

40-5 The specific heats of gases

Now we shall look at some ways to test the theory, and to see how successful is the classical theory of gases. We saw earlier that if U is the internal energy of N molecules, then $PV = NkT = (\gamma - 1)U$ holds, sometimes, for some gases, maybe. If it is a monatomic gas, we know this is also equal to $\frac{2}{3}$ of the kinetic energy of the center-of-mass motion of the atoms. If it is a monatomic gas, then the kinetic energy is equal to the internal energy, and therefore $\gamma - 1 = \frac{2}{3}$. But suppose it is, say, a more complicated molecule, that can spin and vibrate, and let us suppose (it turns out to be true according to classical mechanics) that the energies of the internal motions are also proportional to kT . Then at a given temperature, in addition to kinetic energy kT , it has internal vibrational or rotational energy. So the total U includes not just the internal kinetic energy, but also the rotational energy, and we get a different value of γ . Technically, the best way to measure γ is by measuring the specific heat, which is the change in energy with temperature. We will return to that approach later. For our present purposes, we may suppose γ is found experimentally from the PV^γ curve for adiabatic compression.

Let us make a calculation of γ for some cases. First, for a monatomic gas U is the total energy, the same as the kinetic energy, and we know already that γ should be $\frac{5}{3}$. For a diatomic gas, we may take, as an example, oxygen, hydrogen iodide, hydrogen, etc., and suppose that the diatomic gas can be represented as two atoms held together by some kind of force like the one of Fig. 40-3. We may also suppose, and it turns out to be quite true, that at the temperatures that are of interest for the diatomic gas, the pairs of atoms tend strongly to be separated by r_0 , the distance of potential minimum. If this were not true, if the probability were not strongly varying enough to make the great majority sit near the bottom, we would have to remember that oxygen gas is a mixture of O_2 and single oxygen atoms in a nontrivial ratio. We know that there are, in fact, very few single oxygen atoms, which means that the potential energy minimum is very much greater in magnitude than kT , as we have seen. Since they are clustered strongly around r_0 , the only part of the curve that is needed is the part near the minimum, which may be approximated by a parabola. A parabolic potential implies a harmonic oscillator, and in fact, to an excellent approximation, the oxygen molecule can be represented as two atoms connected by a spring.

Now what is the total energy of this molecule at temperature T ? We know that for each of the two atoms, each of the kinetic energies should be $\frac{3}{2}kT$, so the kinetic energy of both of them is $\frac{3}{2}kT + \frac{3}{2}kT$. We can also put this in a different way: the same $\frac{3}{2}$ plus $\frac{3}{2}$ can also be looked at as kinetic energy of the center of mass

Table 40-1

Values of the specific heat ratio, γ , for various gases

Gas	T ($^{\circ}\text{C}$)	γ
He	-180	1.660
Kr	19	1.68
Ar	15	1.668
H ₂	100	1.404
O ₂	100	1.399
HI	100	1.40
Br ₂	300	1.32
I ₂	185	1.30
NH ₃	15	1.310
C ₂ H ₆	15	1.22

($\frac{3}{2}$), kinetic energy of rotation ($\frac{2}{2}$), and kinetic energy of vibration ($\frac{1}{2}$). We know that the kinetic energy of vibration is $\frac{1}{2}$, since there is just one dimension involved and each degree of freedom has $\frac{1}{2}kT$. Regarding the rotation, it can turn about either of two axes, so there are two independent motions. We assume that the atoms are some kind of points, and cannot spin about the line joining them; this is something to bear in mind, because if we get a disagreement, maybe that is where the trouble is. But we have one more thing, which is the potential energy of vibration; how much is that? In a harmonic oscillator the average kinetic energy and average potential energy are equal, and therefore the potential energy of vibration is $\frac{1}{2}kT$, also. The grand total of energy is $U = \frac{7}{2}kT$, or kT is $\frac{2}{7}U$ per atom. That means, then, that γ is $\frac{9}{7}$ instead of $\frac{5}{3}$, i.e., $\gamma = 1.286$.

