



Instructor Solutions Manual to Accompany Atkins' Physical Chemistry

ELEVENTH EDITION

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Preface

This manual provides detailed solutions to the (b) *Exercises* and the even-numbered *Discussion questions* and *Problems* from the 11th edition of *Atkins' Physical Chemistry*.

Conventions used in presenting the solutions

We have included page-specific references to equations, sections, figures and other features of the main text. Equation references are denoted [14B.3b–595], meaning eqn 14B.3b located on page 595 (the page number is given in italics). Other features are referred to by name, with a page number also given.

Generally speaking, the values of physical constants (from the first page of the main text) are used to 5 significant figures except in a few cases where higher precision is required. In line with the practice in the main text, intermediate results are simply truncated (not rounded) to three figures, with such truncation indicated by an ellipsis, as in 0.123...; the value is used in subsequent calculations to its full precision.

The final results of calculations, generally to be found in a box, are given to the precision warranted by the data provided. We have been rigorous in including units for all quantities so that the units of the final result can be tracked carefully. The relationships given on the back of the front cover are useful in resolving the units of more complex expressions, especially where electrical quantities are involved.

Some of the problems either require the use of mathematical software or are much easier with the aid of such a tool. In such cases we have used *Mathematica* (Wolfram Research, Inc.) in preparing these solutions, but there are no doubt other options available. Some of the *Discussion questions* relate directly to specific section of the main text in which case we have simply given a reference rather than repeating the material from the text.

Acknowledgements

In preparing this manual we have drawn on the equivalent volume prepared for the 10th edition of *Atkins' Physical Chemistry* by Charles Trapp, Marshall Cady, and Carmen Giunta. In particular, the solutions which use quantum chemical calculations or molecular modelling software, and some of the solutions to the *Discussion questions*, have been quoted directly from the solutions manual for the 10th edition, without significant modification. More generally, we have benefited from the ability to refer to the earlier volume and acknowledge, with thanks, the influence that its authors have had on the present work.

This manual has been prepared by the authors using the \LaTeX typesetting system, in the implementation provided by MiKTeX (miktex.org); the vast majority of the figures and graphs have been generated using PGFPlots. We are grateful to the community who maintain and develop these outstanding resources.

Finally, we are grateful to the editorial team at OUP, Jonathan Crowe and Roseanna Levermore, for their invaluable support in bringing this project to a conclusion.

Errors and omissions

In such a complex undertaking some errors will no doubt have crept in, despite the authors' best efforts. Readers who identify any errors or omissions are invited to pass them on to us by email to pchem@ch.cam.ac.uk.



The properties of gases

1A The perfect gas

Answers to discussion questions

D1A.2 The partial pressure of gas J, p_J , in a mixture of gases is given by [1A.6–9], $p_J = x_J p$, where p is the total pressure and x_J is the mole fraction of J.

If the gases are perfect, the partial pressure is also the pressure the gas would exert if it occupied on its own the same container as the mixture at the same temperature. This leads to Dalton's law, which is that the pressure of a mixture of gases is the sum of the pressures that each one would exert if it occupied the container alone.

Dalton's law is a limiting law because it holds exactly only in the limit that there are no interactions between the molecules, which for real gases will be in the limit of zero pressure.

Solutions to exercises

E1A.1(b) From inside the front cover the conversion between pressure units is: $1 \text{ atm} \equiv 101.325 \text{ kPa} \equiv 760 \text{ Torr}$.

(i) A pressure of 22.5 kPa is converted to atm as follows

$$22.5 \text{ kPa} \times \frac{1 \text{ atm}}{101.325 \text{ kPa}} = \boxed{0.222 \text{ atm}}$$

(ii) A pressure of 770 Torr is converted to Pa as follows

$$770 \text{ Torr} \times \frac{1 \text{ atm}}{760 \text{ Torr}} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 103 \text{ kPa} = \boxed{1.03 \times 10^5 \text{ Pa}}$$

E1A.2(b) 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 Ar, 39.95 g mol^{-1} .

$$p = \frac{\overbrace{(25 \text{ g})}^n}{(39.95 \text{ g mol}^{-1})} \frac{(8.3145 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times (303.15 \text{ K})}{1.5 \text{ dm}^3} \\ = 10.4 \text{ bar}$$

So $\boxed{\text{no}}$, the sample would not exert a pressure of 2.0 bar, but $\boxed{10.4 \text{ bar}}$ if it were a perfect gas.

- E1A.3(b)** 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 1.80 dm^3 greater than the final volume so $V_i = 2.14 + 1.80 = 3.94 \text{ dm}^3$.

$$p_i = \frac{V_f}{V_i} \times p_f = \frac{2.14 \text{ dm}^3}{3.94 \text{ dm}^3} \times (1.97 \text{ bar}) = 1.07 \text{ bar}$$

- (i) The initial pressure is 1.07 bar
 (ii) Because 1 atm is equivalent to 1.01325 bar and also to 760 Torr, the initial pressure expressed in Torr is

$$\frac{1 \text{ atm}}{1.01325 \text{ bar}} \times \frac{760 \text{ Torr}}{1 \text{ atm}} \times 1.07 \text{ bar} = \text{803 Torr}$$

- E1A.4(b)** 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: $p_f/p_i = T_f/T_i$. Solving for the final pressure p_f (remember to use absolute temperatures) gives

$$\begin{aligned} p_f &= \frac{T_f}{T_i} \times p_i \\ &= \frac{(11 + 273.15) \text{ K}}{(23 + 273.15) \text{ K}} \times (125 \text{ kPa}) = \text{120 kPa} \end{aligned}$$

- E1A.5(b)** The perfect gas law $pV = nRT$ is rearranged to give $n = pV/RT$.

$$\begin{aligned} n &= \frac{pV}{RT} \\ &= \frac{(1.00 \times 1.01325 \times 10^5 \text{ Pa}) \times (4.00 \times 10^3 \text{ m}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ([20 + 273.15] \text{ K})} = \text{1.66...} \times 10^5 \text{ mol} \end{aligned}$$

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.

The molar mass of CH_4 is $12.01 + 4 \times 1.0079 = 16.0416 \text{ g mol}^{-1}$, so the mass of CH_4 is $(1.66... \times 10^5 \text{ mol}) \times (16.0416 \text{ g mol}^{-1}) = 2.67 \times 10^6 \text{ g}$ or $2.67 \times 10^3 \text{ kg}$.

- E1A.6(b)** 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 ρ , so $p = \rho RT/M$, which rearranges to $M = \rho RT/p$; this is the required relationship between M and the density.

$$M = \frac{\rho RT}{p} = \frac{(0.6388 \text{ kg m}^{-3}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ([100 + 273.15] \text{ K})}{16.0 \times 10^3 \text{ Pa}}$$

$$= 0.123... \text{ kg mol}^{-1}$$

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 P is 30.97 g mol^{-1} , so the number of P atoms in the molecules comprising the vapour is $(0.123... \times 10^3 \text{ g mol}^{-1}) / (30.97 \text{ g mol}^{-1}) = 4.00$. The result is expected to be an integer, so the formula is likely to be P_4 .

- E1A.7(b)** 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 0.53 times the saturated vapour pressure

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

$$= \frac{(18.0158 \text{ g mol}^{-1}) \times (0.53 \times 0.0281 \times 10^5 \text{ Pa}) \times (250 \text{ m}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ([23 + 273.15] \text{ K})}$$

$$= 2.7 \times 10^3 \text{ g} = \boxed{2.7 \text{ kg}}$$

- E1A.8(b)** Once the total amount and the total pressure p_{tot} are known, the volume is found using the perfect gas law. The total amount in moles of the mixture of gases is

$$n_{\text{tot}} = n_{\text{CH}_4} + n_{\text{Ar}} + n_{\text{Ne}} = \frac{m_{\text{CH}_4}}{M_{\text{CH}_4}} + \frac{m_{\text{Ar}}}{M_{\text{Ar}}} + \frac{m_{\text{Ne}}}{M_{\text{Ne}}}$$

$$= \frac{0.320 \text{ g}}{(12.01 + 4 \times 1.0079) \text{ g mol}^{-1}} + \frac{0.175 \text{ g}}{39.95 \text{ g mol}^{-1}} + \frac{0.225 \text{ g}}{20.18 \text{ g mol}^{-1}}$$

$$= 3.54... \times 10^{-2} \text{ mol}$$

The mole fraction of neon is

$$x_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{tot}}} = \frac{0.225 \text{ g}}{20.18 \text{ g mol}^{-1}} \times \frac{1}{3.54... \times 10^{-2} \text{ mol}} = 0.314...$$

Because $p_{\text{Ne}} = x_{\text{Ne}} \times p_{\text{tot}}$ it follows that

$$p_{\text{tot}} = \frac{p_{\text{Ne}}}{x_{\text{Ne}}} = \frac{8.87 \text{ kPa}}{0.314...} = \boxed{28.2 \text{ kPa}}$$

The volume is calculated using the perfect gas equation with the known total pressure and total amount

$$V = \frac{nRT}{p} = \frac{(3.54... \times 10^{-2} \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{28.2 \times 10^3 \text{ Pa}}$$

$$= 3.14 \times 10^{-3} \text{ m}^3 = \boxed{3.14 \text{ dm}^3}$$

- E1A.9(b)** 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 pressure and volume of a known mass of gas to the molar mass.

