CHAPTER 5

Gases: comparison with experiment

5.1 Introduction

In Chapter 4 we described the theory of a hypothetical *ideal gas*. The extent to which this endeavour has been worthwhile will become apparent as we compare the actual behaviour of real gases with the predictions of the theory. In the sections which follow we will familiarise ourselves with the experimental behaviour of real gases, and then develop ideal gas theory to compare its predictions with the experimental results. By juxtaposing predictions and experimental results we will see both the successes and the failures of ideal gas theory, and see how the theory can be developed to model the properties of real gases more closely.

§5.2 **Density:** As we saw in Example 4.1, ideal gas theory makes astonishingly accurate predictions.

§5.3 **Heat capacity:** If you had been studying physics at the start of the twentieth century rather than at the start of the twenty-first, you would have regarded the data on the heat capacity of gases as utterly mystifying. The explanation requires an understanding of the detailed structure and dynamics of the individual molecules that constitute the gas.

§5.4 **Expansions:** Gases can be compressed much more easily than liquids or solids which leads to interesting connections between their mechanical and thermal properties.

§5.5 **Thermal conductivity:** The key process in the transport of thermal energy through gases is collisions between gas molecules. In this section we will see that the 'hard sphere' model of molecular collisions we introduced in §4.3.4 needs to be significantly modified to explain the experimental data.

§5.6 **Speed of sound:** When we examine the data we will find that to explain the results we will again need to consider the detailed structure of the molecules of the gas. In particular we will find a connection with the heat capacity of gases that I still find surprising.

§5.7 **Electrical properties:** The insulating properties of gases are well known, but when subject to high electric fields gases break down and conduct electricity. At low electric fields, we will find that the properties of the gas again depend on the detailed distribution of electric charge within the molecules of the gas.

§5.8 **Optical properties:** The main optical property of gases is that they are almost completely transparent. It turns out that this property arises from an interesting relationship between the electronic properties of molecules and the process of evolutionary biology! When examining the data we will find interesting links to the electrical properties of gases, and to the detailed structure of the gas molecules.

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In addition to copies of the figures and tables, you will find animations of several of the important equations in this chapter and a computer program which realistically simulates the dynamics of simple molecules in gases, liquids and solids.

5.2 Density

5.2.1. Data on the density of gases

The most striking property of gases is their ability to expand to fill any container. In other words, a fixed number of gas molecules has no fixed volume and hence no fixed density. However, we can reasonably discuss the density of gases so long as we specify the conditions under which the density is determined. Table 5.1 contains data on the density of gases at a temperature of 0 °C (273.15 K) and a pressure 101325 Pa, conditions referred to as *standard temperature and pressure* (STP). Notice that this pressure is usually fairly close (but rarely equal to) the average atmospheric pressure close to sea level on Earth.

Notice that the densities in Table 5.1 are generally of the order of 1 kg m^{-3}. This is much lower than the densities of any solid or liquid substance, which generally have densities of the order of 1000 kg m^{-3} or higher.

Air

Air is a mixture of several gases whose relative abundances vary slightly from place to place. The main relatively constant components of the mixture are given in Table 5.2. The variability of both the composition and the density of air derives mainly from variations in water content. The density of *dry air* (i.e. with zero water content) and containing no carbon dioxide is 1.293 kg m^{-3} at STP. The density of 'normal' air is very sensitive to temperature and pressure. At 20 °C the value is typically 1.200 kg m^{-3}, and falls by roughly 0.004 kg °C^{-1} and increases by $\approx$ 0.012 kg kPa^{-1}. At 20 °C, the density fluctuations due to water content only exceptionally exceed $\pm$ 0.003 kg m^{-3}.

The density data show no apparent structure until we consider not the *mass density* (measured in kg m^{-3}), but the *molar density* (measured in mol m^{-3}). Table 5.3 shows the molar density and its inverse, the molar volume for each of the gases from Table 5.1 (see Example 5.1). The results in Table 5.3 indicate strongly that at STP, *every gas* has the same density of approximately 44.61 mol m^{-3}. We can also restate this in terms of

Table 5.1 The density of various gases at STP in units of kg m^{-3}. The lines in the table separate gases of monatomic, diatomic and polyatomic molecules.

Gas	A (u)	Density (kg m^{-3})
Helium, He	4.0030	0.1786
Neon, Ne	20.180	0.9003
Argon, Ar	39.948	1.782
Krypton, Kr	83.800	3.739
Xenon, Xe	131.29	5.858
Hydrogen, H$_2$	2.0160	0.08995
Nitrogen, N$_2$	28.014	1.250
Oxygen, O$_2$	31.998	1.428
Chlorine, Cl$_2$	70.906	3.164
Methane, CH$_4$	16.043	0.7158
Ethane, C$_2$H$_6$	30.070	1.342
Propane, C$_3$H$_8$	44.097	1.968

Table 5.2 The major components of *dry* atmospheric air. Typically water vapour is also present at a level of roughly 0.5%.

Gas	Molecular mass	% by volume
Nitrogen, N$_2$	28.01	78.09
Oxygen, O$_2$	32.00	20.95
Argon, Ar	39.95	0.93
Carbon dioxide, CO$_2$	44.00	0.03

Table 5.3 The molar volume of various gases at STP in units of 10^{-3} m^3. The lines in the table separate gases of monatomic, diatomic and polyatomic molecules.

Gas	Molar density (m^{-3})	Mass of 1 mol ($\times$ 10^{-3} kg)	Molar volume ($\times$ 10^{-3} m^3)
Helium, He	44.6158	4.0030	22.4136
Neon, Ne	44.6152	20.180	22.4139
Argon, Ar	44.6162	39.948	22.4134
Krypton, Kr	44.6168	83.800	22.4131
Xenon, Xe	44.6174	131.29	22.4128
Hydrogen, H$_2$	44.6160	2.0160	22.4135
Nitrogen, N$_2$	44.6168	28.014	22.4131
Oxygen, O$_2$	44.6162	31.998	22.4134
Chlorine, Cl$_2$	44.6172	70.906	22.4129
Methane, CH$_4$	44.6170	16.043	22.4130
Ethane, C$_2$H$_6$	44.6178	30.070	22.4126
Propane, C$_3$H$_8$	44.6182	44.097	22.4124

Example 5.1

One mole of helium gas (i.e. the Avogadro number 6.022×10^{23} of helium atoms), is held in a container at standard temperature and pressure. As illustrated below, the container is free to expand or contract, allowing the gas to assume its equilibrium volume for STP.

What is the equilibrium molar volume V_m?
First we note that 1 mole of helium gas has a mass of number 4.003×10^{-3} kg. From Table 5.1 the density of helium gas at STP is 0.1786 kg m^{-3}. From the expression *density = mass/volume* we can find the equilibrium volume:

$$V_{\mathrm{m}} = \frac{\text{mass}}{\text{density}} = \frac{4.003 \times 10^{-3}}{0.1786}$$

$$= 22.413 \times 10^{-3} \ \mathrm{m}^3$$

i.e. approximately 22.4 litres.

the molar volume i.e. the Avogadro number of molecules of any gas occupies a volume of roughly $22.41 \times 10^{-3} \ \mathrm{m}^3$ at STP. Let me stress again that this result appears to be completely independent of the mass or complexity of the molecules of the gas.

So the questions raised by our preliminary examination of the experimental data on the density of real gases are:

- Why is the molar density of any of the gases in Table 5.3 approximately 44.61 mol m^{-3}, independent of the substance of which the gas is composed?
- Why are the densities of all gases at STP low when compared with those of solids (Tables 7.1 and 7.2) and liquids (Tables 9.1 and 9.2)?

5.2.2 Understanding the density data

We can answer the first question raised in §5.2.1. by rearranging the perfect gas equation:

$$PV = zRT \qquad \text{(4.29 and 5.1)}$$

into an expression for the molar density. We write this as:

$$\frac{z}{V} = \frac{P}{RT} \qquad (5.2)$$

Putting $P = 101325$ Pa and $T = 273.15$ K we have:

$$\text{molar density} = \frac{101325}{8.314 \times 273.15} \qquad (5.3)$$

$$= 44.6175 \ \mathrm{mol \ m}^{-3}$$

Consulting Table 5.3 reveals that the prediction of Equation 5.3 is strikingly accurate. It is clear that the perfect gas equation realistically describes at least some properties of real gases.

Consider now the second question raised in §5.2.1, the relatively low value of the densities as compared with those of solids and liquids. We can see that this is a natural feature of the model illustrated in Figure 4.1. In this model, we see that compared with the size of the molecules, a gas has large spaces between the molecules. Comparing this picture with the simple pictures of solids (Figure 6.1) and liquids (Figure 8.1) shows that a given number of molecules occupies a much larger volume in the gaseous state than in either of the 'condensed' states of matter.

5.2.3 Data on the thermal expansivity of gases

Gases, like most things, expand when heated. At least, they expand if they are free to do so. If they are constrained to stay at a constant volume, then the pressure they exert on their container increases. So, as with our discussion of density, we need to specify clearly the conditions under which the heating takes place.

Heating at constant pressure

The change in volume ΔV of a gas held at constant pressure in an initial volume V_o due to a temperature change ΔT can be expressed as:

$$\Delta V = V_{o}\beta_{V}\Delta T \qquad (5.4)$$

i.e. the volume change is proportional to the initial volume and the magnitude of the temperature

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Figure 5.1: Heating a gas at constant pressure. Notice the increase in volume and reduction in density.
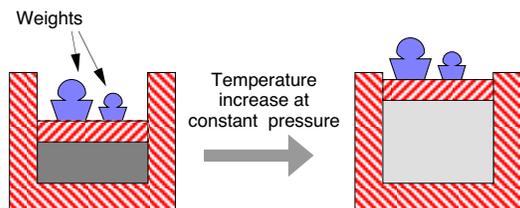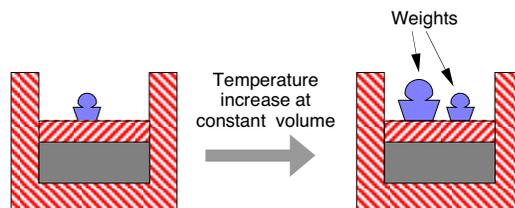

Figure 5.2: Heating a gas at constant volume. Notice the pressure (indicated by the weights) has increased.

change, with constant of proportionally β_V. So the volume of the gas is given by:

$$
\begin{aligned}
V &= V_o + \Delta V \\
&= V_o + V_o \beta_V \Delta T \\
&= V_o (1 + \beta_V \Delta T)
\end{aligned}
\tag{5.5}
$$

The constant β_V is a called the *volume coefficient of thermal expansivity*. If β_V is small then the change in the volume of a gas due to a given temperature change will be small; if β_V is large then the change in the volume will be large.

Heating at constant volume

Similarly, when the temperature changes the increase in pressure of a gas held at *constant volume* (Figure 5.2) at initial pressure P_o is:

$$
\Delta P = P_o \beta_P \Delta T
\tag{5.6}
$$

and so the pressure P of the gas is given by:

$$
\begin{aligned}
P &= P_o + \Delta P \\
&= P_o + P_o \beta_P \Delta T \\
&= P_o (1 + \beta_P \Delta T)
\end{aligned}
\tag{5.7}
$$

where ΔT is the change in temperature.

The constant β_P is called the *pressure coefficient of thermal* expansivity. If β_P is small then the change in the pressure of a gas due to a temperature change will be small; if β_P is large then the change in the pressure of a gas due to a temperature change will be large.

Table 5.4 shows experimental values for β_P and β_V valid at around room temperature and pressure. We see that both the volume and the pressure coefficients of expansivity of all the gases shown

is close to $3.66 \times 10^{-3}\,°C^{-1}$, independent of the type of molecules of which the gas is composed. Looking ahead to Tables 7.7 and 9.5 shows that the figure for β_V is between 10 and 100 times larger than the thermal expansivity of many liquids, and around 100 to 1000 times larger than the expansivity of most solids.

So the main questions raised by our preliminary examination of the experimental data on the expansivity of gases are:

- Why are the expansivities of the five gases in Table 5.4 so similar, independent of the substance of which the gas is composed?
- Why are the expansivities of gases much greater than those shown by solids (Table 7.7) and liquids (Table 9.5)?

5.2.4 Understanding the data on the thermal expansivity of gases

We can answer the questions raised by our examination of the experimental data by rearranging the ideal gas equation $PV = zRT$. Equation 5.5 expressed the expansivity of a gas, β_V in a form

Table 5.4 Values of the expansivity coefficients β_V and β_P for gases whose initial pressure is 0.1333 MPa at 0 °C, valid in the temperature range 0 °C to 100 °C. The pressure 0.1333 MPa is a little greater than normal atmospheric pressure.

Gas	β_V (°C^{-1})	β_P (°C^{-1})
Helium, He	3.6580×10^{-3}	3.6605×10^{-3}
Hydrogen, H_2	3.6588×10^{-3}	3.6620×10^{-3}
Nitrogen, N_2	3.6735×10^{-3}	3.6744×10^{-3}
Air	3.6728×10^{-3}	3.6744×10^{-3}
Neon, Ne	3.6600×10^{-3}	3.6617×10^{-3}

which predicts the volume of a given amount of gas in terms of its volume V_o at some initial temperature T_o:

$$V = V_o(1 + \beta_V \Delta T) \qquad (5.8 \ \& \ 5.5^*)$$

where $\Delta T = T - T_o$. In order to compare the ideal gas theory with experiment, we need to rearrange $PV = zRT$ into a form similar to Equation 5.8. At temperatures T and T_o the volumes of z moles of gas are V and V_o respectively, i.e.

$$V = \frac{zR}{P_o}T \qquad V_o = \frac{zR}{P_o}T_o \qquad (5.9)$$

Notice that both measurements are made at the same pressure P_o. Taking the ratio of the two volumes and simplifying,

$$\frac{V}{V_o} = \frac{(zR/P_o)\, T}{(zR/P_o)\, T_o}$$
$$= \frac{T}{T_o} \qquad (5.10)$$

we predict that:

$$V = \left[\frac{V_o}{T_o}\right]T \qquad (5.11)$$

i.e. the volume is directly proportional to the absolute temperature T, with a constant of proportionality V_o/T_o. Equating the right-hand sides of Equations 5.5 and 5.11, we have:

$$V_o(1 + \beta_V \Delta T) = \left[\frac{V_o}{T_o}\right]T \qquad (5.12)$$

Rearranging this to find β_V :

$$1 + \beta_V(T - T_o) = T/T_o$$
$$\beta_V = \frac{T/T_o - 1}{T - T_o}$$
$$= \frac{(T - T_o)/T_o}{T - T_o} \qquad (5.13)$$
$$= \frac{1}{T_o}$$

Table 5.5 Comparison of experimental and theoretical expansivities of gases. See also Table 5.4.

Gas	β_V (°C^{-1})	% difference between theory and experiment
Helium, He	3.6580×10^{-3}	-0.082
Hydrogen, H$_2$	3.6588×10^{-3}	-0.060
Nitrogen, N$_2$	3.6735×10^{-3}	$+0.342$
Air	3.6728×10^{-3}	$+0.323$
Neon, Ne	3.6600×10^{-3}	-0.027

So the ideal gas theory predicts that all gases should have the same value of β_V. In Table 5.4 $T_o = 0\ °C = 273.15$ K so we expect that:

$$\beta_V = \frac{1}{273.15} = 3.6610 \times 10^{-3}\ °C^{-1} \qquad (5.14)$$

which compares well with the experimental values of Table 5.4 in Table 5.5.

As Table 5.5 shows, the prediction of Equation 5.14 is accurate at the level better than 0.1% for some gases, and better than 1% even for complex mixed gases such as air: impressively close for such a simple theory.

An alternative interpretation of this data is to see it as way of defining the reference temperature T_o in Equation 5.13. Given the 'size' of a degree of temperature, the expansivity of gases provides a way of determining the absolute value of any chosen reference temperature.

Whichever interpretation of the results is chosen, the consistency of the results between different gases is striking. This indicates the general validity of the assumptions of the ideal gas theory outlined in the statements below Equation 4.1:

- The molecules behave as perfect point masses, i.e. they have zero volume
- The molecules do not interact with each other except momentarily as they collide
- The collisions between molecules are elastic

Now we need to consider the second question raised by examining the data: why the expansivities of gases are considerably greater than those of solids and liquids. To understand this, notice the significance of the second assumption above, that the molecules interact with each other only instantaneously as they collide. This amounts to

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Example 5.2

Some helium gas is held in a fixed volume of 1 litre at a pressure of 0.1333 MPa and a temperature T_o = 0 °C. The pressure at another temperature T_1 is measured to be 0.1821 Mpa. What is T_1?

We can solve this problem using Equation 5.9, with the following values:

$$V_o = 1 \text{ litre} = 1 \times 10^{-3} \text{ m}^{-3}$$

$$T_o = 0 \text{ °C}$$

$$P_o = 0.1333 \text{ MPa} = 0.1333 \times 10^6 \text{ Pa}$$

$$P_1 = 0.1821 \text{ MPa} = 0.1821 \times 10^6 \text{ Pa}$$

$$\beta = 3.6605 \times 10^{-3} \text{ °C}^{-1} \text{ or K}^{-1}$$

$$\Delta T = ?$$

We rearrange Equation 5.9:

$$P = P_o(1 + \beta \Delta T)$$

to solve for T_1:

$$\Delta T = T_1 - T_o = \frac{1}{\beta}\left[\frac{P}{P_o} - 1\right]$$

$$T_1 = T_o + \frac{1}{3.6605 \times 10^{-3}}\left[\frac{0.1821}{0.1333} - 1\right]$$

$$= 0 \text{ °C} + 273.186[0.3661]$$

$$= 0 \text{ °C} + 100.01 \text{ °C}$$

$$= 100.01 \text{ °C}$$

This calculation illustrates the mode of operation of *constant volume gas thermometers*. These devices allow the determination of temperature from first principles.

Example 5.3

Some nitrogen gas is held at a fixed pressure of 0.1333 MPa and an initial volume of 1 litre at a temperature of 0 °C. At what temperature (according to Equation 5.7) would the volume reach zero?

We use Equation 5.7 with the following values:

$$V_o = 1 \text{ litre} = 1 \times 10^{-3} \text{ m}^{-3}$$

$$V_1 = 0$$

$$P_o = 0.1333 \text{ MPa}$$

$$\alpha = 3.6735 \times 10^{-3} \text{ °C}^{-1} \text{ or K}^{-1}$$

$$\Delta T = ?$$

We rearrange $V = V_o(1 + \alpha \Delta T)$ to solve for T_1:

$$V = V_o(1 + \alpha \Delta T) = 0$$

$$\Delta T = \frac{-1}{\alpha}$$

$$T_1 = T_o + \frac{-1}{3.6735 \times 10^{-3}}$$

$$= 0 \text{ °C} - 272.2 \text{ °C}$$

$$= 0.93 \text{ K}$$

According to this analysis, the volume should reach zero at a temperature of -272.2 °C (≈ 0.95 K). If this experiment were performed it would be found that before this temperature was reached the nitrogen would first have liquefied at about -196°C (77K) and later solidified at about ≈ 63K. In these states its expansion and contraction would be much smaller than in the gas phase.

assuming that the internal energy of a gas is held entirely by the kinetic energy of its molecules, neglecting the effect of the potential energy of interaction between molecules. The extent of the agreement between ideal gas theory and experiment arises because this neglect of the potential energy is valid.

However, the average kinetic energy of a molecule is proportional to the temperature. Remember that $KE_{\text{average}} = 1.5k_BT$ (Eq. 4.23) so as the temperature is reduced, the average kinetic energy becomes smaller and smaller. At lower temperatures the average kinetic energy will become comparable with the potential energy of interaction between the molecules. As the temperature is lowered, the molecules will tend to appear 'sticky' and form short-lived clusters. Eventually, at low enough

temperatures, they coalesce into a liquid or solid. What constitutes a 'low enough' temperature depends on the strength of interactions between gas molecules.

From the fact that solids and liquids form at low temperatures we can see that the interactions between molecules generally act to reduce the separation between molecules, and hence reduce the volume of the gas. The high expansivity of gases as compared with solids and liquids can be now be understood: it is the high temperature limit of the expansivity of all materials. When the temperature of the gas is high enough to allow us to neglect the molecular interactions that tend to restrict the volume of the gas, the expansivity of real gases approaches that predicted for an ideal gas.

5.3 Heat capacity

The heat capacity of a gas is defined as the limiting value of the ratio of the heat energy input ΔQ to the resulting temperature rise ΔT:

$$C = \frac{\Delta Q}{\Delta T}\bigg|_{\lim \Delta T \to 0} = \frac{dQ}{dT} \ \text{J K}^{-1} \qquad (5.15)$$

The value obtained for this ratio depends on the conditions under which the heat input is made. The two principal measurement conditions are those of:

- *constant pressure*, in which the heat input can cause an expansion of the gas, and
- *constant volume*, in which the heat input can cause a rise in pressure of the gas.

The heat capacity associated with measurements at constant pressure is referred to as C_P and that associated with measurements at constant volume is referred to as C_V. The heat capacity of a substance is usually quoted either for a given *mass* of material, the *specific heat capacity* (e.g. J K^{-1} kg^{-1}), or per mole, the *molar heat capacity* (J K^{-1} mol^{-1}).

Instead of examining data on C_P and C_V independently, we will look first at data for C_P in §5.3.1 and then at data for γ, the ratio of C_P to C_V, in §5.3.2.

5.3.1 Data on the heat capacity of gases at constant pressure

Tables 5.6 and 5.7 show the molar heat capacity C_P at several temperatures for a variety of monatomic and diatomic gases respectively. Figures 5.3 and 5.4 show graphs of the data from Tables 5.6 and 5.7.

The most striking feature of the data is the constancy of the value 20.8 J K^{-1} mol^{-1} for all the monatomic gases shown, independent of temperature. In contrast, the diatomic gases have a rather larger heat capacity at low temperatures, which then increases still further as the temperature is increased, tending to a maximum of around 37 J K^{-1} mol^{-1}.

Thus for either monatomic or diatomic gases, we can make a 'ball park' estimate of the molar heat

Table 5.6 The molar heat capacities at constant pressure C_P(J K^{-1} mol^{-1}) for the monatomic noble gases. These data are graphed in Figure 5.3.

- The shaded figures correspond to data taken in the liquid or solid phase. For each gas the boiling temperature and melting temperature are separated by less than 5 K.
- The data between the two double lines is from a separate source from the rest of the table. Notice that the extra measurement resolution still shows agreement between the heat capacities of the different gases.

T(K)	He	Ne	Ar	Kr	Xe
50	—	—	24.8	25.1	25.1
100	—	—	20.8	31.6	28.2
150	—	—	20.8	20.8	33.6
200	—	—	20.8	20.8	20.8
298.15	20.786	20.786	20.786	20.786	20.786
400	20.8	20.8	20.8	20.8	20.8
600	20.8	20.8	20.8	20.8	20.8
800	20.8	20.8	20.8	20.8	20.8
1000	20.8	20.8	20.8	20.8	20.8
1500	20.8	20.8	20.8	20.8	20.8
2000	20.8	20.8	20.8	20.8	20.8
2500	20.8	20.8	20.8	20.8	20.8

Table 5.7 The molar heat capacities at constant pressure C_P(J K^{-1} mol^{-1}) for some diatomic gases. These data are graphed in Figure 5.4.

- The shaded figures correspond to data taken in the liquid or solid phase.

T(K)	H$_2$	O$_2$	N$_2$	F$_2$	Cl$_2$	Br$_2$	I$_2$
50	—	46.1	41.5	—	29.2	33.3	35.8
100	—	29.1	29.1	—	42.3	43.6	45.6
150	—	29.1	29.1	—	51.0	49.2	49.6
200	—	29.1	29.1	—	54.2	53.8	51.5
400	29.2	30.1	29.2	33.0	35.3	36.7	80.3
600	29.3	32.1	30.1	35.2	36.6	37.3	37.6
800	29.6	33.7	31.4	36.3	37.2	37.5	37.8
1000	30.2	34.9	32.7	37.0	37.5	37.7	37.9
1500	32.3	36.6	34.9	37.9	38.0	38.0	38.2
2000	34.3	37.8	36.0	38.4	38.3	38.2	38.5
2500	36.0	38.9	36.0	38.8	38.6	38.5	38.8

capacity as 30 ± 10 J K^{-1} mol^{-1} at all temperatures.

The main questions raised by our preliminary examination of the experimental data on C_P are:

- Why are the constant pressure heat capacities of monatomic or diatomic gases usually in the range 30 ± 10 J K^{-1} mol^{-1}?
- Why does $C_P = 20.8$ J K^{-1} mol^{-1} for monatomic gases, with almost no dependence on temperature, or on the type of molecule from which the gas is formed?
- Why do some diatomic gases have a low temperature value of C_P rather greater than the value for monatomic gases, but which increases with increasing temperature?

We will consider these questions in §5.3.3, after we have considered data on the ratio of heat capacities $\gamma = C_P/C_V$.

5.3.2 Data on heat capacity ratio ($\gamma = C_P/C_V$)

The data given in Tables 5.6 and 5.7 refer to the heat capacity at constant pressure C_P, i.e. the gas is allowed to expand as the heat input is made. C_P differs significantly from the heat capacity at constant volume C_V. Experimentally it is found that the ratio of C_P to C_V (known as γ, pronounced 'gamma') varies with the number of atoms in a molecule of the gas. Table 5.8 records values of γ classified by the number of atoms in a molecule of the gas.

Figure 5.5 shows a histogram of all the data from Table 5.8, and indicates which values correspond to which type of molecule. It is clear from the histogram that the data cluster according to the number of atoms in a molecule of the gas. Monatomic and diatomic gases have γ values of around 1.66 and 1.4 respectively, and tri- and poly-atomic gases have widely scattered smaller values, but always greater than one.

Interestingly, it seems that for air at high pressures the values for γ are strongly increased, even beyond the values for a monatomic gas.

Figure 5.3: The heat capacity of monatomic gases C_P versus absolute temperature (Table 5.6). Data for temperatures less than the boiling point are not plotted. Notice that at the resolution of the measurement, the gases have the same heat capacity across a temperature variation of over an order of magnitude.
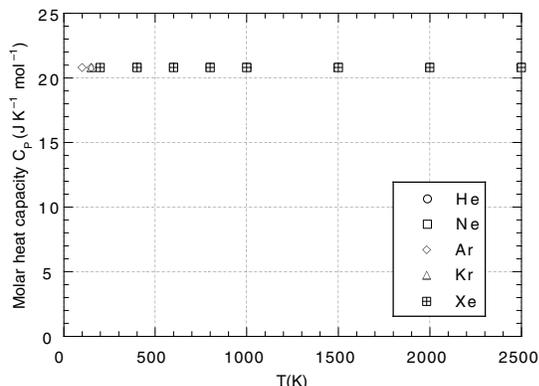

Figure 5.4: The heat capacity of diatomic gases versus absolute temperature (Table 5.7). Data for temperatures below the boiling point are not plotted. Notice that the heat capacities increase with temperature. The lines through the data points are drawn to guide the eye
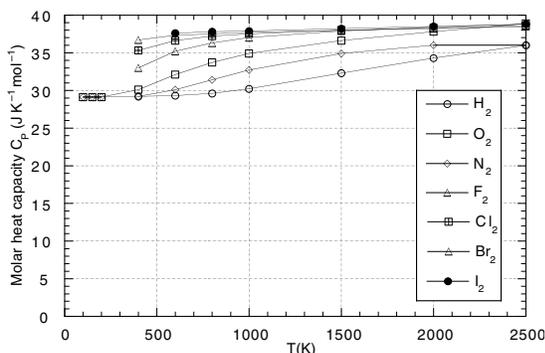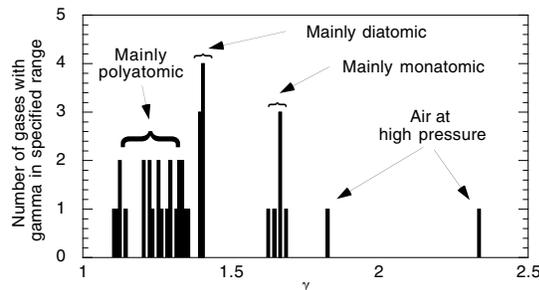

Figure 5.5 Histogram of values of γ in Table 5.8. The column height indicates how common it is to find γ within ± 0.01 of the value specified on the x-axis. Notice how the data are clustered in groups that are identifiable as monatomic, diatomic, polyatomic or high pressure.

Example 5.4

Samples of four gases are heated from room temperature (20 °C or 293K) to 100 °C (373K) in a piston device at a constant pressure of $\approx$ 0.1MPa:

A consists of 1 kg of helium

B consists of 1 kg of xenon

C consists of 1 kg of nitrogen

D consists of 1 kg of unknown *monatomic* gas.

(a) Work out how much heat energy is required to raise samples A, B and C to the required temperature.

(b) Sample D requires 41.65×10^3 joules to raise it to 100 °C. Considering only those gases tabulated in Table 5.6, work out which gas is being heated.

(a) The heating takes place at constant pressure so we use C_P to relate the heat input to the temperature rise.

