6 Ideal Gases and Absolute Temperature

A. Kinetic energy and absolute temperature
B. Pressure, temperature, and volume
C. Measurement of absolute temperature
D. Molecular quantities and Boltzmann's constant
E. Summary

As we have seen, the absolute temperature of a system determines whether the system will be in thermal equilibrium with other systems. The absolute temperature can also profoundly affect the properties of a system. Accordingly, the present chapter discusses ideal gases, systems that are especially simple yet quite important. In particular, we shall examine how the properties of an ideal gas depends on its absolute temperature. This examination will also lead as to practical methods of measuring the absolute temperature of any system.

A. Kinetic energy and absolute temperature

The absolute temperature T of any system specifies how rapidly the system's entropy increases with its energy. Indeed, according to its definition (4F-3), the basic temperature β of a system is related to its basic entropy $\ln\Omega$ so that.

$$\beta = \frac{\ln\Omega}{dE}.$$ (A-1)

Equivalently, since $\beta = 1/(kT)$, the absolute temperature T is related to the entropy $S = k \ln\Omega$ so that

$$\frac{1}{T} = \frac{dS}{dE}.$$ (A-2)

Monatomic gas

Entropy of the gas. Consider a monatomic ideal gas (such as helium or argon) in which every molecule consists of a single atom. The internal energy E of the gas is then merely equal to the total kinetic energy K of all the molecules. Furthermore, this system is sufficiently simple that one can readily calculate how the number Ω of basic states available to the gas depends on its kinetic energy K. This calculation was already carried out in Chapter 4 and led to the result (4E-3) that

$$\Omega = c\, K^{3N/2}.$$ (A-3)

where c is some constant of proportionality. The entropy of this monatomic gas depends thus on its energy $E = K$ so that

$$S = k \ln \Omega = k \ln c + k \left(\frac{3N}{2}\right) \ln E. \qquad (A\text{-}4)$$

Absolute temperature of the gas. According to the general relation (A-2), the absolute temperature T of this gas is related to its energy E so that

$$\frac{1}{T} = \frac{dS}{dE} = 0 + k \left(\frac{3N}{2}\right)\frac{1}{E}$$

since $d(\ln E)/dE = 1/E$. Hence the energy E of the gas (which is solely due to its kinetic energy K) is equal to

Appendix § reviews the properties of logarithms, including the result that $d(\ln x)/dx = 1/x$.

$$\boxed{E = K = \frac{3}{2} N\, kT.} \qquad (A\text{-}5)$$

The average kinetic energy K_1 of any *single* molecule of the gas is, therefore, equal to

$$\boxed{K_1 = \frac{K}{N} = \frac{3}{2} kT.} \qquad (A\text{-}6)$$

The total internal energy of such a monatomic gas (or the average kinetic energy of any one of its molecules) is thus simply proportional to the absolute temperature of the gas. (For example, if the absolute temperature is doubled, the internal energy of the gas is also doubled.)

Polyatomic gas

Polyatomic molecules. Consider now a polyatomic gas where every molecule consists of two or more atoms. (For example, the gas might be nitrogen where every N_2 molecule consists of two nitrogen atoms.) If the gas is ideal, the potential energy of interaction among different molecules is again negligible compared to the kinetic energy associated with the center-of-mass motions of all the molecules. However, the energy of any single molecule includes now not only the kinetic energy due to the motion its center of mass, but also internal molecular energy. (This internal molecular energy includes kinetic energy due to the rotation of the atoms about the center of mass of the molecule. It also includes kinetic and potential energy due to the atoms vibrating relative to each other within the molecule.)

Energy of a polyatomic gas. The total energy E of such an ideal polyatomic gas is thus equal to

$$E = K + E_{mol} \qquad (A\text{-}7)$$

where K is the kinetic energy of the whole gas due to the center-of-mass motions of all the molecules and E_{mol} is the energy of the whole gas due to internal motions within the molecules. The entropy S of the gas is similarly equal to

$$S = S_{kin} + S_{mol} \qquad (A\text{-}8)$$

where S_{kin} is the entropy due to all the possible center-of-mass velocities of the molecules and S_{mol} is the entropy due to all the possible basic states of motion

internal to the molecules. The situation is thus similar to that discussed in the preceding chapter, namely one where the total energy E is shared among two systems (the system consisting of the center-of-mass motions and the system consisting of the internal molecular motions). Correspondingly, the most probable energies of these systems are such that these systems have a common absolute temperature T. The most probable total kinetic energy K of center-of-mass motion is thus still related to the absolute temperature in the way specified by (A-5), i.e.,

$$K = \frac{3}{2} N \, kT. \tag{A-9}$$

Thus the average center-of-mass kinetic energy of any single molecule is

$$K_1 = \frac{K}{N} = \frac{3}{2} kT. \tag{A-10}$$

However, the total internal energy E of the gas is now *not* equal to its total kinetic energy K since the gas has also some additional energy due to internal motions within the molecules.

Energy is independent of volume

Note that the energy E of an ideal gas depends on its absolute temperature T, but does *not* depend on its volume.

If a gas is ideal,	E is independent of volume.

(A-11)

Reasons for independence. If the volume of a gas is changed, the average distance between the gas molecules changes correspondingly. Hence the potential energy U of mutual interaction among molecules also changes. But, if the gas is ideal, this potential energy is negligibly small compared to the kinetic energies of the molecules. Any change of this potential energy has thus no effect on the energy E of the gas.

Furthermore, the *internal* motion within any polyatomic molecule is unaffected by the distances between different molecules in the gas. Hence the energy E_{mol} of internal molecular motions also does not depend on the volume of the gas.

The preceding comments make it clear why the energy of an ideal gas does not depend on its volume. However, they also indicate that the energy of a gas would depend on its volume if the gas is not ideal (i.e., if the average distance between molecules is small enough that their potential energy of interaction is appreciable).

Problems

[A-1] *Temperature variation of molecular speeds*

The molecules of an ideal gas move about in random directions. Suppose that the absolute temperature of the gas is doubled. What is the resulting effect on the average speed of each of its molecules? *<a-12>*

[A-2] *Gas consisting of two kinds of molecules*

A box contains an ideal gas consisting of N_1 molecules of one kind and of N_2 molecules of another kind. The mass m_1 of each molecule of the first kind is larger than the mass m_2 of each molecule of the second kind.

