Chapter 29: Kinetic Theory of Gases:
Equipartition of Energy and the Ideal Gas Law

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29.1 Introduction: Gas

A gas consists of a very large number of particles (typically 10^{24} or many orders of magnitude more) occupying a volume of space that is very large compared to the 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, is a measure of the quantity of matter.

29.1.1 Macroscopic vs. Atomistic Description of a Gas

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? In principle, each point-like atomic particle can be specified by its position and velocity (neglecting any internal structure). 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.

29.1.2 Atoms, Moles, and Avogadro's Number

The Avogadro number was originally defined as the number of molecules in one gram of hydrogen. The number was then redefined to be the number of atoms in 12 grams of the carbon isotope carbon-12. Now the Avogadro number is the fixed numerical value of the Avogadro constant N_A when expressed in the unit mol^{-1}

$$N_A = 6.022\,140\,76 \times 10^{23}\ \text{mol}^{-1}. \tag{29.1.1}$$

Recall that the mole is a base unit in the SI system of units for an amount of substance with symbol [mol]. Based on the new definition of Avogadro constant N_A, one mole contains $6.022\,140\,76 \times 10^{23}$ elementary entities:

$$1\,\text{mol} = \frac{N_A}{6.02214076 \times 10^{23}} \tag{29.2}$$

29.2 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 tend 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 shall refer to this conduction process as '*energy transferred thermally*'. Energy transformed thermally has traditional been called *heat*. 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 isolated 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 energy will transfer thermally between A and B. Thus

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

29.2.1 Thermometers and Ideal-Gas Temperature

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; for example: pressure of a gas, electric resistance of a resistor, thermal electromotive force of a thermocouple, magnetic susceptibility of a paramagnetic salt, or radiant emittance of blackbody radiation.

29.2.2 Gas Thermometer

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 29.1. The volume of the gas is kept constant by raising or lowering the mercury reservoir so that the mercury level on the left arm in Figure 29.1 just reaches the point I. When the bulb is placed in thermal equilibrium with a system whose temperature is to be measured, the difference in height between the mercury levels in the left and right arms is measured. The bulb pressure is atmospheric pressure plus the pressure in mercury a distance h below the surface (Pascal's Law). 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.
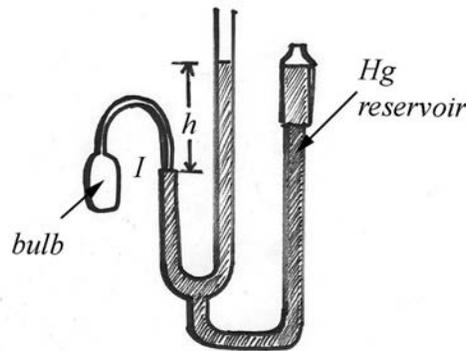
Figure 29.1 Constant volume gas thermometer

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

$$T \propto P. \tag{29.1.3}$$

We define a linear scale for temperature based on the pressure in the bulb by

$$T = aP \tag{29.1.4}$$

where a is a positive constant. In order to fix the constant a in Eq. (29.1.4), 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, the temperature of the triple point of water is chosen to be exactly $273.16\,\text{K}$ on the *Kelvin scale*, at a water-vapor pressure of $610\,\text{Pa}$. Let P_{TP} be the value of the pressure P at the triple point in the gas thermometer. Set the constant a according to

$$a = \frac{273.16\,\text{K}}{P_{\text{TP}}}. \tag{29.1.5}$$

Hence the temperature at any value of P is then

$$T(P) = a\,P = \frac{273.16 \text{ K}}{P_{\text{TP}}} P \,. \qquad (29.1.6)$$

The ratio of temperatures between any two states of a system is then measured by the ratio of the pressures of those states,

$$\frac{T_1}{T_2} = \frac{P_1}{P_2} \,. \qquad (29.1.7)$$

29.2.3 Ideal-Gas Temperature

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 $P_{\text{TP}} \to 0$ is called the *ideal-gas temperature* and is given by the equation

$$T(P) = \lim_{P_{\text{TP}} \to 0} \frac{273.16 \text{ K}}{P_{\text{TP}}} P \,. \qquad (29.1.8)$$

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 ^3He, because this gas becomes a liquid at a lower temperature than any other gas. In this way, temperatures down to $0.5\,\text{K}$ can be measured. We cannot define the temperature of absolute zero, $0\,\text{K}$, using this approach.

