

# 1 The properties of gases

## 1A The perfect gas

### Answers to discussion questions

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- 1A.2** The partial pressure of a gas in a mixture of gases is the pressure the gas would exert if it occupied alone the same container as the mixture at the same temperature. Dalton's law is a limiting law because it holds exactly only under conditions where the gases have no effect upon each other. This can only be true in the limit of zero pressure where the molecules of the gas are very far apart. Hence, Dalton's law holds exactly only for a mixture of perfect gases; for real gases, the law is only an approximation.

### Solutions to exercises

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- 1A.1(b)** The perfect gas law [1A.5] is  $pV = nRT$ , implying that the pressure would be

$$p = \frac{nRT}{V}$$

All quantities on the right are given to us except  $n$ , which can be computed from the given mass of Ar.

$$n = \frac{25 \text{ g}}{39.95 \text{ g mol}^{-1}} = 0.626 \text{ mol}$$

$$\text{so } p = \frac{(0.626 \text{ mol}) \times (8.31 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times (30 + 273) \text{ K}}{1.5 \text{ dm}^3} = \boxed{10.5 \text{ bar}}$$

So  $\boxed{\text{no}}$ , the sample would not exert a pressure of 2.0 bar.

- 1A.2(b)** Boyle's law [1A.4a] applies.

$$pV = \text{constant} \quad \text{so} \quad p_f V_f = p_i V_i$$

Solve for the initial pressure:

$$\text{(i)} \quad p_i = \frac{p_f V_f}{V_i} = \frac{(1.97 \text{ bar}) \times (2.14 \text{ dm}^3)}{(2.14 + 1.80) \text{ dm}^3} = \boxed{1.07 \text{ bar}}$$

**(ii)** The original pressure in Torr is

$$p_i = (1.07 \text{ bar}) \times \left( \frac{1 \text{ atm}}{1.013 \text{ bar}} \right) \times \left( \frac{760 \text{ Torr}}{1 \text{ atm}} \right) = \boxed{803 \text{ Torr}}$$

- 1A.3(b)** The relation between pressure and temperature at constant volume can be derived from the perfect gas law,  $pV = nRT$  [1A.5]

$$\text{so } p \propto T \quad \text{and} \quad \frac{p_i}{T_i} = \frac{p_f}{T_f}$$

The final pressure, then, ought to be

$$p_f = \frac{p_i T_f}{T_i} = \frac{(125 \text{ kPa}) \times (11 + 273) \text{ K}}{(23 + 273) \text{ K}} = \boxed{120 \text{ kPa}}$$

- 1A.4(b)** According to the perfect gas law [1.8], one can compute the amount of gas from pressure, temperature, and volume.

$$pV = nRT$$

$$\text{so } n = \frac{pV}{RT} = \frac{(1.00 \text{ atm}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1}) \times (4.00 \times 10^3 \text{ m}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (20 + 273) \text{ K}} = 1.66 \times 10^5 \text{ mol}$$

Once this is done, the mass of the gas can be computed from the amount and the molar mass:

$$m = (1.66 \times 10^5 \text{ mol}) \times (16.04 \text{ g mol}^{-1}) = 2.67 \times 10^6 \text{ g} = \boxed{2.67 \times 10^3 \text{ kg}}$$

- 1A.5(b)** The total pressure is the external pressure plus the hydrostatic pressure [1A.1], making the total pressure

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

Let  $p_{\text{ex}}$  be the pressure at the top of the straw and  $p$  the pressure on the surface of the liquid (atmospheric pressure). Thus the pressure difference is

$$\begin{aligned} p - p_{\text{ex}} = \rho gh &= (1.0 \text{ g cm}^{-3}) \times \frac{1 \text{ kg}}{10^3 \text{ g}} \times \left( \frac{1 \text{ cm}}{10^{-2} \text{ m}} \right)^3 \times (9.81 \text{ m s}^{-2}) \times (0.15 \text{ m}) \\ &= \boxed{1.5 \times 10^3 \text{ Pa}} = 1.5 \times 10^{-2} \text{ atm} \end{aligned}$$

**1A.6(b)** The pressure in the apparatus is given by

$$p = p_{\text{ex}} + \rho gh \text{ [1A.1]}$$

where  $p_{\text{ex}} = 760 \text{ Torr} = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$ ,

$$\text{and } \rho gh = 13.55 \text{ g cm}^{-3} \times \left( \frac{1 \text{ kg}}{10^3 \text{ g}} \right) \times \left( \frac{1 \text{ cm}}{10^{-2} \text{ m}} \right)^3 \times 0.100 \text{ m} \times 9.806 \text{ m s}^{-2} = 1.33 \times 10^4 \text{ Pa}$$

$$p = 1.013 \times 10^5 \text{ Pa} + 1.33 \times 10^4 \text{ Pa} = 1.146 \times 10^5 \text{ Pa} = \boxed{115 \text{ kPa}}$$

**1A.7(b)** Rearrange the perfect gas equation [1A.5] to give  $R = \frac{pV}{nT} = \frac{pV_{\text{m}}}{T}$

All gases are perfect in the limit of zero pressure. Therefore the value of  $pV_{\text{m}}/T$  extrapolated to zero pressure will give the best value of  $R$ .

The molar mass can be introduced through

$$pV = nRT = \frac{m}{M} RT$$

$$\text{which upon rearrangement gives } M = \frac{m}{V} \frac{RT}{p} = \rho \frac{RT}{p}$$

The best value of  $M$  is obtained from an extrapolation of  $\rho/p$  versus  $p$  to zero pressure; the intercept is  $M/RT$ .

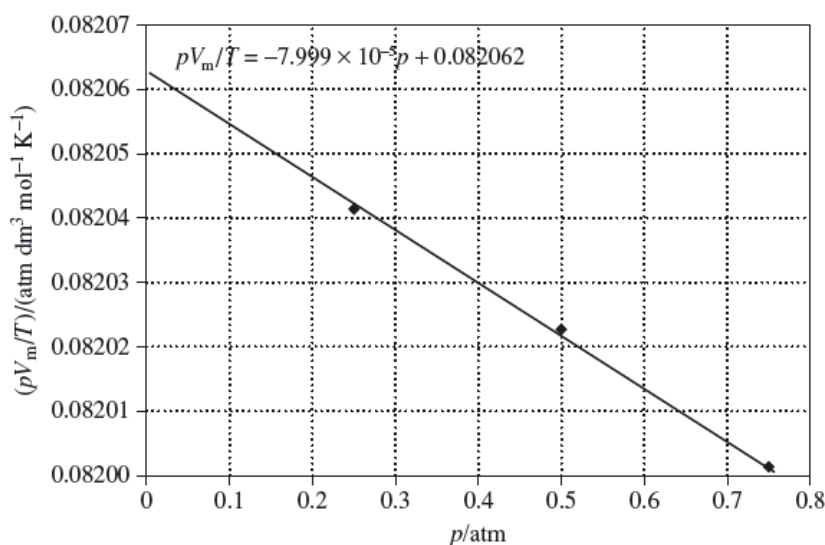
Draw up the following table:

$p/\text{atm}$	$(pV_{\text{m}}/T)/(\text{dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})$	$(\rho/p)/(\text{g dm}^{-3} \text{ atm}^{-1})$
0.750 000	0.082 0014	1.428 59
0.500 000	0.082 0227	1.428 22
0.250 000	0.082 0414	1.427 90

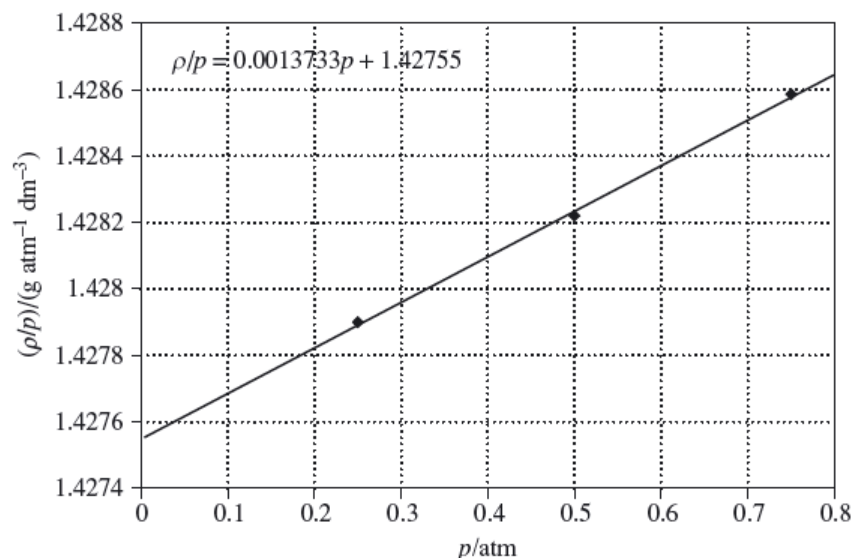
$$\text{From Figure 1A.1(a), } R = \lim_{p \rightarrow 0} \left( \frac{pV_{\text{m}}}{T} \right) = \boxed{0.082 062 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}}$$

**Figure 1A.1**

(a)



(b)



From Figure 1A.1(b),  $\lim_{p \rightarrow 0} \left( \frac{\rho}{p} \right) = 1.42755 \text{ g dm}^{-3} \text{ atm}^{-1}$

$$M = \lim_{p \rightarrow 0} RT \left( \frac{\rho}{p} \right) = (0.082062 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K}) \times (1.42755 \text{ g dm}^{-3} \text{ atm}^{-1})$$
$$= \boxed{31.9988 \text{ g mol}^{-1}}$$

The value obtained for  $R$  deviates from the accepted value by 0.005 per cent, better than can be expected from a linear extrapolation from three data points.