Sample A: Helium

The heat required to raise one mole of gas from T_1 to T_2 is given by:

$$Q = \int_{T_1}^{T_2} C_P dT$$

Consulting Table 5.6 and Figure 5.3 we see that for helium C_P is constant over the range of heating, so the energy required to heat one mole of gas from T_1 to T_2 is given by:

$$Q = C_P \int_{T_1}^{T_2} dT$$
$$= C_P [T_2 - T_1]$$

and similarly for z moles of gas we have:

$$Q = z C_P [T_2 - T_1]$$

1 kg of helium, molecular mass 4, is $1/(4 \times 10^{-3}) = 250$ moles of helium. Substituting for z, C_P, T_2, and T_1 we have:

$$Q = 250 \times 20.8 [373 - 293]$$
$$= 4.16 \times 10^5 \text{ J}$$

Sample B: Xenon

Similarly to sample A we find $Q = z C_P [T_2 - T_1]$. Now however we have 1 kg of Xe, which has a molecular mass of 131.3 and hence contains only:

$$z = \frac{1}{0.1313} = 7.62 \text{ moles}$$

Hence it takes only

$$Q = 7.62 \times 20.8 [373 - 293]$$
$$= 12.68 \times 10^3 \text{ J}$$

to heat the same *mass* of gas through the same temperature rise! The reason for this somewhat counterintuitive result is related to the fact that we have many fewer molecules in sample B than in sample A.

Sample C: Nitrogen

We proceed exactly as with samples A and B except now there is a possibility that C_P will change over the range of heating because nitrogen gas consists of *diatomic* N_2 molecules. Detailed consultation of Table 5.7 shows that the variation from 200 K to 400 K is less than 1% and so may be assumed constant over our more restricted range.

Now however we have 1 kg of N_2 which has a molecular mass of $2 \times 14 = 28$. Notice that it is the mass of the *molecule* that is important. Hence we have :

$$z = \frac{1}{0.028} = 35.71 \text{ moles}$$

So it takes:

$$Q = 35.71 \times 29.1 [373 - 293]$$
$$= 83.132 \times 10^3 \text{ J}$$

(b)
Sample D: Unknown monatomic gas

Sample D requires 41.65×10^3 J to raise it to 100 °C. We can use the formula we derived for helium (sample A) to work out z, the number of moles of gas present:

$$Q = z C_P [T_2 - T_1]$$

We know C_P because for all monatomic gases $C_P = 20.8$ J K^{-1} mol^{-1} and so we can find out how many moles z are contained in 1 kg of the unknown gas. Thus we can work out its relative molecular mass, and identify the gas by its molecular mass. We find that:

$$z = \frac{Q}{C_P [T_2 - T_1]} = \frac{41.65 \times 10^3}{20.8 [373 - 293]}$$
$$= 25.03 \text{ moles}$$

Thus the relative molecular mass is given by:

$$M = \frac{1}{25.03 \times 10^{-3}} = 39.95$$

This identifies the monatomic gas unambiguously as argon.

So the main questions raised by our preliminary examination of the experimental data for γ are:

- Why is the heat capacity at constant pressure always greater than the heat capacity at constant volume, i.e. $\gamma > 1$?
- Why does the value of γ depend on whether the gas is monatomic, diatomic or polyatomic? In particular we would like to understand why:
    - Monatomic gases have values for γ close to 1.66 ($\pm$ 0.02)
    - Diatomic gases in the table have values for γ close to 1.4 ($\pm$ 0.1), except at high pressure
    - Polyatomic gases have lower values of γ than either monatomic or diatomic gases.
- Why is γ for air at extremely high pressures increased to values above those for monatomic gases?

Example 5.5

What is the *specific* heat capacity of helium gas?

One mole of helium gas has a mass of 4×10^{-3} kg and the value of its molar heat capacity at constant pressure C_P is 20.8 J K^{-1} mol^{-1} (Table 5.6). So it takes 20.8 J to raise the temperature of 4×10^{-3} kg of helium by 1 °C. The number of moles in 1 kg of helium is:

$$\frac{1}{4 \times 10^{-3}} = 250 \text{ moles of helium}$$

The *specific* heat capacity at constant pressure is therefore $250 \times 20.8 = 5200$ J K^{-1} kg^{-1}.

Example 5.6

For helium gas, Table 5.8 gives $\gamma = 1.63$ and Table 5.6 gives $C_P = 20.8$ J K^{-1} mol^{-1} over a wide temperature range. What is C_V for helium?

Since $\gamma = C_P / C_V$ we can work out C_V as:

$$C_V = \frac{C_P}{\gamma} = \frac{20.8}{1.63} = 12.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Table 5.8 The ratio of the principal heat capacities ($\gamma = C_P/C_V$) of some gases. The shaded results correspond to a pressure of 200 atmospheres (20 MPa). The notes below each section of the table summarise the results for that class of gases. There appears to be a trend towards a reduction in γ as the temperature is increased. Where no temperature shown, the temperature of the measurement is not known but is probably either 0 °C or close to 20 °C.

Gas	T(°C)	T(K)	γ	Gas	T(°C)	T(K)	γ
Monatomic gases				**Triatomic gases**			
He	0.0	273.20	1.630	O_3	—	—	1.290
Ar	0.0	273.20	1.667	H_2O	100.0	373.20	1.334
Ne	19.0	292.20	1.642	CO_2	10.0	283.20	1.300
Kr	19.0	292.20	1.689	CO_2	300.0	573.20	1.220
Xe	19.0	292.20	1.666	CO_2	500.0	773.20	1.200
Hg	310.0	583.20	1.666	NH_3	—	—	1.336
All the above results are close to 1.66				N_2O	—	—	1.324
Diatomic gases				H_2S	—	—	1.340
H_2	10.0	283.20	1.407	CS_2	—	—	1.239
N_2	20.0	293.20	1.401	SO_2	20.0	293.20	1.260
O_2	10.0	283.20	1.400	SO_2	500.0	773.20	1.200
CO	1800.0	2073.2	1.297	*All the above results are close to 1.3*			
NO	—	—	1.394	**Polyatomic gases**			
Most of the above results are close to 1.4				CH_4	—	—	1.313
C: Air				C_2H_6	—	—	1.220
Air	-79.3	193.90	1.405	C_3H_8	—	—	1.130
Air	10.0	283.20	1.401	C_2H_2	—	—	1.260
Air	500.0	773.20	1.357	C_2H_4	—	—	1.264
Air	900.0	1173.2	1.320	C_6H_6	20.0	293.20	1.400
Air	0.0	273.20	1.828	C_6H_6	99.7	372.90	1.105
Air	-79.3	193.90	2.333	$CHCl_3$	30.0	303.20	1.110
Most of the above results are close to 1.4 except for				$CHCl_3$	99.8	373.00	1.150
those shaded.				CCl_4	—	—	1.130
				The above results are between 1.1 and 1.4			

Example 5.7

What is the *difference* between the values of C_P and C_V for (a) helium and (b) nitrogen, i.e. how much extra energy is needed to raise 1 mole of gas through 1 kelvin if the process takes place at *constant pressure*, as compared with the same process at *constant volume*?

From Example 5.6 we find C_V as $C_V = C_P / \gamma$. So the difference between C_P and C_V is given by:

$$C_P - C_V = C_P - \frac{C_P}{\gamma} = C_P \left[1 - \frac{1}{\gamma} \right]$$

(a) For helium, using Tables 5.6 and 5.8,

$$C_P = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\gamma = 1.63$$

so $\quad C_P - C_V = 20.8 \left[1 - \frac{1}{1.63} \right] = 8.04 \text{ J K}^{-1} \text{ mol}^{-1}$

(b) For nitrogen, using Tables 5.7 and 5.8,
$C_P = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$ at around room temperature
$\gamma = 1.63$:

so $\quad C_P - C_V = 29.2 \left[1 - \frac{1}{1.401} \right] = 8.36 \text{ J K}^{-1} \text{ mol}^{-1}$

5.3.3 Understanding the data on the heat capacity of gases

In this section we will attempt to understand the questions raised in §5.3.1 and §5.3.2 on C_P and γ respectively. In order to do this we will develop the theory of an ideal gas further than we did in Chapter 4. Our plan will be to derive expressions first for C_V, then for C_P and finally for their ratio γ.

Heat capacity: background theory

As we saw in §2.5.2, the first law of thermodynamics can be stated as:

$$\Delta U = \Delta Q + \Delta W \qquad (2.57^*)$$

where:

ΔQ is the heat supplied *to* a substance
ΔW is the work done *on* a substance
ΔU is the change in the internal energy of the substance.

For our purposes, we will rearrange this equation as an expression for ΔQ:

$$\Delta Q = \Delta U - \Delta W \qquad (5.16)$$

Arranged in this way first law tells us that when heat ΔQ is supplied to a substance, it may either:

(a)   increase the internal energy of the substance ΔQ, or
(b)   cause the substance to do ΔW of work on its environment.

This is a statement of the principle of conservation of energy. Notice that ΔW is defined in Equations 2.57 and 5.16 as *the work done on the gas by its*

environment. Thus if the gas does net work on its environment (for example by expanding and pushing a piston) ΔW will be negative. We will develop our theory of the heat capacity of a gas in the following four stages:

Stage 1: We derive an expression the work done by a gas when it changes its volume.

Stage 2: We derive an expression for the heat capacity of a gas when no work is done by the gas during the heating process. This will be our result for C_V.

Stage 3: We combine the first two steps to derive an expression for the heat capacity of a gas when it does work on its environment during the heating process. This will be our result for C_P.

Stage 4: Finally, we combine the previous two results for C_V and C_P to yield an expression for their ratio γ.

Stage 1: Work done by an expanding gas

First of all recall that in general work is done when *a force moves its point of action*. Thus in order to do work, a gas must change its volume. Figure 5.6 illustrates a hypothetical experiment that will allow us to calculate the work done during a volume change.

If the piston apparatus of Figure 5.6 has an area A and the pressure of the gas is P, then the total force on the piston is $F = PA$. Now suppose the piston moves outward an infinitesimal amount dx. In this case the gas volume has increased by a small amount dV. Notice two things: first, the

Figure 5.6 The input of heat into a gas under conditions of constant pressure. The figure shows gas trapped in a thermally insulated piston device with cross-sectional area A. The piston is free to move so that it will finally stop when the net force on the piston is zero.

Weights   Change in volume $\Delta V = A\,\mathrm{d}x$

dx

Before heat input   After heat input
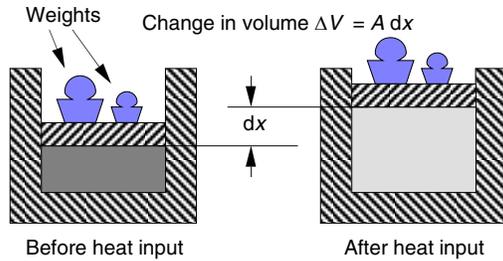
work done *by the environment* on the gas is a negative quantity: this expresses the fact that in an expansion, the gas is doing work on its environment. Second, notice that we can write dW as follows:

$$\mathrm{d}W = -F\mathrm{d}x$$
$$= -PA\mathrm{d}x \qquad (5.17)$$
$$= -P\mathrm{d}V$$

where we noticed that $A\mathrm{d}x$ is an infinitesimal element of volume dV. So the work done *by the environment* on the gas is given by:

$$\mathrm{d}W = -P\mathrm{d}V \qquad (5.18)$$

To obtain the work done *by the environment* on the gas in a finite expansion we must integrate this expression:

$$\Delta W = \int_{V}^{V+\Delta V} -P\mathrm{d}V \qquad (5.19)$$

In general, P will change as the gas expands. However, if we consider the case when heat is added in order to maintain constant pressure during the expansion, then P can slip outside the integral to yield:

$$\Delta W = -P\int_{V}^{V+\Delta V}\mathrm{d}V$$
$$= -P[V]_{V}^{V+\Delta V} \qquad (5.20)$$
$$\Delta W = -P\Delta V$$

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Using the ideal gas equation $PV = zRT$ we may eliminate $P\Delta V$ in favour of $zR\Delta T$, where ΔT is the temperature change required to keep the pressure constant during the expansion. Hence, if z moles of ideal gas expands at constant pressure, the work done *by the environment* on the gas is:

$$\Delta W = -P\Delta V$$
$$= -zR\Delta T \qquad (5.21)$$

Before we move on to stage 2, I would like to remind you that when attempting to solve problems relating to this kind of process, it is important to take care with regard to the sign of ΔW.

Stage 2: Heat capacity at constant volume

If the heat is supplied to a gas at constant volume, then by Equation 5.21 no work is done either by or on the gas. Thus the first law of thermodynamics tells us that:

$$\Delta Q = \Delta U - 0$$
$$\Delta Q = \Delta U \qquad (5.22)$$

Under these conditions the heat energy input goes entirely into increasing the average energy of the molecules, and hence by Equation 4.19, the internal energy, U, of the gas. Recall that for an ideal gas, the internal energy of an ideal gas is just the sum of the kinetic energies of the individual molecules. A molecule of an ideal gas has just three degrees of freedom (§4.2: Complication 3). However we can generalise our calculation to a gas containing real molecules which have other degrees of freedom. If we consider a gas molecule to have p degrees of freedom, each with $0.5k_{\mathrm{B}}T$ of energy, the internal energy of z moles of gas, i.e. zN_{A} molecules will be:

$$U = zN_{\mathrm{A}} \times p \times \tfrac{1}{2}k_{\mathrm{B}}T$$
$$= \tfrac{1}{2}zpN_{\mathrm{A}}k_{\mathrm{B}}T \qquad (5.23)$$

Using $N_{\mathrm{A}}k_{\mathrm{B}} = R$, this simplifies to:

$$U(T) = \tfrac{1}{2}zpRT \qquad (5.24)$$

The internal energy of the gas at $T + \Delta T$ will be given by:

$$U(T + \Delta T) = \tfrac{1}{2}zpR[T + \Delta T] \qquad (5.25)$$

So the change in internal energy ΔU on heating from T to $T + \Delta T$ is:

$$\Delta U = U(T + \Delta T) - U(T)$$
$$= \tfrac{1}{2} zpR[T + \Delta T] - \tfrac{1}{2} zpR[T] \quad (5.26)$$
$$= \tfrac{1}{2} zpR\Delta T$$

By Equation 5.22 this change in internal energy must be supplied by the heat ΔQ, and so we may write:

$$\Delta Q = \tfrac{1}{2} zpR\Delta T \quad (5.27)$$

So the heat capacity at constant volume of z moles of gas is given by:

$$C_V = \frac{\Delta Q}{\Delta T}$$
$$= \frac{\tfrac{1}{2} zpR\Delta T}{\Delta T} \quad (5.28)$$
$$= \tfrac{1}{2} zpR$$

We thus predict that the molar (i.e. $z = 1$) constant-volume heat capacity of a gas will be:

$$C_V = 4.157p \quad \mathrm{J\,K^{-1}\,mol^{-1}} \quad (5.29)$$

in general, and:

$$C_V = 12.471 \quad \mathrm{J\,K^{-1}\,mol^{-1}} \quad (5.30)$$
$$\text{for } p = 3$$

These are simple results. Importantly they indicate that a measurement of C_V for a gas allows us to immediately infer the number of internal degrees of freedom of the molecules of the gas.

Stage 3: Heat capacity at constant pressure

In the previous two stages we developed an expression for the change in internal energy of a gas when it is heated at constant volume:

$$\Delta U = \tfrac{1}{2} pR\Delta T \quad (5.31 \text{ and } 5.26^*)$$

and an expression for the work done *by the environment* on the gas in expanding at constant pressure:

$$\Delta W = -P\Delta V$$
$$= -R\Delta T \quad (5.32 \text{ and } 5.21^*)$$

We can now combine these to arrive at an expression for C_P. Taking note of the sign of ΔW as discussed following Equation 5.16, we may substitute these expressions into the first law of thermodynamics:

$$\Delta Q = \Delta U - \Delta W$$
$$= \tfrac{1}{2} pR\Delta T - [-R\Delta T] \quad (5.33)$$
$$= \left[\tfrac{1}{2} p + 1\right] R\Delta T$$

Remembering that $C_P = \Delta Q/\Delta T$ we find:

$$C_P = \frac{\Delta Q}{\Delta T} = \frac{R\Delta T\left[\tfrac{1}{2} p + 1\right]}{\Delta T} \quad (5.34)$$
$$= R\left[\tfrac{1}{2} p + 1\right]$$

We thus predict that the molar (i.e. $z = 1$) constant-pressure heat capacity of a gas will be:

$$C_P = 8.314 \times \left[\tfrac{1}{2} p + 1\right] \quad \mathrm{J\,K^{-1}\,mol^{-1}} \quad (5.35)$$

in general, and:

$$C_P = 20.785 \quad \mathrm{J\,K^{-1}\,mol^{-1}} \quad (5.36)$$
$$\text{for } p = 3.$$

Stage 4: Gamma (γ)

Finally, we can combine Equation 5.28 for C_V:

$$C_V = \tfrac{1}{2} zpR \quad (5.28^* \text{ and } 5.37)$$

and Equation 5.34 for C_P:

$$C_P = R\left[\tfrac{1}{2} p + 1\right] \quad (5.34^* \text{ and } 5.38)$$

to obtain an expression for γ:

$$\gamma = \frac{C_P}{C_V} = \frac{zR\left[\tfrac{1}{2} p + 1\right]}{\tfrac{1}{2} zpR} = \frac{\left[\tfrac{1}{2} p + 1\right]}{\tfrac{1}{2} p} \quad (5.39)$$

which simplifies to:

$$\gamma = 1 + \frac{2}{p} \quad (5.40)$$

5.3.4 Comparison with experiment

We now have expressions for the heat capacities of a gas at either constant pressure or constant volume, and for their ratio gamma. So we are now in a good position to consider the extent to which they enable us to answer the questions raised at the end of §5.2.2 and §5.2.3 .

Why are the constant-pressure heat capacities of monatomic or diatomic gases usually in the range 30 ± 10 J K^{-1} mol^{-1}?

From Equation 5.38 for C_P, we expect the heat capacity at constant pressure to vary with p, the number of degrees of freedom of the molecules of the gas. We can rearrange Equation 5.38 as an expression for p:

$$p = 2\left[\frac{C_P}{R} - 1\right] \qquad (5.41)$$

in terms of C_P. Now we can interpret the range of values of C_P as being due to the different numbers of internal degrees of freedom of the molecules of the gas. Substituting $C_P = 30 \pm 10$ J K^{-1} mol^{-1} implies values for p in the range 5.2 ± 2.4, or $3 < p < 8$. As we shall see, this is a very plausible range of results.

Why, for monatomic gases, does $C_P = 20.8$ J K^{-1} mol^{-1}, with almost no dependence on temperature or the type of molecule from which the gas is formed?

For monatomic gases, we expect molecules to have no internal degrees of freedom. Therefore, there should be just three degrees of freedom per molecule, corresponding to the kinetic energy of molecule in each of the x-, y- and z- directions. Using $p = 3$ in Equation 5.38 gives a prediction of $C_P = 20.786$ J K^{-1} mol^{-1}. As we can see from Figure 5.7, this value agrees closely with the data for monatomic gases given in Table 5.6 and Figure 5.3. We may take this as an indication that that the internal energy of a monatomic gas really is held in the kinetic energy of its constituent atoms, and in no other way.

Why do diatomic gases have a low temperature value of C_P rather greater than the value for monatomic gases, and which increases with increasing temperature?

Using Equation 5.41

$$p = 2\left[\frac{C_P}{R} - 1\right] \qquad (5.41^*)$$

we can understand these results by supposing that diatomic molecules possess extra degrees of freedom. These would be in addition to the three degrees of freedom associated with the kinetic energy of a molecule as a whole. Furthermore, it appears that not only are there more degrees of freedom, but the number of degrees of freedom required to explain the data gets larger as the temperature increases. In the following section on the heat capacity ratio γ we will see that we can associate these extra degrees of freedom with certain types of *internal* molecular motion. Here we note that the diatomic gases in our sample appear to have a heat capacity corresponding to around 5 degrees of freedom at low temperatures, increasing to around 7 or 8 at higher temperatures.

Gamma, γ
Why is the heat capacity at constant pressure always greater than the heat capacity at constant volume, i.e. γ > 1?

We can see immediately why this must so. The first law of thermodynamics tells us that :

$$\Delta Q = \Delta U - \Delta W \qquad (5.16^* \text{ and } 5.42)$$

In order to achieve a given change in temperature ΔT, Equation 5.26 tells us that we need to increase the internal energy U of the gas by $\Delta U = \frac{1}{2} zpR\Delta T$. So in order to raise the temperature of the gas by ΔT the *minimum* energy required is $\Delta Q = \Delta U$ which occurs when $\Delta W = 0$, i.e. when the gas is held at fixed volume. If the gas is allowed to expand during heating then additional energy must be supplied to do the work ΔW involved in the expansion. Thus C_P must always be greater than C_V and hence γ must always be greater than one.

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Why does the value of γ depend on whether the gas is monatomic, diatomic or polyatomic? In particular we would like to understand why:

- **monatomic gases have values for γ close to 1.66**
- **diatomic gases have values for γ close to 1.4 except at high pressure**
- **polyatomic gases have lower values of γ than either monatomic or diatomic gases.**

From Equation 5.40, we see that we expect γ to depend directly on the number of degrees of freedom per molecule p:

$$\gamma = 1 + \frac{2}{p} \qquad \text{(5.40* and 5.43)}$$

Figure 5.7 Comparison of the prediction of theory with experimental results for monatomic gases. The right-hand axis shows C_P in units of the gas constant R.
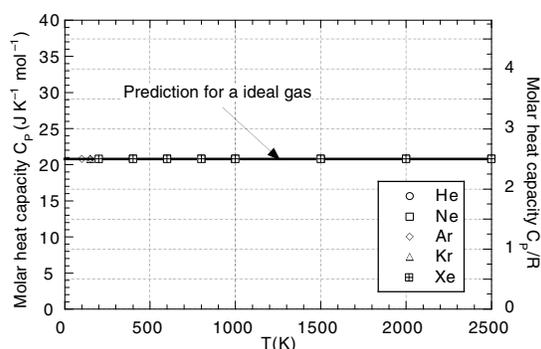
Figure 5.8 The experimental results for diatomic gases compared with the prediction for monatomic gases. The right-hand axis shows C_P in units of the gas constant R. The data exceed the prediction for monatomic gases by at least R at low temperatures, increasing to around 2 to 2.5R at high temperatures.
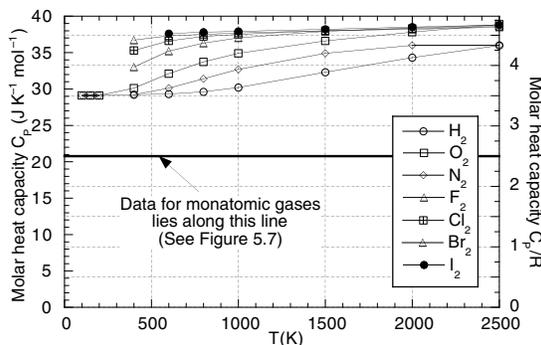
Rearranging this, we can obtain an expression for the number of degrees of freedom per molecule in terms of γ:

$$p = \frac{2}{\gamma - 1} \qquad (5.44)$$

Experimentally, Table 5.8 shows that monatomic gases have values of $\gamma = 1.66 \pm 0.02$. Interpreting this using Equation 5.44 implies $p \approx 3$ (within ± 0.1). Recall that three degrees of freedom are exactly what we expected when we derived the ideal gas equation. Using Equation 5.44 to interpret the values of γ for all the gases in Table 5.8, yields the results in Table 5.9.

We see that we can plausibly explain the data for γ in terms of quite reasonable numbers of degrees of freedom per molecule. By this I mean that the values of p are all greater than three, but are not too much greater. We now need to understand the way in which the values of p vary across Table 5.9. In particular we need to understand why p varies with:

- the different molecules constituting the gas
- the temperature
- the pressure.

Given the answers to the previous questions we are now reasonably sure that all molecules in a gas possess three degrees of freedom associated with their kinetic energy in each of the x-, y- and z-directions. However, there are other possibilities.

Figure 5.9 Three degrees of freedom of a gas molecule are associated with kinetic energy of motion in each of the x-, y-, and z- directions.
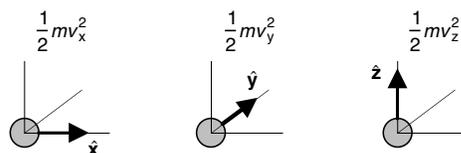
Rotational degrees of freedom

More complicated molecules also possess degrees of freedom associated with *rotation* about each of the x-, y- and z- axes. We can imagine this as a kind of 'tumbling motion', with the molecule spinning round randomly as it moves from one collision to another. The energy associated with

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Figure 5.10 The three degrees of freedom of a diatomic molecule associated with rotation about the *x-, y-* and *z-* axes.
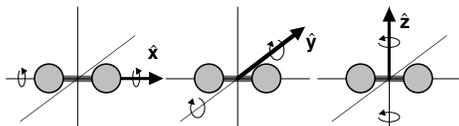
rotations differs depending on the axis of rotation. Figure 5.10 illustrates the rotation of a diatomic molecule. Just by symmetry, we can see that rotation about the *y-* and *z*-axes needs to be considered separately from rotation about the *x*-axis, the one through the centres of the two atoms. A quantum mechanical analysis of this problem shows that rotation about the *x*-axis is much less likely. This is because, as discussed in Table 2.5, the energy separation ΔE between the non-rotating quantum state of the molecule and the rotating quantum state is much greater for rotations about the *x*-axis

than for rotations the *y-* or *z*-axes. The idea that the energy ΔE separating non-rotating states from rotating states is anything other than zero can only be understood through consideration of the quantum mechanics of molecular motion. Classically, we could put as little energy as we chose into the rotation of molecule: there was no lower limit on the rotational speed of a molecule. Quantum mechanically, there is a lower limit to the energy tied up in rotation given by $\Delta E = \hbar\omega$ where ω is the minimum angular frequency of rotation.

It might surprise you that the data on heat capacity of diatomic gases can only be understood with recourse to a quantum mechanical explanation. If so, you would not be alone. At the start of the twentieth century, the fact that classical physics could not explain the heat capacity of gases led Lord Kelvin to call this a 'cloud over the dynamical theory of heat'. At that time, it represented (along with the Michelson–Morley experiment), the greatest challenge to physicists of that era.

Table 5.9 The number of degrees of freedom p for the molecules of a variety of gases predicted from the measured value of γ according to Equation 5.48. Values are plotted only for those gases included in Table 5.8.

Gas	γ	T(K)	p	Gas	γ	T(K)	p
A: Some monatomic gases				**D: Some triatomic gases**			
He	1.630	273.20	3.17	O_3	1.290	—	6.90
Ar	1.667	273.20	3.00	H_2O	1.334	373.20	5.99
Ne	1.642	292.20	3.12	CO_2	1.300	283.20	6.67
Kr	1.689	292.20	2.90	CO_2	1.220	573.20	9.09
Xe	1.666	292.20	3.00	CO_2	1.200	773.20	10.00
Hg	1.666	583.20	3.00	NH_3	1.336	—	5.95
				N_2O	1.324	—	6.17
B: Some diatomic gases				H_2S	1.340	—	5.88
H_2	1.407	283.20	4.91	CS_2	1.239	—	8.37
N_2	1.401	293.20	4.99	SO_2	1.260	293.20	7.69
O_2	1.400	283.20	5.00	SO_2	1.200	773.20	10.00
CO	1.297	2073.2	6.73				
NO	1.394	—	5.08	**E: Some polyatomic gases**			
				CH_4	1.313	—	6.39
C: Air				C_2H_6	1.220	—	9.09
Air	1.405	193.90	4.94	C_3H_8	1.130	—	15.4
Air	1.401	283.20	4.99	C_2H_2	1.260	—	7.69
Air	1.357	773.20	5.60	C_2H_4	1.264	—	7.58
Air	1.320	1173.2	6.25	C_6H_6	1.400	293.20	5.00
Air	1.828	273.20	2.42	C_6H_6	1.105	372.90	19.0
Air	2.333	193.90	1.50	$CHCl_3$	1.110	303.20	18.2
				$CHCl_3$	1.150	373.00	13.3
				CCl_4	1.130	—	15.4

Vibrational degrees of freedom

The rotational degrees of freedom we discussed previously refer to rigid rotation of the molecule, i.e. to motion in which there is no relative motion of the component atoms of the molecule. In general however, the atoms within molecules have several modes of vibration. For example, the relative separation of the two atoms in a diatomic molecule can vary, and the atoms will then oscillate about their average positions. The atoms then possess both kinetic energy of vibration and potential energy of vibration corresponding to a further two degrees of freedom.

