ESSENTIALS OF INTRODUCTORY CLASSICAL MECHANICS

Sixth Edition

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KINETIC THEORY AND THE IDEAL GAS

OVERVIEW

The rigid bodies discussed in the last two chapters can be thought of as 'ideal solids': they have a fixed shape and the application of external forces just moves or rotates the entire object. Though idealized, this provides quite a good description of real solid objects subjected to small external forces. It is clearly quite inadequate to describe liquids and gases, which have no fixed shape and will therefore respond to external and internal forces in different ways. In this chapter we look at the other extreme by considering an ideal gas: a system of identical, independently-moving, non-interacting particles. This model is in fact a very good description of many real gases. We describe the bulk properties of such a gas by a statistical approach, looking at the cumulative effect of many individual particles. This approach, known as *kinetic theory*, introduces the new physical concepts of *pressure*, *heat* and *temperature*. Using Newton's laws, we can define the temperature of a gas in terms of the motion of its molecules, thus relating it to the internal energy of the gas. By using the ideal-gas model we can see how work done on or by a gas can result in a change of the internal energy, and hence the temperature, of the gas.

Some topics, such as the relation between the pressure of an ideal gas and its translational kinetic energy, can be treated very thoroughly with the techniques that we have learned. Other topics, however, such as the precise definition of temperature or the thermal excitation of the vibrations and rotations of molecules, are beyond the level of this book. Since these topics are very important, we will nonetheless discuss them at a qualitative level.

When you have completed this chapter you should:

✔ recognize that kinetic theory uses statistical principles to calculate the bulk properties of systems of many particles from the average behavior of individual particles;

✔ understand the concept of pressure, and be able to relate it to the momentum change of a gas particle colliding with the walls of a container;

✔ know how to define the temperature of a gas in terms of the kinetic energy of its constituent particles, and recognize the distinction between temperature and heat;

✔ be able to calculate the work done when an ideal gas changes its volume.

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ESSENTIALS

In everyday experience, we say that a substance is gaseous if it changes shape and volume according to its surroundings. For example, if a certain mass of gas is enclosed in a box and we then suddenly expand the volume of the box by moving out one of the sides, we expect that the gas will expand to fill the newly enlarged container uniformly, whereas we would not expect a liquid or a solid to behave this way. This experience indicates that the constituent atoms of the gas are moving (so that they can move into the empty space created by enlarging the box), and furthermore that the motion is randomly directed (because we don't find that the behavior of the gas depends on the direction in which we expand the box). Also, the atoms move further apart when the gas expands, so they cannot be confined to deep potential energy minima as is the case with solids. We may conclude that the attractive part of the interatomic forces in a gas is quite weak compared to those acting in a solid.

These experimental properties of gases suggest that a suitable idealized model for a gas would be one in which the interatomic or intermolecular forces are completely negligible. This would be the case if

- the average distance between gas atoms or molecules is very large compared to the size of an individual atom or molecule;

- molecules interact with each other only when they collide;

- collisions between molecules, or between a molecule and the wall of the container, are both rare (i.e. the time spent in collisions is negligible compared to the time spent between collisions) and perfectly elastic.

We further assume that the motions of the gas molecules are randomly directed: that is, if we choose a reference frame in which the center of mass of the gas sample is not moving, the velocity vectors of individual gas molecules have no preferred orientation. It is possible to visualize conditions in which that would not be so (for example, if all our molecules were originally moving exactly perpendicular to one face of a perfectly reflecting cubical box, and there were no collisions between molecules). However, as long as we do allow rare elastic collisions between molecules, it seems reasonable that over a sufficiently long time the velocities of individual molecules should become randomly oriented, even if the container housing the gas is asymmetric in shape. An actual proof of this statement is well beyond the scope of this book, but we shall assume that it is true. The motion of a single particle in the gas will be very complex, but we do not observe it: our experimental measurements are the cumulative result of the action of large numbers of particles, and will thus depend only on the *average* behavior of a particle.

This idealized model is referred to as an *ideal gas*. We would expect that it is likely to be a good approximation to a *low-density* gas.

The observed properties of an ideal gas are bulk properties—any sample of gas we study consists of a very large number of particles whose motions are not individually measured. This is a very different type of system from those we have studied so far, and we will need to develop a new set of concepts to deal with it. We can do this by considering the average behavior of a particle of the gas over time. For simplicity, we will normally assume that the gas is homogeneous and monatomic, i.e. its particles are single atoms, not molecules, and only one kind of atom is present.

As a route to developing the new concepts needed to describe the properties of a gas, we start by investigating an aspect of its behavior which is clearly relevant to classical mechanics: the force exerted by the gas on the walls of its container. To do this, consider a closed box of volume V containing N gas atoms. The total mass of gas in the box is Nm (where m is the mass of one atom), and its density is Nm/V. It's also sometimes useful to think of the *number density*, i.e. the number of atoms per unit volume; this is obviously $n = N/V$. Changing the volume of the box will change the density and the number density, but not the mass, since no atoms are removed from or added to the box.

If the atoms of the gas are all moving randomly around, clearly in any given time interval Δt some of them will collide with the walls of the box. We assume the collisions are elastic, so any particle which does collide will be reflected back with the magnitude of its momentum unchanged, but the sign of the component perpendicular to the wall reversed. Each collision therefore transfers momentum $2mv_x$ to the wall, where x is the direction perpendicular to the wall.
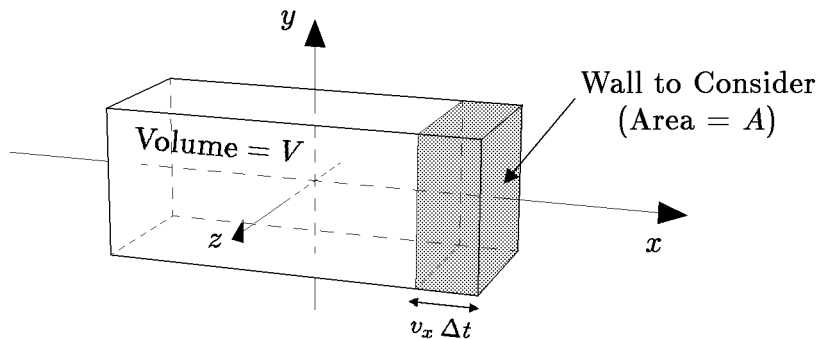
Suppose the box contains just one particle, whose velocity has an x-component of *magnitude* v_x, i.e. at any given time its value is $+v_x$ or $-v_x$ with equal probability. If this particle is to collide with the wall in a specified time interval, then at the start of that interval it

must be within a perpendicular distance $v_x \Delta t$ of the wall (otherwise it won't reach the wall before the end of the time interval). If it could be anywhere in the box, the probability of its being within this distance is $A v_x \Delta t / V$, where A is the area of the wall. If its motion is random, then half the time it spends in this part of the box it will actually be moving away from the wall, so in fact the chance of its colliding with the wall in the specified time is

$$A v_x \Delta t / 2V \ .$$

Therefore, if we consider many time intervals Δt, the average momentum transferred to the wall by this single molecule is the probability that it collides with the wall at all in a particular time interval, times the momentum that it transfers if it does collide:

$$\Delta p = 2 m v_x \frac{A v_x \Delta t}{2V} = \frac{m A \Delta t}{V} v_x^2 \ .$$

Problem 11A.4.

The average force exerted on the wall is given by $F = \Delta p / \Delta t$, so this means that our particle exerts an average force

$$F = \frac{mA}{V} v_x^2 \ .$$

For a box containing N particles, the total force applied to the wall is the sum of the averages for individual particles:

$$F = \frac{mA}{V} \sum_i v_{x,i}^2 \ .$$

The sum of all $v_{x,i}^2$ is just N times the average $v_{x,i}^2$, by the definition of 'average', so we conclude that

$$F = \frac{N m A}{V} \left\langle v_x^2 \right\rangle \ .$$

[Putting a quantity in triangular brackets denotes the average of the quantity for all the particles in the system.]

The factor $\left\langle v_x^2 \right\rangle$ in the above equation can be simplified by noticing that the total speed of each particle is given by $v^2 = v_x^2 + v_y^2 + v_z^2$, and that the randomness of the velocities implies that there is no distinction on average between the x-, y-, and z-directions. It follows that $\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle = \frac{1}{3} \left\langle v^2 \right\rangle$, and therefore

$$F = \frac{2}{3} \frac{N A}{V} \left\langle \frac{1}{2} m v^2 \right\rangle \ .$$

The ideal gas exerts a force on the wall which is proportional to the area of the wall and the average kinetic energy of an atom of the gas.

This means that the force per area, F/A, is a bulk property of the gas: it depends only on the number density of the gas and the average kinetic energy of its particles. We call this property the *pressure*, P, of the gas. The direction of the force exerted on any wall is, from our derivation, always perpendicular to the wall, so we define pressure as a scalar quantity; its units are N/m^2, or pascals ($1 \ Pa = 1 \ N/m^2$).