We may compare these numbers with the relevant measured values shown in Table 40-1. Looking first at helium, which is a monatomic gas, we find very nearly $\frac{5}{3}$, and the error is probably experimental, although at such a low temperature there may be some forces between the atoms. Krypton and argon, both monatomic, agree also within the accuracy of the experiment.

We turn to the diatomic gases and find hydrogen with 1.404, which does not agree with the theory, 1.286. Oxygen, 1.399, is very similar, but again not in agreement. Hydrogen iodide again is similar at 1.40. It begins to look as though the right answer is 1.40, but it is not, because if we look further at bromine we see 1.32, and at iodine we see 1.30. Since 1.30 is reasonably close to 1.286, iodine may be said to agree rather well, but oxygen is far off. So here we have a dilemma. We have it right for one molecule, we do not have it right for another molecule, and we may need to be pretty ingenious in order to explain both.

Let us look further at a still more complicated molecule with large numbers of parts, for example, C₂H₆, which is ethane. It has eight different atoms, and they are all vibrating and rotating in various combinations, so the total amount of internal energy must be an enormous number of kT 's, at least $12kT$ for kinetic energy alone, and $\gamma - 1$ must be very close to zero, or γ almost exactly 1. In fact, it is lower, but 1.22 is not so much lower, and is higher than the $1\frac{1}{2}$ calculated from the kinetic energy alone, and it is just not understandable!

Furthermore, the whole mystery is deep, because the diatomic molecule cannot be made rigid by a limit. Even if we made the couplings stiffer indefinitely, although it might not vibrate much, it would nevertheless keep vibrating. The vibrational energy inside is still kT , since it does not depend on the strength of the coupling. But if we could imagine absolute rigidity, stopping all vibration to eliminate a variable, then we would get $U = \frac{5}{2}kT$ and $\gamma = 1.40$ for the diatomic case. This looks good for H₂ or O₂. On the other hand, we would still have problems, because γ for either hydrogen or oxygen varies with temperature! From the measured values shown in Fig. 40-6, we see that for H₂, γ varies from about 1.6 at -185°C to 1.3 at 2000°C . The variation is more substantial in the case of hydrogen than for oxygen, but nevertheless, even in oxygen, γ tends definitely to go up as we go down in temperature.

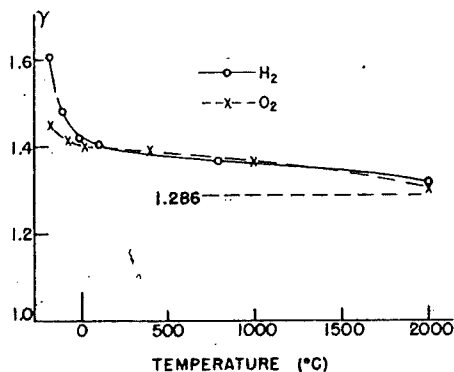


Fig. 40-6. Experimental values of γ as a function of temperature for hydrogen and oxygen. Classical theory predicts $\gamma = 1.286$, independent of temperature.

40-6 The failure of classical physics

So, all in all, we might say that we have some difficulty. We might try some force law other than a spring, but it turns out that anything else will only make γ higher. If we include more forms of energy, γ approaches unity more closely, contradicting the facts. All the classical theoretical things that one can think of will only make it worse. The fact is that there are electrons in each atom, and we know from their spectra that there are internal motions; each of the electrons should have at least $\frac{1}{2}kT$ of kinetic energy, and something for the potential energy, so when these are added in, γ gets still smaller. It is ridiculous. It is wrong.

The first great paper on the dynamical theory of gases was by Maxwell in 1859. On the basis of ideas we have been discussing, he was able accurately to explain a great many known relations, such as Boyle's law, the diffusion theory, the viscosity of gases, and things we shall talk about in the next chapter. He listed all these great successes in a final summary, and at the end he said, "Finally, by

establishing a necessary relation between the motions of translation and rotation (he is talking about the $\frac{1}{2}kT$ theorem) of all particles not spherical, we proved that a system of such particles could not possibly satisfy the known relation between the two specific heats." He is referring to γ (which we shall see later is related to two ways of measuring specific heat), and he says we know we cannot get the right answer.

