

The Kinetic Theory of Gases

Prior to consideration of gas–surface interactions, this chapter and the following will present the kinetic theory of gases and the properties of molecular beams. An understanding of these two subjects is required as a background for understanding both the theoretical and experimental aspects of gas–surface interactions.

First developed by Maxwell, the kinetic theory of gases has been elaborated by many subsequent investigators. This theory explains both the bulk properties of a gas, such as the pressure, molecular impingement rate, and distribution of molecular velocities, and the transport properties, such as viscosity, thermal conductivity, and diffusion, in terms of the dynamics of motion of the individual molecules.

The theory can be developed either in terms of classical mechanics or in terms of quantum statistical mechanics. The classical description is simpler but requires that one make some questionable assumptions which can be shown to be unnecessary by the mathematically more difficult statistical mechanical approach. The classical approach will be used here, as the added rigor of the statistical treatment does not add enough to the physical understanding of gases to warrant the added complexity.

Physical Picture and Assumptions

The physical picture used in the classical approach represents the gas as a collection of a large number of hard, spherical particles, having a small size compared to their separation, in constant rapid motion in random directions. The particles collide with each other and with the walls of the container. The only result of these collisions is to change the momentum and kinetic energy of the particles involved, subject to the constraints imposed by the conservation of momentum and energy. Although the momenta and energies of individual molecules change rapidly with time, the average properties of the collection of particles are time independent if no external process takes place.

The assumptions on which this model is based may be stated formally as

1. Any finite volume of gas contains a large number of molecules.
2. Molecules exert no forces on one another except when they collide. Between collisions with each other or with the container walls they travel in straight lines.

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3. Collisions of one molecule with another or with surfaces exposed to the gas are perfectly elastic. All surfaces are considered smooth.
4. In the absence of external forces, the molecules are distributed uniformly throughout the container.
5. All directions of molecular velocities are equally probable.
6. The speed of a given molecule may have any magnitude, but the number of molecules with speeds in a given range is constant with time. (That is, the speed distribution is time invariant).

Now consider the validity of these assumptions in turn:

1. The number of molecules in 1 cm^3 at atmospheric pressure and room temperature is approximately 3×10^{19} and varies directly with pressure. Consequently, except for extremely low pressures, the number of molecules per cubic centimeter will be large, and assumption 1 is valid.
2. The validity of assumption 2 depends on the definition of collision. If one defines a collision as any approach close enough that there is an interaction, then assumption 2 is valid. In practice, this is a good assumption as long as the distance between particles is very large compared to the particle diameter.
3. Assumption 3 is true only for an ideal gas. Basically, it assumes that there are no intermolecular attractive forces in the gas and no attractive forces between a gas molecule and the surface of the container. At low pressures (or equivalently, at low number densities), the effects of intermolecular attractive forces are small enough that they can be ignored in determining the properties of the gas. However, at high densities, or at low temperatures, these forces must be explicitly accounted for, as they lead to condensation in the case of gas-gas interactions and adsorption in the case of gas-surface interactions. These effects will be discussed in detail. Condensation will be discussed later in this chapter, in the section on molecular interactions. Adsorption is discussed in Chapters 10, 11, and 12.
4. Assumption 4 is generally a good approximation. It breaks down only when assumption 1 breaks down, which is at very low number densities. (This assumption does, however, break down if external forces are present, for example, for the case of an atmosphere in a gravitational field.)
- 5 & 6. Assumptions 5 and 6 are the least tenable of all. They are valid in practice, however, and this is the only justification for their use. There is no *a priori* justification for these assumptions, and one can show by the statistical mechanical approach that they are unnecessary and appear as a consequence of the treatment.

The Molecular Impingement Rate

The first step in the development of the kinetic theory of gases is to develop an expression for the number of gas molecules that strike a given area in the system per unit time. This is called the *molecular impingement rate* and is usually stated in units of

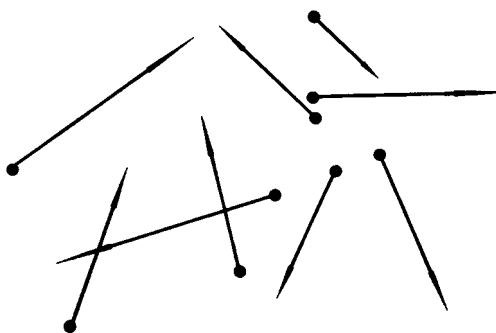


Figure 7.1 Molecular motion in a gas, showing velocity vectors attached to each molecule.

molecules/sec-cm². This is an important parameter in the kinetic theory, as it will be used to develop the expression for pressure and it is often the rate-controlling parameter in gas-surface interactions.