Using the definition of P, we can write the above equation in the form

$$PV = \frac{2}{3}N \left\langle \frac{1}{2}mv^2 \right\rangle \ .$$

This equation closely resembles an equation derived from experimental measurements on real gases in the 17th and 18th centuries, namely

$$PV = \mathcal{N}RT \ ,$$

where $\mathcal{N}$ is related to N and R is a numerical constant. We are therefore encouraged to conclude that (i) our idealized model does indeed describe real gases to some level of accuracy and (ii) *the average kinetic energy of particles in a gas is a measure of its temperature*. We define the scale of temperature in SI units by

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}kT \ ,$$

where T is measured in *kelvin* (K), and k is *Boltzmann's constant*. The scale of T is set, and the value of k determined, by defining the temperature of the *triple point* of water to be exactly 273.16 K. The triple point of a substance is the unique combination of pressure and temperature at which the solid, liquid and gas phases all exist together in equilibrium: its value as a defining point is that it automatically specifies the pressure at which the measurement is made. From the above equation, we see that 0 K, *absolute zero*, corresponds to zero kinetic energy of the gas particles. Absolute zero is thus a physically meaningful concept, unlike the arbitrary zeros of the Centigrade and Fahrenheit scales.

With the scale set in this way, $k = 1.38 \times 10^{-23}$ J/K, and the size of the kelvin is the same as the size of a degree Centigrade (both the Centigrade, or Celsius, scale and the Fahrenheit scale were, of course, in use long before the formal definition of the kelvin). Boltzmann's constant can be thought of as a unit conversion: we could in principle measure temperature in joules, and have $k = 1$.

This definition of temperature is called the *kinetic temperature*. Our earlier definition of an ideal gas ensures that the potential energy associated with intermolecular forces is negligible compared to the kinetic energy of the molecules, so if the gas forms a closed system, with no energy transfer in or out, it will have constant kinetic temperature.

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Kinetic temperature is a fairly recent concept. There is an older, logically independent, definition of temperature, the *thermodynamic temperature*, first formalized by Lord Kelvin, which does not rely on the molecular picture of gases. If two closed systems have each been left undisturbed until they settle into a steady state (this is called 'reaching *thermal equilibrium*'), and are then placed in contact so that energy can flow between them, they are said to be at the same thermodynamic temperature if there is, in fact, no net energy flow. If energy does flow, it flows from the system at higher temperature to the system at lower temperature. The thermodynamic temperature *scale* relates the temperature ratio of the two systems to the heat exchanged with them by an idealized *heat engine*.

To show that these definitions are consistent, which they must be if our concept of temperature is to make scientific sense, we need to demonstrate that if two gases in contact are in thermal equilibrium, with no net energy transfer, their molecules have the same average kinetic energy. This sounds intuitively plausible, and it is in fact true, but a rigorous mathematical proof is beyond the scope of this book. We would also need to show that the scales are consistent, i.e. that an increase of 10% in the average kinetic energy corresponds to an increase of 10% in the thermodynamic temperature: this is done by showing that the kinetic temperature has the same relation to the exchanged heat as does the thermodynamic temperature.

The equivalence of the kinetic and thermodynamic definitions of temperature implies that if we mix two different gases in a box, one gas having molecular mass m_1 and the other m_2, and let the box stand until equilibrium is reached, we will have

$$\left\langle \frac{1}{2}m_1 v_1^2 \right\rangle = \left\langle \frac{1}{2}m_2 v_2^2 \right\rangle \ .$$

Giving the temperature of an ideal gas is equivalent to stating the average kinetic energy of its component molecules (measured in the reference frame of the center of mass of the gas).

We can now restate our relation between pressure and volume using the kinetic temperature:

$$\boxed{PV = NkT \ .}$$

This is called the *ideal gas law*. Note that there is *no* dependence here on the mass of the atoms making up the gas. Given the same conditions, N atoms of helium occupy the same space and exert the same pressure as N atoms of xenon, although xenon has a mass 33 times greater than helium. The xenon atoms hit the walls $\sqrt{33}$ times

less often than the helium atoms would, but impart $\sqrt{33}$ times more momentum on each impact.

Because a single atom is such a small object, for macroscopic applications it is convenient to work in larger units, which would correspond to large numbers of atoms. For historical reasons, the large number used is the number of atoms contained in 0.012 kg of carbon 12, ^{12}C: this is called *Avogadro's number*, after the nineteenth-century Italian scientist who first suggested that equal volumes of different gases at the same temperature and pressure contain equal numbers of molecules. One *mole* of a substance is the amount of that substance that contains Avogadro's number of elementary entities (atoms, molecules, ions, etc.). The mass of a mole therefore depends on the mass of the individual atom or molecule. Atomic and molecular masses are measured in *atomic mass units* (symbol u); 1 u is defined such that an atom of ^{12}C has a mass of exactly 12 u. The mole (abbreviated 'mol') is the SI base unit of "amount of substance". Quantities defined in terms of moles are dimensionally different from similar quantities defined in terms of mass.

In units of moles, the ideal gas law is written

$$PV = \mathcal{N}RT$$

where $\mathcal{N}$ is the number of moles and the gas constant R is 8.31 J/mol·K (joules per mole per kelvin). This is the experimental law that we quoted above. In physical applications one tends to work in terms of atoms and k, but moles and R are widely used in chemistry. Avogadro's number is experimentally measured to be $N_A = 6.02 \times 10^{23}$; from the definitions above we see that $R = N_A k$.

The translational kinetic energy of gas molecules, relative to the center of mass of the gas sample as a whole, is clearly energy internal to the gas-sample system. If a gas has a complicated molecular structure (e.g. methane, CH_4), energy can also be stored in vibrations or rotations of individual molecules. The total energy, both kinetic and potential, stored in these various internal motions is called the *internal energy* of the gas and is given the symbol U. The *principle of equipartition* states that the internal energy of the gas is divided equally amongst the available degrees of freedom (i.e. possible directions of motion). Each mode of rotation within the gas molecule will on average contribute $\frac{1}{2}kT$ to the internal energy, just like each of the three components of the molecule's overall velocity, while each mode of vibration will contribute $\frac{1}{2}kT$ from its kinetic energy and $\frac{1}{2}kT$ from its associated potential energy, making kT in all.

Problem 11D.6

Changing the temperature of an ideal gas therefore implies changing its internal energy. This can obviously be done by doing work on the gas. It can also be done, through transfer of kinetic energy in intermolecular collisions, by placing the gas in contact with a substance at higher temperature. Energy transferred by this second route is called *heat*. Heat and temperature are not equivalent concepts, as can be seen by considering the energy change corresponding to a given temperature change:

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- Temperature measures the average *translational kinetic energy* of the gas particles. If two gases have different numbers of degrees of freedom, e.g. if one consists of single atoms and the other of diatomic molecules, the change in energy per gas particle required for a given temperature change is higher for the gas with more degrees of freedom, because of the principle of equipartition.

- Since heat measures the *total* energy transferred rather than the average per molecule, the amount of heat corresponding to a given temperature change depends on the number of degree of freedom—it will be higher for a gas of diatomic molecules than for a monatomic gas—*and* on the mass involved: less energy is required to heat a cupful of water than is needed for a gallon.

If a mass M of some substance is heated, the resulting temperature change will be

$$\Delta T = \frac{Q}{Mc},$$

where Q is the heat supplied and c is a constant called the *specific heat capacity* of the substance, measured in $J/kg \cdot K$. For gases, it is often useful to consider the number of moles of the gas instead of its mass, and the resulting ratio $Q/\mathcal{N}\Delta T$ is called the *molar heat capacity*, measured in $J/mol \cdot K$. From the discussion above, we expect the specific heat capacity of a gas to depend on its molecular structure, with more complicated molecules having higher specific heats. In addition, the specific heat capacity depends on the conditions under which we heat the gas: if we maintain a constant volume, all the energy we supply will go into raising the temperature, whereas if we allow the gas to expand (for instance by pushing a piston or inflating a balloon) we must also take into account the work done by the gas pressure in the expansion.

Conservation of energy implies that the total change ΔU in internal energy U of the gas is equal to the total energy supplied to it (or removed from it) as work W and as heat Q:

$$\Delta U = Q + W \qquad \text{(if work } W \text{ is done } \textit{on} \text{ the gas) or}$$

$$\boxed{\Delta U = Q - W \qquad \text{(if work } W \text{ is done } \textit{by} \text{ the gas).}}$$

The first choice of sign seems more logical, but the second one is the standard convention.

(This is a basic principle of the branch of physics known as thermodynamics, and is usually called the *first law of thermodynamics*. However, it is really a specific application of energy conservation rather than an independent law.)

