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Physics, Chapter 16: Kinetic Theory of Gases

Henry Semat
City College of New York

Robert Katz
University of Nebraska-Lincoln, rkatz2@unl.edu

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Kinetic Theory of Gases

16-1 General Gas Law

The behavior of a gas under various conditions of temperature and pressure has already been studied in some detail. When the pressure of a constant mass of gas is not too great, say less than about 2 atm, we find that a gas obeys the following relationships:

$$\text{at constant temperature} \quad PV = \text{constant}; \tag{16-1}$$

$$\text{at constant volume} \quad P = KT; \tag{16-2}$$

$$\text{at constant pressure} \quad V = K'T. \tag{16-3}$$

These three equations are special cases of a single experimental equation which gives the relationship between the pressure P, the volume V, and the

$$P_i V_i = P_f V_2 \qquad \frac{V_2}{T_i} = \frac{V_f}{T_f}$$
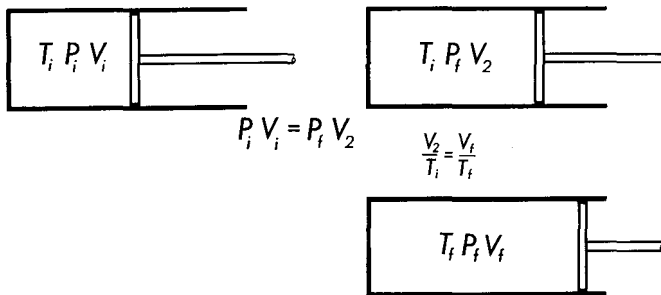
Fig. 16-1 Two steps in the derivation of the general gas law; an isothermal process followed by a constant-pressure process.

absolute temperature T of a constant mass of gas. We may derive the general form of the gas law from the above equations.

Let us consider a gas contained in a cylinder with a closely fitting piston, as shown in Figure 16-1. The initial condition of the gas may be

described in terms of its initial pressure P_i, its initial volume V_i, and its initial temperature T_i. The gas is allowed to expand at constant temperature, say by keeping the cylinder immersed in a bath of melting ice, until its new pressure is P_f and its new volume is V_2. Since the expansion was at constant temperature, we find from Equation (16-1) that

$$P_i V_i = P_f V_2.$$

Now suppose that the gas is heated to a higher temperature T_f, the volume being allowed to expand to a new value V_f, but the pressure on the piston being maintained at the same value P_f throughout this process. Then, from Equation (16-3) we may write

$$\frac{V_2}{T_i} = \frac{V_f}{T_f} = K',$$

or
$$V_2 = V_f \frac{T_i}{T_f}.$$

Substituting for V_2 into the first of the above equations, we find

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}. \tag{16-4}$$

Equation (16-4) is one form of the general gas law. Since the initial state, described by the subscript i, and the final state, described by the subscript f, are entirely arbitrary, the only way in which the quantities on the right- and left-hand sides of the equation can be equal is for each quantity to be separately equal to the same constant. Thus we may rewrite the gas law as

$$\boxed{\frac{PV}{T} = c,} \tag{16-5}$$

where c is a constant whose value depends upon the mass of the enclosed gas. Any convenient units may be used for the pressure and volume, but the temperature T must always be the absolute temperature.

Illustrative Example. A given mass of air occupies a volume of 2,000 cm^3 at 27°C when its pressure corresponds to the pressure at the base of a column of mercury 75 cm high. The air is compressed until its volume is 1,200 cm^3, and its pressure corresponds to 225 cm of mercury. Determine the temperature of the gas after it has been compressed.

From Equation (16-4) we have

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}.$$

The pressure at the base of a column of mercury h cm high is given by $P = h\rho g$, where ρ is the density of the mercury. Substituting numerical values, we have

$$\frac{75 \text{ cm} \times \rho g \times 2,000 \text{ cm}^3}{300.2° \text{ abs}} = \frac{225 \text{ cm} \times \rho g \times 1,200 \text{ cm}^3}{T_f},$$

from which $T_f = 540.4°$ abs.

16-2   The Universal Gas Constant R

The constant c appearing in Equation (16-5) can be evaluated for any given mass of a gas. Let us designate the value of this constant for a *gram molecular weight*, or *mole*, of a gas by the symbol R. *A gram molecular weight of any substance is an amount of that substance whose mass, expressed in grams, is numerically equal to the molecular weight of the substance.* In the limit of low pressures, the value of R is independent of the chemical nature of the gas, so that R is known as the *universal* gas constant. In the event that n moles of gas are present in a container, Equation (16-5) may be rewritten as

$$PV = nRT. \tag{16-6}$$

The numerical value of the gas constant R can be determined by noting that 1 mole of any gas occupies a volume of 22.4 liters at a pressure of 76 cm of mercury at 0°C; putting these values into Equation (16-6), we get

$$R = 8.31 \times 10^7 \frac{\text{erg}}{\text{mole } °\text{K}} = 1.99 \frac{\text{cal}}{\text{mole } °\text{K}} = 8.21 \times 10^{-2} \frac{\text{liter atm}}{\text{mole } °\text{K}}.$$