Figure 5.11 The degree of freedom of a diatomic molecule associated with internal vibration.
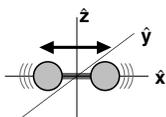
Diatomic molecules

For diatomic molecules we can understand how a molecule can have:

- three translational degrees of freedom
- three rotational degrees of freedom
- two vibrational degrees of freedom

making a total of eight degrees of freedom in all. Using Equation 5.38 $C_P = nR[p/2 + 1]$ with $p = 8$ predicts a maximum value of $C_P = 5R$ or $41.6 \text{ J K}^{-1} \text{ mol}^{-1}$. This is just greater than the largest value in Figure 5.4. However C_P takes this value only at high temperatures. We can understand this as being due to the fact that some types of motion do not take place at low temperatures. Or in the language of statistical mechanics, some degrees of freedom are inaccessible at low temperatures (§2.5.3).

Table 5.10 (and Table 2.5) Illustration of the use of the term *accessibility* of quantum states. Notice that increasing the temperature always increases the number of 'accessible' quantum states.

Inaccessible	Marginal accessibility	Fully accessible
$k_B T \ll \Delta E$	$k_B T \approx \Delta E$	$k_B T \gg \Delta E$
e.g. $k_B T < 0.1\Delta E$	e.g. $0.1\,\Delta E < k_B T < 1.5\Delta E$	e.g. $k_B T > 1.5\Delta E$
In this case, only occasionally do molecules make transitions to the higher quantum state. We can consider the degrees of freedom associated with these transitions to be inaccessible.	In this case, molecules make transitions to the higher quantum state. Detailed calculations are required to assess the extent to which the quantum state can be considered accessible	In this case, molecules frequently make transitions to the higher quantum state. We can consider the degrees of freedom associated with these transitions to be fully accessible.
In colloquial terms, the process associated with transitions between quantum states occurs so infrequently that it may generally be ignored.		In colloquial terms, the process associated with transitions between quantum states occurs so frequently that the quantum nature of the states may generally be ignored.

Figure 5.12 The experimental C_P results for helium and oxygen plotted as a function of temperature, extracted from Figures 5.3 and 5.4 respectively. The left-hand axis gives C_P in units of J K^{-1} mol^{-1} while the right-hand axis shows the number of accessible degrees of freedom inferred using Equation 5.48.
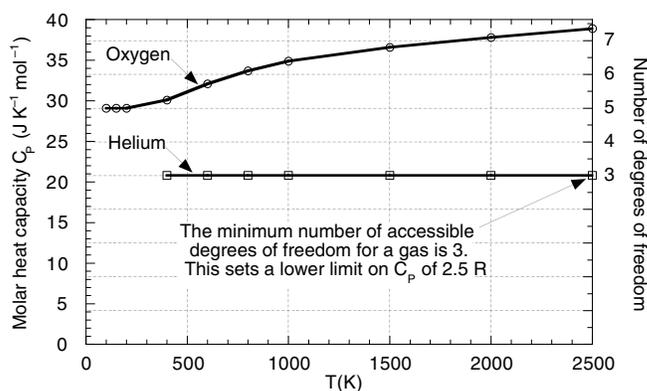
Tri- and polyatomic molecules

In general, we expect the number of degrees of freedom to increase as the number of atoms in a molecule increases, since more types of motion will become available. This tendency is clearly borne out by the data of Table 5.9. Diatomic molecules have more degrees of freedom than monatomic molecules, and polyatomic molecules have more degrees of freedom than diatomic molecules. As discussed below, the actual number observed depends on the way in which the atoms within the molecule are bonded together, and the temperature.

Variation of γ with temperature

As the temperature of the gas is increased, by definition the average energy per degree of freedom of the molecules is increased. In order to assess whether a particular degree of freedom is accessible or not, we compare $k_B T$ with ΔE, the energy difference between the quantum states of the molecule. There are three general situations, which are summarised in Tables 2.5 and 5.10.

The data for oxygen (O_2) (Figures 5.4 and 5.12) clearly indicate the gradual transition in which quantum states are inaccessible at low temperature, but become accessible at higher temperature.

If we compare the data at around 2000 K with that at 100 K, we see that oxygen molecules have acquired two extra degrees of freedom. Based on the discussion above we can tentatively assign these degrees of freedom to either the two easier modes

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of rotation, or the potential and kinetic energies of internal molecular vibration. Detailed calculations indicate that (for diatomic molecules) the two extra degrees of freedom already accessible at low temperatures are due to molecular rotation. We thus infer that the two or three extra degrees of freedom becoming available over the temperature range up to 1000 K are associated with internal vibration of the molecule. From this we infer that the separation of the energy levels involved in these vibrational degrees of freedom is:

$$\Delta E \approx k_B T \approx 1.38 \times 10^{-23} \times 2000 \ \text{J}$$
$$\approx 2.76 \times 10^{-20} \ \text{J} \qquad (5.45)$$
$$\approx 0.173 \ \text{eV}$$

In §2.4 we noted that the frequency of vibration f_o of a simple harmonic oscillator is related to the energy separation between quantum states by $\Delta E = h f_o$. Since h is the Planck constant (6.62×10^{-34} J s), this implies a vibrational frequency of $\approx 4.2 \times 10^{-13}$ Hz, a frequency in the infra-red part of the electromagnetic spectrum.

So as more degrees of freedom become available, we expect that γ (given by Equation 5.40 as $\gamma = 1 + 2/p$) should fall at higher temperatures, in broad agreement with the data.

Variation of γ with pressure

The data for air in Table 5.8 indicate that γ increases with increasing pressure. Comparing the datum for air at around atmospheric pressure (≈ 0.1 MPa) and $T = 283.2$ K with the datum at

around 200 atmospheres ($\approx$20 MPa) and $T = 273.2$ K, we see that increasing the pressure has reduced the number of accessible degrees of freedom. The extent of the reduction is quite dramatic, from a plausible 4.99 (i.e. 5), to a value of 2.42. This latter value is less than the three degrees of freedom that must be possessed by a gas whose molecules are free to move in three dimensions. How can we understand this?

Increasing the pressure of a gas at a fixed temperature implies an increase in the number density of molecules and hence a reduction in the average separation between molecules. This increases the frequency of molecular collisions and interactions, and these interactions restrict the motion of molecules. And so the associated degrees of freedom become inaccessible.

Consider the degrees of freedom associated with rotation. Because of its inertia, an O_2 molecule requires a certain time to rotate, typically 10^{-10} seconds, and if the molecules on average collide before this rotation can be completed then the degree of freedom is restricted. Calculations of the extent of this restriction are complicated, and we will not go through them here. However, we note that if the pressure is increased sufficiently the gas

will condense into a liquid. (Or it will enter a state where the molecules are so close together that it is not clear whether it should be called a liquid or a gas.) Gases compressed to this extent begin to show significant deviations from ideal gas behaviour, and the simple interpretation of γ according to Equation 5.40 is no longer realistic. Gases compressed so much that they cannot be distinguished from a liquid are discussed in §10.7.2, on the critical point.

Summary of heat capacity

Broadly speaking, we have been able to plausibly explain the behaviour of the heat capacity of gases on the basis of a relatively simple extension of the ideal gas theory. The key feature of the theory was the assumption that the internal energy of the gas is 'held' in the individual degrees of freedom of the gas molecules. Importantly we introduced the idea that molecules possessed *internal* degrees of freedom associated with vibrations and rotations of gas molecules. In order to understand the temperature dependence, it was necessary to develop the idea of the *accessibility* of degrees of freedom. This required acknowledgement of the quantum mechanical nature of the vibrations and rotations of gas molecules.

5.4 Compressibility: a discussion

5.4.1 Introduction

I would have liked at this point to present you with data on the compressibility of gases. However, there are two reasons why I cannot do this. The first is that the data are not tabulated in the reference books that I have consulted. And the second is *the reason* that the data are not tabulated: we need additional information about the constraints on the gas before we can say what its compressibility will be.

When we considered the heat capacity of a gas in §5.3, we calculated two special values C_P and C_V. These corresponded to *mechanical constraints* where, respectively, the pressure or the volume was kept constant during the heating or cooling

process. Similarly, when we consider the compressibility of a gas, we will have to specify the *thermal constraints* on the gas. In particular we will consider two specific types of volume changes: *adiabatic* and *isothermal*.

In an *adiabatic* volume change, no heat flows into or out of the gas. Thus if the gas expands and does some work, then the first law of thermodynamics tells us that the work must be done at the expense of the internal energy of the gas, and so the gas will cool.

In an *isothermal* volume change, the temperature of the gas is kept constant, and so heat must flow into or out of the gas. Thus if the gas expands and

Figure 5.13 (a) The variation of pressure with volume during an isothermal and adiabatic expansion. (b) An apparatus for realising an isothermal expansion requires some means of adding heat to the gas. (c) In an adiabatic expansion no heat flows into or out of the gas. Notice in (b) and (c) that the pressure in both cases is the same at the end of the expansion, but the volume is larger in the isothermal case, as indicated in (a).
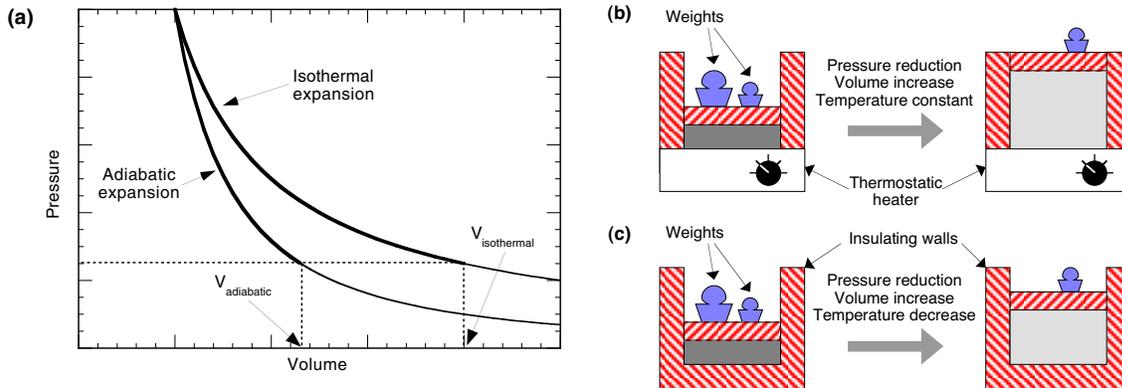
does some work, then work that is done is at the expense of the heat energy supplied to the gas during the expansion.
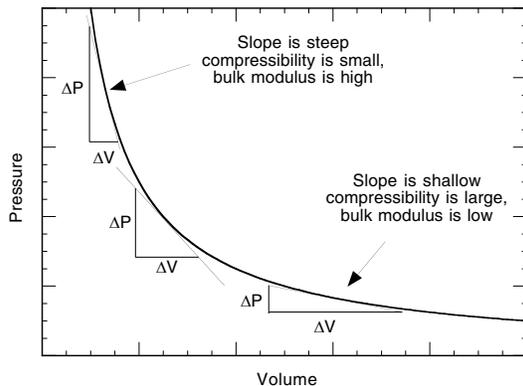
These effects are illustrated in Figure 5.13. We will look in some detail at both adiabatic and isothermal expansions below.

Compressibility and bulk modulus

The compressibility K, of a substance is defined as:

$$K = -\frac{1}{V}\frac{\partial V}{\partial P} \qquad (5.46)$$

Figure 5.14 PV diagram showing the gradient of the pressure volume curve and the relationship to the bulk modulus and compressibility.

The bulk modulus, B, of a substance is the inverse of the compressibility, i.e.

$$B = \frac{1}{K} = -V\frac{\partial P}{\partial V} \qquad (5.47)$$

There are three points you should note about these expressions. The first is that they are both related to the slope of the pressure versus volume graph. (Figure 5.13). If material is incompressible, then the volume changes slowly with applied pressure (i.e. $\partial V/\partial P$ is small). This means that a small compressibility implies a large bulk modulus. The second point to note is the minus sign: this is because the slope $\partial V/\partial P$ is always negative, and it is conventional for physical properties of materials to be defined as positive quantities. Finally we note the factor V: this just normalises the data. You can see the effect of the factor V by considering that when pressurised, a large volume will have a bigger rate of change of volume than a small volume. However this is just to do with the size of the sample, and is not an intrinsic property of the gas.

5.4.2 Isothermal volume changes

In both isothermal and adiabatic expansions we assume that at all times the gas is in equilibrium. This allows us to make use of the fact that whatever the gas is doing, its pressure, volume and temperature are related by $PV = zRT$. In other

words, the pressure is related to the volume by:

$$P = \frac{zRT}{V} \qquad (5.48)$$

and so differentiating we find:

$$\frac{\partial P}{\partial V} = \frac{\partial}{\partial V}\left[\frac{zRT}{V}\right] \qquad (5.49)$$

In an isothermal expansion, the temperature is by definition constant, and so the pressure and volume are related by:

$$\frac{\partial P}{\partial V} = zRT\frac{\partial}{\partial V}\left[\frac{1}{V}\right] \qquad (5.50)$$

i.e.

$$\frac{\partial P}{\partial V} = zRT\left[\frac{-1}{V^2}\right] \qquad (5.51)$$

Substituting for V using $PV = zRT$ and then cancelling we arrive at:

$$\begin{aligned}\frac{\partial P}{\partial V} &= zRT\left[\frac{-1}{V^2}\right]\\ &= \frac{-zRT}{V}\left[\frac{1}{V}\right] \qquad (5.52)\\ &= \frac{-P}{V}\end{aligned}$$

This gives us a surprisingly simple result for the isothermal bulk modulus B_{iso}:

$$\begin{aligned}B_{iso} &= -V\frac{\partial P}{\partial V}\\ &= -V\left[\frac{-P}{V}\right] \qquad (5.53)\\ B_{iso} &= P\end{aligned}$$

5.4.3 Adiabatic volume changes

To derive the adiabatic bulk modulus we start with Equation 5.49

$$\frac{\partial P}{\partial V} = \frac{\partial}{\partial V}\left[\frac{zRT}{V}\right] \qquad (5.49^*)$$

Unlike an isothermal expansion where the temperature does not change, the temperature does

Figure 5.15 Two-step analysis of an adiabatic expansion. An adiabatic expansion can be considered as the sum of two steps which are simpler to analyse: an isothermal expansion, and then an isochoric (constant volume) cooling. This analysis allows us to determine the relationship between the initial pressure and volume and the final pressure and volume.
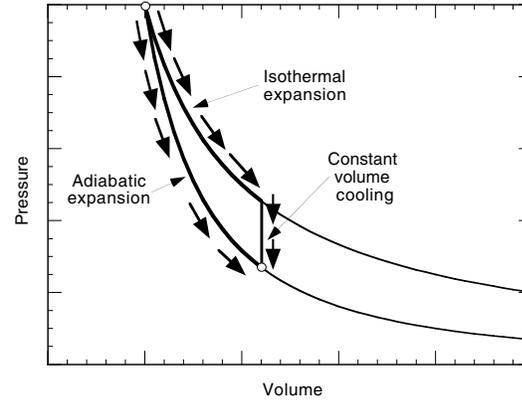
change during an adiabatic expansion. This makes analysis of the expansion curve rather more complicated. However, we can analyse the adiabatic curve in two steps (Figure 5.15). We can consider a small adiabatic expansion as the sum of:
- an isothermal expansion in which heat ΔQ flows *into* the gas
- a constant volume temperature change in which heat ΔQ flows *out* of the gas.

We can then write:

$$\Delta P = \left.\frac{\partial P}{\partial V}\right|_{iso}\Delta V + \left.\frac{\partial P}{\partial T}\right|_{V}\Delta T \qquad (5.54)$$

Now we can evaluate the two parts of the differential of $P = zRT/V$ relatively easily. The first part is our previous result (Equation 5.52) and the second is a straightforward differentiation:

$$\Delta P = \frac{-P}{V}\Delta V + \frac{zR}{V}\Delta T \qquad (5.55)$$

However, we still do not know ΔT, the temperature change during the expansion. We can derive an expression for ΔT by considering the first law of thermodynamics:

$$\Delta U = \Delta Q + \Delta W \qquad (2.57^* \text{ \& } 5.56)$$

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Analysing the adiabatic expansion as the sum of two steps, we notice that in the first step, the internal energy of the gas does not change (since its temperature remains constant). So in this first step heat ΔQ_1 flows *into* the gas during the isothermal expansion:

$$\Delta Q_1 = -\Delta W \qquad (5.57)$$

where ΔW is equal to the work done *on* (not by) the gas. As we saw in the steps leading to Equation 5.21, the work done *on* the gas during an expansion is:

$$\Delta W = -P\Delta V \qquad (5.58)$$

So at the end of the first step in our analysis we can state that the heat which has flowed into the gas is:

$$\Delta Q_1 = +P\Delta V \qquad (5.59)$$

In the second step in our analysis, the gas is cooled at constant volume until all the heat supplied in the first step has been removed. In terms of the constant volume heat capacity of the gas we can write:

$$\Delta Q_2 = zC_V\Delta T \qquad (5.60)$$

In order to make our two steps add up to an adiabatic change, the sum of Equations 5.58 and 5.59 must amount to zero, i.e. $\Delta Q_1 + \Delta Q_2 = 0$. Substituting we can derive an expression for the temperature change during an adiabatic expansion:

$$\Delta T = -\frac{P\Delta V}{zC_V} \qquad (5.61)$$

We can now substitute for ΔT into Equation 5.55:

$$\Delta P = -\frac{P}{V}\Delta V - \frac{zR}{V}\times\frac{P\Delta V}{zC_V} \qquad (5.62)$$

We can now separate terms and take the limiting value for small changes as follows:

$$\frac{\Delta P}{\Delta V} = -\frac{P}{V} - \frac{P}{V}\times\frac{R}{C_V}$$
$$\left.\frac{\partial P}{\partial V}\right|_{ad} = -\frac{P}{V}\left[1+\frac{R}{C_V}\right] \qquad (5.63)$$

Remembering that $C_P = C_V + R$ (Equations 5.40 and 5.41) and that we can express the ratio of the principle heat capacities as γ, we can simplify this expression:

$$\left.\frac{\partial P}{\partial V}\right|_{ad} = -\frac{P}{V}\left[1+\frac{R}{C_V}\right]$$
$$= -\frac{P}{V}\left[\frac{C_V+R}{C_V}\right]$$
$$= -\frac{P}{V}\left[\frac{C_P}{C_V}\right] \qquad (5.64)$$
$$\left.\frac{\partial P}{\partial V}\right|_{ad} = -\frac{\gamma P}{V}$$

We can then evaluate the adiabatic bulk modulus and arrive at another surprisingly simple result:

$$B_{ad} = -V\left.\frac{\partial P}{\partial V}\right|_{ad} = -V\left[\frac{-\gamma P}{V}\right] \qquad (5.65)$$
$$B_{ad} = \gamma P$$

5.2.6 Summary

Results
The previous sections have been quite mathematically involved, so it worthwhile pausing here to review the results of our calculations. We have calculated $\partial P/\partial V$ for both adiabatic and isothermal expansions. This is just the slope of the graph of pressure versus volume. For an isothermal expansion, we found $\partial P/\partial V = -P/V$. For adiabatic expansions, we found that the curve was always steeper than for isothermal expansions by a factor γ, i.e. $\partial P/\partial V = -\gamma P/V$.

From these results we derived expressions for the bulk modulus for both adiabatic and isothermal expansions:

$$B_{iso} = P \qquad (5.53^*)$$

$$B_{ad} = \gamma P \qquad (5.65^*)$$

We can also state values for the compressibility of the gas:

$$K_{ad} = \frac{1}{\gamma P} \qquad K_{iso} = \frac{1}{P} \qquad (5.66)$$

Example 5.8

A mixture of air and fuel in the cylinder of a motor car engine is ignited and increases temperature essentially instantaneously from ambient temperature to around to 1000 °C. The combustion products then rapidly expand from an initial volume of 100×10^{-6} m³ to 400×10^{-6} m³. If there is 0.005 mol of N_2 in the cylinder, estimate the work done in the expansion. If there were 4 such cylinders executing 40 such expansions each second, estimate the power that could be delivered by the engine.

The work done is given by the integral PdV (Eq. 5.60):

$$W = \int_i^f P dV$$

We can substitute for P using Equation 5.69 to find:

$$W = \int_i^f P dV = \int_i^f C V^{-\gamma} dV = C \int_i^f V^{-\gamma} dV$$

This can be integrated to yield:

$$W = C \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_i^f = \frac{C}{-\gamma+1} \left[V^{-\gamma+1} \right]_i^f$$

Before we can evaluate this we need to work out the constant C. To do this we use the ideal gas law to work out the initial pressure:

$$P = \frac{zRT}{V} = \frac{0.005 \times 8.31 \times [273.15+30]}{100 \times 10^{-6}} = 1.26 \times 10^5 \text{ Pa}$$

which allows us to evaluate C. We use $\gamma = 1.4$ for nitrogen from Table 5.8:

$$C = PV^\gamma = 1.26 \times 10^5 \left[100 \times 10^{-6} \right]^{1.4} = 0.316$$

We can now calculate the work done in the expansion:

$$= \frac{0.316}{0.4} \left[\left[100 \times 10^{-6} \right]^{-0.4} - \left[400 \times 10^{-6} \right]^{-0.4} \right]$$

$$= 0.791[39.81 - 22.87] = 13.4 \text{ J}$$

If there are 4 cylinders executing 40 similar expansions per second then the power delivered by the engine is:

$$\text{Power} = 13.4 \times 4 \times 40 = 2144 \text{ W} = 2.144 \text{ kW}$$

PVᵞ constant

The result that $\partial P / \partial V = -\gamma P / V$ for an adiabatic expansion is often stated in more succinct and easily memorable manner:

$$PV^\gamma = \text{constant} \tag{5.67}$$

for an adiabatic expansion. To see how we arrive at this result we start with Equation 5.64:

$$\frac{\partial P}{\partial V} = -\frac{\gamma P}{V} \tag{5.64*}$$

We then rearrange this equation and integrate the results to find a relationship between P and V that holds during all adiabatic processes.

$$\frac{dP}{P} = -\frac{\gamma dV}{V}$$
$$\int \frac{dP}{P} = \int -\frac{\gamma dV}{V} = -\gamma \int \frac{dV}{V} \tag{5.68}$$

We now use the result that $\int dx / x = \ln x + C$, where C is a constant. We find:

$$\ln P = -\gamma \ln V + C$$
$$\ln P + \gamma \ln V = C \tag{5.69}$$

which simplifies to:

$$\ln P + \ln V^\gamma = C$$
$$\ln PV^\gamma = C \tag{5.70}$$

If the last equation above is valid, i.e. the natural logarithm of PV^γ is a constant, then it must also be true that PV^γ itself is constant during an adiabatic process.

Adiabatic or isothermal compressions?

Having taken all this trouble to compare results for isothermal and adiabatic volume changes, you might think that both results were equally useful. In fact, in a great many circumstances, changes to a gas are effectively adiabatic. This occurs because (as we shall see in the next section) the thermal conductivity of gases is generally very low. This means that when a change in a gas takes place, unless the change takes place very slowly, heat does not have time to flow into the gas to maintain the temperature. For example, when large volumes of air move around in the Earth's atmosphere (what we call 'weather'), the volume changes are effectively adiabatic because the changes take place too quickly. Similarly, the expansions and contractions of a gas in a sound wave are also adiabatic. We shall say more about this in §5.6**.**

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5.5 Thermal conductivity

Heat flow through fluids can be *extremely* complex. This is because in addition to the normal flow of heat that takes place through any material, it is also possible for the fluid itself to move from one place to another. This process, known as *convection*, allows fluid to 'carry' heat with it in the form of its heat capacity. Thus, for example, a fluid flow of z moles per second from a part of a container which is ΔT hotter than a cold part will result in a delivery of heat energy to the colder part of the container of $zC_P\Delta T$ joules per second. This effect is illustrated in Figure 5.16.

Convection arises from the interaction of two effects:

- The density of a gas changes significantly on heating (see §5.1.2 on the expansivity of gases.)
- Most experiments we perform on gases take place in a gravitational field. If this were not so there would be no tendency for the hotter, less-dense, gas to 'rise' or 'fall'.

Both factors are necessary for convection. When heat flow by convection occurs in a fluid it can easily overwhelm any other thermal conduction

Figure 5.16 Convection occurs when heating produces a region of low-density gas (hot) which is beneath a region of high-density gas (cold). This arrangement is unstable and the low-density (hot) gas rises and moves to the colder part of the chamber. When it reaches the colder part of the chamber, it cools. It then gives up thermal energy $zC_P\Delta T$. When convection occurs, the heat flow does not depend on the intrinsic thermal conductivity of gas, but on its heat capacity and the rate of flow of gas.
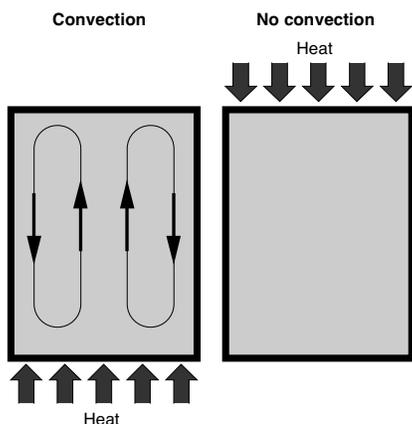
processes through the 'still' fluid. Furthermore, heat flow by convection varies dramatically from one measurement apparatus to another and so is difficult to quantify. For this reason, even though convection is important in many practical situations, more fundamental information can be extracted from experiments on fluids where the fluid itself does not flow. The measurements presented below are made in the absence of convection on 'still gas'.

The thermal conductivity κ of a gas may defined by the equation

$$\frac{dQ}{dT} = -\kappa A \frac{dT}{dx} \qquad (5.71)$$

where:

$\dfrac{dQ}{dT}$ is the rate of heat flow (W)

κ is the thermal conductivity (W m^{-1} K^{-1})

A is the cross sectional area across which heat is flowing (m^2)

$\dfrac{dT}{dx}$ is the temperature gradient (K m^{-1}).

The minus sign in Equation 5.71 indicates that heat flows *down* a temperature gradient, i.e. from regions of high temperature to regions of low temperature.

5.5.1 Data on the thermal conductivity of gases

The data in Table 5.11 show the still-gas values of the thermal conductivity of a selection of monatomic, diatomic and tri-atomic gases at several temperatures. All the data refer to gases at pressures around one atmosphere. A typical value of κ for gases is ≈ 0.1 W m^{-1} K^{-1}. This is much less than for a metal such as copper (≈ 400 W m^{-1} K^{-1}: Table 7.16) or an electrical insulator such as quartz (≈ 1 to 10 W m^{-1} K^{-1} Table 7.17).

Figure 5.14 graphs data from Table 5.11 and shows there is clear qualitative similarity in the thermal conductivity of all the gases. The thermal conductivity increases as temperature rises, but the increase is not linear: the *rate* of increase becomes less at higher temperatures.

More surprisingly, Figure 5.18 shows that the thermal conductivity of a gas is independent of pressure across a wide range of pressures around atmospheric pressure: notice the logarithmic pressure range on the *x*-axis. Thus removing 99% of the molecules from a gas at atmospheric pressure, i.e. reducing the pressure by a factor 100, produces no change in the thermal conductivity of the gas!

The main questions raised by our preliminary examination of the experimental data on the thermal conductivity of gases are:

- Why does the thermal conductivity of gases increase at high temperatures?
- Why is the thermal conductivity of gases independent of pressure across a wide range of pressures around atmospheric pressure?
- Why are the thermal conductivities of gases as low as they are?

5.5.2 Understanding the data on the thermal conductivity of gases

Before considering the theory of the thermal conductivity, we note that the thermal conductivity of a gas is a different type of property from the heat capacity of a gas. The heat capacity relates the temperature at the beginning and end of a heating

Table 5.11 Measured values of the thermal conductivities of some gases. The units are 10^{-2} W m^{-1} K^{-1}. For example, the thermal conductivity of argon at 273.2 K is 1.63×10^{-2} W m^{-1} K^{-1}.