We have previously argued that 'non-conservation' of energy in inelastic collisions and the action of dissipative forces is due to changes in the internal energy of the bodies in question. In the case of gases we are now in a position to test this, because we have a way to measure the internal energy of a gas—for a monatomic gas with no additional degrees of freedom, we can deduce the internal energy from the temperature.

Suppose we have a gas in a box which has a frictionless piston closing one side. The gas exerts a force PA on the piston, where A is the area of the piston, and by Newton's third law the piston exerts a force $-PA$ on the gas. If the pressure of the gas pushes the piston out by a distance Δx, the work done by the gas on the piston (which is minus the work done by the piston on the gas) is

$$\Delta W = F\,\Delta x = PA\,\Delta x \ .$$

But $A\,\Delta x$ is just the change in the volume of the box, so in fact

$$\boxed{\Delta W = P\,\Delta V.}$$

Thus if a gas initially has pressure P_i and volume V_i, and undergoes some process leading to a final state with pressure and volume (P_f, V_f), *we can calculate the work done by the gas by integrating $P\mathrm{d}V$ from V_i to V_f*, i.e. by measuring the area under the curve that the process traces out on a plot of P against V. Note that the value of this integral will depend on the exact path traced by the pressure and volume of the gas during the process.
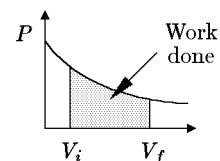
This path dependence of the integral is the principle on which internal-combustion engines, refrigerators, etc. operate: *by changing the conditions under which a gas expands and contracts, we can return to the initial pressure and volume by a different route and have done some net work during the process.* (Of course, energy conservation requires that this is 'paid for' in energy supplied, for example, by burning gasoline.)

The relations between internal energy, heat, and work are at the heart of *thermodynamics*. Thermodynamics is an important field with many practical applications, notably the study of the efficiency of energy generation (i.e. the proportion of the total energy of a given system which can be transformed into work).

How useful in practical applications is the concept of an ideal gas? The answer turns out to be "extremely useful"—most 'everyday' gases, such as air, methane, or carbon dioxide, are very good approximations to an ideal gas. This is in contrast to the situation in the next chapter, where the 'ideal liquid' that we shall consider is *not* a very good approximation to real liquids.

SUMMARY

* The *ideal gas* model consists of free, non-interacting particles which move randomly and may undergo elastic collisions with each other or with other objects in the vicinity. This model is a very good approximation to many real gases at room temperature and atmospheric pressure.

* Gases exert a force on any surrounding wall which is directed perpendicular to the wall and is proportional to its area. The force exerted divided by the area is called the *pressure* of the gas.

* The pressure exerted by an ideal gas is proportional to the average kinetic energy of its constituent particles and to the number of particles present, and inversely proportional to the volume in which the gas is contained.

* The *temperature* of an ideal gas is the average translational kinetic energy of its constituents (times a numerical conversion factor). Temperature is defined relative to an *absolute zero*, at which the average kinetic energy of the atoms of an ideal gas would be zero, and is measured in *kelvin*.

* The *internal energy* of a gas is the mechanical energy, both kinetic and potential, stored in the motions of the individual molecules of the gas. This includes both translational kinetic energy of whole molecules and rotational and vibrational energy within a molecule.

* The temperature of an object can be increased by supplying energy, either by doing work on the object or by placing it in contact with something at a higher temperature. The energy transferred in the second case is called *heat*. The *specific heat capacity* of a substance, in $J/kg \cdot K$, is the heat required to raise the temperature of 1 kg of the substance by 1 K; the *molar heat capacity* of a gas is the heat required to raise the temperature of one mole (Avogadro's number of molecules) of the gas by 1 K. The values of specific and molar heat capacity for a given gas depend on the conditions under which the gas is heated; for different gases they depend on the complexity of the gas molecule, i.e. the number of degrees of freedom for motion within a single molecule.

* Physical concepts introduced in this chapter: pressure, heat, temperature, internal energy (of a gas); Avogadro's Number, mole; specific heat capacity, molar heat capacity.

* Mathematical concepts introduced in this chapter: notation $\langle x \rangle$ for 'average value of x'.

* Equations introduced in this chapter:

$$PV = \frac{2}{3} N \left\langle \frac{1}{2} mv^2 \right\rangle \quad \text{(pressure of an ideal gas)};$$

$$\left\langle \frac{1}{2} mv^2 \right\rangle = \frac{3}{2} kT \quad \text{(definition of kinetic temperature)};$$

$$PV = NkT = \mathcal{N}RT \quad \text{(ideal-gas law)};$$

$$\Delta U = Q - W \quad \text{(first law of thermodynamics)};$$

$$\Delta W = P \, \Delta V \quad \text{(work done by expanding gas)}.$$

* Useful constants:

$$R = 8.3 \text{ J/mol} \cdot \text{K} \qquad \text{(gas constant)};$$

$$k = 1.38 \times 10^{-23} \text{ J/K} \qquad \text{(Boltzmann's constant)};$$

$$N_A = 6.02 \times 10^{23} \text{ molecules/mole} \qquad \text{(Avogadro's number)};$$

$$1 \text{ u} = 1.66 \times 10^{-27} \text{ kg} \qquad \text{(atomic mass unit)}.$$

* Temperature scales:

$$T(\text{K}) = T(°\text{C}) + 273.15 \text{ K} \qquad \text{(Centigrade to Kelvin)};$$

$$T(°\text{F}) = 32°\text{F} + \tfrac{9}{5}T(°\text{C}) \qquad \text{(Centigrade to Fahrenheit)};$$

$$T(°\text{C}) = \tfrac{5}{9}\left(T(°\text{F}) - 32°\text{F}\right) \qquad \text{(Fahrenheit to Centigrade)}.$$

The triple point of water corresponds to 273.16 K, or 0.01°C, by definition.

PROBLEMS AND QUESTIONS

By the end of this chapter you should be able to answer or solve the types of questions or problems stated below.

Note: throughout this book, in multiple-choice problems, the answers have been rounded off to 2 significant figures, unless otherwise stated.

At the end of the chapter there are answers to all the problems. In addition, for problems with an (H) or (S) after the number, there are respectively hints on how to solve the problems or completely worked-out solutions.

11A   FUNDAMENTAL CONCEPTS (THE IDEAL GAS)

11A.1   A strong wind has a velocity of 80 km/h. Compare this with the typical speed of an air molecule at 290 K. What do we mean by 'wind velocity', and why is the effect of a wind so different from that of still air?

11A.2 (H)   Small dust particles suspended in air seem to dance randomly about, a phenomenon called *Brownian motion*. Explain why this occurs. Why is Brownian motion only perceptible for small particles?

11A.3   Give briefly, in your own words, the microscopic description of a gas and, in the context of your description, explain the origin and meaning of the term "pressure of a gas".

11A.4   In this chapter we have introduced the new concepts of the *pressure* and (kinetic) *temperature* of a large quantity of an ideal gas. What are the measurable properties of a single atom or molecule of that gas which correspond to the bulk properties of pressure and temperature?

Suppose that the pressure and temperature of a quantity of ideal gas are accurately known. Are the corresponding properties of the individual atoms also accurately known? If not, what is known about them?

11B   KINETIC THEORY

11B.1   Air is a mixture of oxygen molecules with a mass of 32 u ($1u = 1.66 \times 10^{-27}$ kg) and nitrogen molecules with a mass of 28 u. What is the ratio of the speed of a typical oxygen molecule to that of a typical nitrogen molecule?

(a) 1.07; (b) 0.94; (c) 0.88; (d) 1.00.

11B.2 (S)   What is the typical speed of (a) a helium atom, (b) a nitrogen molecule, at 300 K? Helium has a mass of 4 u, N_2 a mass of 28 u; $1u = 1.66 \times 10^{-27}$ kg.

11B.3 (H)   At what temperature would (a) the average kinetic energy and (b) the rms speed of a hydrogen molecule (mass 2 u) be equal to that of an oxygen molecule (mass 32 u) at 300 K?

11B.4   Air contains a small proportion (about 1% of the total number of molecules) of argon, a monatomic gas with an atomic mass of 40 u (1 u = 1.66×10^{-27} kg). What is the average kinetic energy of the argon atoms in a room at a typical room temperature of 68°F (20°C)? What is the typical speed of an argon atom at this temperature? What is the total number of argon atoms in a room of size 2.5 m × 3 m × 5 m, and what pressure do they exert on the walls of the room? (Atmospheric pressure is 1.01×10^5 Pa.)

11B.5 (S)   According to quantum physics, a light wave is actually composed of particles, called *photons*. While a complete understanding of photons involves both quantum physics and relativity, the pressure exerted by photons inside a perfectly reflecting box can be calculated using the same method we employed for the ideal gas. The differences are that photons always move at the speed of light, which is denoted by c (i.e. $|\vec{v}| = c$), and the momentum $\vec{p}$ of a photon is not $m\vec{v}$, but

$$\vec{p} = \frac{E}{c^2}\vec{v},$$

where E is the energy of the photon.