29.2.4 Temperature Scales

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 $0.01\,^\circ\text{C}$,

$$T(^\circ\text{C}) = \theta(\text{K}) - 273.15\,^\circ\text{C} \,, \qquad (29.1.9)$$

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

$$T(^\circ\text{F}) = \frac{9}{5} T(^\circ\text{C}) + 32\,^\circ\text{F} \,. \qquad (29.1.10)$$

The freezing point of pure water at standard atmospheric pressure occurs at 0°C and 32°F. The boiling point of pure water at standard atmospheric pressure is 100°C and 212°F.

29.3 Internal Energy vs. Thermal Energy of a Gas

The *internal energy U* of a physical system is defined to be the sum of all contributions to the total energy of the system in a reference frame in which the center of mass of the system is at rest. The internal energy dos not include potential energies that are due to external interactions, for example the gravitational potential energy due to the interaction between the system and an external body such as Earth. For example the internal energy of a gas consists of the kinetic energy, K, of the center-of-mass motions of the gas molecules relative to a container that is at rest in the reference frame; kinetic energy associated with rotational motion. These two motions have no potential energies associated to them. Diatomic and polyatomic atoms have vibrational motions which like a spring have both kinetic and potential energies. The internal energy also includes other contributions to internal energy of the system: the rest –mass energy of the constituents and nuclear binding energies associated with the nuclear structure of the constituents.

Thermal energy is the sum of all the energies except the binding energies and rest energies. **Temperature is a measure of the thermal energy of a system.** At absolute zero temperature, the thermal energy of a gas is zero even though the internal energy is still a positive constant due the binding energies and rest energies.

Internal energy of a Solid or Liquid:

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.

29.3.1 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 term in some generalized coordinate to the internal energy is called a *degree of freedom*. Examples include the displacement x of a particle undergoing one-dimensional simple harmonic motion position with a corresponding contribution of $(1/2)kx^2$ to the potential energy, the x-component of the velocity v_x for translational motion with a corresponding contribution of $(1/2)mv_x^2$ to the kinetic energy, and z-component of angular velocity ω_z for rotational motion with a corresponding contribution of $(1/2)I_z\omega_z^2$ to the rotational kinetic energy where I_z is the moment of inertia about the z-axis. 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.

29.3.2 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

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

The total internal energy of the ideal gas is then

$$E_{\text{internal}} = N(\text{\# of degrees of freedom})\frac{1}{2}kT \ . \tag{29.3.1}$$

This equal division of the energy is called the *equipartition of the energy.* The Boltzmann constant is an arbitrary constant and fixes a choice of temperature scale. Its value is chosen such that the temperature scale in Eq. (29.3.1) closely agrees with the temperature scales discussed in Section 29.2.

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 needed to correctly describe 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, 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 (the theory of quantum mechanics in necessary to understand this phenomena). Diatomic nitrogen also has an intramolecular vibrational degree of freedom that does not contribute to the internal energy at room temperatures. As discussed in Section 29.6, N_2 constitutes most of the earth's atmosphere ($\sim 78\%$).

Example 29.1: Diatomic Nitrogen Gas

What is the internal energy of the diatomic N_2 gas?

Solution: 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,

$$E_{internal} = N\frac{5}{2}kT .$$
(29.3.2)

As discussed above, at temperatures well above room temperature, but low enough for nitrogen to form diatomic molecules, there is an additional vibrational degree of freedom. Therefore there are six degrees of freedom and so the internal energy is

$$E_{internal} = N(\# \text{ of degrees of freedom})\frac{1}{2}kT = 3N\,kT .$$
(29.3.3)

29.4 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.