(a) When the gas is in equilibrium, is the absolute temperature of the system consisting of all the molecules of the first kind the same as the absolute temperature of the system consisting of all the molecules of the second kind?

(b) Is the average kinetic energy (of center-of-mass motion) of a molecule of the first kind larger than, smaller than, or equal to the average kinetic energy of a molecule of the second kind? *<h-4>*

(c) Is the average speed of a molecule of the first kind larger than, smaller than, or equal to the average speed of a molecule of the second kind?

(d) What is the ratio v_1/v_2 of the average speed v_1 of a molecule of the first kind compared to the average speed v_2 of a molecule of the second kind?

(e) Suppose that the molecules of the first kind are oxygen molecules (each of which consists of two oxygen atoms) and that the molecules of the second kind are helium molecules (each of which consists of a single helium atom). The mass m_1 of an oxygen molecule is known to be 8 times larger than the mass m_2 of a helium molecule. What then is the numerical value of the ratio v_1/v_2? *<a-7>*

[A-3] *Free expansion of a gas*

A box, with rigid walls and thermally insulated from its environment, is divided into two parts by a partition. As indicated in Fig. A-1a, the left half of the container is filled with a gas while the right half is empty. A valve is now opened in the partition. No work is thereby done on the gas which then expands freely until it reaches the equilibrium situation where it fills the entire box (as indicated in Fig. A-1b).

(a) Is the final internal energy of the gas larger than, smaller than, or the same as its initial internal energy when it was in the left half of the container?

(b) If the gas is ideal, is its final absolute temperature larger than, smaller than, or the same as its initial absolute temperature? Why? *<h-7>*

(c) If the number n of gas molecules per unit volume is sufficiently large, the molecules are sufficiently close together that the potential energy U due to their interactions is appreciable.

(1) As the gas expands so as to fill the entire box, does this potential energy then change? Why?

(2) Does the total kinetic energy K of the gas molecules then change? Why?

(3) Does the temperature of the gas then change? [The equation (A-9), relating the kinetic energy K to the absolute temperature T of the gas, is true even if the potential energy U is appreciable.] *<a-3>*
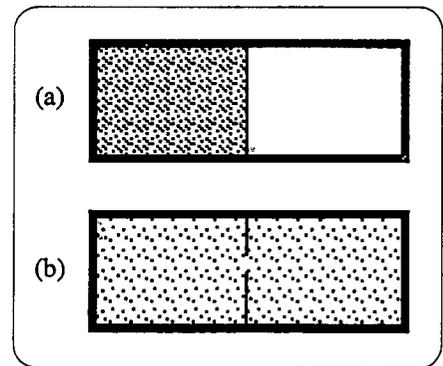

Fig. A-1. Free expansion of a gas throughout an entire box.

B. Pressure, temperature, and volume

What is the pressure exerted by an ideal gas? And how is it related to the absolute temperature of the gas?

Pressure produced by molecular impacts

The pressure exerted on the surface of any object immersed in the gas (or on any wall of the container enclosing the gas) is due to the continual collisions of

the gas molecules with this surface. These collisions produce a slightly fluctuating force on this surface. The pressure p of the gas is, by definition, equal to the magnitude of this force exerted per unit area.

Force and molecular momentum change. To calculate the pressure produced by these molecular collisions, consider an ideal gas in the box of Fig. B-1a. The colliding molecules exert on the right wall of this box a net force to the right (i.e., along the indicated x-direction). The magnitude F of this force is the same as the magnitude of the force exerted on the molecules by the wall — and this force is equal to the rate of change of momentum of the molecules. Thus

These statements are based on a knowledge of mechanics, i.e., on the relation between mutual forces (Newton's third law of motion) and on the momentum law $d\vec{P}/dt = \vec{F}_{ext}$.

$$F = \text{(magnitude of momentum change in one collision)} \times \text{(number of wall collisions per unit time)} \tag{B-1}$$

Momentum change in a single collision. To make a simplified calculation of the force F, assume that all the gas molecules are moving with the same speed v in random directions. Fig. B-1b shows such a molecule which is near the right wall and moves toward it with a speed v to the right. After striking the wall, the molecule then rebounds from it with a speed v to the left. If the molecule has a mass m, the magnitude of its momentum change during a collision with the wall is then mv − (−mv) so that

$$\text{magnitude of momentum change in one collision} = 2mv. \tag{B-2}$$

Number of collisions per unit time. During a small time dt, a molecule with speed v travels a distance v dt. Consider any molecule which moves to the right with this speed, as indicated in Fig. B-2. If this molecule is within a distance v dt of the right wall, it will strike the wall during the time dt. (But if it is farther from the wall than this distance, it will *not* strike the wall.) The molecules which strike the wall, of area A, during the time dt are thus all those molecules which move to the right and are contained in a cylinder of length v dt and area A.

$$\text{Volume of cylinder in Fig. B-2} = A \, v \, dt.$$

Suppose that the gas contains n molecules per unit volume. On the average, one third of these (i.e., n/3 per unit volume) then move parallel to the x-direction, one third move parallel to the y-direction, and one third move parallel to the z-direction. Half of those moving parallel to the x-direction (i.e., n/6 molecules per unit volume) move toward the right wall (while the remaining half move away from it). Hence

$$\text{number of molecules moving to the right within the cylinder of Fig. B-2} = \frac{n}{6} (A \, v \, dt)$$

Dividing this by the time dt, we get

$$\text{number of wall collisions per unit time} = \frac{nAv}{6}. \tag{B-3}$$
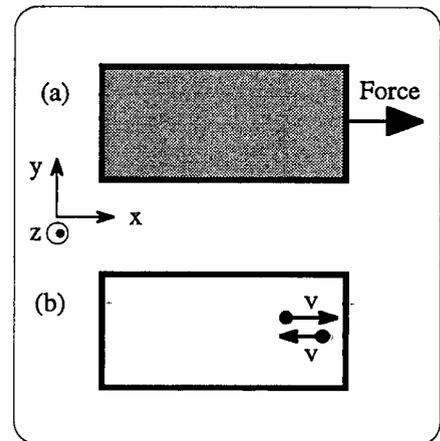
Fig. B-1. (a) A gas inside a box. (b) A gas molecule striking the right wall of the box and rebounding from it.