The amount n is expressed as the mass m divided by the molar mass M to give $pV = (m/M)RT$; this rearranges to $M = mRT/pV$ which is the required relationship. The pressure in Torr is converted to Pa by noting that 760 Torr is equivalent to 1 atm.

$$\begin{aligned} M &= \frac{mRT}{pV} \\ &= \frac{(33.5 \times 10^{-6} \text{ kg}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(152 \text{ Torr}/760 \text{ Torr}) \times (1.01325 \times 10^5 \text{ Pa}) \times (250 \times 10^{-6} \text{ m}^3)} \\ &= \boxed{0.0164 \text{ kg mol}^{-1}} \end{aligned}$$

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; note the conversion of the volume to m^3 .

- E1A.10(b)** The idea here is that the volume will go to zero at absolute zero. The data given are the slope of the volume/temperature plot, together with one fixed point, so the equation of the straight line can be found, and then the required intercept.

The equation of the line is

$$(V/\text{dm}^3) = (0.0741) \times (\theta/^\circ\text{C}) + (c/\text{dm}^3)$$

The fixed point given is that the volume at $\theta = 0^\circ\text{C}$ is 20.00 dm^3 , so the constant c is equal to this volume

$$(V/\text{dm}^3) = (0.0741) \times (\theta/^\circ\text{C}) + 20.00$$

This is solved for $V = 0$ to give $(\theta/^\circ\text{C}) = (-20.00)/(0.0741) = -270$, hence $\boxed{\theta = -270^\circ\text{C}}$. This is the estimate of absolute zero.

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

$$x_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{H}_2} + n_{\text{N}_2}} = \frac{1.5 \text{ mol}}{1.5 \text{ mol} + 2.5 \text{ mol}} = \boxed{\frac{3}{8}} \quad x_{\text{N}_2} = 1 - x_{\text{H}_2} = \boxed{\frac{5}{8}}$$

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

$$\begin{aligned} p_{\text{H}_2} &= x_{\text{H}_2} p_{\text{tot}} = \frac{3}{8} \times \frac{(4.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.4 \times 10^{-3} \text{ m}^3} \\ &= \boxed{1.5 \times 10^5 \text{ Pa}} \end{aligned}$$

$$\begin{aligned} p_{\text{N}_2} &= x_{\text{N}_2} p_{\text{tot}} = \frac{5}{8} \times \frac{(4.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.4 \times 10^{-3} \text{ m}^3} \\ &= \boxed{2.5 \times 10^5 \text{ Pa}} \end{aligned}$$

Expressed in atmospheres these are 1.5 atm and 2.5 atm, respectively.

(iii) The total pressure is

$$\frac{(3.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.4 \times 10^{-3} \text{ m}^3} = \boxed{4.0 \times 10^5 \text{ Pa}}$$

or 4.0 atm.

Alternatively, note that 1 mol at STP occupies a volume of 22.4 dm³ which is the stated volume. As there are a total of 4.0 mol present the (total) pressure must therefore be 4.0 atm.

Solutions to problems

PIA.2 Perfect gas behaviour indicates that $pV \propto T$, where T is the absolute temperature. In terms of the temperature θ in °N, T is written $T = \theta + \theta_0$, where θ_0 is the absolute temperature of zero on the °N scale. The proportionality is made an equality by inserting a constant

$$pV = \alpha(\theta + \theta_0)$$

The two data points given are expressed as the following two equations:

$$28 = \alpha(0 + \theta_0) \quad 40 = \alpha(100 + \theta_0)$$

These are solved simultaneously to give $\theta_0 = 233 \text{ K}$. This means that 0 °N corresponds to an absolute temperature of 233 K. It follows that, on the °N scale, absolute zero is $\boxed{-233 \text{ °N}}$.

PIA.4 At absolute zero the volume will go to zero so the temperature corresponding to absolute zero θ_0 is found by solving

$$0 = V_0(1 + \alpha\theta_0) \quad \text{hence} \quad \theta_0 = -1/\alpha$$

The quantity α varies with pressure, and what is required is its value in the limit that the pressure goes to zero, because in this limit perfect gas behaviour is achieved. A plot of α against pressure, Fig. 1.1, reveals a gentle curve which fits well to a polynomial of order 2.

The equation of the fitted line is

$$(10^3 \alpha)/^\circ\text{C}^{-1} = 4.5000 \times 10^{-9} \times (p/\text{Torr})^2 + 7.5870 \times 10^{-6} \times (p/\text{Torr}) + 3.6635$$

The intercept at $p = 0$ gives the low pressure limit of α as $3.6635 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$, and hence

$$\theta_0 = -1/\alpha = -1/(3.6635 \times 10^{-3} \text{ }^\circ\text{C}^{-1}) = \boxed{-273.96 \text{ }^\circ\text{C}}$$

PIA.6 For a given setting of the pivot, the balance point is reached for a given density of gas, because it is the density which affects the buoyancy of the bulb. The density of the gas depends on its pressure and its molar mass: the greater the molar mass, the higher the density for a given pressure.

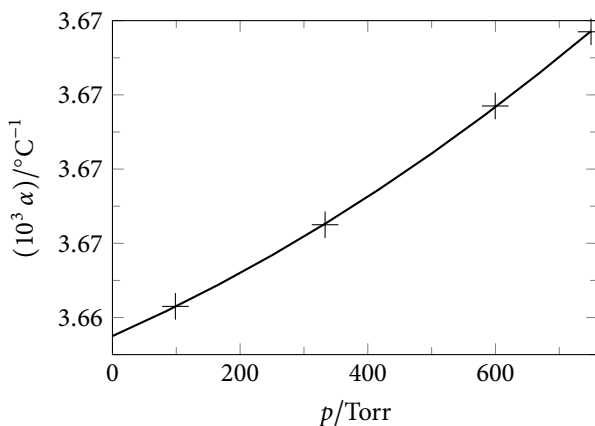


Figure 1.1

The exact relationship is derived for a perfect gas by starting with $pV = nRT$. The amount in moles is $n = m/M$, where M is the molar mass and m is the mass of the gas. It follows that $pV = (m/M)(RT)$ which rearranges to $pM = (m/V)(RT)$. The quantity m/V is the mass density ρ , and hence $pM = \rho RT$.

If the first gas has molar mass M_1 and balances the pivot at pressure p_1 , and likewise M_2 and p_2 for the second gas, then because the densities must be the same it follows that (at fixed temperature)

$$p_1 M_1 = p_2 M_2 \quad \text{hence} \quad M_1 = \frac{p_2 M_2}{p_1}$$

For the first experiment

$$M_1 = \frac{p_2 M_2}{p_1} = \frac{(423.22 \text{ Torr}) \times (70.014 \text{ g mol}^{-1})}{(327.10 \text{ Torr})} = 90.588 \text{ g mol}^{-1}$$

For the second experiment

$$M_1 = \frac{p_2 M_2}{p_1} = \frac{(427.22 \text{ Torr}) \times (70.014 \text{ g mol}^{-1})}{(293.22 \text{ Torr})} = 102.01 \text{ g mol}^{-1}$$

If the gases are behaving ideally, the two experiments should give the same molar mass – which evidently they do not. Because the lower pressure is closer to ideality, the second experiment is perhaps to be preferred, but high precision is not justified in quoting the result for the molar mass as 102 g mol^{-1} .

The compounds CH_2FCF_3 and CHF_2CHF_2 have molar masses close to this value.