Gas	Temperature (K)				
---	73.2	173.2	273.2	373.2	1273
Monatomic gases					
Helium, He	5.95	10.45	14.22	17.77	41.90
Neon, Ne	1.74	3.37	4.65	5.66	12.80
Argon, Ar	—	1.09	1.63	2.12	5.00
Krypton, Kr	—	0.57	0.87	1.15	2.90
Xenon, Xe	—	0.34	0.52	0.70	1.90
Radon, Ra	—	—	0.33	0.45	—
Diatomic gases					
Hydrogen, H_2	5.09	11.24	16.82	21.18	—
Fluorine, Fl_2	—	1.56	2.54	3.47	—
Chlorine, Cl_2	—	—	0.79	1.15	—
Bromine, Br_2	—	—	0.40	0.60	—
Nitrogen, N_2	—	1.59	2.40	3.09	7.40
Oxygen, O_2	—	1.59	2.45	3.23	8.60
Carbon monoxide, CO	—	1.51	2.32	3.04	—
Air, N_2/O_2	—	1.58	2.41	3.17	7.60
Polyatomic gases					
Ammonia, NH_4	—	—	2.18	3.38	—
Carbon dioxide, CO_2	—	—	1.45	2.23	7.90
Ethane, C_2H_6	—	1.80	—	—	—
Ethene, C_2H_4	—	1.40	—	—	—
Methane, CH_4	—	1.88	3.02	—	—
Sulpur dioxide, SO_2	—	—	0.77	—	—
Water/Steam, H_2O	—	—	1.58	2.35	—

Figure 5.17 Variation of the thermal conductivity of the gases from Table 5.11 with absolute temperature. All the curves, monatomic, diatomic and polyatomic behave broadly similarly, but the absolute magnitude of conductivity varies significantly from one gas to another. The lines joining the data points are a guide to the eye only.
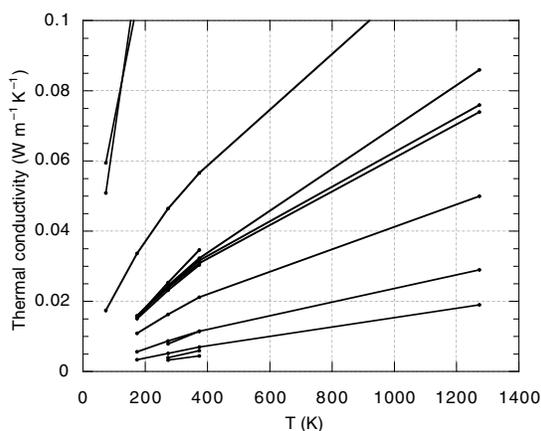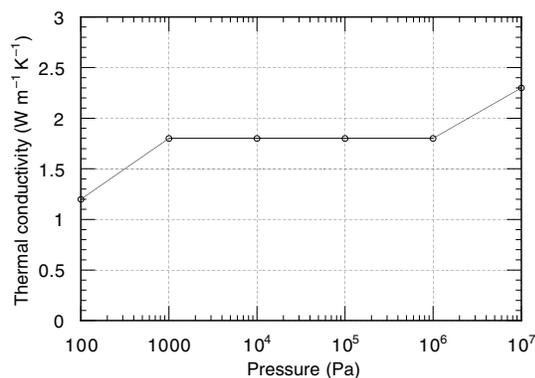
Figure 5.18 Variation of the thermal conductivity of argon with pressure. The lines join the data points and are a guide to the eye only. Notice that the pressure scale is logarithmic and represents a pressure range of 5 orders of magnitude.

process to the heat added to the gas. In each state (before and after heating) the gas is in thermal equilibrium. In contrast, the thermal conductivity relates to the process of heat flow, which necessarily implies that the gas is not in equilibrium. It is a general feature of physics that equilibrium properties are easier to understand than transport processes.

Background theory

In order to understand the thermal conductivity of gases, we will need to use some of the ideas that we developed in §4.3. In particular we will use the following results:

- The mean free path, λ_{mfp}, of a gas molecule, is given by:

$$\lambda_{\text{mfp}} = \frac{1}{\sqrt{2}\pi n a^2} \qquad (4.45^* \ \& \ 5.72)$$

where n is number density of molecules and a is the effective diameter of a gas molecule.

- The average energy of a molecule with p degrees of freedom is given by:

$$\bar{u} = \tfrac{1}{2} p k_{\text{B}} T \qquad (5.73)$$

- The number of molecular collisions with an area A per second is given by:

$$\tfrac{1}{4} n \bar{v} A \qquad (4.39^* \ \& \ 5.74)$$

where n is number density of molecules and $\bar{v}$ is the mean speed of a gas molecule.

Figure 5.19 illustrates a gas in which there is a temperature gradient, and highlights an area A perpendicular to the temperature gradient. Molecules strike area A from both the hotter side and the colder side. On average, molecules striking A have travelled a distance λ_{mfp}, and so have come from within a sphere of radius λ_{mfp}. In order to work out the net energy transported across A per second we will make a simplifying assumption. We will assume that the molecules have come not from a sphere, but from two planes a distance λ_{mfp} from A in either direction along the temperature gradient. The energy transported from these planes will be in the form of the kinetic energy of the molecules, plus the energy associated with any internal degrees of freedom.

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Example 5.9

A container of cross-sectional area 25 cm^2 and length 30 cm is heated from the top such that air at the bottom is at approximately 100 °C and that air at the top is approximately 10 °C warmer. What is the rate at which energy is transported down the tube?

110 °C

We first note the situation is stable against convection, and so we may use the intrinsic values of the thermal conductivity listed in Table 5.11. We then note that the pressure is not mentioned in the question so we assume it is within an order of magnitude of atmospheric pressure and will thus be same as the figures listed in Table 5.11. We are now in a position to use Equation 5.72 in a fairly straightforward manner. We have:

$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dx}$$

with:
100 °C

$$\kappa = 3.17 \times 10^{-2} \ \text{W m}^{-1} \text{K}^{-1}$$

$$A = 25 \times 10^{-4} \ \text{m}^2$$

The temperature difference across the length of tube is 10 °C and the length of tube is 30×10^{-2} m, so we can estimate the temperature gradient within the tube as:

$$\frac{dT}{dx} \approx \frac{\Delta T}{\Delta x} = \frac{10}{0.3} \approx 33 \ \text{°C m}^{-1}$$

Thus the rate of heat flow down the tube is given by:

$$\frac{dQ}{dt} = -3.17 \times 10^{-2} \times 25 \times 10^{-4} \times 33$$

$$= 2.62 \times 10^{-3} \ \text{W}$$

Thus the maintenance of a 10 °C temperature difference across the length of the tube requires a heat input of only around 2.6 mW.
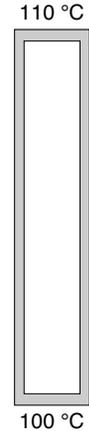

The number of molecules crossing unit area per second from each direction is given by Equation 5.74 as $\frac{1}{4} n \bar{v}$ and each molecule brings with it on average $\frac{1}{2} k_{\text{B}} T$ of energy per accessible degree of freedom. Thus if each molecule has p accessible degrees of freedom, on average the energy crossing area A per second from each side is:

$$\tfrac{1}{4} n \bar{v} \times A \times p \times \tfrac{1}{2} k_{\text{B}} T \qquad (5.75)$$

Now at $x + \lambda_{\text{mfp}}$, the temperature is approximately:

Figure 5.19 Illustration of the basic process by which we imagine heat flow to take place. Notice that the *average* speed of molecules (represented by the length of the arrows) in the hotter region is greater than the *average* speed in the colder region.

Hotter   Heat flow   Colder
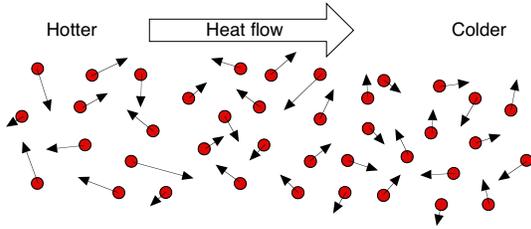
$$T + \frac{\partial T}{\partial x}\lambda_{\text{mfp}} \qquad (5.76)$$

and at $x - \lambda_{\text{mfp}}$, the temperature is approximately:

$$T - \frac{\partial T}{\partial x}\lambda_{\text{mfp}} \qquad (5.77)$$

The small difference in temperature between Equations 5.76 and 5.77 means that molecules striking area A from $x + \lambda_{\text{mfp}}$ carry on average slightly more energy than molecules striking area A from $x - \lambda_{\text{mfp}}$. The difference between the two energy fluxes gives the net energy transported across A per second. Notice that in Figure 5.20 the temperature increases in the positive x-direction and so heat flow will be in negative x-direction.

So the energy flow per second across area A in the positive x-direction is:

$$\tfrac{1}{8}n\bar{v}Apk_{\text{B}}\left[T - \frac{\partial T}{\partial x}\lambda_{\text{mfp}}\right] \qquad (5.78)$$

and the energy flow per second across area A in the negative x-direction is:

$$\tfrac{1}{8}n\bar{v}Apk_{\text{B}}\left[T + \frac{\partial T}{\partial x}\lambda_{\text{mfp}}\right] \qquad (5.79)$$

Subtracting Equation 5.79 from Equation 5.78 yields the net energy per second in the positive x-direction:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{1}{8}n\bar{v}Apk_{\text{B}}\left[T - \frac{\partial T}{\partial x}\lambda_{\text{mfp}} - T - \frac{\partial T}{\partial x}\lambda_{\text{mfp}}\right]$$

$$= \frac{1}{8}n\bar{v}Apk_{\text{B}}\left[-2\frac{\partial T}{\partial x}\lambda_{\text{mfp}}\right]$$

$$= -\underbrace{\left[\tfrac{1}{4}n\bar{v}pk_{\text{B}}\lambda_{\text{mfp}}\right]}_{\kappa}A\frac{\partial T}{\partial x}$$

$$(5.80)$$

Comparing Equation 5.80 with the standard form of the heat flow Equation 5.71 we see that the expression within the square brackets is just κ:

$$\kappa = \tfrac{1}{4}n\bar{v}pk_{\text{B}}\lambda_{\text{mfp}} \qquad (5.81)$$

This expression requires only refinement and rearrangement before we can compare it with experimental results. If we had been more careful in our averaging of the heat flows across area A, we would have found an expression identical to Equation 5.81 but with the '4' in the denominator replaced by a '6'. This modified expression is the one we will now work with, namely:

$$\kappa = \tfrac{1}{6}n\bar{v}pk_{\text{B}}\lambda_{\text{mfp}} \qquad (5.82)$$

Figure 5.20 Simplified illustration of the calculation of thermal conductivity of a gas. The figure shows three planes in the gas perpendicular to a temperature gradient. The separation of the planes is λ_{mfp}. the mean free path of the molecules. Thus molecules that are travelling in the appropriate direction in either the top or the bottom plane will (probably) cross the central plane before colliding. Energy is carried across A in both directions, but *on average* more energy flows across A from the plane in the hotter region of the gas. The analysis of the thermal conductivity centres on the problem of evaluating the net energy flow across an area A.

$x + \Delta x$ Hotter   Area, A
λ_{mfp}
x
λ_{mfp}
$x - \Delta x$ Colder
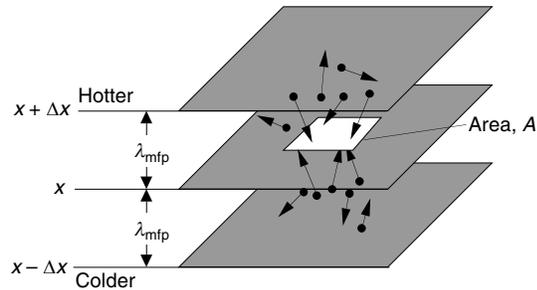
Example 5.10

Evaluate Equation 5.84 for argon gas at temperature T.

$$\kappa = \frac{\bar{v}pk_B}{6\sqrt{2}\pi a^2}$$

There are three quantities in Equation 5.84 that we need to estimate:
* the number of accessible degrees of freedom p
* the average molecular speed $\bar{v}$
* the effective molecular diameter a.

Let us look at each of these in turn.
* From the analysis of heat capacity measurements (§5.3.3) we can be sure that for a monatomic gas there are exactly three degrees of freedom, $p=3$.
* We can make an estimate of $\bar{v}$ in terms of the *root mean square velocity* $\sqrt{\overline{v^2}}$. Remember that for any molecule there are three degrees of freedom associated with kinetic energy. Because of the equipartition of energy between degrees of freedom, we can write the *average* kinetic energy:

$$\frac{1}{2}m\overline{v^2} = 3 \times \frac{1}{2}k_B T$$

where m is the mass of a molecule. As mentioned in §4.32,

$$\sqrt{\overline{v^2}} = 1.085\bar{v}$$

so we can estimate $\bar{v}$ as:

$$\bar{v} = \frac{1}{1.085}\sqrt{\overline{v^2}}$$

$$= \frac{1}{1.085}\sqrt{\frac{3k_B T}{m}}$$

* Finally we estimate a from a typical value for the separation between atoms in the solid state, which is $a \approx 0.3 \times 10^{-10}$ m. This is not a very accurate estimate, and it does not allow us to quantitatively compare results for different gases. However, it should be a constant for each type of gas and be of the correct order of magnitude.

Putting these estimates together and substituting them into the equation for the thermal conductivity:

$$\kappa = \frac{\bar{v}pk_B}{6\sqrt{2}\pi a^2}$$

$$= \frac{1}{1.085}\sqrt{\frac{3k_B T}{m}} \times \frac{3k_B}{6\sqrt{2}\pi a^2}$$

$$= \left[\frac{3}{1.085 \times 6 \times \sqrt{2}}\sqrt{\frac{3k_B}{m}} \times \frac{k_B}{\pi a^2}\right]\sqrt{T}$$

$$= \left[0.326\sqrt{\frac{3k_B}{m}} \times \frac{k_B}{\pi a^2}\right]\sqrt{T}$$

Substituting for argon (relative atomic mass 39.95):

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$a = 0.3 \times 10^{-9} \text{ m}$$

$$m = 39.95u = 39.95 \times 1.66 \times 10^{-27} \text{ kg}$$

we find:

$$\kappa = \left[0.326\sqrt{\frac{3 \times 1.38 \times 10^{-23}}{39.95 \times 1.66 \times 10^{-27}}} \times \frac{1.38 \times 10^{-23}}{\pi\left(0.3 \times 10^{-9}\right)^2}\right]\sqrt{T}$$

$$= 3.98 \times 10^{-4}\sqrt{T} \text{ W m}^{-1} \text{ K}^{-1}$$

If we substitute for λ_{mfp} using Equation 5.72, we arrive at an expression which has no reference to n, the number density of molecules

$$\kappa = \frac{1}{6}n\bar{v}pk_B \times \frac{1}{\sqrt{2}\pi n a^2} \tag{5.83}$$

$$\kappa = \frac{\bar{v}pk_B}{6\sqrt{2}\pi a^2} \tag{5.84}$$

We are now in a position to compare our theoretical prediction with the experimental results of §5.5.1.

Comparison with experiment

Let us consider the questions raised at the end of §5.5.1 in turn

Why does the thermal conductivity of gases increase at high temperatures?

Example 5.10 below shows how we may use Equation 5.84 to estimate the thermal conductivity of a gas. The example shows that we expect a $T^{0.5}$ dependence for κ. Broadly speaking, this describes the behaviour of all the gases in Figure 5.17. However, we shall see that the theory as we have developed it is not able to fully explain the experimental in more than this qualitative manner.

We can make some more progress if we concentrate on results for argon, and examine the extent of detailed agreement between the calculation of κ in Example 5.10 and the experimental data. Table 5.12 shows this calculation repeated for each of the temperatures for which we have data. The predictions are clearly of the correct order of magnitude, but differ by a factor of roughly 2 to 3 from the data. Noting that our estimate of the diameter of an argon atom in Example 5.10 was just a ball-park guess, we could improve the overall level of agreement between theory and experiment if we revised our estimate for the diameter of an argon atom. The diameter required to match experimental data is shown on the rightmost column of Table 5.12. The magnitude of the diameters are entirely plausible; however in order to explain the data we have to suppose that the molecules become effectively smaller at higher temperatures.

A more quantitative approach

We can quantitatively examine the deviations of the data from the dependence if we re-plot some of the data from Figure 5.17 in a different form. Example 5.10 predicts that $\kappa = AT^{0.5}$ and so a plot of $\log \kappa$ versus $\log T$ should have a slope of 0.5 and an intercept of $\log A$ where:

$$A = \frac{k_B}{2.17 \pi a^2} \sqrt{\frac{3k_B}{2m}} \qquad (5.85)$$

Figure 5.21 plots the data for the monatomic gases in this way. The slopes and intercepts of the best-fit lines of the form AT^x are recorded in Table 5.13. The intercepts A behave qualitatively as expected, becoming smaller for the gases with the larger molecules. In the bottom line of Table 5.13 we have used the experimental values for A to extract a value for the low-temperature limit of the effective diameter a of the noble gas atoms from Equation 5.85. The data indicate a low-temperature effective diameter of an argon atom of 0.391 nm which can be compared with a value of 0.21 nm at 173.2 K. We see that the effective diameter at low temperatures is considerably greater than the effective diameter at high temperature.

The origin of this effect lies in the effect discussed in §4.4.3 (Figure 4.13) concerning the detailed

Table 5.12 Calculated and experimental values for κ for argon at various temperatures. Also shown is the inferred value(a) for the molecular diameter.

T (K)	Data (W m^{-1} K^{-1})	Prediction (W m^{-1} K^{-1})	Ratio	a (nm)
173.2	1.09×10^{-2}	5.23×10^{-3}	2.08	0.21
273.2	1.63×10^{-2}	6.57×10^{-3}	2.48	0.19
373.2	2.12×10^{-2}	7.68×10^{-3}	2.76	0.18
1273	5.00×10^{-2}	14.19×10^{-3}	3.52	0.16

Figure 5.21 A log–log plot of thermal conductivity κ of the monatomic gases versus temperature. Thick lines connect data points. Thin dotted lines are the best-fit lines of the form AT^x. The thin solid line illustrates what a line of slope 0.5 looks like. The parameters of the lines fitted to the data are shown in Table 5.13.
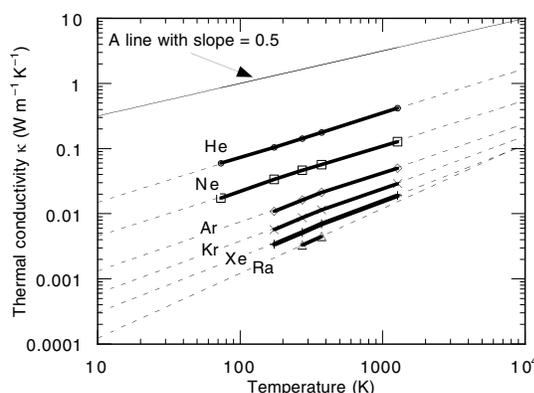

Table 5.13 Results from an analysis of the thermal conductivity data assuming the data has the form $\kappa = AT^x$. The significance of a is discussed in the text.

Gas	A	x	a (nm)
Helium, He	30.91×10^{-4}	0.685	0.108
Neon, Ne	9.14×10^{-4}	0.695	0.198
Argon, Ar	2.34×10^{-4}	0.754	0.391
Krypton, Kr	0.93×10^{-4}	0.806	0.620
Xenon, Xe	0.42×10^{-4}	0.857	0.923
Radon, Ra	0.12×10^{-4}	0.994	1.73

nature of molecular collisions. At low temperatures, the average speed of molecules is relatively slow, and molecules may be strongly affected by the weak attraction between molecules. At higher temperatures, the higher average speed of molecules causes their trajectories to be only slightly affected by the weak inter-molecular interactions.

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We can find further evidence for the idea that molecular interactions are the source of the deviations of the thermal conductivity theory from the data. If we examine the slopes x from Figure 5.21 (Table 5.13) we note that the experimental values are all higher than the predicted 0.5, and that the difference from 0.5 becomes larger for the gases with heavier atoms.

We have not yet discussed the detailed nature of the interactions between molecules, but we will do so in §6.2. Perhaps surprisingly, §6.2 is concerned with the properties of noble gas molecules *in their solid state*. This does in fact make sense since in the properties of these molecular solids are dominated by interactions between molecules. This can be compared with the properties of the gas phase, in which we have had to search quite hard even to detect the properties of molecular interactions. In §6.2 we will see that the strength of the interaction between molecules is related to the *electrical polarisability* of a molecule (§5.7). This property is related to the ease with which the electron distribution around an atom may be distorted. The heavy noble gas atoms (such as xenon) have relatively large, easily distorted (i.e. highly polarisable) electron distributions. Hence they also have relatively strong interatomic interactions. In contrast the light noble gas atoms (such as helium) have small, very rigid (i.e. weakly polarisable) electron distribution, and hence relatively weak interatomic interactions. This picture corresponds well with the data of Table 5.13

Before moving on we note that we have come to an explanation of the deviations from a $T^{0.5}$ dependence of the thermal conductivity of gases. However in order to achieve this we have had to consider details of the interatomic interactions in the gas. In contrast we could understand the heat capacity data on monatomic gases without any consideration of the details of interatomic interactions. This is typical of the difference between an equilibrium property of a substance and a non-equilibrium transport property. It is generally a more straightforward matter to interpret equilibrium properties than it is to interpret transport properties. However, by studying the deviations from a $T^{0.5}$ dependence, we were able (in princi-

ple) to compare particular models of molecular interactions with experiment.

Why is the thermal conductivity of gases independent of pressure across a wide range of pressures around atmospheric pressure?

Figure 5.18 shows that, for argon at least, the thermal conductivity is independent of pressure over a range of at least three orders of magnitude. We can understand this immediately from the form of Equation 5.84:

$$\kappa = \frac{\bar{v}pk_B}{6\sqrt{2}\pi a^2} \qquad (5.84^*)$$

This equation does not mention pressure, and so the theory predicts correctly that κ is independent of pressure. But how does this come about? If we examine the precursor equations to 5.84, such as Equation 5.81, we can see that the formula includes the product of n and λ_{mfp}. This makes sense since the thermal conductivity will maximised if:

- there are more molecules to carry the thermal energy (i.e. n is large)
- each molecule can travel unimpeded through the gas (i.e. λ_{mfp} is large).

However λ_{mfp} is inversely proportional to n and so increasing n reduces λ_{mfp} by an exactly compensating factor.

Figure 5.18 shows that κ is independent of pressure only over a certain (large) range. At lower pressures κ gets smaller, and at higher pressures κ gets larger. We can understand the low-pressure behaviour quite simply. As the pressure is reduced, the number density of molecules n falls, and so λ_{mfp} gets larger. However a point will be reached where λ_{mfp} is so large that the molecules are simply bouncing from side to side in their container and only rarely colliding with each other. Lowering the pressure beyond this point will not cause any further increases in λ_{mfp} and κ will simply be proportional to n. We can estimate the pressure at which this occurs: if we fix $\lambda_{mfp} \approx L,$ the dimension of the gas container which might be, say, 1 cm (10^{-2} m). From Equation 5.72 λ_{mfp} will reach this value when:

$$n = \frac{1}{\sqrt{2}\pi L a^2} \qquad (5.86)$$

Using our usual estimate of a molecular diameter of $a = 0.3$ nm we find $n = 2.5 \times 10^{20}$ m^{-3}. We can estimate the pressure and temperature at which this occurs using the formula from Example 4.2:

$$n = \frac{P}{k_B T} \qquad (5.87)$$

Assuming a temperature of 300 K, we have

$$
\begin{aligned}
P &= n k_B T \\
&= 2.5 \times 10^{20} \times 1.38 \times 10^{-23} \times 300 \\
&\approx 1.04 \text{ Pa} \\
&\approx 1.04 \times 10^{-2} \text{ mBar}
\end{aligned}
\qquad (5.88)
$$

Atmospheric pressure is approximately 10^5 Pa (1000 mbar) so this phenomenon does not occur until relatively low pressure, a regime known as the high-vacuum regime. For example, the pressure inside the wall of a 'vacuum flask' is typically 10^{-5} mbar (approximately 10^{-8} Pa) and so the thermal conductivity of the gas in the flask is well into the high-vacuum regime. Notice that lowering the pressure through five orders of magnitude from atmospheric pressure would have had no effect on the thermal conductivity! Only when the pressure is reduced below the critical pressure indicated by Equation 5.88 is the thermal conductivity affected.

The rise in thermal conductivity at higher pressures occurs because the molecules are becoming so densely packed that the assumptions about molecular trajectories become invalid. Again, the mean free path is becoming fixed, but now at a distance of approximately one atomic diameter.

Why are the thermal conductivities of gases as low as they are?

The rise in thermal conductivity at very high pressures (Fig 5.18) gives a clue to the origin of the small absolute magnitude of the thermal conductivity in gases as compared with solids or liquids. The smallness of κ arises because the number density of molecules, n, is so small for a gas. If we consider a highly compressed gas in which λ_{mfp} is estimated as a small fraction of a molecular diameter a, and n as approximately $1/a^3$, then estimates of the order of magnitude of κ from Equation 5.84 produce answers similar to those found for liquids. We will consider this regime further when analysing the thermal conductivity of liquids in §9.11.

5.6 Speed of sound

5.6.1 Data on the speed of sound in gases

Sound is a displacement wave, or pressure wave, which propagates through a gas. At any particular moment, the wave consists of layers of compressed gas at a pressure slightly higher than ambient pressure, and rarefied gas at a pressure slightly lower than ambient pressure. Figure 5.20 illustrates the variation of the pressure/density within the wave.

Notice that only one type of sound wave, a longitudinal pressure wave, is able to propagate in gas. This is in contrast with solids, which can support three types of sound wave: one longitudinal and two transverse. This is because in order for a wave to propagate, there must be a restoring force which acts to reverse any strain in the material. For gases, there is no restoring force for so-called shear strains, and so transverse waves cannot be sustained.

Some illustrations and a more rigorous discussion of wave propagation are given in Appendix A2.

Sound travels considerably slower through gases than through solids or liquids. As shown in Table 5.14, the maximum speed at 0°C is approximately 1000 ms^{-1} for the gases with the lightest molecules, helium and hydrogen. This may be

compared with the values for solids (Table 7.6) and liquids (Table 9.5) which are typically of the order of 3000 ms^{-1}.

One important datum not included in Table 5.14 is for the speed of sound in air. At 1.0 kHz, in dry air with 0.03 % CO_2, at a temperature of 273.15 K and a pressure of 101325 Pa, the speed of sound is 331.45 ± 0.05 ms^{-1}.

Figure 5.19 shows a graph of c_{sound} versus M, the relative molecular mass of the molecules of the gas. It is fairly clear that the mass of the molecules of the gas plays a significant role in determining the speed of sound. Table 5.14 does not contain enough data to allow a systematic study of the effects of temperature and other factors on the speed of sound. However, we can obtain some clues about which other factors affect the speed of sound by looking in detail at the shaded entries in the table. These have at least one other 'partner entry' referring either to a gas with the same molecular mass, or to the same gas but at a different temperature. We will examine each of the shaded entries in turn.

Extract from Table 5.14

Gas		*M*	*T*(K)	c_{sound} (ms^{-1})
Helium	He	4.0	273.2	971.9
Deuterium	D$_2$	4.0	273.2	890

The data for helium and deuterium are taken at the same temperature, but the sound velocities differ by $\approx$ 9%. So there must be a factor other than temperature and molecular weight affecting c_{sound}.

Extract from Table 5.14

Gas		*M*	*T*(K)	c_{sound} (ms^{-1})
Water (steam)	H$_2$O	18.0	373.2	473
Water (steam)	H$_2$O	18.0	407.2	494

The data for steam show an increase in the speed of sound with increasing temperature.

Extract from Table 5.14

Gas	*M*	*T*(K)	c_{sound} (ms^{-1})
Nitrogen, N$_2$	28.0	273.2	337
Carbon monoxide, CO	28.0	273.2	337
Ethylene, C$_2$H$_4$	28.0	273.2	318

Table 5.14 The speed of sound in a selection of gases listed in order of increasing molecular mass *M* in atomic mass units u. The shaded entries in the table are gases that have a 'partner' gas in the table with the same molecular mass. See the text for more details.

Gas	*M*	*T*(K)	c_{sound} (ms^{-1})
Hydrogen, H$_2$	2.0	273.2	1286
Helium, He	4.0	273.2	971.9
Deuterium, D$_2$	4.0	273.2	890
Methane, CH$_4$	16.0	273.2	430
Ammonia, NH$_3$	18.0	273.2	415
Water (steam), H$_2$O	18.0	373.2	473
Water (steam), H$_2$O	18.0	407.2	494
Fluorine, F$_2$	19.0	373.2	332
Heavy Water (steam), D$_2$O	20.0	373.2	451
Neon, Ne	20.2	273.2	434
Acetylene, C$_2$H$_2$	26.0	273.2	329
Nitrogen, N$_2$	28.0	273.2	337
Carbon monoxide, CO	28.0	273.2	337
Ethylene, C$_2$H$_4$	28.0	273.2	318
Ethane, C$_2$H$_6$	30.0	283.2	308
Ethane, C$_2$H$_6$	30.0	304.2	316
Nitric oxide, NO	30.0	283.2	324
Nitric oxide, NO	30.0	289.2	334
Oxygen, O$_2$	32.0	303.2	332
Methanol, CH$_3$OH	32.0	370.2	335
Hydrogen sulphide, H$_2$S	33.1	273.2	310
Hydrogen chloride, HCl	36.5	273.2	296
Argon, Ar	40.0	273.2	307.8
Nitrous oxide, N$_2$O	44.0	298.2	268
Propane, C$_3$H$_8$	44.0	273.2	238
Carbon dioxide, CO$_2$	44.0	273.2	259
Ethanol, C$_2$H$_5$OH	46.0	326.2	258
Sulphur dioxide, SO$_2$	64.0	273.2	211
Chlorine, Cl$_2$	70.9	293.2	219
Carbon disulphide, CS$_2$	76.0	273.2	192
Benzene, C$_6$H$_6$	78.0	273.2	177
Bromine, Br$_2$	79.9	331.2	149
Hydrogen bromide, HBr	80.9	273.2	200
Krypton, Kr	83.8	273.2	213
Cyclohexane, C$_6$H$_{12}$	84.0	303.2	181
Hydrogen iodide, HI	127.9	273.2	157
Xenon, Xe	131.3	273.2	170
Sulphur hexafluoride, SF$_6$	146.0	284.2	133
Carbon tetrachloride, CCl$_4$	153.8	370.2	145
Iodine, I$_2$	263.8	453.2	138

The data for nitrogen and carbon monoxide are taken at the same temperature, and have the same speed of sound: the level of agreement is striking. However ethylene with the same molecular mass and at the same temperature has a sound velocity about 6% lower. Let us hypothesise that the number of atoms in the gas molecule is also a factor affecting c_{sound} .