16-3   Kinetic Theory of Gases

From the preceding discussion we have seen that all gases exhibit similar thermal and mechanical properties, regardless of their chemical composition, as long as their pressure is sufficiently small. This behavior is quite unlike that of the same substances in liquid or solid form, where these substances exhibit widely different thermal and elastic properties. We are led to infer that the molecules of a gas are sufficiently far apart so that they rarely interact with each other. The pressure of a gas then results from the collisions of the molecules of the gas with the walls of the container. The moving molecules of the gas completely fill every container in which the gas is placed.

We may construct a theory of an ideal gas which is in good agreement with the experimental results described in the preceding sections on the basis of a few simple assumptions. We shall assume that *a gas is composed of molecules that are so small that, to a first approximation, they may be considered as point masses.* We assume further that the molecules *do not*

exert forces on each other except during collisions. We shall further assume that *the molecules of the gas are perfectly elastic*, and that the container is made of perfectly elastic, rigid walls. This implies that mechanical energy is conserved in collisions between molecules. If this were not the case, we would expect to observe that the pressure of a tank of gas would diminish with time, as the molecules lost mechanical energy in inelastic collisions. For the sake of simplicity we shall assume that the gas is in a cubical container of edge d and of volume $V = d^3$.
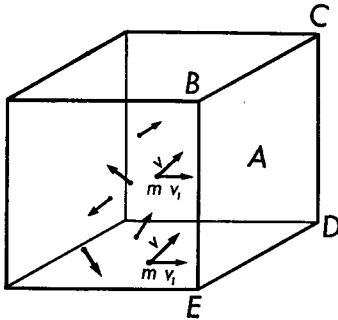

Fig. 16-2 Molecules with equal velocity components v_1 near face $BCDE$ of the cube.

The pressure exerted by the gas on the walls of the container is due to the impact of the molecules on the walls, and, when in equilibrium, is equal to the pressure throughout the gas. To calculate this pressure let us assume that the impact of a molecule with a wall is an elastic impact; that is, if a molecule is approaching the wall with a velocity v and momentum mv, then it will leave the wall with a velocity $-v$ and a momentum $-mv$. The change in momentum of the molecule produced by this impact will thus be $-2mv$. To determine the pressure on the walls of the container, let us first calculate the force exerted by the molecules on one of the six faces of the cube, say the face $BCDE$ of Figure 16-2, and then divide by its area.

Let us consider those molecules which at some instant are very close to this face. Only those molecules whose velocities have components perpendicular to this face, and directed toward it, will strike it and rebound. Suppose we consider a small number of molecules which have the same value v_1 for this velocity component. The number of these molecules which will strike this face during a small time interval Δt will be one half of the number contained in a small volume $A \, \Delta l$, where A is equal to the area of the face of the cube and $\Delta l = v_1 \, \Delta t$; the other half having a velocity component of magnitude v_1 are moving away from the wall. If n_1 represents the number of molecules per unit volume which have a velocity component of magnitude v_1, then the number striking this face of the cube in time Δt will be

$$\frac{n_1}{2} \, A v_1 \, \Delta t.$$

Since each such molecule will have its momentum changed by $-2mv_1$ as a result of this impact, the impulse imparted to the wall will be equal and opposite to it, or $+2mv_1$. The impulse $F_1 \, \Delta t$ on the wall produced by these collisions in time Δt will then be

$$F_1 \, \Delta t = \frac{n_1}{2} \, Av_1 \, \Delta t \times 2mv_1,$$

from which $\quad\quad\quad\quad F_1 = An_1mv_1^2.$

The pressure on the wall produced by the impact of these molecules is

$$p_1 = \frac{F_1}{A} = n_1mv_1^2.$$

We can now consider another group of molecules, n_2 per unit volume, which have a slightly different velocity component v_2 in this direction; they will produce an additional pressure p_2 given by

$$p_2 = n_2mv_2^2.$$

In this way, we can break up the gas into different groups of molecules, each group contributing a similar term to the pressure on this face of the cube. The total pressure P due to all the different groups of molecules will therefore be of the form

$$P = n_1mv_1^2 + n_2mv_2^2 + n_3mv_3^2 + \cdots.$$

This equation can be simplified by introducing a new term called *the average of the squares of the components of the velocities of all the molecules moving perpendicular to face A* and defined by the equation

$$\overline{v_A^2} = \frac{n_1v_1^2 + n_2v_2^2 + n_3v_3^2 + \cdots}{n},$$

in which n represents the total number of molecules per unit volume. Substituting this value of $\overline{v_A^2}$ in the equation for the pressure, we get

$$P = nm\overline{v_A^2}. \quad\quad\quad\quad\quad\quad \text{(16-7)}$$

There will be a similar expression for the pressure on each of the six faces of the cube, except that the factor $\overline{v_A^2}$ will be replaced by the appropriate average of the squares of the components of the velocities of the molecules for that particular face.

