

Chapter 16: Kinetic Theory of Gases

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Contents

16 Kinetic Theory of Gases	1
16.1 Introduction: Gas	1
16.1.1 Macroscopic vs. Atomistic Description of a Gas	2
16.1.2 Atoms, Moles, and Avogadro's Number	2
16.2 Temperature and Thermal Equilibrium	2
16.2.1 Thermometers and Ideal-Gas Temperature	3
16.2.2 Gas Thermometer	3
16.2.3 Ideal-Gas Temperature	4
16.2.4 Temperature Scales	5
16.3 Internal Energy vs. Thermal Energy of a Gas	5
16.3.1 Internal energy of a Solid or Liquid	5
16.3.2 Degrees of Freedom	6
16.3.3 Equipartition of Energy	6
16.3.4 Example: Diatomic Nitrogen Gas	7
16.4 Ideal Gas	7
16.4.1 Internal Energy of a Monatomic Gas	8
16.4.2 Pressure of an Ideal Gas	8
16.5 Atmosphere	12
16.5.1 Isothermal Ideal Gas Atmosphere	13
16.5.2 Example: Ideal Gas Atmospheric Pressure	15
16.5.3 Earth's Atmosphere	16

Chapter 16

Kinetic Theory of Gases

I will therefore conclude by considering it as demonstrated by the experiments contained in this paper;—

1st. That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the quantity of force expended. And,

2nd. That the quantity of heat capable of increasing the temperature of a pound of water (weighed in vacuo, and taken at between 55° and 60°) by 1° Fahr., requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lbs. through the space of one foot.

1

James Prescott Joule

16.1 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 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.

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16.1.1 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.

16.1.2 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 (^{12}C). Now the Avogadro number is the fixed numerical value of the Avogadro constant N_A when expressed in the unit mol^{-1}

$$N_A = 6.022\ 140\ 76 \times 10^{23} \text{ mol}^{-1}. \quad (16.1)$$

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 $6.02214076 \times 10^{23}$ elementary entities:

$$1 \text{ mol} = \frac{N_A}{6.02214076 \times 10^{23}}. \quad (16.2)$$

16.2 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 traditionally 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.

16.2.1 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.

16.2.2 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 16.1. 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 16.1 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. At constant volume, and at ordinary temperatures, the pressure of gases is proportional to the temperature, $P \propto T$. We define a linear scale for temperature based on the pressure in the bulb by

$$T = a P. \quad (16.3)$$

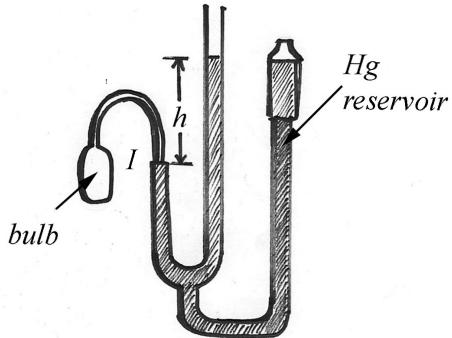


Figure 16.1: Constant volume gas thermometer .

where is a positive constant. In order to fix the constant a in Equation 16.3, 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 273.16K on the Kelvin scale, at a water-vapor pressure of 610Pa. Let P_{TP} be the value of the pressure P at the triple point in the gas thermometer. Set the constant a according to

$$a = \frac{273.16 \text{ K}}{P_{\text{TP}}}. \quad (16.4)$$

Hence the temperature at any value of P is then

$$T(P) = a P = \frac{273.16 \text{ K}}{P_{\text{TP}}} P. \quad (16.5)$$

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

$$\frac{T_1}{T_2} = \frac{P_1}{P_2}. \quad (16.6)$$

16.2.3 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 $P_{\text{TP}} \rightarrow 0$ is called the ideal-gas temperature and is given by

$$T(P) = \lim_{P_{\text{TP}} \rightarrow 0} \frac{273.16 \text{ K}}{P_{\text{TP}}} P. \quad (16.7)$$

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 ${}^3\text{He}$,

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

16.2.4 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°C,

$$T(\text{°C}) = \theta(\text{K}) - 273.15 \text{ °C}. \quad (16.8)$$

In the Celsius scale the freezing and boiling points of water at standard atmospheric pressure are 0°C and 100°C.

The *Fahrenheit* scale is related to the Celsius scale by

$$T(\text{°F}) = \frac{9}{5}T(\text{°C}) + 32 \text{ °F}. \quad (16.9)$$

In the Fahrenheit scale the freezing and boiling points of water at standard atmospheric pressure are 32°F and 212°F.