PIA.8

The stoichiometric equation for the production of NH_3 is $3\text{H}_2 + \text{N}_2 \longrightarrow 2\text{NH}_3$. Conversion of all of the H_2 (2 moles) to ammonia results in the formation of $\frac{4}{3}$ mol of NH_3 and consumes $\frac{2}{3}$ mol of N_2 . After the reaction is complete

the amounts are therefore

$$n_{\text{H}_2} = 0 \quad n_{\text{N}_2} = 1 - \frac{2}{3} = \frac{1}{3} \text{ mol} \quad n_{\text{NH}_3} = \frac{4}{3} \text{ mol}$$

The total amount is $\frac{1}{3} + \frac{4}{3} = \frac{5}{3}$ mol, from which the total pressure is calculated using the perfect gas law

$$p = \frac{nRT}{V} = \frac{(\frac{5}{3} \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.4 \times 10^{-3} \text{ m}^3} = \boxed{1.69 \times 10^5 \text{ Pa}}$$

The partial pressures are calculated from the mole fractions and the total pressure

$$p_{\text{N}_2} = x_{\text{N}_2} p = \frac{n_{\text{N}_2}}{n_{\text{tot}}} p = \frac{1/3 \text{ mol}}{5/3 \text{ mol}} \times (1.69 \times 10^5 \text{ Pa}) = \boxed{0.338 \times 10^5 \text{ Pa}}$$

$$p_{\text{NH}_3} = x_{\text{NH}_3} p = \frac{n_{\text{NH}_3}}{n_{\text{tot}}} p = \frac{4/3 \text{ mol}}{5/3 \text{ mol}} \times (1.69 \times 10^5 \text{ Pa}) = \boxed{1.35 \times 10^5 \text{ Pa}}$$

P1A.10 It is useful to recall that at STP 1 mol occupies a volume of 22.414 dm^3 .

A concentration of 250 DU means that when all of the ozone in a column of cross-sectional area 1.00 dm^2 is compressed into a disc with the same cross-sectional area and at STP the thickness of the disc is $250/1000 \text{ cm}$. Expressed in dm, the thickness is therefore $2.50 \times 10^{-2} \text{ dm}$, and so the volume of the disc is (thickness \times area) $= (2.50 \times 10^{-2} \text{ dm}) \times (1.00 \text{ dm}^2) = 2.50 \times 10^{-2} \text{ dm}^3$. The amount in moles of ozone is therefore

$$n_{\text{O}_3} = \frac{2.50 \times 10^{-2} \text{ dm}^3}{22.414 \text{ dm}^3 \text{ mol}^{-1}} = 1.11 \times 10^{-3} \text{ mol} = \boxed{1.12 \times 10^{-3} \text{ mol}}$$

The amount in moles corresponding to 100 DU is found by using a ratio

$$n_{\text{O}_3, 100 \text{ DU}} = \frac{100}{250} \times n_{\text{O}_3, 250 \text{ DU}} = \frac{100}{250} \times (1.11 \times 10^{-3} \text{ mol}) = \boxed{4.46 \times 10^{-3} \text{ mol}}$$

The volume of a column of cross-sectional area 1.00 dm^2 and height $(50 - 10) = 40 \text{ km}$ is $(1.00 \times 10^{-2} \text{ m}^2) \times (40 \times 10^3 \text{ m}) = 400 \text{ m}^3$. If the amount in moles in this column is $1.11 \times 10^{-3} \text{ mol}$ (corresponding to 250 DU) the concentration is

$$c_{\text{O}_3} = \frac{1.11 \times 10^{-3} \text{ mol}}{400 \text{ m}^3} = 2.79 \times 10^{-6} \text{ mol m}^{-3}$$

or $\boxed{2.79 \times 10^{-9} \text{ mol dm}^{-3}}$. Using a ratio as before, the concentration corresponding to 100 DU is $(100/250) \times 2.79 \times 10^{-9} \text{ mol dm}^{-3} = \boxed{1.12 \times 10^{-9} \text{ mol dm}^{-3}}$.

P1A.12 (a) From the perfect gas law $pV = nRT$, the amount in moles is calculated using $n = pV/RT$; the volume of the balloon is $(4/3)\pi r^3$.

$$n = \frac{pV}{RT} = \frac{(1.01325 \times 10^5 \text{ Pa}) \times (\frac{4}{3}\pi [3.0 \text{ m}]^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ([25 + 273.15] \text{ K})}$$

$$= 4.62 \times 10^3 \text{ mol} = \boxed{4.6 \times 10^3 \text{ mol}}$$

(b) The mass of the volume of air displaced by the balloon is

$$\text{mass} = \text{volume} \times \text{density} = \left(\frac{4}{3}\pi[3.0\text{ m}]^3\right) \times (1.22\text{ kg m}^{-3}) = 1.37... \times 10^2\text{ kg}$$

The mass of the hydrogen in the balloon is

$$\begin{aligned}\text{mass} &= \text{amount in moles} \times \text{molar mass} \\ &= (4.62... \times 10^3\text{ mol}) \times (2 \times 1.0079 \times 10^{-3}\text{ kg mol}^{-1}) = 9.31... \text{ kg}\end{aligned}$$

The mass that can be lifted (the payload) is the difference between the displaced mass and the mass of the gas in the balloon (ignoring the mass of the material making up the balloon itself)

$$\text{payload} = (1.37... \times 10^2\text{ kg}) - (9.31... \text{ kg}) = \boxed{1.3 \times 10^2\text{ kg}}$$

(c) If the gas is helium, the mass of the gas in the balloon is

$$(4.62... \times 10^3\text{ mol}) \times (4.00 \times 10^{-3}\text{ kg mol}^{-1}) = 1.84... \times 10^1\text{ kg}$$

and the payload is

$$\text{payload} = (1.37... \times 10^2\text{ kg}) - (1.84... \times 10^1\text{ kg}) = \boxed{1.2 \times 10^2\text{ kg}}$$

PIA.14 To solve this problem it is necessary to assume that the *partial pressure* of each gas obeys a barometric formula in which the constant H depends on the identity of the gas

$$p_{\text{N}_2} = p_{0,\text{N}_2} \exp(-h/H_{\text{N}_2}) \quad H_{\text{N}_2} = \frac{RT}{M_{\text{N}_2}g}$$

and likewise for O_2 . The mole fractions of the two gases at sea level, and hence their partial pressures, are found from the mass composition at this level. Likewise, the mole fractions and partial pressures are found at the higher altitude from the stated mass composition.

Imagine 1000 g of atmosphere: at sea level this contains 800 g of N_2 and 200 g of O_2 . The mole fractions are

$$x_{\text{N}_2} = \frac{(800\text{ g})/(2 \times 14.01\text{ g mol}^{-1})}{(800\text{ g})/(2 \times 14.01\text{ g mol}^{-1}) + (200\text{ g})/(2 \times 16.00\text{ g mol}^{-1})} = 0.820$$

Hence $x_{\text{O}_2} = 1 - x_{\text{N}_2} = 0.180$.

At the higher altitude the same mass of atmosphere contains 900 g of N_2 and 100 g of O_2 . The mole fractions are

$$x'_{\text{N}_2} = \frac{(900\text{ g})/(2 \times 14.01\text{ g mol}^{-1})}{(900\text{ g})/(2 \times 14.01\text{ g mol}^{-1}) + (100\text{ g})/(2 \times 16.00\text{ g mol}^{-1})} = 0.911$$

Hence $x'_{\text{O}_2} = 1 - x'_{\text{N}_2} = 0.089$.

At altitude h the partial pressures of the two gases are

$$p_{\text{N}_2} = p_{0,\text{N}_2} \exp(-h/H_{\text{N}_2}) \quad p_{\text{O}_2} = p_{0,\text{O}_2} \exp(-h/H_{\text{O}_2})$$

Taking the ratio of these two equations gives

$$\frac{p_{\text{N}_2}}{p_{\text{O}_2}} = \frac{p_{0,\text{N}_2}}{p_{0,\text{O}_2}} \exp(-h/H_{\text{N}_2} + h/H_{\text{O}_2})$$

The ratio of the partial pressures is the same as the ratio of the mole fractions

$$\frac{x'_{\text{N}_2}}{x'_{\text{O}_2}} = \frac{x_{\text{N}_2}}{x_{\text{O}_2}} \exp(-h/H_{\text{N}_2} + h/H_{\text{O}_2})$$

where x_{N_2} is the mole fraction at $h = 0$. This equation is rearranged to find h

$$\begin{aligned} \frac{x'_{\text{N}_2} x_{\text{O}_2}}{x'_{\text{O}_2} x_{\text{N}_2}} &= \exp(-h/H_{\text{N}_2} + h/H_{\text{O}_2}) \\ \ln \left(\frac{x'_{\text{N}_2} x_{\text{O}_2}}{x'_{\text{O}_2} x_{\text{N}_2}} \right) &= -\frac{h}{H_{\text{N}_2}} + \frac{h}{H_{\text{O}_2}} \\ \ln \left(\frac{x'_{\text{N}_2} x_{\text{O}_2}}{x'_{\text{O}_2} x_{\text{N}_2}} \right) &= -\frac{hM_{\text{N}_2}g}{RT} + \frac{hM_{\text{O}_2}g}{RT} \\ \frac{RT}{g(M_{\text{O}_2} - M_{\text{N}_2})} \ln \left(\frac{x'_{\text{N}_2} x_{\text{O}_2}}{x'_{\text{O}_2} x_{\text{N}_2}} \right) &= h \end{aligned}$$