The velocity v of any one molecule may be in any direction; it can be resolved into three mutually perpendicular components v_x, v_y, v_z. The magnitude of v in terms of the magnitudes of these components is given by

$$v^2 = v_x^2 + v_y^2 + v_z^2.$$

There will be a similar equation for the square of the velocity of each molecule of the gas in terms of the squares of its three mutually perpendicular components. If we add the squares of the component velocities in the x direction and divide this sum by the total number of molecules, we will get the average value of the square of this velocity component; it will be represented by $\overline{v_x^2}$. Similarly, $\overline{v_y^2}$ and $\overline{v_z^2}$ will represent the average squares of the velocities in the y and z directions, respectively. By adding these average squares of the three velocity components, we get

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2},$$

where $\overline{v^2}$ is the average of the squares of the velocities of all the molecules. Since the velocities of the molecules have all possible directions, the average value of the squares of the velocity in any one direction should be the same as in any other direction, or

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2},$$

so that

$$\overline{v^2} = 3\overline{v_x^2}.$$

If we take the x direction as perpendicular to the face A, we can write

$$\overline{v^2} = 3\overline{v_A^2},$$

so that Equation (16-7) becomes

$$\boxed{P = \tfrac{1}{3}nm\overline{v^2}.} \tag{16-8}$$

Recalling that the kinetic energy of a moving molecule is equal to $\tfrac{1}{2}mv^2$, Equation (16-8) may be written as

$$P = \tfrac{2}{3}n(\tfrac{1}{2}m\overline{v^2}).$$

Since n is the number of molecules per unit volume, we see that the pressure is numerically equal to two thirds the kinetic energy of the molecules in a unit volume of gas.

   Let us suppose that N_0 is the total number of molecules in a mole of gas, called *Avogadro's number*, which is contained in a volume V. Then the number of molecules per unit volume n is given by the expression

$$n = \frac{N_0}{V}.$$

Substituting for n into Equation (16-8), we find

$$PV = \tfrac{2}{3}N_0 \times \tfrac{1}{2}m\overline{v^2}. \tag{16-9}$$

Equation (16-9) is a theoretical result obtained from our hypotheses about an ideal gas, relating the pressure and volume of 1 mole of an ideal gas.

If we compare this result to the experimental equation given in Equation (16-6), which for 1 mole of gas becomes

$$PV = RT,$$

we find the theoretical and experimental results to be in agreement if

$$RT = \tfrac{2}{3} N_0 \tfrac{1}{2} \overline{mv^2},$$

or if
$$\tfrac{1}{2} \overline{mv^2} = \frac{3}{2} \frac{R}{N_0} T.$$

It is customary to define a new constant k, called *Boltzmann's constant*, such that

$$k = \frac{R}{N_0} . \qquad\qquad (16\text{-}10)$$

Since R is the gas constant per mole, and N_0 is the number of molecules in a mole of gas, the constant k may be described as the gas constant per molecule. In terms of k the preceding equation becomes

$$\tfrac{1}{2} \overline{mv^2} = \tfrac{3}{2} kT; \qquad\qquad (16\text{-}11)$$

that is, the mean kinetic energy of translation of a molecule of gas is given by $\tfrac{3}{2}$ the product of Boltzmann's constant by the absolute temperature. This equation gives us some physical meaning of temperature for an ideal gas. For such a gas the temperature is associated with the kinetic energy of the random translational motion of the molecules of the gas. According to Equation (16-11) the average energy of each molecule, and therefore the total internal energy of an ideal gas, is associated with its temperature. Thus the *internal energy of an ideal gas is a function of its temperature only*, and not of its pressure or volume.

In our derivation of the gas law in the form of Equation (16-9), we used the word "molecules" to describe the particles with which we were dealing. These molecules were described by the condition that they were small, relatively far apart, and perfectly elastic. Thus this equation might be used to describe the behavior of any aggregate of particles whose physical dimensions were small compared to their average separation, provided that these particles were elastic and rarely interacted with each other. The neutrons in a nuclear reactor satisfy these conditions. If the neutrons are in equilibrium with the material of the reactor at a temperature T, we speak of them as *thermal neutrons*. The mean velocity $\bar{v}$ of these thermal neutrons may be obtained from Equation (16-11). The particles of a *colloidal suspension* may also be thought of as though they were molecules of an ideal gas, and it is found that these also obey the gas laws.

