



# The properties of gases

## 1A The perfect gas

### Answers to discussion questions

**D1A.1** An equation of state is an equation that relates the variables that define the state of a system to each other. Boyle, Charles, and Avogadro established these relations for gases at low pressures (perfect gases) by appropriate experiments. Boyle determined how volume varies with pressure ( $V \propto 1/p$ ), Charles how volume varies with temperature ( $V \propto T$ ), and Avogadro how volume varies with amount of gas ( $V \propto n$ ). Combining all of these proportionalities into one gives

$$V \propto \frac{nT}{p}$$

Inserting the constant of proportionality,  $R$ , yields the perfect gas equation

$$V = R \frac{nT}{p} \quad \text{or} \quad pV = nRT$$

### Solutions to exercises

**E1A.1(a)** From the inside the front cover the conversion between pressure units is: 1 atm  $\equiv$  101.325 kPa  $\equiv$  760 Torr; 1 bar is  $10^5$  Pa exactly.

(i) A pressure of 108 kPa is converted to Torr as follows

$$108 \text{ kPa} \times \frac{1 \text{ atm}}{101.325 \text{ kPa}} \times \frac{760 \text{ Torr}}{1 \text{ atm}} = \boxed{810 \text{ Torr}}$$

(ii) A pressure of 0.975 bar is  $0.975 \times 10^5$  Pa, which is converted to atm as follows

$$0.975 \times 10^5 \text{ Pa} \times \frac{1 \text{ atm}}{101.325 \text{ kPa}} = \boxed{0.962 \text{ atm}}$$

**E1A.2(a)** The perfect gas law [1A.4–8],  $pV = nRT$ , is rearranged to give the pressure,  $p = nRT/V$ . The amount  $n$  is found by dividing the mass by the molar mass of Xe,  $131.29 \text{ g mol}^{-1}$ .

$$p = \frac{\overbrace{(131 \text{ g})}^n}{(131.29 \text{ g mol}^{-1})} \frac{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{1.0 \text{ dm}^3}$$
$$= 24.4 \text{ atm}$$

So **no**, the sample would not exert a pressure of 20 atm, but **24.4 atm** if it were a perfect gas.

**EIA.3(a)** Because the temperature is constant (isothermal) Boyle's law applies,  $pV = \text{const}$ . Therefore the product  $pV$  is the same for the initial and final states

$$p_f V_f = p_i V_i \quad \text{hence} \quad p_i = p_f V_f / V_i$$

The initial volume is  $2.20 \text{ dm}^3$  greater than the final volume so  $V_i = 4.65 + 2.20 = 6.85 \text{ dm}^3$ .

$$p_i = \frac{V_f}{V_i} \times p_f = \frac{4.65 \text{ dm}^3}{6.85 \text{ dm}^3} \times (5.04 \text{ bar}) = 3.42 \text{ bar}$$

(i) The initial pressure is **3.42 bar**

(ii) Because a pressure of 1 atm is equivalent to 1.01325 bar, the initial pressure expressed in atm is

$$\frac{1 \text{ atm}}{1.01325 \text{ bar}} \times 3.40 \text{ bar} = \mathbf{3.38 \text{ atm}}$$

**EIA.4(a)** If the gas is assumed to be perfect, the equation of state is [1A.4–8],  $pV = nRT$ . In this case the volume and amount (in moles) of the gas are constant, so it follows that the pressure is proportional to the temperature:  $p \propto T$ . The ratio of the final and initial pressures is therefore equal to the ratio of the temperatures:  $p_f/p_i = T_f/T_i$ . The pressure indicated on the gauge is that in excess of atmospheric pressure, thus the initial pressure is  $24 + 14.7 = 38.7 \text{ lb in}^{-2}$ . Solving for the final pressure  $p_f$  (remember to use absolute temperatures) gives

$$\begin{aligned} p_f &= \frac{T_f}{T_i} \times p_i \\ &= \frac{(35 + 273.15) \text{ K}}{(-5 + 273.15) \text{ K}} \times (38.7 \text{ lb in}^{-2}) = 44.4... \text{ lb in}^{-2} \end{aligned}$$

The pressure indicated on the gauge is this final pressure, minus atmospheric pressure:  $44.4... - 14.7 = \mathbf{30 \text{ lb in}^{-2}}$ . This assumes that (i) the gas is behaving perfectly and (ii) that the tyre is rigid.

**EIA.5(a)** The perfect gas law  $pV = nRT$  is rearranged to give the pressure

$$\begin{aligned} p &= \frac{nRT}{V} \\ &= \frac{\overbrace{255 \times 10^{-3} \text{ g}}^n}{20.18 \text{ g mol}^{-1}} \times \frac{(8.3145 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times (122 \text{ K})}{3.00 \text{ dm}^3} \\ &= \mathbf{0.0427 \text{ bar}} \end{aligned}$$

Note the choice of  $R$  to match the units of the problem. An alternative is to use  $R = 8.3154 \text{ J K}^{-1} \text{ mol}^{-1}$  and adjust the other units accordingly, to give a pressure in Pa.

$$p = \frac{[(255 \times 10^{-3} \text{ g}) / (20.18 \text{ g mol}^{-1})] \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (122 \text{ K})}{3.00 \times 10^{-3} \text{ m}^3}$$

$$= \boxed{4.27 \times 10^5 \text{ Pa}}$$

where  $1 \text{ dm}^3 = 10^{-3} \text{ m}^3$  has been used along with  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ .

- E1A.6(a)** The vapour is assumed to be a perfect gas, so the gas law  $pV = nRT$  applies. The task is to use this expression to relate the measured mass density to the molar mass.

First, the amount  $n$  is expressed as the mass  $m$  divided by the molar mass  $M$  to give  $pV = (m/M)RT$ ; division of both sides by  $V$  gives  $p = (m/V)(RT/M)$ . The quantity  $(m/V)$  is the mass density  $\rho$ , so  $p = \rho RT/M$ , which rearranges to  $M = \rho RT/p$ ; this is the required relationship between  $M$  and the density.

$$M = \frac{\rho RT}{p} = \frac{(3.710 \text{ kg m}^{-3}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ([500 + 273.15] \text{ K})}{93.2 \times 10^3 \text{ Pa}}$$

$$= 0.255... \text{ kg mol}^{-1}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$  have been used. The molar mass of S is  $32.06 \text{ g mol}^{-1}$ , so the number of S atoms in the molecules comprising the vapour is  $(0.255... \times 10^3 \text{ g mol}^{-1}) / (32.06 \text{ g mol}^{-1}) = 7.98$ . The result is expected to be an integer, so the formula is likely to be  $\boxed{\text{S}_8}$ .

- E1A.7(a)** The vapour is assumed to be a perfect gas, so the gas law  $pV = nRT$  applies; the task is to use this expression to relate the measured data to the mass  $m$ . This is done by expressing the amount  $n$  as  $m/M$ , where  $M$  is the molar mass. With this substitution it follows that  $m = MPV/RT$ .

The partial pressure of water vapour is 0.60 times the saturated vapour pressure

$$m = \frac{MpV}{RT}$$

$$= \frac{(18.0158 \text{ g mol}^{-1}) \times (0.60 \times 0.0356 \times 10^5 \text{ Pa}) \times (400 \text{ m}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ([27 + 273.15] \text{ K})}$$

$$= 6.2 \times 10^3 \text{ g} = \boxed{6.2 \text{ kg}}$$

- E1A.8(a)** Consider  $1 \text{ m}^3$  of air: the mass of gas is therefore 1.146 kg. If perfect gas behaviour is assumed, the amount in moles is given by  $n = pV/RT$

$$n = \frac{pV}{RT} = \frac{(0.987 \times 10^5 \text{ Pa}) \times (1 \text{ m}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ([27 + 273.15] \text{ K})} = 39.5... \text{ mol}$$

- (i) The total amount in moles is  $n = n_{\text{O}_2} + n_{\text{N}_2}$ . The total mass  $m$  is computed from the amounts in moles and the molar masses  $M$  as

$$m = n_{\text{O}_2} \times M_{\text{O}_2} + n_{\text{N}_2} \times M_{\text{N}_2}$$

These two equations are solved simultaneously for  $n_{\text{O}_2}$  to give the following expression, which is then evaluated using the data given

$$\begin{aligned} n_{\text{O}_2} &= \frac{m - M_{\text{N}_2} n}{M_{\text{O}_2} - M_{\text{N}_2}} \\ &= \frac{(1146 \text{ g}) - (28.02 \text{ g mol}^{-1}) \times (39.5\dots \text{ mol})}{(32.00 \text{ g mol}^{-1}) - (28.02 \text{ g mol}^{-1})} = 9.50\dots \text{ mol} \end{aligned}$$

The mole fractions are therefore

$$x_{\text{O}_2} = \frac{n_{\text{O}_2}}{n} = \frac{9.50\dots \text{ mol}}{39.5\dots \text{ mol}} = \boxed{0.240} \quad x_{\text{N}_2} = 1 - x_{\text{O}_2} = \boxed{0.760}$$

The partial pressures are given by  $p_i = x_i p_{\text{tot}}$

$$p_{\text{O}_2} = x_{\text{O}_2} p_{\text{tot}} = 0.240(0.987 \text{ bar}) = \boxed{0.237 \text{ bar}}$$

$$p_{\text{N}_2} = x_{\text{N}_2} p_{\text{tot}} = 0.760(0.987 \text{ bar}) = \boxed{0.750 \text{ bar}}$$

- (ii) The simultaneous equations to be solved are now

$$n = n_{\text{O}_2} + n_{\text{N}_2} + n_{\text{Ar}} \quad m = n_{\text{O}_2} M_{\text{O}_2} + n_{\text{N}_2} M_{\text{N}_2} + n_{\text{Ar}} M_{\text{Ar}}$$

Because it is given that  $x_{\text{Ar}} = 0.01$ , it follows that  $n_{\text{Ar}} = n/100$ . The two unknowns,  $n_{\text{O}_2}$  and  $n_{\text{N}_2}$ , are found by solving these equations simultaneously to give

$$\begin{aligned} n_{\text{N}_2} &= \frac{100m - n(M_{\text{Ar}} + 99M_{\text{O}_2})}{100(M_{\text{N}_2} - M_{\text{O}_2})} \\ &= \frac{100 \times (1146 \text{ g}) - (39.5\dots \text{ mol}) \times [(39.95 \text{ g mol}^{-1}) + 99 \times (32.00 \text{ g mol}^{-1})]}{100 \times [(28.02 \text{ g mol}^{-1}) - (32.00 \text{ g mol}^{-1})]} \\ &= 30.8\dots \text{ mol} \end{aligned}$$

From  $n = n_{\text{O}_2} + n_{\text{N}_2} + n_{\text{Ar}}$  it follows that

$$\begin{aligned} n_{\text{O}_2} &= n - n_{\text{Ar}} - n_{\text{N}_2} \\ &= (39.5\dots \text{ mol}) - 0.01 \times (39.5\dots \text{ mol}) - (30.8\dots \text{ mol}) = 8.31\dots \text{ mol} \end{aligned}$$

The mole fractions are

$$x_{\text{N}_2} = \frac{n_{\text{N}_2}}{n} = \frac{30.8\dots \text{ mol}}{39.5\dots \text{ mol}} = \boxed{0.780} \quad x_{\text{O}_2} = \frac{n_{\text{O}_2}}{n} = \frac{8.31\dots \text{ mol}}{39.5\dots \text{ mol}} = \boxed{0.210}$$

The partial pressures are

$$p_{\text{N}_2} = x_{\text{N}_2} p_{\text{tot}} = 0.780 \times (0.987 \text{ bar}) = \boxed{0.770 \text{ bar}}$$

$$p_{\text{O}_2} = x_{\text{O}_2} p_{\text{tot}} = 0.210 \times (0.987 \text{ bar}) = \boxed{0.207 \text{ bar}}$$

Note: the final values are quite sensitive to the precision with which the intermediate results are carried forward.

- E1A.9(a)** The vapour is assumed to be a perfect gas, so the gas law  $pV = nRT$  applies. The task is to use this expression to relate the measured mass density to the molar mass.

First, the amount  $n$  is expressed as the mass  $m$  divided by the molar mass  $M$  to give  $pV = (m/M)RT$ ; division of both sides by  $V$  gives  $p = (m/V)(RT/M)$ . The quantity  $(m/V)$  is the mass density  $\rho$ , so  $p = \rho RT/M$ , which rearranges to  $M = \rho RT/p$ ; this is the required relationship between  $M$  and the density.

$$\begin{aligned} M &= \frac{\rho RT}{p} \\ &= \frac{(1.23 \text{ kg m}^{-3}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (330 \text{ K})}{20.0 \times 10^3 \text{ Pa}} \\ &= \boxed{0.169 \text{ kg mol}^{-1}} \end{aligned}$$

The relationships  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$  have been used.

- E1A.10(a)** Charles' law [1A.3b–7] states that  $V \propto T$  at constant  $n$  and  $p$ , and  $p \propto T$  at constant  $n$  and  $V$ . For a fixed amount the density  $\rho$  is proportional to  $1/V$ , so it follows that  $1/\rho \propto T$ . At absolute zero the volume goes to zero, so the density goes to infinity and hence  $1/\rho$  goes to zero. The approach is therefore to plot  $1/\rho$  against the temperature (in  $^{\circ}\text{C}$ ) and then by extrapolating the straight line find the temperature at which  $1/\rho = 0$ . The plot is shown in Fig 1.1.

$\theta/^{\circ}\text{C}$	$\rho/(\text{g dm}^{-3})$	$(1/\rho)/(\text{g}^{-1} \text{ dm}^3)$
-85	1.877	0.532 8
0	1.294	0.772 8
100	0.946	1.057 1

The data are a good fit to a straight line, the equation of which is

$$(1/\rho)/(\text{g}^{-1} \text{ dm}^3) = 2.835 \times 10^{-3} \times (\theta/^{\circ}\text{C}) + 0.7734$$

The intercept with  $1/\rho = 0$  is found by solving

$$0 = 2.835 \times 10^{-3} \times (\theta/^{\circ}\text{C}) + 0.7734$$

This gives  $\boxed{\theta = -273^{\circ}\text{C}}$  as the estimate of absolute zero.