To begin this development, one must first put assumption 5, concerning the equal probability of all directions of molecular velocities, into analytical form. This is done by imagining first that there is attached to each molecule in the system, at any moment, a vector representing the direction and magnitude of its velocity, as shown in Figure 7.1. All of these vectors are transferred to a common origin, as shown in Figure 7.2, and a sphere of radius r constructed around this origin. In this construction, the velocity vectors (or their extensions for those molecules whose speeds have amplitudes less than r) intersect the surface of the sphere in as many points as there are molecules in the system. The assumption of uniform distribution of directions of velocity simply means that each unit of area on the surface of the sphere that we have constructed is intersected by the same number of vectors (or their extensions). The average number of intersections per unit area is thus

$$\frac{N}{S} = \frac{N}{4\pi r^2}, \quad 7.1$$

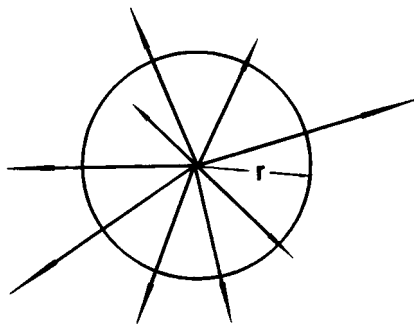


Figure 7.2 Velocity vectors transferred to a common origin.

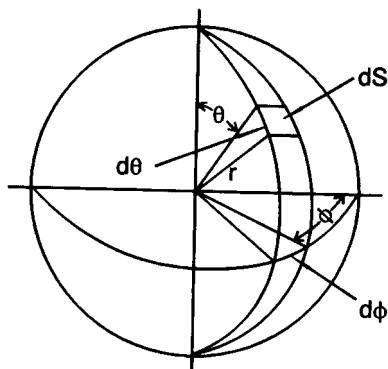


Figure 7.3 Definition of an element of surface on a sphere in terms of the polar angle θ and the azimuthal angle Φ .

where N is the total number of molecules in the system and S is the surface area of the sphere. The number of intersections on any element of the surface of the sphere, dS , is thus

$$dN = \left(\frac{N}{4\pi r^2} \right) dS, \quad 7.2$$

independent of where dS is located on the sphere.

Carrying this development one step further and defining a specific surface element, dS , in terms of the polar coordinates θ , Φ as shown in Figure 7.3, leads to

$$dS = r d\theta r \sin\theta d\Phi,$$

or

$$dS = r^2 \sin\theta d\theta d\Phi. \quad 7.3$$

The number of molecules whose velocity vectors intersect this element of area, that is, the number of molecules whose velocities are directed within a polar angle from θ to $\theta + d\theta$ and azimuthal angle from Φ to $\Phi + d\Phi$, which is called $d^2N_{\theta,\Phi}$, is

$$d^2N_{\theta,\Phi} = \left(\frac{N}{4\pi r^2} \right) (r^2 \sin\theta d\theta d\Phi)$$

or

$$d^2N_{\theta,\Phi} = \left(\frac{N}{4\pi} \right) (\sin\theta d\theta d\Phi). \quad 7.4$$

As a final step, divide both sides by the system volume, V , to get

$$d^2n_{\theta,\Phi} = \left(\frac{n}{4\pi} \right) (\sin\theta d\theta d\Phi), \quad 7.5$$

where $n = N/V$. Equation 7.5 is the desired analytical expression of assumption 5.

The foregoing result can be used to develop the expression for molecular impingement rate. This is the rate at which molecules from the gas strike a unit area of surface exposed to the gas—either the container surface or any area constructed within the bulk of the gas. To do this, consider an arbitrary element, dA , of any surface exposed to the gas. (Note that this dA is an element of real surface, as opposed to the dS discussed previously which was an element of area on an arbitrarily constructed sphere in vector space.) Construct a line normal to the plane of dA , and a reference plane perpendicular to the normal as shown in Figure 7.4. The question now is that of how many molecules impinge on this area, dA , in the time interval, dt , traveling in a direction specified by θ , Φ , and having a specified speed, v . Such a collision of a molecule having direction defined by θ , Φ , with speed v , is called a θ , Φ , v collision (that is, a molecule with directions between θ and $\theta + d\theta$, Φ and $\Phi + d\Phi$ and speed between v and $v + dv$).