Equation (16-9) incorporates another result called Avogadro's hypothesis, first stated by Avogadro in 1811, that *all gases occupying equal*

volumes at the same temperature and pressure contain equal numbers of mole-cules. The accepted value for the number of molecules in a mole of gas N_0 is

$$N_0 = 6.023 \times 10^{23} \text{ molecules/gm molecular wt.}$$

As we have already seen, 1 mole of gas occupies a volume of 22.4 liters at 0°C and at a pressure of 76 cm of mercury. If we perform the calculation indicated in Equation (16-10) to find the numerical value of Boltzmann's constant, we obtain

$$k = 1.38 \times 10^{-16} \text{ erg/°K.}$$

16-4   Work Done by a Gas

Whenever a gas expands against some external force, it does work on the external agency; conversely, whenever a gas is compressed by the action of some outside force, work is done on the gas. To calculate the work done
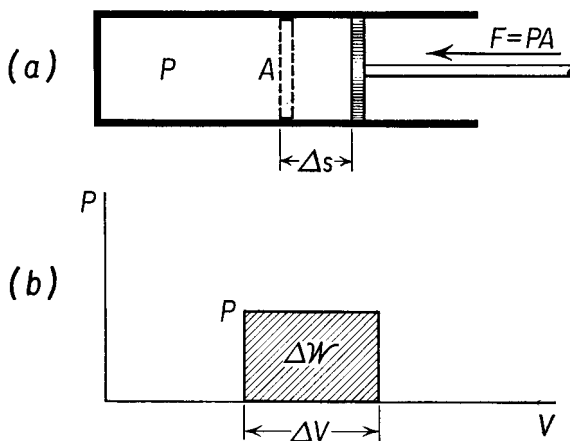

Fig. 16-3   (a) Expansion of a gas at constant pressure.   (b) Graphical representation of the work done ΔW as an area on the PV diagram.

by a gas, consider a gas enclosed in a cylinder with a tight fitting piston. The piston may be connected to a mechanical device on which it exerts some force. The force F acting on the piston owing to the pressure P of the gas is given by

$$F = PA,$$

in which A is the cross-sectional area of the piston, as shown in Figure 16-3. Suppose that the piston is pushed out a small distance Δs, while the pressure of the gas remains essentially constant. The work ΔW done by the gas in

moving the piston is given by

$$\Delta W = F\,\Delta s = PA\,\Delta s,$$

or $$\Delta W = P\,\Delta V. \tag{16-12}$$

Thus the work done by an expanding gas at constant pressure is equal to the product of the pressure by the change in volume. No mechanical work is done by a gas unless there is a change in the volume of the gas. The first law of thermodynamics,

$$\Delta Q = \Delta U + \Delta W, \tag{15-6}$$

may be rewritten for processes involving gases as

$$\Delta Q = \Delta U + P\,\Delta V. \tag{16-13}$$

Thus, in any process in which the volume of the gas remains constant, called an *isovolumic process*, any heat delivered to the gas must appear as internal energy and is therefore exhibited as a change in the temperature of the gas.

Let us calculate the work done by an ideal gas which expands *isothermally*, that is, at constant temperature, from an initial volume V_1 to a final volume V_2. From the gas law the relationship between the variables of pressure, volume, and temperature for one mole of gas may be stated as

$$PV = RT.$$

The work done may be represented as an integral, from Equation (16-12), as

$$W = \int dW = \int_V^{V_2} P\,dV,$$

and, substituting for P its value from the gas law,

$$P = \frac{RT}{V},$$

we find $$W = RT\int_{V_1}^{V_2} \frac{dV}{V}$$

at constant temperature. Recalling that

$$\int \frac{dx}{x} = \ln x + C,$$

where C is a constant of integration, we find that

$$W = RT\ln\frac{V_2}{V_1} \tag{16-14}$$

for the work done by one mole of an ideal gas in an isothermal expansion

at temperature T from an initial volume V_1 to a final volume V_2. From Equation (16-14) we see that when the gas expands, that is, when V_2 is greater than V_1, the work done is positive, as is consistent with the sign convention developed in Section 15-6. The work done is shown as the area under the isotherm in Figure 16-4.
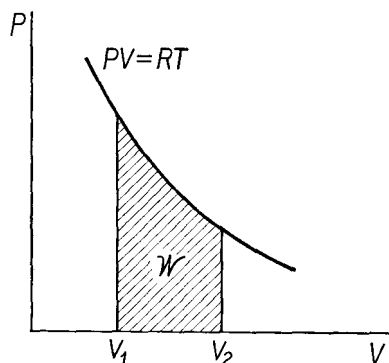
16-5 Molar Heat Capacity of a Gas