Using this information, calculate the pressure exerted by a 'gas' of N photons confined inside a rectangular box of volume V. Assume the walls of the box are perfectly reflecting, so that a photon-wall interaction is an elastic collision.

11C   THE IDEAL GAS LAW

11C.1   A closed box containing air at 72°F is placed in a refrigerator so that its temperature decreases to 36°F. If the original pressure of the air in the box was 10^5 Pa, what is its pressure at the new temperature?

(a) 5.0×10^4 Pa; (b) 2.0×10^5 Pa; (c) 9.3×10^4 Pa; (d) 1.1×10^5 Pa.

11C.2   Atmospheric pressure is about 10^5 Pa, and a typical room temperature might be 300 K. Approximately how many molecules are there in an air-filled room of dimensions 3 meters by 3 meters by 4 meters?

(a) 8.7×10^{26}; (b) 2.6×10^{29}; (c) 2.4×10^{25}.

11C.3 (H)   A chemistry laboratory buys supplies of pure gases in pressurized cylinders with a volume of 10 liters (0.01 m³), and later returns the cylinders for refilling. To avoid accidentally sending out empty cylinders, the supply company keeps a record of the masses of its cylinders when 'empty', and weighs each one before sending it back out. When full, the cylinders have a pressure of 2.0×10^7 Pa, when 'empty', they contain the same gas, but at a pressure of 1.0×10^5 Pa (one atmosphere). The weighing is done at room temperature (22°C). What is the mass difference between a full and an empty cylinder of hydrogen (molecular mass 2 u)?

11C.4   A pressure cooker is a pan whose lid can be tightly sealed to prevent gas from escaping. If an empty (but sealed) pressure cooker were inadvertently left on a hot stove, what would be the force on the lid due to air pressure when the air inside the cooker had been heated to 120°C? Assume that the temperature of the room outside is 20°C and that the pressure cooker is 30 cm in diameter. Atmospheric pressure is 1.01×10^5 Pa.

If the pressure relief valve on the lid is now opened, allowing hot air to escape until the pressure inside is reduced to atmospheric, and the pot is then sealed again and removed from the stove, what is the net force on the lid due to air pressure when the contents have cooled back to 20°C?

11C.5 (H)   Air is approximately 80% nitrogen and 20% oxygen by mass (i.e. 1 kg of air contains 800 g of nitrogen and 200 g of oxygen). What is the ratio of the number of nitrogen molecules to the number of oxygen molecules? Estimate the density (in kg/m^3) of air at 20°C and 10^5 Pa. By how much does this change if the air is at 0°C and the same pressure? A molecule of nitrogen has a mass of 28 u, oxygen 32 u.

11C.6 (S)   If the atmosphere of a planet is all at the same temperature T and consists of a gas whose molecules have mass m, how does the density of the atmosphere vary with height above the ground? Assume that the atmosphere does not extend far enough from the planet for g to change significantly.

11D   INTERNAL ENERGY AND WORK DONE BY IDEAL GAS

11D.1 (H)   Explain, on both a microscopic and macroscopic level, why a bicycle pump gets hot when you use it. Does the temperature it reaches depend on the speed at which you pump?

> Note for problems 11D.2–11D.5: a monatomic ideal gas such as helium has no internal molecular degrees of freedom. Hence the internal energy of the gas is entirely stored in the translational kinetic energy of the atoms.

11D.2 (H)   A monatomic ideal gas, originally at a pressure P_i, volume V_i and temperature T_i, expands to three times its initial volume. Calculate the final pressure and temperature if this expansion takes place (a) isothermally (i.e. at constant temperature); (b) isobarically (at constant pressure). In each case, how much heat is supplied to the gas and how much work is done by the gas during the expansion?

11D.3 (H) (a)   A standard tool in thermodynamics is a plot of pressure as a function of volume (i.e. a plot with P as the y-axis and V as the x-axis). On such a PV plot, draw lines representing each of the expansion processes you calculated in problem 11D.2. What is the graphical representation of the work done during each expansion?

(b)   A *cycle* on a PV plot is a closed loop, i.e. a series of expansions and compressions which eventually brings the gas back to its starting point. What is the *net* change in the internal energy of an ideal gas after it has completed such a cycle? Is it possible that a net amount of *work* has been done during the cycle? If so, draw a cycle in which a net amount of work is done. Explain how this satisfies energy conservation.

11D.3, continued:

(c) Use the *PV* plot you drew in part (a) to construct a cycle in which a gas expands isobarically to three times its initial volume, is then allowed to cool at constant volume back to its original temperature, and finally is compressed isothermally back to its original volume. How much net work is done by the gas during this cycle?

11D.4 (S) Obtain expressions for the molar heat capacities of a monatomic ideal gas at constant volume and at constant pressure, and hence show that their ratio is 5/3.

We saw in the *Essentials* that the conditions under which a gas is heated affect its measured heat capacity. These two extremes (heating without change of volume, which implies an increase in pressure, and conversely heating at constant pressure, which requires expansion) are the standard ways to quote specific or molar heat capacities: the corresponding values are labeled C_V and C_P respectively.

11D.5 (H) If the volume of a sealed vessel filled with helium at atmospheric pressure (1.01×10^5 Pa) and room temperature (295 K) is 0.5 m^3, calculate the internal energy of the helium gas at 295 K and at 77 K. Hence calculate the heat transferred from the vessel during the cooling process. What is the molar heat capacity of helium at constant volume?

The following problem demonstrates how the number of atoms in each molecule of a polyatomic gas affects the heat capacity of that gas. This material is quite difficult— consider it a challenge problem.

11D.6 (S) The **principle of equipartition** states that internal energy is equally shared amongst the available degrees of freedom, i.e. $\langle \frac{1}{2}mv_x^2 \rangle = \langle \frac{1}{2}mv_y^2 \rangle = \langle \frac{1}{2}mv_z^2 \rangle = \frac{1}{2}kT$ for a monatomic gas, and each internal degree of freedom for a polyatomic gas also contributes $\frac{1}{2}kT$. What effect will this have on the molar heat capacities of polyatomic ideal gases? For a diatomic molecule, what do you expect the ratio of heat capacities to be (a) if only rotational internal motion occurs, and (b) if vibration also contributes?

11D.7 (S) An *adiabatic* expansion or contraction is one in which $Q = 0$, i.e. no heat is transferred to or from the gas.

(a) Show that this implies that $P_i V_i^\gamma = P_f V_f^\gamma$, where i denotes the initial state, f the final state, and $\gamma = C_P/C_V$ is the ratio of specific heat capacities.

(b) Suppose that $\mathcal{N}$ moles of an ideal gas expand isothermally from (P_a, V_a) to (P_b, V_b), and then adiabatically from (P_b, V_b) to (P_c, V_c). The gas is then compressed isothermally from (P_c, V_c) to (P_d, V_d), and finally compressed adiabatically back to its starting point. How much heat is (i) supplied to, (ii) lost by, the gas during this cycle? What is the *efficiency* of the cycle, where efficiency is defined as the work done divided by the heat supplied?

COMPLETE SOLUTIONS TO PROBLEMS WITH AN (S)

11B.2   *What is the typical speed of (a) a helium atom, (b) a nitrogen molecule, at* 300 K*?*
Helium has a mass of 4 u, N_2 *a mass of* 28 u; 1 u = 1.66×10^{-27} kg.

Conceptualize
The kinetic temperature of an ideal gas is defined in terms of the average kinetic energy
of its constituent atoms or molecules. Therefore we can calculate the average kinetic
energy of a gas atom/molecule corresponding to a temperature of 300 K. This gives us
the average value of v^2, and the square root of this will presumably represent a 'typical'
speed.

Formulate and Solve
The average kinetic energy of the molecules of an ideal gas is $\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}kT$. Thus any
ideal gas at 300 K has an average molecular kinetic energy of 6.2×10^{-21} J. Dividing by
$\frac{1}{2}m$ gives $\left\langle v^2 \right\rangle = 1.9 \times 10^6 \text{m}^2/\text{s}^2$ for helium and $2.7 \times 10^5 \text{m}^2/\text{s}^2$ for nitrogen. A typical
speed would be the square root of this, so 1.4 km/s for helium and 520 m/s for nitrogen.

Scrutinize and Learn
These speeds are high by everyday standards, though much less than the speed of light
(we are still safely in the realm of classical mechanics). However, the velocities of
individual gas molecules will be randomly oriented in space, so the speed of the center
of mass of a volume of gas remains essentially zero.

The square root of $\left\langle v^2 \right\rangle$ is called the **root-mean-square** or **rms** speed. It is **not** equal to
the average speed, $\langle v \rangle$: for example, two point masses with speeds 2.0 and 6.0 m/s have
average speed 4.0 m/s, but rms speed 4.5 m/s—and their average *velocity* depends on
the directions in which they are moving. Both $\langle v \rangle$ and the rms speed represent 'typical'
speeds, but the rms speed is more useful for problems in more than one dimension, since
$\left\langle v^2 \right\rangle$ is easier to express in component form than $\langle v \rangle$.