Reviewing the data so far we have some evidence that:
- c_{sound} is increased at higher temperatures
- c_{sound} is decreased if a molecule of the gas has many atoms.

These hypotheses are consistent with all the data so far. Let us examine the rest of the data:

Extract from Table 5.14

Gas	*M*	*T*(K)	c_{sound} (ms^{-1})
Ethane, C_2H_6	30.0	283.2	308
Ethane, C_2H_6	30.0	304.2	316
Nitric oxide, NO	30.0	283.2	324
Nitric oxide, NO	30.0	289.2	334

We now have data that allow comparison of the effects of both temperature (over a limited range) and molecular complexity. We see that these data

Figure 5.22. A graph of c_{sound} (ms^{-1}) versus *M*, the relative molecular mass (u). The graph seems to show that the molecular weight of the molecules of the gas plays a significant role in determining the velocity of sound through the gas.
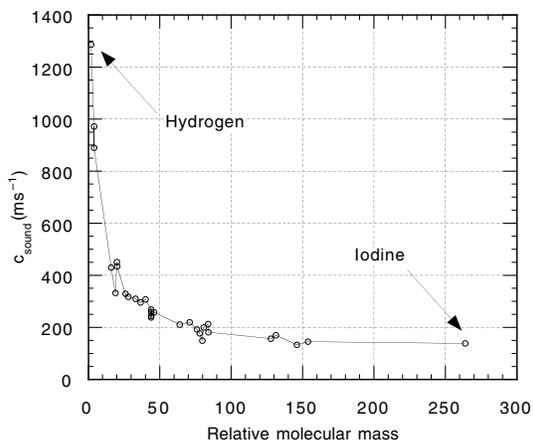
are again consistent with the hypotheses above: the more complex molecule has the lower c_{sound}; the higher temperature data have higher values of c_{sound}.

Extract from Table 5.14

Gas	*M*	*T*(K)	c_{sound} (ms^{-1})
Oxygen, O_2	32.0	303.2	332
Methanol, CH_3OH	32.0	370.2	335

These data correspond both to different numbers of atoms per molecule, and to different temperatures. The data are not inconsistent with the hypotheses because the effects of temperature and molecular complexity could be compensating one another.

Extract from Table 5.14

Gas	*M*	*T*(K)	c_{sound} (ms^{-1})
Nitrous oxide, N_2O	44.0	298.2	268
Propane, C_3H_8	44.0	273.2	238
Carbon dioxide, CO_2	44.0	273.2	259

Again the hypotheses are confirmed. Comparing propane and carbon dioxide we see that the molecule with more atoms has the lower c_{sound}. Comparing nitrous oxide and carbon dioxide, both triatomic molecules, we see that the substance at the higher temperature has the greater c_{sound}. Thus, our hypotheses set out above seem to be confirmed by all the data in Table 5.14. There is little data available on the dependence of the speed of sound on pressure, because, surprisingly, the speed of sound is broadly independent of the pressure.

So the questions raised by our preliminary examination of the experimental data on the velocity of sound in gases are:
- Why is the speed of sound greater at higher temperatures, but roughly independent of pressure?
- Why is the speed of sound reduced by molecular complexity, i.e. for different gases of the same molecular mass, sound travels faster in the gas with the least complex molecules?
- Why is the speed of sound higher in gases with low molecular mass?
- Why is the speed of sound in gases at about atmospheric pressure around a few hundred metres per second?

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5.5.2 Understanding the data on the speed of sound

Appendix A2 contains a derivation of an expression for the speed of sound in any medium: solid, liquid or gas. There we predict that the speed of sound, c_{sound} in a gas is given in terms of its mass density ρ, and either the compressibility K or the bulk modulus B:

$$c_{\text{sound}} = \sqrt{\frac{1}{K\rho}}$$
$$= \sqrt{\frac{B}{\rho}} \qquad (5.89)$$

We can see that this prediction makes physical sense by considering a region of compressed gas. The ease with which the gas will 'spring back' to try to restore ambient pressure depends on the quantities in Equation 5.89.

- It depends on the compressibility of the gas K because if the gas is easily compressed, then the restoring force will be small, i.e. the gas is not very 'springy'. Thus, highly compressible gases will tend to have a low speed of sound.
- It depends on the density of the gas ρ because if the density of the gas is high then the mass per unit volume will be high. This means that a given restoring force will produce less acceleration of the gas. Thus dense gases will 'spring back' slower and hence tend to have lower speed of sound.

The compressibility and its inverse ($1/K$), the bulk modulus, were discussed at some length in §5.4. They are defined as:
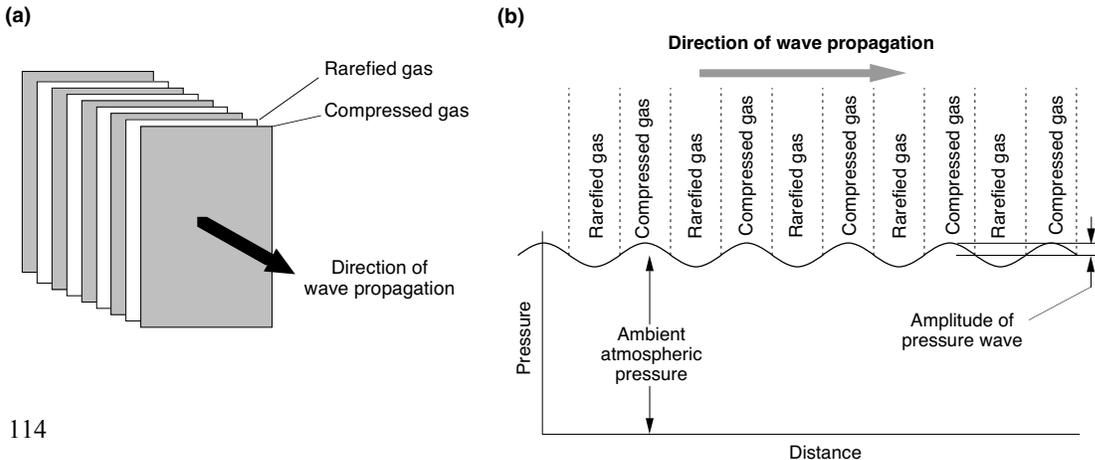
$$K = -\frac{1}{V}\frac{\partial V}{\partial P} \quad \text{and} \quad B = -V\frac{\partial P}{\partial V} \qquad (5.90)$$

There we saw that compressibility has different values depending on whether the gas is compressed at constant temperature, or whether the gas is isolated during the compression, in which case the temperature may rise on compression. In the former case the compressions are said to be *isothermal*; in the latter, the compressions are said to be *adiabatic*. The value of K corresponding to each of these types of compression is discussed below.

Adiabatic or isothermal compressions?

It is not obvious at first sight which type of compression takes place in a sound wave. We are not aware of temperature oscillations when a sound wave passes by, but this doesn't mean they don't exist: if they are small and oscillating at several hundred times per second, we may not notice them. In order to decide which type of compression takes place in a sound wave we will work out the predicted speed of sound in air (Equation 5.89) for each of the two cases in turn. Then by comparing the predictions with experiment we will see that it is possible to deduce which type of compression actually occurs. We saw in §5.4 that the

Figure 5.23 Two illustrations of the variation of pressure within a sound wave at a given time. (a) A perspective drawing of planes of constant pressure: shaded planes represent compressed regions of the gas, un-shaded planes represent rarefied regions of gas. (b) The pressure as a function of position in a sound wave. The pressure amplitude of a sound wave rarely exceeds 1% of the ambient pressure.

(a)

Rarefied gas
Compressed gas
Direction of wave propagation

(b)

Direction of wave propagation

Rarefied gas | Compressed gas | Rarefied gas | Compressed gas | Rarefied gas | Compressed gas | Rarefied gas | Compressed gas | Rarefied gas | Compressed gas

Pressure

Ambient atmospheric pressure

Amplitude of pressure wave

Distance

isothermal compressibility of an ideal gas is:

$$K_{iso} = \frac{1}{P} \qquad (5.66^*)$$

where P is the pressure of the gas and the subscript 'iso' indicates that compression is isothermal. Similarly, we saw that the adiabatic compressibility of a ideal gas is given by:

$$K_{ad} = \frac{1}{\gamma P} \qquad (5.66^*)$$

where γ is the ratio of the principal heat capacities C_P/C_V and the subscript 'ad' indicates that compression is adiabatic.

Taking the Equations 5.66 for K_{iso} and K_{ad} we can compare predictions for the speed of sound with experimental values. For air under the standard conditions of $0\,°C$ (273.15 K) and pressure 1.013×10^5 Pa we find (§5.2) that the density of air is 1.293 kg m^{-3}. Taking a value of $\gamma = 1.4$ (Table 5.8) we can predict values for the speed of sound assuming either isothermal or adiabatic compressions in the sound wave.

$$c_{sound} = \sqrt{\frac{1}{K\rho}} \qquad (5.91)$$

Isothermal prediction

$$c_{sound} = \sqrt{\frac{1}{K_{iso}\rho}}$$

$$= \sqrt{\frac{P}{\rho}}$$

$$= \sqrt{\frac{1.013 \times 10^5}{1.293}}$$

$$c_{sound} = 279.9 \text{ m s}^{-1}$$

Adiabatic prediction

$$c_{sound} = \sqrt{\frac{1}{K_{ad}\rho}}$$

$$= \sqrt{\frac{\gamma P}{\rho}}$$

$$= \sqrt{\frac{1.4 \times 1.013 \times 10^5}{1.293}}$$

$$c_{sound} = 331.2 \text{ m s}^{-1}$$

Comparing these predictions with the experimental value of 331.45 ± 0.05 ms^{-1} clearly favours the theory in which the compressions of the gas are adiabatic. In retrospect, we can understand this fairly easily. The wavelength of a sound wave is typically of the order of one metre at a frequency of 1 kHz. If the compressions and rarefactions of the wave are adiabatic, then there will be small temperature differences created in the wave. In order for the compressions and rarefactions of the wave to be isothermal, heat would have to flow between compressed and rarefied regions of the wave in about half a cycle of the sound wave. The small temperature differences in the wave would have to equalise over a distance of half a wavelength (roughly 0.5 metre) in around 0.5 ms. For a poor thermal conductor such as a gas this is unrealistic. Thus for all sound waves in gases over all practical frequencies, the compressions and rarefactions are adiabatic, and the speed of sound is given by:

$$c_{sound} = \sqrt{\frac{\gamma P}{\rho}} \qquad (5.92)$$

The temperature oscillations associated with sound waves are considered in Exercise P34 at the end of this Chapter and Exercise 6 in Chapter 12.

Comparison with experiment

The pressure and temperature dependence of the speed of sound

Equation 5.92 allows us to understand immediately why the speed of sound is not significantly dependent on pressure: the density of a gas is proportional to its pressure. Thus changing the pressure of a gas affects the compressibility of a gas, but changes its density by an exactly compensating amount. This lack of pressure dependence becomes clearer if we rearrange Equation 5.92 by substituting for P and ρ: this allows direct comparison with the results of Table 5.14. We use the perfect gas equation to substitute for both $P = zRT/V$, and for $\rho = zM/V$ (where z/V is the number of moles per unit volume, and M is the mass in kg of one mole of gas). We find the speed of sound may thus be expressed as:

$$c_{sound} = \sqrt{\frac{\gamma zRT}{V} \times \frac{V}{zM}}$$

$$= \sqrt{\frac{\gamma RT}{M}} \qquad (5.93)$$

Equation 5.93 shows that if the temperature of the

Example 5.11

What is the predicted speed of sound in helium at 0 °C?

Equation 5.93 tells us that:

$$c_{sound} = \sqrt{\frac{\gamma RT}{M}}$$

The data for helium is:

$\gamma = 1.63$ (from Table 5.8)

$R = 8.31$ J K^{-1} mol^{-1}

$T = 273.1$ K

$M = 4.0 \times 10^{-3}$ kg

So we find:

$$c_{sound} = \sqrt{\frac{1.63 \times 8.31 \times 273.1}{4.0 \times 10^{-3}}}$$

$$= 961.3 \ \text{m s}^{-1}$$

This compares with the experimental value (Table 5.14) of 971.9 ms^{-1} an error of around 1 %.

gas is kept constant, then we expect to find no variation with pressure.

It is actually rather hard to compare the predictions of Equation 5.93 with experiment. It might seem to be a fairly straightforward task to look up the values of γ and M for the gas, and then note the temperature T at which c_{sound} was measured. However the tables of c_{sound} are commonly compiled by assuming that Equation 5.93 holds true and then deducing γ from measurements of c_{sound} and T. Hence we cannot then use the γ values to check the values of c_{sound}! However, we can look

at questions raised by examination of the data, with the aim of checking the overall consistency of Equation 5.93 in describing gases of different types of molecules.

The effect of molecular complexity

We saw in §5.3.2 that the number of degrees of freedom of a molecules could be determined from measurements of γ using Equation 5.44:

$$p = \frac{2}{\gamma - 1} \qquad (5.44*)$$

This predicts that more complex molecules have more degrees of freedom (p) and hence lower values of c_{sound}. Thus through Equation 5.93:

$$c_{sound} = \sqrt{\frac{\gamma RT}{M}} \qquad (5.93*)$$

we expect gases of more complex molecules to have a lower speed of sound. We can examine the dependence on p and γ by looking for gases which have the same molecular mass M but different numbers of molecules, and hence different values of γ. Searching through Table 5.14 we see that we have several examples of which I have chosen just the two whose details are set out in Table 5.15 below.

For the monatomic or diatomic molecules, the agreement is excellent if we assume that at around room temperature there are two accessible rotational degrees of freedom, but no vibrational degrees of freedom. However, for more complex molecules such as ethylene (CH_2CH_2), it is difficult to arrive at an estimate for γ which is any-

Table 5.15 Details of gases whose molecules have relative molecular mass of 4 and 28. The table enables a detailed comparison of theoretical expectations and experimental results for the dependence of the speed of sound upon molecular complexity.

Gas	M	Number of atoms per molecule	Expected γ	T(K)	c_{sound} (theoretical) $\sqrt{(\gamma RT/M)}$	c_{sound} (experimental) Table 5.14
He	4.0	1	1.667 (p=3)	273.2	972.8	971.9
D_2	4.0	2	1.400 (p=5)	273.2	891.5	890.0
N_2	28	2	1.400 (p=5)	273.2	336.9	337.0
CO	28	2	1.400 (p=5)	273.2	336.9	337.0
CH_2CH_2	28	6	1.2 (p=10?)	273.2	≈312	318.0

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thing more than a guess. In order to improve on guess work we would need to carefully calculate the molecular dynamics of an ethylene molecule, a task well beyond the scope of this book.

Why gamma?

It is interesting to ask why γ, the ratio of the heat capacities C_P / C_V, is involved in an expression for the speed of sound. The answer lies in the effect that extra degrees of freedom have on the magnitude of the temperature oscillations in the sound wave. We can see how this happens by considering the compression/expansion of the gas that occurs in the wave. Since the compression/expansion is adiabatic, the gas is successively heated/cooled. By the equipartition theorem (§2.5), the increased/decreased internal energy of the gas caused by the compression/expansion is shared equally amongst the p accessible degrees of freedom of the molecules. So if the average energy of each molecule is increased/decreased by Δu, the temperature rise/fall ΔT will be such that $\Delta u = 0.5 p k_B \Delta T$. So ΔT is given by:

$$\Delta T = \frac{\Delta u}{0.5 p k_B} \tag{5.94}$$

Equation 5.94 implies that ΔT is inversely proportional to p. So, for example, if $p = 3$ then the temperature rise/fall ΔT will be larger than if $p = 5$

Figure 5.24. Graph of the speed of sound (m s^{-1}) versus $1/\sqrt{A}$ where A is the molecular mass in atomic mass units u. The data show a clear linear relationship as indicated by the least-squares fit shown as a line on the graph.
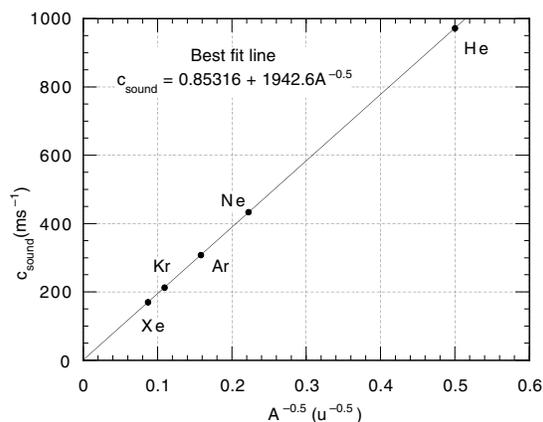
because the energy of compression/expansion is shared amongst fewer degrees of freedom. This temperature rise/fall causes the gas pressure to increase/decrease more quickly as its volume is reduced/enlarged. In other words, having fewer degrees of freedom increases the magnitude of the temperature oscillations that accompany the pressure oscillations in the sound wave. The temperature oscillations act to oppose the pressure oscillations that cause them, and so make the gas less compressible. And the larger the temperature rise, the greater the reduction in compressibility. Thus if two types of gas have molecules of the same mass, the gas whose molecules have fewer internal degrees of freedom will be 'springier'.

Dependence of c_{sound} on M

The strong dependence of c_{sound} on the molecular mass M was clearly shown in Figure 5.22. With hindsight we can now see how this dependence arises, and by plotting c_{sound} versus $M^{-\frac{1}{2}}$ we should find that the data lie close to a straight line through the origin. Further, if we draw this plot using a set of gases for which γ is the same we should be able to reduce the apparently random scatter on Figure 5.22. Figure 5.24 shows such a plot for the monatomic gases for which we are confident from analysis of heat capacity data that there are exactly three degrees of freedom, i.e. $p = 3$.

If we substitute the expression for γ (Equation 5.40) into Equation 5.93, and then separate out the dependence on molecular mass, we find:

$$c_{sound} = \sqrt{\left[1 + \tfrac{2}{3}\right] R T} \times M^{-\frac{1}{2}} \tag{5.95}$$

Now M is the mass of one mole of gas i.e. N_A times the mass of a molecule, Au. Evaluating this yields:

$$\begin{aligned} \text{slope} &= \sqrt{\left[1 + \tfrac{2}{3}\right] R T} \\ &= \sqrt{\left[1 + \tfrac{2}{3}\right] \frac{8.314 \times 273.1}{6.022 \times 10^{23} \times 1.661 \times 10^{-27}}} \\ &= 1945.1 \ \text{m s}^{-1} \text{kg}^{-1/2} \end{aligned} \tag{5.96}$$

which differs from the experimental slope (1942.6 m s^{-1} kg$^{-1/2}$) by $\approx 0.13\%$ i.e. less than two

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parts in 1000. Clearly we understand all the factors at play in determining the speed of sound, in monatomic gases at least.

Order of magnitude of c_{sound}

Why does c_{sound} have the value it has for a gas? One answer is to refer to Equation 5.93 and its derivation and say 'it just does'. Another answer is to consider whether we could have said anything about the speed of sound in a gas before considering the derivation of Equation 5.93. In fact we can establish a rough upper limit for the maximum possible speed of sound in a gas. It is reasonable to suppose that *a sound wave cannot travel through a gas more quickly than the molecules of the gas are moving*. We can see this by noting that if we have a compressed region of gas, the pressure changes that constitute the sound wave clearly cannot move faster than the fastest molecules, and will probably move at a speed related to the average speed of molecules. Since the average speed of molecules in air at room temperature is ≈ 500 m s^{-1}, and the speed of sound is ≈ 340 m s^{-1}, we can see that there is some experimental support for this idea. We can in fact do better than this and convert Equation 5.93 for c_{sound} into a relationship between c_{sound} and $\overline{v^2}$.

First, we recall that T is defined by the fact that the average energy per accessible degree of freedom is $0.5k_BT$. So for the three degrees of freedom of the kinetic energy of the gas we have:

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}k_BT \qquad \text{(4.23 and 5.97)}$$

Substituting for T in Equation 5.93 yields:

$$c_{sound} = \sqrt{\frac{\gamma RT}{M}}$$
$$= \sqrt{\frac{\gamma Rm\overline{v^2}}{3k_BM}} \qquad (5.98)$$

Now M is the mass in kilograms of one mole of the gas, i.e. $M = N_Am$ where m is the mass of one molecule. Remembering that by definition $R = k_BN_A$ we have:

$$c_{sound} = \sqrt{\frac{\gamma Rm\overline{v^2}}{3k_BM}}$$
$$= \sqrt{\frac{\gamma Rm\overline{v^2}}{3k_BN_Am}} = \sqrt{\frac{\gamma \overline{v^2}}{3}} \qquad (5.99)$$
$$= \left[\sqrt{\frac{\gamma}{3}}\right]\sqrt{\overline{v^2}} = \left[\sqrt{\frac{\gamma}{3}}\right]v_{RMS}$$

Since γ ranges from roughly 1.7 to 1, c_{sound} should vary between 58% and 75% of the root mean square speed of the molecules.

5.7 Electrical properties

The electrical properties of gases are complex, and difficult to describe succinctly. However we can simplify our discussion by dividing the properties of the gas into behaviour observed in weak electric fields and strong electric fields.

In this section we will look mainly at the properties of gases under weak, static electric fields. The term 'static' in this context refers to electric fields varying at frequencies much lower than the frequencies of molecular vibration and rotation, i.e. less than approximately 10^9 Hz. The response to electric fields varying at infrared frequencies or higher is discussed in the §5.8 on the optical properties of gases.

We will look briefly at the phenomenon of electrical breakdown that occurs in strong electric fields in §5.7.3.

5.7.1 Data on the electrical properties of gases in weak electric fields

The application of a weak electric field to a gas does not produce any dramatic effects. A 'weak'

electric field may be defined as one which is less than the *dielectric strength* of the gas. The dielectric strength varies with temperature and pressure, but at around room temperature and normal atmospheric pressure, it is of the order of 10^6 volts per metre ($V\,m^{-1}$).

For electric fields less than the dielectric strength of the gas it is not a trivial matter to detect *any* effect of the electric field on the gas! To a first approximation we may ignore the presence of a gas in a region of weak electric field and treat the situation as if there were no matter present, i.e. as a vacuum. However, careful experiments show that there is a small effect which may be described in terms of the *dielectric constant*, ε (§2.3.2). The dielectric constant has the value unity for a vacuum and is often tabulated as ($\varepsilon - 1$). Tabulations in this form emphasise the difference between the presence and absence of molecules of the substance. For gases, ε usually differs only slightly from unity with typical values (Table 5.16) in the range 1.0001 to 1.001.

A gas weakens the interaction between electric charges by reducing the electric field around a charge, and so we find $\varepsilon \geq 1$. The quantity ($\varepsilon - 1$) is tabulated for various gases around room temperature and atmospheric pressure in Table 5.16.

Table 5.16 and Figure 5.25(a) both show a good deal of apparently random variability. However despite this, it is possible to discern some systematic trends in the data. From Figure 5.22 it appears that, with striking exceptions, there is a weak trend towards larger dielectric constants in gases with large molecules. Further, in the two cases where Table 5.16 has data for a gas at several temperatures (carbon dioxide and ammonia), the data show a systematic decrease of ($\varepsilon - 1$) with increasing temperature.

Figure 5.25(b) shows the variation of ($\varepsilon - 1$) for carbon dioxide as a function of pressure at a temperature of 100 °C. We see that ($\varepsilon - 1$) depends linearly on the pressure, with a slight sign of curvature at the highest pressures.

The main questions raised by our preliminary examination of experimental data on the dielectric

Table 5.16 The relative dielectric permittivity ε of various gases at atmospheric pressure (1.013×10^5 Pa). For pressures below atmospheric pressure ε varies linearly with pressure. The relative permittivity of vacuum is exactly 1, and all the gases in the table have values of ε within 1% of unity. The table shows the value of $10^4\,(\varepsilon - 1)$, which clearly shows the variation between gases. The table also shows the relative molecular mass of the molecules of the gas.

Different experimenters find different values of ε and the data for $10^4\,(\varepsilon - 1)$ should all be treated as accurate to only about 10%. The entry for ethanol has two alternative values to indicate two particularly divergent values for $10^4\,(\varepsilon - 1)$. For other entries I have taken averages of tabulated results, or ignored entries in tables that were clearly in error.

The data refer to values obtained with electric fields oscillating at radio frequencies, $\approx 10^6$ Hz. The shaded entries in the table, i.e. helium, hydrogen, argon, oxygen, nitrogen, and air, are typical results for ε valid from DC up to optical frequencies $\approx 10^{15}$ Hz. The variation over that range is within ±2 of the least significant figure in the table.

Gas	M	T (°C)	$10^4(\varepsilon - 1)$
Monatomic gases			
Helium, He	4.0	20	0.65
Neon, Ne	20.2	0	1.3
Argon, Ar	40.0	20	5.16
Mercury, Hg	200.6	180	7.4
Mercury, Hg	200.6	180	7.4
Diatomic gases			
Hydrogen, H_2	2.0	0	2.72
Hydrogen, H_2	2.0	20	2.54
Nitrogen, N_2	28.0	20	5.47
Oxygen, O_2	32.0	20	4.94
Air (dry, no CO_2)	28.8	20	5.36
Carbon monoxide, CO	28.0	23	6.92
Triatomic gases			
Carbon dioxide, CO_2	44.0	0	9.88
Carbon dioxide, CO_2	44.0	20	9.22
Carbon dioxide, CO_2	44.0	100	7.23
Nitrous oxide, N_2O	44.0	25	11
Water (steam) H_2O	18.0	100	60
Polyatomic gases			
Ethane, C_2H_6	30.0	0	15
Benzene, C_6H_6	65.0	100	32.7
Methanol, CH_3OH	32.0	100	57
Ethanol, C_2H_5OH	44.0	100	61 or 78
Ammonia, NH_3	18.0	0	8.34
Ammonia, NH_3	18.0	100	4.87

permittivity of gases are:

- Why does the value of $(\varepsilon - 1)$ depends linearly on pressure?
- Why does the value of $(\varepsilon - 1)$ decreases with increasing temperature?
- Why does the value of $(\varepsilon - 1)$ depend on the type of molecule of the gas? There is some indication that $(\varepsilon - 1)$ may be larger for larger molecules. However, some molecules display particularly large dielectric constants.
- Why, under the action of weak electric fields, is the relative dielectric permittivity $(\varepsilon - 1)$ so close to unity?

5.7.2 Understanding the electrical properties of gases in weak electric fields

In order to understand the phenomena described above, we must first develop a theory of the dielectric constant of a gas. We do this in the following sections and then later proceed to compare the predictions of the theory with experiment.

Background theory

The theory we develop below models a gas as a collection of molecules which do not interact with one another. Thus the properties of the gas will depend directly on just two factors: the response of individual molecules to an applied electric field, and the number density of the molecules. Our previous discussion of ideal gas theory gives us the tools we need to understand how to calculate the number density of molecules. From Example 4.2 we can write that:

$$n = \frac{P}{k_B T} \tag{5.100}$$

So let us now turn our attention to the response of individual molecules to an applied electric field. It is found that the responses fall into two distinct classes:

- Atoms or molecules which, in the absence of an applied electric field, possess no *electric dipole moment*. Such atoms and molecules are called *non-polar*. All atoms are non-polar, but only a few molecules (those with a high degree of symmetry such as N_2 or O_2) fall into this category.

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Figure 5.25 (a) The data of Table 5.16 showing $10^4(\varepsilon - 1)$ as a function of the mass of the molecules of the gas. Uncertainty indications represent ±10% of the values in the Table 5.16. The value for Mercury (Hg) has not been plotted because its large molecular mass distorts the scale of the graph. (b) The variation of the dielectric constant plotted as $10^4(\varepsilon - 1)$ for carbon dioxide as a function of pressure at a temperature of 100 °C. We see that $(\varepsilon - 1)$ is depends linearly on the pressure, with a slight sign of curvature at the highest pressures.