When a quantity of heat ΔQ is delivered to a gas, it may change the internal energy of the gas by an amount ΔU and may also result in the performance of an amount of external work ΔW by the gas upon the outside world, in accordance with the first law of thermodynamics. If the volume of the gas is kept constant, all the heat is converted into internal energy. Since the internal energy U of a mole of gas is a function of temperature only, we may define the molar heat capacity at constant volume of a mole of gas C_V as

$$C_V = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} \quad \text{(at constant volume)}, \tag{16-15}$$

so that the change in internal energy ΔU may be expressed as

$$\Delta U = C_V \, \Delta T. \tag{16-16}$$

From Equation (16-13) the first law of thermodynamics as applied to an ideal gas may be rewritten as

$$\Delta Q = C_V \, \Delta T + P \, \Delta V. \tag{16-17}$$

Let us consider the change in temperature of a mole of gas when a quantity of heat ΔQ is delivered to the gas while the pressure is held constant but the volume is permitted to change. The thermal energy delivered to the gas must now be used to do external work as well as to change the internal energy of the gas. The rise in temperature of the gas will therefore be less than in the case where the volume of the gas is kept constant. The molar heat capacity at constant pressure C_P might be expressed in such units as calories per mole per degree, and may be defined through the equation

$$C_P = \frac{\Delta Q}{\Delta T} \quad \text{(at constant pressure)}, \tag{16-18}$$

Fig. 16-4 Work done by a mole of a gas in an isothermal expansion at temperature T from volume V_1 to volume V_2.

and from Equation (16-17) we find

$$C_P = \frac{C_V \, \Delta T + P \, \Delta V}{\Delta T}.$$

From the gas law for a mole of gas we have

$$PV = RT,$$

or

$$V = \frac{R}{P} \, T.$$

At constant pressure both R and P are constant, so that a change of volume ΔV is related to a change in temperature ΔT through the equation

$$\Delta V = \frac{R}{P} \, \Delta T.$$

Substituting this result into the preceding equation for C_P, we find that

$$C_P = C_V + R. \tag{16-19}$$

The molar heat capacity of a gas at constant pressure is always greater than the molar heat capacity at constant volume by the gas constant R.

The internal energy of a monatomic gas, such as helium, is entirely in the form of kinetic energy of translation of the random motions of the atoms of the gas. From Section 16-3 this internal energy may be stated as

$$U = N_0 \times \tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}RT. \tag{16-20}$$

Since R is a constant, we find that the change in internal energy ΔU associated with a change in temperature ΔT is given by

$$\Delta U = \tfrac{3}{2}R \, \Delta T.$$

Thus the molar heat capacity of a monatomic gas at constant volume may be found by substituting the preceding result into Equation (16-15), to find

$$C_V = \tfrac{3}{2}R \quad \text{(monatomic gas)}. \tag{16-21a}$$

Substituting this result into Equation (16-19), we obtain

$$C_P = \tfrac{5}{2}R \quad \text{(monatomic gas)}. \tag{16-21b}$$

It is customary to designate the ratio of the specific heat at constant pressure to the specific heat at constant volume by the letter γ (gamma). Thus

$$\gamma = \frac{C_P}{C_V}. \tag{16-22}$$

Substituting from Equations (16-21) into (16-22), we find the value of γ for a monatomic gas to be

$$\gamma = \tfrac{5}{3} \quad \text{(monatomic gas)}.$$

In our development of the kinetic theory of an ideal gas we assumed that a molecule could be considered as a point mass and showed that the average kinetic energy of translation per molecule is $\frac{3}{2}kT$ (Equation 16-11). There are three independent directions of motion of translation, say the x, y, and z directions. We say that the molecule has three *degrees of freedom*; that is, three coordinates are necessary to specify the position of the molecule at any instant, one for each degree of freedom. Since there is no reason for preferring one direction rather than another, we postulate the principle of *equipartition of energy*, that each degree of freedom should have the same amount of energy. Referring to Equation 16-11, the amount of energy to be associated with each degree of freedom per molecule is $\frac{1}{2}kT$. The internal energy of a mole of a monatomic gas will then be $\frac{3}{2}RT$, as given by Equation 16-20.

The idea of degrees of freedom can be extended to diatomic and polytomic gases. It can be shown that the value of γ can be expressed as

$$\gamma = \frac{f+2}{f},$$

where f is the number of degrees of freedom per molecule. For a monatomic gas we find that $\gamma = \dfrac{3+2}{3} = \dfrac{5}{3} = 1.67$, in agreement with measured values as shown in Table 16-1.

We may extend these ideas to a diatomic molecule which we may imagine to be two point masses a fixed distance apart; the line joining the two atoms is the axis of the molecule. If the diatomic molecule is considered as a rigid body, then it will have three degrees of freedom owing to the translational motion of the entire molecule, plus a certain number of degrees of freedom owing to the rotational motion of the molecule. A glance at Table 16-1 shows that $\gamma = 1.4$ for diatomic gas, indicating that $f = 5$; thus there must be two additional degrees of freedom of rotation. These would correspond to rotations about two mutually perpendicular axes in a plane at right angles to the line joining the two atoms.