**1A.8(b)** The mass density  $\rho$  is related to the molar volume  $V_m$  by

$$V_m = \frac{V}{n} = \frac{V}{m} \times \frac{m}{n} = \frac{M}{\rho}$$

where  $M$  is the molar mass. Putting this relation into the perfect gas law [1A.5] yields

$$pV_m = RT \quad \text{so} \quad \frac{pM}{\rho} = RT$$

Rearranging this result gives an expression for  $M$ ; once we know the molar mass, we can divide by the molar mass of phosphorus atoms to determine the number of atoms per gas molecule.

$$M = \frac{RT\rho}{p} = \frac{(8.3145 \text{ Pa m}^3 \text{ mol}^{-1}) \times [(100 + 273) \text{ K}] \times (0.6388 \text{ kg m}^{-3})}{1.60 \times 10^4 \text{ Pa}}$$
$$= 0.124 \text{ kg mol}^{-1} = 124 \text{ g mol}^{-1}$$

The number of atoms per molecule is

$$\frac{124 \text{ g mol}^{-1}}{31.0 \text{ g mol}^{-1}} = 4.00$$

suggesting a formula of  $\boxed{\text{P}_4}$ .

**1A.9(b)** Use the perfect gas equation [1A.5] to compute the amount; then convert to mass.

$$pV = nRT \quad \text{so} \quad n = \frac{pV}{RT}$$

We need the partial pressure of water, which is 53 per cent of the equilibrium vapour pressure at the given temperature and standard pressure. (We must look it up in a handbook like the *CRC* or other resource such as the NIST Chemistry WebBook.)

$$p = (0.53) \times (2.81 \times 10^3 \text{ Pa}) = 1.49 \times 10^3 \text{ Pa}$$

so 
$$n = \frac{(1.49 \times 10^3 \text{ Pa}) \times (250 \text{ m}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (23 + 273) \text{ K}} = 151 \text{ mol}$$

and 
$$m = (151 \text{ mol}) \times (18.0 \text{ g mol}^{-1}) = 2.72 \times 10^3 \text{ g} = \boxed{2.72 \text{ kg}}$$

- 1A.10(b)** (i) The volume occupied by each gas is the same, since each completely fills the container. Thus solving for  $V$  we have (assuming a perfect gas, eqn. 1A.5)

$$V = \frac{n_j RT}{p_j}$$

We have the pressure of neon, so we focus on it

$$n_{\text{Ne}} = \frac{0.225 \text{ g}}{20.18 \text{ g mol}^{-1}} = 1.115 \times 10^{-2} \text{ mol}$$

Thus

$$V = \frac{1.115 \times 10^{-2} \text{ mol} \times 8.3145 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{8.87 \times 10^3 \text{ Pa}} = 3.14 \times 10^{-3} \text{ m}^3 = \boxed{3.14 \text{ dm}^3}$$

- (ii) The total pressure is determined from the total amount of gas,  $n = n_{\text{CH}_4} + n_{\text{Ar}} + n_{\text{Ne}}$ .

$$n_{\text{CH}_4} = \frac{0.320 \text{ g}}{16.04 \text{ g mol}^{-1}} = 1.995 \times 10^{-2} \text{ mol} \quad n_{\text{Ar}} = \frac{0.175 \text{ g}}{39.95 \text{ g mol}^{-1}} = 4.38 \times 10^{-3} \text{ mol}$$

$$n = (1.995 + 0.438 + 1.115) \times 10^{-2} \text{ mol} = 3.55 \times 10^{-2} \text{ mol}$$

and 
$$p = \frac{nRT}{V} = \frac{3.55 \times 10^{-2} \text{ mol} \times 8.3145 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{3.14 \times 10^{-3} \text{ m}^3}$$
  

$$= \boxed{2.82 \times 10^4 \text{ Pa}} = \boxed{28.2 \text{ kPa}}$$

- 1A.11(b)** This exercise uses the formula,  $M = \frac{\rho RT}{p}$ , which was developed and used in Exercise

1A.8(b). First the density must first be calculated.

$$\rho = \frac{33.5 \times 10^{-3} \text{ g}}{250 \text{ cm}^3} \times \left( \frac{10^3 \text{ cm}^3}{\text{dm}^3} \right) = 0.134 \text{ g dm}^{-3}$$

$$M = \frac{(0.134 \text{ g dm}^{-3}) \times (62.36 \text{ dm}^3 \text{ torr K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{152 \text{ torr}} = \boxed{16.4 \text{ g mol}^{-1}}$$

- 1A.12(b)** This exercise is similar to Exercise 1.12(a) in that it uses the definition of absolute zero as that temperature at which the volume of a sample of gas would become zero if the substance remained a gas at low temperatures. The solution uses the experimental fact that the volume is a linear function of the Celsius temperature:

$$V = V_0 + \alpha \theta \quad \text{where} \quad V_0 = 20.00 \text{ dm}^3 \text{ and } \alpha = 0.0741 \text{ dm}^3 \text{ } ^\circ\text{C}^{-1}.$$

At absolute zero,  $V = 0 = V_0 + \alpha \theta$

so 
$$\theta(\text{abs.zero}) = -\frac{V_0}{\alpha} = -\frac{20.00 \text{ dm}^3}{0.0741 \text{ dm}^3 \text{ } ^\circ\text{C}^{-1}} = \boxed{-270^\circ\text{C}}$$

which is close to the accepted value of  $-273^\circ\text{C}$ .

- 1A.13(b)** (i) Mole fractions are

$$x_{\text{N}} = \frac{n_{\text{N}}}{n_{\text{total}}} [1\text{A.9}] = \frac{2.5 \text{ mol}}{(2.5 + 1.5) \text{ mol}} = \boxed{0.63}$$

Similarly,  $x_{\text{H}} = \boxed{0.37}$

According to the perfect gas law

$$p_{\text{tot}} V = n_{\text{tot}} RT$$

$$\text{so } p_{\text{tot}} = \frac{n_{\text{tot}} RT}{V} = \frac{(4.0 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (273.15 \text{ K})}{22.4 \text{ dm}^3} = \boxed{4.0 \text{ atm}}$$

(ii) The partial pressures are

$$p_{\text{N}} = x_{\text{N}} p_{\text{tot}} = (0.63) \times (4.0 \text{ atm}) = \boxed{2.5 \text{ atm}}$$

$$\text{and } p_{\text{H}} = (0.37) \times (4.0 \text{ atm}) = \boxed{1.5 \text{ atm}}$$

$$\text{(iii) } p = p_{\text{H}} + p_{\text{N}} [1\text{A.10}] = (2.5 + 1.5) \text{ atm} = \boxed{4.0 \text{ atm}}$$

## Solutions to problems

**1A.2** Solving for  $n$  from the perfect gas equation [1A.5] yields  $n = \frac{pV}{RT}$ . From the definition of molar mass  $n = \frac{m}{M}$ , hence  $\rho = \frac{m}{V} = \frac{Mp}{RT}$ . Rearrangement yields the desired relation, namely

$$\boxed{p = \rho \frac{RT}{M}}.$$

Therefore, for ideal gases  $\frac{p}{\rho} = \frac{RT}{M}$  and  $M = \frac{RT}{p/\rho}$ . For real gases, find the zero-pressure

limit of  $\frac{p}{\rho}$  by plotting it against  $p$ . Draw up the following table.