- E1A.11(a)** (i) The mole fractions are

$$x_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{H}_2} + n_{\text{N}_2}} = \frac{2.0 \text{ mol}}{2.0 \text{ mol} + 1.0 \text{ mol}} = \boxed{\frac{2}{3}} \quad x_{\text{N}_2} = 1 - x_{\text{H}_2} = \boxed{\frac{1}{3}}$$

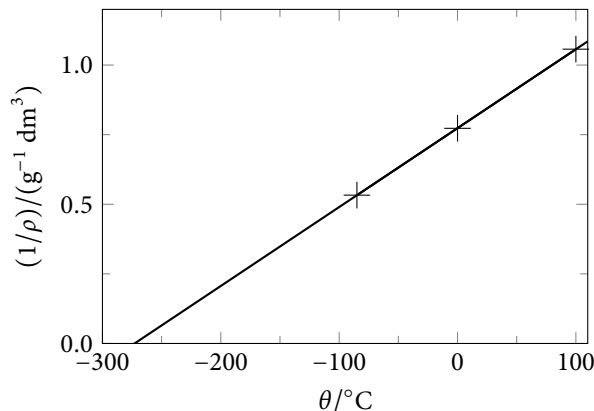


Figure 1.1

- (ii) The partial pressures are given by  $p_i = x_i p_{\text{tot}}$ . The total pressure is given by the perfect gas law:  $p_{\text{tot}} = n_{\text{tot}}RT/V$

$$p_{\text{H}_2} = x_{\text{H}_2} p_{\text{tot}} = \frac{2}{3} \times \frac{(3.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.4 \times 10^{-3} \text{ m}^3}$$

$$= \boxed{2.0 \times 10^5 \text{ Pa}}$$

$$p_{\text{N}_2} = x_{\text{N}_2} p_{\text{tot}} = \frac{1}{3} \times \frac{(3.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.4 \times 10^{-3} \text{ m}^3}$$

$$= \boxed{1.0 \times 10^5 \text{ Pa}}$$

Expressed in atmospheres these are 2.0 atm and 1.0 atm, respectively.

- (iii) The total pressure is

$$\frac{(3.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.4 \times 10^{-3} \text{ m}^3} = \boxed{3.0 \times 10^5 \text{ Pa}}$$

or 3.00 atm.

Alternatively, note that 1 mol at STP occupies a volume of  $22.4 \text{ dm}^3$ , which is the stated volume. As there are a total of 3.0 mol present the (total) pressure must therefore be 3.0 atm.

## Solutions to problems

- PIA.1** (a) The expression  $\rho gh$  gives the pressure in Pa if all the quantities are in SI units, so it is helpful to work in Pa throughout. From the front cover, 760 Torr is exactly 1 atm, which is  $1.01325 \times 10^5 \text{ Pa}$ . The density of  $13.55 \text{ g cm}^{-3}$  is equivalent to  $13.55 \times 10^3 \text{ kg m}^{-3}$ .

$$p = p_{\text{ex}} + \rho gh$$

$$= 1.01325 \times 10^5 \text{ Pa} + (13.55 \times 10^3 \text{ kg m}^{-3}) \times (9.806 \text{ m s}^{-2})$$

$$\times (10.0 \times 10^{-2} \text{ m}) = \boxed{1.15 \times 10^5 \text{ Pa}}$$

(b) The calculation of the pressure inside the apparatus proceeds as in (a)

$$p = 1.01325 \times 10^5 \text{ Pa} + (0.9971 \times 10^3 \text{ kg m}^{-3}) \times (9.806 \text{ m s}^{-2}) \\ \times (183.2 \times 10^{-2} \text{ m}) = 1.192... \times 10^5 \text{ Pa}$$

The value of  $R$  is found by rearranging the perfect gas law to  $R = pV/nT$

$$R = \frac{pV}{nT} = \frac{(1.192... \times 10^5 \text{ Pa}) \times (20.000 \times 10^{-3} \text{ m}^3)}{[(1.485 \text{ g})/(4.003 \text{ g mol}^{-1})] \times ([500 + 273.15] \text{ K})} \\ = \boxed{8.315 \text{ J K}^{-1} \text{ mol}^{-1}}$$

### PIA.3

The perfect gas law  $pV = nRT$  implies that  $pV_m = RT$ , where  $V_m$  is the molar volume (the volume when  $n = 1$ ). It follows that  $p = RT/V_m$ , so a plot of  $p$  against  $T/V_m$  should be a straight line with slope  $R$ .

However, real gases only become ideal in the limit of zero pressure, so what is needed is a method of extrapolating the data to zero pressure. One approach is to rearrange the perfect gas law into the form  $pV_m/T = R$  and then to realise that this implies that for a real gas the quantity  $pV_m/T$  will tend to  $R$  in the limit of zero pressure. Therefore, the intercept at  $p = 0$  of a plot of  $pV_m/T$  against  $p$  is an estimate of  $R$ . For the extrapolation of the line back to  $p = 0$  to be reliable, the data points must fall on a reasonable straight line. The plot is shown in Fig 1.2.

$p/\text{atm}$	$V_m/(\text{dm}^3 \text{ mol}^{-1})$	$(pV_m/T)/(\text{atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1})$
0.750 000	29.8649	0.082 001 4
0.500 000	44.8090	0.082 022 7
0.250 000	89.6384	0.082 041 4

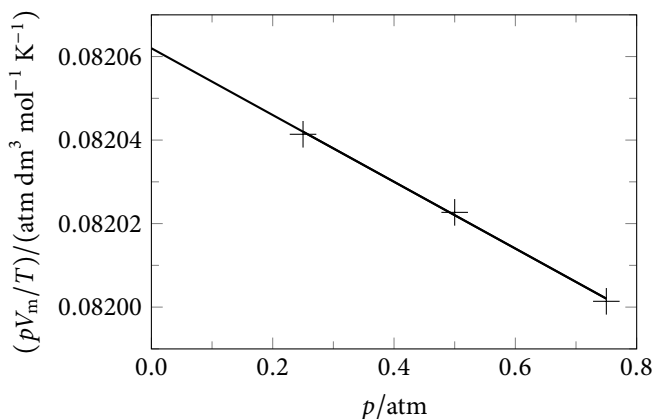


Figure 1.2

The data fall on a reasonable straight line, the equation of which is

$$(pV_m/T)/(\text{atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}) = -7.995 \times 10^{-5} \times (p/\text{atm}) + 0.082062$$

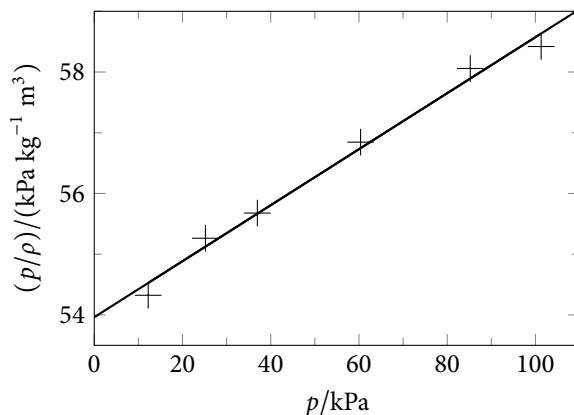
The estimate for  $R$  is therefore the intercept,  $0.082062 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ . The data are given to 6 figures, but they do not fall on a very good straight line so the value for  $R$  has been quoted to one fewer significant figure.

**PIA.5** For a perfect gas  $pV = nRT$  which can be rearranged to give  $p = nRT/V$ . The amount in moles is  $n = m/M$ , where  $M$  is the molar mass and  $m$  is the mass of the gas. Therefore  $p = (m/M)(RT/V)$ . The quantity  $m/V$  is the mass density  $\rho$ , and hence

$$p = \rho RT/M$$

It follows that for a perfect gas  $p/\rho$  should be a constant at a given temperature. Real gases are expected to approach this as the pressure goes to zero, so a suitable plot is of  $p/\rho$  against  $p$ ; the intercept when  $p = 0$  gives the best estimate of  $RT/M$ . The plot is shown in Fig. 1.3.

$p/\text{kPa}$	$\rho/(\text{kg m}^{-3})$	$(p/\rho)/(\text{kPa kg}^{-1} \text{ m}^3)$
12.22	0.225	54.32
25.20	0.456	55.26
36.97	0.664	55.68
60.37	1.062	56.85
85.23	1.468	58.06
101.30	1.734	58.42



**Figure 1.3**

The data fall on a reasonable straight line, the equation of which is

$$(p/\rho)/(\text{kPa kg}^{-1} \text{ m}^3) = 0.04610 \times (p/\text{kPa}) + 53.96$$



The intercept is  $(p/\rho)_{\lim p \rightarrow 0}$ , which is equal to  $RT/M$ .

$$M = \frac{RT}{(p/\rho)_{\lim p \rightarrow 0}} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{53.96 \times 10^3 \text{ Pa kg}^{-1} \text{ m}^3} = 4.594 \times 10^{-2} \text{ kg mol}^{-1}$$

The estimate of the molar mass is therefore  $\boxed{45.94 \text{ g mol}^{-1}}$ .

- PIA.7** (a) For a perfect gas  $pV = nRT$  so it follows that for a sample at constant volume and temperature,  $p_1/T_1 = p_2/T_2$ . If the pressure increases by  $\Delta p$  for an increase in temperature of  $\Delta T$ , then with  $p_2 = p_1 + \Delta p$  and  $T_2 = T_1 + \Delta T$  it follows that

$$\frac{p_1}{T_1} = \frac{p_1 + \Delta p}{T_1 + \Delta T} \quad \text{hence} \quad \Delta p = \frac{p_1 \Delta T}{T_1}$$

For an increase by 1.00 K,  $\Delta T = 1.00 \text{ K}$  and hence

$$\Delta p = \frac{p_1 \Delta T}{T_1} = \frac{(6.69 \times 10^3 \text{ Pa}) \times (1.00 \text{ K})}{273.16 \text{ K}} = \boxed{24.5 \text{ Pa}}$$

Another way of looking at this is to write the rate of change of pressure with temperature as

$$\frac{\Delta p}{\Delta T} = \frac{p_1}{T_1} = \frac{6.69 \times 10^3 \text{ Pa}}{273.16 \text{ K}} = 24.5... \text{ Pa K}^{-1}$$

- (b) A temperature of  $100.00 \text{ }^\circ\text{C}$  is equivalent to an increase in temperature from the triple point by  $100.00 + 273.15 - 273.16 = 99.99 \text{ K}$

$$\Delta p' = \Delta T' \times \left( \frac{\Delta p}{\Delta T} \right) = (99.99 \text{ K}) \times \frac{6.69 \times 10^3 \text{ Pa}}{273.16 \text{ K}} = 2.44... \times 10^3 \text{ Pa}$$

The final pressure is therefore  $6.69 + 2.44... = \boxed{9.14 \text{ kPa}}$ .

- (c) For a perfect gas  $\Delta p/\Delta T$  is independent of the temperature so at  $100.0 \text{ }^\circ\text{C}$  a 1.00 K rise in temperature gives a pressure rise of  $\boxed{24.5 \text{ Pa}}$ , just as in (a).

- PIA.9** The molar mass of  $\text{SO}_2$  is  $32.06 + 2 \times 16.00 = 64.06 \text{ g mol}^{-1}$ . If the gas is assumed to be perfect the volume is calculated from  $pV = nRT$

$$V = \frac{nRT}{p} = \left( \frac{200 \times 10^6 \text{ g}}{64.06 \text{ g mol}^{-1}} \right) \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((800 + 273.15) \text{ K})}{1.01325 \times 10^5 \text{ Pa}}$$

$$= \boxed{2.7 \times 10^5 \text{ m}^3}$$

Note the conversion of the mass in t to mass in g; repeating the calculation for 300 t gives a volume of  $\boxed{4.1 \times 10^5 \text{ m}^3}$ .

The volume of gas is therefore between  $\boxed{0.27 \text{ km}^3}$  and  $\boxed{0.41 \text{ km}^3}$ .

**PIA.11** Imagine a column of the atmosphere with cross sectional area  $A$ . The pressure at any height is equal to the force acting down on that area; this force arises from the gravitational attraction on the gas in the column *above* this height – that is, the ‘weight’ of the gas.

Suppose that the height  $h$  is increased by  $dh$ . The force on the area  $A$  is reduced because less of the atmosphere is now bearing down on this area. Specifically, the force is reduced by that due to the gravitational attraction on the gas contained in a cylinder of cross-sectional area  $A$  and height  $dh$ . If the density of the gas is  $\rho$ , the mass of the gas in the cylinder is  $\rho \times A dh$  and the force due to gravity on this mass is  $\rho g A dh$ , where  $g$  is the acceleration due to free fall. The change in pressure  $dp$  on increasing the height by  $dh$  is this force divided by the area, so it follows that

$$dp = -\rho g dh$$

The minus sign is needed because the pressure decreases as the height increases.

The density is related to the pressure by starting from the perfect gas equation,  $pV = nRT$ . If the mass of gas is  $m$  and the molar mass is  $M$ , it follows that  $n = m/M$  and hence  $pV = (m/M)RT$ . Taking the volume to the right gives  $p = (m/MV)RT$ . The quantity  $m/V$  is the mass density  $\rho$ , so  $p = (\rho/M)RT$ ; this is rearranged to give an expression for the density:  $\rho = Mp/RT$ .

This expression for  $\rho$  is substituted into  $dp = -\rho g dh$  to give  $dp = -(Mp/RT)gdh$ . Division by  $p$  results in separation of the variables  $(1/p) dp = -(M/RT)gdh$ . The left-hand side is integrated between  $p_0$ , the pressure at  $h = 0$  and  $p$ , the pressure at  $h$ . The right-hand side is integrated between  $h = 0$  and  $h$

$$\begin{aligned} \int_{p_0}^p \frac{1}{p} dp &= \int_0^h -\frac{Mg}{RT} dh \\ [\ln p]_{p_0}^p &= -\frac{Mg}{RT} [h]_0^h \\ \ln \frac{p}{p_0} &= -\frac{Mgh}{RT} \end{aligned}$$

The exponential of each side is taken to give

$$p = p_0 e^{-h/H} \quad \text{with} \quad H = \frac{RT}{Mg}$$

It is assumed that  $g$  and  $T$  do not vary with  $h$ .