Thus if at ordinary temperatures the molecules of a diatomic gas may be thought of as rigid, and possessing no vibrational energy, the mean energy of each molecule must be $\frac{5}{2}kT$. The total internal energy of a mole of such a gas is given by

$$U = N_0 \times \tfrac{5}{2}kT = \tfrac{5}{2}RT \quad \text{(diatomic gas).} \tag{16-23}$$

From this expression we find the molar heat capacities of a diatomic gas to be

$$C_V = \tfrac{5}{2}R, \qquad C_P = \tfrac{7}{2}R \quad \text{(diatomic gas),} \tag{16-24}$$

and the ratio of the specific heats γ is

$$\gamma = \tfrac{7}{5} \quad \text{(diatomic gas)}. \tag{16-25}$$

These results are in rather remarkable agreement with experiment, as shown in Table 16-1.

TABLE 16-1   THE MOLAR HEAT CAPACITY AT CONSTANT VOLUME, AND THE RATIO OF SPECIFIC HEATS FOR SEVERAL GASES

Gas	Atoms per Molecule	C_V*		γ	
		Theory	Experiment	Theory	Experiment
Argon	1	2.98	2.98	1.67	1.67
Helium	1	2.98	2.98	1.67	1.66
Oxygen	2	4.97	5.04	1.40	1.40
Nitrogen	2	4.97	4.93	1.40	1.40
Carbon monoxide	2	4.97	4.94	1.40	1.40

    * The units of C_V are given as calories per mole per degree centigrade.

At high temperatures the classical theory of the specific heats of gases is no longer adequate to describe the experimental determinations. Additional rotational and vibrational modes are excited at high temperatures in a manner which is best described by the quantum theory of specific heats; this is beyond the scope of this book.

16-6   Adiabatic Processes

An adiabatic process is one in which no heat enters or leaves the system. In the form of an equation

$$\Delta Q = 0.$$

If we apply the first law of thermodynamics, in the form of Equation (16-17), to adiabatic processes, we find

$$\Delta Q = 0 = C_V \, \Delta T + P \, \Delta V.$$

Thus
$$\Delta T = -P \frac{\Delta V}{C_V}.$$

The general gas law describes the behavior of a gas under all circumstances. Thus for a mole of gas we have

$$PV = RT.$$

If P, V, and T are permitted small variations, we find, on taking differentials, that

$$P \, \Delta V + V \, \Delta P = R \, \Delta T.$$

If we replace the gas constant R by

$$R = C_P - C_V$$

from Equation (16-19), and substitute the value of ΔT into the above equation, we find

$$P\,\Delta V + V\,\Delta P = -(C_P - C_V)\frac{P\,\Delta V}{C_V} = -(\gamma - 1)\,P\,\Delta V,$$

for, from Equation (16-22), $\gamma = C_P/C_V$. On transposing, and dividing the above equation by the product PV, we find

$$\frac{\Delta P}{P} + \gamma\,\frac{\Delta V}{V} = 0.$$

In the limit of small increments we may replace Δ by d, and integrate to find

$$\ln P + \gamma \ln V = \text{constant,}$$

or $\qquad\qquad\qquad\qquad PV^{\gamma} = \text{constant.} \qquad\qquad\qquad$ **(16-26)**

The value of the constant is determined by the quantity of gas present, so that Equation (16-26) may be used to describe the relationship between the pressure and the volume of any quantity of gas undergoing an adiabatic change. If a gas originally at pressure P_1, volume V_1, and temperature T_1 is compressed adiabatically, as in an insulated cylinder, to a new pressure P_2, the new volume of the gas V_2 may be found from Equation (16-26) by writing

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}. \qquad\qquad\qquad \textbf{(16-27)}$$

The final temperature of the gas T_2 may then be obtained from the gas law

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2},$$

in which all quantities except T_2 are now known.

    Illustrative Example. A mass of gas occupies a volume of 8 liters at a pressure of 1 atm and a temperature of 300° abs. It is compressed adiabatically to a volume of 2 liters. Determine (a) the final pressure and (b) the final temperature, assuming it to be an ideal gas whose value of $\gamma = 1.5$.