(a)

(b)
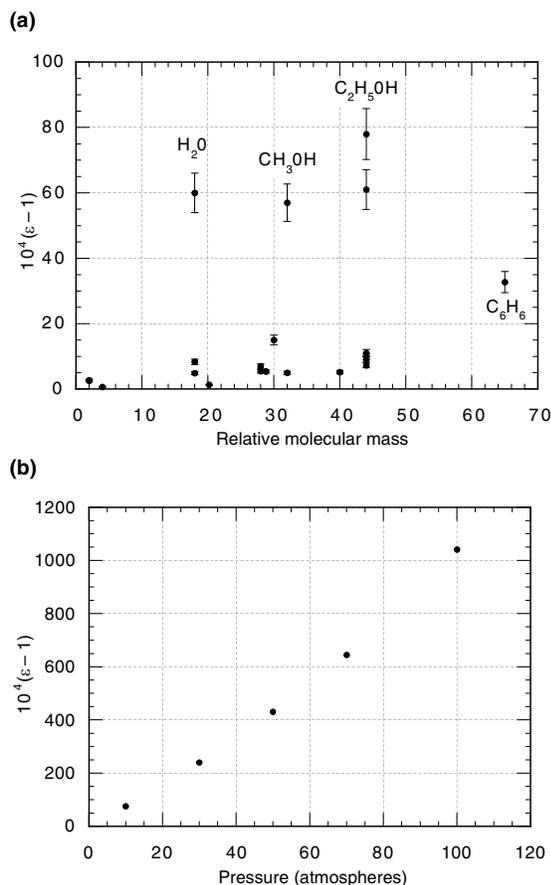
- Molecules which, in the absence of an applied electric field, possess a finite *electric dipole moment*. Such atoms and molecules are called *polar*. Most molecules fall into this category, though the magnitude of their dipole moment varies considerably from one type of molecule to another.

Let us examine the cases of non-polar and polar molecules in turn.

Non-polar molecules

The situation when a weak applied field is applied to an atom (or molecule) with no intrinsic electric dipole moment is illustrated in Figure 5.26. The electric field perturbs the electronic charge distribution around the nucleus of each atom, drawing the electrons slightly to one side of the nucleus. Thus an electric dipole moment is induced on each atom and the atoms are said to be *polarised*. However the atoms are still electrically neutral and so there is no net force on them in the applied electric field. The magnitude of the induced dipole moment p_i is given by the product of the total charge on the nucleus Ze multiplied by Δx, the distance between the centres of symmetry of the electronic and nuclear charge distributions. In general Δx is extremely small, typically a small fraction of an atomic diameter. Atomic dipole moments are sometimes tabulated in units of 10^{-30} C m, called *debye* units.

Physically we can see that the extent of the disturbance of the charge distribution depends on the ratio of the *applied* electric field to the *internal* field. Usually this ratio is extremely small (Example 2.1)

Polar molecules

The situation when a weak external field is applied to a molecule which has a permanent electric dipole moment p_p is illustrated in Figure 5.27.

Commonly, the permanent electric dipole moment p_p is much larger than the induced electric dipole moment p_i. In this case the main effect of the electric field is to rotate the molecule. Recall (§2.2.3) that the energy of an electric dipole **p** in a field **p** is $-\mathbf{p} \cdot \mathbf{E}$ and that the torque on an electric dipole **p** in a field **E** is $\Gamma = \mathbf{p} \times \mathbf{E}$.
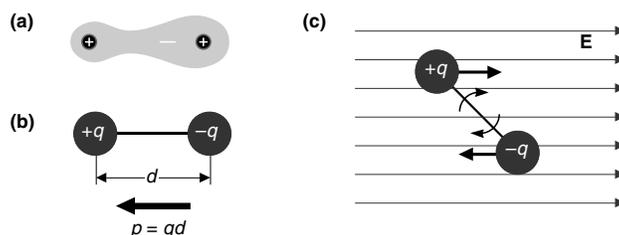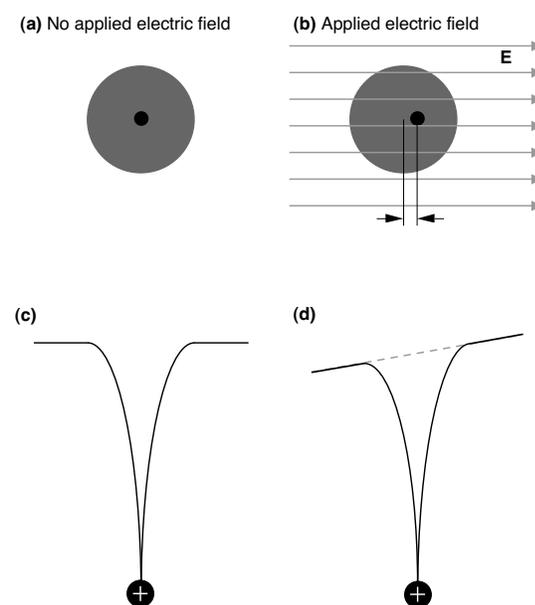
Figure 5.26 The effect of an applied electric field on a non-polar molecule.

Diagrams (a) and (c) refer to the situation when there is no electric field applied. In (a) the charge distribution of the electrons is symmetrically arranged around the nucleus. This is because the coulomb potential energy of an electron, which varies approximately as $1/r$ as shown in (c), is symmetric.

Diagrams (b) and (d) refer to the situation when there is an external electric field applied. In (b) the charge distribution of the electrons is now asymmetrically arranged around the nucleus. This is because the coulomb potential energy of an electron (d) is now asymmetric.

The extent of the disturbance of the charge distribution depends on the ratio of the applied electric field to the internal field. Usually this ratio is extremely small (Example 2.1).

(a) No applied electric field

(b) Applied electric field

(c)

(d)

Figure 5.27 (a) Schematic illustration of a charge distribution which possesses a dipole moment. (b) For many purposes, a real molecule may be modelled as a permanent dipole moment. (c) The forces acting on a dipole moment form a torque that twists the molecule until **p** lies parallel to **E**.

(a)

(b)

$+q$ — $-q$

d

$p = qd$

(c)

E

$+q$

$-q$

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Dielectric constant of a non-polar gas

We start off by assuming that the electric field $\mathbf{E}$ around each molecule induces a electric dipole moment $\mathbf{p}_i$ on the molecule, given by:

$$\mathbf{p}_i = \alpha \mathbf{E} \qquad (2.12^* \ \& \ 5.101)$$

where α is called the *molecular polarisability*. If there are n such molecules per unit volume then the total polarisation per unit volume $\mathbf{P}$ is:

$$\begin{aligned} \mathbf{P} &= n\mathbf{p}_i \\ &= n\alpha\mathbf{E} \end{aligned} \qquad (5.102)$$

Now the average electric field $\mathbf{E}$ around each molecule is slightly reduced from the applied electric field $\mathbf{E}_{app}$ according to two relations. The first is:

Example 5.12

In an applied electric field, the centre of electronic symmetry of an argon atom moves a distance of around 10^{-13} m away from the nucleus. What is the magnitude of the electric dipole moment induced on the atom?

An argon nucleus has a charge $+18e$ and the electrons have a total charge $-18e$. If we assume that the entire charge distribution moves rigidly by a distance 10^{-13} m then the induced electric dipole moment is (§ 2.2.3):

$$\begin{aligned} p &= qd \\ &= 18 \times 1.6 \times 10^{-19} \times 10^{-13} \\ &= 2.88 \times 10^{-31} \ \text{C m} \\ &= 0.288 \ \text{Debye units} \end{aligned}$$

In fact, it is unlikely that the entire charge distribution would shift rigidly in the applied field. The electric field of the nucleus falls of as $\sim 1/r^2$ and so is much weaker in the outer regions of the atom than near the nucleus. (Figure 5.26) The electrons respond to the *total electric field* due to both the nucleus and the applied electric field. Near the nucleus, the applied electric field is a small fraction of the total electric field, but for electrons in the outer regions of the atom, the applied electric field may be a significant fraction of the total field. Thus, the outer (valence) electrons tend to move more than the inner electrons in an applied field. These considerations would reduce the actual dipole moment below that predicted above.

$$\mathbf{E} = \frac{\mathbf{E}_{app}}{\varepsilon} \qquad (5.103)$$

which defines the dielectric constant ε. The second expression defines the polarisation (*Bleaney and Bleaney*: see §1.4.1 for a detailed reference):

$$\mathbf{E} = \mathbf{E}_{app} - \frac{\mathbf{P}}{\varepsilon_o} \qquad (5.104)$$

The minus sign arises because the induced electric field $\mathbf{P}/\varepsilon_o$ at a molecule due to all the other molecules opposes the applied field. Combining Equation 5.103 with Equation 5.104 we have:

$$\frac{\mathbf{E}_{app}}{\varepsilon} = \mathbf{E}_{app} - \frac{\mathbf{P}}{\varepsilon_o} \qquad (5.105)$$

Substituting for $\mathbf{P}$ using Equation 5.102 we find:

$$\frac{\mathbf{E}_{app}}{\varepsilon} = \mathbf{E}_{app} - \frac{n\alpha\mathbf{E}}{\varepsilon_o} \qquad (5.106)$$

Neglecting the small difference between the applied field $\mathbf{E}_{app}$ and average field around each molecule $\mathbf{E}$ we arrive at:

$$\frac{1}{\varepsilon} = 1 - \frac{n\alpha}{\varepsilon_o} \qquad (5.107)$$

which simplifies to:

$$\begin{aligned} \varepsilon &= \left[1 - \frac{n\alpha}{\varepsilon_o} \right]^{-1} \\ &\approx \left[1 + \frac{n\alpha}{\varepsilon_o} + \ldots \right] \end{aligned} \qquad (5.108)$$

where we have used the fact that $n\alpha/\varepsilon_o$ is very much less unity. We finally arrive at:

$$\varepsilon - 1 = \frac{n\alpha}{\varepsilon_o} \qquad (5.109)$$

This final expression may be compared with the exact expression for $\varepsilon - 1$ obtained after considerably more trouble (*Bleaney and Bleaney*) by *Clausius and Mossotti*:

$$\varepsilon - 1 = \frac{n\alpha}{\varepsilon_o}\left[\frac{\varepsilon+2}{3}\right] \qquad (5.110)$$

Expressions 5.109 and 5.110 yield a prediction for $\varepsilon - 1$ expressed in terms of the number density of molecules n, the permittivity of free space ε_o, and the molecular polarisability α. The molecular polarisability may (with some difficulty) be calculated from first principles for each type of molecule. Its magnitude depends on the ease with which the electronic charge around a molecule may be deformed by an applied electric field.

Dielectric constant of a polar gas

For a gas of polar molecules we have to take account of two different effects of the applied electric field.

- First the molecules will have an electric dipole moment $\mathbf{p}_i$ *induced* on them as described in the preceding section.
- Second, the orientation of molecules will be affected by the torque on their permanent electric dipole moment $\mathbf{p}_p$.

The first of these effects has been discussed in the previous section, so we will consider here only the second effect. In the absence of an applied electric field, the permanent electric dipole moments are randomly oriented, resulting in zero net polarisation of the gas. In the presence of an applied field, there will be a tendency for more molecules to orient their permanent dipole moments $\mathbf{p}_p$ parallel to the applied field, resulting in a net polarisation $\mathbf{P}$. We thus expect that the polarisation to be:

$$P \propto n \times fraction \times \mathbf{p}_p \qquad (5.111)$$

where n is the number density of molecules, and *fraction* (the fractional excess of molecules oriented parallel to $\mathbf{E}$) varies between 0 and 1. The *fraction* depends on the ratio of two energies: the random kinetic energy of the molecules which is of the order of k_BT; and the orientational energy of the molecule in the applied field, which is $\mathbf{p}_p \cdot \mathbf{E} \approx p_pE$. We thus expect the *fraction* in Equation 5.111 to be of the form:

$$fraction \propto \frac{p_pE}{k_BT} \qquad (5.112)$$

at least for small electric fields. Hence, we expect the polarisation of the gas to be given by an expression of the form:

$$\mathbf{P} \propto n \times fraction \times \mathbf{p}_p$$
$$\mathbf{P} \propto n \times \frac{p_pE}{k_BT} \times \mathbf{p}_p \qquad (5.113)$$

or dropping the vector notation:

$$P \propto \frac{np_p^2E}{k_BT} \qquad (5.114)$$

An exact calculation (*Bleaney and Bleaney*) shows the constant of proportionality in Equation 5.114 to be $\frac{1}{3}$ and so the polarisation is then:

$$P = \frac{np_p^2E}{3k_BT} \qquad (5.115)$$

This expression has exactly the same form as the expression known as the *Curie Law* for the magnetisation of a substance containing freely-rotating permanent magnetic dipole moments (See Web Chapter W2). Following the argument of Equations 5.105 to 5.110 in the preceding section, we can convert this expression for the polarisation into an expression for the dielectric constant due to the re-orientation of the permanent dipole moments:

$$\varepsilon - 1 = \frac{np_p^2}{3\varepsilon_o k_BT}. \qquad (5.116)$$

Comparison with experiment

We are now in a position to compare the data on the dielectric constants of gases with the predictions of the preceding sections. We expect that for gases of non-polar molecules $\varepsilon - 1$ should be given by:

$$\varepsilon - 1 = \frac{n\alpha}{\varepsilon_o} \qquad (5.109^*)$$

where the molecular polarisability α is an intrinsic property of a molecule. For gases of polar molecules we expect that in addition to any induced

dipole moment there should be an additional term given by:

$$\varepsilon - 1 = \frac{n p_p^2}{3 \varepsilon_o k_B T} \qquad (5.116*)$$

where p_p is an intrinsic property of a molecule.

Let us now turn to the questions raised by the data.

Pressure dependence

We notice that both expressions for $\varepsilon - 1$ (Equations 5.109 and 5.116) depend linearly on n, the number density of molecules. Hence at fixed temperature, we expect $\varepsilon - 1$ to vary linearly with pressure in accord with the experimental behaviour of CO_2 in Figure 5.25 (b).

Temperature dependence of non-polar molecules

The temperature dependence of $\varepsilon - 1$ is slightly harder to understand than the pressure dependence. From a wider understanding of the structure of molecules, we expect that the CO_2 molecule should have no permanent dipole moment and so it should obey Equation 5.109 for non-polar molecules. If this is so then we would expect $\varepsilon - 1$ to show no temperature dependence. However the data below (extracted from Table 5.16) show a clear dependence on temperature.

From Table 5.16

Gas	T (°C)	T (K)	$10^4 (\varepsilon - 1)$
Carbon dioxide, CO_2	0	273	9.88
Carbon dioxide, CO_2	20	293	9.22
Carbon dioxide, CO_2	100	373	7.23

In fact, the temperature dependence is 'hidden' in the expression for the number density n. The data in Table 5.16 are taken at constant pressure, and increasing the temperature at constant pressure implies a reduction in the number density n according to:

$$n = \frac{P}{k_B T} \qquad (5.100*)$$

This shows that, at constant pressure, n is proportional to $1/T$. Substitution into Equation 5.109 predicts that:

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$$\varepsilon - 1 = \frac{P \alpha}{\varepsilon_o k_B T} \qquad (5.117)$$

If this is the origin of the temperature dependence, then we should expect the value of $\varepsilon - 1$ at 373 K to be a factor $273/373 = 0.732$ less than its value at 273 K. Comparing this with the data from Table 5.16 predicts that the value at 100 °C should be $0.732 \times 9.88 \times 10^{-4} = 7.23 \times 10^{-4}$, in agreement with the experimental value.

Temperature dependence of polar molecules

Using this knowledge of the of the 'hidden' temperature dependence of n we now expect the value of $\varepsilon - 1$ for polar molecules to vary as:

$$\begin{aligned} \varepsilon - 1 &= \frac{p_p^2}{3 \varepsilon_o k_B T} \\ &= \frac{P p_p^2}{3 \varepsilon_o k_B^2 T^2} \end{aligned} \qquad (5.118)$$

i.e. with a $1/T^2$ temperature dependence. Examining the data for the polar molecule ammonia in Table 5.16, we expect the value of $\varepsilon - 1$ at 373 K to be a factor $(273/373)^2 = 0.536$ less than its value at 273 K. Comparing this with the data from Table 5.16 predicts that the value at 100 °C should be $0.536 \times 8.34 \times 10^{-4} = 4.46 \times 10^{-4}$, in rough agreement with the experimental value of 4.87×10^{-4}.

From Table 5.16

Gas	T (°C)	T (K)	$10^4 (\varepsilon - 1)$
Ammonia, NH_3	0	273	8.34
Ammonia, NH_3	100	373	4.87

The discrepancy between experiment and theory can be understood as arising from the fact that polar molecules have contributions to $\varepsilon - 1$ from both the re-orientation of their permanent electric dipole moments, and from their induced dipole moment. Thus we can plausibly assign the difference between the observed and predicted value to the induced electric dipole moment.

Dependence of $(\varepsilon - 1)$ on the type of molecule

The final points we need to understand concern the general magnitude of $\varepsilon - 1$ and the occasional occurrence of some extremely large values (Figure

5.25). We can understand this by considering as examples the distribution of electric charge within two simple diatomic molecules: O_2 and CO.

Even without knowing the details of the charge distribution within an oxygen molecule, we can say that we would expect the charge to be distributed symmetrically between the two atoms. We say this because each oxygen atom is identical and hence has an equal attraction (or *affinity*) for electrons. If we think now about carbon monoxide CO, we would expect the charge to be distributed asymmetrically between the two atoms. We say this because each atom is different and so has a different characteristic electron affinity. In this case, the electrons are more attracted to the oxygen atom than the carbon atom and so the oxygen atom becomes negatively charged with respect to the carbon atom. In other words, a CO molecule has permanent electric dipole moment.

We can estimate the magnitude of the permanent dipole moment p_p by considering the CO datum from Table 5.16: $10^4(\varepsilon - 1) = 6.92$ at 23 °C (296 K). Rearranging Equation 5.118, into an expression for p_p we obtain:

$$p_p = \sqrt{\frac{3k_B^2 T^2 (\varepsilon - 1)\varepsilon_o}{P}} \qquad (5.119)$$

Evaluating this at atmospheric pressure we find:

$$p_p = \sqrt{\frac{3\left(1.38\times10^{-23}\times296\right)^2 \times 6.92\times10^{-4} \times 8.85\times10^{-12}}{1.013\times10^5}}$$

$$= 1.74\times10^{-30} \quad Cm \qquad (5.120)$$

$$= 1.74 \quad debye$$

Does this make sense? Imagine that some fraction f of an entire electronic charge e is transferred from CO. The separation r_o of the atoms in a CO molecule is given in *Kaye and Laby* as 0.1131 nm. We thus expect that the permanent dipole moment will be given by:

$$p_p = 1.74\times10^{-30}$$

$$= r_o fe \qquad (5.121)$$

$$= 0.113\times10^{-9} \times f \times 1.6\times10^{-19}$$

which predicts $f = 0.096 \approx 0.1$, which seems reasonable. Notice that the magnitude of p_p yields the product of *fe* and r_o and so we may interpret the magnitude of p_p as being:

- the transfer of a fractional charge *fe* across the entire length of the molecule, or
- the transfer of an entire electronic charge *e* across a fraction *f* of the entire length of the molecule, or
- any combination of the above two effects.

The discussion above allows us to understand why larger molecules tend to possess larger dipole moments. In larger molecules it is possible for an amount of charge of the order of *e* to be transferred across relatively large distances, and hence give rise to relatively large dipole moments. This charge transfer arises as part of the processes of chemical interaction between the atoms within a molecule. The larger physical extent of larger molecules allows charge to be spread across larger distances and hence give rise to larger permanent electric dipole moments.

Considering the non-polar gases in Table 5.16, we see that $\varepsilon - 1$, and hence the *induced* dipole moments, tends to increase with increasing atomic number, i.e. the molecular polarisability α is larger for larger atoms. We can understand this by considering the electric field which acts on the valence electrons in an atom (Figure 5.26 (c) and (d)). For an atom such as helium, the two electrons are extremely close to the electric charge on the nucleus $+2e$. In an atom such as xenon, however, the outer electrons are further away from the nucleus and experience a much weaker electric field. As a consequence the electric field around the valence electrons in xenon is much less than that around the valence electrons in helium. Thus an applied electric field of a given strength affects the valence electrons around a xenon atom more strongly than the electrons around a helium atom. This amounts to making a xenon atom more deformable (i.e. more polarisable) than a helium atom.

Finally we note that in Figure 5.25(a), all three of the substances with anomalously large dipole moments contain an OH group of atoms. A wide range of chemical experiments indicate that the

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OH group, known as a hydroxyl group, has a particularly strong affinity for electrons, thus causing a large amount of charge to be transported away from the centre of the molecule.

5.7.3 Data on the electrical properties of gases in strong electric field

In weak electric fields, gases form effective electrical insulators with low values of electrical conductivity. In strong electric fields however, electric charge can move through a gas producing a variety of interesting phenomena. The value of electric field at which this change in behaviour takes place is known as the *breakdown electric field* or *dielectric strength* of the gas.

Taking air as a typical gas, the dielectric strength of air at 25 °C and normal atmospheric pressure (0.1013 MPa) is 3.13×10^6 V m^{-1}. The variation of dielectric strength of air with temperature and pressure is shown in Figure 5.28.

The value of electric field at which breakdown occurs varies between gases, and also depends critically on several 'minor' properties of the gas. In particular, the presence of ions, i.e. atoms which are not electrically neutral, significantly lowers the dielectric strength of a gas. In practice, we must also consider the humidity of the gas: humid air can deposit a microscopic layer of water on solid surfaces with which it is in contact. Although this extremely thin layer is only a weak conductor of electricity, it can 'short circuit' the even more highly resistive air. In different experiments this can lead to anomalous apparent increases or decreases in the dielectric strength of humid air.

In the nineteenth century great efforts were put into understanding the nature of the flow of electric current through a gas, and a considerable understanding of the phenomena associated with 'cathode rays' was achieved. These experiments advanced our understanding of the nature of gases and of the internal structure of atoms enormously. A selection of the phenomena we have to understand are succinctly described by one of the fore-

Figure 5.28 The variation of dielectric strength of air with temperature and pressure in the region of ambient temperature and pressure. The dielectric strength is increased at low temperatures and high pressures.
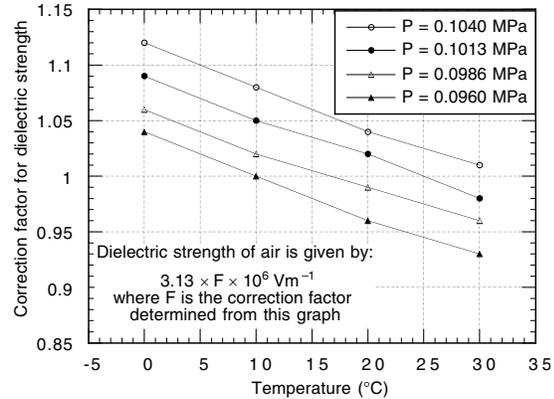
Example 5.13

An air-cored parallel-plate capacitor has a plate separation of $d = 1$ mm. If the air pressure is 0.1 MPa and the temperature is 5 °C, what is the maximum voltage that can be applied between the plates before sparking occurs?

From the text, the dielectric strength of air at 25 °C and normal atmospheric pressure (0.1013 MPa) is 3.13×10^6 Vm^{-1}. We use the graph (Figure 5.28) to find a corrected value for our temperature and pressure. Looking up the 5 °C line on the graph reveals that the correction factor will be between 1.04 (which would be appropriate at a pressure of 0.0986 MPa) and 1.07 (which would be appropriate at a pressure of 0.1013 MPa). Our pressure lies roughly midway between these values and so we estimate a value of 1.055. The dielectric strength of air at 5 °C and 0.100 MPa is therefore:

$$= 1.055 \times 3.13 \times 10^6 \text{ V m}^{-1} = 3.30 \times 10^6 \text{ V m}^{-1}$$

The electric field between the plates of a capacitor is given approximately by $E = V/d$. If we work out the voltage which will yield the maximum sustainable field we have:

$$V = Ed = \left[3.30 \times 10^6\right] \times \left[10^{-3}\right] = 3.30 \times 10^3 \text{ V}$$

Thus the capacitor can, in principle, be used up to 3.3 kV. However, the electric field around the edge of a capacitor plate can be significantly greater the field between the plates, and breakdown would occur there before it would between the plates. A more likely value of maximum working voltage is ≈ 1 kV. Notice that for very small gaps of the order of a micron (10^{-6} m) this breakdown voltage can be only a few volts.

most scientists of that age, J.J. Thomson, in his book *Conduction of Electricity Through Gases*. In the following extract he describes the general nature of the phenomena which occur when an electric current is passed through a glass tube containing gas at low pressure.

> When the electric discharge passes through a gas at low pressure, differences in the appearance of the gas at various points in its path become very clearly marked. The discharge, as illustrated [in Figure 5.29], presents the following features: starting from the cathode (negative terminal) there is a thin layer of luminosity (1) spread over its surface; next to this there is a comparatively dark space called 'Crookes dark space' (2), the width of which depends on the pressure of the gas, increasing as the pressure diminishes – it also depends, under some conditions on the intensity of the current. The boundary of the dark space is approximately the surface traced out by normals of constant length drawn to the surface of the cathode. Beyond the dark space there is a luminous region (3) called the 'negative glow'. Beyond this again is another comparatively dark region (4) called by some writers the 'second negative dark space' and by others the 'Faraday dark space'. Its length is very variable, even when the pressure is constant. Beyond this again there is a luminous column (5) reaching right up to the anode and called the positive column. When the current and pressure are within certain limits this column exhibits remarkable alternations of dark and bright spaces: these are called striations. In long tubes the positive column constitutes by far the greater part of the discharge, for the Crookes space, negative glow and Faraday dark space do not depend markedly on the length of the tube. So that when the length of the discharge is increased, the increase is practically only in the length of the positive column. Thus for example in a tube about 15 metres used by one of us, the positive column occupied the whole of the tube with the exception of two or three centimetres close to the cathode.

J. J. Thomson

Conduction of Electricity Through Gases,
published by Cambridge University Press in 1933

The colour of the 'luminosity', particularly within the positive column (feature 5 in Figure 5.29) depends on the type of gas. Hydrogen for instance has a red glow, as does neon, but argon has a bluish tint. If one examines the spectrum of the light then one finds that the spectrum is characteristic of the type of gas in the tube. More details of these

Figure 5.29 An illustration of the pattern of light emitted when an electric current flows through a gas, called a *discharge*. The details of the pattern (1 to 5) are discussed in the text. The shaded areas in the figure represent luminous regions of the gas and the unshaded regions represent regions from which no light is emitted.
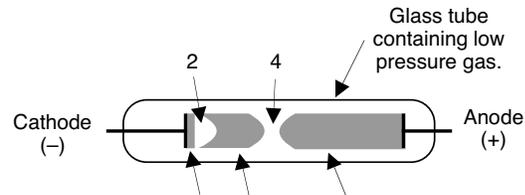
emission spectra are given in §5.7.5 on the optical properties of gases.

The main questions raised by our preliminary examination of the experimental data for on the properties of gases under strong electric fields are:

- Why is the dielectric strength largest at low temperatures and high pressures, i.e. when the gas is most dense?
- Why, below a critical electric field, the dielectric strength, do gases behave as electrical insulators, while above that they behave as electrical conductors, displaying a variety of optical effects?

5.7.4 Understanding the data on the electrical properties of gases in strong electric fields

When the electric field exceeds the dielectric strength, the gas changes from behaving like an insulator to become an electrical conductor. In this section, we will propose a formula for the dielectric strength of a gas, and then using the ideas developed for this formula we will qualitatively discuss the phenomena observed in a discharge tube by J.J. Thompson.

Background theory

In order to understand how the breakdown of the insulating properties of the gas occurs we need to consider the situation where a single charged particle, an ion, is present in the gas when an electric field E is applied. The ion might be the result of an interaction between an atom and a fast-moving particle from a cosmic ray shower. In the absence

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of an electric field, the electron and ion created by the ionisation will quickly recombine (Figure 5.30).

In the presence of an electric field, the electron and ion created by the ionisation may be prevented from recombining and can be accelerated through the gas by the applied electric field (Figure 5.30).

Given that a free ion, separated from 'its' electron, has been created, it will experience force qE which will accelerate it. Hence its speed will increase and it will acquire more kinetic energy the further it travels in the field. If the *mean free path* λ_{mfp} of the ion in the gas is long enough, or the electric field strength is great enough, then it may acquire enough kinetic energy to ionise the atom with which it next collides. The consequences of this can be enormous.

There will now be two ions, instead of just one. What happened to the first ion may also happen to the second one, and if it does, the two ions will cause further ions to be created. Hence starting with just a single ion, the number of ions in a gas can increase in an effect called an *avalanche*. Also under the influence of the applied electric field, the second ion will move along in the same direction as the first, whereas the electron released from the second ion will travel in the opposite direction (Figure 5.30). After many collisions an electric current flows through the gas, with electrons travelling in one direction and ions travelling in the other.

Thus the presence of a single ion has caused the gas to become an electrical conductor instead of an electrical insulator. The electric field which must be applied to a gas to cause it to become a conductor is called the *breakdown electric field*, or the *dielectric strength* of the gas.