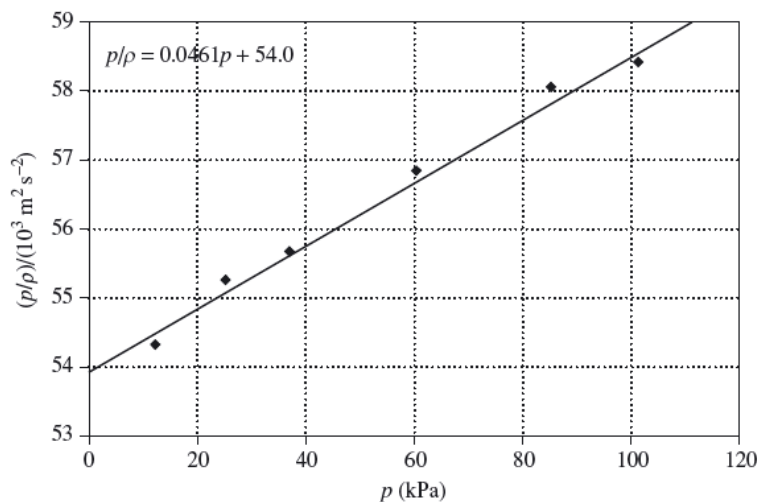
$p/(\text{kPa})$	12.223	25.20	36.97	60.37	85.23	101.3
$\rho/(\text{kg m}^{-3})$	0.225	0.456	0.664	1.062	1.468	1.734
$\frac{p/\rho}{10^3 \text{ m}^2 \text{ s}^{-2}}$	54.3	55.3	55.7	56.8	58.1	58.4

Bear in mind that  $1 \text{ kPa} = 10^3 \text{ kg m}^{-1} \text{ s}^{-2}$ .

$\frac{p}{\rho}$  is plotted in Figure 1A.2. A straight line fits the data rather well. The extrapolation to  $p = 0$  yields an intercept of  $54.0 \times 10^3 \text{ m}^2 \text{ s}^{-2}$ . Then

$$\begin{aligned} M &= \frac{RT}{5.40 \times 10^4 \text{ m}^2 \text{ s}^{-2}} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{5.40 \times 10^4 \text{ m}^2 \text{ s}^{-2}} \\ &= 0.0459 \text{ kg mol}^{-1} = \boxed{45.9 \text{ g mol}^{-1}} \end{aligned}$$

**Figure 1A.2**



**Comment.** This method of the determination of the molar masses of gaseous compounds is due to Cannizzarro who presented it at the Karlsruhe Congress of 1860. That conference had been called to resolve the problem of the determination of the molar masses of atoms and molecules and the molecular formulas of compounds.

- 1A.4** The mass of displaced gas is  $\rho V$ , where  $V$  is the volume of the bulb and  $\rho$  is the density of the displaced gas. The balance condition for the two gases is

$$m(\text{bulb}) = \rho V(\text{bulb}) \quad \text{and} \quad m(\text{bulb}) = \rho' V(\text{bulb})$$

which implies that  $\rho = \rho'$ . Because [Problem 1.2]  $\rho = \frac{pM}{RT}$

the balance condition is  $pM = p'M'$ ,

which implies that  $M' = \frac{p}{p'} \times M$

This relation is valid in the limit of zero pressure (for a gas behaving perfectly).

In experiment 1,  $p = 423.22$  Torr,  $p' = 327.10$  Torr;

$$\text{hence} \quad M' = \frac{423.22 \text{ Torr}}{327.10 \text{ Torr}} \times 70.014 \text{ g mol}^{-1} = 90.59 \text{ g mol}^{-1}$$

In experiment 2,  $p = 427.22$  Torr,  $p' = 293.22$  Torr;

$$\text{hence} \quad M' = \frac{427.22 \text{ Torr}}{293.22 \text{ Torr}} \times 70.014 \text{ g mol}^{-1} = 102.0 \text{ g mol}^{-1}$$

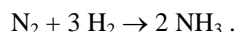
In a proper series of experiments one should reduce the pressure (e.g. by adjusting the balanced weight). Experiment 2 is closer to zero pressure than experiment 1, so it is more likely to be close to the true value:

$$M' \approx 102 \text{ g mol}^{-1}$$

The molecules  $\text{CH}_2\text{FCF}_3$  and  $\text{CHF}_2\text{CHF}_2$  have molar mass of  $102 \text{ g mol}^{-1}$ .

**Comment.** The substantial difference in molar mass between the two experiments ought to make us wary of confidently accepting the result of Experiment 2, even if it is the more likely estimate.

- 1A.6** We assume that no  $\text{H}_2$  remains after the reaction has gone to completion. The balanced equation is



We can draw up the following table

	$\text{N}_2$	$\text{H}_2$	$\text{NH}_3$	Total
Initial amount	$n$	$n'$	0	$n + n'$
Final amount	$n - \frac{1}{3}n'$	0	$\frac{2}{3}n'$	$n + \frac{1}{3}n'$
Specifically	0.33 mol	0	1.33 mol	1.66 mol
Mole fraction	0.20	0	0.80	1.00

$$p = \frac{nRT}{V} = (1.66 \text{ mol}) \times \left( \frac{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (273.15 \text{ K})}{22.4 \text{ dm}^3} \right) = 1.66 \text{ atm}$$

$$p(\text{H}_2) = x(\text{H}_2)p = 0$$

$$p(\text{N}_2) = x(\text{N}_2)p = 0.20 \times 1.66 \text{ atm} = 0.33 \text{ atm}$$

$$p(\text{NH}_3) = x(\text{NH}_3)p = 0.80 \times 1.66 \text{ atm} = 1.33 \text{ atm}$$

- 1A.8** The perfect gas law is  $pV = nRT$  so  $n = \frac{pV}{RT}$

At mid-latitudes

$$n = \frac{(1.00 \text{ atm}) \times \{(1.00 \text{ dm}^2) \times (250 \times 10^{-3} \text{ cm}) / 10 \text{ cm dm}^{-1}\}}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} = 1.12 \times 10^{-3} \text{ mol}$$

In the ozone hole

$$n = \frac{(1.00 \text{ atm}) \times \{(1.00 \text{ dm}^2) \times (100 \times 10^{-3} \text{ cm}) / 10 \text{ cm dm}^{-1}\}}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} = 4.46 \times 10^{-4} \text{ mol}$$

The corresponding concentrations are

$$\frac{n}{V} = \frac{1.12 \times 10^{-3} \text{ mol}}{(1.00 \text{ dm}^2) \times (40 \times 10^3 \text{ m}) \times (10 \text{ dm m}^{-1})} = \boxed{2.8 \times 10^{-9} \text{ mol dm}^{-3}}$$

and 
$$\frac{n}{V} = \frac{4.46 \times 10^{-4} \text{ mol}}{(1.00 \text{ dm}^2) \times (40 \times 10^3 \text{ m}) \times (10 \text{ dm m}^{-1})} = \boxed{1.1 \times 10^{-9} \text{ mol dm}^{-3}}$$

respectively.

**1A.10** The perfect gas law [1A.5] can be rearranged to  $n = \frac{pV}{RT}$

The volume of the balloon is 
$$V = \frac{4\pi}{3} r^3 = \frac{4\pi}{3} \times (3.0 \text{ m})^3 = 113 \text{ m}^3$$

(a) 
$$n = \frac{(1.0 \text{ atm}) \times (113 \times 10^3 \text{ dm}^3)}{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})} = \boxed{4.62 \times 10^3 \text{ mol}}$$

(b) The mass that the balloon can lift is the difference between the mass of displaced air and the mass of the balloon. We assume that the mass of the balloon is essentially that of the gas it encloses:

$$m = m(\text{H}_2) = nM(\text{H}_2) = (4.62 \times 10^3 \text{ mol}) \times (2.02 \text{ g mol}^{-1}) = 9.33 \times 10^3 \text{ g}$$

$$\text{Mass of displaced air} = (113 \text{ m}^3) \times (1.22 \text{ kg m}^{-3}) = 1.38 \times 10^2 \text{ kg}$$

Therefore, the mass of the maximum payload is

$$138 \text{ kg} - 9.33 \text{ kg} = \boxed{1.3 \times 10^2 \text{ kg}}$$

(c) For helium,  $m = nM(\text{He}) = (4.62 \times 10^3 \text{ mol}) \times (4.00 \text{ g mol}^{-1}) = 18 \text{ kg}$

The maximum payload is now  $138 \text{ kg} - 18 \text{ kg} = \boxed{1.2 \times 10^2 \text{ kg}}$

**1A.12** Avogadro's principle states that equal volumes of gases contain equal amounts (moles) of the gases, so the volume mixing ratio is equal to the mole fraction. The definition of partial pressures is

$$p_i = x_i p$$

The perfect gas law is

$$pV = nRT \quad \text{so} \quad \frac{n_i}{V} = \frac{p_i}{RT} = \frac{x_i p}{RT}$$

(a) 
$$\frac{n(\text{CCl}_3\text{F})}{V} = \frac{(261 \times 10^{-12}) \times (1.0 \text{ atm})}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (10 + 273) \text{ K}} = \boxed{1.1 \times 10^{-11} \text{ mol dm}^{-3}}$$

and 
$$\frac{n(\text{CCl}_2\text{F}_2)}{V} = \frac{(509 \times 10^{-12}) \times (1.0 \text{ atm})}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (10 + 273) \text{ K}} = \boxed{2.2 \times 10^{-11} \text{ mol dm}^{-3}}$$

(b) 
$$\frac{n(\text{CCl}_3\text{F})}{V} = \frac{(261 \times 10^{-12}) \times (0.050 \text{ atm})}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (200 \text{ K})} = \boxed{8.0 \times 10^{-13} \text{ mol dm}^{-3}}$$

and 
$$\frac{n(\text{CCl}_2\text{F}_2)}{V} = \frac{(509 \times 10^{-12}) \times (0.050 \text{ atm})}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (200 \text{ K})} = \boxed{1.6 \times 10^{-12} \text{ mol dm}^{-3}}$$

## 1B The kinetic model

### Answers to discussion questions

**1B.2** The formula for the mean free path [eqn 1B.13] is

$$\lambda = \frac{kT}{\sigma p}$$

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 are dependences on size. As pointed out in the text, 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 set 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 molecules' radius).