    (a) The final pressure of the gas can be determined with the aid of Equation (16-27) thus,

$$P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma},$$

so that $\qquad\qquad\qquad\qquad P_2 = 1\ \text{atm}\left(\frac{8}{2}\right)^{1.5},$

from which $\qquad\qquad\qquad\qquad P_2 = 8\ \text{atm.}$

(b) The final temperature can be found with the aid of the general gas law thus,

$$T_2 = T_1 \frac{P_2 V_2}{P_1 V_1},$$

so that

$$T_2 = 300° \text{ abs} \frac{8 \text{ atm} \times 2l}{1 \text{ atm} \times 8l},$$

or

$$T_2 = 600° \text{ abs}.$$

16-7   The Maxwell Distribution Function

In Section 16-3 we showed how the properties of a gas could be accounted for on the basis of a very simple set of hypotheses about the nature of a gas. We assumed that the gas was made up of many molecules in rapid motion, and that the molecules were sufficiently far apart so that the forces
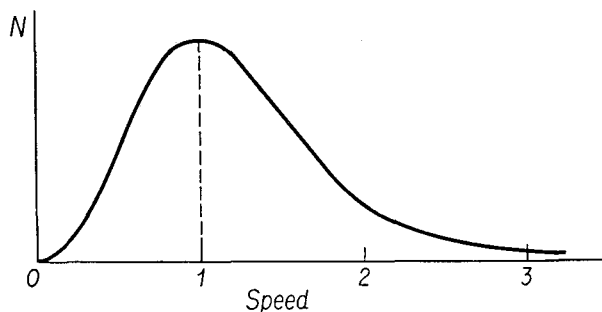

Fig. 16-5 The Maxwellian distribution of molecular speeds. Relative numbers of molecules having speeds in a unit speed interval at various speeds are shown as ordinate, while speeds in units of the most probable speed are shown as abscissa.

that one molecule exerted on another were of minor importance and could be neglected. We assumed that the molecules were perfectly elastic so that there was no loss in mechanical energy in collisions between molecules of the gas and the walls of the container. On the basis of such arguments, we could account for the gas law, and we were able to show that the temperature of a gas was directly related to the average value of the kinetic energy of its molecules.

When a gas is in equilibrium at an absolute temperature T, the distribution of velocities of the molecules of the gas is given by Figure 16-5, called the Maxwellian distribution, according to the theory first developed by Maxwell (1831–1879). This theory has now been well verified by experiment as actually describing the behavior of gas molecules. In fact, the Maxwellian distribution may be taken as the meaning of the temperature

of a gas, for, if a collection of gas molecules has a velocity distribution which differs from Figure 16-5, then we may say that the gas has not yet reached thermal equilibrium and therefore does not have a well-defined temperature.

The average of the velocity components of the molecules of a gas in a particular direction must be zero. If this were not so, the gas and its container would be in translational motion. However, the average value of the squares of the molecular velocities is not zero, and is given by Equation (16-11). From Figure 16-5 we see that molecules whose speeds are more than three times the most probable speed are extremely rare. Nevertheless, there are some molecules in the gas which have very large speeds, for the distribution curve approaches the horizontal axis asymptotically. We must also note that, at a given temperature, the molecules of a gas of low molecular weight are in more rapid motion than the molecules of a gas of high molecular weight. This has the interesting consequence that hydrogen and helium are steadily diffusing out of the earth's atmosphere, for, at the temperature of the outer air, some of these lighter molecules are moving sufficiently rapidly to attain the escape velocity of 11 km/sec necessary for a projectile to escape the gravitational pull of the earth.

If we call the energy required to disrupt a chemical molecule its *binding energy*, we see that, as the temperature of a gas is raised, a greater proportion of gas molecules may have kinetic energies greater than the binding energy, so that a molecule may be decomposed as a result of energy transfer during a collision. Thus molecules which are stable at ordinary temperatures must have binding energies which are large compared to the mean kinetic energy of a molecule at room temperature, as given by Equation (16-11).

It is interesting that modern theories of the structure of atoms and molecules have provided a justification of a basic assumption of the kinetic theory of gases. According to the *quantum theory*, molecules exist only in certain *quantum states*, each having a fixed amount of energy. These are sometimes called *energy levels*. The molecule normally exists in its state of lowest energy, called its *ground state*, and can only absorb energy in a collision with another molecule in exactly the right amount to raise it to a state of higher energy, called an *excited state*, or to disrupt it completely. In general, it is very unlikely that the colliding molecules will have just the right amount of energy for excitation, so that the collisions between the molecules of a gas result in no absorption of energy by the molecules. The kinetic energy is conserved in the collision rather than being transferred to internal excitation energy of one molecule. The collisions are therefore perfectly elastic.

Problems

16-1. A closed vessel contains dry air at 25°C and 76 cm of mercury pressure. Its temperature is raised to 100°C. Determine the pressure of the air, neglecting the change in volume of the container.

16-2. A mass of oxygen occupies a volume of 1 liter at a pressure of 76 cm of mercury when its temperature is 40°C. The gas is allowed to expand until its volume is 1.5 liters and its pressure is 80 cm of mercury. (a) Determine its final temperature. (b) Determine the number of moles of oxygen in the system.