11B.5   *According to quantum physics, a light wave is actually composed of particles, called*
photons. *While a complete understanding of photons involves both quantum physics*
and relativity, the pressure exerted by photons inside a perfectly reflecting box can be
calculated using the same method we employed for the ideal gas. The differences are
that photons always move at the speed of light, which is denoted by c (i.e. $|\vec{v}| = c$*), and*
the momentum $\vec{p}$ *of a photon is not* $m\vec{v}$*, but*

$$\vec{p} = \frac{E}{c^2}\vec{v},$$

where E is the energy of the photon.

Using this information, calculate the pressure exerted by a 'gas' of N photons confined
inside a rectangular box of volume V . Assume the walls of the box are perfectly reflecting,
so that a photon-wall interaction is an elastic collision.

Conceptualize
Our basic premise is that photons behave like the particles of an ideal gas: they move
randomly around the box and undergo elastic collisions with the walls. We can therefore
use the same line of attack that we used to calculate the pressure of an ideal gas in the

11B.5, continued:

Essentials. We consider one wall of the rectangular box and define the x-axis so that it is perpendicular to our chosen wall. We then calculate the average momentum transferred to the wall in a time interval Δt by a single photon of energy E, and finally sum over all N photons to obtain the total force.
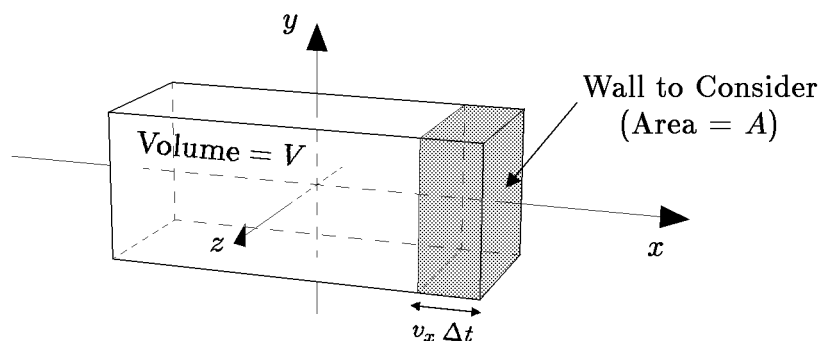
Formulate

Let the wall in question have area A as shown, and consider a photon reflected off the wall. The effect of the reflection is to reverse the sign of the x-component of the photon's velocity, while leaving its magnitude unchanged; the y- and z-components are unaffected. If the magnitude of the x-component is v_x, the photon's velocity changes by $\Delta v_x = -2v_x$ in the collision, so its momentum change is

$$\Delta p_x = -2\frac{E}{c^2}v_x,$$

and, by conservation of momentum, the momentum transferred to the wall is $-\Delta p_x$.

To determine the average force exerted by the photon on the wall, we need to calculate the momentum transferred per unit time, since $\vec{\mathbf{F}} = \mathrm{d}\vec{\mathbf{p}}/\mathrm{d}t$. This means that we have to find the probability that the photon collides with the wall in a given time interval Δt. The average momentum transferred in a time Δt is then the probability of a collision times the momentum transferred if a collision does occur, and the force is $\langle \vec{\mathbf{p}} \rangle / \Delta t$.

Solve

For the photon to collide with our chosen wall in a given time interval Δt, its x-velocity must be positive (otherwise it is moving away from the wall). If it moves randomly, there is a 50% probability that this will be so. Given that it is moving in the right direction, it must be close enough to the wall to reach it in the specified time: that is, when we start the clock it must be not more than $v_x \Delta t$ away from the wall, in the shaded volume in the diagram. If it could be anywhere in volume V, the probability that it is within the shaded volume is

$$\frac{Av_x\Delta t}{V}.$$

The average momentum transferred to the wall is therefore

$$\langle p \rangle = \frac{1}{2} \times \frac{Av_x\Delta t}{V} \times 2v_x\frac{E}{c^2}$$

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11B.5, continued:

and the average force exerted on the wall is

$$\langle F \rangle = \frac{EA}{c^2 V} v_x^2.$$

For N photons we need to sum over the individual photons. Since all photons travel at the speed of light c, we know

$$c^2 = v_x^2 + v_y^2 + v_z^2,$$

and if the photons are moving randomly they will (by definition of "random") have no preferred direction, so

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \tfrac{1}{3} c^2.$$

The pressure exerted by our N photons is the total force per unit area:

$$P = \frac{F}{A} = \frac{1}{3} \frac{N \langle E \rangle}{V}.$$

Scrutinize
If we compare this expression with the ideal gas pressure

$$P_{\text{gas}} = \frac{2}{3} \frac{N \langle K \rangle}{V},$$

where $K = \frac{1}{2} m v^2$, we see that the two are extremely similar, as we might expect since we derived them in the same way. However, the difference between E and K is very significant when we take into account Einstein's famous equation $E = mc^2$. For the ideal gas, most of the energy is actually locked up in the mass of the gas particles, so the pressure is quite a small effect; for the massless photons, the pressure is related to the *total* energy E, and is therefore a much larger effect in relative terms. In absolute terms, however, it is very small under normal everyday conditions, and therefore we do not think of light as exerting a pressure (whereas we do recognize in everyday life the pressures exerted by gases and liquids).

Learn
The term $N \langle E \rangle / V$ is simply the total energy per unit volume, or *energy density*, associated with the light (or other electromagnetic radiation, such as radio waves or X-rays) in our box. As discussed above, the energy density associated with light is very small under typical experimental conditions, but this is emphatically not true in more exotic locations. Radiation pressure plays a significant role in the evolution of stars, and probably also in the processes which power quasars and other active galaxies. In addition, cosmologistsbelieve that for the first 10,000 to 100,000 years of the history of the universe, its mass density was not dominated by matter as we know it, but by radiation. During this period the pressure—equal to one-third of the energy density—was enormous. This huge pressure prevented matter from clumping under the influence of gravity. The process of galaxy formation, therefore, could not begin until the universe

11B.5, continued:

had cooled enough to lower the radiation energy density to the point where gravity could win out over radiation pressure.

11C.6   *If the atmosphere of a planet is all at the same temperature T and consists of a gas whose molecules have mass m, how does the density of the atmosphere vary with height above the ground? Assume that the atmosphere does not extend far enough from the planet for g to change significantly.*

Conceptualize

It seems reasonable to assume that the planet's atmosphere is basically stable, that is, it is not condensing onto the ground or leaking away into space. If that is the case, there must be no net force acting on a typical small volume element of atmosphere at some height h above the planet's surface. The individual forces acting on this small volume element are

- $g\Delta m$ downwards, where $\Delta m = \rho_h \mathrm{d}V = \rho_h A \Delta h$;

- $P(h) \cdot A$ upwards;

- $P(h + \Delta h) \cdot A$ downwards;

- various horizontal pressure forces.

The symmetry of the situation implies that the horizontal pressure forces all cancel. The vertical pressure forces, however, must not cancel, since they must contribute a net upward force to balance $g\Delta m$. If the atmosphere is an ideal gas, then $P = nkT$, where n is the number density. We are told T does not vary with height, so the only way to have pressure decreasing with height is to have n decrease with height: $\Delta P = kT\Delta n$.
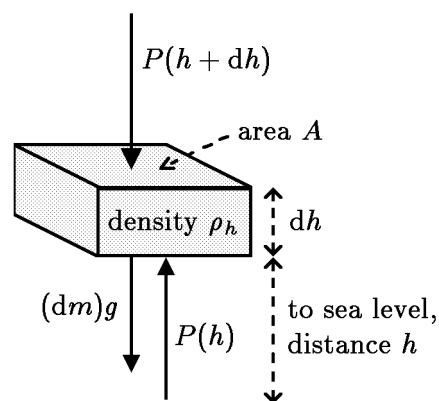
Formulate

The net force on our small volume element is

$$P(h + \Delta h) \cdot A - P(h) \cdot A = -\rho_h A g \Delta h,$$

or, writing $P = nkT$ and $\rho_h = nm$, where m is the average mass of one molecule of atmosphere,

$$\frac{\mathrm{d}n}{\mathrm{d}h} = \lim_{\Delta h \to 0} \frac{\Delta n}{\Delta h} = -\frac{nmg}{kT}.$$

Solve

If we rearrange this slightly we have

$$\frac{\mathrm{d}n}{n} = -\frac{mg}{kT}\mathrm{d}h,$$

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11C.6, continued:

which we can integrate from zero, or ground level, to height H to give

$$\ln n_H - \ln n_0 = -\frac{mgH}{kT}$$

or

$$n_H = n_0 \exp\left(-\frac{mgH}{kT}\right),$$

where n_0 is the number density at ground level. (The mass density has the same form, since $\rho_H = n_H m$.) The density of the atmosphere decreases exponentially with height: at $H = kT/mg$ it has decreased to 37% of its value at ground level, at twice that height to 14%, and so on. For the Earth, taking nitrogen gas at 290 K to be representative of the atmosphere, $kT/mg \simeq 9$ km.