### Solutions to exercises

**1B.1(b)** The mean speed is [1B.8]

$$v_{\text{mean}} = \left( \frac{8RT}{\pi M} \right)^{1/2}$$

The mean translational kinetic energy is

$$\langle E_k \rangle = \langle \frac{1}{2} m v^2 \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m v_{\text{rms}}^2 = \frac{m}{2} \left( \frac{3RT}{M} \right) [1B.3] = \frac{3kT}{2}$$

The ratios of species 1 to species 2 at the same temperature are

$$\frac{v_{\text{mean},1}}{v_{\text{mean},2}} = \left( \frac{M_2}{M_1} \right)^{1/2} \quad \text{and} \quad \frac{\langle E_k \rangle_1}{\langle E_k \rangle_2} = 1$$

$$(i) \quad \frac{v_{\text{mean,H}_2}}{v_{\text{mean,Hg}}} = \left( \frac{200.6}{4.003} \right)^{1/2} = \boxed{7.079}$$

(ii) The mean translation kinetic energy is independent of molecular mass and depends upon temperature alone! Consequently, because the mean translational kinetic energy for a gas is proportional to  $T$ , the ratio of mean translational kinetic energies for gases at the same temperature always equals 1.

**1B.2(b)** The root mean square speed [1B.3] is

$$v_{\text{rms}} = \left( \frac{3RT}{M} \right)^{1/2}$$

For  $\text{CO}_2$  the molar mass is

$$M = (12.011 + 2 \times 15.9994) \times 10^{-3} \text{ kg mol}^{-1} = 44.010 \times 10^{-3} \text{ kg mol}^{-1}$$

$$\text{so} \quad v_{\text{rms}} = \left( \frac{3(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(20 + 273) \text{ K}}{44.01 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{1/2} = \boxed{408 \text{ m s}^{-1}}$$

For He

$$v_{\text{rms}} = \left( \frac{3(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(20 + 273) \text{ K}}{4.003 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{1/2} = \boxed{1.35 \times 10^3 \text{ m s}^{-1}} = \boxed{1.35 \text{ km s}^{-1}}$$

**1B.3(b)** The Maxwell-Boltzmann distribution of speeds [1B.4] is

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

and the fraction of molecules that have a speed between  $v$  and  $v+dv$  is  $f(v)dv$ . The fraction of molecules to have a speed in the range between  $v_1$  and  $v_2$  is, therefore,  $\int_{v_1}^{v_2} f(v)dv$ . If the range is relatively small, however, such that  $f(v)$  is nearly constant over that range, the integral may be approximated by  $f(v)\Delta v$ , where  $f(v)$  is evaluated anywhere within the range and  $\Delta v = v_2 - v_1$ . Thus, we have, with  $M = 44.010 \times 10^{-3} \text{ kg mol}^{-1}$  [Exercise 1B.2(b)],

$$\int_{v_1}^{v_2} f(v)dv \approx f(v)\Delta v = 4\pi \left( \frac{44.010 \times 10^{-3} \text{ kg mol}^{-1}}{2\pi(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(400 \text{ K})} \right)^{3/2} (402.5 \text{ m s}^{-1})^2$$



$$\times \exp\left(-\frac{(44.010 \times 10^{-3} \text{ kg mol}^{-1})(402.5 \text{ m s}^{-1})^2}{2(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(400 \text{ K})}\right) \times (405 - 400) \text{ m s}^{-1}$$

$$= \boxed{0.0107}, \text{ just over 1\%}$$

**1B.4(b)** The most probable, mean, and mean relative speeds are, respectively

$$v_{\text{mp}} = \left(\frac{2RT}{M}\right)^{1/2} \quad [1\text{B.9}] \quad v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2} \quad [1\text{B.8}] \quad v_{\text{rel}} = \left(\frac{8RT}{\pi \mu}\right)^{1/2} \quad [1\text{B.10b}]$$

The temperature is  $T = (20+273) \text{ K} = 293 \text{ K}$ .

$$\text{so } v_{\text{mp}} = \left(\frac{2(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293 \text{ K})}{2 \times 1.008 \times 10^{-3} \text{ kg mol}^{-1}}\right)^{1/2} = \boxed{1.55 \times 10^3 \text{ m s}^{-1}}$$

$$\text{and } v_{\text{mean}} = \left(\frac{8(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293 \text{ K})}{\pi(2 \times 1.008 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} = \boxed{1.75 \times 10^3 \text{ m s}^{-1}}$$

For many purposes, air can be considered as a gas with an average molar mass of  $29.0 \text{ g mol}^{-1}$ . In that case, the reduced molar mass [1B.10b] is

$$\mu = \frac{M_A M_B}{M_A + M_B} = \frac{(29.0 \text{ g mol}^{-1})(2 \times 1.008 \text{ g mol}^{-1})}{(29.0 + 2 \times 1.008) \text{ g mol}^{-1}} = 1.88 \text{ g mol}^{-1}$$

$$\text{and } v_{\text{rel}} = \left(\frac{8(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(293 \text{ K})}{\pi(1.88 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} = \boxed{1.81 \times 10^3 \text{ m s}^{-1}}$$

**Comment.** One computes the average molar mass of air just as one computes the average molar mass of an isotopically mixed element, namely by taking an average of the species that have different masses weighted by their abundances.

**Comment.** Note that  $v_{\text{rel}}$  and  $v_{\text{mean}}$  are very nearly equal. This is because the reduced mass between two very dissimilar species is nearly equal to the mass of the lighter species (in this case,  $\text{H}_2$ ).

**1B.5(b)** (i)  $v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2} \quad [1\text{B.8}] = \left(\frac{8(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{\pi(2 \times 14.007 \times 10^{-3} \text{ kg mol}^{-1})}\right)^{1/2} = \boxed{475 \text{ m s}^{-1}}$

(ii) The mean free path [1B.13] is

$$\lambda = \frac{kT}{\sigma p} = \frac{kT}{\pi d^2 p} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{\pi(395 \times 10^{-12} \text{ m})^2(1 \times 10^{-9} \text{ Torr})} \times \frac{1 \text{ Torr}}{133.3 \text{ Pa}}$$

$$= \boxed{6.3 \times 10^4 \text{ m}} = \boxed{63 \text{ km}}$$

The mean free path is much larger than the dimensions of the pumping apparatus used to generate the very low pressure.

(iii) The collision frequency is related to the mean free path and relative mean speed by [1B.12]

$$\lambda = \frac{v_{\text{rel}}}{z} \quad \text{so} \quad z = \frac{v_{\text{rel}}}{\lambda} = \frac{2^{1/2} v_{\text{mean}}}{\lambda} \quad [1\text{B.10a}]$$

$$z = \frac{2^{1/2}(475 \text{ m s}^{-1})}{6.3 \times 10^4 \text{ m}} = \boxed{1.1 \times 10^{-2} \text{ s}^{-1}}$$

**1B.6(b)** The collision diameter is related to the collision cross section by

$$\sigma = \pi d^2 \quad \text{so} \quad d = (\sigma/\pi)^{1/2} = (0.36 \text{ nm}^2/\pi)^{1/2} = 0.34 \text{ nm}.$$

The mean free path [1B.13] is

$$\lambda = \frac{kT}{\sigma p}$$

Solve this expression for the pressure and set  $\lambda$  equal to  $10d$ :

$$p = \frac{kT}{\sigma\lambda} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(293 \text{ K})}{0.36 \times (10^{-9} \text{ m})^2 (10 \times 0.34 \times 10^{-9} \text{ m})} = 3.3 \times 10^6 \text{ J m}^{-3} = \boxed{3.3 \text{ MPa}}$$

**Comment.** This pressure works out to 33 bar (about 33 atm), conditions under which the assumption of perfect gas behavior and kinetic model applicability at least begins to come into question.