16-3. Derive the general gas law from Equations (16-1) to (16-3) by considering that the gas is taken from $T_i P_i V_i$ by a constant-volume process to $T_2 P_f V_i$, and thence by a constant-pressure process to $T_f P_f V_f$.

16-4. A certain gas has a density of 0.001 gm/cm^3 when its temperature is 50°C and its pressure is 4 atm. What pressure will be needed to change the density of the gas to 0.002 gm/cm^3 when its temperature is 100°C?

16-5. An automobile tire has a volume of 1,000 in.^{3} and contains air at a gauge pressure of 24 lb/in.^{2} when the temperature is 0°C. What will be the gauge pressure of the air in the tires when its temperature rises to 27°C and its volume increases to 1,020 in.^{3}?

16-6. Determine the pressure of 4.032 gm of hydrogen which occupies a volume of 16.8 liters at a temperature of 0°C. The molecular weight of hydrogen is 2.016.

16-7. Determine the average value of the kinetic energy of the molecules of a gas (a) at 0°C and (b) at 100°C.

16-8. (a) What is the mass of a hydrogen molecule? (b) Determine the average velocity of a molecule of hydrogen at 27°C.

16-9. The molecules of a certain gas have a mass of 5×10^{-24} gm. What is the number of molecules per cubic centimeter of this gas when its pressure is 10^6 dynes/cm^2 and its temperature is 27°C?

16-10. Calculate the work done in compressing one mole of oxygen from a volume of 22.4 liters at 0°C and 1 atm pressure to 16.8 liters at the same temperature.

16-11. A cylinder contains a mole of hydrogen at 0°C and 76 cm of mercury pressure. Calculate the amount of heat required to raise the temperature of this hydrogen to 50°C (a) keeping the pressure constant, and (b) keeping the volume constant. (c) What is the volume of the hydrogen when at 0°C?

16-12. A cylinder contains 32 gm of oxygen at 0°C and 76 cm of mercury pressure. Calculate the amount of heat required to raise the temperature of this mass of oxygen to 80°C (a) keeping the pressure constant and (b) keeping the volume constant. (c) How much mechanical work is done by the oxygen in each case?

16-13. A mass of a monatomic gas occupies a volume of 400 cm^3 at a temperature of 17°C and a pressure of 76 cm of mercury. The gas is compressed adiabatically until its pressure is 90 cm of mercury. Determine (a) the final volume of the gas and (b) the final temperature of the gas.

16-14. A mass of a diatomic gas occupies a volume of 6 liters at a temperature

of 27°C and 75 cm of mercury pressure. The gas expands adiabatically until its volume is 8 liters. What is the final temperature of the gas?

16-15. A mole of gas at atmospheric pressure and 0°C is compressed isothermally until its pressure is 2 atm. How much mechanical work is done on the gas during this operation?

16-16. Ten grams of oxygen are heated at constant atmospheric pressure from 27°C to 127°C. (a) How much heat is delivered to the oxygen? (b) What fraction of the heat is used to raise the internal energy of the oxygen?

16-17. An air bubble of volume 20 cm^3 is at the bottom of a lake 40 m deep where the temperature is 4°C. The bubble rises to the surface where the temperature is 20°C. Assuming that the temperature of the bubble is the same as that of the surrounding water, what is its volume just as it reaches the surface?

16-18. An ideal gas for which $\gamma = 1.5$ is enclosed in a cylinder of volume 1 m^3 under a pressure of 3 atm. The gas is expanded adiabatically to a pressure of 1 atm. Find (a) the final volume and (b) the final temperature of the gas if its initial temperature was 20°C.

16-19. A mass of 1.3 kg of oxygen of molecular weight 32 is enclosed in a cylinder of volume 1 m^3 at a pressure of 10^5 nt/m^2 and a temperature of 20°C. From these data find the universal gas constant R assuming oxygen to be an ideal gas.

16-20. A gas of mass m and molecular weight M undergoes an isothermal expansion from an initial pressure P_1 and volume V_1 to a final pressure P_2 and volume V_2 while at temperature T. Find (a) the work done by the gas in this expansion, (b) the heat flow to the gas, and (c) the change in internal energy of the gas in terms of these symbols.

16-21. A piece of putty is placed in a vise with insulating jaws. A constant force of 100 nt is applied through a distance of 2 cm. The putty is found not to have its volume changed in this process. What is the change in the internal energy of the putty?

16-22. Prove that $TV^{\gamma-1} =$ constant for an adiabatic process.

16-23. Show that the work done by a gas in an adiabatic expansion from initial conditions P_i, V_i to final conditions P_f, V_f is given by

$$W = \frac{P_i V_i^\gamma}{1 - \gamma} (V_f^{1-\gamma} - V_i^{1-\gamma}).$$