Inserting the data gives

$$\begin{aligned} h &= \frac{RT}{g(M_{\text{O}_2} - M_{\text{N}_2})} \ln \left(\frac{x'_{\text{N}_2} x_{\text{O}_2}}{x'_{\text{O}_2} x_{\text{N}_2}} \right) \\ &= \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})([25 + 273.15] \text{ K})}{(9.807 \text{ m s}^{-2}) \times [(2 \times 16.00 \times 10^{-3} \text{ kg mol}^{-1}) - (2 \times 14.01 \times 10^{-3} \text{ kg mol}^{-1})]} \\ &\quad \times \ln \left(\frac{0.911}{0.0890} \frac{0.180}{0.820} \right) \\ &= 51.4... \text{ km} = \boxed{51 \text{ km}} \end{aligned}$$

At this height the total pressure is found by summing the partial pressures at this height. The partial pressure at sea level is given by $p_{0,\text{N}_2} = x_{\text{N}_2}p_0$, so it follows that

$$p_{\text{N}_2} = x_{\text{N}_2}p_0 \exp(-h/H_{\text{N}_2}) \quad p_{\text{O}_2} = x_{\text{O}_2}p_0 \exp(-h/H_{\text{O}_2})$$

It is convenient to compute the scale heights H separately

$$\begin{aligned} H_{\text{N}_2} &= \frac{RT}{M_{\text{N}_2}g} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})([25 + 273.15] \text{ K})}{(2 \times 14.01 \times 10^{-3} \text{ kg mol}^{-1}) \times (9.807 \text{ m s}^{-2})} \\ &= 9.02... \times 10^3 \text{ m} \\ H_{\text{O}_2} &= \frac{RT}{M_{\text{O}_2}g} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})([25 + 273.15] \text{ K})}{(2 \times 16.00 \times 10^{-3} \text{ kg mol}^{-1}) \times (9.807 \text{ m s}^{-2})} \\ &= 7.90... \times 10^3 \text{ m} \end{aligned}$$

The total pressure at height h is therefore

$$\begin{aligned}
 p &= x_{\text{N}_2} p_0 \exp(-h/H_{\text{N}_2}) + x_{\text{O}_2} p_0 \exp(-h/H_{\text{O}_2}) \\
 &= (0.820 \times 1 \text{ atm}) \exp\left(-\frac{51.4... \times 10^3 \text{ m}}{9.02... \times 10^3 \text{ m}}\right) \\
 &\quad + (0.180 \times 1 \text{ atm}) \exp\left(-\frac{51.4... \times 10^3 \text{ m}}{7.90... \times 10^3 \text{ m}}\right) \\
 &= \boxed{0.0030 \text{ atm}}
 \end{aligned}$$

The calculation is incomplete as it assumes that composition is affected only by the mass and ignores the entropically driven mixing of gases. In fact, the composition of the atmosphere remains pretty much constant up to 100 km.

1B The kinetic model

Answer to discussion questions

D1B.2 The mean free path is given by [1B.14–18], $\lambda = kT/\sigma p$. In a container of constant volume, the mean free path is directly proportional to temperature and inversely proportional to pressure. The former dependence can be rationalized by noting that the faster the molecules travel, the farther on average they go between collisions. The latter also makes sense in that the lower the pressure, the less frequent are collisions, and therefore the further the average distance between collisions.

Perhaps more fundamental than either of these considerations is the dependence on the size of the container and on the size of the molecules. The ratio T/p is directly proportional to volume for a perfect gas, so the average distance between collisions is directly proportional to the size of the container holding a given number of gas molecules. Finally, the mean free path is inversely proportional to the size of the molecules as given by the collision cross section (and therefore inversely proportional to the square of the radius of the molecule).

Solutions to exercises

E1B.1(b) (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

$$\frac{v_{\text{mean,He}}}{v_{\text{mean,Hg}}} = \left(\frac{M_{\text{Hg}}}{M_{\text{He}}}\right)^{1/2} = \left(\frac{200.59 \text{ g mol}^{-1}}{4.00 \text{ g mol}^{-1}}\right)^{1/2} = \boxed{7.08}$$

(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 He 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(b) The rms speed is given by [1B.8–15], $v_{\text{rms}} = (3RT/M)^{1/2}$; $M_{\text{CO}_2} = 44.01 \text{ g mol}^{-1}$.

$$\begin{aligned} v_{\text{rms, CO}_2} &= \left(\frac{3RT}{M_{\text{CO}_2}} \right)^{1/2} = \left(\frac{3 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{44.01 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{1/2} \\ &= \boxed{408 \text{ m s}^{-1}} \end{aligned}$$

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

$$v_{\text{rms, He}} = \left(\frac{3 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{4.00 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{1/2} = \boxed{1.35 \text{ km s}^{-1}}$$

E1B.3(b) 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_{mid} is the mid-point of the velocity range: $v_{\text{mid}} = \frac{1}{2}(v_2 + v_1)$. In this exercise $v_{\text{mid}} = 402.5 \text{ m s}^{-1}$ and $\delta v = 5 \text{ m s}^{-1}$. $M_{\text{CO}_2} = 12.01 + 2 \times 16.00 = 44.01 \text{ g mol}^{-1}$.

$$\begin{aligned} \text{fraction} &= f(v_{\text{mid}}) \delta v = 4\pi \times \left(\frac{M}{2\pi RT} \right)^{3/2} v_{\text{mid}}^2 \exp\left(\frac{-Mv_{\text{mid}}^2}{2RT} \right) \delta v \\ &= 4\pi \times \left(\frac{44.01 \times 10^{-3} \text{ kg mol}^{-1}}{2\pi \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})} \right)^{3/2} \times (402.5 \text{ m s}^{-1})^2 \\ &\quad \times \exp\left(\frac{-(44.01 \times 10^{-3} \text{ kg mol}^{-1}) \times (402.5 \text{ m s}^{-1})^2}{2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})} \right) \times (5 \text{ m s}^{-1}) \\ &= \boxed{0.0107} \end{aligned}$$

where $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ has been used. Thus, 1.07% of molecules have velocities in this range.

E1B.4(b) 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_{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 N_2 and O_2 this effective mass is

$$N_A \mu = \frac{M_{\text{N}_2} M_{\text{O}_2}}{M_{\text{N}_2} + M_{\text{O}_2}} = \frac{(2 \times 14.01 \text{ g mol}^{-1}) \times (2 \times 16.00 \text{ g mol}^{-1})}{(2 \times 14.01 \text{ g mol}^{-1}) + (2 \times 16.00 \text{ g mol}^{-1})} = 14.9... \text{ g mol}^{-1}$$

$$v_{\text{rel}} = \left(\frac{8RT}{\pi N_A \mu} \right)^{1/2} = \left(\frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{\pi \times (14.9... \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} = \boxed{650 \text{ m s}^{-1}}$$

E1B.5(b) 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], $v_{\text{rel}} = \sqrt{2} v_{\text{mean}}$. $M_{\text{H}_2} = 2 \times 1.0079 = 2.0158 \text{ g mol}^{-1}$.

$$v_{\text{mp}} = \left(\frac{2RT}{M} \right)^{1/2} = \left(\frac{2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{2.0158 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{1/2} \\ = \boxed{1.56 \times 10^3 \text{ m s}^{-1}}$$

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M} \right)^{1/2} = \left(\frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293.15 \text{ K})}{\pi \times (2.0158 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ = \boxed{1.75 \times 10^3 \text{ m s}^{-1}}$$

$$v_{\text{rel}} = \sqrt{2} v_{\text{mean}} = \sqrt{2} \times (1.75 \times 10^3 \text{ m s}^{-1}) = \boxed{2.48 \times 10^3 \text{ m s}^{-1}}$$

E1B.6(b) 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 *Re-source section* the collision cross-section σ is 0.40 nm^2 .

$$z = \frac{\sigma v_{\text{rel}} p}{kT} = \frac{\sigma p}{kT} \times \sqrt{2} \times \left(\frac{8RT}{\pi M} \right)^{1/2} \\ = \frac{(0.40 \times 10^{-18} \text{ m}^2) \times (1.01325 \times 10^5 \text{ Pa})}{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})} \times \sqrt{2} \\ \times \left(\frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{\pi \times (2 \times 16.00 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ = \boxed{6.2 \times 10^9 \text{ s}^{-1}}$$

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. Note the conversion of the collision cross-section σ to m^2 : $1 \text{ nm}^2 = (1 \times 10^{-9})^2 \text{ m}^2 = 1 \times 10^{-18} \text{ m}^2$.