**1B.7(b)** The mean free path [1B.13] is

$$\lambda = \frac{kT}{\sigma p} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(217 \text{ K})}{0.43 \times (10^{-9} \text{ m})^2 (12.1 \times 10^3 \text{ Pa atm}^{-1})} = \boxed{5.8 \times 10^{-7} \text{ m}}$$

## Solutions to problems

**1B.2** The number of molecules that escape in unit time is the number per unit time that would have collided with a wall section of area  $A$  equal to the area of the small hole. This quantity is readily expressed in terms of  $Z_w$ , the collision flux (collisions per unit time with a unit area), given in eqn 19A.6. That is,

$$\frac{dN}{dt} = -Z_w A = \frac{-Ap}{(2\pi mkT)^{1/2}}$$

where  $p$  is the (constant) vapour pressure of the solid. The change in the number of molecules inside the cell in an interval  $\Delta t$  is therefore  $\Delta N = -Z_w A \Delta t$ , and so the mass loss is

$$\Delta w = m \Delta N = -Ap \left( \frac{m}{2\pi kT} \right)^{1/2} \Delta t = -Ap \left( \frac{M}{2\pi RT} \right)^{1/2} \Delta t$$

Therefore, the vapour pressure of the substance in the cell is

$$p = \left( \frac{-\Delta w}{A \Delta t} \right) \times \left( \frac{2\pi RT}{M} \right)^{1/2}$$

For the vapour pressure of germanium

$$p = \left( \frac{43 \times 10^{-9} \text{ kg}}{\pi (0.50 \times 10^{-3} \text{ m}) (7200 \text{ s})} \right) \times \left( \frac{2\pi (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (1273 \text{ K})}{72.64 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{1/2} \\ = 7.3 \times 10^{-3} \text{ Pa} = \boxed{7.3 \text{ mPa}}$$

**1B.4** We proceed as in Justification 1B.2 except that, instead of taking a product of three one-dimensional distributions in order to get the three-dimensional distribution, we make a product of two one-dimensional distributions.

$$f(v_x, v_y) dv_x dv_y = f(v_x^2) f(v_y^2) dv_x dv_y = \left( \frac{m}{2\pi kT} \right) e^{-mv^2/2kT} dv_x dv_y$$

where  $v^2 = v_x^2 + v_y^2$ . The probability  $f(v)dv$  that the molecules have a two-dimensional speed,  $v$ , in the range  $v$  to  $v + dv$  is the sum of the probabilities that it is in any of the area elements  $dv_x dv_y$  in the circular shell of radius  $v$ . The sum of the area elements is the area of the circular shell of radius  $v$  and thickness  $dv$  which is  $\pi(v+dv)^2 - \pi v^2 = 2\pi v dv$ . Therefore,

$$f(v) = \left[ \left( \frac{m}{kT} \right) v e^{-mv^2/2kT} \right] = \left[ \left( \frac{M}{RT} \right) v e^{-Mv^2/2RT} \right] \left[ \frac{M}{R} = \frac{m}{k} \right]$$

The mean speed is determined as

$$v_{\text{mean}} = \int_0^\infty v f(v) dv = \left( \frac{m}{kT} \right) \int_0^\infty v^2 e^{-mv^2/2kT} dv$$

Using integral G.3 from the Resource Section yields

$$v_{\text{mean}} = \left( \frac{m}{kT} \right) \times \left( \frac{\pi^{1/2}}{4} \right) \times \left( \frac{2kT}{m} \right)^{3/2} = \left( \frac{\pi kT}{2m} \right)^{1/2} = \left( \frac{\pi RT}{2M} \right)^{1/2}$$

**1B.6** The distribution [1B.4] is

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

The proportion of molecules with speeds less than  $v_{\text{rms}}$  is

$$P = \int_0^{v_{\text{rms}}} f(v) dv = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \int_0^{v_{\text{rms}}} v^2 e^{-Mv^2/2RT} dv$$

Defining  $a \equiv R / 2RT$ ,

$$P = 4\pi \left( \frac{a}{\pi} \right)^{3/2} \int_0^{v_{\text{rms}}} v^2 e^{-av^2} dv = -4\pi \left( \frac{a}{\pi} \right)^{3/2} \frac{d}{da} \int_0^{v_{\text{rms}}} e^{-av^2} dv$$

Defining  $\chi^2 \equiv av^2$ . Then,  $dv = a^{-1/2} d\chi$  and

$$\begin{aligned} P &= -4\pi \left( \frac{a}{\pi} \right)^{3/2} \frac{d}{da} \left\{ \frac{1}{\chi^{1/2}} \int_0^{v_{\text{rms}} a^{1/2}} e^{-\chi^2} d\chi \right\} \\ &= -4\pi \left( \frac{a}{\pi} \right)^{3/2} \left\{ -\frac{1}{2} \left( \frac{1}{a} \right)^{3/2} \int_0^{v_{\text{rms}} a^{1/2}} e^{-\chi^2} d\chi + \left( \frac{1}{a} \right)^{1/2} \frac{d}{da} \int_0^{v_{\text{rms}} a^{1/2}} e^{-\chi^2} d\chi \right\} \end{aligned}$$

Then we use the error function [Integral G.6]:

$$\begin{aligned} \int_0^{v_{\text{rms}} a^{1/2}} e^{-\chi^2} d\chi &= (\pi^{1/2} / 2) \text{erf}(v_{\text{rms}} a^{1/2}). \\ \frac{d}{da} \int_0^{v_{\text{rms}} a^{1/2}} e^{-\chi^2} d\chi &= \left( \frac{dv_{\text{rms}} a^{1/2}}{da} \right) \times (e^{-av_{\text{rms}}^2}) = \frac{1}{2} \left( \frac{c}{a^{1/2}} \right) e^{-av_{\text{rms}}^2} \end{aligned}$$

where we have used  $\frac{d}{dz} \int_0^z f(y) dy = f(z)$

Substituting and cancelling we obtain  $P = \text{erf}(v_{\text{rms}} a^{1/2}) - (2v_{\text{rms}} a^{1/2} / \pi^{1/2}) e^{-av_{\text{rms}}^2}$

Now  $v_{\text{rms}} = \left( \frac{3RT}{M} \right)^{1/2}$  so  $v_{\text{rms}} a^{1/2} = \left( \frac{3RT}{M} \right)^{1/2} \times \left( \frac{M}{2RT} \right)^{1/2} = \left( \frac{3}{2} \right)^{1/2}$

and  $P = \text{erf} \left( \sqrt{\frac{3}{2}} \right) - \left( \frac{6}{\pi} \right)^{1/2} e^{-3/2} = 0.92 - 0.31 = \boxed{0.61}$

Therefore,

- (a)  $1 - P = \boxed{39\%}$  have a speed greater than the root mean square speed.
- (b)  $P = \boxed{61\%}$  of the molecules have a speed less than the root mean square speed.
- (c) For the proportions in terms of the mean speed  $v_{\text{mean}}$ , replace  $v_{\text{rms}}$  by

$$v_{\text{mean}} = (8kT / \pi m)^{1/2} = (8 / 3\pi)^{1/2} v_{\text{rms}} \quad \text{so} \quad v_{\text{mean}} a^{1/2} = 2 / \pi^{1/2}.$$

Then  $P = \text{erf}(v_{\text{mean}} a^{1/2}) - (2v_{\text{mean}} a^{1/2} / \pi^{1/2}) \times (e^{-av_{\text{mean}}^2})$   
 $= \text{erf} \left( 2 / \pi^{1/2} \right) - (4 / \pi) e^{-4/\pi} = 0.889 - 0.356 = \boxed{0.533}$

That is,  $\boxed{53\%}$  of the molecules have a speed less than the mean, and  $\boxed{47\%}$  have a speed greater than the mean.

**1B.8** The average is obtained by substituting the distribution (eqn 1B.4) into eqn 1B.7:

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

For even values of  $n$ , use Integral G.8:

$$\langle v^n \rangle = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \frac{(n+1)!!}{2^{\left(\frac{n+4}{2}\right)}} \left( \frac{2RT}{M} \right)^{\left(\frac{n+2}{2}\right)} \left( \frac{2\pi RT}{M} \right)^{1/2} = (n+1)!! \left( \frac{RT}{M} \right)^{\left(\frac{n}{2}\right)}$$

where  $(n+1)!! = 1 \times 3 \times 5 \dots \times (n+1)$

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

For odd values of  $n$ , use Integral G.7:

$$\langle v^n \rangle = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \frac{\left( \frac{n+1}{2} \right)!}{2} \left( \frac{2RT}{M} \right)^{\left( \frac{n+3}{2} \right)} = \frac{2}{\pi^{1/2}} \left( \frac{2RT}{M} \right)^{n/2}$$

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

**Question.** Show that these expressions reduce to  $v_{\text{mean}}$  and  $v_{\text{rms}}$  for  $n = 1$  and 2 respectively.