♦ number of molecules, per unit volume, which move to right = n/6
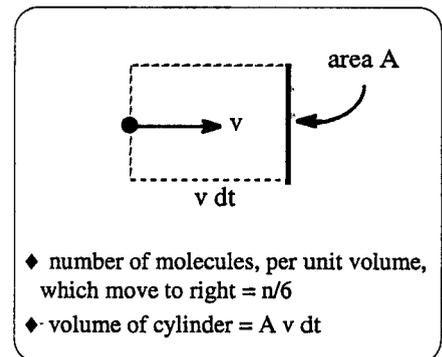
♦ volume of cylinder = A v dt

Fig. B-2. Cylinder containing the molecules which strike the wall within a time dt.

Calculation of pressure. The magnitude of the force in (B-1) is obtained by multiplying (B-2) by (B-3) so that

$$F = (mv) \left(\frac{nAv}{6}\right) = \frac{1}{6} n A mv^2.$$

The pressure p exerted by the gas molecules on the wall is then

$$\boxed{p = \frac{F}{A} = \frac{1}{6} n mv^2.}$$ (B-4)

More exact reasoning should take into account the fact that not all molecules of the gas move with the same speed. This reasoning merely leads to the result that v^2 in (B-4) should be replaced by the average value of this quantity.

One can readily verify that this result makes sense. (a) If the number n of molecules per unit volume were twice as large, the pressure would be twice as large (since twice as many molecules would then hit the wall during any second). (b) If the mass m of a molecule were twice as large, the pressure would also be twice as large (since the momentum change of a molecule during any collision would be twice as large. (c) If the speed v of the molecules were twice as large, the pressure would be *four* times as large (since the momentum change of a molecule during any collision would be twice as large and the number of such collisions during any second would also be twice as large).

Relation among the properties of an ideal gas

Pressure and absolute temperature. The quantity mv^2 in (B-4) is related to the kinetic energy $K_1 = \frac{1}{2} mv^2$ of a single molecule. Hence the pressure in (B-4) is also equal to

$$p = \frac{2}{3} n K_1 .$$ (B-5)

But we know from (A-6) and (A-9) that the kinetic energy of a molecule (whether monatomic or polyatomic) is related to the absolute temperature T of the gas so that

$$K_1 = \frac{3}{2} kT.$$ (B-6)

By combining these two relations, we obtain the result

$$\boxed{p = n kT}$$ (B-7)

which relates the pressure of the gas to its absolute temperature. This relation implies that the pressure of the gas is directly proportional to its absolute temperature. (For example, if the absolute temperature is doubled, the pressure exerted by the gas is also doubled).

Ideal-gas law. The number n of molecules per unit volume is equal to N/V where N is the total number N of molecules in the gas and V is the volume of the gas. Hence (B-7) can also be expressed in the form

$$p = \frac{N}{V} kT$$

or $\boxed{pV = NkT .}$ (B-8)

This equation relates the pressure, volume, and temperature of an ideal gas and is called the ideal-gas law.

> In Chapter 8 this ideal-gas law will also be obtained by a simpler and more general method.

Note that ideal-gas law (B-8) is the same for *every* ideal gas, independent of the nature of its molecules. For example, the pressure depends on the number of gas molecules in a container, but it does not matter whether these molecules are helium atoms or nitrogen molecules

Implications of the ideal-gas law. The ideal-gas law (B-8) has several obvious, but important, implications. For example,

> *if T is constant,* $\qquad$ pV = constant. $\qquad\qquad$ (B-9)

(This relation is called Boyle's law.) It implies that, if the temperature remains constant, the pressure of an ideal gas is inversely proportional to its volume. (For instance, if the volume of the gas is doubled, its pressure becomes half as large.) A graph of pressure versus volume has, therefore, the shape shown in Fig. B-3.

> This law was discovered experimentally in 1662 by the British chemist and physicist Robert Boyle (1627-1691).

As another example, the ideal-gas law (B-8) implies that

> *if V is constant,* $\qquad$ $p \propto T$, $\qquad\qquad$ (B-10)

> *if p is constant,* $\qquad$ $V \propto T$. $\qquad\qquad$ (B-11)

(These relations are called Charles's law or Gay-Lussac's law.) Thus (B-10) asserts that, if the volume of an ideal gas is kept constant, its pressure is simply proportional to its absolute temperature. Similarly, (B-11) asserts that, if the pressure of an ideal gas is kept constant, its volume is simply proportional to its absolute temperature.
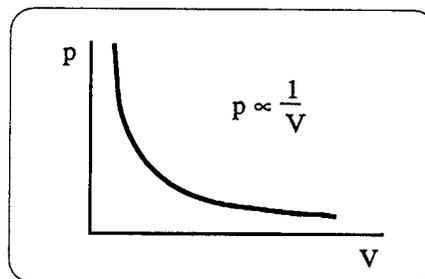
Fig. B-3. Graph showing how the pressure p of an ideal gas varies with its volume V if the temperature of the gas remains constant.

> Jacques Charles (1746-1823) and Joseph Gay-Lussac (1778-1850) were both French scientists.

Problems

[B-1] *Isothermal compression of a gas*

A gas, which can be considered ideal, is contained in a cylinder closed by a piston. When the volume occupied by the gas is 150 cm^3, the gas pressure at room temperature is 1.0×10^5 N/m^2. The piston is now slowly moved so as to reduce the volume of the gas to 60 cm^3 while maintaining the gas at room temperature. What then is the final pressure of the gas? *<a-14>*

[B-2] *Comparison of absolute temperatures*

A glass bulb contains a small amount of argon gas. When the bulb is immersed in water containing melting ice, the measured pressure of the gas inside the bulb is 3.97×10^4 N/m^2. When the bulb is immersed in boiling water, the measured pressure of the gas inside the bulb is 5.42×10^4 N/m^2. What is the ratio T_b/T_m of the absolute temperature T_b of the boiling water compared to the absolute temperature T_m of the water containing melting ice? *<a-1>*

[B-3] *Temperature dependence of quantities in an ideal gas*

Suppose that the absolute temperature of an ideal gas is doubled. By what factor is each of the following quantities then multiplied?