Ten years later, in a lecture, he said, "I have now put before you what I consider to be the greatest difficulty yet encountered by the molecular theory." These words represent the first discovery that the laws of classical physics were wrong. This was the first indication that there was something fundamentally impossible, because a rigorously proved theorem did not agree with experiment. About 1890, Jeans was to talk about this puzzle again. One often hears it said that physicists at the latter part of the nineteenth century thought they knew all the significant physical laws and that all they had to do was to calculate more decimal places. Someone may have said that once, and others copied it. But a thorough reading of the literature of the time shows they were all worrying about something. Jeans said about this puzzle that it is a very mysterious phenomenon, and it seems as though as the temperature falls, certain kinds of motions "freeze out."

If we could assume that the vibrational motion, say, did not exist at low temperature and did exist at high temperature, then we could imagine that a gas might exist at a temperature sufficiently low that vibrational motion does not occur, so $\gamma = 1.40$, or a higher temperature at which it begins to come in, so γ falls. The same might be argued for the rotation. If we can eliminate the rotation, say it "freezes out" at sufficiently low temperature, then we can understand the fact that the γ of hydrogen approaches 1.66 as we go down in temperature. How can we understand such a phenomenon? Of course that these motions "freeze out" cannot be understood by classical mechanics. It was only understood when quantum mechanics was discovered.

Without proof, we may state the results for statistical mechanics of the quantum-mechanical theory. We recall that according to quantum mechanics, a system which is bound by a potential, for the vibrations, for example, will have a discrete set of energy levels, i.e., states of different energy. Now the question is: how is statistical mechanics to be modified according to quantum-mechanical theory? It turns out, interestingly enough, that although most problems are more difficult in quantum mechanics than in classical mechanics, problems in statistical mechanics are much easier in quantum theory! The simple result we have in classical mechanics, that $n = n_0 e^{-\text{energy}/kT}$, becomes the following very important theorem: If the energies of the set of molecular states are called, say, $E_0, E_1, E_2, \dots, E_i, \dots$, then in thermal equilibrium the probability of finding a molecule in the particular state of having energy E_i is proportional to $e^{-E_i/kT}$. That gives the probability of being in various states. In other words, the relative chance, the probability, of being in state E_1 relative to the chance of being in state E_0 , is

$$\frac{P_1}{P_0} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}}, \quad (40.10)$$

which, of course, is the same as

$$n_1 = n_0 e^{-(E_1 - E_0)/kT}, \quad (40.11)$$

since $P_1 = n_1/N$ and $P_0 = n_0/N$. So it is less likely to be in a higher energy state than in a lower one. The ratio of the number of atoms in the upper state to the number in the lower state is e raised to the power (minus the energy difference, over kT)—a very simple proposition.

Now it turns out that for a harmonic oscillator the energy levels are evenly spaced. Calling the lowest energy $E_0 = 0$ (it actually is not zero, it is a little different, but it does not matter if we shift all energies by a constant), the first one is then $E_1 = \hbar\omega$, and the second one is $2\hbar\omega$, and the third one is $3\hbar\omega$, and so on.

Now let us see what happens. We suppose we are studying the vibrations of a diatomic molecule, which we approximate as a harmonic oscillator. Let us ask