- (a) The pressure decrease across such a small distance will be very small because  $h/H \ll 1$ . It is therefore admissible to expand the exponential and retain just the first two terms:  $e^x \approx 1 + x$

$$p = p_0(1 - h/H)$$

This is rearranged to give an expression for the pressure decrease,  $p - p_0$

$$p - p_0 = -p_0 h/H$$

If it is assumed that  $p_0$  is one atmosphere and that  $H = 8$  km,

$$p - p_0 = -\rho_0 h/H = -\frac{(1.01325 \times 10^5 \text{ Pa}) \times (15 \times 10^{-2} \text{ m})}{8 \times 10^3 \text{ m}} = \boxed{-2 \text{ Pa}}$$

(b) The pressure at 11 km is calculated using the full expression

$$p = p_0 e^{-h/H} = (1 \text{ atm}) \times e^{-(11 \text{ km})/(8 \text{ km})} = \boxed{0.25 \text{ atm}}$$

**PIA.13** Imagine a volume  $V$  of the atmosphere, at temperature  $T$  and pressure  $p_{\text{tot}}$ . If the concentration of a trace gas is expressed as  $X$  parts per trillion (ppt), it means that if that gas were confined to a volume  $X \times 10^{-12} \times V$  at temperature  $T$  it would exert a pressure  $p_{\text{tot}}$ . From the perfect gas law it follows that  $n = pV/RT$ , which in this case gives

$$n_{\text{trace}} = \frac{p_{\text{tot}}(X \times 10^{-12} \times V)}{RT}$$

Taking the volume  $V$  to the left gives the molar concentration,  $c_{\text{trace}}$

$$c_{\text{trace}} = \frac{n_{\text{trace}}}{V} = \frac{X \times 10^{-12} \times p_{\text{tot}}}{RT}$$

An alternative way of looking at this is to note that, at a given temperature and pressure, the volume occupied by a gas is proportional to the amount in moles. Saying that a gas is present at  $X$  ppt implies that the volume occupied by the gas is  $X \times 10^{-12}$  of the whole, and therefore that the amount in moles of the gas is  $X \times 10^{-12}$  of the total amount in moles

$$n_{\text{trace}} = (X \times 10^{-12}) \times n_{\text{tot}}$$

This is rearranged to give an expression for the mole fraction  $x_{\text{trace}}$

$$x_{\text{trace}} = \frac{n_{\text{trace}}}{n_{\text{tot}}} = X \times 10^{-12}$$

The partial pressure of the trace gas is therefore

$$p_{\text{trace}} = x_{\text{trace}} p_{\text{tot}} = (X \times 10^{-12}) \times p_{\text{tot}}$$

The concentration is  $n_{\text{trace}}/V = p_{\text{trace}}/RT$ , so

$$c_{\text{trace}} = \frac{n_{\text{trace}}}{V} = \frac{X \times 10^{-12} \times p_{\text{tot}}}{RT}$$

(a) At 10 °C and 1.0 atm

$$\begin{aligned}
 c_{\text{CCl}_3\text{F}} &= \frac{X_{\text{CCl}_3\text{F}} \times 10^{-12} \times p_{\text{tot}}}{RT} \\
 &= \frac{261 \times 10^{-12} \times (1.0 \text{ atm})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times ([10 + 273.15] \text{ K})} \\
 &= \boxed{1.1 \times 10^{-11} \text{ mol dm}^{-3}} \\
 c_{\text{CCl}_2\text{F}_2} &= \frac{X_{\text{CCl}_2\text{F}_2} \times 10^{-12} \times p_{\text{tot}}}{RT} \\
 &= \frac{509 \times 10^{-12} \times (1.0 \text{ atm})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times ([10 + 273.15] \text{ K})} \\
 &= \boxed{2.2 \times 10^{-11} \text{ mol dm}^{-3}}
 \end{aligned}$$

(b) At 200 K and 0.050 atm

$$\begin{aligned}
 c_{\text{CCl}_3\text{F}} &= \frac{X_{\text{CCl}_3\text{F}} \times 10^{-12} \times p_{\text{tot}}}{RT} \\
 &= \frac{261 \times 10^{-12} \times (0.050 \text{ atm})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (200 \text{ K})} \\
 &= \boxed{8.0 \times 10^{-13} \text{ mol dm}^{-3}} \\
 c_{\text{CCl}_2\text{F}_2} &= \frac{X_{\text{CCl}_2\text{F}_2} \times 10^{-12} \times p_{\text{tot}}}{RT} \\
 &= \frac{509 \times 10^{-12} \times (0.050 \text{ atm})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (200 \text{ K})} \\
 &= \boxed{1.6 \times 10^{-12} \text{ mol dm}^{-3}}
 \end{aligned}$$

## 1B The kinetic model

### Answer to discussion questions

**DIB.1** The three assumptions on which the kinetic model is based are given in Section 1B.1 on page 11.

1. The gas consists of molecules in ceaseless random motion obeying the laws of classical mechanics.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions; they are 'point-like'.
3. The molecules interact only through brief elastic collisions.

An elastic collision is a collision in which the total translational kinetic energy of the molecules is conserved.

None of these assumptions is strictly true; however, many of them are good approximations under a wide range of conditions including conditions of ambient temperature and pressure. In particular,

- Molecules are subject to laws of quantum mechanics; however, for all but the lightest gases at low temperatures, non-classical effects are not important.
- With increasing pressure, the average distance between molecules will decrease, eventually becoming comparable to the dimensions of the molecules themselves.
- Intermolecular interactions, such as hydrogen bonding, and the interactions of dipole moments, operate when molecules are separated by small distances. Therefore, as assumption (2) breaks down, so does assumption (3), because the molecules are often close enough together to interact even when not colliding.

**D1B.3** For an object (be it a space craft or a molecule) to escape the gravitational field of the Earth it must acquire kinetic energy equal in magnitude to the gravitational potential energy the object experiences at the surface of the Earth. The gravitational potential between two objects with masses  $m_1$  and  $m_2$  when separated by a distance  $r$  is

$$V = -\frac{Gm_1m_2}{r}$$

where  $G$  is the (universal) gravitational constant. In the case of an object of mass  $m$  at the surface of the Earth, it turns out that the gravitational potential is given by

$$V = -\frac{GmM}{R}$$

where  $M$  is the mass of the Earth and  $R$  its radius. This expression implies that the potential at the surface is the same as if the mass of the Earth were localized at a distance equal to its radius.

As a mass moves away from the surface of the Earth the potential energy increases (becomes less negative) and tends to zero at large distances. This change in potential energy must all be converted into kinetic energy if the mass is to escape. A mass  $m$  moving at speed  $v$  has kinetic energy  $\frac{1}{2}mv^2$ ; this speed will be the *escape velocity*  $v_e$  when

$$\frac{1}{2}mv_e^2 = \frac{GmM}{R} \quad \text{hence} \quad v_e = \sqrt{\frac{2GM}{R}}$$

The quantity in the square root is related to the acceleration due to free fall,  $g$ , in the following way. A mass  $m$  at the surface of the Earth experiences a gravitational *force* given  $GMm/R^2$  (note that the force goes as  $R^{-2}$ ). This force accelerates the mass towards the Earth, and can be written  $mg$ . The two expressions for the force are equated to give

$$\frac{GMm}{R^2} = mg \quad \text{hence} \quad \frac{GM}{R} = gR$$

This expression for  $GM/R$  is substituted into the above expression for  $v_e$  to give

$$v_e = \sqrt{\frac{2GM}{R}} = \sqrt{2Rg}$$

The escape velocity is therefore a function of the radius of the Earth and the acceleration due to free fall.

The radius of the Earth is  $6.37 \times 10^6$  m and  $g = 9.81$  m s<sup>-2</sup> so the escape velocity is  $1.11 \times 10^4$  m s<sup>-1</sup>. For comparison, the mean speed of He at 298 K is  $1300$  m s<sup>-1</sup> and for N<sub>2</sub> the mean speed is  $475$  m s<sup>-1</sup>. For He, only atoms with a speed in excess of eight times the mean speed will be able to escape, whereas for N<sub>2</sub> the speed will need to be more than twenty times the mean speed. The fraction of molecules with speeds many times the mean speed is small, and because this fraction goes as  $e^{-v^2}$  it falls off rapidly as the multiple increases. A tiny fraction of He atoms will be able to escape, but the fraction of heavier molecules with sufficient speed to escape will be utterly negligible.

### Solutions to exercises

- E1B.1(a)** (i) The mean speed is given by [1B.9–16],  $v_{\text{mean}} = (8RT/\pi M)^{1/2}$ , so  $v_{\text{mean}} \propto \sqrt{1/M}$ . The ratio of the mean speeds therefore depends on the ratio of the molar masses

$$\frac{v_{\text{mean,H}_2}}{v_{\text{mean,Hg}}} = \left(\frac{M_{\text{Hg}}}{M_{\text{H}_2}}\right)^{1/2} = \left(\frac{200.59 \text{ g mol}^{-1}}{2 \times 1.0079 \text{ g mol}^{-1}}\right)^{1/2} = \boxed{9.975}$$

- (ii) The mean translational kinetic energy  $\langle E_k \rangle$  is given by  $\frac{1}{2}m\langle v^2 \rangle$ , where  $\langle v^2 \rangle$  is the mean square speed, which is given by [1B.7–15],  $\langle v^2 \rangle = 3RT/M$ . The mean translational kinetic energy is therefore

$$\langle E_k \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m\left(\frac{3RT}{M}\right)$$

The molar mass  $M$  is related to the mass  $m$  of one molecule by  $M = mN_A$ , where  $N_A$  is Avogadro's constant, and the gas constant can be written  $R = kN_A$ , hence

$$\langle E_k \rangle = \frac{1}{2}m\left(\frac{3RT}{M}\right) = \frac{1}{2}m\left(\frac{3kN_A T}{mN_A}\right) = \frac{3}{2}kT$$

The mean translational kinetic energy is therefore independent of the identity of the gas, and only depends on the temperature: it is the same for H<sub>2</sub> and Hg.

This result is related to the principle of equipartition of energy: a molecule has three translational degrees of freedom ( $x$ ,  $y$ , and  $z$ ) each of which contributes  $\frac{1}{2}kT$  to the average energy.

**E1B.2(a)** The rms speed is given by [1B.8–15],  $v_{\text{rms}} = (3RT/M)^{1/2}$ .

$$v_{\text{rms,H}_2} = \left( \frac{3RT}{M_{\text{H}_2}} \right)^{1/2} = \left( \frac{3 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{2 \times 1.0079 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{1/2} \\ = \boxed{1.90 \text{ km s}^{-1}}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  has been used. Note that the molar mass is in  $\text{kg mol}^{-1}$ .

$$v_{\text{rms,O}_2} = \left( \frac{3 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{2 \times 16.00 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{1/2} = \boxed{478 \text{ m s}^{-1}}$$

**E1B.3(a)** The Maxwell–Boltzmann distribution of speeds,  $f(v)$ , is given by [1B.4–14]. The fraction of molecules with speeds between  $v_1$  and  $v_2$  is given by the integral

$$\int_{v_1}^{v_2} f(v) dv$$

If the range  $v_2 - v_1 = \delta v$  is small, the integral is well-approximated by

$$f(v_{\text{mid}}) \delta v$$

where  $v_{\text{mid}}$  is the mid-point of the velocity range:  $v_{\text{mid}} = \frac{1}{2}(v_2 + v_1)$ . In this exercise  $v_{\text{mid}} = 205 \text{ m s}^{-1}$  and  $\delta v = 10 \text{ m s}^{-1}$ .

$$\text{fraction} = f(v_{\text{mid}}) \delta v = 4\pi \times \left( \frac{M}{2\pi RT} \right)^{3/2} v_{\text{mid}}^2 \exp\left( \frac{-Mv_{\text{mid}}^2}{2RT} \right) \delta v \\ = 4\pi \times \left( \frac{2 \times 14.01 \times 10^{-3} \text{ kg mol}^{-1}}{2\pi \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})} \right)^{3/2} \times (205 \text{ m s}^{-1})^2 \\ \times \exp\left( \frac{-(2 \times 14.01 \times 10^{-3} \text{ kg mol}^{-1}) \times (205 \text{ m s}^{-1})^2}{2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})} \right) \times (10 \text{ m s}^{-1}) \\ = \boxed{6.87 \times 10^{-3}}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  has been used. Thus, 0.687% of molecules have velocities in this range.

**E1B.4(a)** The mean relative speed is given by [1B.11b–16],  $v_{\text{rel}} = (8kT/\pi\mu)^{1/2}$ , where  $\mu = m_A m_B / (m_A + m_B)$  is the effective mass. Multiplying top and bottom of the expression for  $v_{\text{rel}}$  by  $N_A$  and using  $N_A k = R$  gives  $v_{\text{rel}} = (8RT/\pi N_A \mu)^{1/2}$  in which  $N_A \mu$  is the molar effective mass. For the relative motion of  $\text{N}_2$  and  $\text{H}_2$  this effective mass is

$$N_A \mu = \frac{M_{\text{N}_2} M_{\text{H}_2}}{M_{\text{N}_2} + M_{\text{H}_2}} = \frac{(2 \times 14.01 \text{ g mol}^{-1}) \times (2 \times 1.0079 \text{ g mol}^{-1})}{(2 \times 14.01 \text{ g mol}^{-1}) + (2 \times 1.0079 \text{ g mol}^{-1})} = 1.88... \text{ g mol}^{-1}$$

$$v_{\text{rel}} = \left( \frac{8RT}{\pi N_A \mu} \right)^{1/2} = \left( \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{\pi \times (1.88... \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} = \boxed{1832 \text{ m s}^{-1}}$$

The value of the effective mass  $\mu$  is dominated by the mass of the lighter molecule, in this case  $\text{H}_2$ .

