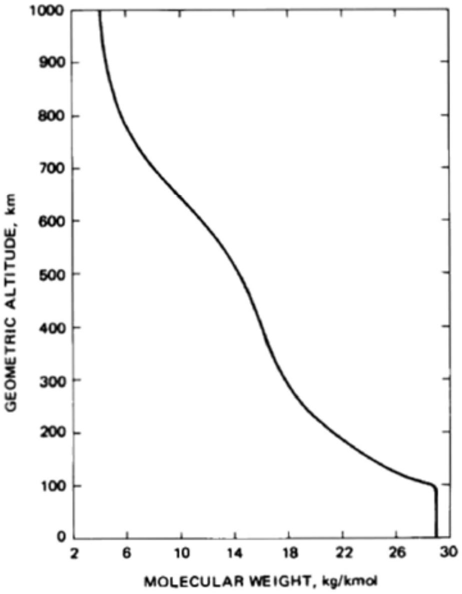


**Figure 12.8** Mean molecular weight as a function of geometric height

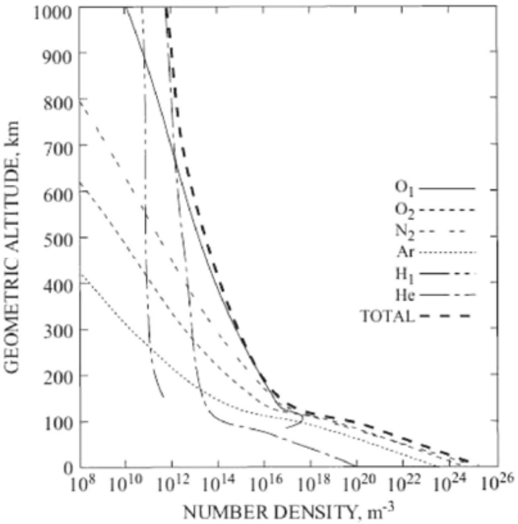


**Figure 12.9** Number density of individual species and total number as a function of geometric altitude.

(Note that in the above axis label and caption for Figure 12.8, the term "molecular weight" is used instead of the more appropriate "molecular mass" or "molar mass.")