what is the relative chance of finding a molecule in state E_1 instead of in state E_0 . The answer is that the chance of finding it in state E_1 , relative to that of finding it in state E_0 , goes down as $e^{-\hbar\omega/kT}$. Now suppose that kT is much less than $\hbar\omega$, and we have a low-temperature circumstance. Then the probability of its being in state E_1 is extremely small. Practically all the atoms are in state E_0 . If we change the temperature but still keep it very small, then the chance of its being in state $E_1 = \hbar\omega$ remains infinitesimal—the energy of the oscillator remains nearly zero; it does not change with temperature so long as the temperature is much less than $\hbar\omega$. All oscillators are in the bottom state, and their motion is effectively “frozen”; *there is no contribution of it to the specific heat*. We can judge, then, from Table 40-1, that at 100°C, which is 373 degrees absolute, kT is much less than the vibrational energy in the oxygen or hydrogen molecules, but not so in the iodine molecule. The reason for the difference is that an iodine atom is very heavy, compared with hydrogen, and although the forces may be comparable in iodine and hydrogen, the iodine molecule is so heavy that the natural frequency of vibration is very low compared with the natural frequency of hydrogen. With $\hbar\omega$ higher than kT at room temperature for hydrogen, but lower for iodine, only the latter, iodine, exhibits the classical vibrational energy. As we increase the temperature of a gas, starting from a very low value of T , with the molecules almost all in their lowest state, they gradually begin to have an appreciable probability to be in the second state, and then in the next state, and so on. When the probability is appreciable for many states, the behavior of the gas approaches that given by classical physics, because the quantized states become nearly indistinguishable from a continuum of energies, and the system can have almost any energy. Thus, as the temperature rises, we should again get the results of classical physics, as indeed seems to be the case in Fig. 40-6. It is possible to show in the same way that the rotational states of atoms are also quantized, but the states are so much closer together that in ordinary circumstances kT is bigger than the spacing. Then many levels are excited, and the rotational kinetic energy in the system participates in the classical way. The one example where this is not quite true at room temperature is for hydrogen.

This is the first time that we have really deduced, by comparison with experiment, that there was something wrong with classical physics, and we have looked for a resolution of the difficulty in quantum mechanics in much the same way as it was done originally. It took 30 or 40 years before the next difficulty was discovered, and that had to do again with statistical mechanics, but this time the mechanics of a photon gas. That problem was solved by Planck, in the early years of this century.

The Brownian Movement

41-1 Equipartition of energy

The Brownian movement was discovered in 1827 by Robert Brown, a botanist. While he was studying microscopic life, he noticed little particles of plant pollens jiggling around in the liquid he was looking at in the microscope, and he was wise enough to realize that these were not living, but were just little pieces of dirt moving around in the water. In fact he helped to demonstrate that this had nothing to do with life by getting from the ground an old piece of quartz in which there was some water trapped. It must have been trapped for millions and millions of years, but inside he could see the same motion. What one sees is that very tiny particles are jiggling all the time.

This was later proved to be one of the effects of *molecular motion*, and we can understand it qualitatively by thinking of a great push ball on a playing field, seen from a great distance, with a lot of people underneath, all pushing the ball in various directions. We cannot see the people because we imagine that we are too far away, but we can see the ball, and we notice that it moves around rather irregularly. We also know, from the theorems that we have discussed in previous chapters, that the mean kinetic energy of a small particle suspended in a liquid or a gas will be $\frac{3}{2}kT$ even though it is very heavy compared with a molecule. If it is very heavy, that means that the speeds are relatively slow, but it turns out, actually, that the speed is not really so slow. In fact, we cannot see the speed of such a particle very easily because although the mean kinetic energy is $\frac{3}{2}kT$, which represents a speed of a millimeter or so per second for an object a micron or two in diameter, this is very hard to see even in a microscope, because the particle continuously reverses its direction and does not get anywhere. How far it does get we will discuss at the end of the present chapter. This problem was first solved by Einstein at the beginning of the present century.