29.4.1 Internal Energy of a Monatomic Gas

An ideal monatomic gas atom has no internal structure, so we treat it as point particle. Therefore 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

$$E_{\text{internal}} = N\frac{3}{2}kT .$$ (29.4.1)

Eq. (29.4.1) is called the *thermal equation of state* of a monatomic ideal gas. The average kinetic energy of each ideal gas atom is then

$$\frac{1}{2}m(v^2)_{\text{ave}} = \frac{3}{2}kT$$ (29.4.2)

where $(v^2)_{\text{ave}}$ is the average of the square of the speeds and is given by

$$(v^2)_{\text{ave}} = \frac{3kT}{m} .$$ (29.4.3)

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 Eq. (29.4.2).

29.4.2 Pressure of an Ideal Gas

Consider an ideal gas consisting of a large number N of identical gas molecules, each of of mass m, inside a container of volume V and pressure P. The number of gas molecules per unit volume is then $n = N/V$. The density of the gas is $\rho = nm$. 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 concepts 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.
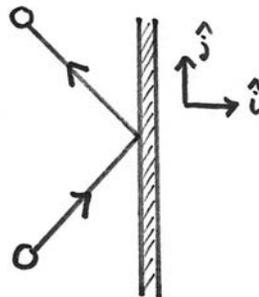
**Figure 29.2** Collision of a gas molecule with a wall of a container

We 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 29.2). Suppose the molecule has mass m and is moving with velocity $\vec{\mathbf{v}} = v_x \hat{\mathbf{i}} + v_y \hat{\mathbf{j}} + v_z \hat{\mathbf{k}}$. Because the collision with the wall is elastic, the y-and z-components of the velocity of the molecule remain constant and the x-component of the velocity changes sign (Figure 29.2), resulting in a change of momentum of the gas molecule;

$$\Delta \vec{\mathbf{p}}_m = \vec{\mathbf{p}}_{m,f} - \vec{\mathbf{p}}_{m,i} = -2mv_x \hat{\mathbf{i}}. \qquad (29.4.4)$$

Therefore the momentum transferred by the gas molecule to the wall is

$$\Delta \vec{\mathbf{p}}_w = 2mv_x \hat{\mathbf{i}}. \qquad (29.4.5)$$

Now, let's consider the effect of the collisions of a large number of randomly moving molecules. 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.

Area A

n *number of gas molecules per unit volume*

$nA\Delta x$ *molecules in volume*
$\Delta V = A\Delta x$

Δx
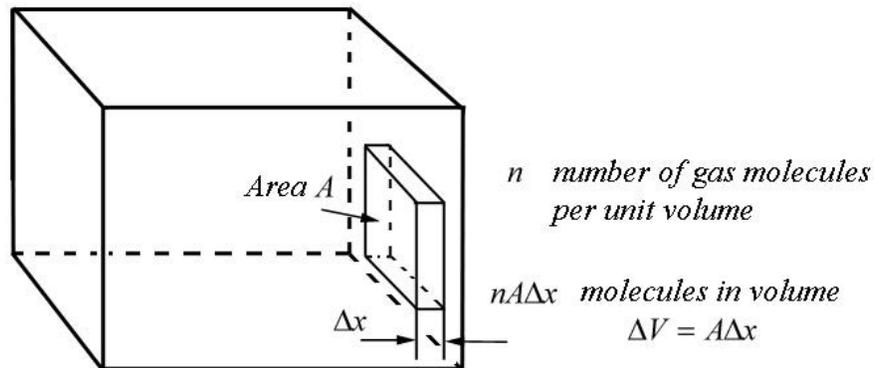
Figure 29.3 Small volume adjacent to the wall of container