To determine the number of such collisions per unit area per unit time, construct a prism of height $v dt$, and base dA , inclined to the plane of dA at angles θ , Φ , again as shown in Figure 7.4. The volume of this figure is

$$dV = v dA dt \cos \theta. \tag{7.6}$$

Because of the fact that this volume element was defined by direction–speed coordinates, θ , Φ , v , all of the molecules that were within this volume element at $t = 0$ will strike dA in time dt . In order to determine the contribution to the impingement rate from this volume element, the number of molecules in this element having velocities from v to $v + dv$ must be determined. One must then integrate over all possible values of θ , Φ , v to get the total impingement rate. To do this one must make one further assumption, namely, that just it was assumed that the distribution of all of the molecules throughout the volume of the system was uniform, it is now assumed that the distribution of any subgroup of molecules is uniform throughout the volume. That is, the fraction of the molecules in the prism constructed that are θ , Φ , v molecules is the same as the fraction of the molecules in the total system that are θ , Φ , v molecules.

Having made this assumption, one may now define dn_v as the number of

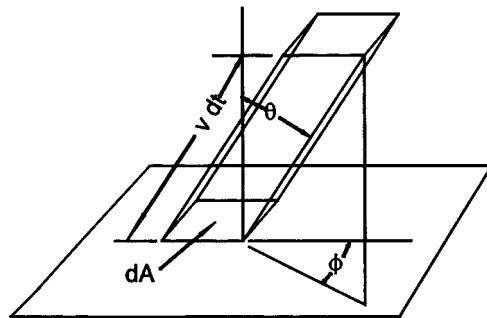


Figure 7.4 Reference element of a real surface area, dA , with prism defined by θ , Φ , v .

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molecules per unit volume having speeds from v to $v + dv$, irrespective of the direction of their velocity. If the number density of molecules with directions described by θ, Φ , is

$$d^2 n_{\theta, \Phi} = \left(\frac{1}{4\pi} \right) n \sin \theta \, d\theta \, d\Phi, \quad 7.7$$

one may similarly define

$$d^3 n_{\theta, \Phi, v} = \left(\frac{1}{4\pi} \right) dn_v \sin \theta \, d\theta \, d\Phi, \quad 7.8$$

the number of molecules per unit volume having speeds between v and $v + dv$, traveling in a direction defined by θ, Φ . The total number of θ, Φ, v molecules in the prism constructed is simply the product of $d^3 n_{\theta, \Phi, v}$ and the volume of the prism, dV , or

$$\begin{aligned} N_{\theta, \Phi, v} &= d^3 n_{\theta, \Phi, v} dV \\ &= dA \, dt \left(\frac{v dn_v}{4\pi} \right) \sin \theta \cos \theta \, d\theta \, d\Phi. \end{aligned} \quad 7.9$$

From this one may write the impingement rate of θ, Φ, v molecules per unit area per unit time as

$$I_{\theta, \Phi, v} = \frac{N_{\theta, \Phi, v}}{dA \, dt} = \left(\frac{1}{4\pi} \right) v dn_v \sin \theta \cos \theta \, d\theta \, d\Phi. \quad 7.10$$

One may define the total impingement rate of molecules having speeds from v to $v + dv$, over the whole of the space above the reference area, by integrating Equation 7.10 with respect to θ from zero to $\pi/2$ and with respect to Φ from zero to 2π , yielding

$$I_v = \left(\frac{1}{4\pi} \right) v dn_v (2\pi) \left(\frac{1}{2} \right),$$

or

$$I_v = \frac{1}{4} v dn_v. \quad 7.11$$

Furthermore, the total impingement rate for all molecules, irrespective of their speeds, is

$$I = \frac{1}{4} \int v dn_v. \quad 7.12$$

This may finally be expressed in terms of the arithmetic mean speed of the molecules, which is defined as

$$\bar{v} = \frac{\sum_i n_i v_i}{\sum_i n_i} \quad 7.13$$

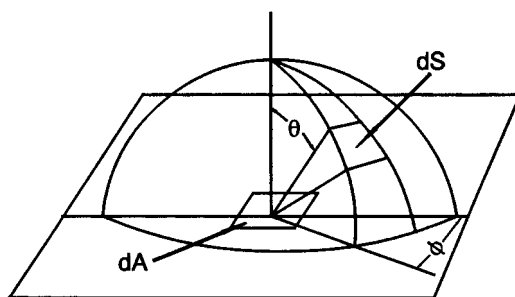


Figure 7.5 Defining geometry for calculation of impingement rate as a function of polar angle.