16.3 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 does 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, 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.

16.3.1 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.

16.3.2 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.

16.3.3 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

$$k = 1.3806505 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}. \quad (16.10)$$

The total internal energy of the gas is then

$$E_{\text{internal}} = N(\# \text{ of degrees of freedom}) \frac{1}{2}kT. \quad (16.11)$$

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 Equation 16.11, closely agrees with the temperature scales discussed in Section 16.2.

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 is 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 ($\approx 78\%$).

16.3.4 Example: 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,

$$E_{\text{internal}} = N \frac{5}{2} kT. \quad (16.12)$$

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

$$E_{\text{internal}} = N(\# \text{ of degrees of freedom}) \frac{1}{2} kT = 3N kT. \quad (16.13)$$

16.4 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.

16.4.1 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

$$E_{\text{internal}} = N \frac{3}{2} kT. \quad (16.14)$$

Equation 16.14 is called the *thermal equation of state* of a monatomic ideal gas. The average kinetic energy of each ideal gas atom is then

$$\frac{1}{2}m(v^2)_{\text{ave}} = \frac{3}{2}kT. \quad (16.15)$$

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

$$(v^2)_{\text{ave}} = \frac{3kT}{m}. \quad (16.16)$$

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 16.16.

16.4.2 Pressure of an Ideal Gas

Consider an ideal gas consisting of a large number N of identical gas molecules, each 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 .

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 16.2). Suppose the molecule has mass m and is moving with velocity $\vec{v} = v_x \hat{\mathbf{i}} + v_y \hat{\mathbf{j}} + v_z \hat{\mathbf{k}}$. 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

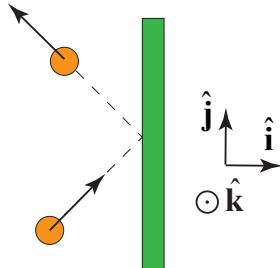


Figure 16.2: Collision of a gas molecule with a wall of a container.

the velocity changes sign (Figure 16.2), resulting in a change of momentum of the gas molecule;

$$\Delta \vec{p} = \vec{p}_f - \vec{p}_i = -2m v_x \hat{i}. \quad (16.17)$$

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

$$\Delta \vec{p}_w = -\Delta \vec{p} = 2m v_x \hat{i}. \quad (16.18)$$

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. Consider a small rectangular volume $\Delta V = A\Delta x$ of the gas adjacent to one

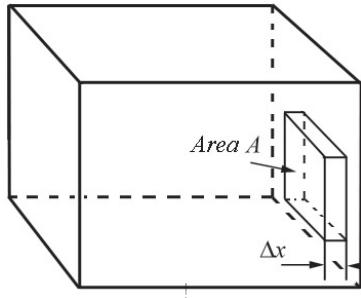


Figure 16.3: Small volume adjacent to the wall of container.

of the walls of the container as shown in . 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 j^{th} 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

$$\Delta n_j = \frac{1}{2} n_j A \Delta x. \quad (16.19)$$

(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 $\Delta x \rightarrow 0$, the number leaving the edges also approaches zero.) The number of gas molecules per second is then

$$\frac{\Delta n_j}{\Delta t_j} = \frac{1}{2} n_j A \frac{\Delta x}{\Delta t_j} = \frac{1}{2} n_j A v_{x,j}. \quad (16.20)$$

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

$$\frac{\Delta \vec{p}_j}{\Delta t_j} = \frac{\Delta n_j}{\Delta t_j} 2m v_{x,j} \hat{i} = n_j m A v_{x,j}^2 \hat{i}. \quad (16.21)$$

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;

$$(\vec{F}_{j,w})_{ave} = \frac{\Delta \vec{p}_j}{\Delta t_j} = n_j m A v_{x,j}^2 \hat{i}. \quad (16.22)$$

The pressure contributed by this group of gas molecules is then

$$P_j = \frac{|(\vec{F}_{j,w})_{ave}|}{A} = n_j m v_{x,j}^2. \quad (16.23)$$

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

$$P = \sum_{j=1}^{j=N_g} (P_j)_{ave} = m \sum_{j=1}^{j=N_g} n_j v_{x,j}^2. \quad (16.24)$$