- E1B.7(b)** From inside the front cover 760 Torr is equivalent to 1 atm, which is 1.01325×10^5 Pa. Therefore a pressure of 1 nTorr is expressed in Pa as

$$1 \text{ nTorr} = (1 \times 10^{-9} \text{ Torr}) \times \frac{1 \text{ atm}}{760 \text{ Torr}} \times \frac{1.01325 \times 10^5 \text{ Pa}}{1 \text{ atm}} = 1.33... \times 10^{-7} \text{ Pa}$$

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 σ 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

$$\lambda = \frac{kT}{\sigma p} = \frac{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}{(4.90... \times 10^{-19} \text{ m}^2) \times (1.33... \times 10^{-7} \text{ Pa})} = \boxed{6.30 \times 10^4 \text{ m}}$$

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 mean free path is 63 km, a distance very much greater than the dimensions of the apparatus.

- (iii) The collision rate is calculated as

$$\begin{aligned} z &= \frac{\sigma v_{\text{rel}} p}{kT} = \frac{\sigma p}{kT} \times \sqrt{2} \times \left(\frac{8RT}{\pi M} \right)^{1/2} \\ &= \frac{(4.90 \times 10^{-19} \text{ m}^2) \times (1.33... \times 10^{-7} \text{ Pa})}{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})} \times \sqrt{2} \\ &\quad \times \left(\frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{\pi \times (2 \times 14.01 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \\ &= \boxed{1.07 \times 10^{-2} \text{ s}^{-1}} \end{aligned}$$

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

$$z = \frac{v_{\text{rel}}}{\lambda} = \frac{\sqrt{2} v_{\text{mean}}}{\lambda} = \frac{\sqrt{2} \times (475 \text{ m s}^{-1})}{6.30 \times 10^4 \text{ m}} = \boxed{1.07 \times 10^{-2} \text{ s}^{-1}}$$

As expected for such a low pressure, collisions are very infrequent, occurring about once every 100 s.

E1B.8(b) The collision cross section σ is written in terms of a diameter as $\sigma = \pi d^2$, hence $d = \sqrt{\sigma/\pi}$

$$d = \sqrt{\sigma/\pi} = \sqrt{(0.36 \times 10^{-18} \text{ m}^2)/\pi} = 3.38... \times 10^{-10} \text{ m}$$

The mean free path is given by [1B.14–18], $\lambda = kT/\sigma p$. This is rearranged to give the pressure p with λ equal to 10 times the estimate for the diameter of the atoms

$$p = \frac{kT}{\sigma(10d)} = \frac{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}{(0.36 \times 10^{-18} \text{ m}^2) \times 10 \times (3.38... \times 10^{-10} \text{ m})} = \boxed{3.4 \times 10^6 \text{ Pa}}$$

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

$$\lambda = \frac{kT}{\sigma p} = \frac{(1.3806 \times 10^{-23} \text{ J K}^{-1}) \times (217 \text{ K})}{(0.43 \times 10^{-18} \text{ m}^2) \times (12.1 \times 10^3 \text{ Pa})} = \boxed{5.8 \times 10^{-7} \text{ m} = 0.58 \text{ }\mu\text{m}}$$

Solutions to problems

P1B.2 The Maxwell–Boltzmann distribution of speeds in one dimension (here x) is given by [1B.3–13]

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

An analogous expression gives the distribution in the y direction, $f(v_y)$. The probability of finding a particle with velocity between v_x and $v_x + dv_x$ is given by $f(v_x) dv_x$, and similarly in the y direction. The overall probability of finding a particle with velocity between v_x and $v_x + dv_x$, and between v_y and $v_y + dv_y$, is therefore

$$\begin{aligned} & \left[\left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/2kT} \right] \left[\left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_y^2/2kT} \right] dv_x dv_y \\ &= \left(\frac{m}{2\pi kT} \right) e^{-m(v_x^2 + v_y^2)/2kT} dv_x dv_y \\ &= \underbrace{\left(\frac{m}{2\pi kT} \right) e^{-mv^2/2kT}}_A dv_x dv_y \end{aligned}$$

On the last line the speed v , given by $v^2 = v_x^2 + v_y^2$, is introduced.

As discussed in Section 1B.1(b) on page 13, the ‘area element’ $dv_x dv_y$ can be interpreted by imagining a velocity space with axes labelled (v_x, v_y) . In this space, particles with speed v lie on a circle of radius v , so particles with speeds between v and $v + dv$ lie in a ring of radius v and thickness dv . Because the ring is very thin, its area is given by the circumference of the circle times the width: $2\pi v dv$.

The *total* probability of a particle having speed v and $v + dv$, $f(v)dv$, is therefore found by multiplying the term A in the above expression, not by the area element $dv_x dv_y$ but by the area of the ring because this gives the total probability

of having this range of speeds, regardless of direction

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

The distribution of speeds in two dimension is therefore

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

The average speed is found using [1B.6–15], $\langle v^n \rangle = \int_0^\infty v^n f(v) dv$. In this case

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

The required integral is of the form of G.3 from the *Resource section*

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4} \left(\frac{\pi}{a^3} \right)^{1/2}$$

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

$$\langle v \rangle = \frac{1}{4} \left(\frac{m}{kT} \right) \left(\frac{\pi}{(m/2kT)^3} \right)^{1/2} = \left(\frac{\pi kT}{2m} \right)^{1/2}$$

P1B.4

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 root mean square speed is given by [1B.8–15], $v_{\text{rms}} = (3RT/M)^{1/2}$, and mean speed is given by [1B.9–16], $v_{\text{mean}} = (8RT/\pi M)^{1/2}$. The required proportions are found by integrating $f(v)$ between the relevant limits for v .

(a) The fraction having speed greater than v_{rms} is given by

$$\int_{v_{\text{rms}}}^\infty f(v) dv$$

Mathematical software is used to evaluate the integral to give $\sqrt{6/\pi} e^{3/2} + \text{erfc}(\sqrt{3/2})$, where $\text{erfc}(x)$ is the complementary error function, $\text{erfc}(x) = 1 - \text{erf}(x)$. The result is evaluated numerically to give 0.391, that is 39% of molecules have speeds greater than the root mean square speed.

(b) The remaining fraction, $1 - 0.391 = 0.608$, have speeds smaller than v_{rms} . Thus 61% of molecules have speeds smaller than the root mean square speed.

(c) The integral is as in (a), but with lower limit v_{mean} . Mathematical software gives the result $4/\pi e^{-4/\pi} + \text{erfc}(2/\sqrt{\pi})$. The result is evaluated numerically to give 0.467, that is 47% of molecules have speeds greater than the mean speed, and so 53% of molecules have speeds smaller than the mean speed.

PIB.6 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 mean of v^n is found using [1B.6–15], $\langle v^n \rangle = \int_0^\infty v^n f(v) dv$. The required integral is therefore

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

For the case where $n + 2$ is odd, integral G.7 from the *Resource section* is used

$$\int_0^\infty x^{2m+1} e^{-ax^2} dx = \frac{m!}{2a^{m+1}} \quad m = 1, 2, 3, \dots$$

The relationship between m and n is found by noting that for $n = 1, 3, 5, \dots$, m will be $1, 2, 3, \dots$ (note that these generate only the odd values of $n + 2$). It therefore follows that $m = \frac{1}{2}(n + 1)$ and $m + 1 = \frac{1}{2}(n + 3)$. These substitutions, along with $a = M/2RT$ allow the integral to be evaluated.

$$\begin{aligned} \langle v^n \rangle &= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_0^\infty v^{n+2} e^{-Mv^2/2RT} dv \\ &= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \frac{1}{2} \frac{[\frac{1}{2}(n + 1)]!}{(M/2RT)^{\frac{1}{2}(n+3)}} \\ &= 2\pi \left(\frac{1}{\pi} \right)^{3/2} \left(\frac{M}{2RT} \right)^{3/2} \left(\frac{M}{2RT} \right)^{-\frac{1}{2}(n+3)} [\frac{1}{2}(n + 1)]! \\ &= 2 \left(\frac{1}{\pi} \right)^{1/2} \left(\frac{2RT}{M} \right)^{\frac{1}{2}n} [\frac{1}{2}(n + 1)]! \quad \text{odd } n \end{aligned}$$

Hence

$$\boxed{\langle v^n \rangle^{1/n} = \frac{2^{1/n}}{\pi^{1/2n}} \left(\frac{2RT}{M} \right)^{\frac{1}{2}} ([\frac{1}{2}(n + 1)]!)^{1/n} \quad \text{odd } n}$$

For the case where $n + 2$ is even, integral G.8 from the *Resource section* is used

$$\int_0^\infty x^{2m} e^{-ax^2} dx = \frac{(2m - 1)!!}{2^{m+1} a^m} \left(\frac{\pi}{a} \right)^{1/2} \quad m = 1, 2, 3, \dots$$

where $(2m - 1)!! = (2m - 1) \times (2m - 3) \times (2m - 5) \times \dots \times 1$ or 2 .