- 1B.10** Dry atmospheric air is 78.08% N<sub>2</sub>, 20.95% O<sub>2</sub>, 0.93% Ar, 0.04% CO<sub>2</sub>, plus traces of other gases. Nitrogen, oxygen, and carbon dioxide contribute 99.06% of the molecules in a volume with each molecule contributing an average rotational energy equal to  $kT$ . (Linear molecules can rotate in two dimensions, contributing two “quadratic terms” of rotational energy, or  $kT$  by the equipartition theorem [Topic B.3(b)]. The rotational energy density is given by

$$\begin{aligned} \rho_R &= \frac{E_R}{V} = \frac{0.9906N \langle \varepsilon^R \rangle}{V} = \frac{0.9906NkT}{V} = 0.9906p \\ &= 0.9906(1.013 \times 10^5 \text{ Pa}) = 1.004 \times 10^5 \text{ J m}^{-3} = 0.1004 \text{ J cm}^{-3} \end{aligned}$$

The total energy density is translational plus rotational (vibrational energy contributing negligibly):

$$\rho_{\text{tot}} = \rho_T + \rho_R = 0.15 \text{ J cm}^{-3} + 0.10 \text{ J cm}^{-3} = \boxed{0.25 \text{ J cm}^{-3}}$$

- 1B.12** The fraction of molecules (call it  $F$ ) between speeds  $a$  and  $b$  is given by

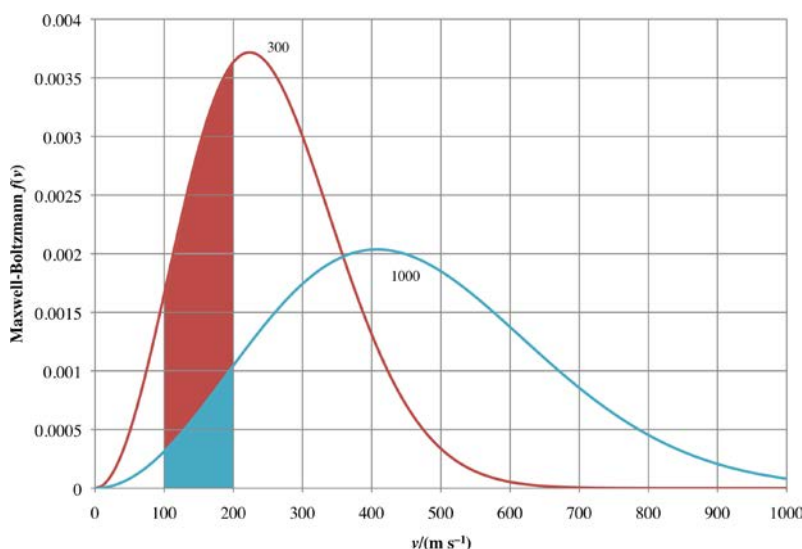
$$F(a, b) = \int_a^b f(v) dv$$

where  $f(v)$  is given by eqn 1B.4. This integral can be approximated by a sum over a discrete set of velocity values. For convenience, let the velocities  $v_i$  be evenly spaced within the interval such that  $v_{i+1} = v_i + \Delta v$ :

$$F(a, b) \approx \sum f(v_i) \Delta v$$

On a spreadsheet or other mathematical software, make a column of velocity values and then a column for  $f(v)$  [1B.4] at 300 K and at 1000 K. Figure 1B.1 shows  $f(v)$  plotted against  $v$  for these two temperatures. Each curve is labeled with the numerical value of  $T/\text{K}$ , and each is shaded under the curve between the speeds of 100 and 200 m s<sup>-1</sup>.  $F(a, b)$  is simply the area under the curve between  $v = a$  and  $v = b$ . One should take some care to avoid double counting at the edges of the interval, that is, not including both endpoints of the interval with full weight. example, beginning the sum with the area under the curve at those speeds. Using a spreadsheet that evaluates  $f(v)$  at 5-m s<sup>-1</sup> intervals, and including points at both 100 and 200 m s<sup>-1</sup> with half weight,  $F(100 \text{ m s}^{-1}, 200 \text{ m s}^{-1}) \approx \boxed{0.281}$  at 300 K and  $\boxed{0.066}$  at 1000 K.

**Figure 1B.1**



## 1C Real gases

### Answers to discussion questions

- 1C.2** The critical constants represent the state of a system at which the distinction between the liquid and vapour phases disappears. We usually describe this situation 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.
- 1C.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

- 1C.1(b)** The van der Waals equation [1C.5a] is

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

From Table 1C.3 for  $\text{H}_2\text{S}$ ,  $a = 4.484 \text{ dm}^6 \text{ atm mol}^{-1}$  and  $b = 0.0434 \text{ dm}^3 \text{ mol}^{-1}$ .

- (i) 
$$p = \frac{(1.0 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (273.15 \text{ K})}{22.414 \text{ dm}^3 - (1.0 \text{ mol}) \times (4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} - \frac{(4.484 \text{ dm}^6 \text{ atm mol}^{-1}) \times (1.0 \text{ mol})^2}{(22.414 \text{ dm}^3)^2} = \boxed{0.99 \text{ atm}}$$
- (ii) 
$$p = \frac{(1.0 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (500 \text{ K})}{0.150 \text{ dm}^3 - (1.0 \text{ mol}) \times (4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} - \frac{(4.484 \text{ dm}^6 \text{ atm mol}^{-1}) \times (1.0 \text{ mol})^2}{(0.150 \text{ dm}^3)^2} = \boxed{190 \text{ atm}} \text{ (2 sig. figures)}$$

- 1C.2(b)** The conversions needed are as follows:

$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$ ,  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ ,  $1 \text{ dm}^6 = (10^{-1} \text{ m})^6 = 10^{-6} \text{ m}^6$ ,  $1 \text{ dm}^3 = 10^{-3} \text{ m}^3$ .  
Therefore,

$$a = 1.32 \text{ atm dm}^6 \text{ mol}^{-2} \times \frac{1.013 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}}{1 \text{ atm}} \times \frac{10^{-6} \text{ m}^6}{\text{dm}^6} = \boxed{1.34 \times 10^{-1} \text{ kg m}^5 \text{ s}^{-2} \text{ mol}^{-2}}$$

$$\text{and } b = 0.0426 \text{ dm}^3 \text{ mol}^{-1} \times \frac{10^{-3} \text{ m}^3}{\text{dm}^3} = \boxed{4.26 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

- 1C.3(b)** The compression factor  $Z$  is [1C.1]

$$Z = \frac{V_{\text{m}}}{V_{\text{m}}^{\circ}} = \frac{pV_{\text{m}}}{RT}$$

- (i) Because  $V_{\text{m}} = V_{\text{m}}^{\circ} + 0.12 V_{\text{m}}^{\circ} = (1.12)V_{\text{m}}^{\circ}$ , we have  $Z = \boxed{1.12}$

- (ii) The molar volume is

$$V_m = (1.12)V_m^o = (1.12) \times \left( \frac{RT}{p} \right)$$

$$= (1.12) \times \left( \frac{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (350 \text{ K})}{12 \text{ atm}} \right) = \boxed{2.7 \text{ dm}^3 \text{ mol}^{-1}}$$

Since  $V_m > V_m^o$  **repulsive** forces dominate.

**1C.4(b)** (i) According to the perfect gas law

$$V_m^o = \frac{RT}{p} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{(200 \text{ bar}) \times (10^5 \text{ Pa bar}^{-1})} \times \left( \frac{1 \text{ dm}}{10^{-1} \text{ m}} \right)^3 = \boxed{0.124 \text{ dm}^3 \text{ mol}^{-1}}$$

(ii) The van der Waals equation [1C.5b] is a cubic equation in  $V_m$ . Cubic equations can be solved analytically. However, this approach is cumbersome, so we proceed as in Example 1C.1. The van der Waals equation is rearranged to the cubic form

$$V_m^3 - \left( b + \frac{RT}{p} \right) V_m^2 + \left( \frac{a}{p} \right) V_m - \frac{ab}{p} = 0$$

$$\text{or} \quad x^3 - \left( b + \frac{RT}{p} \right) x^2 + \left( \frac{a}{p} \right) x - \frac{ab}{p} = 0 \quad \text{with} \quad x = V_m / (\text{dm}^3 \text{ mol}^{-1}).$$

It will be convenient to have the pressure in atm:

$$200 \text{ bar} \times \frac{1 \text{ atm}}{1.013 \text{ bar}} = 197.4 \text{ atm}$$

The coefficients in the equation are

$$b + \frac{RT}{p} = (3.183 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}) + \frac{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})}{197.4 \text{ atm}}$$

$$= (3.183 \times 10^{-2} + 0.1239) \text{ dm}^3 \text{ mol}^{-1} = 0.1558 \text{ dm}^3 \text{ mol}^{-1}$$

$$\frac{a}{p} = \frac{1.360 \text{ dm}^6 \text{ atm mol}^{-2}}{197.4 \text{ atm}} = 6.89 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2}$$

$$\frac{ab}{p} = \frac{(1.360 \text{ dm}^6 \text{ atm mol}^{-2}) \times (3.183 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})}{197.4 \text{ atm}} = 2.193 \times 10^{-4} \text{ dm}^9 \text{ mol}^{-3}$$

Thus, the equation to be solved is  $x^3 - 0.1558x^2 + (6.89 \times 10^{-3})x - (2.193 \times 10^{-4}) = 0$ .