Consider a small rectangular volume $\Delta V = A\Delta x$ of gas adjacent to one of the walls of the container as shown in Figure 29.3. There are $nA\Delta x$ gas molecules in this small volume. Let each group have the same x-component of the velocity. Let n_j denote the number of gas molecules in the jth group with x-component of the velocity $v_{x,j}$. Because the gas molecules are moving randomly, only half of the gas molecules in each group will be moving towards the wall in the positive x-direction. Therefore in a time interval $\Delta t_j = \Delta x / v_{x,j}$, the number of gas molecules that strike the wall with x-component of the velocity $v_{x,j}$ is given by

$$\Delta n_j = \frac{1}{2} n_j A \Delta x.$$ (29.4.6)

(During this time interval some gas molecules may leave the edges of the box, but because the number that cross the area per second is proportional to the area, in the limit as $\Delta x \to 0$, the number leaving the edges also approaches zero.) The number of gas molecules per second is then

$$\frac{\Delta n_j}{\Delta t_j} = \frac{1}{2} n_j A \frac{\Delta x}{\Delta t_j} = \frac{1}{2} n_j A v_{x,j}.$$ (29.4.7)

The momentum per second that the gas molecules in this group deliver to the wall is

$$\frac{\Delta \vec{\mathbf{p}}_j}{\Delta t_j} = \frac{\Delta n_j}{\Delta t_j} 2 m v_{x,j} \hat{\mathbf{i}} = n_j m A v_{x,j}^2 \hat{\mathbf{i}}.$$ (29.4.8)

By Newton's Second Law, the average force on the wall due to this group of molecules is equal to the momentum per second delivered by the gas molecules to the wall;

$$(\vec{\mathbf{F}}_{j,w})_{\text{ave}} = \frac{\Delta \vec{\mathbf{p}}_j}{\Delta t_j} = n_j m A v_{x,j}^2 \hat{\mathbf{i}}.$$ (29.4.9)

The pressure contributed by this group of gas molecules is then

$$P_j = \frac{\left| (\vec{\mathbf{F}}_{j,w})_{\text{ave}} \right|}{A} = n_j m v_{x,j}^2.$$ (29.4.10)

The pressure exerted by all the groups of gas molecules is the sum

$$P = \sum_{j=1}^{j=N_g} (P_j)_{\text{ave}} = m \sum_{j=1}^{j=N_g} n_j v_{x,j}^2.$$ (29.4.11)

The average of the square of the x-component of the velocity is given by

$$(v_x^2)_{\text{ave}} = \frac{1}{n} \sum_{j=1}^{j=N_g} n_j v_{x,j}^2,$$ (29.4.12)

where n is the number of gas molecules per unit volume in the container. Therefore we can rewrite Eq. (29.4.11) as

$$P = mn(v_x^2)_{\text{ave}} = \rho (v_x^2)_{\text{ave}},$$ (29.4.13)

where ρ is the density of the gas. Because we assumed that the gas molecules are moving randomly, the average of the square of the x-, y- and z-components of the velocity of the gas molecules are equal,

$$(v_x^2)_{\text{ave}} = (v_y^2)_{\text{ave}} = (v_z^2)_{\text{ave}} .$$ (29.4.14)

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

$$(v^2)_{\text{ave}} = (v_x^2)_{\text{ave}} + (v_y^2)_{\text{ave}} + (v_z^2)_{\text{ave}} .$$ (29.4.15)

Therefore

$$(v^2)_{\text{ave}} = 3(v_x^2)_{\text{ave}} .$$ (29.4.16)

Substituting Eq. (29.4.16) into Eq. (29.4.13) for the pressure of the gas yields

$$P = \frac{1}{3}\rho(v^2)_{\text{ave}} .$$ (29.4.17)

The square root of $(v^2)_{\text{ave}}$ is called the **root-mean-square** ("rms") speed of the molecules.

Substituting Eq. (29.4.3) into Eq. (29.4.17) yields

$$P = \frac{\rho k T}{m} .$$ (29.4.18)

Recall that the density of the gas

$$\rho = \frac{M}{V} = \frac{Nm}{V} .$$ (29.4.19)

Therefore Eq. (29.4.18) can be rewritten as

$$P = \frac{NkT}{V} .$$ (29.4.20)

Eq. (29.4.20) can be re-expressed as

$$PV = NkT .$$ (29.4.21)

Eq. (29.4.21) 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 $N = n_m N_A$ where n_m is the number of moles and N_A is the Avogadro constant. The ideal gas law becomes

$$PV = n_m N_A kT .$$
(29.4.22)

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

$$PV = n_m RT .$$
(29.4.23)

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, number of moles, 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,

$$N = \frac{1}{k} \frac{PV}{T} .$$
(29.4.24)

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.