**E1B.5(a)** The most probable speed is given by [1B.10-16],  $v_{\text{mp}} = (2RT/M)^{1/2}$ , the mean speed is given by [1B.9-16],  $v_{\text{mean}} = (8RT/\pi M)^{1/2}$ , and the mean relative speed between two molecules of the same mass is given by [1B.11a-16],  $v_{\text{rel}} = \sqrt{2}v_{\text{mean}}$ .

$$M_{\text{CO}_2} = 12.01 + 2 \times 16.00 = 44.01 \text{ g mol}^{-1}.$$

$$v_{\text{mp}} = \left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{44.01 \times 10^{-3} \text{ kg mol}^{-1}}\right)^{1/2} = \boxed{333 \text{ m s}^{-1}}$$

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{\pi \times (44.01 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} = \boxed{376 \text{ m s}^{-1}}$$

$$v_{\text{rel}} = \sqrt{2}v_{\text{mean}} = \sqrt{2} \times (376 \text{ m s}^{-1}) = \boxed{531 \text{ m s}^{-1}}$$

**E1B.6(a)** The collision frequency is given by [1B.12b-17],  $z = \sigma v_{\text{rel}} p / kT$ , with the relative speed for two molecules of the same type given by [1B.11a-16],  $v_{\text{rel}} = \sqrt{2}v_{\text{mean}}$ . The mean speed is given by [1B.9-16],  $v_{\text{mean}} = (8RT/\pi M)^{1/2}$ . From the *Resource section* the collision cross-section  $\sigma$  is  $0.27 \text{ nm}^2$ .

$$\begin{aligned} z &= \frac{\sigma v_{\text{rel}} p}{kT} = \frac{\sigma p}{kT} \times \sqrt{2} \times \left(\frac{8RT}{\pi M}\right)^{1/2} \\ &= \frac{(0.27 \times 10^{-18} \text{ m}^2) \times (1.01325 \times 10^5 \text{ Pa})}{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})} \times \sqrt{2} \\ &\quad \times \left(\frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{\pi \times (2 \times 1.0079 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} \\ &= \boxed{1.7 \times 10^{10} \text{ s}^{-1}} \end{aligned}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$  have been used. Note the conversion of the collision cross-section  $\sigma$  to  $\text{m}^2$ :  $1 \text{ nm}^2 = (1 \times 10^{-9})^2 \text{ m}^2 = 1 \times 10^{-18} \text{ m}^2$ .

**E1B.7(a)** The mean speed is given by [1B.9-16],  $v_{\text{mean}} = (8RT/\pi M)^{1/2}$ . The collision frequency is given by [1B.12b-17],  $z = \sigma v_{\text{rel}} p / kT$ , with the relative speed for two molecules of the same type given by [1B.11a-16],  $v_{\text{rel}} = \sqrt{2}v_{\text{mean}}$ . The mean free path is given by [1B.14-18],  $\lambda = kT/\sigma p$

(i) The mean speed is calculated as

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{\pi \times (2 \times 14.01 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} = \boxed{475 \text{ m s}^{-1}}$$

(ii) The collision cross-section  $\sigma$  is calculated from the collision diameter  $d$  as  $\sigma = \pi d^2 = \pi \times (395 \times 10^{-9} \text{ m})^2 = 4.90... \times 10^{-19} \text{ m}^2$ . With this value the mean free path is calculated as

$$\lambda = \frac{kT}{\sigma p} = \frac{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}{(4.90... \times 10^{-19} \text{ m}^2) \times (1.01325 \times 10^5 \text{ Pa})} = 82.9 \times 10^{-9} \text{ m} = \boxed{82.9 \text{ nm}}$$

where  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$  have been used.



(iii) The collision rate is calculated as

$$\begin{aligned} z &= \frac{\sigma v_{\text{rel}} p}{kT} = \frac{\sigma p}{kT} \times \sqrt{2} \times \left( \frac{8RT}{\pi M} \right)^{1/2} \\ &= \frac{(4.90... \times 10^{-19} \text{ m}^2) \times (1.01325 \times 10^5 \text{ Pa})}{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})} \times \sqrt{2} \\ &\quad \times \left( \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{\pi \times (2 \times 14.01 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ &= \boxed{8.10 \times 10^9 \text{ s}^{-1}} \end{aligned}$$

An alternative for the calculation of  $z$  is to use [1B.13–18],  $\lambda = v_{\text{rel}}/z$ , rearranged to  $z = v_{\text{rel}}/\lambda$

$$z = \frac{v_{\text{rel}}}{\lambda} = \frac{\sqrt{2} v_{\text{mean}}}{\lambda} = \frac{\sqrt{2} \times (475 \text{ m s}^{-1})}{82.9 \times 10^{-9} \text{ m}} = \boxed{8.10 \times 10^9 \text{ s}^{-1}}$$

**E1B.8(a)** The container is assumed to be spherical with radius  $r$  and hence volume  $V = \frac{4}{3}\pi r^3$ . This volume is expressed in terms of the required diameter  $d = 2r$  as  $V = \frac{1}{6}\pi d^3$ . Rearrangement of this expression gives  $d$

$$d = \left( \frac{6V}{\pi} \right)^{1/3} = \left( \frac{6 \times 100 \text{ cm}^3}{\pi} \right)^{1/3} = 5.75... \text{ cm}$$

The mean free path is given by [1B.14–18],  $\lambda = kT/\sigma p$ . This is rearranged to give the pressure  $p$  with  $\lambda$  equal to the diameter of the vessel

$$p = \frac{kT}{\sigma d} = \frac{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}{(0.36 \times 10^{-18} \text{ m}^2) \times (5.75... \times 10^{-2} \text{ m})} = \boxed{0.20 \text{ Pa}}$$

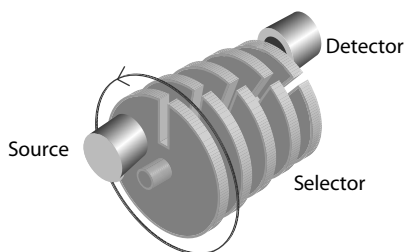
Note the conversion of the diameter from cm to m.

**E1B.9(a)** The mean free path is given by [1B.14–18],  $\lambda = kT/\sigma p$ .

$$\begin{aligned} \lambda &= \frac{kT}{\sigma p} = \frac{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (217 \text{ K})}{(0.43 \times 10^{-18} \text{ m}^2) \times (0.05 \times 1.01325 \times 10^5 \text{ Pa})} \\ &= \boxed{1.4 \times 10^{-6} \text{ m} = 1.4 \text{ }\mu\text{m}} \end{aligned}$$

## Solutions to problems

**P1B.1** A rotating slotted-disc apparatus consists of a series of disks all mounted on a common axle (shaft). Each disc has a narrow radial slot cut into it, and the slots on successive discs are displaced from one another by a certain angle. The discs are then spun at a constant angular speed.



Imagine a molecule moving along the direction of the axle with a certain velocity such that it passes through the slot in the first disc. By the time the molecule reaches the second disc the slot in that disc will have moved around, and the molecule will only pass through the slot if the speed of the molecule is such that it arrives at the second disc at just the time at which the slot appears in the path of the molecule. In this way, only molecules with a specific velocity (or, because the slot has a finite width, a small range of velocities) will pass through the second disc. The velocity of the molecules which will pass through the second disc is set by the angular speed at which the discs are rotated and the angular displacement of the slots on successive discs.

The angular velocity of the discs is  $2\pi\nu \text{ rad s}^{-1}$  so in time  $t$  the discs move through an angle  $\theta = 2\pi\nu t$ . If the spacing of the discs is  $d$ , a molecule with velocity  $v_x$  will take time  $t = d/v_x$  to pass from one disc to the next. If the second slit is set at an angle  $\alpha$  relative to the first, such a molecule will only pass through the second slit if

$$2\pi\nu \left( \frac{d}{v_x} \right) = \alpha \quad \text{hence} \quad v_x = \frac{2\pi\nu d}{\alpha}$$

If the angle  $\alpha$  is expressed in degrees,  $\alpha = \pi(\alpha^\circ/180^\circ)$ , this rearranges to

$$v_x = \frac{2\pi\nu d}{\pi(\alpha^\circ/180^\circ)} = \frac{360^\circ \nu d}{\alpha^\circ}$$

With the values given the velocity of the molecules is computed as

$$v_x = \frac{360^\circ \nu d}{\alpha^\circ} = \frac{360^\circ \nu (0.01 \text{ m})}{2^\circ} = 180\nu (0.01 \text{ m})$$

The Maxwell-Boltzmann distribution of speeds in one dimension is given by [1B.3-13]

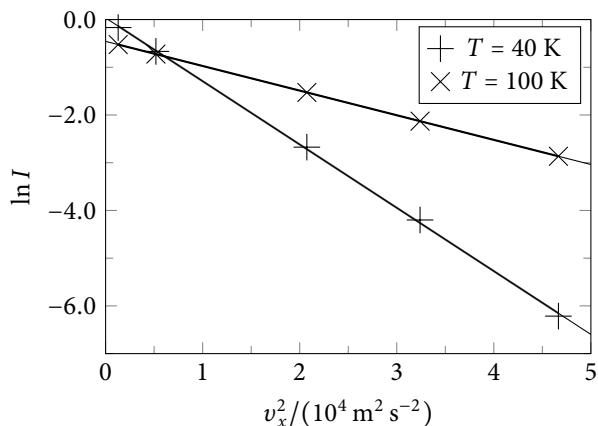
$$f(v_x) = \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/2kT}$$

The given data on the intensity of the beam is assumed to be proportional to  $f(v_x)$ :  $I \propto f(v_x) = Af(v_x)$ . Because the constant of proportionality is not known and the variation with  $v_x$  is to be explored, it is convenient to take logarithms to give

$$\ln I = \ln[Af(v_x)] = \ln A + \ln \left( \frac{m}{2\pi kT} \right)^{1/2} - \frac{mv_x^2}{2kT}$$

A plot of  $\ln I$  against  $v_x^2$  is expected to be a straight line with slope  $-m/2kT$ ; such a plot is shown in Fig. 1.4.

$\nu/\text{Hz}$	$v_x/\text{m s}^{-1}$	$v_x^2/(10^4 \text{ m}^2 \text{ s}^{-2})$	$I(40 \text{ K})$	$\ln I(40 \text{ K})$	$I(100 \text{ K})$	$\ln I(100 \text{ K})$
20	36	0.13	0.846	-0.167	0.592	-0.524
40	72	0.52	0.513	-0.667	0.485	-0.724
80	144	2.07	0.069	-2.674	0.217	-1.528
100	180	3.24	0.015	-4.200	0.119	-2.129
120	216	4.67	0.002	-6.215	0.057	-2.865



**Figure 1.4**

At both temperatures the data fall on reasonable straight lines, with slope  $-1.33$  at  $40 \text{ K}$  and  $-0.516$  at  $100 \text{ K}$ .

If the Maxwell-Boltzmann distribution applies the expected slope at  $40 \text{ K}$  is computed as

$$-\frac{m}{2kT} = -\frac{M}{2RT} = -\frac{83.80 \times 10^{-3} \text{ kg mol}^{-1}}{2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (40 \text{ K})} = -1.26 \times 10^{-4} \text{ m}^{-2} \text{ s}^2$$

where  $R = N_A k$  has been used. The expected slope of the above graph is therefore  $-1.26$ , which compares reasonably well with that found experimentally.

At  $100 \text{ K}$  the expected slope is

$$-\frac{83.80 \times 10^{-3} \text{ kg mol}^{-1}}{2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K})} = -5.04 \times 10^{-5} \text{ m}^{-2} \text{ s}^2$$

Again, the expected slope  $-0.504$  compares reasonably well with that found experimentally.

**PIB.3** The Maxwell-Boltzmann distribution of speeds in one dimension (here  $x$ ) is given by [1B.3-13]

$$f(v_x) = \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/2kT}$$

The first task is to find an expression for the mean speed, which is found using [1B.6–15],  $\langle v^n \rangle = \int_0^\infty v^n f(v) dv$ . In this case

$$\langle v_x \rangle = \int_0^\infty v_x \left( \frac{m}{kT} \right)^{1/2} e^{-mv_x^2/2kT} dv$$

The required integral is of the form of G.2 from the *Resource section*

$$\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a}$$

With  $a = m/2kT$  the mean speed is

$$v_{\text{mean}} = \langle v_x \rangle = \left( \frac{m}{kT} \right)^{1/2} \left( \frac{1}{2(m/2kT)} \right) = \left( \frac{kT}{2\pi m} \right)^{1/2}$$

After the beam emerges from the velocity selector,  $f(v_x)$  is zero for  $v_x > v_{\text{mean}}$ . The probability distribution is therefore changed and so needs to be re-normalized such that

$$K_x \int_0^{v_{\text{mean}}} e^{-mv_x^2/2kT} dv_x = 1$$

This integral is best evaluated using mathematical software which gives

$$\int_0^{v_{\text{mean}}} e^{-mv_x^2/2kT} dv_x = \left( \frac{\pi kT}{2m} \right)^{1/2} \text{erf}\left(\frac{1}{2\sqrt{\pi}}\right)$$

where  $\text{erf}(x)$  is the *error function*. The normalized distribution is therefore

$$f_{\text{new}}(v_x) = \left( \frac{2m}{\pi kT} \right)^{1/2} \frac{1}{\text{erf}\left(\frac{1}{2\sqrt{\pi}}\right)} e^{-mv_x^2/2kT}$$

The new mean speed is computed using this distribution; again this integral is best evaluated using mathematical software. Note that the integral extends up to  $v_{\text{mean}}$

$$\begin{aligned} v_{\text{mean, new}} &= \left( \frac{2m}{\pi kT} \right)^{1/2} \frac{1}{\text{erf}\left(\frac{1}{2\sqrt{\pi}}\right)} \int_0^{v_{\text{mean}}} v_x e^{-mv_x^2/2kT} dv_x \\ &= (1 - e^{1/4\pi}) \left( \frac{2kT}{\pi m} \right)^{1/2} \frac{1}{\text{erf}\left(\frac{1}{2\sqrt{\pi}}\right)} = (1 - e^{1/4\pi}) 2 \overbrace{\left( \frac{kT}{2\pi m} \right)^{1/2}}^{v_{\text{mean}}} \frac{1}{\text{erf}\left(\frac{1}{2\sqrt{\pi}}\right)} \\ &= (1 - e^{1/4\pi}) 2v_{\text{mean}} \frac{1}{\text{erf}\left(\frac{1}{2\sqrt{\pi}}\right)} \end{aligned}$$

The error function is evaluated numerically to give  $v_{\text{mean, new}} \approx 0.493 v_{\text{mean}}$ .