(a) The average kinetic energy of a molecule?
(b) The average speed of a molecule?

(c) The number of molecules hitting a wall every second?
(d) The average change of momentum of a molecule hitting a wall?
(e) The average force exerted by the molecules on a wall?
(f) The pressure of the gas? *<a-11>*

[B-4] *Dependence of gas pressure on number of molecules*

When a steel cylinder is filled with 1.4 grams of helium gas at room temperature, the pressure of the gas is 1.2×10^5 N/m^2.

(a) Suppose that this cylinder is filled with 2.8 grams of helium gas at room temperature. What then is the pressure of the gas?
(b) Suppose that the cylinder is filled with 1.4 grams of oxygen gas at room temperature. What then is the pressure of the gas? (The mass of an oxygen molecule is 8 times as large as the mass of a helium molecule.)
(c) With how many grams of oxygen gas at room temperature must the cylinder be filled so that the gas pressure is 1.2×10^5 N/m^2? *<a-10>*

[B-5] *Pressure of a gas mixture*

A box, of volume V, contains an ideal gas at an absolute temperature T. The gas consists of N_1 molecules of one kind and of N_2 molecules of another kind. Each molecule of the first kind has a mass m_1 and each molecule of the second kind has a mass m_2. The total force exerted on a wall of the box is then simply the sum of the forces exerted by these two kinds of molecules.

(a) What is the pressure p_1 exerted on a wall of the box by the molecules of the first kind? What is the pressure p_2 exerted on this wall by the molecules of the second kind? Express your answer in terms of kT and the other specified quantities.
(b) What is the total pressure p exerted on a wall of the box by all the molecules? Express your answer in terms of kT and the other specified quantities.
(c) Suppose that the numbers of molecules of each kind are the same, but that the masses of these molecules are different. Do the molecules of one kind then strike a wall as frequently as the molecules of the other kind? Is the pressure exerted on this wall by the molecules of one kind then the same as the pressure exerted by the molecules of the other kind? *<a-5>*

[B-6] *Internal energy of a monatomic gas*

A monatomic ideal gas at a pressure p has a volume V.

(a) What is the internal energy of this gas?
(b) What is the internal energy of 1.00 m^3 of argon gas at the atmospheric pressure of 1.013×10^5 N/m^2? *<h-1>* *<a-22>*

C. Measurement of absolute temperature

Measurement strategy. As we have seen, an ideal gas is a sufficiently simple system that one calculate how its absolute temperature is related to its other measurable properties. Any such simple system can then be used to measure the absolute temperature of any other system X, no matter how complex. Indeed, if one lets the simple system come to thermal equilibrium with the system X, one knows that the absolute temperatures of the two systems must be equal. Since one can determine the absolute temperature of the simple system, on has then also obtained information about the absolute temperature of X.

Gas thermometers. The ideal-gas law (B-8) provides the relation $pV = NkT$. The quantity kT (or the basic temperature $\beta = 1/kT$ of the gas) can then be measured by determining the pressure p of the gas, its volume V, and the number N of molecules in the gas. But such measurements of kT are not easy since the number of molecules in a gas cannot readily be measured with great accuracy.

Constant-volume gas thermometer. On the other hand, it is much easier to measure the *ratio* of two absolute temperatures. For example, consider any fixed amount of gas in a container of fixed volume (so that N and V are constant). Then one can readily compare the absolute temperatures T and T' of the gas in two situations by comparing the corresponding measured pressures p and p' of the gas. For then it must be true that

$$pV = NkT \quad \text{and} \quad p'V = NkT'$$

so that
$$\frac{T}{T'} = \frac{p}{p'} ,$$
(C-1)

i.e., the ratio of the absolute temperatures is simply equal to the ratio of the measurable pressures of the gas. An ideal gas within a container of constant volume can thus be used as a *constant-volume gas thermometer* to measure the ratios of any two absolute temperatures.

Examples of gas thermometers

Fig. C-1 shows a gas contained in a glass bulb which is connected to a flexible tube partially filled with mercury. The volume of gas in the bulb can be kept constant if the level of the mercury in the left side of the tube is kept fixed. The height difference h between the mercury levels in both sides of the tube provides a direct indication of the pressure of the gas. The apparatus in Fig. C-1 can thus be used as a simple kind of constant-volume gas thermometer. (To make sure that the gas is ideal, the amount of gas in the bulb must be sufficiently small.)

Fig. C-2 shows a constant-volume gas thermometer used to measure the absolute temperature of a liquid. Here a small bulb, filled with gas, is immersed in the liquid. The thermometer then consists of this bulb which is connected by a thin tube to a *manometer*, i.e., to some pressure-measuring device. (For example, such a manometer might consist of mercury in a tube like that in Fig. C, or it might be a device where the pressure distorts a flexible metal membrane and thus causes the deflection of a pointer.)

Standard of absolute temperature. The preceding measuring procedures can be readily implemented, but determine only the *ratio* of two absolute temperatures. Hence it is convenient to introduce a standard temperature against which all other absolute temperatures can be compared. The standard temperature adopted by international convention is the unique temperature where liquid water, ice, and water vapor can coexist in equilibrium. This is called the *triple point* of water.
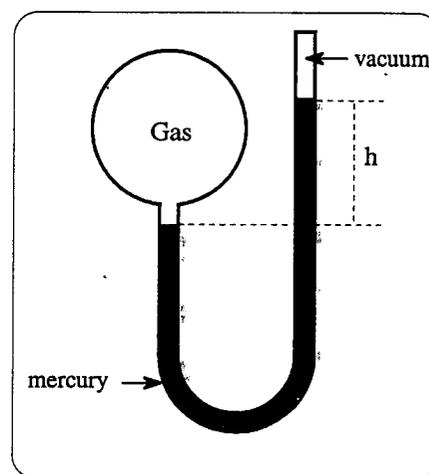

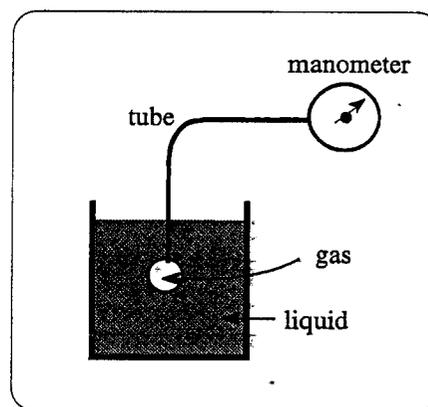**Fig. C-1.** Apparatus for measuring the pressure of a gas in a glass bulb.