The relationship between m and n is found by noting that for $n = 2, 4, 6, \dots$, m will be $1, 2, 3, \dots$ (note that these generate only the even values of $n + 2$). It therefore follows that $m = \frac{1}{2}(n + 2)$, $m + 1 = \frac{1}{2}(n + 4)$ and $(2m - 1) = (n + 1)$.

These substitutions, along with $a = M/2RT$ allow the integral to be evaluated.

$$\begin{aligned}
 \langle v^n \rangle &= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_0^\infty v^{n+2} e^{-Mv^2/2RT} dv \\
 &= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \frac{(2m-1)!!}{2^{m+1} a^m} \left(\frac{\pi}{a} \right)^{1/2} \\
 &= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \frac{(n+1)!!}{2^{\frac{1}{2}(n+4)} (M/2RT)^{\frac{1}{2}(n+2)}} \left(\frac{\pi}{(M/2RT)} \right)^{1/2} \\
 &= \left(\frac{1}{2} \right)^{n/2} \left(\frac{M}{2RT} \right)^{3/2} \left(\frac{M}{2RT} \right)^{-\frac{1}{2}(n+2)} \left(\frac{M}{2RT} \right)^{-1/2} (n+1)!! \\
 &= \left(\frac{1}{2} \right)^{n/2} \left(\frac{2RT}{M} \right)^{n/2} (n+1)!! \\
 &= \left(\frac{RT}{M} \right)^{n/2} (n+1)!! \quad \text{even } n
 \end{aligned}$$

Hence

$$\langle v^n \rangle^{1/n} = \left(\frac{RT}{M} \right)^{1/2} [(n+1)!!]^{1/n} \quad \text{even } n$$

Mathematical software gives a solution for both even and odd n

$$\begin{aligned}
 \langle v^n \rangle &= \int_0^\infty v^n f(v) dv = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_0^\infty v^{n+2} e^{-Mv^2/2RT} dv \\
 &= \frac{1}{\sqrt{\pi}} 2^{(n+2)/2} \left(\frac{RT}{M} \right)^{n/2} \Gamma\left(\frac{1}{2}[n+3]\right)
 \end{aligned}$$

where $\Gamma(x)$ is the Euler gamma function.

If the argument x is an integer then $\Gamma(x) = (x-1)!$. This will be the case for odd n , in which case

$$\langle v^n \rangle = \frac{1}{\sqrt{\pi}} 2^{(n+2)/2} \left(\frac{RT}{M} \right)^{n/2} \left(\frac{1}{2}[n+1] \right)! \quad \text{odd } n$$

which is the same result as found above.

If the argument of the Gamma function is an odd multiple of $\frac{1}{2}$ (that is $\frac{1}{2}m$, with $m = 1, 3, 5, \dots$) then

$$\Gamma\left(\frac{1}{2}m\right) = \frac{(m-2)!!\sqrt{\pi}}{2^{(m-1)/2}}$$

This will be the case for even n , in which case

$$\begin{aligned}
 \langle v^n \rangle &= \frac{1}{\sqrt{\pi}} 2^{(n+2)/2} \left(\frac{RT}{M} \right)^{n/2} \frac{(n+3-2)!!\sqrt{\pi}}{2^{(n+3-1)/2}} \\
 &= \frac{1}{\sqrt{\pi}} 2^{(n+2)/2} \left(\frac{RT}{M} \right)^{n/2} \frac{(n+1)!!\sqrt{\pi}}{2^{(n+2)/2}} \\
 &= \left(\frac{RT}{M} \right)^{n/2} (n+1)!! \quad \text{even } n
 \end{aligned}$$

which again is the same result as above.

PIB.8 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, here taken to be 0.1 kg mol^{-1} . Plots of $f(v)$ are shown in Fig. 1.2.

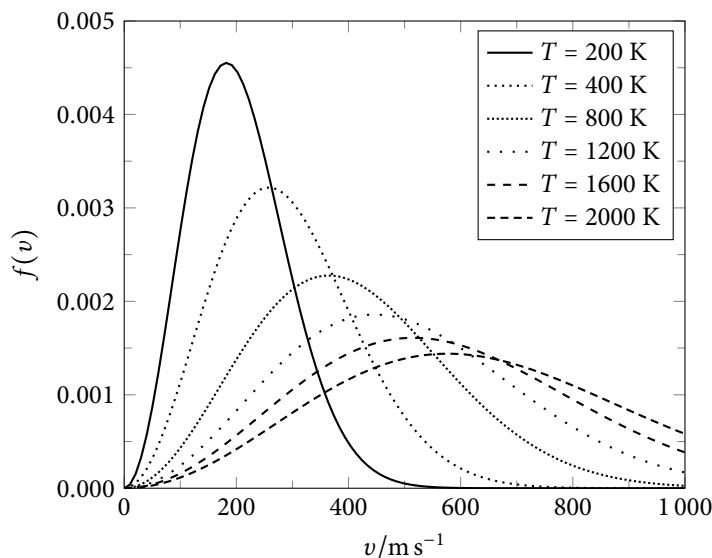


Figure 1.2

PIB.10 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 speed at which this function is a maximum is found by setting the derivative $df(v)/dv$ equal to zero. The derivative is found using the product rule and the chain rule

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

The derivative is set to zero and factors of $e^{-Mv^2/2RT}$ and v are identified to give

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

The solution when $v = 0$ is not a maximum, and the solution $e^{-Mv^2/2RT} = 0$ corresponds to the asymptotic behavior at large speeds. This leaves the maximum

to be given by

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

That this is a maximum can be verified by inspecting a plot of $f(v)$.

1C Real gases

Answer to discussion questions

- DIC.2** The critical constants represent the state of a system at which the distinction between the liquid and vapour phases disappears. This situation is usually described by saying that above the critical temperature the liquid phase cannot be produced by the application of pressure alone. The liquid and vapour phases can no longer coexist, though supercritical fluids have both liquid and vapour characteristics.
- DIC.4** The van der Waals equation is a cubic equation in the volume V . Every cubic equation has some values of the coefficients for which the number of real roots passes from three to one. In fact, any equation of state of odd degree $n > 1$ can in principle account for critical behavior because for equations of odd degree in V there are necessarily some values of temperature and pressure for which the number of real roots of V passes from n to 1. That is, the multiple values of V converge from n to 1 as the temperature approaches the critical temperature. This mathematical result is consistent with passing from a two phase region (more than one volume for a given T and p) to a one phase region (only one V for a given T and p), and this corresponds to the observed experimental result as the critical point is reached.

Solutions to exercises

- E1C.1(b)** 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 H_2S are given in the *Resource section* as $a = 4.484 \text{ atm dm}^6 \text{ mol}^{-2}$ and $b = 4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$. With these units it is convenient to use $R = 8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$. The pressure is computed by substituting in the relevant data.

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

$$\begin{aligned} p &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{(1.0 \text{ mol}) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{(22.414 \text{ dm}^3) - (1.0 \text{ mol}) \times (4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} \\ &\quad - \frac{(4.484 \text{ atm dm}^6 \text{ mol}^{-2}) \times (1.0 \text{ mol})^2}{(22.414 \text{ dm}^3)^2} = \boxed{0.99 \text{ atm}} \end{aligned}$$

(ii) $T = 500 \text{ K}$, $V = 150 \text{ cm}^3 = 0.150 \text{ dm}^3$, $n = 1.0 \text{ mol}$

$$\begin{aligned}
 p &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\
 &= \frac{(1.0 \text{ mol}) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}{(0.150 \text{ dm}^3) - (1.0 \text{ mol}) \times (4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} \\
 &\quad - \frac{(4.484 \text{ atm dm}^6 \text{ mol}^{-2}) \times (1.0 \text{ mol})^2}{(0.150 \text{ dm}^3)^2} = \boxed{1.9 \times 10^2 \text{ atm}}
 \end{aligned}$$

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

$$\begin{aligned}
 a &= (1.32 \text{ atm dm}^6 \text{ mol}^{-2}) \times \frac{1.01325 \times 10^5 \text{ Pa}}{1 \text{ atm}} \times \frac{10^{-6} \text{ m}^6}{1 \text{ dm}^6} = 0.134 \text{ Pa m}^6 \text{ mol}^{-2} \\
 &= 0.134 \text{ kg m}^{-1} \text{ s}^{-2} \text{ m}^6 \text{ mol}^{-2} = \boxed{0.134 \text{ kg m}^5 \text{ s}^{-2} \text{ mol}^{-2}}
 \end{aligned}$$

$$b = (0.0436 \text{ dm}^3 \text{ mol}^{-1}) \times \frac{10^{-3} \text{ m}^3}{1 \text{ dm}^3} = \boxed{4.36 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

E1C.3(b) The compression factor Z is defined in [1C.1–20] as $Z = V_m/V_m^\circ$, where V_m° 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% larger than the molar volume of a perfect gas, it follows that $V_m = V_m^\circ(1 + 0.12) = 1.12V_m^\circ$. The compression factor is then computed directly as

$$Z = \frac{V_m}{V_m^\circ} = \frac{1.12 \times V_m^\circ}{V_m^\circ} = \boxed{1.12}$$

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

$$\begin{aligned}
 V_m &= \frac{ZRT}{p} = \frac{1.12 \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (350 \text{ K})}{12 \text{ atm}} \\
 &= \boxed{2.7 \text{ dm}^3 \text{ mol}^{-1}}
 \end{aligned}$$

Because $Z > 1$, implying that $V_m > V_m^\circ$, repulsive forces are dominant.