**PIB.5** The Maxwell–Boltzmann distribution of speeds in three dimensions is given by [1B.4–14]

$$f(v) = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

with  $M$  the molar mass. The most probable speed is given by [1B.10–16],  $v_{\text{mp}} = (2RT/M)^{1/2}$ . If the interval of speeds,  $\Delta v$  is small, the fraction of molecules with speeds in this range, centred at speed  $v_{\text{mp}}$  is well-approximated by  $f(v_{\text{mp}})\Delta v$ .

The required fraction of molecules with speeds in the range  $\Delta v$  around  $n \times v_{\text{mp}}$  compared to that centred around  $v_{\text{mp}}$  is given by

$$\frac{f(n \times v_{\text{mp}})\Delta v}{f(v_{\text{mp}})\Delta v} = \frac{(n \times v_{\text{mp}})^2 e^{-M(nv_{\text{mp}})^2/2RT}}{v_{\text{mp}}^2 e^{-Mv_{\text{mp}}^2/2RT}} = n^2 e^{-Mv_{\text{mp}}^2(n^2-1)/2RT}$$

In taking the ratio, with the exception of the term  $v^2$ , all of the terms in  $f(v)$  which multiply the exponential cancel. In this expression the term  $v_{\text{mp}}$  is replaced by  $(2RT/M)^{1/2}$  to give

$$\frac{f(n \times v_{\text{mp}})\Delta v}{f(v_{\text{mp}})\Delta v} = n^2 e^{-Mv_{\text{mp}}^2(n^2-1)/2RT} = n^2 e^{-M(2RT/M)(n^2-1)/2RT} = n^2 e^{-(1-n^2)}$$

For  $n = 3$  this expression evaluates to  $3.02 \times 10^{-3}$  and for  $n = 4$  it evaluates to  $4.89 \times 10^{-6}$ . These numbers indicate that very few molecules have speeds several times greater than the most probable speed.

**PIB.7** The key idea here is that for an object to escape the gravitational field of the Earth it must acquire kinetic energy equal in magnitude to the gravitational potential energy the object experiences at the surface of the Earth. The gravitational potential energy between two objects with masses  $m_1$  and  $m_2$  when separated by a distance  $r$  is

$$V = -\frac{Gm_1m_2}{r}$$

where  $G$  is the (universal) gravitational constant. In the case of an object of mass  $m$  at the surface of the Earth, it turns out that the gravitational potential energy is given by

$$V = -\frac{GmM}{R}$$

where  $M$  is the mass of the Earth and  $R$  its radius. This expression implies that the potential at the surface is the same as if the mass of the Earth were localized at a distance equal to its radius.

As a mass moves away from the surface of the Earth the potential energy increases (becomes less negative) and tends to zero at large distances. If the mass is to escape its kinetic energy must be greater than or equal to this change in potential energy. A mass  $m$  moving at speed  $v$  has kinetic energy  $\frac{1}{2}mv^2$ ; this speed will be the *escape velocity*  $v_e$  when

$$\frac{1}{2}mv_e^2 = \frac{GmM}{R} \quad \text{hence} \quad v_e = \left( \frac{2GM}{R} \right)^{1/2}$$

The quantity in the square root is related to the acceleration due to free fall,  $g$ , in the following way. A mass  $m$  at the surface of the Earth experiences a gravitational *force* given  $GMm/R^2$  (note that the force goes as  $R^{-2}$ ). This force accelerates the mass towards the Earth, and can be written  $mg$ . The two expressions for the force are equated to give

$$\frac{GMm}{R^2} = mg \quad \text{hence} \quad \frac{GM}{R} = gR \quad (1.1)$$

This expression for  $GM/R$  is substituted into the above expression for  $v_e$  to give

$$v_e = \left( \frac{2GM}{R} \right)^{1/2} = (2Rg)^{1/2}$$

The escape velocity is therefore a function of the radius of the Earth and the acceleration due to free fall.

The quoted values for the Earth give

$$v_e = \sqrt{2Rg} = \sqrt{2 \times (6.37 \times 10^6 \text{ m}) \times (9.81 \text{ m s}^{-2})} = \boxed{1.12 \times 10^4 \text{ m s}^{-1}}$$

For Mars, data is not given on the acceleration due to free fall. However, it follows from eqn 1.1 that  $g = GM/R^2$ , and hence

$$\frac{g_{\text{Mars}}}{g_{\text{Earth}}} = \frac{M_{\text{Mars}}}{M_{\text{Earth}}} \left( \frac{R_{\text{Earth}}}{R_{\text{Mars}}} \right)^2$$

The acceleration due to freefall on Mars is therefore computed as

$$\begin{aligned} g_{\text{Mars}} &= g_{\text{Earth}} \frac{M_{\text{Mars}}}{M_{\text{Earth}}} \left( \frac{R_{\text{Earth}}}{R_{\text{Mars}}} \right)^2 \\ &= (9.81 \text{ m s}^{-2}) \times (0.108) \times \left( \frac{6.37 \times 10^6 \text{ m}}{3.38 \times 10^6 \text{ m}} \right)^2 = 3.76... \text{ m s}^{-2} \end{aligned}$$

The escape velocity on Mars is therefore

$$v_e = \sqrt{2Rg} = \sqrt{2 \times (3.38 \times 10^6 \text{ m}) \times (3.76... \text{ m s}^{-2})} = \boxed{5.04 \times 10^3 \text{ m s}^{-1}}$$

The mean speed is given by [1B.9–16],  $v_{\text{mean}} = (8RT/\pi M)^{1/2}$ . This expression is rearranged to give the temperature  $T$  at which the mean speed is equal to the escape velocity

$$T = \frac{v_e^2 \pi M}{8R}$$

For  $\text{H}_2$  on the Earth the calculation is

$$T = \frac{(1.12 \times 10^4 \text{ m s}^{-1})^2 \times \pi \times (2 \times 1.0079 \times 10^{-3} \text{ kg mol}^{-1})}{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})} = 1.19 \times 10^4 \text{ K}$$

The following table gives the results for all three gases on both planets

planet	$v_e/\text{m s}^{-1}$	$T/10^4 \text{ K (H}_2\text{)}$	$T/10^4 \text{ K (He)}$	$T/10^4 \text{ K (O}_2\text{)}$
Earth	$1.12 \times 10^4$	1.19	2.36	18.9
Mars	$5.04 \times 10^3$	0.242	0.481	3.84

The fraction of molecules with speed greater than  $v_e$  is found by integrating the Maxwell–Boltzmann distribution from this speed up to infinity:

$$\text{fraction with speed } \geq v_e = F = \int_{v_e}^{\infty} 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT} dv$$

This integral is best computed using mathematical software, to give the following results for the fraction  $F$ ; an entry of zero indicates that the calculated fraction is zero to within the machine precision.

planet	$T/\text{K}$	$F(\text{H}_2)$	$F(\text{He})$	$F(\text{O}_2)$
Earth	240	0	0	0
	1500	$1.49 \times 10^{-4}$	$9.52 \times 10^{-9}$	0
Mars	240	$1.12 \times 10^{-5}$	$5.09 \times 10^{-11}$	0
	1500	0.025	$4.31 \times 10^{-2}$	$4.61 \times 10^{-14}$

These results indicate that the lighter molecules have the greater chance of escaping (because they are moving faster on average) and that increasing the temperature increases the probability of escaping (again because this increases the mean speed). Escape from Mars is easier than from the Earth because of the lower escape velocity, and heavier molecules are seemingly very unlikely to escape from the Earth.

**P1B.9** The Maxwell–Boltzmann distribution of speeds in three dimensions is given by [1B.4–14]

$$f(v) = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

The fraction with speed between  $v_1$  and  $v_2$  is found by integrating the distribution between these speeds; this is best done using mathematical software

$$\text{fraction with speed between } v_1 \text{ and } v_2 = \int_{v_1}^{v_2} 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT} dv$$

At 300 K and with  $M = 2 \times 16.00 \text{ g mol}^{-1}$  the fraction is 0.0722 and at 1000 K the fraction is 0.0134.

**P1B.11** Two hard spheres will collide if their line of centres approach within  $2r$  of one another, where  $r$  is the radius of the sphere. This distance defines the collision diameter,  $d = 2r$ , and the collision cross-section is the area of a circle with this radius,  $\sigma = \pi d^2 = \pi(2r)^2$ . The pressure is computed from the other parameters using the perfect gas law:  $p = nRT/V$ .

The collision frequency is given by [1B.12b-17],  $z = \sigma v_{\text{rel}} p / kT$ , with the relative speed for two molecules of the same type given by [1B.11a-16],  $v_{\text{rel}} = \sqrt{2} v_{\text{mean}}$ . The mean speed is given by [1B.9-16],  $v_{\text{mean}} = (8RT/\pi M)^{1/2}$ .

Putting this all together gives

$$\begin{aligned} z &= \frac{\sigma v_{\text{rel}} p}{kT} = \frac{\pi(2r)^2}{kT} \times \sqrt{2} \times \left(\frac{8RT}{\pi M}\right)^{1/2} \times \frac{nRT}{V} \\ &= \pi(2r)^2 \times \sqrt{2} \times \left(\frac{8RT}{\pi M}\right)^{1/2} \times \frac{nN_{\text{A}}}{V} \end{aligned}$$

where to go to the second line  $R = N_{\text{A}}k$  has been used. The expression is evaluated to give

$$\begin{aligned} z &= \pi(2 \times (0.38 \times 10^{-9} \text{ m}))^2 \times \sqrt{2} \times \left(\frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{\pi \times (16.0416 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} \\ &\quad \times \frac{(0.1 \text{ mol}) \times (6.0221 \times 10^{23} \text{ mol}^{-1})}{1 \times 10^{-3} \text{ m}^3} = \boxed{9.7 \times 10^{10} \text{ s}^{-1}} \end{aligned}$$

## 1C Real gases

### Answer to discussion questions

**DIC.1** Consider three temperature regions:

- (1)  $T < T_{\text{B}}$ . At very low pressures, all gases show a compression factor,  $Z \approx 1$ . At high pressures, all gases have  $Z > 1$ , signifying that they have a molar volume greater than a perfect gas, which implies that repulsive forces are dominant. At intermediate pressures, most gases show  $Z < 1$ , indicating that attractive forces reducing the molar volume below the perfect value are dominant.
- (2)  $T \approx T_{\text{B}}$ .  $Z \approx 1$  at low pressures, slightly greater than 1 at intermediate pressures, and significantly greater than 1 only at high pressures. There is a balance between the attractive and repulsive forces at low to intermediate pressures, but the repulsive forces predominate at high pressures where the molecules are very close to each other.
- (3)  $T > T_{\text{B}}$ .  $Z > 1$  at all pressures because the frequency of collisions between molecules increases with temperature.

**DIC.3** The van der Waals equation ‘corrects’ the perfect gas equation for both attractive and repulsive interactions between the molecules in a real gas; see Section 1C.2 on page 23 for a fuller explanation.

The Berthelot equation accounts for the volume of the molecules in a manner similar to the van der Waals equation but the term representing molecular attractions is modified to account for the effect of temperature. Experimentally it is found that the van der Waals parameter  $a$  decreases with increasing temperature. Theory (see Focus 14) also suggests that intermolecular attractions



can decrease with temperature. This variation of the attractive interaction with temperature can be accounted for in the equation of state by replacing the van der Waals  $a$  with  $a/T$ .

### Solutions to exercises

**E1C.1(a)** The van der Waals equation of state in terms of the volume is given by [1C.5a–23],  $p = nRT/(V - b) - an^2/V^2$ . The parameters  $a$  and  $b$  for ethane are given in the *Resource section* as  $a = 5.507 \text{ atm dm}^6 \text{ mol}^{-2}$  and  $b = 6.51 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ .

With these units it is convenient to use  $R = 8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ .

(i)  $T = 273.15 \text{ K}$ ,  $V = 22.414 \text{ dm}^3$ ,  $n = 1.0 \text{ mol}$

$$\begin{aligned} p &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{(1.0 \text{ mol}) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{(22.414 \text{ dm}^3) - (1.0 \text{ mol}) \times (6.51 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} \\ &\quad - \frac{(5.507 \text{ atm dm}^6 \text{ mol}^{-2}) \times (1.0 \text{ mol})^2}{(22.414 \text{ dm}^3)^2} = \boxed{0.99 \text{ atm}} \end{aligned}$$

(ii)  $T = 1000 \text{ K}$ ,  $V = 100 \text{ cm}^3 = 0.100 \text{ dm}^3$ ,  $n = 1.0 \text{ mol}$

$$\begin{aligned} p &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{(1.0 \text{ mol}) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (1000 \text{ K})}{(0.100 \text{ dm}^3) - (1.0 \text{ mol}) \times (6.51 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} \\ &\quad - \frac{(5.507 \text{ atm dm}^6 \text{ mol}^{-2}) \times (1.0 \text{ mol})^2}{(0.100 \text{ dm}^3)^2} = \boxed{1.8 \times 10^3 \text{ atm}} \end{aligned}$$

**E1C.2(a)** Recall that  $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$ ,  $1 \text{ dm}^6 = 10^{-6} \text{ m}^6$ , and  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$\begin{aligned} a &= (0.751 \text{ atm dm}^6 \text{ mol}^{-2}) \times \frac{1.01325 \times 10^5 \text{ Pa}}{1 \text{ atm}} \times \frac{10^{-6} \text{ m}^6}{1 \text{ dm}^6} = 0.0761 \text{ Pa m}^6 \text{ mol}^{-2} \\ &= 0.0760 \text{ kg m}^{-1} \text{ s}^{-2} \text{ m}^6 \text{ mol}^{-2} = \boxed{0.0761 \text{ kg m}^5 \text{ s}^{-2} \text{ mol}^{-2}} \end{aligned}$$

$$b = (0.0226 \text{ dm}^3 \text{ mol}^{-1}) \times \frac{10^{-3} \text{ m}^3}{1 \text{ dm}^3} = \boxed{2.26 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

**E1C.3(a)** The compression factor  $Z$  is defined in [1C.1–20] as  $Z = V_m/V_m^\circ$ , where  $V_m^\circ$  is the molar volume of a perfect gas under the same conditions. This volume is computed from the equation of state for a perfect gas, [1A.4–8], as  $V_m^\circ = RT/p$ , hence  $Z = pV_m/RT$  [1C.2–20].