29.5 Atmosphere

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

$$M_{\text{atm}} \simeq (0.78)(28.0 \, \text{g} \cdot \text{mol}^{-1}) + (0.21)(32.0 \, \text{g} \cdot \text{mol}^{-1}) = 28.6 \, \text{g} \cdot \text{mol}^{-1}. \quad (29.5.1).$$

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

$$\rho = \frac{M^{\text{total}}}{V} = \frac{n_{\text{m}} M_{\text{molar}}}{V}. \quad (29.5.2)$$

How does the pressure of the atmosphere vary a function of height above the surface of the earth? In Figure 29.4, 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.)
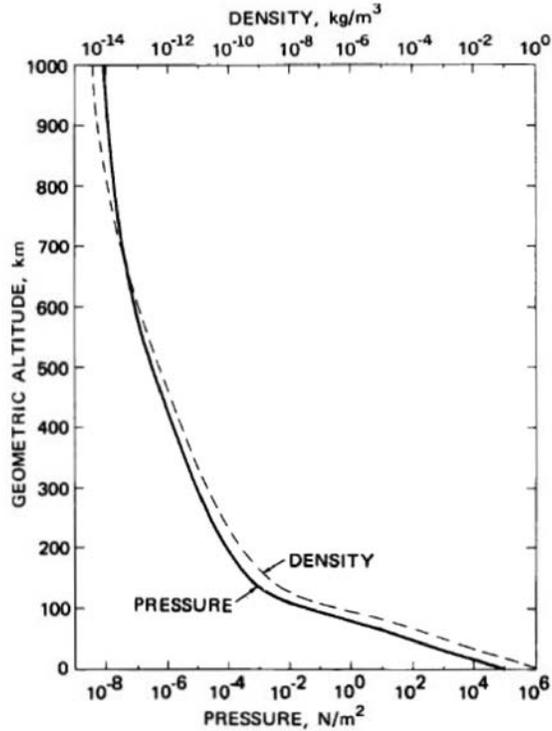
Figure 29.4 Total pressure and density as a function of geometric altitude

29.5.1 Isothermal Ideal Gas Atmosphere

Let's model the atmosphere as an ideal gas in static equilibrium at constant temperature $T = 250\,\text{K}$. The pressure at the surface of the earth is $P_0 = 1.02 \times 10^5\,\text{Pa}$. The pressure of an ideal gas, using the ideal gas equation of state (Eq. (29.4.23)) can be expressed in terms of the pressure P, the universal gas constant R, molar mass of the atmosphere M_{atm}, and the temperature T,

$$P = n_{\text{m}} R \frac{T}{V} = \frac{M^{\text{total}}}{V} \frac{RT}{M_{\text{atm}}} = \rho \frac{RT}{M_{\text{atm}}}. \qquad (29.5.3)$$

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

$$\rho = \frac{M_{\text{atm}}}{RT} P. \qquad (29.5.4)$$

We use Newton's Second Law determine the condition on the forces that are acting on a small cylindrical volume of atmosphere (Figure 29.5a) in static equilibrium of cross section area A located between the heights z and $z + \Delta z$.