Scrutinize

The value we obtain for the Earth seems reasonable: it explains why commercial airplanes flying at about 10 km have to be pressurized, and why climbers of high mountains often use oxygen masks. We have, however, cheated somewhat: our coordinate system implicitly assumes that the Earth is flat. If you are confident of your calculus, you might like to investigate the surprising results of trying to do this calculation for an isothermal atmosphere about a spherical planet. Further, the isothermal approximation is not a very good one—anyone who has climbed a mountain will be aware that the Earth's atmosphere is not at all isothermal! Despite these approximations, the actual numerical value for the scale height of the atmosphere is not too bad.

Learn

Taking this result together with that from problem 11B.2, we can also understand why the Earth has an atmosphere of nitrogen and oxygen, the Moon has no atmosphere at all, and Jupiter has an atmosphere of hydrogen and helium. Although the speed of a typical helium atom is not high enough to escape from Earth's gravity, gas atoms actually have a wide range of speeds about this typical value, and helium (having smaller m) also extends out to greater heights than heavier elements. A helium atom which happens to be moving fast is therefore quite likely to escape from the atmosphere before a collision with another atom slows it down, and over the five billion years of Earth's history we have lost any gaseous hydrogen and helium we originally possessed. The Moon, with only one-sixth of Earth's surface gravity, is unable to retain any gaseous atmosphere at all, whereas Jupiter, with both a higher gravity and a lower temperature, keeps even the least massive gases.

Notice that the form of the exponential is $-(\text{potential energy})/kT$. This turns out not to be a special coincidence for height, but instead a very general feature of gas distributions. Potential energy and kinetic energy are very closely related, so it is not too surprising to find that the distribution of molecular speeds follows a similar law: the probability of finding a molecule with speed in the range v to $v + \Delta v$ does indeed include a factor of $\exp\left(-\frac{1}{2}mv^2/kT\right)\Delta v$. The full formula, including normalization, is the *Maxwell-Boltzmann distribution*,

$$f(v)dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{1}{2}mv^2/kT} dv.$$

11C.6, continued:

The significance of this formula is that it tells us the *spread* of molecular speeds about the average we deduce from the temperature. This is important when one considers, for example, the evaporation of a liquid (fast molecules escape as vapor) or—as above—the loss of light gases from a planetary atmosphere.

11D.4   *Obtain expressions for the molar heat capacities of a monatomic ideal gas at constant volume and at constant pressure, and hence show that their ratio is 5/3.*

Conceptualize

For a monatomic ideal gas, the internal energy U is just the total kinetic energy $N \left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} N k T$. If we heat the gas at constant volume, no work is done by the gas, and therefore all the energy we transfer to the gas just increases its internal energy. Therefore the amount of energy needed to raise the temperature of one mole of gas by an amount ΔT under these conditions is simply $C_V \Delta T = \frac{3}{2} N_A k \left((T + \Delta T) - T \right)$, where N_A is Avogadro's number.

In the case of constant pressure, the change in internal energy for a given temperature change ΔT must be the same, $C_V \Delta T$, because the kinetic temperature of a gas depends *only* on the kinetic energy of its constituent particles, and not on the volume they happen to be occupying. However, to maintain constant pressure while changing the temperature the volume occupied by the gas must change, and so the gas must do work—e.g. in pushing out a piston, as in the *Essentials*. Conservation of energy implies that additional energy must be supplied to the gas to allow it to do this work, and therefore the molar heat capacity at constant pressure, C_P, must be greater than C_V.

Formulate

We have already seen that the work done by the gas for a change of volume ΔV is $P \Delta V$. To raise the temperature of a mole of gas by ΔT at constant pressure P, the total energy that must be supplied to the gas is therefore

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

(Denoting the heat transferred by Q is standard notation, because the obvious abbreviation, H, unfortunately has a technical meaning in thermodynamics.)

Solve

The molar heat capacity at constant volume is

$$C_V = \frac{dU}{dT} = \lim_{\Delta T \to 0} \frac{\Delta U}{\Delta T} = \frac{3}{2} N_A k.$$

Since $N_A k = R$ by definition, this implies $C_V = \frac{3}{2} R$. Numerically this comes to 12.47 J/mol·K.

The molar heat capacity at constant pressure is

$$C_P = \frac{dQ}{dT} = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} = P \frac{dV}{dT} + C_V.$$

11D.4, continued:

What is dV/dT? From the ideal-gas law,

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

for one mole of gas, and both R and P are constant if the heating is done at constant pressure. Hence

$$\frac{dV}{dT} = \frac{R}{P},$$

and so

$$C_P = R + C_V = \tfrac{5}{2}R,$$

which comes to 20.79 J/mol·K. The ratio of molar heats is

$$\frac{C_P}{C_V} = \frac{\tfrac{5}{2}R}{\tfrac{3}{2}R} = \frac{5}{3}.$$

Scrutinize

We have assumed here that the energy transferred to the gas goes **_either_** into increasing the kinetic energy of its constituent particles **_or_** doing work on its surroundings. This is reasonable for the **_monatomic ideal gas_** specified in the question.

The dimensions of C_V and C_P must be [energy]/[temperature]·[mole], since they both represent the amount of energy needed to raise the temperature of one mole of the gas by 1 K. From the equation $PV = \mathcal{N}RT$ we see that the dimensions of R are [force] × [length]/([temperature] × [$\mathcal{N}$]). As $\mathcal{N}$ is measured in moles, this is consistent. Note that the units of the **_specific_** heat capacity, which is the energy required to raise the temperature of **_one kilogram_** of material through 1 K, are slightly different: J/kg·K, rather than J/mol·K. The specific heat capacity, not the molar heat capacity, is the quantity normally tabulated in data books, since in practical applications the amount of material is more likely to be given in kilograms than in moles. The ratio of specific heats is of course equal to the ratio of molar heats.

Learn

For ideal gases which are not monatomic, the ratio of molar heats (or specific heats) depends on the structure of the molecule (see Problem 11D.6). This ratio also arises in other contexts in thermodynamics—for example, in describing the path followed on the PV plot by a mass of gas expanding or contracting without exchanging heat with its surroundings. For this reason, the ratio of specific heats is given its own symbol: $C_P/C_V \equiv \gamma$.

11D.6   _The **principle of equipartition** states that internal energy is equally shared amongst the available degrees of freedom, i.e._ $\left\langle \tfrac{1}{2}mv_x^2 \right\rangle = \left\langle \tfrac{1}{2}mv_y^2 \right\rangle = \left\langle \tfrac{1}{2}mv_z^2 \right\rangle = \tfrac{1}{2}kT$ _for a monatomic gas, and each internal degree of freedom for a polyatomic gas also contributes_ $\tfrac{1}{2}kT$. _What effect will this have on the molar heat capacities of polyatomic ideal gases?_

11D.6, continued:

For a diatomic molecule, what do you expect the ratio of heat capacities to be (a) if only rotational internal motion occurs and (b) if vibration also contributes?

Conceptualize and Formulate

The kinetic temperature of a gas is defined in terms of the translational kinetic energy of its constituent molecules. Internal kinetic or potential energy plays no part in this definition. Therefore, to raise the temperature of a mole of a polyatomic ideal gas from T to $T + \Delta T$, we still have to increase $\left\langle \frac{1}{2}mv^2 \right\rangle$ by an amount $\frac{3}{2}k\Delta T$. The principle of equipartition states that this implies raising the energy stored in all the other degrees of freedom by $\frac{1}{2}k\Delta T$ each. This implies that the molar heat capacity at constant volume will increase to $\frac{1}{2}fR$, where f is the total number of degrees of freedom (including the three for translational kinetic energy).

The calculation in Problem 11D.4 which gave $C_P = C_V + R$ was not in any way dependent on the actual value of C_V. Therefore it still holds for our polyatomic gas, which must have $C_P = R + C_V = (1 + \frac{1}{2}f)R$. The ratio of molar heats is then

$$\gamma = \frac{C_P}{C_V} = \frac{1 + \frac{1}{2}f}{\frac{1}{2}f} = \frac{2}{f} + 1.$$

Solve

To solve this problem for a diatomic molecule, we therefore have to count the number of degrees of freedom—the number of coordinates required to specify the motion of one molecule. We already know that three degrees of freedom are taken up by the three independent directions of translational motion, i.e. the three coordinates needed to specify the velocity vector of the molecule's center of mass.