Fig. C-2. A constant-volume gas thermometer used to measure the absolute temperature of a liquid.

Def: | **Triple point:** The situation where all three forms of a substance (liquid, solid, and gas) can coexist in mutual equilibrium. | (C-2)

Unit of absolute temperature. The *unit* of absolute temperature (i.e., the algebraic symbol associated with the standard) is called *kelvin* (abbreviated as K) and is defined so that the absolute temperature T_t of water at the triple point has the following value:

$$\text{At the triple point of water,} \qquad T_t = 273.16 \text{ K.} \qquad (C-3)$$

Any absolute temperature can then be expressed in terms of the unit *kelvin*. For example, suppose that a constant-volume gas thermometer indicates the pressure p when it is in thermal equilibrium with some system X, and that it indicates the pressure p_t when it is in thermal equilibrium with water at its triple point. Then (C-1) implies that

$$\frac{T}{273.16 \text{ K}} = \frac{p}{p_t} \qquad \text{or} \qquad T = (273.16) \left(\frac{p}{p_t}\right) \text{ K.}$$

On this temperature scale, room temperature is about 300 K.

Celsius temperature scale. Other temperature scales are today all defined in terms of the absolute temperature. For example, the *Celsius temperature* (or *centigrade temperature*) θ_C is measured in terms of a the unit *degree Celsius* (abbreviated as *°C*) and is defined so that

$$\frac{\theta_C}{°C} = \frac{T}{K} - 273.15. \qquad (C-4)$$

Stated in words, this says that

temperature (expressed in °C) = temperature (expressed in K) – 273.15.

On this temperature scale (commonly used in all countries that use the metric system) the triple point of water has a temperature of exactly 0.01 °C. Furthermore, water freezes at a temperature very close to 0 °C and water boils (at atmospheric pressure) at a temperature very close to 100·°C.

Fahrenheit temperature scale. The *Fahrenheit temperature* θ_F (still used in the United States) is measured in terms of the unit *degree Fahrenheit* (abbreviated as *°F*). It is related to the Celsius temperature so that

$$\frac{\theta_F}{°F} = \frac{9}{5} \left(\frac{\theta_C}{°C}\right) - 32. \qquad (C-5)$$

On this temperature scale water freezes at a temperature very close to 32 °F and water boils (at atmospheric pressure) at a temperature very close to 212·°F.

Problems

[C-1] *Temperature measurements with a gas thermometer*

When the bulb of a constant-volume gas thermometer, like that illustrated in Fig. C-2, is in thermal equilibrium with water at the triple point, the measured pressure of the gas is 4.82×10^4 N/m^2. When the bulb is immersed in molten lead, the measured pressure is 1.06×10^5 N/m^2. When it is immersed in liquid nitrogen, the measured pressure is 1.36×10^4 N/m^2.

(a) What is the absolute temperature of the molten lead? What is its Celsius temperature?

(b) What is the absolute temperature of the liquid nitrogen? What is its Celsius temperature? *<a-8>*

[C-2] *Absolute temperature of the human body*

The Celsius temperature of a normal human body is 37 °C. What is the absolute temperature of a human body? *<a-18>*

[C-3] *Lowering a gas pressure by cooling*

A flask contains helium gas at room temperature (20 °C) and at a pressure of 1.00 atmosphere (i.e., 1.01×10^5 N/m^2. What is the pressure of this helium gas when the flask is immersed in liquid hydrogen whose temperature is -253 °C? *<a-27>*

D. Molecular quantities and Boltzmann's constant

The ideal-gas law $pV = NkT$ can be used not only to measure the *ratio* of two absolute temperatures, but should also allow one to measure the quantity kT itself (i.e., the basic temperature $\beta = 1/kT$). However, in order to do this, one needs information about the number N of molecules in a gas. The next few paragraphs review some concepts familiar from chemistry to indicate how such information can conveniently be specified.

Specification of molecular masses. Information about the number of molecules in a substance can most readily be obtained from information about masses. The mass of a molecule (or single atom) can conveniently be specified in terms of the *atomic mass unit* u which is approximately equal to the mass of the hydrogen atom. More precisely, the atomic mass unit is defined in terms of the mass m_C a particular species of carbon atom (the *isotope* carbon-12).

Def:

Atomic mass unit:	$u = \dfrac{m_C}{12}$.

(D-1)

The mass m of any molecule can then be specified as a multiple of this atomic mass unit by writing $m = \mu\, u$ where the quantity μ (denoted by the Greek letter *mu*) is called the *molecular weight* of the molecule.

Def:

Molecular weight:	$\mu = \dfrac{m}{u}$.

(D-2)

The term *molecular weight* is really a misnomer since it refers to a mass (and not a weight). Since it denotes a ratio, it is also a pure number *without* any associated units.

For example, the molecular weight of the carbon-12 atom is exactly 12 and the molecular weight of the hydrogen atom is approximately 1.

Number of molecules and amount. The number N of particles (molecules or atoms) can conveniently be expressed as a multiple of some standard number N_a called *Avogadro's number* or *mole*. By international convention, this number is defined so that

Def: | *Avogadro's number (mole):* The number N_a of carbon-12 atoms having a total mass of 12 gram. | (D-3)

Amadeo Avogadro (1776-1856) was an Italian physicist who inferred from experiments on gases that the number of molecules per unit volume is the same for all gases at the same temperature. His conclusions became only accepted after his death.