Pressure and temperature dependence of the dielectric strength

We can consider the ionisation process which initiates and maintains the density of ions responsible for conduction in gas, as a two-step process. In the first stage, an electron or ion (charge q) accelerates for a distance λ under the action of the electric field and gains energy u, given by:

Figure 5.30 Ionisation of an atom in the absence and the presence of a strong electric field.
(a) Initially (1) we have a neutral atom, then (2) one of the causes described in the text causes an ionisation event. In the absence of an applied field the negatively-charged electron and the positively-charged ion quickly recombine (3). Finally we return to the situation (1) we started with. Thus the gas is stable against the formation of ions.
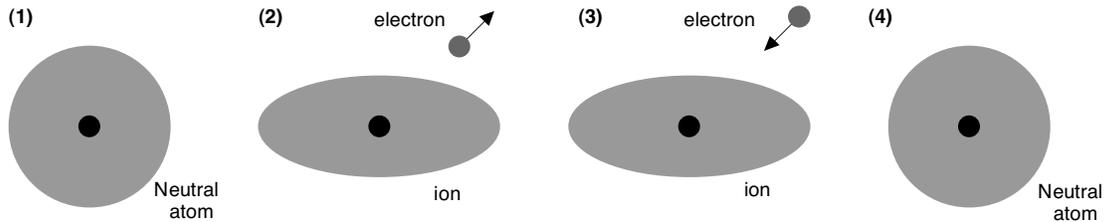
(b) Initially (1) we have a neutral atom, then (2) one of the causes described in the text causes an ionisation event. In contrast with (a), an applied electric field (3) acts to draw apart the negatively-charged electron and the positively-charged ion, and recombination is prevented.

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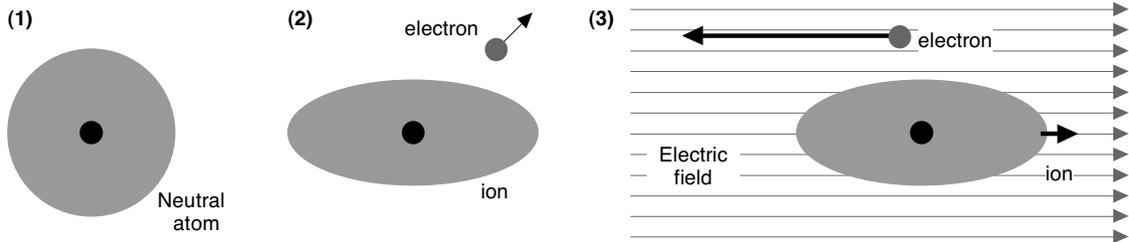
$$u = \int_0^\lambda q\mathbf{E} \cdot \mathrm{d}s \qquad (5.122)$$
$$= qE\lambda$$

In the second stage, some of this energy (typically of the order of few hundredths of an eV) is given up in collisions with molecules. These collisions lead, on average, to a further ionisation process.

However, although this two-stage process is easy to describe at this level, working out λ, the average path length of an ion or an electron between collisions, is rather difficult. Notice that because the ions and electrons are electrically charged, ion–molecule and electron–molecule interactions are considerably stronger than molecule–molecule interactions. Calculating the effective diameters or cross-sectional areas of molecules for ionic collisions is not an easy problem. However, we can say one thing for sure: whatever λ is, it will be inversely proportional to n, the number density of molecules in the gas.

So from Equation 5.122 we expect that the break down field E_B will be defined when the work done in accelerating an ion or electron is sufficient to ionise a molecule, i.e. when:

$$u_o = qE_B\lambda \qquad (5.123)$$

where u_o is the ionisation energy. Since u_o is characteristic of the molecules of the gas we therefore expect to find that E_B is proportional to $1/\lambda$. Hence based on the arguments in the preceding paragraph we expect quite generally to find:

$$E_B \propto \frac{1}{\lambda} \propto n \qquad (5.124)$$

Recalling that $n = P/k_B T$ we therefore expect that:

$$E_B \propto A\frac{P}{T} \qquad (5.125)$$

where A is an expression involving λ and u_o. Thus we expect the dielectric strength to be proportional to pressure and inversely proportional to absolute temperature.

Examining Figure 5.28, we see that at 0 °C, the correction factor increases from 1.04 at a pressure of 0.096 MPa to 1.12 at 0.104 MPa. Thus the dielectric strength increases by a factor $(1.12/1.04) = 1.08$ as a result of a pressure increase of $(0.104/0.0960) = 1.08$. At limited resolution, this is fairly good agreement.

Similarly, at a pressure of 0.1013 MPa, the correction factor of 1.09 at $T = 273.2$ K falls to a correction factor of 0.98 at a $T = 273.2 + 30$ K. Thus the dielectric strength decreases by a factor $(0.98/1.09) = 0.90$ as a result of a temperature increase by a factor $(303.2/273.2) = 1.11$. Since $1/1.11 = 0.90$ this is fairly good agreement, albeit at limited resolution.

At first sight, this result may appear counter-intuitive. It might be thought that the best way to stop a gas from conducting would be to use a low gas pressure i.e. an approximation to a vacuum, which is an excellent insulator. It is not too difficult to reduce the pressure of a gas by a factor of about 10^9 from atmospheric pressure (10^{-6} mbar $\approx 10^{-4}$ Pa). However even here there are still $\approx 10^{16}$ molecules m^{-3}. In these circumstances, if a single ion is created it will travel straight across the vacuum chamber with virtually no chance of collision with another molecule. Thus the mean free path becomes fixed at the dimension of the container and does not get any longer as the pressure is lowered. This situation is similar to the behaviour of the pressure dependence of the thermal conductivity of a gas (§5.5). The relevant ionisation energy is then that of the atoms in the walls in the container. If an ion hits the walls and creates more ions, then ions will simply bounce between the walls of the container. Lowering the gas pressure will make no difference until there are no atoms at all, something which is not technically achievable.

The phenomena within a discharge tube
In the light of our discussions above, Table 5.17 explains the phenomena described by J.J. Thomson, in the passage from his book *Conduction of Electricity Through Gases* that was reproduced in §5.7.3. The spectra of the 'luminosity' is discussed below in §5.8 on the optical properties of gases. The state in which a substantial fraction of gas

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molecules are ionised is generally referred to as a *plasma*. By far the majority of the matter in the universe exists in this state, but on Earth it is rela-

tively rare, and we pass it by without further mention.

Figure 5.29 (Reproduced here for your convenience) The details of the pattern (1 to 5) are discussed in Table 5.17. The shaded areas in the figure represent luminous regions of the gas and the unshaded regions represent regions from which no light is emitted.
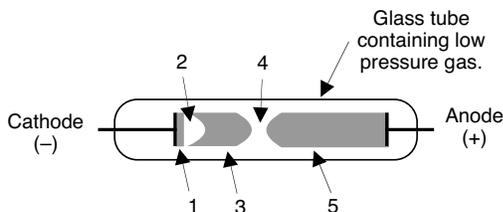

Table 5.17

Thompson's description	What is happening
Starting from the cathode (negative terminal) there is a thin layer of luminosity (1) spread over its surface.	The luminosity is caused by positive ions striking the surface of the cathode.
Next to this there is a comparatively dark space called 'Crookes dark space' (2), the width of which depends on the pressure of the gas, increasing as the pressure diminishes — it also depends, under some conditions on the intensity of the current. The boundary of the dark space is approximately the surface traced out by normals of constant length drawn to the surface of the cathode.	In this region electrons liberated from the cathode (by the impact of positive ions) are being accelerated by the electric field in the tube. They are colliding with atoms and ions in this region but give off no light because they do not have sufficient energy to excite the atoms. The boundary of the region has this form because electrons have travelled in straight lines for a distance of around one ionic mean free path from the cathode.
Beyond the dark space there is a luminous region (3) called the 'negative glow'.	Now electrons *do* have sufficient energy to excite the atoms.
Beyond this again is another comparatively dark region (4) called by some writers the 'second negative dark space' and by others the 'Faraday dark space'. Its length is very variable, even when the pressure is constant.	Having collided inelastically with atoms of the gas in region (3), the electrons lost kinetic energy and are now being accelerated again.
Beyond this again there is a luminous column (5) reaching right up to the anode and called the positive column. When the current and pressure are within certain limits this column exhibits remarkable alternations of dark and bright spaces: these are called striations. In long tubes the positive column constitues by far the greater part of the discharge, for the Crookes space, negative glow and Faraday dark space do not depend markedly on the length of the tube. So that when the length of the discharge is increased, the increase is practically only in the length of the positive column. Thus for example in a tube about 15 metres used by one of us, the positive column occupied the whole of the tube with the exception of two or three centimetres close to the cathode.	The striations are caused by alternating regions of the gas in which: • electrons and ions are accelerated and do not yet have sufficient energy to ionise/excite the atoms of the gas: these are the non-luminous dark regions • electrons and ions accelerated in the above 'dark' regions now have sufficient energy to ionise/excite the atoms of the gas; these are the luminous regions. In some circumstances where the geometry of the acceleration is not very well defined, or where the cathode is heated to created a spread of initial electron velocities, the dark and light striations become blurred and overlap one another.

5.8 Optical properties

'Light' is the name given to oscillations of the electromagnetic field which take place with frequencies in the range 400 THz (Red) to 1000 THz (Blue). Remember that 1 THz = 10^{12} Hz. Below we concentrate entirely on the effect of the oscillations of the *electric* component of the electromagnetic field.

5.8.1 Data on the speed of light in gases: refractive index

Light travels at a slightly slower speed, c_g, through a gas than its speed through vacuum c. You may be forgiven for not having noticed this difference because it is generally rather small; typically a small fraction of a per cent. An apparatus illustrating how such changes may be measured is illustrated in Figure 3.9. The ratio c/c_g is known as the *refractive index* of the gas (§2.3.3), and normally has the symbol n. In order to avoid confusion with n used to signify number density, the refractive index in this text has the symbol n_{light}. The refractive indices of various gases are shown in Table 5.18 and plotted as a function of
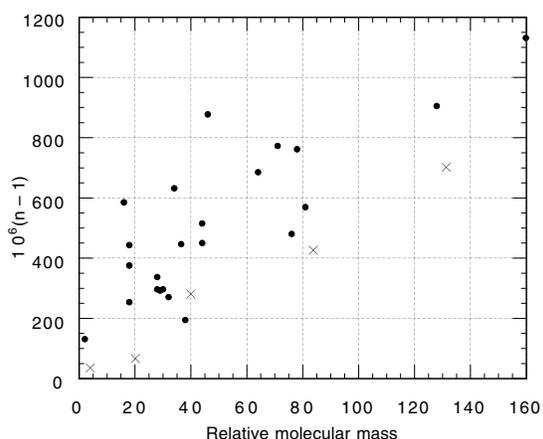
relative molecular mass in Figure 5.31. Because n_{light} for gases is close to unity, the table records data in the form $10^6(n_{light} - 1)$. Thus the refractive index of air recorded as 293 is actually 1.000293 and so the speed of light in air is $c/1.000293$, 99.97% of the speed of light in vacuum.

Figure 5.31 shows that there is a general trend towards large molecular mass molecules display-

Figure 5.31 The refractive index n of gases from Table 5.17 plotted as a function of the relative molecular weight of the gas molecules. The refractive indices of the gases are all within 0.2 % of unity and so the quantity $10^6(n-1)$ has been plotted so as to make visible differences in the data. The crosses (×) mark the data points for the noble gases helium, neon, argon, krypton, and xenon.

Table 5.18 The refractive index of various gases as $10^6(n_{light}-1)$ together with the molecular weight of the molecules of the gas. The data refer to gases at STP (P = 0.1013 MPa: T = 0 °C). The refractive index is that appropriate to the bright yellow 'D' lines in the emission spectrum of sodium vapour and varies slightly with frequency.

Gas	M	$(n_{light}-1) \times 10^6$
Hydrogen, H_2	2	132
Helium, He	4	36
Methane, CH_4	18	444
Water vapour, H_2O	18	254
Ammonia, NH_4	18	376
Neon, Ne	20	67
Nitrogen, N_2	28	297
Carbon monoxide, CO	28	338
Air	29	293
Nitric oxide, NO	30	297
Oxygen, O_2	32	271
Methanol, CH_3OH	32	586
Hydrogen sulphide, H_2S	34	633
Hydrogen chloride, HCl	36	447
Fluorine, F_2	38	195
Argon, Ar	40	281
Nitrous oxide, N_2O	44	516
Carbon dioxide, CO_2	44	451
Ethanol, C_2H_5OH	46	878
Sulphur dioxide, SO_2	64	686
Chlorine, Cl_2	71	773
Carbon disulphide, CS_2	76	481
Benzene, C_6H_6	78	1762
Hydrogen bromide, HBr	81	570
Krypton, Kr	84	427
Hydrogen iodide, HI	128	906
Xenon, Xe	131	702
Bromine, Br_2	160	1132

ing a higher refractive index, but the wide variation in n_{light} shows that there are significant factors other than molecular mass. Figure 5.31 shows the data for monatomic noble gases helium, neon, argon, krypton, and xenon as crosses ($\times$), indicating that amongst similar molecules, the link between n_{light} and M is relatively direct.

The main questions raised by our preliminary examination of the experimental data on the refractive indices of gases are:

- Why do the refractive indices of a wide variety of gases at STP all lie between 1.000 and 1.002?
- Why, within this range, is there a significant dependence of n_{light} upon the molecular mass?

5.8.2 Understanding data on the refractive index of gases

Introduction
Our explanation of the interaction of light with gases follows on from the discussion of the dielectric constant data (§5.7.2). We assume that each molecule responds independently to the oscillating electric field of the light wave, and that in response to this field the molecule either:

- acquires an induced dipole moment p_i, or
- orients its own permanent dipole moment p_p (if it has one) parallel to the instantaneous value of the electric field.

As we shall see, in general the second process is not as important as the first because the time taken for a molecule to rotate is typically of the order 10^{-10} seconds (Example 5.15). Although this may seem like a short time, it is much longer than the period of the electric field oscillation in a light wave, which is of the order 10^{-15} seconds.

So the main effect of a light wave is to induce an oscillating electric dipole moment on the molecules of the gas (Figure 5.33). In general, the magnitude of the induced dipole moment varies with frequency, and generally grows resonantly large at a frequency in the ultraviolet region of the spectrum. The frequency dependence of the dipole moments induced on atoms and molecules is considered more fully in the analysis of the optical

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Example 5.14

It is required to split a laser beam in two, and to delay one beam with respect the other travelling through vacuum by 4.7 ps (4.7×10^{-12} s). To achieve this delay one part of the split beam light is passed through a length L of gas. For reasons of its inertness and cost, argon is thought suitable to fill the tube. What length of tube is required if the gas within is at STP? Is this method really practical?

We require a tube which will take a light signal 4.7 ps longer to traverse than an equivalent tube filled with vacuum. If the tube were evacuated the transit time would be:

$$t_o = \frac{L}{c}$$

but when filled with gas will be:

$$t_g = \frac{L}{c_g}$$

We need a device in which $t_g - t = 4.7$ ps, i.e.

$$t_g - t = \frac{L}{c_g} - \frac{L}{c} = 4.7 \times 10^{-12}$$

We now note that Table 4.10 tells us that for argon at STP the refractive index is given by:

$$n - 1 = 281 \times 10^{-6}$$
$$n = 1.000281$$

From the definition of the refractive index this implies

$$\frac{c}{c_g} = 1.000281$$

Rearranging our equation we have:

$$4.7 \times 10^{-12} = L \left[\frac{1}{c_g} - \frac{1}{c} \right] = L \left[\frac{1}{c/1.000281} - \frac{1}{c} \right]$$
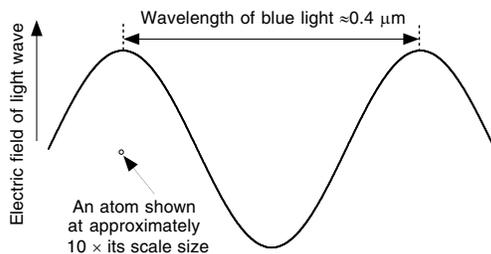
This simplifies to:

$$4.7 \times 10^{-12} = \frac{L}{c} [1.000281 - 1]$$

which can be solved for L:

$$L = \frac{4.7 \times 10^{-12} \times 2.998 \times 10^8}{0.000281} = 5.01 \text{ m}$$

This is rather an inconveniently long tube for practical use, given that the tube needs to be kept temperature stabilised. However, the technique can be (and is) used by reflecting the light backwards and forwards (say) ten times between an array of mirrors 0.5 m apart.

Figure 5.32 Comparison of the wavelength of blue light with the size of an atom. Notice that in order to be clearly printed the atom has been shown at approximately 10 times its correct scale size.

Figure 5.33 Illustration of the origin of the oscillating dipole moment on a non-polar molecule subject to an oscillating electric field. Notice that in the very short time between successive periods of the light field, only the low-mass electrons can move a significant distance. The heavy nucleus moves relatively little.

properties of solids (§7.5). Here we concentrate on the effect of these induced dipole moments on the speed of light through the gas.

As outlined in §2.3.3, for most substances the refractive index is given by:

$$n_{light} = \sqrt{\varepsilon} \qquad (2.17^*)$$

We can check Equation 2.17 by using values of $\varepsilon - 1$ from Table 5.16 to predict values for $n_{light} - 1$ (Table 5.19).

The non-polar gases (helium, neon, argon) show excellent agreement. Recalling that $\varepsilon - 1$ is determined at low frequencies (i.e. $<10^9$ Hz), this indi-

cates that the molecular polarisability of these atoms is relatively constant from radio frequencies (MHz) up to optical frequencies (1000 THz).

When we consider the polar molecules in Table 5.19 we find that this agreement is not as good: knowing the value of $\varepsilon - 1$ does not enable us to predict the value of $n_{light} - 1$. This disagreement is slight in the case of ammonia, but for water vapour the difference is dramatic. The reason is that the value of $\varepsilon - 1$ for polar molecules (determined at low frequency) is generally dominated by the effect of molecular rotation. However, as we mentioned above, the oscillations of electric field at optical frequencies are too rapid to allow molecules to rotate. So the refractive index is sensitive

Table 5.19 Comparison of the experimental values of the refractive index of gases with the prediction of their refractive index based on Equation 2.17. Before comparing the data, the dielectric constant data have been corrected to STP using factors discussed in §5.6.2. The first three entries in the table are for non-polar gases and the last two are for polar gases. Notice the good agreement between theory and experiment for the non-polar gases, and the massive disagreement for water vapour.

Gas	$10^4(\varepsilon - 1)$	T	Correction factor	$10^4(\varepsilon - 1)$ (STP)	Prediction $10^6(\sqrt{\varepsilon} - 1)$	Experiment $10^6(n_{light} - 1)$
Non-polar gases						
He	0.65	20	293/273	0.70	35	36
Ne	1.3	0	1	1.3	65	67
Ar	5.16	20	293/273	5.54	277	281
Polar gases						
NH_3	8.34	0	1	8.34	416	376
H_2O	60	100	$(293/273)^2$	69.1	3449	254

only to the induced component of the electric dipole moment of a molecule.

Turning to the questions raised at the end of §5.8.1, we can understand both these phenomena in terms of the connection outlined in Equation 2.17 between n_{light} and ε. The small magnitude of $n_{light} - 1$ results from the small magnitude of $\varepsilon - 1$ (Equation 5.109)

$$\varepsilon - 1 = \frac{n\alpha}{\varepsilon_o} \qquad (5.109^*)$$

which in turn is small because of the intrinsic magnitude of molecular polarisability α and the low number density of molecules in the gas. The dependence of $n_{light} - 1$ upon molecular mass arises because larger molecules tend to have larger values of molecular polarisability.

Example 5.15

Consider a diatomic polar molecule (i.e. one with a 'built-in' electric dipole moment) which has a permanent electric dipole moment of approximately 0.1×10^{-30} Cm.
(a) Estimate the torque on the molecule in an electric field of 1000 Vm^{-1}.
(b) Calculate the time for it to rotate through 90 °.

(a) Assuming the moment is oriented perpendicular to the field, then Γ is given by:

$$\Gamma \approx pE = 0.1 \times 10^{-30} \times 10^3 = 10^{-28} \ \text{N m}$$

(b) This is tricky if you are unfamiliar with dealing with rotational calculations. We recall that we use the rotational analogues to the equations of linear motion analogous to $F = ma$ we have:

$$\Gamma = I \frac{d^2\theta}{dt^2}$$

where Γ is the torque described above, I is the *moment of inertia* defined below, and $d^2\theta/dt^2$ is the *angular acceleration*. Similarly, one familiar equation states that $s = ut + \frac{1}{2}at^2$, or with $u = 0$ this becomes $s = \frac{1}{2}at^2$. The rotational analogue of that equation is:

$$\theta = \frac{1}{2}\left[\frac{d^2\theta}{dt^2}\right]t^2$$

These two equations allow us to calculate the time taken for a rotation due to a particular torque. The final formula we need is for the moment of inertia of the molecule and this is given by:

$$I = m_1 \times d_1^2 + m_2 \times d_2^2$$

where d_1 and d_2 are the distances to the two atoms from the centre of mass of the molecule. Approximately this amounts to:

$$I \approx [\text{average mass of the two atoms}] \times \left[\frac{1}{2}r\right]^2$$

where r is the distance between the two atoms, typically $\approx 1.3 \times 10^{-10}$ m (*CRC Handbook*)

Assuming average masses of the two atoms of $\approx 14u$ (i.e. like CO), the moment of inertia is approximately:

$$I \approx [14u] \times \left[\frac{1}{2} \times 1.3 \times 10^{-10}\right]^2$$

$$\approx [14 \times 1.66 \times 10^{-27}] \times \left[0.65 \times 10^{-10}\right]^2$$

$$= 9.8 \times 10^{-47} \approx 10^{-46} \ \text{kg m}^2$$

Substituting this into the analogue of $F = ma$, we find an angular acceleration of:

$$\frac{d^2\theta}{dt^2} = \frac{\Gamma}{I} \approx \frac{10^{-28}}{10^{-46}} \approx 10^{18} \ \text{rad s}^{-2}$$

So, we can now find out how long it takes the molecule to rotate. Starting with:

$$\theta = \frac{1}{2}\frac{d^2\theta}{dt^2}t^2$$

we can rearranging this to solve for *t*:

$$t = \sqrt{\frac{2\theta}{\frac{d^2\theta}{dt^2}}}$$

Substituting $\theta = \pi/2$ (i.e. 90°) we find:

$$t = \sqrt{\frac{2 \times \pi/2}{10^{18}}} \approx \sqrt{\pi \times 10^{-18}} \approx 1.8 \times 10^{-9} \ \text{s}.$$

So we find that it takes a molecule a couple of nanoseconds to rotate in a weak electric field. This has been a very approximate calculation, but the result is still valid. Molecules take a time of the order of nanoseconds to rotate in an applied electric field.

This may seem like a short time, but in fact when compared to some other processes it is rather slow. For example, the electric field of a light wave oscillates at around 10^{15} times per second. In a field oscillating this fast the molecule will have no time to rotate, whereas in a DC field the molecule will have plenty of time to rotate. This causes a difference between the electrical properties of gases at DC and optical frequencies.

5.8.3 The scattering of light by gases

At optical frequencies, most gases are extremely transparent. However they are not 100% transparent. This can be easily seen by looking through a few kilometres of our most readily available gas, air: objects viewed at a distance can appear 'hazy' or 'coloured'. Also, looking upwards into the air, we see mainly blue light coming apparently from nowhere (we say 'the sky is blue'). If the atmosphere were truly transparent, we would instead see the blackness of space and the stars. Furthermore, the Sun, which appears to be yellow during the day, appears red as it rises or sets. All these effects are due to the scattering of light by the molecules of the gases in the atmosphere. The main questions raised by our qualitative observations of the scattering of light are:

- Why are gases highly, but not completely, transparent?
- Why are some colours scattered more strongly than others?

Let us begin our attempt to answer these questions by first considering the nature of the scattering process.

What is scattering?

The scattering of light caused by atoms in a gas is known as *Rayleigh scattering* (Figure 5.34). The process may be considered in two stages:

- An incoming electromagnetic wave polarises molecules of the gas, and induces an oscillating electric dipole moment.
- The induced oscillating electric dipole moment re-radiates energy in a complicated pattern. The re-radiated (or scattered) wave is at the same frequency as the incoming wave, but travels radially away from the centre of the scattering.

The 'scattering power' of an individual molecule depends on the magnitude of the dipole moment induced on it by the electric field of the light wave. Clearly, if no dipole moment is induced, then there will be no scattering. Recall that as we saw in examining the data on the refractive indices of gases (§5.8.2), at optical frequencies, only the *induced* dipole moment needs to be considered. This is because polar molecules have no time to rotate in a single cycle of the oscillating electric

Figure 5.34 Rayleigh scattering. An incoming plane wave causes an oscillating electric dipole moment (Figure 5.33). The oscillating dipole moment then re-radiates some of the incoming wave as a spherical wave emanating from the molecule. The figure shows a two-dimensional analogue to the scattering such as might occur with water waves on the surface of a pond.
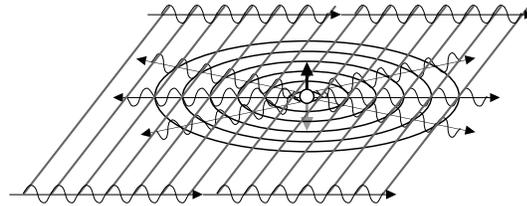
field of the light wave. The theory of an oscillating dipole radiator (*Bleaney and Bleaney*: see §1.4.1 for a detailed reference) indicates that the power radiated by a dipole whose magnitude varies as $p = p_o \cos(2\pi f t)$ is given by:

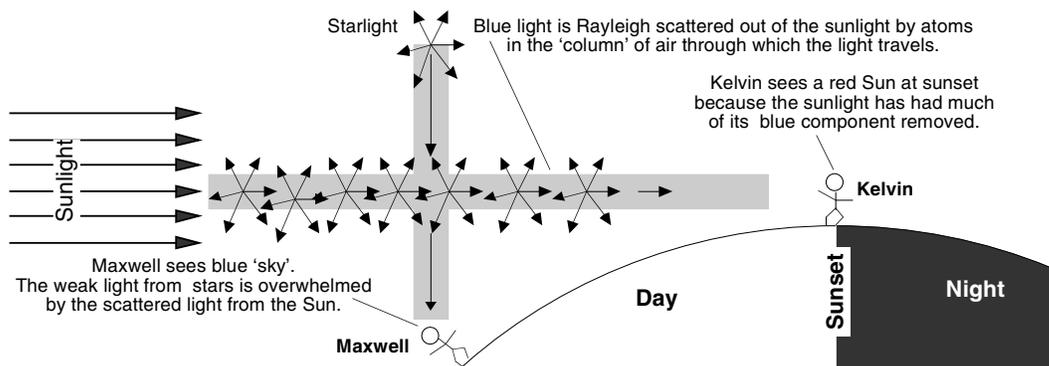$$\text{Power} = \left[\frac{4\mu_o \pi^3 p_o^2}{3c} \right] \times f^4 \qquad (5.126)$$

Equation 5.126 shows that the scattered power depends on the fourth power of the frequency i.e. f^4. Blue light has a frequency of $f \approx 10^{15}$ Hz and red light has a frequency of $f \approx 4 \times 10^{14}$ Hz, so according to Equation 5.126, blue light should be scattered at least $(10/4)^4 \approx 2.5^4 \approx 39$ times more strongly than red light.

Blue skies, sunsets, and the difficulty of seeing stars in the daytime

We all know that we cannot see the stars in the daytime. But why not? And we all know that the sky is blue. But what exactly is it that is blue? Let us look at how our understanding of Rayleigh scattering helps us to answer these questions

First of all let us consider a person standing on Earth looking out into space, attempting to gaze at the stars during the daytime (Figure 5.35). They are looking out into space through a column of gas (air) which is about 20 km long. Intense light from the Sun is passing through this column, though it is not travelling directly towards the stargazer. The reason he or she cannot see the stars is because the small amount of light which has been Rayleigh

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scattered from the sunlight, is *much* brighter than the feeble light from the stars.

The scattered light is primarily blue, because as we noted above, blue light is more strongly scattered than red light. So what we see when we look at blue 'sky' is a kind of glow from the atmosphere caused by its illumination with sunlight.

Furthermore, if our stargazer waited for a more conventional time to observe the stars, he or she might spend a few moments observing the light from the Sun at sunset. They would notice that the Sun appears considerable dimmer as it nears the horizon, and that its colour is distinctly redder than during the daytime. We can understand both these phenomena by noting that in order for sunlight to reach our stargazer at sunset, the sunlight must pass through a considerably greater thickness of the atmosphere than it would have had to during the day. As Figure 5.35 shows, this is a very large effect because the atmosphere is so thin (roughly 20 km) in comparison with the diameter of the Earth (roughly 12800 km).

This immediately allows us to understand why the Sun is less bright at sunset than at midday: more light has been scattered out of sunlight. Furthermore, because the blue light has been scattered more strongly than the red (in order to make blue skies for other observers) the light reaching our sunset stargazer has a stronger yellow/red component than the original spectrum of sunlight.

Another way of looking at it

There is another way of arriving at Equation 5.126 for the Rayleigh scattered power, which starts from quite different assumptions about the scattering process.

We start by noting that the theory of the propagation of electromagnetic waves through substances predicts that a *homogeneous substance* does not scatter light at all. A homogeneous substance is one in which there is no change in refractive index from one region of the substance to another. This is in fact correct. It is perhaps most dramatically demonstrated by the ability of light to travel through the glass of optical fibres with attenuation as low as 1 % per kilometre! What happens in a homogeneous substance is that the light which is re-radiated from the oscillations of the atomic dipoles interferes constructively only in the forward direction. The homogeneity of the medium ensures that destructive interference in the sideways direction is complete.