in which one sums over all possible values of v_i . Assuming that the velocity distribution is continuous, that dn_v represents the number density of molecules with speed v , and that the total number density of molecules is large, then one can replace the sums in Equation 7.13 by integrals and write

$$\bar{v} = \frac{\int v dn_v}{\int dn_v} = \frac{\int v dn_v}{n}. \quad 7.14$$

Thus,

$$\int v dn_v = n\bar{v}, \quad 7.15$$

and

$$I = \frac{1}{4} n\bar{v}, \quad 7.16$$

the desired result. Thus, the molecular impingement rate depends directly on the number density and the mean velocity. The next section in this chapter will show that \bar{v} depends on the temperature, T , and that n is directly related to the pressure, p .

One further property related to the subject of impingement rate may be derived, namely, the impingement rate as a function of the polar angle θ . To do this, consider a reference area element located at the center of a sphere, as shown in Figure 7.5, in the plane defined by the x and y axes. Molecules impinging on dA from a direction defined by θ , Φ are those that enter the sphere drawn within the cone defined by θ to $\theta + d\theta$ and Φ to $\Phi + d\Phi$, which intersects the surface of the sphere in an area element dS . As previously shown

$$dS = r^2 \sin\theta \, d\theta \, d\Phi, \quad 7.17$$

and the solid angle subtended by the cone is

$$d\omega = \sin\theta \, d\theta \, d\Phi = \frac{dS}{r^2}. \quad 7.18$$

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One may rewrite Equation 7.10 in terms of ω as

$$I_{\theta,\Phi,v} = I_{\omega,v} = \left(\frac{1}{4\pi}\right) v dn_v \cos \theta d\omega, \quad 7.19$$

an expression giving the impingement rate of molecules having a velocity from v to $v + dv$ and coming from a direction defined by the solid angle from ω to $\omega + d\omega$. From this, one can write an expression for the impingement rate of molecules in the velocity range from $v + dv$ per unit solid angle as

$$(I_v)_{\omega} = \frac{I_{\omega,v}}{d\omega} = \left(\frac{1}{4\pi}\right) v dn_v \cos \theta. \quad 7.20$$

The total impingement rate for all velocities per unit solid angle is thus

$$I_{\omega} = \left(\frac{1}{4\pi}\right) \cos \theta \int v dn_v$$

or

$$I_{\omega} = \left(\frac{1}{4\pi}\right) n\bar{v} \cos \theta = \frac{1}{4} n\bar{v} \frac{\cos \theta}{\pi}. \quad 7.21$$

This is known as the cosine law. The greatest value of I_{ω} is associated with the element of solid angle located normal to the surface. I_{ω} decreases uniformly as the polar angle increases toward the surface. This result will be used in Chapter 8, in the discussion of effusion from orifices and molecular beam technology.

Pressure

Knowledge of the impingement rate may be used to develop an expression for the pressure exerted on the container walls arising from the collisions of the gas molecules with the walls. The pressure may be defined either as the force exerted per unit area by the gas molecules on the walls of the container or as the rate at which momentum is imparted to unit area of wall surface. Mathematically, this latter definition can be written as

$$p = \frac{\dot{\mu}}{dA dt}, \quad 7.22$$

where $\dot{\mu}$ is the rate of momentum transfer. To develop an expression for pressure, one must thus calculate the average momentum transfer from a molecule to the wall per collision, then multiply this by the impingement rate, I , to get the pressure.

To make this calculation, begin by recalling assumption number 3, that the collisions are perfectly elastic and the walls perfectly smooth. Assume in addition that the

walls are so massive relative to the molecular mass that the wall velocity is unaffected in the collision process. If this is the case, then the change in velocity experienced by a colliding molecule having an initial velocity v , coming from a direction defined by θ , Φ is, as before,

$$\Delta v = 2v \cos \theta . \quad 7.23$$

This is essentially a billiard-ball collision. Because the wall is smooth, only the component of the velocity perpendicular to the wall is affected. The change in momentum per collision is then

$$\mathcal{A} = m\Delta v = 2mv \cos \theta \quad 7.24$$

for a molecule having an initial velocity v , coming from a direction defined by θ , Φ . Recall that Equation 7.9 showed that the number of such molecules is

$$N_{\theta, \Phi, v} = \left(\frac{1}{4\pi} \right) v dn_v \sin \theta \cos \theta d\theta d\Phi dAdt .$$