Calculators and computer software for the solution of polynomials are readily available. In this case we find

$$x = 0.112 \quad \text{and} \quad V_m = \boxed{0.112 \text{ dm}^3 \text{ mol}^{-1}}.$$

The perfect-gas value is about 15 percent greater than the van der Waals result.

**1C.5(b)** The molar volume is obtained by solving  $Z = \frac{pV_m}{RT}$  [1C.2], for  $V_m$ , which yields

$$V_m = \frac{ZRT}{p} = \frac{(0.86) \times (0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (300 \text{ K})}{20 \text{ atm}} = 1.06 \text{ dm}^3 \text{ mol}^{-1}$$

$$\text{(i) Then,} \quad V = nV_m = (8.2 \times 10^{-3} \text{ mol}) \times (1.06 \text{ dm}^3 \text{ mol}^{-1}) = 8.7 \times 10^{-3} \text{ dm}^3 = \boxed{8.7 \text{ cm}^3}$$

(ii) An approximate value of  $B$  can be obtained from eqn 1C.3b by truncation of the series expansion after the second term,  $B/V_m$ , in the series. Then,

$$B = V_m \left( \frac{pV_m}{RT} - 1 \right) = V_m \times (Z - 1)$$

$$= (1.06 \text{ dm}^3 \text{ mol}^{-1}) \times (0.86 - 1) = \boxed{-0.15 \text{ dm}^3 \text{ mol}^{-1}}$$

**1C.6(b)** Equations 1C.6a are solved for  $b$  and  $a$ , respectively, and yield

$$b = V_c/3 \quad \text{and} \quad a = 27b^2 p_c = 3V_c^2 p_c.$$

Substituting the critical constants

$$b = \frac{148 \text{ cm}^3 \text{ mol}^{-1}}{3} = 49.3 \text{ cm}^3 \text{ mol}^{-1} = 0.0493 \text{ dm}^3 \text{ mol}^{-1}$$

and  $a = 3 \times (0.148 \text{ dm}^3 \text{ mol}^{-1})^2 \times (48.20 \text{ atm}) = 3.17 \text{ dm}^6 \text{ atm mol}^{-2}$

But this problem is overdetermined. We have another piece of information

$$T_c = \frac{8a}{27Rb}$$

If we use  $T_c$  along with  $V_c$  as above, we would arrive at the same value of  $b$  along with

$$\begin{aligned} a &= \frac{27RbT_c}{8} = \frac{9RV_cT_c}{8} \\ &= \frac{9(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})(0.148 \text{ dm}^3 \text{ mol}^{-1})(305.4 \text{ K})}{8} \\ &= 4.17 \text{ dm}^6 \text{ atm mol}^{-2} \end{aligned}$$

Or we could use  $T_c$  along with  $p_c$ . In that case, we can solve the pair of equations for  $a$  and  $b$  by first setting the two expressions for  $a$  equal to each other:

$$a = 27b^2p_c = \frac{27RbT_c}{8}$$

Solving the resulting equation for  $b$  yields

$$b = \frac{RT_c}{8p_c} = \frac{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})(305.4 \text{ K})}{8(48.20 \text{ atm})} = 0.06499 \text{ dm}^3 \text{ mol}^{-1}$$

and then

$$a = 27(0.06499 \text{ dm}^3 \text{ mol}^{-1})^2(48.20 \text{ atm}) = 5.497 \text{ dm}^6 \text{ atm mol}^{-2}$$

These results are summarized in the following table

Using	$a/\text{dm}^6 \text{ atm mol}^{-2}$	$b/\text{dm}^3 \text{ mol}^{-1}$
$V_c$ & $p_c$	3.17	0.0493
$V_c$ & $T_c$	4.17	0.0493
$p_c$ & $T_c$	5.497	0.06499

One way of selecting best values for these parameters would be to take the mean of the three determinations, namely  $a = 4.28 \text{ dm}^6 \text{ atm mol}^{-2}$  and  $b = 0.0546 \text{ dm}^3 \text{ mol}^{-1}$ .

By interpreting  $b$  as the excluded volume of a mole of spherical molecules, we can obtain an estimate of molecular size. The centres of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e., twice their radius); that volume times the Avogadro constant is the molar excluded volume  $b$

$$\begin{aligned} b &= N_A \left( \frac{4\pi(2r)^3}{3} \right) \quad \text{so} \quad r = \frac{1}{2} \left( \frac{3b}{4\pi N_A} \right)^{1/3} \\ r &= \frac{1}{2} \left( \frac{3(0.0546 \text{ dm}^3 \text{ mol}^{-1})}{4\pi(6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 1.39 \times 10^{-9} \text{ dm} = 0.139 \text{ nm} \end{aligned}$$

**1C.7(b)** The Boyle temperature,  $T_B$ , is the temperature at which the virial coefficient  $B = 0$ . In order to express  $T_B$  in terms of  $a$  and  $b$ , the van der Waals equation [1C.5b] must be recast into the form of the virial equation.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Factoring out  $\frac{RT}{V_m}$  yields  $p = \frac{RT}{V_m} \left\{ \frac{1}{1 - b/V_m} - \frac{a}{RTV_m} \right\}$

So long as  $b/V_m < 1$ , the first term inside the brackets can be expanded using

$$(1-x)^{-1} = 1 + x + x^2 + \dots,$$

which gives

$$p = \frac{RT}{V_m} \left\{ 1 + \left( b - \frac{a}{RT} \right) \times \left( \frac{1}{V_m} \right) + \dots \right\}$$

We can now identify the second virial coefficient as  $B = b - \frac{a}{RT}$

At the Boyle temperature

$$B = 0 = b - \frac{a}{RT_B} \quad \text{so} \quad T_B = \frac{a}{bR} = \frac{27T_c}{8}$$

(i) From Table 1C.3,  $a = 4.484 \text{ dm}^6 \text{ atm mol}^{-2}$  and  $b = 0.0434 \text{ dm}^3 \text{ mol}^{-1}$ . Therefore,

$$T_B = \frac{(4.484 \text{ dm}^6 \text{ atm mol}^{-2})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (0.0434 \text{ dm}^3 \text{ mol}^{-1})} = \boxed{1259 \text{ K}}$$

(ii) As in Exercise 1C.6(b),

$$b = N_A \left( \frac{4\pi(2r)^3}{3} \right) \quad \text{so} \quad r = \frac{1}{2} \left( \frac{3b}{4\pi N_A} \right)^{1/3}$$

$$r = \frac{1}{2} \left( \frac{3(0.0434 \text{ dm}^3 \text{ mol}^{-1})}{4\pi(6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 1.29 \times 10^{-9} \text{ dm} = 1.29 \times 10^{-10} \text{ m} = \boxed{0.129 \text{ nm}}$$

**1C.8(b)** States that have the same reduced pressure, temperature, and volume [1C.8] are said to correspond. The reduced pressure and temperature for  $\text{N}_2$  at 1.0 atm and  $25^\circ\text{C}$  are [Table 1C.2]

$$p_r = \frac{p}{p_c} = \frac{1.0 \text{ atm}}{33.54 \text{ atm}} = 0.030 \quad \text{and} \quad T_r = \frac{T}{T_c} = \frac{(25 + 273) \text{ K}}{126.3 \text{ K}} = 2.36$$

The corresponding states are

(i) For  $\text{H}_2\text{S}$  (critical constants obtained from *NIST Chemistry WebBook*)

$$T = 2.36(373.3 \text{ K}) = \boxed{881 \text{ K}}$$

$$p = 0.030(89.7 \text{ atm}) = \boxed{2.67 \text{ atm}}$$

(ii) For  $\text{CO}_2$

$$T = 2.36(304.2 \text{ K}) = \boxed{718 \text{ K}}$$

$$p = 0.030(72.9 \text{ atm}) = \boxed{2.2 \text{ atm}}$$

(iii) For Ar

$$T = 2.36(150.7 \text{ K}) = \boxed{356 \text{ K}}$$

$$p = 0.030(48.0 \text{ atm}) = \boxed{1.4 \text{ atm}}$$

**1C.9(b)** The van der Waals equation [1C.5b] is

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

which can be solved for  $b$

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

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

The compression factor is

$$Z = \frac{pV_m}{RT} [1C.2] = \frac{(4.0 \times 10^6 \text{ Pa}) \times (4.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (288 \text{ K})} = \boxed{0.67}$$