E1C.4(b) (i) The molar volume is computed from the equation of state for a perfect gas, [1A.4–8], as $V_m = RT/p$

$$V_m = \frac{RT}{p} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times ([25 + 273.15] \text{ K})}{200 \times 10^5 \text{ Pa}} = 1.24 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

hence $\boxed{V_m = 0.124 \text{ dm}^3 \text{ mol}^{-1}}$.

- (ii) 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

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

The values of the constants are given, as is the pressure and temperature. Given the units of the quoted values of a and b it is convenient to convert the pressure of 200 bar (200×10^5 Pa) to atm, $p = (200 \times 10^5 \text{ Pa}) \times (1 \text{ atm})/(1.01325 \times 10^5 \text{ Pa}) = 197.4 \text{ atm}$, and to use $R = 8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$. Inserting all of these values gives the polynomial

$$197.4V_m^3 - 30.762V_m^2 + 1.364V_m - 0.04351 = 0$$

The roots of this polynomial are found numerically using Mathematical software and of these roots only $V_m = 0.112 \text{ dm}^3 \text{ mol}^{-1}$ is a physically plausible value for the molar volume (the other roots are complex). This molar volume is smaller than the molar volume of the corresponding perfect gas by about 10%.

An alternative approach is to approximate the term a/V_m^2 as $a/(V_m^\circ)^2$ and then rearrange the van der Waals equation to give a simpler expression for V_m

$$p = \frac{RT}{(V_m - b)} - \frac{a}{(V_m^\circ)^2} \quad \text{hence} \quad V_m = \frac{RT}{p + [a/(V_m^\circ)^2]} + b$$

$$\begin{aligned} V_m &= \frac{RT}{p + [a/(V_m^\circ)^2]} + b \\ &= \frac{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{(197.4 \text{ atm}) + [(1.364 \text{ atm dm}^6 \text{ mol}^{-2})/(0.124 \text{ dm}^3 \text{ mol}^{-1})^2]} \\ &\quad + 3.19 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} = 0.117 \text{ dm}^3 \text{ mol}^{-1} \end{aligned}$$

This approximate value for V_m is then used in place of V_m° and the whole process repeated. After a few iterations the value of V_m settles as $0.112 \text{ dm}^3 \text{ mol}^{-1}$, which is the same as the value found by solving the cubic.

- E1C.5(b)** (i) The compression factor Z is given in terms of the molar volume and pressure by [1C.2-20], $Z = pV_m/RT$, hence $V_m = ZRT/p$. The volume occupied by n mol is therefore $V = nV_m = nZRT/p$

$$\begin{aligned} V &= \frac{nZRT}{p} \\ &= \frac{(8.2 \times 10^{-3} \text{ mol}) \times (0.86) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{20 \text{ atm}} \\ &= \boxed{8.7 \times 10^{-3} \text{ dm}^3} = \boxed{8.7 \text{ cm}^3} \end{aligned}$$

- (ii) The virial expansion in terms of V_m is given by [1C.3b–2I], $pV_m = RT(1 + B/V_m + \dots)$. The relationship in [1C.2–20], $Z = pV_m/RT$, is used to rewrite the term pV_m as ZRT . If only the first two terms of the expansion are retained it follows that

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

and therefore $B = V_m(Z - 1)$. The relationship $V_m = ZRT/p$ is used to give

$$\begin{aligned} B &= V_m(Z - 1) = \frac{ZRT}{p}(Z - 1) \\ &= \frac{(0.86) \times (8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{20 \text{ atm}} \times (0.86 - 1) \\ &= \boxed{-0.15 \text{ dm}^3 \text{ mol}^{-1}} \end{aligned}$$

- E1C.6(b)** 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 dm^3 .

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

$$\begin{aligned} V_c &= 3b \quad \text{hence} \quad b = V_c/3 = (0.148 \text{ dm}^3 \text{ mol}^{-1})/3 = 0.0493 \text{ dm}^3 \text{ mol}^{-1} \\ p_c &= \frac{a}{27b^2} = \frac{a}{27(V_c/3)^2} \quad \text{hence} \quad a = 27(V_c/3)^2 p_c \\ a &= 27(V_c/3)^2 p_c = 27([0.148 \text{ dm}^3 \text{ mol}^{-1}]/3)^2 \times (48.2 \text{ atm}) \\ &= 3.17 \text{ atm dm}^6 \text{ mol}^{-2} \end{aligned}$$

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 3.17, 5.50, and 4.17, giving an average of $\boxed{4.28 \text{ atm dm}^6 \text{ mol}^{-2}}$. For b the values are 0.0493, 0.0650, and 0.0493, giving an average of $\boxed{0.0546 \text{ dm}^3 \text{ mol}^{-1}}$.

In Section 1C.2(a) on page 23 it is argued that $b = 4V_{\text{molec}}N_A$, where V_{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 $r = (3b/16\pi N_A)^{1/3}$.

$$r = \left(\frac{3b}{16\pi N_A} \right)^{1/3} = \left(\frac{3 \times (0.0546 \text{ dm}^3 \text{ mol}^{-1})}{16\pi \times (6.0221 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 1.76 \times 10^{-9} \text{ dm} = \boxed{176 \text{ pm}}$$

- E1C.7(b)** (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 are the expressions for the product pV_m in each case ([1C.5b–24] and [1C.3b–21])

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

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

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

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

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*

$$\begin{aligned} T_b &= \frac{a}{Rb} = \frac{4.484 \text{ atm dm}^6 \text{ mol}^{-2}}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} \\ &= \boxed{1.26 \times 10^3 \text{ K}} \end{aligned}$$

- (ii) In Section 1C.2(a) on page 23 it is argued that $b = 4V_{\text{molec}}N_A$, where V_{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 $r = (3b/16\pi N_A)^{1/3}$.

$$\begin{aligned} r &= \left(\frac{3b}{16\pi N_A} \right)^{1/3} = \left(\frac{3 \times (4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})}{16\pi \times (6.0221 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} \\ &= 1.63 \times 10^{-9} \text{ dm} = \boxed{163 \text{ pm}} \end{aligned}$$

- E1C.8(b)** The reduced variables are defined in terms of the critical constants in [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 N_2 $p_c = 33.54$ atm, $T_c = 126.3$ K, and for H_2O $p_c = 218.3$ atm, $T_c = 647.4$ K. Taking gas (1) as N_2 and gas (2) as H_2O , the pressure and temperature of H_2O corresponding to $p^{(\text{N}_2)} = 1.0$ atm and $T^{(\text{N}_2)} = 298.15$ K is calculated as

$$p^{(\text{H}_2\text{O})} = \frac{p^{(\text{N}_2)}}{p_c^{(\text{N}_2)}} \times p_c^{(\text{H}_2\text{O})} = \frac{1.0 \text{ atm}}{33.54 \text{ atm}} \times (218.3 \text{ atm}) = \boxed{6.5 \text{ atm}}$$

$$T^{(\text{H}_2\text{O})} = \frac{T^{(\text{N}_2)}}{T_c^{(\text{N}_2)}} \times T_c^{(\text{H}_2\text{O})} = \frac{298.15 \text{ K}}{126.3 \text{ K}} \times (647.4 \text{ K}) = \boxed{1.5 \times 10^3 \text{ K}}$$

- (ii) For CO_2 $p_c = 72.9$ atm, $T_c = 304.2$ K.