The total change in momentum due to collisions of this type on the area dA in the time dt is thus

$$N_{\theta, \Phi, v} \mathcal{A} = \left(\frac{1}{2\pi} \right) mv^2 dn_v \sin \theta \cos^2 \theta d\theta d\Phi dAdt . \quad 7.25$$

This expression may be integrated as before over θ from zero to $\pi/2$ and over Φ from zero to 2π to get the total momentum transfer due to molecules in a given velocity range as

$$\begin{aligned} \mathcal{A}_v &= \left(\frac{1}{2\pi} \right) mv^2 dn_v dAdt (2\pi) \left(\frac{1}{3} \right) \\ &= \left(\frac{1}{3} \right) mv^2 dn_v dAdt . \end{aligned} \quad 7.26$$

Again, as before, one may integrate over all possible values of velocity to get the total momentum transferred to the area dA in the time dt as

$$\mathcal{A} = \frac{1}{3} m \int v^2 dn_v dAdt \quad 7.27$$

and, using the definition of pressure in Equation 7.22,

$$p = \frac{\mathcal{A}}{dAdt} = \frac{1}{3} m \int v^2 dn_v . \quad 7.28$$

Here again, as in the case of the impingement rate, this is an integral over velocity

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increments, only this time it is over increments of v^2 . One may proceed as before to define the average value of v^2 , the mean square velocity, as

$$\overline{v^2} = \frac{\sum_i v_i^2 n_i}{\sum_i n_i}. \quad 7.29$$

Again, making the same assumptions as before concerning the continuity of the distributions of velocities, one may replace the summations with integrals to obtain

$$\overline{v^2} = \frac{\int v^2 dn_v}{\int dn_v} = \frac{\int v^2 dn_v}{n} \quad 7.30$$

or

$$\int v^2 dn_v = n\overline{v^2}, \quad 7.31$$

yielding as the expression for pressure

$$p = \frac{1}{3} m (n\overline{v^2})$$

or

$$p = \frac{1}{3} nm\overline{v^2}. \quad 7.32$$

Note at this point that $\overline{v}^2 \neq \overline{v^2}$. The difference between these two parameters will become more apparent in the next section of this chapter, a discussion of the distribution of velocities.

Before leaving the subject of pressure, consider pressure from another viewpoint. The assumptions made in developing the kinetic theory of gases are equivalent to those that define the ideal gas on a thermodynamic basis. For example, the assumptions of elastic collisions and no intermolecular attractive forces are equivalent to the thermodynamic criterion that

$$\left(\frac{\partial E}{\partial V} \right)_T = 0. \quad 7.33$$

Consequently, a kinetic theory gas should have the same equation of state as an ideal gas—that is, it should obey Boyle's and Charles's laws and should have as an equation of state

$$pV = \left(\frac{N}{N_{av}} \right) RT. \quad 7.34$$

If the equation for pressure derived above is correct, it must be identical to the pressure defined by Equation 7.34, which can be derived from purely thermodynamic considerations. That is,

$$P_{\text{kin}} = P_{\text{thermo}}$$

or

$$\frac{1}{3}nm\overline{v^2} = \left(\frac{N}{V}\right)\left(\frac{R}{N_{\text{av}}}\right)T \quad 7.35$$

or, substituting into the right-hand side

$$n = \frac{N}{V}, \quad \frac{R}{N_{\text{av}}} = k, \quad 7.36$$

where k is Boltzmann's constant,

$$\frac{1}{3}m\overline{v^2} = kT \quad 7.37$$

The kinetic energy of a kinetic theory gas is thus,

$$\frac{1}{2}m\overline{v^2} = \left(\frac{3}{2}\right)kT. \quad 7.38$$

It is apparent that this energy is a function of temperature only, as it must be if the thermodynamic criterion for an ideal gas, $(\partial E/\partial V)_T = 0$, is to be satisfied. Note in passing that one can rearrange Equation 7.37 to obtain

$$\overline{v^2} = \frac{3kT}{m}, \quad 7.39$$

a relation that will be used the next section of this chapter, the distribution of velocities.

Finally, substitution of the identities shown in Equation 7.36 into Equation 7.34 yields

$$p = nkT. \quad 7.40$$

This will be a very convenient form for p in much of this work, as it gives p as a function of the gas density and the temperature.

Distribution of Molecular Velocities

To this point it has been assumed that the gas molecules at equilibrium have some given distribution of velocities and that this distribution is time invariant. Now consider the form of this distribution.