What about rotational motion? We can consider a diatomic molecule as two point particles connected by a spring (representing the interatomic force binding the molecule together). If we put the origin of coordinates at the molecule's center of mass and the x-axis runs along the line joining the two atoms, the molecule can
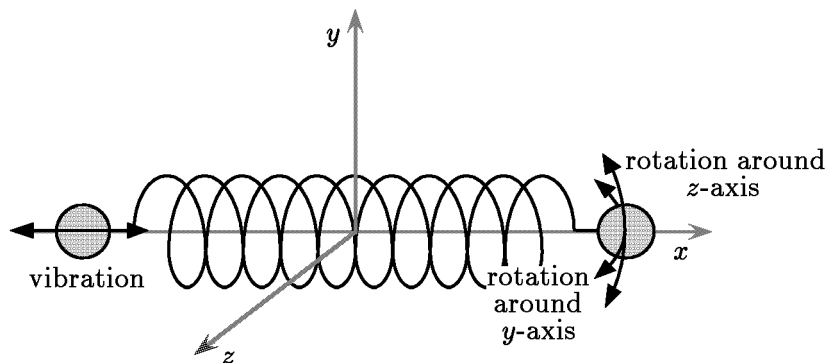
rotate about the y- or z-axis or some combination of these, so the angular motion has two components. (Rotation about the x-axis is meaningless if we assume the atoms are

11D.6, continued:

point particles.) Adding these to the three components of the velocity of the molecule's center of mass, we have $f = 5$, and so we would predict $\gamma = 1.4$.

Vibration adds only one degree of freedom, because the molecule has only one possible way to vibrate. Hence we must add another $\frac{1}{2}kT$ for the average *kinetic* energy of vibration of the molecule. However, if we think of the atoms as being connected by a spring, there is also *potential* energy associated with this vibration, and we can work out from our knowledge of simple harmonic motion that the average potential energy is equal to the average kinetic energy. (It is reasonably obvious that this must be so, since the total energy in the oscillation varies from all kinetic, when the spring is at its natural length, to all potential at the points of greatest compression or extension, and back again.) We must account for this in our sum, so effectively $f = 7$ and the expected ratio is 1.286.

Scrutinize and Learn

Writing the ideal-gas law in terms of internal energy rather than temperature gives us

$$PV = \frac{2}{f}U = (\gamma - 1)U.$$

This expression allows us to calculate the internal energy, and to count the number of degrees of freedom, from the *measured* ratio of molar heats. We can therefore check our understanding of kinetic theory by measuring this ratio for a variety of different diatomic gases. The results are surprising: for most diatomic molecules the ratio of specific heats comes out close to 1.4 (see any standard data book). This suggests that the bond between the molecules is more like a rigid rod than a spring, and vibration is not possible. However, this explanation cannot be right, because (i) some heavy diatomic gases, such as iodine, have molar heat ratios close to 1.3 and (ii) the ratio of molar heats for diatomic gases varies with temperature, approaching 1.286 as the temperature gets very high, even for those gases which have ratios of 1.4 at room temperature.

This is a real failure of our model, since there is nothing in our calculation which suggests a temperature dependence. In the 19th century, when the kinetic theory of gases was first developed, this disagreement was not understood (it is not that these gases are not ideal, because they obey the ideal-gas law very well; they just have the 'wrong' value of γ!). We now know that it occurs because at these small distances and energies it is necessary to apply the rules of quantum mechanics. Under these rules, a diatomic molecule may not actually be able to 'use' all its potential degrees of freedom at low energy, and therefore our calculation represents the high-energy (or high temperature) limit of the specific heat ratio, which will be different at lower temperatures.

11D.7 *An adiabatic expansion or contraction is one in which $Q = 0$, i.e. no heat is transferred to or from the gas.*

(a) *Show that this implies that $P_i V_i^\gamma = P_f V_f^\gamma$, where i denotes the initial state, f the final state, and $\gamma = C_P/C_V$ is the ratio of specific heat capacities.*

11D.7, continued:

Conceptualize

If $Q = 0$, then the work done by the gas must be equal to the change in its internal energy. We can express both of these in terms of P, V, and T, and then use the ideal gas law to eliminate T. This will leave a relation between P and V.

Because the work done depends on the specific path taken on the PV plot, it will be best to start by considering *small* changes of pressure and volume. We can then integrate to find the result for large changes.

Formulate

For the case $Q = 0$, the first law of thermodynamics reduces to $\Delta U = -\Delta W$, where we use ΔW to denote a *small* amount of work. We know that $\Delta W = P\Delta V$, and the definition of the molar heat capacity tells us that $\Delta U = \mathcal{N} C_V \Delta T$. (When heating at constant volume, no work is done, and so C_V relates the heat supplied directly to the change in internal energy of the gas.) Thus,

$$\mathcal{N} C_V \Delta T = -P\Delta V.$$

This equation describes a small adiabatic change of volume in an ideal gas. To solve the problem, we need to express ΔT in terms of P, V, ΔP and ΔV.

Solve

The ideal gas law is $\mathcal{N} RT = PV$. If we differentiate this with respect to some variable, say time, then the product rule for differentiation gives

$$\frac{\mathrm{d}}{\mathrm{d}t}(\mathcal{N} RT) = \mathcal{N} R\frac{\mathrm{d}T}{\mathrm{d}t} = P\frac{\mathrm{d}V}{\mathrm{d}t} + V\frac{\mathrm{d}P}{\mathrm{d}t}.$$

This gives us the *differential form* of the ideal gas law:

$$\mathcal{N} R\Delta T = P\Delta V + V\Delta P.$$

Using this, we can substitute for ΔT in our adiabatic volume change:

$$\frac{C_V}{R}(P\Delta V + V\Delta P) = -P\Delta V$$

$$\implies (C_V + R)P\Delta V = -C_V V\Delta P.$$

But we saw in Problem 11D.4 that $C_V + R = C_P$, so this equation reduces to

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

We can now integrate this equation from the initial state (P_i, V_i) to the final state (P_f, V_f):

$$\gamma \int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} = -\int_{P_i}^{P_f} \frac{\mathrm{d}P}{P}$$

$$\implies \gamma \ln\frac{V_f}{V_i} = -\ln\frac{P_f}{P_i},$$

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11D.7, continued:

where $\gamma = C_P/C_V$ as in Problem 11D.4. Taking antilogs, using the fact that $\ln(x^a) = a \ln x$, we have

$$P_i V_i^{\gamma} = P_f V_f^{\gamma}$$

as required.

Scrutinize

The dimensions of the equation are OK: in particular, γ, being a ratio of two quantities with the same units, is dimensionless (it would be meaningless to speak of "x to the power of (y joules)", for example). We can use the ideal gas law to eliminate P, giving $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$, and since $\gamma > 1$ this correctly implies that T must decrease if V increases (as no heat is supplied from outside, the work done by the gas in expanding must come from a loss of internal energy, i.e. a reduction in temperature).

Learn

Adiabatic expansion and compression is a useful idealization in describing **rapid** changes in volume, when there is no time for significant heat exchange with the surroundings. An example would be the motion of the piston in an automobile engine: both the compression stroke and the power stroke are approximately adiabatic.

(b) *Suppose that $\mathcal{N}$ moles of an ideal gas expand isothermally from (P_a, V_a) to (P_b, V_b), and then adiabatically from (P_b, V_b) to (P_c, V_c). The gas is then compressed isothermally from (P_c, V_c) to (P_d, V_d), and finally compressed adiabatically back to its starting point. How much heat is (i) supplied to, (ii) lost by, the gas during this cycle? What is the **efficiency** of the cycle, where efficiency is defined as the work done divided by the heat supplied?*

Conceptualize

By definition, no heat is lost by or supplied to the gas in the adiabatic legs of the cycle, so when calculating the heat supplied we need consider only the isothermal legs $a \to b$ and $c \to d$. The gas does positive work in expanding from a to b, and as its internal energy does not change (the expansion is isothermal) heat must be supplied to balance this work: conversely, the gas does negative work, and loses heat, during the isothermal compression from c to d. Since the gas winds up back at its starting point, its internal energy does not change over a complete cycle, and so, by the first law of thermodynamics, the work done during the cycle must be the difference between the heat **supplied** in the ab leg and the heat **lost** during the cd leg. Thus we do not need to calculate the work done during the adiabatic stages. We will, however, have to use the adiabatic legs to work out the relationship between the temperatures of the two isothermal stages.

Formulate

Since $PV = \mathcal{N}RT$ and T is constant, the work done during an isothermal expansion or compression is

$$W = \int_{V_i}^{V_f} P \, dV = \mathcal{N}RT \int_{V_i}^{V_f} \frac{dV}{V} = \mathcal{N}RT \ln \frac{V_f}{V_i}.$$

11D.7, continued:

As we saw in part (a), the relation between temperature and volume for an adiabatic expansion or compression is
$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}.$$

This is all we need to solve the problem.