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

$$(v_x^2)_{ave} = \frac{1}{n} \sum_{j=1}^{j=N_g} n_j v_{x,j}^2, \quad (16.25)$$

where n is the number of gas molecules per unit volume in the container. Therefore we can rewrite Equation 16.24 as

$$P = mn(v_x^2)_{ave} = \rho(v_x^2)_{ave}, \quad (16.26)$$

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 three components of the velocity of the gas molecules are equal,

$$(v_x^2)_{ave} = (v_y^2)_{ave} = (v_z^2)_{ave}. \quad (16.27)$$

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

$$(v^2)_{ave} = (v_x^2)_{ave} + (v_y^2)_{ave} + (v_z^2)_{ave} = 3(v_x^2)_{ave}. \quad (16.28)$$

Substituting Equation 16.28 into Equation 16.26 for the pressure of the gas yields

$$P = \frac{1}{3}\rho(v^2)_{\text{ave}}. \quad (16.29)$$

The square root of $(v^2)_{\text{ave}}$ is called the *root-mean-square* (“rms”) speed of the molecules. Substituting Equation 16.16 into Equation 16.29 yields

$$P = \frac{\rho kT}{m}. \quad (16.30)$$

The density of the gas is

$$\rho = \frac{M}{V} = \frac{Nm}{V}. \quad (16.31)$$

Therefore Equation 16.30 can be rewritten as

$$P = \frac{NkT}{V}, \quad (16.32)$$

which can be rewritten as

$$PV = NkT. \quad (16.33)$$

Equation 16.33 is known as the *ideal gas equation of state*, also known as the *Perfect Gas Law* or as the *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

$$PV = n_m N_A kT. \quad (16.34)$$

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

$$PV = n_m RT. \quad (16.35)$$

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,

$$N = \frac{1}{k} \frac{PV}{T}. \quad (16.36)$$

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.

16.5 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 16.1: Average composition of the atmosphere up to an altitude of 25 km.

Gas Name	Chemical Formula	Percent Volume
Nitrogen	N ₂ (s)	78.084%
Oxygen	O ₂ (m)	20.947%
Argon	Ar	0.934%
Water vapor	H ₂ O	0 to 4%
Carbon Dioxide	C ₂ O	0.035%
Neon	Ne	18.182 parts per million
Helium	He	5.24 parts per million
Methane	CH ₄	18.182 parts per million
Krypton	Kr	1.14 parts per million
Hydrogen	H ₂	0.53 parts per million
Nitrous Oxide	N ₂ O	0.334 parts per million
Carbon Monoxide	CO	0.10 parts per million
Xenon	Xe	0.09 parts per million
Ozone	O ₃	0.07 parts per million
Nitrogen dioxide	NO ₂	0.02 parts per million
Iodine	I ₂	0.01 parts per million
Ammonia	NH ₃	trace

In the atmosphere, nitrogen forms a diatomic molecule N₂ with molar mass $M_{N_2} = 28.0 \text{ g} \cdot \text{mol}^{-1}$ and oxygen also forms a diatomic molecule O₂ with molar mass $M_{O_2} = 32.0 \text{ g} \cdot \text{mol}^{-1}$. Because these two gases combine to form 99% of the atmosphere, the average molar mass of the atmosphere is

$$M_{\text{atm}} \approx (0.78)(28.0 \text{ g} \cdot \text{mol}^{-1}) + (0.21)(32.0 \text{ g} \cdot \text{mol}^{-1}) = 28.6 \text{ g} \cdot \text{mol}^{-1}. \quad (16.37)$$

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

$$\rho = \frac{M^{\text{total}}}{V} = \frac{n_m M_{\text{molar}}}{V}. \quad (16.38)$$

How does the pressure of the atmosphere vary a function of height above the surface of the earth? In Figure 16.4, 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.)

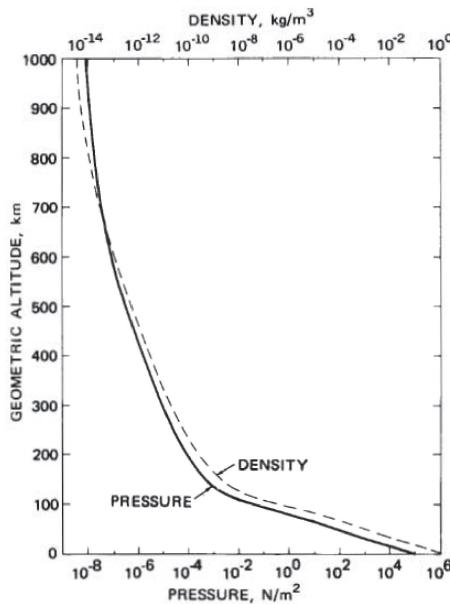


Figure 16.4: Total pressure and density as a function of geometric altitude.