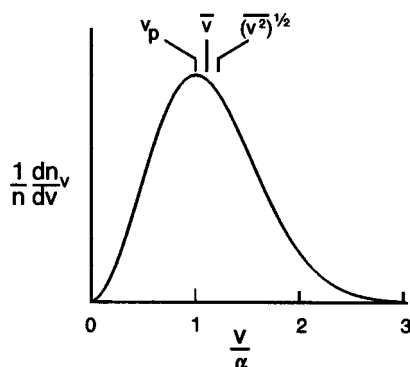


Figure 7.6 The equilibrium distribution of molecular velocities in a kinetic theory gas. v_p : \bar{v} : $(\bar{v}^2)^{1/2}$ as 1.000 : 1.128 : 1.225.

The mathematics required in developing the distribution in detail would take more time than is justified for present purposes. The development proceeds, however, by assuming that the three orthogonal components of the velocity of a given molecule are independent of one another, then uses a variational process involving the use of an undetermined multiplier, α . This involves essentially varying the velocity components of the various molecules, subject to the constraint of constant total system energy, in order to determine the equilibrium distribution. The result of this process gives the relation for the fraction of the molecules in the system in a given velocity range in terms of the velocity and the multiplier α . The resulting relation is

$$\frac{dN_v}{N} = \frac{dn_v}{n} = \left(\frac{4}{\pi^{1/2} \alpha^3} \right) \exp\left(\frac{-v^2}{\alpha^2} \right) v^2 dv. \quad 7.41$$

Figure 7.6 is a graph of this relation. From the graph one may define three characteristic velocities:

1. The most probable velocity, v_p —the velocity associated with the maximum in the distribution. That is, the velocity for which

$$\left(\frac{1}{n} \right) \left(\frac{dn_v}{dv} \right) = 0 \quad 7.42$$

This can be found by differentiation to be

$$v_p = \alpha. \quad 7.43$$

2. The mean velocity, \bar{v} . Using the definition of \bar{v} ,

$$\bar{v} = \frac{\int v dn_v}{\int dn_v}, \quad 7.44$$

and plugging in dn_v from Equation 7.41 it can be determined that

$$\bar{v} = \left(\frac{2}{\pi^{1/2}} \right) \alpha \quad 7.45$$

3. The mean square velocity $\overline{v^2}$. Again, using the definition

$$\overline{v^2} = \frac{\int v^2 dn_v}{\int dn_v} \quad 7.46$$

one determines that

$$\overline{v^2} = \frac{3}{2} \alpha^2. \quad 7.47$$

Recall that it has already been determined, by comparing kinetic theory results to thermodynamics, that

$$\overline{v^2} = \frac{3kT}{m}; \quad 7.48$$

thus one may write that

$$\bar{v} = \left(\frac{8kT}{\pi m} \right)^{1/2} \quad 7.49$$

and

$$v_p = \left(\frac{2kT}{m} \right)^{1/2}. \quad 7.50$$

A comparison of the numerical values of these three characteristic velocities yields:

$$v_p : \bar{v} : (\overline{v^2})^{1/2} = 1.000 : 1.128 : 1.225. \quad 7.51$$

Note finally that now that \bar{v} has been evaluated in terms of observables, one may write as the final expression for the molecular impingement rate that

$$I = \frac{1}{4} n \bar{v}$$

$$I = \frac{1}{4} \left(\frac{p}{kT} \right) \left(\frac{8kT}{\pi m} \right)^{1/2}$$

or

$$I = \frac{p}{(2\pi mkT)^{1/2}}. \quad 7.52$$

This expression will be used throughout the book.

Finite Molecular Size Effects

Up to this point, the gas molecules have been treated as point masses. Allowing for the fact that the molecules, in reality, are of finite size, leads to three new concepts, namely, excluded volume, collision frequency, and mean free path.

Excluded volume arises from the fact that because the molecules take up space, not all of the volume of the container is available to any given molecule at any given time. One may account for this effect by assuming first that the molecules are spheres of radius ρ . Consequently, each molecule excludes the centers of all of the other molecules in the system from a sphere of radius 2ρ , or a volume of $8V_m$, where

$$V_m = \left(\frac{4}{3}\right)\pi\rho^3. \quad 7.53$$

If one calculates the average volume available to a given molecule on this basis, by effectively adding molecules one at a time to an empty volume and calculating the volume available to each incremental molecule, the result is

$$V_A = V - 4NV_m. \quad 7.54$$

The equation of state for the gas, including the effect of this term is

$$p(V - b) = NkT, \quad 7.55$$

where

$$b = 4NV_m = \left(\frac{16}{3}\right)\pi N\rho^3 \quad 7.56$$

and is a constant for any given molecular species.