$$p^{(\text{CO}_2)} = \frac{p^{(\text{N}_2)}}{p_c^{(\text{N}_2)}} \times p_c^{(\text{CO}_2)} = \frac{1.0 \text{ atm}}{33.54 \text{ atm}} \times (72.9 \text{ atm}) = \boxed{2.2 \text{ atm}}$$

$$T^{(\text{CO}_2)} = \frac{T^{(\text{N}_2)}}{T_c^{(\text{N}_2)}} \times T_c^{(\text{CO}_2)} = \frac{298.15 \text{ K}}{126.3 \text{ K}} \times (304.2 \text{ K}) = \boxed{7.2 \times 10^2 \text{ K}}$$

- (iii) For Ar $p_c = 48.0$ atm, $T_c = 150.7$ K.

$$p^{(\text{Ar})} = \frac{p^{(\text{N}_2)}}{p_c^{(\text{N}_2)}} \times p_c^{(\text{Ar})} = \frac{1.0 \text{ atm}}{33.54 \text{ atm}} \times (48.0 \text{ atm}) = \boxed{1.4 \text{ atm}}$$

$$T^{(\text{Ar})} = \frac{T^{(\text{N}_2)}}{T_c^{(\text{N}_2)}} \times T_c^{(\text{Ar})} = \frac{298.15 \text{ K}}{126.3 \text{ K}} \times (150.7 \text{ K}) = \boxed{3.6 \times 10^2 \text{ K}}$$

E1C.9(b) 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

$$\begin{aligned} p &= \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{hence} \quad p + \frac{a}{V_m^2} = \frac{RT}{V_m - b} \\ \text{hence} \quad \frac{pV_m^2 + a}{V_m^2} &= \frac{RT}{V_m - b} \quad \text{hence} \quad \frac{V_m^2}{pV_m^2 + a} = \frac{V_m - b}{RT} \\ \text{hence} \quad b &= V_m - \frac{RTV_m^2}{pV_m^2 + a} \end{aligned}$$

With the data given

$$b = V_m - \frac{RTV_m^2}{pV_m^2 + a} = (4.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}) - \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (288 \text{ K}) \times (4.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})^2}{(4.0 \times 10^6 \text{ Pa}) \times (4.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})^2 + (0.76 \text{ m}^6 \text{ Pa mol}^{-2})}$$

$$= \boxed{1.3 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}$$

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° 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

$$Z = \frac{pV_m}{RT} = \frac{(4.0 \times 10^6 \text{ Pa}) \times (4.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (288 \text{ K})} = \boxed{0.67}$$

Solutions to problems

P1C.2 (a) Using the perfect gas law, $pV = nRT$, the molar volume is calculate as

$$V_m = \frac{RT}{p} = \frac{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (350 \text{ K})}{2.30 \text{ atm}} = \boxed{12.5 \text{ dm}^3 \text{ mol}^{-1}}$$

(b) The van der Waals equation of state in terms of the molar volume is given by [1C.5b–24], $p = RT/(V_m - b) - a/V_m^2$; the term a/V_m^2 is due to attractive interactions.

This equation is a cubic in V_m which can be solved numerically. A simpler approach is to approximate a/V_m^2 as $a/(V_m^\circ)^2$, where V_m° is the molar volume of a perfect gas under the prevailing conditions. The van der Waals equation is then rearranged to give a simpler expression for V_m

$$p = \frac{RT}{(V_m - b)} - \frac{a}{(V_m^\circ)^2} \quad \text{hence} \quad V_m = \frac{RT}{p + [a/(V_m^\circ)^2]} + b$$

The van der Waals constants for Cl_2 are $a = 6.260 \text{ atm dm}^6 \text{ mol}^{-2}$ and $b = 5.42 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$. With these values, the first approximation to the molar volume is calculated as

$$V_m = \frac{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (350 \text{ K})}{(2.30 \text{ atm}) + [(6.260 \text{ atm dm}^6 \text{ mol}^{-2})/(12.5 \text{ dm}^3 \text{ mol}^{-1})^2]} + 5.42 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} = 12.3 \text{ dm}^3 \text{ mol}^{-1}$$

This approximate value for V_m is then used in place of V_m° and the process repeated, to give $V_m = 12.3 \text{ dm}^3 \text{ mol}^{-1}$ – the same value. The process has converged (to this level of precision).

PIC.4 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

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

Division of the numerator and denominator of the first fraction by V_m , and then taking a factor of RT on the right gives the required expression

$$pV_m = RT \left(\frac{1}{(1 - b/V_m)} - \frac{a}{RTV_m} \right) \quad (1.1)$$

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

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

The virial equation in terms of the molar volume is given by [1C.3b-21]

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

Comparison of this equation with eqn 1.1 shows that $B = b - a/RT$, as required.

The value of the second virial coefficient at the critical temperature of 126.3 K is found from the given van der Waals parameters as

$$\begin{aligned} B &= b - \frac{a}{RT} \\ &= (0.0391 \text{ dm}^3 \text{ mol}^{-1}) - \frac{1.390 \text{ atm dm}^6 \text{ mol}^{-2}}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (126.3 \text{ K})} \\ &= -0.0950... \text{ dm}^3 \text{ mol}^{-1} \end{aligned}$$

With this value for B , the molar volume is computed using the virial equation and with the approximation that the molar volume or the right-hand side of the expression can be replaced by the molar volume of a perfect gas, V_m° , under the same conditions

$$\begin{aligned} V_m &= \frac{RT}{p} \left(1 + \frac{B}{V_m} \right) \approx \frac{RT}{p} \left(1 + \frac{B}{V_m^\circ} \right) = \frac{RT}{p} \left(1 + \frac{B}{RT/p} \right) \\ \text{hence } V_m &= \frac{RT}{p} + B \\ &= \frac{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (126.3 \text{ K})}{10 \text{ atm}} - 0.0950... \text{ dm}^3 \text{ mol}^{-1} \\ &= 0.941... = \boxed{0.94 \text{ dm}^3 \text{ mol}^{-1}} \end{aligned}$$

Repeating the calculation at the Boyle temperature, 327.2 K, gives $B = -0.0126... \text{ dm}^3 \text{ mol}^{-1}$ and $V_m = 2.67... \text{ dm}^3 \text{ mol}^{-1}$ hence $\boxed{V_m = 2.7 \text{ dm}^3 \text{ mol}^{-1}}$.

How close a gas under particular conditions is to perfect behaviour is assessed by computing the compression factor Z , given by [1C.2–20], $Z = pV_m/RT$. At 126.3 K

$$Z = \frac{pV_m}{RT} = \frac{(10 \text{ atm}) \times (0.941... \text{ dm}^3 \text{ mol}^{-1})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (126.3 \text{ K})} = 0.91$$

and at 327.2 K

$$Z = \frac{pV_m}{RT} = \frac{(10 \text{ atm}) \times (2.67... \text{ dm}^3 \text{ mol}^{-1})}{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (327.2 \text{ K})} = 1.00$$

The latter conditions give $Z = 1$, as expected at the Boyle temperature, whereas in the former case Z differs significantly from 1. The gas is closer to perfect behaviour at the Boyle temperature than at the critical temperature.

P1C.6 The molar volume for a perfect gas is computed from $V_m = RT/p$

$$V_m = \frac{RT}{p} = \frac{(8.2057 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})}{3 \text{ atm}} = 10.941 \text{ dm}^3 \text{ mol}^{-1}$$

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

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

Inserting the values of the van der Waals constants, $a = 1.337 \text{ atm dm}^6 \text{ mol}^{-2}$ and $b = 3.20 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$, and the stated temperature and pressure gives the polynomial

$$3V^3 - 32.919V_m^2 + 1.337V_m - 0.042784 = 0$$

The roots of this polynomial are found numerically using mathematical software and of these roots only $V_m = 10.932 \text{ dm}^3 \text{ mol}^{-1}$ is a physically plausible value for the molar volume.

The difference between the molar volume and that of a perfect gas is expressed in terms of the fraction

$$\frac{V_m - V_m^\circ}{V_m^\circ} = \frac{(10.932 \text{ dm}^3 \text{ mol}^{-1}) - (10.941 \text{ dm}^3 \text{ mol}^{-1})}{10.941 \text{ dm}^3 \text{ mol}^{-1}} = -8.2 \times 10^{-4}$$

The difference between the molar volumes is therefore $\boxed{-0.082\%}$ of the molar volume of the perfect gas.

P1C.8 According to Table 1C.4 on page 25, for the Berthelot equation of state the critical constants are given by

$$p_c = \frac{1}{12} \left(\frac{2aR}{3b^3} \right)^{1/2} \quad V_c = 3b \quad T_c = \frac{2}{3} \left(\frac{2a}{3bR} \right)^{1/2}$$