Solve
The heat supplied during stage ab is

$$Q_S = \mathcal{N} R T_H \ln \frac{V_b}{V_a},$$

where T_H is the temperature of the gas during this expansion (the subscript H indicates that it is **higher** than the temperature during the cd compression). Likewise, the heat lost in stage cd is

$$Q_L = -\mathcal{N} R T_L \ln \frac{V_c}{V_d}.$$

From stage bc we know that

$$\left(\frac{V_c}{V_b}\right)^{\gamma-1} = \frac{T_H}{T_L},$$

and likewise from da

$$\left(\frac{V_d}{V_a}\right)^{\gamma-1} = \frac{T_H}{T_L}.$$

Comparing these, we see that

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}$$

$$\implies \frac{V_c}{V_d} = \frac{V_b}{V_a}.$$

From the first law of thermodynamics, we know that over this cycle $Q = W$, i.e. $Q_S + Q_L = W$. Hence the efficiency is given by

$$\epsilon = \frac{W}{Q_S} = 1 + \frac{Q_L}{Q_S}$$

$$= 1 - \frac{T_L}{T_H}.$$

Scrutinize
The efficiency is dimensionless, as it should be, and lies in the range 0 to 1 (or 0% to 100%), as energy conservation dictates that it must. Note that 100% efficiency can only be attained if $T_L = 0$, which is never true in practice—this cycle cannot transform **all** the energy supplied to it into useful work.

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11D.7, continued:

☺ ***Learn***
The cycle we have analyzed here was first studied by the nineteenth-century French engineer N.L. Sadi Carnot, and is called the ***Carnot cycle*** in his honor. It can be shown that ***for a given T_L and T_H, no engine can convert heat to work more efficiently than the Carnot cycle***. An engine using the Carnot cycle is not in fact practical, but it is possible to approximate real engines by different cycles on the PV plot and calculate their maximum efficiencies: for example, the operation of an automobile engine is approximately described by the ***Otto cycle***, which consists of an adiabatic compression (the compression stroke of the piston), heating at constant volume (the ignition of gasoline by the spark), adiabatic expansion (the piston power stroke), and cooling at constant volume (the exhaust). The efficiency of the Otto cycle turns out to be $1 - (V_{\min}/V_{\max})^{\gamma-1}$, which means that high auto engine efficiencies require a high ***compression ratio*** $(V_{\max}/V_{\min})$. Real engines always have lower efficiencies than their idealized counterparts on the PV plot, owing to the effects of friction, turbulence, etc.

The statement that for a Carnot cycle (or other ideal reversible engine) working between temperatures T_H and T_L, the ratio of heat lost to heat supplied

$$\frac{|Q_L|}{|Q_S|} = \frac{T_L}{T_H}$$

was used by Lord Kelvin to ***define*** the thermodynamic temperature scale. The fact that we have derived it using our kinetic temperature scale shows that the two are equivalent. Historically, this is not surprising: although the two definitions are logically independent, in practice they are both rigorous formulations of the empirical ideal-gas temperature scale, which states that the temperature of an ideal gas at constant volume is proportional to its pressure.

HINTS FOR PROBLEMS WITH AN (H)
The number of the hint refers to the number of the problem

11A.2 If instead of small dust particles in the air you had a small admixture of a different gas, what would the average kinetic energy of a molecule of this gas be? Does this depend on the mass of the molecule?

11B.3 How does the average kinetic energy at a given temperature depend on mass and on temperature? If you are having trouble with this problem, study the solution to problem 11B.2

11C.3 How many molecules of gas does a cylinder contain when full? When 'empty'?

11C.5 How many molecules of mass m are there in a total mass M of a given gas?

What is the total number of molecules (of any kind) per unit volume of air at the given pressure and temperature?

11D.1 If the compression is *rapid*, there is no time for air to escape through the delivery valve of the pump or for the compressed gas to cool. Under these circumstances, what will happen to the internal energy of the air in the pump? Where does the energy come from?

11D.2 What is the internal energy of N molecules of a monatomic gas?

What is the work done by the gas as a result of a small change of volume ΔV? If the pressure is *constant*, can you integrate this over a large volume change?

How is the change in internal energy related to the heat supplied and the work done?

11D.3 (a) What is the expression for work done in terms of pressure and change in volume? What is the graphical equivalent of this?

(b) Can the temperature of the ideal gas be different if it has returned to the same point on the PV plot? Can the path it traces out on its return be different from the path it followed originally?

11D.5 What is the change in internal energy of the gas as a result of the temperature change? Has any work been done on or by the gas?

What is the definition of molar heat capacity? How many moles of gas are there in the vessel?

ANSWERS TO HINTS

11A.2 Same as the air molecules; no.

11B.3 Independent of mass; proportional to temperature.

11C.3 4.92×10^{25}; 2.46×10^{23}.

11C.5 M/m; 2.47×10^{25} m^{-3}.

11D.1 It will increase. You did work on the piston of the pump, which in turn did work on the gas.

11D.2 $\frac{3}{2}NkT$; $\Delta W = P\Delta V$;

$W = P(V_f - V_i)$ where f and i are final and initial values.

Change in internal energy of gas = heat supplied to gas minus work done by gas.

11D.3 (a) $W = \int_{start}^{end} P dV$; the integral is the area under the graph.

(b) No; yes.

11D.5 -56 kJ; no.

Heat transferred per mole of gas for a temperature change of 1 K; 20.6 moles.

ANSWERS TO ALL PROBLEMS

11A.1 Typical speed about 500 m/s (1800 km/h).

Wind velocity represents a net velocity of large quantities of air, whereas net velocity of a large quantity of still air is zero (individual velocities have random orientation). Wind can therefore exert a net force on large objects, whereas pressure exerts no **net** force on any object large enough for random fluctuations to average out.

11A.2 The motion of the dust particles is caused by their collisions with randomly moving air molecules. For large particles the characteristic kinetic energy for room temperature corresponds to an unmeasurably small speed.

11A.3 All answers to this question should, of course, be different! A reasonable response would be:

"A gas consists of an extremely large number of small particles (usually atoms or molecules) moving randomly about with some distribution of speeds. The interparticle forces are very small (zero, for an ideal gas), and all collisions are elastic. Each collision of a gas particle with a container wall or other object will impart an impulse to the object struck: the time averaged sum of all these small impulses, divided by the area of the object, is the pressure exerted by the gas."

11A.4 Change of momentum per unit time; translational kinetic energy. No; the average over all the atoms or molecules in the sample.

11B.1 b

11B.2 See complete solution.

11B.3 (a) 300 K; (b) 19 K (if hydrogen were still an ideal gas at this low temperature!).

11B.4 6.1×10^{-21} J; 430 m/s; 9.4×10^{24}; 1.0×10^3 Pa.

11B.5 See complete solution.

11C.1 c

11C.2 a

11C.3 0.16 kg

11C.4 2.4 kN upwards; 1.8 kN downwards.

11C.5 4.57:1; 1.18 kg/m^3; by a factor of 1.07, to 1.27 kg/m^3.

11C.6 See complete solution.

11D.1 The piston of the pump does work in compressing the gas, which increases its internal energy—microscopically, each gas molecule bouncing off the moving piston rebounds with a slightly higher speed. The average kinetic energy of a gas molecule increases and therefore so does its temperature. On the return stroke, fresh air is drawn in from outside the pump, so when the piston returns to its initial position the gas in the pump has not returned to its initial temperature—unlike a pendulum, this is not a closed, isolated system. Yes, both because the piston does more work if you apply more force in moving it, and because given time the gas will exchange heat with its surroundings.

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11D.2 (a) $P_f = P_i/3$, $T_f = T_i$, $Q = (\ln 3) P_i V_i,$; $W = (\ln 3) P_i V_i$.

  (b) $P_f = P_i$, $T_f = 3T_i$, $Q = 5P_i V_i$, $W = 2P_i V_i$.

11D.3 (a)
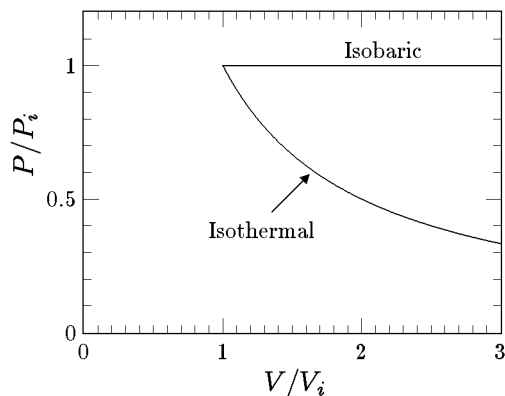
Work done in each case is area under curve.

  (b) Zero; yes; any cycle where the line representing the *expansion* phase is higher than the line representing the *compression* phase.

  Some of the heat supplied during the cycle has been converted to work.

  (c) 0.9 $P_i V_i$

11D.4 See complete solution.

11D.5 12.5 J/mol·K.

11D.6 See complete solution.

11D.7 See complete solution.