- (i) If  $V_m$  is 12% smaller than the molar volume of a perfect gas, it follows that  $V_m = V_m^\circ(1 - 0.12) = 0.88 V_m^\circ$ . The compression factor is then computed directly as

$$Z = \frac{V_m}{V_m^\circ} = \frac{0.88 \times V_m^\circ}{V_m^\circ} = \boxed{0.88}$$

- (ii) From [1C.2–20] it follows that  $V_m = ZRT/p$

$$\begin{aligned} V_m &= \frac{ZRT}{p} = \frac{0.88 \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (250 \text{ K})}{15 \text{ atm}} \\ &= \boxed{1.2 \text{ dm}^3 \text{ mol}^{-1}} \end{aligned}$$

Because  $Z < 1$ , implying that  $V_m < V_m^\circ$ , attractive forces are dominant.

- E1C.4(a)** The van der Waals equation of state in terms of the volume is given by [1C.5a–23],  $p = nRT/(V-b) - an^2/V^2$ . The molar mass of  $\text{N}_2$  is  $M = 2 \times 14.01 \text{ g mol}^{-1} = 28.02 \text{ g mol}^{-1}$ , so it follows that the amount in moles is

$$n = m/M = (92.4 \text{ kg})/(0.02802 \text{ kg mol}^{-1}) = 3.29... \times 10^3 \text{ mol}$$

The pressure is found by substituting the given parameters into [1C.5a–23], noting that the volume needs to be expressed in  $\text{dm}^3$

$$\begin{aligned} p &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{(3.29... \times 10^3 \text{ mol}) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}{(1000 \text{ dm}^3) - (3.29... \times 10^3 \text{ mol}) \times (0.0387 \text{ dm}^3 \text{ mol}^{-1})} \\ &\quad - \frac{(1.352 \text{ atm dm}^6 \text{ mol}^{-2}) \times (3.29... \times 10^3 \text{ mol})^2}{(1000 \text{ dm}^3)^2} = \boxed{140 \text{ atm}} \end{aligned}$$

- E1C.5(a)** (i) The pressure is computed from the equation of state for a perfect gas, [1A.4–8], as  $p = nRT/V$

$$\begin{aligned} p &= \frac{nRT}{V} = \frac{(10.0) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times ([27 + 273.15] \text{ K})}{4.860 \text{ dm}^3} \\ &= \boxed{50.7 \text{ atm}} \end{aligned}$$

- (ii) The van der Waals equation of state in terms of the volume is given by [1C.5a–23],  $p = nRT/(V - b) - an^2/V^2$ . This is used to calculate the pressure

$$\begin{aligned} p &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{(10.0 \text{ mol}) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times ([27 + 273.15] \text{ K})}{(4.860 \text{ dm}^3) - (10.0 \text{ mol}) \times (0.0651 \text{ dm}^3 \text{ mol}^{-1})} \\ &\quad - \frac{(5.507 \text{ atm dm}^6 \text{ mol}^{-2}) \times (10.0 \text{ mol})^2}{(4.860 \text{ dm}^3)^2} = 35.2... = \boxed{35.2 \text{ atm}} \end{aligned}$$

The compression factor  $Z$  is given in terms of the molar volume and pressure by [1C.2–20],  $Z = pV_m/RT$ . The molar volume is  $V/n$

$$Z = \frac{pV_m}{RT} = \frac{pV}{nRT} = \frac{(35.2\dots \text{atm}) \times (4.860 \text{ dm}^3)}{(10.0 \text{ mol}) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (300.15 \text{ K})} = \boxed{0.695}$$

**E1C.6(a)** The relation between the critical constants and the van der Waals parameters is given by [1C.6–26]

$$V_c = 3b \quad p_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb}$$

All three critical constants are given, so the problem is over-determined: any pair of these expressions is sufficient to find values of  $a$  and  $b$ . It is convenient to use  $R = 8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$  and volumes in units of  $\text{dm}^3$ .

If the expressions for  $V_c$  and  $p_c$  are used,  $a$  and  $b$  are found in the following way

$$\begin{aligned} V_c = 3b \quad \text{hence} \quad b &= V_c/3 = (0.0987 \text{ dm}^3 \text{ mol}^{-1})/3 = 0.0329 \text{ dm}^3 \text{ mol}^{-1} \\ p_c &= \frac{a}{27b^2} = \frac{a}{27(V_c/3)^2} \quad \text{hence} \quad a = 27(V_c/3)^2 p_c \\ a &= 27(V_c/3)^2 p_c = 27([0.0987 \text{ dm}^3 \text{ mol}^{-1}]/3)^2 \times (45.6 \text{ atm}) \\ &= 1.33 \text{ atm dm}^6 \text{ mol}^{-2} \end{aligned}$$

There are three possible ways of choosing two of the expressions with which to find  $a$  and  $b$ , and each choice gives a different value. For  $a$  the values are 1.33, 1.74, and 2.26, giving an average of  $\boxed{1.78 \text{ atm dm}^6 \text{ mol}^{-2}}$ . For  $b$  the values are 0.0329, 0.0329, and 0.0429, giving an average of  $\boxed{0.0362 \text{ dm}^3 \text{ mol}^{-1}}$ .

In Section 1C.2(a) on page 23 it is argued that  $b = 4V_{\text{molec}}N_A$ , where  $V_{\text{molec}}$  is the volume occupied by one molecule. This volume is written in terms of the radius  $r$  as  $4\pi r^3/3$  so it follows that  $r = (3b/16\pi N_A)^{1/3}$ .

$$r = \left( \frac{3b}{16\pi N_A} \right)^{1/3} = \left( \frac{3 \times (0.0362 \text{ dm}^3 \text{ mol}^{-1})}{16\pi \times (6.0221 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 1.53 \times 10^{-9} \text{ dm} = \boxed{153 \text{ pm}}$$

**E1C.7(a)** (i) In Section 1C.1(b) on page 20 it is explained that at the Boyle temperature  $Z = 1$  and  $dZ/dp = 0$ ; this latter condition corresponds to the second virial coefficient,  $B$  or  $B'$ , being zero. The task is to find the relationship between the van der Waals parameters and the virial coefficients, and the starting point for this is the expressions for the product  $pV_m$  in each case ([1C.5b–24] and [1C.3b–21])

$$\text{van der Waals: } p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2} \quad \text{hence} \quad pV_m = \frac{RTV_m}{(V_m - b)} - \frac{a}{V_m}$$

$$\text{virial: } pV_m = RT \left( 1 + \frac{B}{V_m} \right)$$

The van der Waals expression for  $pV_m$  is rewritten by dividing the denominator and numerator of the first fraction by  $V_m$  to give

$$pV_m = \frac{RT}{(1 - b/V_m)} - \frac{a}{V_m}$$

The dimensionless parameter  $b/V_m$  is likely to be  $\ll 1$ , so the approximation  $(1 - x)^{-1} \approx 1 + x$  is used to give

$$pV_m = RT(1 + b/V_m) - \frac{a}{V_m} = RT \left[ 1 + \frac{1}{V_m} \left( b - \frac{a}{RT} \right) \right]$$

Comparison of this expression with the virial expansion shows that

$$B = b - \frac{a}{RT}$$

It therefore follows that the Boyle temperature, when  $B = 0$ , is  $T_b = a/Rb$ .

For the van der Waals parameters from the *Resource section*

$$\begin{aligned} T_b &= \frac{a}{Rb} = \frac{6.260 \text{ atm dm}^6 \text{ mol}^{-2}}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (5.42 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} \\ &= \boxed{1.41 \times 10^3 \text{ K}} \end{aligned}$$

- (ii) In Section 1C.2(a) on page 23 it is argued that  $b = 4V_{\text{molec}}N_A$ , where  $V_{\text{molec}}$  is the volume occupied by one molecule. This volume is written in terms of the radius  $r$  as  $4\pi r^3/3$  so it follows that  $r = (3b/16\pi N_A)^{1/3}$ .

$$\begin{aligned} r &= \left( \frac{3b}{16\pi N_A} \right)^{1/3} = \left( \frac{3 \times (5.42 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})}{16\pi \times (6.0221 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} \\ &= 1.75 \times 10^{-9} \text{ dm} = \boxed{175 \text{ pm}} \end{aligned}$$

**EIC.8(a)** The reduced variables are defined in terms of the critical constants, [1C.8–26]

$$V_r = V_m/V_c \quad p_r = p/p_c \quad T_r = T/T_c$$

If the reduced pressure is the same for two gases (1) and (2) it follows that

$$\frac{p^{(1)}}{p_c^{(1)}} = \frac{p^{(2)}}{p_c^{(2)}} \quad \text{hence} \quad p^{(2)} = \frac{p^{(1)}}{p_c^{(1)}} \times p_c^{(2)}$$

and similarly

$$T^{(2)} = \frac{T^{(1)}}{T_c^{(1)}} \times T_c^{(2)}$$

These relationships are used to find the pressure and temperature of gas (2) corresponding to a particular state of gas (1); it is necessary to know the critical constants of both gases.

- (i) From the tables in the *Resource section*, for  $\text{H}_2$   $p_c = 12.8$  atm,  $T_c = 33.23$  K, and for  $\text{NH}_3$   $p_c = 111.3$  atm,  $T_c = 405.5$  K. Taking gas (1) as  $\text{H}_2$  and gas (2) as  $\text{NH}_3$ , the pressure and temperature of  $\text{NH}_3$  corresponding to  $p^{(\text{H}_2)} = 1.0$  atm and  $T^{(\text{H}_2)} = 298.15$  K is calculated as

$$p^{(\text{NH}_3)} = \frac{p^{(\text{H}_2)}}{p_c^{(\text{H}_2)}} \times p_c^{(\text{NH}_3)} = \frac{1.0 \text{ atm}}{12.8 \text{ atm}} \times (111.3 \text{ atm}) = \boxed{8.7 \text{ atm}}$$

$$T^{(\text{NH}_3)} = \frac{T^{(\text{H}_2)}}{T_c^{(\text{H}_2)}} \times T_c^{(\text{NH}_3)} = \frac{298.15 \text{ K}}{33.23 \text{ K}} \times (405.5 \text{ K}) = \boxed{3.6 \times 10^3 \text{ K}}$$

- (ii) For  $\text{Xe}$   $p_c = 58.0$  atm,  $T_c = 289.75$  K.

$$p^{(\text{Xe})} = \frac{p^{(\text{H}_2)}}{p_c^{(\text{H}_2)}} \times p_c^{(\text{Xe})} = \frac{1.0 \text{ atm}}{12.8 \text{ atm}} \times (58.0 \text{ atm}) = \boxed{4.5 \text{ atm}}$$

$$T^{(\text{Xe})} = \frac{T^{(\text{H}_2)}}{T_c^{(\text{H}_2)}} \times T_c^{(\text{Xe})} = \frac{298.15 \text{ K}}{33.23 \text{ K}} \times (289.75 \text{ K}) = \boxed{2.6 \times 10^3 \text{ K}}$$

- (iii) For  $\text{He}$   $p_c = 2.26$  atm,  $T_c = 5.2$  K.

$$p^{(\text{He})} = \frac{p^{(\text{H}_2)}}{p_c^{(\text{H}_2)}} \times p_c^{(\text{He})} = \frac{1.0 \text{ atm}}{12.8 \text{ atm}} \times (2.26 \text{ atm}) = \boxed{0.18 \text{ atm}}$$

$$T^{(\text{He})} = \frac{T^{(\text{H}_2)}}{T_c^{(\text{H}_2)}} \times T_c^{(\text{He})} = \frac{298.15 \text{ K}}{33.23 \text{ K}} \times (5.2 \text{ K}) = \boxed{47 \text{ K}}$$

- E1C.9(a)** The van der Waals equation of state in terms of the molar volume is given by [1C.5b–24],  $p = RT/(V_m - b) - a/V_m^2$ . This relationship is rearranged to find  $b$

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{hence} \quad p + \frac{a}{V_m^2} = \frac{RT}{V_m - b}$$

$$\text{hence} \quad \frac{pV_m^2 + a}{V_m^2} = \frac{RT}{V_m - b} \quad \text{hence} \quad \frac{V_m^2}{pV_m^2 + a} = \frac{V_m - b}{RT}$$

$$\text{hence} \quad b = V_m - \frac{RTV_m^2}{pV_m^2 + a}$$

With the data given

$$b = V_m - \frac{RTV_m^2}{pV_m^2 + a} = (5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}) - \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K}) \times (5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})^2}{(3.0 \times 10^6 \text{ Pa}) \times (5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})^2 + (0.50 \text{ m}^6 \text{ Pa mol}^{-2})}$$

$$= \boxed{4.6 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

where  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$  and  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  have been used.