16.5.1 Isothermal Ideal Gas Atmosphere

Let's model the atmosphere as an ideal gas in static equilibrium at constant temperature $T = 250$ K. The pressure at the surface of the earth is $P_0 = 1.02 \times 10^5$ Pa. The pressure of an ideal gas, using the ideal gas equation of state (Equation 16.35) 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 ,

$$P = n_m R \frac{T}{V} = \frac{M^{\text{total}}}{V} \frac{RT}{M_{\text{atm}}} = \rho \frac{RT}{M_{\text{atm}}}. \quad (16.39)$$

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

$$\rho = \frac{M_{\text{atm}}}{RT} P. \quad (16.40)$$

Use Newton's Second Law determine the condition on the forces that are acting on a small cylindrical volume of atmosphere. Choose a coordinate system such that the z -axis points vertical upward and the plane $z = 0$ is at the surface. Choose a small cylindrical volume element of the atmosphere at a height z , with cross-sectional area A , thickness Δz and mass $\Delta m = \rho A \Delta z$ as shown in the Figure 16.5.

The cylindrical column of the atmosphere has now been divided into three pieces, an upper piece, the small mass element, and a lower piece.

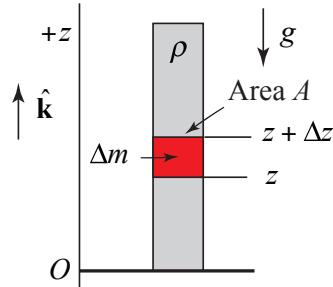


Figure 16.5: Coordinate system and small mass element in an ideal gas atmosphere.

The free-body force diagram on the small mass element of the atmosphere of thickness Δz is shown in Figure 16.6. The pressure force of the atmosphere on the bottom surface of the mass element is directed away from the surface and is given by $\vec{F}(z) = F(z)\hat{k}$. The pressure force of the atmosphere on the upper surface of the mass element is directed towards the surface and is given by $\vec{F}(z + \Delta z) = F(z + \Delta z)\hat{k}$. The magnitudes of the two forces are related to the pressure by $F(z) = P(z)A$ and $F(z + \Delta z) = P(z + \Delta z)A$. The gravitational force is directed downward and given by $\vec{F}^g = -\Delta m g \hat{k} = -\rho A \Delta z g \hat{k}$.

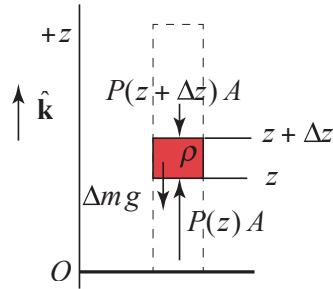


Figure 16.6: Force diagram for small mass element in an ideal gas atmosphere.

We now apply Newton's Second Law to the small element noting that the acceleration is zero

$$-(P(z) + \Delta P)A + P(z)A - \rho A \Delta z g = 0. \quad (16.41)$$

The difference in the pressure $\Delta P \equiv P(z + \Delta z) - P(z)$ divided by the thickness Δz is then

$$\frac{\Delta P}{\Delta z} = -\rho g. \quad (16.42)$$

Now take the limit as $\Delta z \rightarrow 0$:

$$\lim_{\Delta z \rightarrow 0} \frac{\Delta P}{\Delta z} = \rho g, \quad (16.43)$$

therefore the differential equation describing how pressure varies with depth is given by

$$\frac{dP}{dz} = -\rho g. \quad (16.44)$$

Now substitute the density of the gas determined by the Ideal Gas Law (Equation 16.40) into the differential equation 16.44:

$$\frac{dP}{dz} = -\frac{Mg}{RT} P. \quad (16.45)$$

In order to find the pressure as a function of height from the surface, integrate Equation 16.45 using the technique of separation of variables. first rewrite the differential equation in terms of differentials and two integration variables P' and z'

$$\frac{dP'}{P'} = -\frac{Mg}{RT} z'. \quad (16.46)$$

Now integrate both sides, with the following limits for the definite integrals: integrate the pressure from $P' = P_0$ to $P' = P(z)$ and the depth variable $z' = 0$ to $z' = z$,

$$\int_{P'=P_0}^{P'=P(z)} \frac{dP'}{P'} = - \int_{z'=0}^{z'=z} \frac{Mg}{RT} dz'. \quad (16.47)$$