29-14
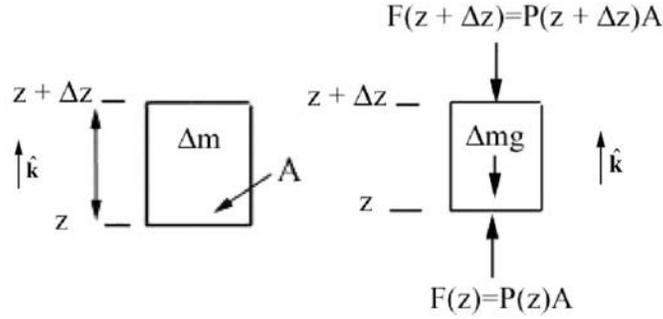
Figures 29.5 (a) (left), mass element of atmosphere, and
(b) (right), force diagram for the mass element

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

$$\Delta m = \rho \Delta V = \rho A \Delta z . \qquad (29.5.5)$$

The force due to the pressure on the top of the cylinder is directed downward and is equal to $\vec{F}(z + \Delta z) = -P(z + \Delta z) A \, \hat{k}$ (Figure 29.5(b)) where $\hat{k}$ 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 $\vec{F}(z) = P(z) A \, \hat{k}$. 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 29.5b.

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

$$\vec{F}^{\text{total}} = \Delta m \, \vec{a} = \vec{0} . \qquad (29.5.6)$$

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

$$-P(z + \Delta z) A + P(z) A - \Delta m g = 0 . \qquad (29.5.7)$$

The change is pressure is then given by

$$\Delta P A = -\Delta m g . \qquad (29.5.8)$$

Using Eq. (29.5.5) for the mass Δm, substitute into Eq. (29.5.8), yielding

$$\Delta P \, A = -\rho A \Delta z \, g = -\frac{M_{\text{atm}} g}{RT} A \Delta z \, P . \qquad (29.5.9)$$

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

$$\frac{dP}{dz} = \lim_{\Delta z \to 0} \frac{\Delta P}{\Delta z} = -\frac{M_{\text{atm}} g}{RT} P \ . \tag{29.5.10}$$

This is a separable differential equation; separating the variables,

$$\frac{dP}{P} = -\frac{M_{\text{atm}} g}{RT} dz \ . \tag{29.5.11}$$

Integrate Eq. (29.5.11) to yield

$$\int_{P_0}^{P(z)} \frac{dP}{P} = \ln\left(\frac{P(z)}{P_0}\right) = -\int_0^z \frac{M_{\text{atm}} g}{RT} dz = -\frac{M_{\text{atm}} g}{RT} z \ . \tag{29.5.12}$$

Exponentiate both sides of Eq. (29.5.12) to find the pressure $P(z)$ in the atmosphere as a function of height z above the surface of the earth,

$$P(z) = P_0 \exp\left(-\frac{M_{\text{atm}} g}{RT} z\right). \tag{29.5.13}$$

Example 29.2 Ideal Gas Atmospheric Pressure

What is the ratio of atmospheric pressure at $z = 9.0 \text{ km}$ to the atmospheric pressure at the surface of the earth for our ideal-gas atmosphere?

$$\frac{P(9.0 \text{ km})}{P_0} = \exp\left(-\frac{(28.6 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1})(9.8 \text{ m} \cdot \text{s}^{-2})}{(8.31 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(250 \text{ K})}(9.0 \times 10^3 \text{ m})\right) \tag{29.5.14}$$
$$= 0.30.$$