The compression factor  $Z$  is defined in [1C.1–20] as  $Z = V_m/V_m^\circ$ , where  $V_m^\circ$  is the molar volume of a perfect gas under the same conditions. This volume is computed from the equation of state for a perfect gas, [1A.4–8], as  $V_m^\circ = RT/p$ , hence  $Z = pV_m/RT$ , [1C.2–20]. With the data given

$$Z = \frac{pV_m}{RT} = \frac{(3.0 \times 10^6 \text{ Pa}) \times (5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} = \boxed{0.66}$$

### Solutions to problems

**PIC.1** The virial equation is given by [1C.3b–21],  $pV_m = RT(1 + B/V_m + \dots)$ , and from the *Resource section* the second virial coefficient  $B$  for  $\text{N}_2$  at 273 K is  $-10.5 \text{ cm}^3 \text{ mol}^{-1}$ . The molar mass of  $\text{N}_2$  is  $2 \times 14.01 = 28.02 \text{ g mol}^{-1}$ , hence the molar volume is

$$V_m = \frac{V}{n} = \frac{V}{m/M} = \frac{2.25 \text{ dm}^3}{(4.56 \text{ g})/(28.02 \text{ g mol}^{-1})} = 13.8... \text{ dm}^3 \text{ mol}^{-1}$$

This is used to calculate the pressure using the virial equation. It is convenient to use  $R = 8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$  and express all the volumes in  $\text{dm}^3$

$$\begin{aligned} p &= \frac{RT}{V_m} \left( 1 + \frac{B}{V_m} \right) \\ &= \frac{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{13.8... \text{ dm}^3 \text{ mol}^{-1}} \left( 1 + \frac{-1.05 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}}{13.8... \text{ dm}^3 \text{ mol}^{-1}} \right) \\ &= \boxed{1.62 \text{ atm}} \end{aligned}$$

**PIC.3** The virial equation is [1C.3b–21],  $pV_m = RT(1 + B/V_m + C/V_m^2 + \dots)$ . The compression factor is defined in [1C.1–20] as  $Z = V_m/V_m^\circ$ , and the molar volume of a perfect gas,  $V_m^\circ$  is given by  $V_m^\circ = RT/p$ .

It follows that

$$\begin{aligned} V_m &= (RT/p)(1 + B/V_m + C/V_m^2) = V_m^\circ(1 + B/V_m + C/V_m^2) \\ \text{hence } Z &= \frac{V_m}{V_m^\circ} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} \end{aligned}$$

To evaluate this expression, the molar volume is approximated by the molar volume of a perfect gas under the prevailing conditions

$$V_m^\circ = \frac{RT}{p} = \frac{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{100 \text{ atm}} = 0.224... \text{ dm}^3 \text{ mol}^{-1}$$

This value of the molar volume is then used to compute  $Z$ ; note the conversion of all the volume terms to  $\text{dm}^3$

$$\begin{aligned} Z &= 1 + \frac{B}{V_m} + \frac{C}{V_m^2} \\ &= 1 + \frac{-21.3 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}}{0.224... \text{ dm}^3 \text{ mol}^{-1}} + \frac{1200 \times 10^{-6} \text{ dm}^6 \text{ mol}^{-2}}{(0.224... \text{ dm}^3 \text{ mol}^{-1})^2} = 0.928... = \boxed{0.929} \end{aligned}$$

The molar volume is computed from the compression factor

$$Z = \frac{V_m}{V_m^\circ} = \frac{V_m}{RT/p}$$

hence  $V_m = \frac{ZRT}{p} = \frac{0.928... \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{100 \text{ atm}}$

$$= \boxed{0.208 \text{ dm}^3 \text{ mol}^{-1}}$$

**PIC.5** In Section 1C.1(b) on page 20 it is explained that at the Boyle temperature  $Z = 1$  and  $dZ/dp = 0$ ; this latter condition corresponds to the second virial coefficient,  $B$  or  $B'$ , being zero. The Boyle temperature is found by setting the given expression for  $B(T)$  to zero and solving for  $T$

$$0 = a + be^{-c/T^2} \quad \text{hence} \quad -a/b = e^{-c/T^2}$$

Taking logarithms gives  $\ln(-a/b) = -c/T^2$  hence

$$T = \left( \frac{-c}{\ln(-a/b)} \right)^{1/2} = \left( \frac{-1131 \text{ K}^2}{\ln[-(-0.1993 \text{ bar}^{-1})/(0.2002 \text{ bar}^{-1})]} \right)^{1/2}$$

$$= \boxed{501.0 \text{ K}}$$

**PIC.7** (a) The molar mass  $M$  of  $\text{H}_2\text{O}$  is  $18.02 \text{ g mol}^{-1}$ . The mass density  $\rho$  is related to the molar density  $\rho_m$  by  $\rho_m = \rho/M$ , and the molar volume is simply the reciprocal of the molar density  $V_m = 1/\rho_m = M/\rho$

$$V_m = \frac{M}{\rho} = \frac{18.02 \times 10^{-3} \text{ kg mol}^{-1}}{133.2 \text{ kg m}^{-3}} = 1.352... \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

The molar volume is therefore  $\boxed{0.1353 \text{ dm}^3 \text{ mol}^{-1}}$

(b) The compression factor  $Z$  is given by [1C.2–20],  $Z = pV_m/RT$

$$Z = \frac{pV_m}{RT} = \frac{(327.6 \text{ atm}) \times (0.1352... \text{ dm}^3 \text{ mol}^{-1})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (776.4 \text{ K})} = \boxed{0.6957}$$

(c) The virial equation (up to the second term) in terms of the molar volume is given by [1C.3b–21]

$$pV_m = RT \left( 1 + \frac{B}{V_m} \right)$$

Division of each side by  $p$  gives

$$V_m = \frac{RT}{p} \left( 1 + \frac{B}{V_m} \right)$$

The quantity  $RT/p$  is recognised as the molar volume of a perfect gas,  $V_m^\circ$ , so it follows that

$$V_m = V_m^\circ \left(1 + \frac{B}{V_m}\right) \quad \text{hence} \quad \frac{V_m}{V_m^\circ} = Z = \left(1 + \frac{B}{V_m}\right)$$

In *Problem P1C.4* it is shown that  $B$  is related to the van der Waals constants by  $B = b - a/RT$ ; using this, it is then possible to compute the compression factor

$$\begin{aligned} B &= b - \frac{a}{RT} = (0.03049 \text{ dm}^3 \text{ mol}^{-1}) \\ &\quad - \frac{(5.464 \text{ atm dm}^6 \text{ mol}^{-2})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (776.4 \text{ K})} \\ &= -0.552... \text{ dm}^3 \text{ mol}^{-1} \end{aligned}$$

$$Z = 1 + \frac{B}{V_m} = 1 + \frac{-0.552... \text{ dm}^3 \text{ mol}^{-1}}{0.1352... \text{ dm}^3 \text{ mol}^{-1}} = \boxed{0.5914}$$

**PI C.9** According to Table 1C.4 on page 25, for the Dieterici equation of state the critical constants are given by

$$p_c = \frac{a}{4e^2 b^2} \quad V_c = 2b \quad T_c = \frac{a}{4bR}$$

From the *Resource section* the values for Xe are  $T_c = 289.75 \text{ K}$ ,  $p_c = 58.0 \text{ atm}$ ,  $V_c = 118.8 \text{ cm}^3 \text{ mol}^{-1}$ . The coefficient  $b$  is computed directly from  $V_c$

$$b = V_c/2 = (118.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1})/2 = \boxed{0.0594 \text{ dm}^3 \text{ mol}^{-1}}$$

The expressions for  $p_c$  and  $V_c$  are combined to eliminate  $b$

$$p_c = \frac{a}{4e^2 b^2} = \frac{a}{4e^2 V_c^2/4}$$

This is then rearranged to find  $a$

$$\begin{aligned} a &= p_c e^2 V_c^2 = (58.0 \text{ atm}) \times e^2 \times (118.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1})^2 \\ &= \boxed{6.049 \text{ atm dm}^6 \text{ mol}^{-2}} \end{aligned}$$

Alternatively, the expressions for  $T_c$  and  $V_c$  are combined to eliminate  $b$

$$T_c = \frac{a}{4bR} = \frac{a}{4RV_c/2}$$

This is then rearranged to find  $a$

$$\begin{aligned} a &= 2T_c V_c R \\ &= 2 \times (289.75 \text{ K}) \times (118.8 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}) \\ &\quad \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) = \boxed{5.649 \text{ atm dm}^6 \text{ mol}^{-2}} \end{aligned}$$



The two values of  $a$  are not the same; their average is  $5.849 \text{ atm dm}^6 \text{ mol}^{-2}$ .

From Table 1C.4 on page 25 the expression for the pressure exerted by a Dieterici gas is

$$p = \frac{nRT \exp(-a/[RTV/n])}{V - nb}$$

With the parameters given the exponential term evaluates to

$$\exp\left(\frac{-(5.849 \text{ atm dm}^6 \text{ mol}^{-2})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times (1.0 \text{ dm}^3)/(1.0 \text{ mol})}\right) = 0.787\dots$$

and hence the pressure evaluates to

$$p = \frac{(1.0 \text{ mol}) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \times (0.787\dots)}{(1.0 \text{ dm}^3) - (1.0 \text{ mol}) \times (0.0594 \text{ dm}^3 \text{ mol}^{-1})} = \boxed{20.48 \text{ atm}}$$

**PIC.11** The van der Waals equation in terms of the molar volume is given by [1C.5b–24],  $p = RT/(V_m - b) - a/V_m^2$ . Multiplication of both sides by  $V_m$  gives

$$pV_m = \frac{RTV_m}{(V_m - b)} - \frac{a}{V_m}$$

and then division of the numerator and denominator of the first fraction by  $V_m$  gives

$$pV_m = \frac{RT}{(1 - b/V_m)} - \frac{a}{V_m}$$

The approximation  $(1-x)^{-1} \approx 1+x+x^2$  is used to approximate  $1/(1-b/V_m)$  to give

$$pV_m = RT \left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2}\right) - \frac{a}{V_m}$$

The terms in  $1/V_m$  and  $1/V_m^2$  are gathered together to give

$$pV_m = RT \left(1 + \frac{1}{V_m} \left[b - \frac{a}{RT}\right] + \frac{b^2}{V_m^2}\right)$$

This result is then compared with the virial equation in terms of the molar volume, [1C.3b–21]

$$pV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2}\right)$$

This comparison identifies the virial coefficients as

$$B = b - \frac{a}{RT} \quad C = b^2$$

From the given value  $C = 1200 \text{ cm}^6 \text{ mol}^{-2}$  it follows that  $b = \sqrt{C} = 34.64 \text{ cm}^3 \text{ mol}^{-1}$ . Expressed in the usual units this is  $b = \boxed{0.03464 \text{ dm}^3 \text{ mol}^{-1}}$ . The value of  $a$  is found by rearranging  $B = b - a/RT$  to

$$\begin{aligned} a &= RT(b - B) = (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K}) \times \\ &\quad [(0.03464 \text{ dm}^3 \text{ mol}^{-1}) - (-21.7 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1})] \\ &= \boxed{1.262 \text{ atm dm}^6 \text{ mol}^{-2}} \end{aligned}$$

**PIC.13** In Section 1C.2(b) on page 24 it is explained that critical behaviour is associated with oscillations in the isotherms predicted by a particular equation of state, and that at the critical point there is a point of inflexion in the isotherm. At this point it follows that

$$\frac{dp}{dV_m} = 0 \quad \frac{d^2p}{dV_m^2} = 0$$

The procedure is first to find expressions for the first and second derivatives. Then these are both set to zero give two simultaneous equations which can be solved for the critical pressure and volume.

$$\frac{dp}{dV_m} = -\frac{RT}{V_m^2} + \frac{2B}{V_m^3} - \frac{3C}{V_m^4} = 0 \quad \frac{d^2p}{dV_m^2} = \frac{2RT}{V_m^3} - \frac{6B}{V_m^4} + \frac{12C}{V_m^5} = 0$$

The first of these equations is multiplied through by  $V_m^4$  and the second by  $V_m^5$  to give

$$-RTV_m^2 + 2BV_m - 3C = 0 \quad 2RTV_m^2 - 6BV_m + 12C = 0$$

The first equation is multiplied by 2 and added to the second, thus eliminating the terms in  $V_m^2$  and giving

$$4BV_m - 6C - 6BV_m + 12C = 0 \quad \text{hence} \quad V_m = 3C/B$$

This expression for  $V_m$  is then substituted into  $-RTV_m^2 + 2BV_m - 3C = 0$  to give

$$-RT \frac{(3C)^2}{B^2} + 2B \frac{3C}{B} - 3C = 0$$

A term  $3C$  is cancelled and the equation is multiplied through by  $B^2$  to give

$$-RT(3C) + 2B^2 - B^2 = 0 \quad \text{hence} \quad T = B^2/3RC$$

Finally the pressure is found by substituting  $V_m = 3C/B$  and  $T = B^2/3RC$  into the equation of state

$$\begin{aligned} p &= \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3} \\ &= \frac{B^2R}{3RC} \frac{B}{3C} - \frac{B^3}{9C^2} + \frac{CB^3}{27C^3} = \frac{B^3}{9C^2} - \frac{B^3}{9C^2} + \frac{B^3}{27C^2} = \frac{B^3}{27C^2} \end{aligned}$$

In summary, the critical constants are

$$V_m = 3C/B \quad T = B^2/3CR \quad p = B^3/27C^2$$

**PI.C.15** The virial equation in terms of the pressure, [1C.3a–2l], is (up to the second term)

$$pV_m = RT(1 + B'p)$$

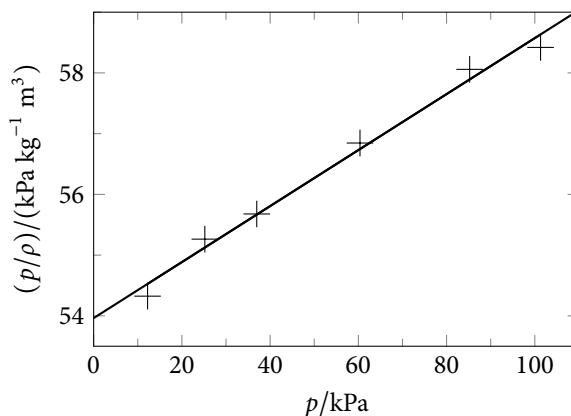
The mass density  $\rho$  is given by  $m/V$ , and the mass  $m$  can be written as  $nM$ , where  $n$  is the amount in moles and  $M$  is the molar mass. It follows that  $\rho = nM/V = M/V_m$ , where  $V_m$  is the molar volume. Rearranging gives  $V_m = M/\rho$ : measurements of the mass density therefore lead to values for the molar volume.