Incidentally, when we say that the mean kinetic energy of this particle is $\frac{3}{2}kT$, we claim to have derived this result from the kinetic theory, that is, from Newton's laws. We shall find that we can derive all kinds of things—marvelous things—from the kinetic theory, and it is most interesting that we can apparently get so much from so little. Of course we do not mean that Newton's laws are "little"—they are enough to do it, really—what we mean is that we did not do very much. How do we get so much out? The answer is that we have been perpetually making a certain important assumption, which is that if a given system is in thermal equilibrium at some temperature, it will also be in thermal equilibrium with *anything else* at the same temperature. For instance, if we wanted to see how a particle would move if it was really colliding with water, we could imagine that there was a gas present, composed of another kind of particle, little fine pellets that (we suppose) do not interact with water, but only hit the particle with "hard" collisions. Suppose the particle has a prong sticking out of it; all our pellets have to do is hit the prong. We know all about this imaginary gas of pellets at temperature T —it is an ideal gas. Water is complicated, but an ideal gas is simple. Now, *our particle has to be in equilibrium with the gas of pellets*. Therefore, the mean motion of the particle must be what we get for gaseous collisions, because if it were not moving at the right speed relative to the water but, say, was moving faster, that would mean that the pellets would pick up energy from it and get hotter than the water. But we had started them at the same temperature, and we assume that if a thing is once in equilibrium, it stays in equilibrium—parts of it do not get hotter and other parts colder, spontaneously.

41-1 Equipartition of energy

41-2 Thermal equilibrium of radiation

41-3 Equipartition and the quantum oscillator

41-4 The random walk

This proposition is true and can be proved from the laws of mechanics, but the proof is very complicated and can be established only by using advanced mechanics. It is much easier to prove in quantum mechanics than it is in classical mechanics. It was proved first by Boltzmann, but for now we simply take it to be true, and then we can argue that our particle has to have $\frac{3}{2}kT$ of energy if it is hit with artificial pellets, so it also must have $\frac{3}{2}kT$ when it is being hit with water at the same temperature and we take away the pellets; so it is $\frac{3}{2}kT$. It is a strange line of argument, but perfectly valid.

In addition to the motion of colloidal particles for which the Brownian movement was first discovered, there are a number of other phenomena, both in the laboratory and in other situations, where one can see Brownian movement. If we are trying to build the most delicate possible equipment, say a very small mirror on a thin quartz fiber for a very sensitive ballistic galvanometer (Fig. 41-1), the mirror does not stay put, but jiggles all the time—all the time—so that when we shine a light on it and look at the position of the spot, we do not have a perfect instrument because the mirror is always jiggling. Why? Because the average kinetic energy of rotation of this mirror has to be, on the average, $\frac{1}{2}kT$.

What is the mean-square angle over which the mirror will wobble? Suppose we find the natural vibration period of the mirror by tapping on one side and seeing how long it takes to oscillate back and forth, and we also know the moment of inertia, I . We know the formula for the kinetic energy of rotation—it is given by Eq. (19.8): $T = \frac{1}{2}I\omega^2$. That is the kinetic energy, and the potential energy that goes with it will be proportional to the square of the angle—it is $V = \frac{1}{2}I\omega_0^2\theta^2$. But, if we know the period t_0 and calculate from that the natural frequency $\omega_0 = 2\pi/t_0$, then the potential energy is $V = \frac{1}{2}I\omega_0^2\theta^2$. Now we know that the average kinetic energy is $\frac{1}{2}kT$, but since it is a harmonic oscillator the average potential energy is also $\frac{1}{2}kT$. Thus

$$\frac{1}{2}I\omega_0^2\langle\theta^2\rangle = \frac{1}{2}kT,$$

or

$$\langle\theta^2\rangle = kT/I\omega_0^2. \quad (41.1)$$

In this way we can calculate the oscillations of a galvanometer mirror, and thereby find what the limitations of our instrument will be. If we want to have smaller oscillations, we have to cool the mirror. An interesting question is, *where* to cool it. This depends upon where it is getting its “kicks” from. If it is through the fiber, we cool it at the top—if the mirror is surrounded by a gas and is getting hit mostly by collisions in the gas, it is better to cool the gas. As a matter of fact, if we know where the *damping* of the oscillations comes from, it turns out that that is always the *source* of the fluctuations also, a point which we will come back to.