29.5.2 Earth's Atmosphere

We made two assumptions about the atmosphere, that the temperature was uniform and that the different gas molecules were uniformly mixed. The actual temperature varies according to the specific region of the atmosphere. A plot of temperature as a function of height is shown in Figure 29.6.
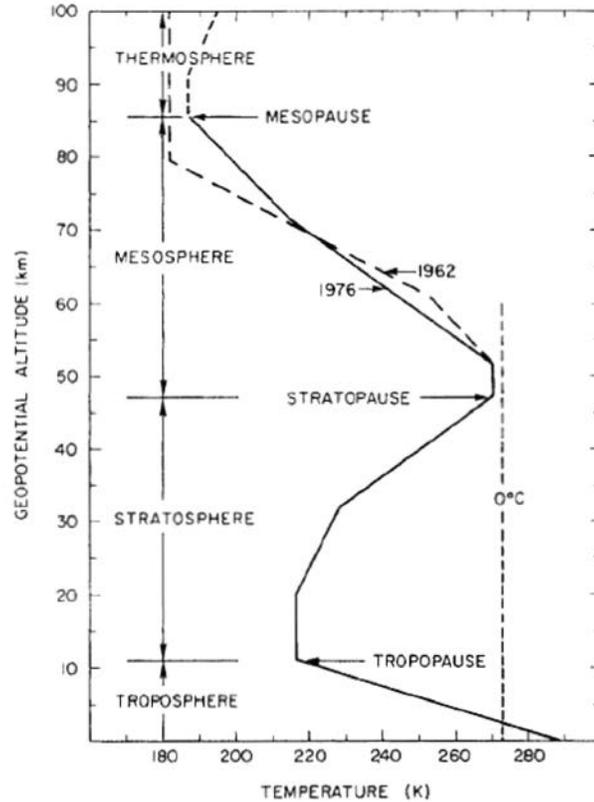
Figure 29.6 Temperature-height profile for U.S. Standard Atmosphere

In the *troposphere*, the temperature decreases with altitude; the earth is the main heat source in which there is absorption of infrared (IR) radiation by trace gases and clouds, and there is convection and conduction of thermal energy. In the *stratosphere*, the temperature increases with altitude due to the absorption of ultraviolet (UV) radiation from the sun by ozone. In the *mesosphere*, the temperature decreases with altitude. The atmosphere and earth below the mesosphere are the main source of IR that is absorbed by ozone. In the *thermosphere*, the sun heats the thermosphere by the absorption of X-rays and UV by oxygen. The temperatures ranges from 500 K to 2000 K depending on the solar activity.

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. 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 radiation from the earth. The graph of height vs. mean molecular weight is shown in Figure 29.7. The number density of individual species and the total number density are plotted in Figure 29.8.
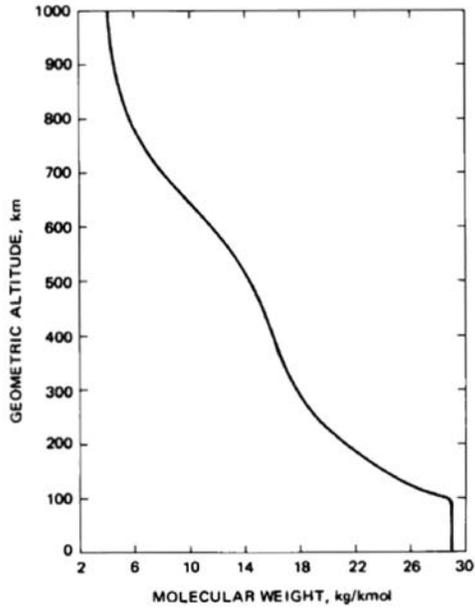
Figure 29.7 Mean molecular weight as a function of geometric height
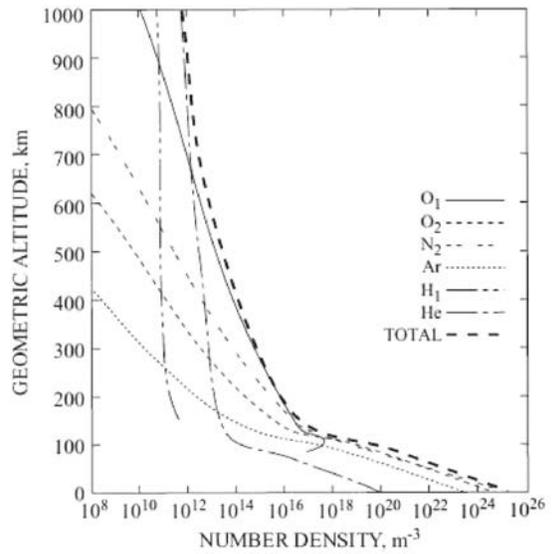
Figure 29.8 Number density of individual species and total number as a function of geometric altitude.

(Note that in the above axis label and caption for Figure 29.8, the term "molecular weight" is used instead of the more appropriate "molecular mass" or "molar mass.")

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