Perform the integrals on both sides of Equation ??:

$$\ln \left(\frac{P(z)}{P_0} \right) = -\frac{M_{\text{atm}} g}{RT} z. \quad (16.48)$$

Exponentiate both sides of this equation using the fact that $e^{\ln z} = z$ yielding

$$\frac{P(z)}{P_0} = e^{-(M_{\text{atm}} g / RT) z}. \quad (16.49)$$

The pressure at a height z is then

$$P(z) = P_0 e^{-(M_{\text{atm}} g / RT) z}. \quad (16.50)$$

16.5.2 Example: 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?

Solution:

$$\frac{P(9.0 \text{ km})}{P_0} = \exp \left(-\frac{(28.6 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1})(9.8 \text{ m} \cdot \text{s}^{-2})}{(8.31 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(250 \text{ K})} (9.0 \times 10^3 \text{ m}) \right) \\ = 0.30. \quad (16.51)$$

16.5.3 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 16.7. In the *troposphere*, the temperature decreases with

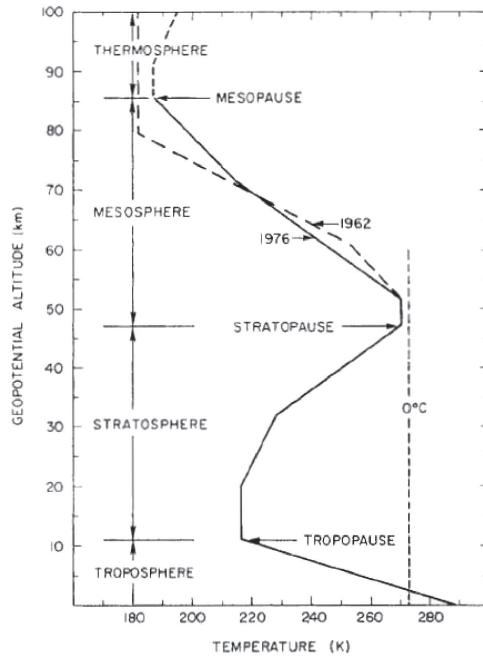


Figure 16.7: Temperature-height profile for U.S. Standard Atmosphere.

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 16.8. The number density of individual species and the total number density are plotted in Figure 16.9. (Note that

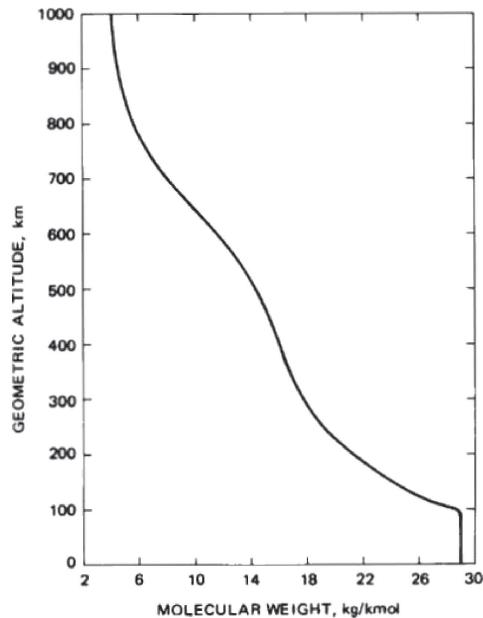


Figure 16.8: Mean molecular weight as a function of geometric height.

in the above axis label and caption for Figure 16.9, the term “molecular weight” is used instead of the more appropriate “molecular mass” or “molar mass.”)

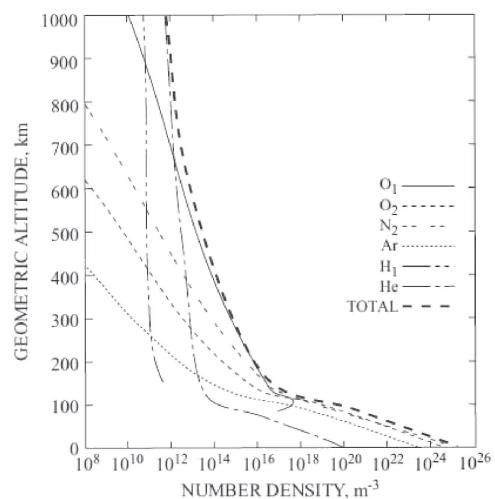


Figure 16.9: Number density of individual species and total number as a function of geometric altitude.