Equivalently, this is the number of particles, of mass u, having a total mass of one gram. (Thus N_a = gram/u so that Avogadro's number can been determined by measuring the atomic mass unit in terms of grams.) The numerical value of Avogadro's number is found to be approximately

$$N_a = \text{mole} = 6.02 \times 10^{23}.$$ (D-4)

Any number N of particles can then be expressed in terms of moles (i.e., as a multiple of Avogadro's number) by writing $N = \nu \, N_a$ where the quantity ν (denoted by the Greek letter *nu*) is called the *amount* of particles. This amount (or number of moles of particles) is thus defined as follows:

Def: | *Amount:* $\nu = \dfrac{N}{N_a} = \dfrac{N}{\text{mole}}.$ | (D-5)

A *mole* is thus a unit of amount in the same way that a *dozen* (denoting twelve things) is a unit of amount.

Molar expression of the ideal-gas law: The ideal-gas law (B-8) can be conveniently expressed in terms of the *amount* ν of gas instead of the number N of molecules. Since $N = \nu \, N_a$, one gets

$$pV = \nu \, N_a \, kT$$

or $$\boxed{pV = \nu \, RT}$$ (D-6)

where the constant R is called the *gas constant*.

Def: | *Gas constant:* $R = N_a k.$ | (D-7)

Determination of Boltzmann's constant. The ideal-gas law (D-6) can be used to measure the gas constant R. This can be done by enclosing a known amount of ideal gas (i.e., a known number ν of moles) in a container of known volume V, and then measuring the pressure p of the gas at a known absolute temperature (e.g., at the triple point of water where T = 273.16 K). All the quantities in (D-7) are then known so that one can find the value of the gas constant R. Thus one finds the numerical value

$$R = 8.31 \text{ J/(K mole)}.$$ (D-8)

By combining this with the known value (D-5) of Avogadro's number, one then obtains the corresponding value of Boltzmann's constant $k = R/N_a$. Thus one finds that

$$k = 1.38 \times 10^{-23} \text{ J/K.} \qquad \text{(D-9)}$$

Since the entropy of a system was defined so that $S = k \ln\Omega$, the entropy has the same units as k (i.e., it too has the units of joule/kelvin).

Once that measurements have been used to determine the values of the fundamental constants N_a and k, all other quantities of interest can be readily measured or calculated. For example, the ideal-gas law (D-6) allows one to find the pressure produced by any amount of gas in any volume at any temperature. Many other quantities depending on the absolute temperature can be similarly calculated.

Example: Molecular speeds in a gas

We know from (A-6) or (A-10) that the average center-of-mass kinetic energy K_1 of a molecule in any ideal gas is

$$K_1 = \frac{3}{2} kT. \qquad \text{(D-10)}$$

Room temperature is about 20 °C corresponding to an absolute temperature of about $(20 + 273)$ K or 293 K. Hence the average kinetic energy of a gas molecule at room temperature is

$$K_1 = \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K}) (293 \text{ K}) = 6.1 \times 10^{-21} \text{ J.} \qquad \text{(D-11)}$$

Let us then estimate the typical speed v of such a molecule. If the mass of the molecule is m,

$$K_1 = \frac{1}{2} mv^2$$

so that
$$v = \sqrt{\frac{2K_1}{m}}. \qquad \text{(D-12)}$$

Suppose that the gas is nitrogen gas consisting of N_2 molecules each of which consists of two nitrogen atoms. Since the atomic weight of a nitrogen atom is 14, the molecular weight of a nitrogen molecule is 28. This means that one mole of nitrogen molecules (i.e., 6.023×10^{23} such molecules) have a mass of 28 gram. The mass m of a single nitrogen molecule is then

$$m = \frac{28 \times 10^{-3} \text{ kg}}{6.023 \times 10^{23}} = 4.6 \times 10^{-26} \text{ kg.} \qquad \text{(D-13)}$$

Hence (D-12) leads to the following estimate of a typical speed of a nitrogen molecule

$$v = \sqrt{\frac{2 (6.1 \times 10^{-21} \text{ J})}{4.6 \times 10^{-26} \text{ kg}}} \approx 500 \text{ m/s.} \qquad \text{(D-14)}$$

This speed is roughly the same as the speed of sound in air.

Problems

[D-1] Ideal gas under standard conditions

A gas is conventionally considered to be under "standard conditions" when it is at a temperature of 0 °C and at atmospheric pressure $(1.01 \times 10^5 \text{ N/m}^2)$.

(a) What is the volume of one mole of such an ideal gas under standard conditions?

(b) How many molecules per cubic centimeter are there in such a gas under standard conditions? <a-20>

[D-2] *Carbon dioxide molecules in air*

Carbon dioxide molecules are commonly introduced in our surrounding air as a result of combustion or respiration processes. Such a carbon dioxide molecule (CO_2) consists of one carbon atom and two oxygen atoms. The atomic weight of a carbon atom is 12 and that of an oxygen atom is 16.

(a) What is the mass (in kilograms) of such a carbon dioxide molecule?

(b) Estimate the average speed of such a carbon dioxide molecule in air at a temperature of 20 °C. <a-25>

[D-3] *Volume change of a rising weather balloon*

A weather balloon at ground level is loosely inflated with helium gas at a temperature of 20 °C and at an atmospheric pressure of 1.01×10^5 N/m^2. When the balloon reaches a height several kilometers above the earth's surface, the pressure of the helium gas is very nearly that of the surrounding atmosphere (5.20×10^4 N/m^2) whose temperature is -43 °C. What then is the volume of the balloon if its volume at ground level was V_0? <a-17>

E. Summary

Definitions

Triple point: The situation where all three forms of a substance (liquid, solid, and gas) can coexist in mutual equilibrium.

Absolute temperature at the triple point of water:

The kelvin unit of absolute temperature is defined so that $T_t = 273.16$ K.

Celsius temperature θ_C: $\theta_C/°C = T/K - 273.15$.

Atomic mass unit: $u = m_C/12$ (m_C = mass of a carbon-12 atom).