With this substitution for the molar volume the virial equation becomes

$$\frac{pM}{\rho} = RT(1 + B'p) \quad \text{hence} \quad \frac{p}{\rho} = \frac{RT}{M}(1 + B'p)$$

Therefore a plot of  $p/\rho$  against  $p$  is expected to be a straight line whose slope is related to  $B'$ ; such a plot is shown in Fig. 1.5.

$p/\text{kPa}$	$\rho/(\text{kg m}^{-3})$	$(p/\rho)/(\text{kPa kg}^{-1} \text{ m}^3)$
12.22	0.225	54.32
25.20	0.456	55.26
36.97	0.664	55.68
60.37	1.062	56.85
85.23	1.468	58.06
101.30	1.734	58.42



**Figure 1.5**

The data fall on a reasonable straight line, the equation of which is

$$(p/\rho)/(\text{kPa kg}^{-1} \text{ m}^3) = 0.04610 \times (p/\text{kPa}) + 53.96$$

The slope is  $B'RT/M$

$$\frac{B'RT}{M} = 0.04610 \text{ kg}^{-1} \text{ m}^3$$

For methoxymethane,  $\text{CH}_3\text{OCH}_3$ ,  $M = 2 \times 12.01 + 6 \times 1.0079 + 16.00 = 46.0674 \text{ g mol}^{-1}$ .

$$B' = \frac{(0.04610 \text{ kg}^{-1} \text{ m}^3) \times (46.0674 \times 10^{-3} \text{ kg mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})} = 8.57 \times 10^{-7} \text{ m}^3 \text{ J}^{-1}$$

The units of the result can be simplified by noting that  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ , so  $1 \text{ m}^3 \text{ J}^{-1} = 1 \text{ m kg}^{-1} \text{ s}^2$ . Recall that  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ , so the units of the  $B'$  are  $\text{Pa}^{-1}$ , an inverse pressure, as expected:  $B' = 8.57 \times 10^{-7} \text{ Pa}^{-1}$  or  $\boxed{B' = 0.0868 \text{ atm}^{-1}}$ .

The virial coefficient  $B$  is found using the result from *Problem PIC.14*,  $B = B'RT$

$$\begin{aligned} B &= B'RT \\ &= (0.0868 \text{ atm}^{-1}) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \\ &= \boxed{2.12 \text{ dm}^3 \text{ mol}^{-1}} \end{aligned}$$

**PIC.17** A gas can only be liquefied by the application of pressure if the temperature is below the critical temperature, which for  $\text{N}_2$  is 126.3 K.

**PIC.19** The compression factor is given by [1C.1-20],  $Z = V_m/V_m^\circ = V_m p/RT$ . The given equation of state is rearranged to give an expression for  $V_m$  after putting  $n = 1$

$$p(V - nb) = nRT \quad \text{becomes} \quad p(V_m - b) = RT \quad \text{hence} \quad V_m = \frac{RT}{p} + b$$

It follows that the compression factor is given by

$$Z = \frac{V_m p}{RT} = \frac{(RT/p + b)p}{RT} = \boxed{1 + \frac{bp}{RT}}$$

If  $V_m = 10b$  it follows from the previous equation that

$$\frac{V_m p}{RT} = \frac{10bp}{RT} = 1 + \frac{bp}{RT} \quad \text{hence} \quad b = \frac{RT}{9p}$$

With this expression for  $b$  the compression factor is computed from  $Z = 1 + bp/RT$  as

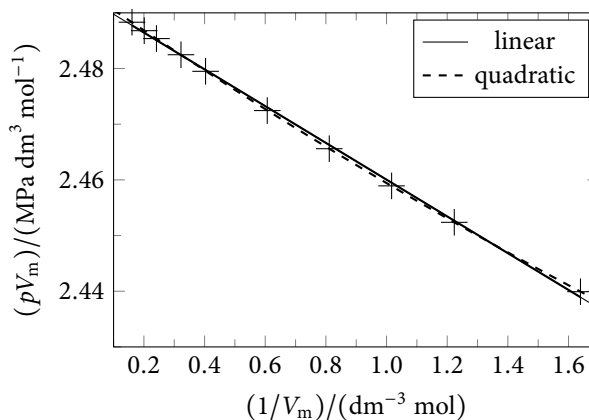
$$Z = 1 + \frac{bp}{RT} = 1 + \frac{RT}{9p} \frac{p}{RT} = 1 + \frac{1}{9} = \boxed{1.11}$$

**PIC.21** The virial equation in terms of the molar volume, [1C.3b-2l], is (up to the third term)

$$pV_m = RT \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} \right)$$

For part (a) only the first two terms are considered, and it then follows that a plot of  $pV_m$  against  $1/V_m$  is expected to be a straight line with slope  $BRT$ ; such a plot is shown in Fig. 1.6.

$p/\text{MPa}$	$V_m/(\text{dm}^3 \text{mol}^{-1})$	$(pV_m)/(\text{MPa dm}^3 \text{mol}^{-1})$	$(1/V_m)/(\text{dm}^{-3} \text{mol})$
0.4000	6.2208	2.4883	0.16075
0.5000	4.9736	2.4868	0.20106
0.6000	4.1423	2.4854	0.24141
0.8000	3.1031	2.4825	0.32226
1.000	2.4795	2.4795	0.40331
1.500	1.6483	2.4725	0.60669
2.000	1.2328	2.4656	0.81116
2.500	0.98357	2.4589	1.0167
3.000	0.81746	2.4524	1.2233
4.000	0.60998	2.4399	1.6394



**Figure 1.6**

The data fall on a reasonable straight line, the equation of which is

$$(pV_m)/(\text{MPa dm}^3 \text{mol}^{-1}) = -0.03302 \times (1/V_m)/(\text{dm}^{-3} \text{mol}) + 2.4931$$

The slope is  $BRT$

$$BRT = (-0.03302 \text{ MPa dm}^6 \text{mol}^{-2})$$

It is convenient to convert to atm giving  $BRT = (-0.3259 \text{ atm dm}^6 \text{mol}^{-2})$   
hence

$$\begin{aligned}
 B &= \frac{(-0.3259 \text{ atm dm}^6 \text{mol}^{-2})}{RT} \\
 &= \frac{(-0.3259 \text{ atm dm}^6 \text{mol}^{-2})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{atm K}^{-1} \text{mol}^{-1}) \times (300 \text{ K})} \\
 &= \boxed{-0.01324 \text{ dm}^3 \text{mol}^{-1}}
 \end{aligned}$$

For part (b) the data points are fitted to polynomial of order 2 in  $1/V_m$  using mathematical software; the data are a slightly better fit to such a function (see the dashed line in the graph above) which is

$$(pV_m)/(\text{MPa dm}^3 \text{ mol}^{-1}) = 0.002652 \times (1/V_m)^2/(\text{dm}^{-6} \text{ mol}^2) - 0.03748 \times (1/V_m)/(\text{dm}^{-3} \text{ mol}) + 2.494$$

The coefficient of the term in  $(1/V_m)^2$  is  $CRT$

$$CRT = (0.002652 \text{ MPa dm}^9 \text{ mol}^{-3})$$

It is convenient to convert to atm giving  $CRT = (0.02617 \text{ atm dm}^9 \text{ mol}^{-3})$  hence

$$\begin{aligned} C &= \frac{(0.02617 \text{ atm dm}^9 \text{ mol}^{-3})}{RT} \\ &= \frac{(0.02617 \text{ atm dm}^9 \text{ mol}^{-3})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})} \\ &= \boxed{1.063 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2}} \end{aligned}$$

**FIG. 23** The van der Waals equation of state in terms of the molar volume is given by [1C.5b-24],  $p = RT/(V_m - b) - a/V_m^2$ . This equation is a cubic in  $V_m$ , as is seen by multiplying both sides by  $(V_m - b)V_m^2$  and then gathering the terms together

$$pV_m^3 - V_m^2(pb + RT) + aV_m - ab = 0$$

From the *Resource section* the van der Waals parameters for  $\text{Cl}_2$  are

$$a = 6.260 \text{ atm dm}^6 \text{ mol}^{-2} \quad b = 5.42 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$$

It is convenient to convert the pressure to atm

$$p = (150 \times 10^3 \text{ Pa}) \times (1 \text{ atm})/(1.01325 \times 10^5 \text{ Pa}) = 1.4804 \text{ atm}$$

and to use  $R = 8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ ; inserting all of these values and the temperature gives the polynomial

$$1.4804V_m^3 - 20.5946V_m^2 + 6.260V_m - 0.3393 = 0$$

The roots of this polynomial are found numerically using mathematical software and of these roots only  $\boxed{V_m = 13.6 \text{ dm}^3 \text{ mol}^{-1}}$  is a physically plausible value for the molar volume.

The molar volume of a perfect gas under corresponding conditions is

$$V_m = \frac{RT}{p} = \frac{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (250 \text{ K})}{1.48 \text{ atm}} = 13.9 \text{ dm}^3 \text{ mol}^{-1}$$

The molar volume of the van der Waals gas is about 2% smaller than that of the perfect gas.

**Answers to integrated activities**

- II.1** The Maxwell–Boltzmann distribution of speeds in three dimensions is given by [1B.4–14]

$$f(v) = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

with  $M$  the molar mass. The most probable speed is found by taking the derivative of  $f(v)$  with respect to  $v$ , and setting this to zero; calculating the derivative requires the use of the chain rule

$$\frac{df(v)}{dv} = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \left[ 2ve^{-Mv^2/2RT} + v^2 \left( \frac{-2Mv}{2RT} \right) e^{-Mv^2/2RT} \right] = 0$$

The multiplying constant and factors of  $v$  and  $e^{-Mv^2/2RT}$  are cancelled (these do not correspond to maxima) leaving

$$2 - \frac{Mv^2}{RT} = 0 \quad \text{hence} \quad \boxed{v = \left( \frac{2RT}{M} \right)^{1/2}}$$

Inspection of the form of the distribution shows that this is a maximum.

The average kinetic energy is calculated from the average of the square of the speed:  $\langle E_k \rangle = \frac{1}{2}m\langle v^2 \rangle$ . The task is therefore to calculate this average using the Maxwell–Boltzmann distribution: the required integral is

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v) dv = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \int_0^\infty v^4 e^{-Mv^2/2RT} dv$$

This integral is of the form of G.8 from the *Resource section*

$$\int_0^\infty x^{2m} e^{-ax^2} dx = \frac{(2m-1)!!}{2^{m+1} a^m} \left( \frac{\pi}{a} \right)^{1/2}$$

with  $m = 2$ ,  $(2m-1)!! = 3 \times 1 = 3$ ,  $2^{m+1} = 8$ ,  $a^m = a^2$  and  $a = M/2RT$ .

$$\begin{aligned} \langle v^2 \rangle &= 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \times \frac{3}{8} \times \left( \frac{4R^2 T^2}{M^2} \right) \times \left( \frac{2RT\pi}{M} \right)^{1/2} \\ &= \frac{3RT}{M} = \frac{3kT}{m} \end{aligned}$$

To go to the last line from the previous one involves a deal of careful algebra, and for the final step  $R = N_A k$  and  $M = mN_A$  have been used, with  $m$  the mass of the molecule.

With this result

$$\langle E_k \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m \left( \frac{3kT}{m} \right) = \frac{3}{2}kT$$

which is in accord with the equipartition principle.

**11.3** In Section 1C.2(a) on page 23 it is argued that  $b = 4V_{\text{molec}}N_{\text{A}}$ , where  $V_{\text{molec}}$  is the volume occupied by one molecule. The collision cross-section  $\sigma$  is defined in terms of a collision diameter  $d$  as  $\sigma = \pi d^2$ , and in turn the diameter is interpreted as twice the radius of the colliding spheres:  $d = 2r$ . It follows that  $r = (\sigma/4\pi)^{1/2}$

$$\begin{aligned} b &= 4V_{\text{molec}}N_{\text{A}} \\ &= 4\left(\frac{4}{3}\pi r^3\right)N_{\text{A}} = \frac{16\pi N_{\text{A}}}{3}\left(\frac{\sigma}{4\pi}\right)^{3/2} \\ &= \frac{16\pi(6.0221 \times 10^{23} \text{ mol}^{-1})}{3}\left(\frac{0.46 \times 10^{-18} \text{ m}^2}{4\pi}\right)^{3/2} \\ &= 7.1 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} = \boxed{0.071 \text{ dm}^3 \text{ mol}^{-1}} \end{aligned}$$





# Internal energy

## 2A Internal energy

### Answers to discussion questions

**D2A.1** In physical chemistry, the universe is considered to be divided into two parts: the system and its surroundings. In thermodynamics, the system is the object of interest which is separated from its surroundings, the rest of the universe, by a boundary. The characteristics of the boundary determine whether the system is open, closed, or isolated.

An open system has a boundary that permits the passage of both matter and energy. A closed system has a boundary that allows the passage of energy but not of matter. Closed systems can be either adiabatic or diathermic. The former do not allow the transfer of energy as a result of a temperature difference, but the latter do. An isolated system is one with a boundary that allows neither the transfer of matter nor energy between the system and the surroundings.

**D2A.3** Table 2A.1 on page 39 lists four varieties of work: expansion, surface expansion, extension, and electrical. There is also work associated with processes in magnetic and gravitational fields which we will not describe in detail.

**D2A.5** An isothermal expansion of a gas may be achieved by making sure that the gas and its container are in thermal contact with a large 'bath' which is held at a constant temperature – that is, a thermostat.

### Solutions to exercises

**E2A.1(a)** *The chemist's toolkit 7* in Topic 2A gives an explanation of the equipartition theorem. The molar internal energy is given by

$$U_m = \frac{1}{2} \times (\nu_t + \nu_r + 2\nu_v) \times RT$$

where  $\nu_t$  is the number of translational degrees of freedom,  $\nu_r$  is the number of rotational degrees of freedom and  $\nu_v$  is the number of vibrational degrees of freedom. As each gas molecule can move independently along the  $x$ ,  $y$  and  $z$  axis, the number of translational degrees of freedom is three.

- (i) Molecular iodine is a diatomic molecule, therefore it has two degrees of rotational freedom. On account of its heavy atoms, molecular iodine is