We might then ask why gases produce Rayleigh scattered light when solids do not. Surely, gases are homogeneous? The answer is that optically they are not. Example 4.2 tells us that the number density of molecules in a gas, $n = P/k_{B}T$, is of the order of 10^{25} molecules per cubic metre. Since the molecules move independently of each other, statistically, we would then expect that this number should show fluctuations of the order of $\sqrt{n}$. This means that if we counted the molecules in one cubic metre, and compared the result with a

count of the molecules in a neighbouring cubic metre, we would expect both results to be close to 10^{25}, with differences of the order $\sqrt{10^{25}} \approx 3 \times 10^{12}$. Thus the fluctuations represent changes of around 3 parts in 10^{12} of the overall number density. We thus expect the refractive index (Equation 2.17) of each cubic metre to be the same to roughly 3 parts in 10^{12}. However, if we consider how the refractive index might vary from one wavelength of light to the next we arrive at quite a different conclusion.

If we consider a cube of side equal to a wavelength of light λ then the average number of molecules in such a cube is $n\lambda^3$ and the fluctuations from one wavelength to the next are of the order $\sqrt{n\lambda^3}$. The refractive index of each small cube will vary by roughly $\sqrt{n\lambda^3}/n\lambda^3 = 1/\sqrt{n\lambda^3}$. Substituting $n \approx 10^{25}$ molecules per cubic metre and $\lambda = 4 \times 10^{-7}$ m (blue light) we note that there are only around 6.4×10^5 molecules in each small volume. So the fluctuations in this number are around one part in a thousand. These fluctuations in density from one wavelength to the next mean that the amplitude of radiation scattered from each small volume is not quite the same. This in turn leads to the result that the destructive interference between neighbouring sources of scattered radiation is not quite total. In this view of Rayleigh scattering, it is not the molecules themselves which we consider to do the scattering, but the fluctuations in their density on the scale of a wavelength of light.

5.8.4 Data on the emission spectra of gases

As outlined in §5.7.3 on the electrical properties of gases, when an electric current is passed through a gas, the gas gives off light from its *positive column*. The colour of the light is indicative of the type of gas through which the current is passed. However 'colour' is a subjective description of the light which can be made quantitative by examination of the *spectrum* of the light.

A spectrometer is a device which separates out the different frequencies of electromagnetic wave present in light by means of a prism or, more usu-

Figure 5.36 A prism spectrometer. Light is collimated by passing it through slits and then reaches a prism. The different speeds (refractive indices) of different frequencies of light through the glass of the prism (Table 7.49) causes the different colours to take different paths through the prism. The light is then projected onto a screen (or other detector). If the light is from an incandescent lamp, then the intensity varies across the screen in a way similar to that illustrated as *A*. This would look like our familiar 'rainbow' spectrum. However light from the positive column of a discharge tube (*B*) produces a line spectrum, and the precise positions and relative intensities of the lines are uniquely characteristic of the type of gas within the discharge tube.
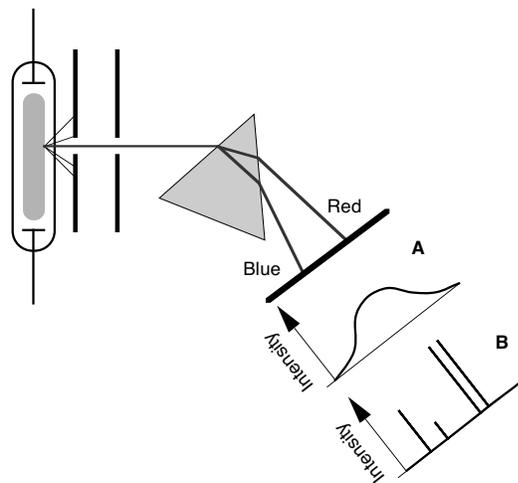
ally, a diffraction grating (Figure 5.36). If we examine the spectrum of a narrow slit illuminated by light from the gas, then we observe striking differences between white light from a heated filament lamp or the Sun, and light from the gas.

The emission spectrum of a gas is discrete: only certain frequencies (colours) characteristic of the molecules of the gas are present. For example, the presence of two very bright 'lines' close together with an average frequency of 509×10^{12} Hz (i.e. a wavelength of 589 nm in vacuum indicates the presence of sodium atoms in the gas. These lines appear 'yellow' to our eyes. Details of the spectra of sodium (vapour) and neon are shown in Figure 5.37.

By spectroscopic investigations, the composition of an unknown gas can be assessed by comparing its spectrum with reference spectra for known sub-

stances. This technique is used to determine the composition of the outer layers of stars, and in the examination of unknown materials as an alternative to 'wet' chemical analysis. This is the technique used to obtain the data on the composition of the outer part of the Sun detailed in Figure 2.1.

Historically, it was from studying the emission spectra of gases that our understanding of atomic structure was derived and checked. Thus the emission spectra of gases have played a key role in the development of the theory of quantum mechanics used to describe the electronic structure of atoms.

So the main question raised by this preliminary discussion of the experimental data on the emission spectra gases fields is:

* Why are the emission spectra of gases in the positive column of a discharge tube discrete, and characteristic of the atoms of the gas?

5.8.5 Understanding the data on the emission spectra of gases

The emission spectra of gases is more properly the subject of a book on atomic physics, but we can see roughly why the emission spectra are characteristic, without trying to calculate why the spectra have the particular form they have.

First we notice that within the positive column of a discharge tube we have molecules in several different states: electrically-neutral molecules, singly-ionised molecules, doubly-ionised molecules, and possibly higher ionisation states of the molecule. The internal electronic structure of each

Figure 5.37 The intensity of the light emitted as function of wavelength for sodium vapour and neon gas. On each spectrum the dotted curve represents the average sensitivity of the human eye. Note that:

* The vertical axis is logarithmic and is plotted in arbitrary units.
* Only about half the lines (those with intensities greater than 300) have been plotted.
* The positive column of a sodium vapour discharge lamp appears bright yellow because of the two closely spaced intense lines (the 'D' lines) at around 589nm, close to the peak of the spectral sensitivity of the eye.
* The positive column of a neon discharge lamp appears red because of the relative scarcity of *any* intense lines near the peak of the eye's sensitivity. The intense cluster of peaks at the red of the spectrum thus dominates the appearance of the spectrum even though the eye is very insensitive in this region of the spectrum.

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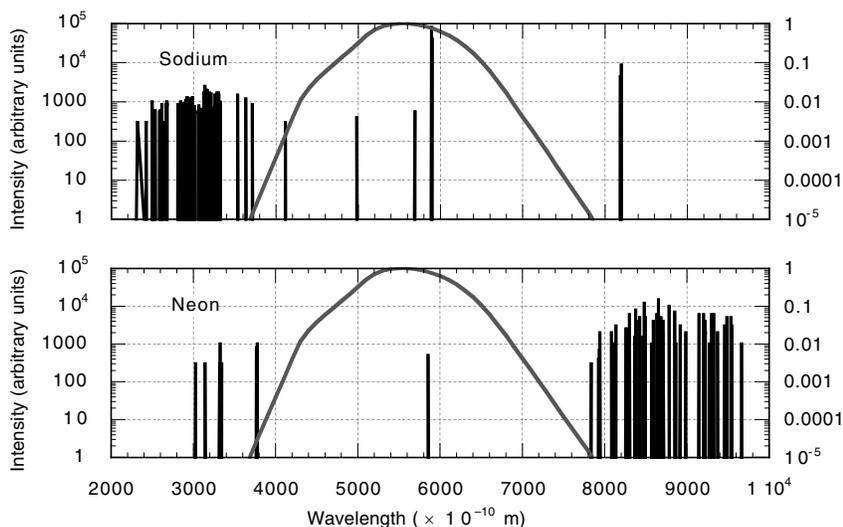
of these states of the molecule is similar, but slightly different. Let us assume for the moment that the molecules within the positive column are predominantly electrically neutral. These molecules are being continually bombarded by (a) other molecules as in a non-conducting gas, and (b) by ions and electrons with energies ranging up to the ionisation energy of the molecules.

Taking the analogy of a mechanical object, this high-energy bombardment sets a molecule 'ringing' at its natural resonant frequencies. In the same way, striking a bell sets it oscillating in characteristic patterns. Importantly, the resonant frequencies of a bell and the sound it produces are more characteristic of the size, shape and mass of the bell than they are of the way it was struck. Similarly, the molecules in a discharge tube oscillate in a characteristic manner, with characteristic frequencies depending on their internal electronic structure. These frequencies and their relative amplitudes depend more on the structure of the

molecules than on the nature of what is exciting them. The oscillation of charge density within the molecules causes radiation of energy according to Equation 5.126. The radiated power is proportional to the magnitude of the oscillating dipole moment p. If the resonant vibration of the charge within the atom is large, then the oscillating dipole moment p also becomes resonantly large, and the radiated power at that frequency is intense.

As mentioned in §2.4, quantum mechanically the phenomenon of resonance is described as a transition between quantum states. Thus in the correct quantum mechanical description, a resonance of frequency f_o is described in terms of the emission or absorption of quanta of radiation with energy $E = hf_o$. Thus the frequencies of light (the colours) emitted from the positive column of a discharge tube are the characteristic frequencies of the oscillation of electric charge within the molecules of the gas.

5.9 Magnetic Properties.

Gases in general have subtle magnetic properties, which may for many purposes be ignored, i.e. the magnetic permeability of the gas is very close to unity. However in detailed studies of the emission spectra (see above) of gases in magnetic fields it was observed that under the action of a strong

applied magnetic field, some of the lines in the spectrum of light from a gas could either change their position, or split into several lines. The observation and explanation of this *Zeeman effect* historically proved important in attempts to understand atomic structure.

5.10 Exercises

Exercises marked with a P prefix are 'normal' exercises. Those marked with a C prefix are best solved numerically by using a computer program or spreadsheet. Exercises marked with an E prefix are in general rather more challenging that the P and C exercises. Answers to all the exercises are downloadable from www.physicsofmatter.com

P1. Of the properties of gases listed below, which properties do not depend strongly on the microscopic properties of gas molecules other than their mass?

(a) Thermal conductivity (§ 5.4)

(b) Heat capacity at constant volume (§ 5.3)

(c) Heat capacity at constant pressure (§ 5.3)

(d) Density (§ 5.2)

(e) Thermal Expansivity (§ 5.2)

(f) Speed of Sound (§ 5.5)

(g) Dielectric Constant (§ 5.6)

(h) Refractive Index (§ 5.7)

(i) Emission Spectrum (§ 5.7)

Density and expansivity

P2. What is the approximate volume of 1 mole of any gas (a) at STP and (b) at room temperature and pressure? Work out the volume of the room you are in *now*:

Considering air to be made of 80% nitrogen and 20% oxygen (Table 5.2) approximately how many moles of oxygen and nitrogen are in the room? What is the mass of the air? If all the air were condensed into a solid, what volume would it occupy (Table 5.2 and Table 7.2)?

P3. Air held in a fixed volume of 1 litre has a pressure of 0.1333 MPa and a temperature of 0 °C. What is the mass of air in the container and what is the expected pressure at 100 °C (§ 5.2.2)?

P4. Compare the experimental results on the pressure coefficient β_P (Table 5.4) with those of a theory of your own devising. What is the relationship between the deviations from theory of the pressure and volume coefficients (Table 5.5)?

E5. The cylinder of a petrol engine initially contains approximately 10^{-3} mole of gas in a volume of 60 cm^3 at a temperature of around 200 °C. During the subsequent explosion, the gas pressure peaks at approximately 3×10^5 Pa before the cylinder expands adiabatically to a volume of 240 cm^3.

(a) What is the initial pressure of the gas (§ 5.2.3)?

(b) What is the peak force on the piston if its diameter is 5 cm?

(c) What is the peak temperature of the gas (§ 5.2.3)?

(d) Assuming the gas obeys:

$$PV^{\gamma} = \text{constant}$$

throughout the expansion, with $\gamma = 1.3$, estimate the pressure and temperature at the end of the expansion.

P6. Objects float if their *average* density is less than the density of the fluid in which they are immersed. A balloon of mass 10 g is made of a material with negligible wall thickness which does not stretch under pressure (a fair approximation for the plastic *Mylar*). It is filled with helium gas at 0°C and 1.1×10^5 Pa until it just floats in air at STP. (a) What is the volume of the balloon? (You should find that the volume of the balloon (expressed in m^3) is very roughly the same as the total load on the balloon (expressed in kg). (b) What volume must the balloon have if it is to lift the weight of an adult human being, say 70 kg? (c) If the balloon just floats at STP, will it float or sink if the temperature is increased to room temperature? (Assume the volume of the balloon stays constant.)

P7. A solid object of density 2000 kg m^{-3} is weighed on a simple balance against weights of density 8000 kg m^{-3}. (a) Derive an expression for the buoyancy (uplift) force on both the object and the weights if the measurement is carried out in air at room temperature and normal atmospheric pressure. (§5.2 and Tables 5.1 & 5.2). (b) Use the answer to (a) to show that no balance can be read with an accuracy greater than around 1 part in 10^4 unless the relative densities of the weights

and the object being weighed are considered.

P8. Approximately how many moles of gas are there in the Earth's atmosphere? What is the mass of this gas? Assume that: (i) the atmosphere exists at a uniform pressure of around half the normal atmospheric pressure at sea level; (ii) the average temperature is around 0 °C; (iii) that the atmosphere exists only up to a height of 10 km and (iv) that the atmosphere has the same composition as given in Table 5.2. The radius of the Earth is approximately 6400 km.

Assuming that the atmosphere has the same composition as given in Table 5.2, estimate the mass of CO_2 in the atmosphere. If the concentration of CO_2 increases by 1% each year, what mass of carbon joins the atmosphere each year? (§5.2.3). **Note:** The concentration of CO_2 in the atmosphere reflects the balance between processes which produce CO_2 (e.g. animals breathing, fuel-burning) and processes which remove CO_2 (e.g. rain, plant-growth). Understanding the actual concentrations is rather complex.

Heat capacity

P9. What is the molar heat capacity at constant pressure of (a) argon at 2000 K, (b) oxygen at −73.15 °C, (c) oxygen at 1000 K? (Tables 5.6 & 5.7)

P10. What is the molar heat capacity at constant pressure of the three major components of air (Table 5.2) at around room temperature? (Tables 5.6 & 5.7)

P11. At around room temperature and pressure, what is the value of γ (the ratio of the heat capacity at constant pressure to the heat capacity at constant volume), for (a) oxygen, (b) nitrogen (c) argon (d) carbon dioxide and (e) air. (Table 5.8). For each gas work out the number of degrees of freedom per molecule according to Equation 5.44 and compare your calculated values with mine in Table 5.9. To what extent is it fair to assume that, with regard to thermal properties, air behaves similarly to nitrogen?

P12. What is the ratio of the principal heat capacities γ for (a) helium at 0 °C, (b) mercury vapour at 0 °C, (c) krypton at 20 °C, (d) air at 500 °C, (e) steam at 100 °C, (f) methane and (g) ethane (Table 5.8)?

For each gas estimate the number of degrees of freedom of molecules of the gas according to Equation 5.44 and write a paragraph suggesting the molecular motions to which these degrees of freedom might correspond.(Tables 5.8 & 5.9)

P13. (a) What is the *heat capacity per kilogram* (at constant pressure) of argon gas at STP? Is it greater than or less than the *heat capacity per kilogram* of helium? (b) What is the heat capacity per cubic metre (at constant pressure) of argon gas at STP? Is it greater than or less than the heat capacity per cubic metre of helium?

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P14. The room in which I am writing this question is approximately 3m × 4m × 5m in size. Assuming that no heat is lost through the walls or my newly double-glazed windows, estimate how long I will have to run a 1 kW fan heater if I am to raise the air temperature in the room from 8 °C to 25 °C? (Tables 5.2, 5.8 & Question P2 above)

Do this experiment in your own room and compare the results of your experiment with your calculation. Based on the results of your experiment, state to what extent the heat in a room is stored in the air, and to what extent it is stored in a thin layer of plaster on the inside of the walls.

P15. From analysis of the variation with temperature of the heat capacity of oxygen, the text estimates that oxygen molecules vibrate with a frequency of around $f_o = 4.2 \times 10^{13}$ Hz. Following a similar method, estimate the vibrational frequencies of (a) hydrogen (H_2) and (b) chlorine (Cl_2) (Table 5.7, Figure 5.4). By considering the relative mass of hydrogen, oxygen and chlorine atoms, estimate the effective 'spring constant' K for each type of molecular bond (Equation 2.24 and Example 2.4).

Note: as discussed following Example 2.4 and Question P9 of Chapter 2, the correct mass to use in Equation 2.24 is actually the so-called *reduced mass*. However, since this calculation is 'order of magnitude' only, this does not affect our general conclusions.

P16. Following on from Question P8, estimate the heat capacity at constant pressure of the Earth's atmosphere.

Expansions and contractions

P17. Following on from the statement in §5.4.4 that:

$$PV^\gamma = \text{constant}$$

during an adiabatic volume change, show that it is also true that:

$$TV^{\gamma-1} = \text{another constant}$$

during an adiabatic volume change.

C18. To appreciate the distinctions between isothermal and adiabatic expansions try the following computer exercise. (a) For a given amount of gas, use a spreadsheet to evaluate P as a function of V for a range of different values of γ for both adiabatic and isothermal expansions. (b) Plot a graph of both (i) P as a function of V and (ii) T as a function of V for both adiabatic and isothermal expansions.

P19. If the 10 cc of air at atmospheric pressure in a bicycle pump are adiabatically compressed to 2.5 cc, work out the expected pressure and temperature of the gas. If you have a bicycle pump, see if the compression ratio of four that I have suggested above is about right and check whether the air really does get this hot.

Thermal conductivity

C20. Plot the thermal conductivity at 100 °C of the noble gases (Table 5.11) as a function of molecular mass, m. By re-plotting the data as a function of $m^{-1/2}$, discuss to what the extent the data agree with the theory summarised in Example 5.9. Now repeat the analysis for diatomic gases in Table 5.11 at both 0 °C and 100 °C: do the same general conclusions apply?

C21. From www.physicsofmatter.com you can download a small program illustrating the dynamics of molecules in 2-dimensions. In the 'help' section of the demo are some suggestions for phenomena you might like to observe. In particular you should set the program going with the option to plot molecular trajectories ON and MOLECULAR INTERACTIONS switched ON. You should look carefully to see if you can observe the 'orbiting collisions' referred to at the end of Chapter 4.

P22. Estimate the mean free path λ_{mfp} of helium molecules at a pressure of 1 Pa based on the molecular size data of Table 5.13. If the gas is contained in a region where the walls are separated by a distance of 1 mm, will the gas still be in the plateau region of thermal conductivity, or will the thermal conductivity have begun to decrease? (Figure 5.18).

P23. A *Pirani gauge* is a device to measure the pressure of a gas at low pressures. The device consists of a heated filament which is cooled by the gas. In the pressure range where the thermal conductivity of the gas changes with pressure, the temperature of the filament varies with gas pressure. Thus, after calibration, measurement of the temperature of the filament by a thermocouple or resistance thermometer (Chapter 2) allows determination of the pressure. By considering Figure 5.18 and Equation 5.85, estimate the size of the container in which the element should be suspended if the device works only at pressures below 100 Pa.

P24. A cubic container of volume 1 m³ is heated from the bottom such that air at the bottom is approximately 10 °C hotter than air at the top (Figure 5.13). (a) If the box is at a temperature around room temperature and at normal atmospheric pressure, approximately how many moles of gas are in the box? (b) Convection lifts 0.1 mole per second of air from the bottom to the top. Estimate the heat flow across the container due to convection? Is it greater or less than would be expected due to the 'still air' thermal conductivity listed in Table 5.11 alone?

C25. Table 5.12 shows the reduction of the effective diameter a of monatomic gas molecules as the temperature is increased. Plot a graph of a^2 versus $1/T$. You should see straight-line behaviour, a phenomenon noted by Sutherland. From the $1/T = 0$ intercept (i.e. corresponding to $T = \infty$), estimate the high-temperature 'hard core' diameter of an argon atom.

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Analyse the data for the thermal conductivity of a diatomic gas (e.g. N_2) in same way as the text analyses the thermal conductivity of the monatomic gases. Does this analysis support or contradict the conclusions that the text draws from the analysis of the monatomic gas data?

Speed of sound

P26. What is the speed of sound in (a) helium and (b) deuterium at STP? What conclusion can be drawn from the difference between these results? (Table 5.14)

P27. What is the speed of sound in dry air at STP? (§5.6.1) What value would you expect for the speed of sound in air at normal room temperature (approximately 20 °C)? (Equation 5.93 and Example 5.11).

P28. During a thunderstorm, you observe that a lightning flash and the start of a peel of thunder are separated by t seconds. By considering the likely speed of sound in the atmosphere (§5.6.1 and Equation 5.93), derive a rule of thumb for estimating the distance of a lightning strike (in kilometres), based on a measurement of t.

E29. A siren in a flat region of England emits sound waves upwards and outwards in a hemispherical pattern. If the speed of sound were constant, the wave-fronts would form concentric hemispheres centred on the siren. However the speed of sound falls with decreasing temperature, and since the atmosphere becomes progressively colder with increasing altitude, the wave-fronts become distorted. Sketch the wave-fronts for (a) the normal situation and (b) the rare occasion (known as a *temperature inversion*) when warm air is trapped above colder air. In (b) show graphically how sound can be 'focussed' back onto the ground at large distances from the siren.

[**Aside**: Its interesting that the fall in pressure with height in the atmosphere does not affect this problem to first order, but look at Chapter 12: Q6 to discover the link between the decline in pressure with altitude and the decline in temperature.]

P30. You may have learned in your school years that 'sound cannot travel in a vacuum'. This is certainly true, but interestingly Equation 5.93 for the speed of sound has no explicit dependence on pressure. So consider a chamber into which a loud speaker is emitting a continuous tone. Write a short discussion of what will happen to the sound wave as the air is removed.

P31. If a volcano explosion near Australia were loud enough to be heard in England, roughly how long after the explosion would it be heard? (§5.6.1) If, instead, seismometers were used to detect the sound waves that travelled directly through the earth, estimate very roughly (Table 7.9) when the explosion would be detected. The radius of the Earth is 6,400 km

P32. Could a device be built which would measure the temperature of the air by measuring the speed of sound through it (§5.6)? If you did build such a device, what problems would you expect to have? What frequency of sound would you choose if the device were to be portable?

E33. A *flame* is a region of very hot gas (typically in the range 1500 °C to 2000 °C) that occurs close to exothermic chemical reactions. Determining the temperature of flames is important for optimising the combustion process, i.e. reducing unwanted combustion products and maximising energy output. However determining the temperature accurately is very difficult by conventional means. One way is to measure the speed of sound through a small region of the flame. An intense laser heats a small region of the gas rapidly. A pressure pulse (sound wave) moves away from the heated region and the change in refractive index a short distance away is measured by the effect on a second pulse beam. By measuring the time delay between the laser pulse and the effect on the probe beam the speed of sound can be determined. By considering Equation 5.93, estimate the uncertainty with which the temperature can be determined given a plausible level of uncertainty in (a) knowledge of the molecules present in the flame and (b) the change of γ with temperature.

P34. In Chapter 12 Question 6 you are asked to show that the magnitude of the temperature oscillations, ΔT, in a sound wave in a gas at temperature T and pressure P is given by:

$$\frac{\Delta T}{T} = \left(1 - \frac{1}{\gamma}\right)\frac{\Delta P}{P}$$

where ΔP is the magnitude of the pressure oscillations in the sound wave. For a sound wave in air with a pressure amplitude of 0.2 Pa estimate the magnitude of the temperature oscillations. How could you imagine measuring such oscillations? [Aside: if a sound wave has this amplitude is said to have a sound pressure level in decibels of 80 db. At a frequency of around 1 kHz, sound waves of this amplitude would be subjectively experienced as very loud — equivalent to standing near a road as a lorry passes by]

P35. Based on the speed of sound in air at STP (§5.6.1) estimate the root mean square (RMS) speed of molecules in air at STP according to Equation 5.99. How does this estimate compare with the one derived from the Maxwell speed distribution for nitrogen at 0 °C. (Table 5.8, Question C3 in §4.5).

P36. Describe, with the aid of labelled sketches, an apparatus that could be used to determine γ for gases at a range of temperatures by measuring the speed of sound in the gas. In analysis of your results, how would you separate out the $T^{1/2}$ dependence of the speed of

sound from the variations of γ with temperature? (Equation 5.93)

P37. We saw in §5.6.2 that the compressions and expansions in sound waves are always adiabatic. This is because the thermal conductivity of gases is so poor that the hotter (high-pressure) and colder (low-pressure) regions cannot communicate over a distance of half a wavelength, in the half-period before the wave reverses phase. If we wanted to observe a hypothetical isothermal sound wave, should we try moving to very low frequencies, or very high frequencies?

Electrical properties

P38. A parallel-plate capacitor of plate area $A = 1$ cm^2 and plate separation $d = 1$ mm has a capacitance of $C = \varepsilon\varepsilon_0 A/d$. Work out the capacitance if there is a vacuum between the two plates. What would be the percentage change in the capacitance if the space between the two plates was filled with (a) air at STP (b) CO_2 at STP (c) CO_2 at 1 atmosphere and 100 °C and (d) CO_2 at 100 atmospheres and 100 °C. (Table 5.16, Figure 5.25)

P39. What is the dielectric constant of (a) helium, (b) neon (c) argon and (d) nitrogen at STP? (Table 5.16) Use Equation 5.109 to estimate the polarisability of a single molecule of the each of the gases (a) to (d). State which molecule is the least polarisable, and which the most, and briefly suggest the features of each kind of atom which determine its polarisability (Figure 5.24).

P40. What is the dielectric constant of water (steam) at 100 °C (Table 5.16) Use Equation 5.116 to estimate the size of the permanent dipole moment on a water molecule in Debye units.

P41. What is the approximate breakdown field of air around room temperature and atmospheric pressure (Figure 5.28)?

P42. Around high voltage apparatus such as *Van der Graaf* generators, electrical breakdown may be prevented by enclosing the entire apparatus in an atmosphere of sulphur hexafluoride gas (SF_6). Given that the device must operate at around room temperature, should the gas be at high or low pressure (Figure 5.28)? What is the maximum conceivable breakdown field for the gas?

Optical properties

P43. What are (i) the refractive index and (ii) the speed of light, in (a) a vacuum (b) air at STP (c) helium at STP and (d) xenon at STP.(Table 5.18)?

P44. What is the ratio of the wavelength of light to the approximate diameter of an argon atom (Table 5.13 and Figure 5.32)?

P45. Equations 5.117 and 5.118 predict that at constant temperature, the difference of the dielectric constant of a gas from unity ($\varepsilon - 1$) is proportional to pressure. By considering Equation 2.17, show that as long as ($\varepsilon - 1$) $\ll$ 1, the difference between the refractive index of a gas and unity is also proportional to pressure.

P46. What is the wavelength of (yellow) light with a frequency of 5.09×10^{14} Hz (a) in a vacuum and (b) in air at STP (0 °C and 1.013×10^5 Pa). As you may have shown in the previous question, the difference of the refractive index of a gas from unity is proportional to pressure. (c) Use the answers to part (a) and (b) to estimate the wavelength of the light in air at 0 °C and 1.023×10^5 Pa. (Table 5.18)

Why is the above calculation relevant? Before it reaches us, light from stars passes through the atmosphere, which is not quite uniform. The pressure of the air fluctuates slightly over a time scale of a few seconds, and differs slightly above neighbouring points on the ground. Show with the aid of a sketch how this effect can lead to distortions of the initially parallel wavefronts from a distant star. Explain how this leads to the 'twinkling' of stars when observed from the ground.

P47. A star is observed through a ground-based telescope to be at an angle of 45° above the horizon. Taking account of the refraction by the Earth's atmosphere, estimate the actual angle above the horizon.

P48. Figure 3.8 shows the use of an optical interferometer to determine the refractive index of light in a gas. Initially the sample arm of the apparatus is at vacuum. For a path length in the gas of 50 cm and yellow light with a frequency of 5.09×10^{14} Hz, calculate the pressure of helium gas required to produce a single wavelength phase shift between the two beams. (See also problem P11 in Chapter 3)

P49. The intensity, I, of a light beam is reduced (due to scattering) as it travels a distance x through the atmosphere according to $I = I_0 \exp(-x/\lambda)$. Derive an order of magnitude estimate of λ for air under typical conditions based on your own observations of the atmosphere.

P50. Figure 5.37 shows the emission spectra of sodium and neon. Both spectra have emission peaks in the range 580 nm to 590 nm, close to the peak sensitivity of the human eye. Taking note of the logarithmic scale, explain why an electrical discharge through sodium vapour appears yellow and through neon appears red.

P51. Estimate the refractive index of water vapour at STP by extrapolation from the refractive index of liquid water. How accurate is your estimate? (Table 5.18, §9.13 and Table 9.21)