Molecular weight: $\mu = m/u$ (m = mass of particle)

Avogadro's number (mole):

The number N_a of carbon-12 atoms having a total mass of 12 gram.

Amount of particles: $v = N/N_a = N/\text{mole}$.

Gas constant: $R = N_a k$.

Important knowledge

Average kinetic energy (of center-of-mass motion) of a gas molecule:

$$K_1 = \frac{3}{2} kT.$$

Internal energy of an ideal gas is independent of its volume.

Ideal-gas law: Relation between pressure, volume, and absolute temperature.

$$pV = NkT = vRT.$$

Numerical values of physical constants:

     Avogadro's number: $N_a = 6.023 \times 10^{23}$

     Bolzmann's constant: $k = 1.38 \times 10^{-23}$ J/K

     Gas constant: $R = N_a k = 8.31$ J/(K mole).

New abilities

You should now be able to do the following:

(1) Relate the kinetic energy of gas molecules their absolute temperature, and relate the total energy of an ideal gas to its volume.

(2) Apply the ideal-gas law ($pV = NkT = \nu RT$) to find any of the quantities in this law from a knowledge of the others.

(3) Describe how ideal-gas thermometers can be used to measure the absolute temperature of a system.

Problems

[E-1] *Properties of air*

About 75% of the molecules of air are nitrogen (N_2) molecules and about 25% of them are oxygen (O_2) molecules. The atomic weight of a nitrogen (N) atom is 14 and the atomic weight of an oxygen atom (O) if 16.

(a) What is the total number of molecules contained in 1.00 m^3 of air at room temperature (20 °C) and at atmospheric pressure (1.01×10^5 N/m^2)?

(b) What is the mass of this volume of air? *<a-19>*

[E-2] *Typical distance between molecules in a gas*

A gas consists of N molecules in some container of volume V. Consider this gas at room temperature (20 °C) and at atmospheric pressure (1.01×10^5 N/m^2).

(a) What is the average volume 7V/N occupied by a single molecule in this gas?

(b) Imagine that each molecule is at the center of a sphere having this volume. How large would be the radius of this sphere? *<h-5>*

(c) By imagining that all these spheres fill the volume of the container, estimate the average distance between neighboring molecules in the gas.

(d) Roughly how much larger is this distance than the typical size of a molecule (about 10^{-10} m)? *<a-15>*

[E-3] *Thermal diffusion of uranium isotopes*

Uranium (U) atoms consist mostly of ^{238}U atoms which have an atomic weight or 238. However, the chain reaction leading to nuclear fission (and thus to the production of nuclear energy) occurs predominantly in the nuclei of ^{235}U atoms which have an atomic weight of 235 because they contain fewer neutrons in the atomic nucleus. To produce uranium rich in ^{235}U atoms, one needs then to separate these atoms from the much more abundant ^{238}U atoms. This can be done by a process of gaseous diffusion which exploits the fact that in uranium hexafluoride (UF_6) gas the molecules containing ^{235}U atoms move with slightly different speeds than the molecules containing ^{238}U atoms.

In such a gas of hexafluoride, what is the ratio v_{235}/v_{238} of the average speed v_{235} of molecules containing ^{235}U atoms compared to the average speed v_{238} of molecules containing ^{238}U atoms? [The atomic weight of a fluorine (F) atom is 19.] *<a-24>*

[E-4] *Free expansion of a dense gas*

A gas is *dense* if the number n of molecules per unit volume is large enough that the potential energy U of interaction between the molecules is appreciable. The total energy E of the gas is then the sum K + U of the kinetic energy K to the velocities of all the molecules and the potential energy U due to the positions of all the molecules. Similarly, the total entropy of the gas is the sum of the entropy due to all the possible velocities of its molecules and the entropy due to

The situation here is analogous to that discussed in Sec. 5A where two systems are in thermal equilibrium. In the present case the two systems are the system consisting of all molecular velocities and the system consisting of all molecular positions.

all the possible positions of these molecules. In equilibrium, where this total entropy is maximum, both positions and velocities are then characterized by the same absolute temperature T. The kinetic energy K is then related to T by the familiar relation $K = \frac{3}{2} NkT$ and the potential energy U is related to T in some way depending on the nature of the intermolecular interactions.

Suppose that the molecules in the gas interact by mutually attractive forces. Consider the free expansion of this gas, as previously illustrated in Fig. A-1 and discussed in Problem A-3.

(a) In this expansion, does the total energy of the gas increase, decrease, or remain the same?

(b) Does the potential energy U of intermolecular interaction increase, decrease, or remain the same? Why? *<h-11>*

(c) Does the kinetic energy K of the molecules increase, decrease, or remain the same? Why?

(d) Does the absolute temperature of the gas increase, decrease, or remain the same? *<a-9>*

[E-5] *Mixture of helium and nitrogen gas*

An ideal gas, consisting of 0.80 moles of helium gas (consisting of He atoms) and of 0.20 moles of nitrogen gas (consisting of N_2 molecules) is contained in a vessel at a fixed temperature. The atomic weight of a helium atom is 4 and the atomic weight of a nitrogen atom is 14.

(a) What is the mass of the gas in the container?

(b) What is the ratio $\mathcal{N}_{hel}/\mathcal{N}_{nit}$ where $\mathcal{N}_{hel}$ is the number of helium atoms striking a wall of the vessel per second and where $\mathcal{N}_{nit}$ is the number of nitrogen molecules striking this wall per second?

(c) Suppose that the 0.80 moles of helium gas is replaced by 0.80 moles of oxygen gas (consisting of O_2 molecules having a molecular weight of 32). If everything else remains the same, is the pressure exerted by the gas mixture than larger than, smaller than, or the same as before? *<a-16>*

[E-6] *Air bubble rising in a lake*

The temperature of the water at the bottom of a 30 m deep lake is 4 °C and the pressure there is about 4.0×10^5 N/m². An air bubble, formed at the bottom of this lake, slowly rises to its surface where the temperature is 20 °C and the pressure is 1.0×10^5 N/m². What is the ratio R'/R of the radius R' of this bubble at the surface of the lake compared to its initial radius R when it was at the bottom of the lake? *<h-5> <a-13>*

[E-7] *Measuring the change of basic states available to a system*

The energy of a system is increased by 0.001 joule when the system is illuminated by light from a lamp. Describe how you could actually measure the resulting increase in the basic entropy $\ln\Omega$ of the system (and thus also the corresponding increase in the number Ω of basic states available to the system)? *<a-2>*

[E-8]† *Connected containers of gas*

Fig. E-1 shows two containers, of volume V_1 and V_2, connected by a thin tube and filled with an ideal gas. The gas in both containers is initially at the same absolute temperature T and at the same pressure p. After the absolute temperature of the gas in the second container is raised to a new value T_2, the gas pressure in both containers reaches a new common value p'.