Consider next the concept of *collision frequency*. Because the molecules are of finite size, they will collide if they get within a certain distance of one another. Empirically, one would expect this collision frequency, Z , to be proportional to the number of molecules present, how close they are to one another (the product of these two terms is given by n), the mean molecular velocity, \bar{v} , and the cross-sectional area that one molecule "sees" as it approaches another. That is,

$$Z = \sigma n \bar{v}, \quad 7.57$$

where σ is the collision cross-section. One can develop this relation rigorously, but the intuitive argument given above will suffice here.

Finally, consider the so-called *mean free path*, λ . This is defined as the average distance a molecule travels between collisions. One can get at this parameter simply by dividing the average distance traveled per unit time by the average number of collisions per unit time, or

$$\lambda \propto \frac{\bar{v} dt}{Z dt} \propto \frac{\bar{v}}{\sigma n \bar{v}} = \frac{1}{\sigma n}. \quad 7.58$$

A more rigorous treatment would yield

$$\lambda = \frac{1}{\sqrt{2}n\sigma}. \quad 7.59$$

Note that the mean free path turns out to be independent of temperature and inversely proportional to pressure, through its dependence on n .

Molecular Interactions

To this point, it has been assumed that there were no forces acting between molecules in the gas. This is clearly an unrealistic assumption but one which gives results in agreement with observation at high temperatures and low densities. Now consider these forces and their effect on the behavior of real gases.

The forces in question are the permanent or induced dipole interactions that are always present when molecules approach one another. These are the forces that lead to condensation at low enough temperatures. The net effect of these forces in the case of a gas is to reduce the measured pressure below that which would be calculated using the kinetic theory equations developed above. The magnitude of this effect depends on the type of forces involved in any given case. In general, permanent dipole forces will be stronger than induced dipole, or van der Waals, forces, and the forces will be stronger for heavy molecules than for light molecules. The net effect on the equation of state of allowing for these forces is to modify the pressure dependence, leading to

$$\left(p + \frac{a}{V^2}\right)(V - b) = NkT, \quad 7.60$$

the so-called *van der Waals equation of state*.

Figure 7.7 is a plot of the van der Waals equation of state, showing the relation of p to V for a range of temperatures. At high temperatures, the curves are essentially the

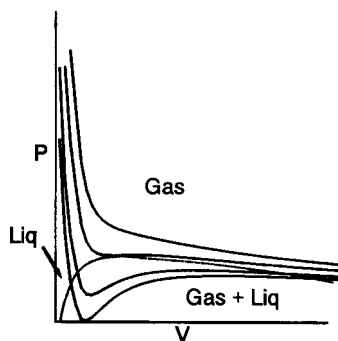


Figure 7.7 Relation between pressure and volume for a gas that obeys the van der Waals equation of state. Isotherms are plotted for a range of temperatures. Below T_c , a gas and a condensed phase may coexist at equilibrium. Two phases will be present inside the dotted area.

hyperbolas predicted by the kinetic theory. As the temperature is reduced, there are increasing deviations in the direction of lower pressure for a given volume. Eventually, a point is reached where the curve becomes double valued in V for a given p . At this point, called the critical temperature, T_c , condensation occurs, and a two-phase mixture of gas and condensed phases is formed. With further decreases in temperature, the equilibrium pressure over the condensed phase is further reduced.

Polyatomic Molecules

As a final topic under the behavior of gases, consider the complications that arise when the details of molecular structure are taken into account. In particular, the concern is the way in which the average total energy per molecule depends on the number and kind of atoms that make up the molecule. For the case of translational kinetic energy, the average energy per molecule is

$$E_{tr} = \frac{1}{2} m \overline{v^2} = \left(\frac{3}{2}\right) kT. \quad 7.61$$

This leads to a value for the heat capacity of $(3/2)N_{Av}k$ per mole.

For the case of polyatomic molecules, one must consider in addition contributions to the total energy from the so-called *internal degrees of freedom*, namely, rotational and vibrational energies.

Rotational motion can generally be treated classically, as the motion of a rigid rotor. The result of such a treatment is a contribution to the total average energy per molecule of kT for the case of diatomic or linear polyatomic molecules and of $(3/2)kT$ per molecule for nonlinear polyatomic molecules. This leads to a total average energy per molecule of $(5/2)kT$ (linear) or $3kT$ (nonlinear) and to heat capacities of $(5/2)N_{Av}k$ and $3N_{Av}k$ per mole, respectively. These considerations will be important in the discussion of molecular beam formation.