The same thing works, amazingly enough, in *electrical circuits*. Suppose that we are building a very sensitive, accurate amplifier for a definite frequency and have a resonant circuit (Fig. 41-2) in the input so as to make it very sensitive to this certain frequency, like a radio receiver, but a really good one. Suppose we wish to go down to the very lowest limit of things, so we take the voltage, say off the inductance, and send it into the rest of the amplifier. Of course, in any circuit like this, there is a certain amount of loss. It is not a perfect resonant circuit, but it is a very good one and there is a little resistance, say (we put the resistor in so we can see it, but it is supposed to be small). Now we would like to find out: How much does the voltage across the inductance fluctuate? *Answer*: We know that $\frac{1}{2}LI^2$ is the “kinetic energy”—the energy associated with a coil in a resonant circuit (Chapter 25). Therefore the mean value of $\frac{1}{2}LI^2$ is equal to $\frac{1}{2}kT$ —that tells us what the rms current is and we can find out what the rms voltage is from the rms current. For if we want the voltage across the inductance the formula is $\hat{V}_L = i\omega L\hat{I}$, and the mean absolute square voltage on the inductance is $\langle V_L^2 \rangle = L^2\omega_0^2\langle I^2 \rangle$, and putting in $\frac{1}{2}L\langle I^2 \rangle = \frac{1}{2}kT$, we obtain

$$\langle V_L^2 \rangle = L\omega_0^2kT. \quad (41.2)$$

So now we can design circuits and tell when we are going to get what is called *Johnson noise*, the noise associated with thermal fluctuations!

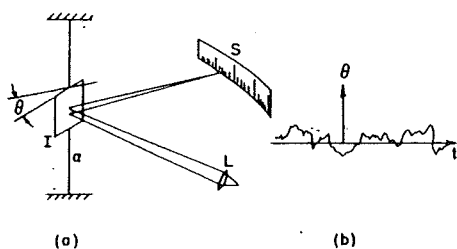


Fig. 41-1. (a) A sensitive light-beam galvanometer. Light from a source L is reflected from a small mirror onto a scale. (b) A schematic record of the reading of the scale as a function of the time.

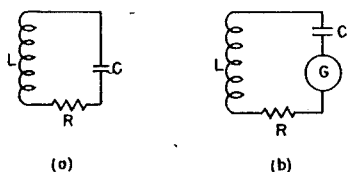


Fig. 41-2. A high-Q resonant circuit. (a) Actual circuit, at temperature T . (b) Artificial circuit, with an ideal (noiseless) resistance and a “noise generator” G .

Where do the fluctuations come from this time? They come again from the resistor—they come from the fact that the electrons in the resistor are jiggling around because they are in thermal equilibrium with the matter in the resistor, and they make fluctuations in the density of electrons. They thus make tiny electric fields which drive the resonant circuit.

Electrical engineers represent the answer in another way. Physically, the resistor is effectively the source of noise. However, we may replace the real circuit having an honest, true physical resistor which is making noise, by an artificial circuit which contains a little generator that is going to *represent* the noise, and now the resistor is otherwise ideal—no noise comes from it. All the noise is in the artificial generator. And so if we knew the characteristics of the noise generated by a resistor, if we had the formula for that, then we could calculate what the circuit is going to do in response to that noise. So, we need a formula for the noise fluctuations. Now the noise that is generated by the resistor is at all frequencies, since the resistor by itself is not resonant. Of course the resonant circuit only “listens” to the part that is near the right frequency, but the resistor has many different frequencies in it. We may describe how strong the generator is, as follows: The mean power that the resistor would absorb if it were connected directly across the noise generator would be $\langle E^2 \rangle / R$, if E were the voltage from the generator. But we would like to know in more detail how much power there is at every frequency. There is very little power in any one frequency; it is a distribution. Let $P(\omega) d\omega$ be the power that the generator would deliver in the frequency range $d\omega$ into the very same resistor. Then we can prove (we shall prove it for another case, but the mathematics is exactly the same) that the power comes out

$$P(\omega) d\omega = (2/\pi)kT d\omega, \quad (41.3)$$

and is *independent of the resistance* when put this way.