(a) What is the value of this pressure?

(b) What is the numerical value of the ratio p'/p if the volume of the second container is twice as large as that of the first (so that $V_2 = 2 V_1$) and if the absolute temperature of the gas in the second container is increased by 25% (so that $T_2 = 1.25$ T)? *<h-3> <a-23>*
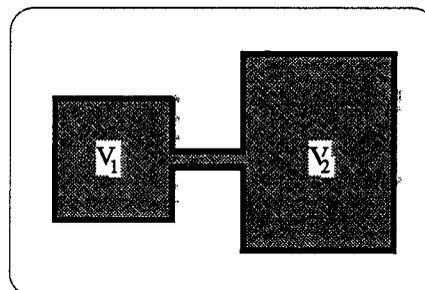

Fig. E-1. Two containers filled with gas and connected by a thin tube.

[E-9] *Volume change of a monatomic gas*

The ideal monatomic gas, enclosed in the cylinder shown in Fig. E-2, is maintained at the constant pressure p of the atmosphere. When the gas is heated, its volume gradually expands from an initial volume V_A to a final volume V_B.

(a) In this process, what is the work done on the gas by the atmosphere?
(b) What is the change of the internal energy of the gas? *<h-2>*
(c) What is the heat absorbed by the gas? *<a-26>*

[E-10]† *Quasi-static process of helium gas*

One mole of helium gas (whose molecules are single helium atoms) is taken quasi-statically from the macrostate A to the macrostate B, and from there to the macrostate C. In the graph of Fig. E-3, these processes are indicated by the straight line connecting the points A and B, and the straight line connecting the points B and C. Use your knowledge of the properties of ideal gases to answer the following questions:

(a) In the process AB, what is the work done on the gas? What is the heat absorbed by the gas? What is the change of the internal energy of the gas? *<h-8>*
(b) In the process BC, what is the work done on the gas? What is the heat absorbed by the gas? What is the change of the internal energy of the gas?
(c) In the entire process ABC, what is the work done on the gas? What is the heat absorbed by the gas? What is the change of the internal energy of the gas? *<a-21>*

[E-11]† *Cyclic process of a monatomic ideal gas*

The graph in Fig. E-4 shows how the pressure p of one mole of a monatomic ideal gas varies with its volume in the quasi-static cyclic process ABCA. In the process AB, the volume of the gas remains constant. The process BC is adiabatic. In the process CA, the pressure of the gas remains constant.

Express the answers to all the following questions solely in terms of the gas constant R and the absolute temperatures T_A, T_B, and T_C of the gas in its macrostates A, B, and C. Indicate your reasoning.

(a) In the process AB, what is the work done on the gas? What is the heat absorbed by the gas? What is the change of the internal energy of the gas? *<h-9>*
(b) Answer the same questions for the process BC.
(c) Answer the same questions for the process CA. *<h-6>*
(d) Answer the same questions for the entire cyclic process ABCA. Is the work done on the gas in this cyclic process positive, negative, or zero? Is the heat absorbed by the gas in this cyclic process positive, negative, or zero? *<a-4>*

[E-12] *Temperature relations in the preceding process*

Consider again the monatomic ideal gas experiencing the cyclic quasi-static process indicated by the graph in Fig. E-§. Answer the following questions and indicate your reasoning.

(a) Is the absolute temperature T_B larger than, smaller than, or equal to the absolute temperature T_A? *<h-2>*
(b) Is T_C larger than, smaller than, or equal to T_B?
(c) Is T_A larger than, smaller than, or equal to T_C?
(d) List the absolute temperatures T_A, T_B, and T_C in the order of their increasing magnitudes. *<a-29>*

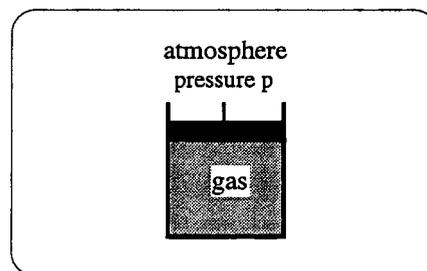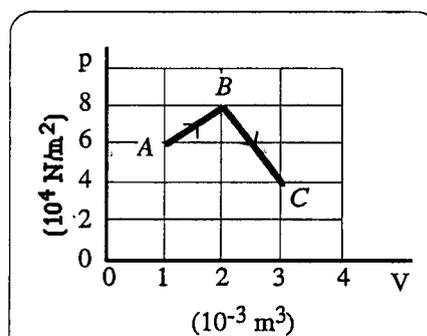**Fig. E-2.** A monatomic gas maintained at constant atmospheric pressure.

$V_A = 1.0 \times 10^{-3} \, m^3$

$p_A = 6.0 \times 10^4 \, N/m^2$

$V_B = 2.0 \times 10^{-3} \, m^3$

$p_B = 8.0 \times 10^4 \, N/m^2$

$V_C = 3.0 \times 10^{-3} \, m^3$

$p_C = 4.0 \times 10^4 \, N/m^2$
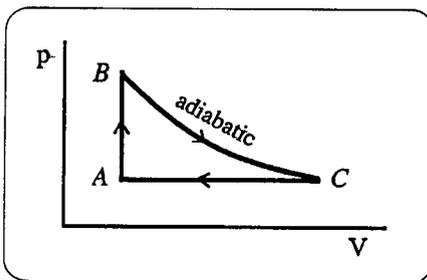
Fig. E-3. Quasi-static process of helium gas.

Fig. E-4. Cyclic process of a monatomic gas.