Because the separation between adjacent vibrational energy levels is generally large compared to kT , vibrational energies must be treated quantum mechanically. The net result of such a treatment is that the fraction of molecules to be found in a given excited vibrational state, i , will be

$$\frac{n_i}{n} = (const) \exp\left(\frac{-h\nu}{kT}\right). \quad 7.62$$

Because of the large energy differences from state to state, vibrational excitation is rare, except at high temperatures. The contribution of vibrational energy to the heat capacity is, in general, correspondingly small.

Summary

By way of summary, Table 7.1 shows the values expected for n , I , Z , λ , the intermolecular spacing, and the time required to form a monolayer of gas on a surface for

Table 7.1

Pressure (P), Number Density (n), Impingement Rate (I), Intermolecular Spacing, Collision Frequency (Z), Mean Free Path (λ) and Monolayer Time for a Gas Having $m = 28$ AMU at $T = 273$ K.

P (Torr)	P (Pascal)	n (molec/cm ³)	I (molec/cm ² sec)	Intermolecular Spacing (cm)	Z sec ⁻¹	λ (cm)	Monolayer Time (sec)
760	10^5	2.7×10^{19}	3×10^{23}	3.3×10^{-7}	7×10^9	6×10^{-6}	3.3×10^{-9}
1	1.3×10^2	3.5×10^{16}	4×10^{20}	3×10^{-6}	9×10^6	4.5×10^{-3}	2.5×10^{-6}
10^{-3}	1.3×10^{-1}	3.5×10^{13}	4×10^{17}	3×10^{-5}	9×10^3	4.5	2.5×10^{-3}
10^{-6}	1.3×10^{-4}	3.5×10^{10}	4×10^{14}	3×10^{-4}	9	4.5×10^3 (150 ft)	2.5
10^{-9}	1.3×10^{-7}	3.5×10^7	4×10^{11}	3×10^{-3}	9×10^{-3}	4.5×10^6 (28 mi)	2.5×10^3 (42 min)
10^{-12}	1.3×10^{-10}	3.5×10^4	4×10^8	3×10^{-2}	9×10^{-6}	4.5×10^9 (28000 mi)	2.5×10^6 (700 hr)
10^{-15}	1.3×10^{-13}	35	4×10^5	3×10^{-1}	9×10^{-9}	4.5×10^{12} (2.8×10^7 mi)	2.5×10^9 (79 yr)

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the case of a gas with $m = 28$ AMU at $T = 273$ K. This table warrants extensive examination, as it contains the information necessary to get a feeling for the physical situation in systems at various pressure levels.

Problems

7.1. Derive an expression equivalent to the kinetic theory expression for pressure ($p = 1/3nm\bar{v}^2$) for a two-dimensional gas, that is, one whose molecules can move only in a plane. Note that instead of force/area in this case it is force/length of the boundary enclosing the available area.

7.2. The pressure in a vacuum system is 10^{-9} Torr, the external pressure is 1 atm, and the temperature is 300 K. There is a pinhole in the wall of the system having an area of 10^{-10} cm². Assuming that every molecule that strikes the hole passes through it:

a. How many molecules leak in in 1 hour?

b. If the system volume is 2 liters, how great a pressure rise will result? (Assume no pumping in the system.)

7.3. A spherical bulb 10 cm in diameter is pumped continuously to a high vacuum. In the bulb is a small vessel, closed except for a 0.2 mm diameter hole, located at the center of the larger bulb. The small vessel contains mercury at 100°C, where its vapor pressure is 0.28 Torr.

a. Calculate \bar{v} for the mercury in the vessel.

b. Calculate the rate of efflux of mercury through the hole in grams per hour.

c. How long a time is required for 10^{-6} g of mercury to be deposited on 1 cm² of bulb surface in a direction making a 45° angle with the normal to the hole? Assume that all mercury atoms that strike the bulb surface stick to it.

7.4. At 300 K, what fraction of the molecules in argon gas have a kinetic energy greater than 1.0 eV/atom?

7.5. The density of N_2 at 273 K and 3000 atm is 0.835 g/cm³. Calculate the average distance between the centers of the molecules. How does this compare with the molecular diameter calculated from the van der Waals equation of state, for which $b = 39.1$ cm³/mole?

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