## Solutions to problems

**1C.2** From the definition of  $Z$  [1C.1] and the virial equation [1C.3b],  $Z$  may be expressed in virial form as

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



Since  $V_m = \frac{RT}{p}$  (by assumption of approximate perfect gas behavior),  $\frac{1}{V_m} = \frac{p}{RT}$ ; hence upon substitution, and dropping terms beyond the second power of  $\left(\frac{1}{V_m}\right)$

$$\begin{aligned}
 Z &= 1 + B\left(\frac{p}{RT}\right) + C\left(\frac{p}{RT}\right)^2 \\
 &= 1 + (-21.7 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}) \times \left(\frac{100 \text{ atm}}{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (273 \text{ K})}\right) \\
 &\quad + (1.200 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2}) \times \left(\frac{100 \text{ atm}}{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (273 \text{ K})}\right)^2 \\
 &= 1 - 0.0968 + 0.0239 = \boxed{0.927} \\
 V_m &= (0.927) \left(\frac{RT}{p}\right) \\
 &= (0.927) \left(\frac{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{100 \text{ atm}}\right) = \boxed{0.208 \text{ dm}^3}
 \end{aligned}$$

**Question.** What is the value of  $Z$  obtained from the next approximation using the value of  $V_m$  just calculated? Which value of  $Z$  is likely to be more accurate?

**1C.4** Since  $B'(T_B) = 0$  at the Boyle temperature [Topic 1.3b]:  $B'(T_B) = a + be^{-c/T_B^2} = 0$

$$\text{Solving for } T_B: \quad T_B = \left\{ \frac{-c}{\ln\left(\frac{-a}{b}\right)} \right\}^{1/2} = \left\{ \frac{-(1131 \text{ K}^2)}{\ln\left(\frac{-(-0.1993 \text{ bar}^{-1})}{(0.2002 \text{ bar}^{-1})}\right)} \right\}^{1/2} = \boxed{5.0 \times 10^2 \text{ K}}$$

**1C.6** From Table 1C.4  $T_c = \left(\frac{2}{3}\right) \times \left(\frac{2a}{3bR}\right)^{1/2}$ ,  $p_c = \left(\frac{1}{12}\right) \times \left(\frac{2aR}{3b^3}\right)^{1/2}$

$$\left(\frac{2a}{3bR}\right)^{1/2} \text{ may be solved for from the expression for } p_c \text{ and yields } \left(\frac{12bp_c}{R}\right).$$

$$\begin{aligned}
 \text{Thus } T_c &= \left(\frac{2}{3}\right) \times \left(\frac{12p_c b}{R}\right) = \left(\frac{8}{3}\right) \times \left(\frac{p_c V_c}{R}\right) \\
 &= \left(\frac{8}{3}\right) \times \left(\frac{(40 \text{ atm}) \times (160 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1})}{0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}}\right) = \boxed{210 \text{ K}}
 \end{aligned}$$

By interpreting  $b$  as the excluded volume of a mole of spherical molecules, we can obtain an estimate of molecular size. The centres of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e., twice their radius); that volume times the Avogadro constant is the molar excluded volume  $b$

$$\begin{aligned}
 b &= N_A \left(\frac{4\pi(2r)^3}{3}\right) \quad \text{so} \quad r = \frac{1}{2} \left(\frac{3b}{4\pi N_A}\right)^{1/3} \quad [\text{Exercise 1C.6(b)}] = \frac{1}{2} \left(\frac{V_c}{4\pi N_A}\right)^{1/3} \\
 r &= \frac{1}{2} \left(\frac{160 \text{ cm}^3 \text{ mol}^{-1}}{4\pi(6.022 \times 10^{23} \text{ mol}^{-1})}\right)^{1/3} = 1.38 \times 10^{-8} \text{ cm} = \boxed{0.138 \text{ nm}}
 \end{aligned}$$

**1C.8** Substitute the van der Waals equation [1C.5b] into the definition of the compression factor [1C.2]

$$Z = \frac{pV_m}{RT} = \frac{1}{\left(1 - \frac{b}{V_m}\right)} - \frac{a}{RTV_m} \quad [\text{Exercise 1C.7(a)}]$$

which upon expansion of  $\left(1 - \frac{b}{V_m}\right)^{-1} = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \dots$  yields

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

We note that all terms beyond the second are necessarily positive, so only if

$$\frac{a}{RTV_m} > \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \dots$$

can  $Z$  be less than one. If we ignore terms beyond  $\frac{b}{V_m}$ , the conditions are simply stated as

$$Z < 1 \quad \text{when} \quad \frac{a}{RT} > b \quad Z > 1 \quad \text{when} \quad \frac{a}{RT} < b$$

Thus  $Z < 1$  when attractive forces predominate and when there is insufficient thermal energy to disrupt those forces, and  $Z > 1$  when size effects (short-range repulsions) predominate.

#### 1C.10 The Dieterici equation is

$$p = \frac{RTe^{-a/RTV_m}}{V_m - b} \quad [\text{Table 1C.4}]$$

At the critical point the derivatives of  $p$  with respect to  $V_m$  equal zero along the isotherm defined by  $T = T_c$ . This means that  $(\partial p / \partial V_m)_T = 0$  and  $(\partial^2 p / \partial V_m^2)_T = 0$  at the critical point.

$$\left(\frac{\partial p}{\partial V_m}\right)_T = p \left\{ \frac{aV_m - ab - RTV_m^2}{V_m^2(V_m - b)(RT)} \right\}$$

and

$$\left(\frac{\partial^2 p}{\partial V_m^2}\right)_T = \left(\frac{\partial p}{\partial V_m}\right)_T \left\{ \frac{aV_m - ab - RTV_m^2}{V_m^2(V_m - b)(RT)} \right\} + p \frac{(-2aV_m^2 + 4V_m ab + RTV_m^3 - 2ab^2)}{\{V_m^3[(V_m - b)^2(RT)]\}}$$

Setting the Dieterici equation equal to the critical pressure and making the two derivatives vanish at the critical point yields three equations:

$$p_c = \frac{RT_c e^{-a/RT_c V_c}}{V_c - b} \quad aV_c - ab - RT_c V_c^2 = 0$$

$$\text{and} \quad -2aV_c^2 + 4V_c ab + RT_c V_c^3 - 2ab^2 = 0$$

Solving the middle equation for  $T_c$ , substitution of the result into the last equation, and solving for  $V_c$  yields the result

$$V_c = 2b \quad \text{or} \quad b = V_c / 2$$

(The solution  $V_c = b$  is rejected because there is a singularity in the Dieterici equation at the point  $V_m = b$ .) Substitution of  $V_c = 2b$  into the middle equation and solving for  $T_c$  gives the result

$$T_c = a / 4bR \quad \text{or} \quad a = 2RT_c V_c$$

Substitution of  $V_c = 2b$  and  $T_c = a / 4bR$  into the first equation gives

$$p_c = \frac{ae^{-2}}{4b^2} = \frac{2RT_c e^{-2}}{V_c}$$

The equations for  $V_c$ ,  $T_c$ ,  $p_c$  are substituted into the equation for the critical compression factor [1C.7] to give

$$Z_c = \frac{p_c V_c}{RT_c} = 2e^{-2} = 0.2707.$$

This is significantly lower than the critical compression factor that is predicted by the van der Waals equation:  $Z_c(\text{vdW}) = p_c V_c / RT_c = 3/8 = 0.3750$ . Experimental values for  $Z_c$  are

summarized in Table 1C.2 where it is seen that the Dieterici equation prediction is often better.

$$1C.12 \quad \frac{pV_m}{RT} = 1 + B'p + C'p^2 + \dots \quad [1C.3a]$$

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \quad [1C.3b]$$

$$\text{Thus} \quad B'p + C'p^2 + \dots = \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

Multiply through by  $V_m$ , replace  $pV_m$  by  $RT\{1+(B/V_m) + \dots\}$ , and equate coefficients of powers of  $1/V_m$ :

$$B'RT + \frac{BB'RT + C'R^2T^2}{V_m} + \dots = B + \frac{C}{V_m} + \dots$$

$$\text{Hence, } B'RT = B, \text{ implying that } \boxed{B' = \frac{B}{RT}}$$

$$\text{Also } BB'RT + C'R^2T^2 = C = B^2 + C'R^2T^2, \text{ implying that } \boxed{C' = \frac{C - B^2}{R^2T^2}}$$

$$1C.14 \quad \text{Write } V_m = f(T, p); \text{ then } dV_m = \left(\frac{\partial V_m}{\partial T}\right)_p dT + \left(\frac{\partial V_m}{\partial p}\right)_T dp$$

Restricting the variations of  $T$  and  $p$  to those which leave  $V_m$  constant, that is  $dV_m = 0$ , we obtain

$$\left(\frac{\partial V_m}{\partial T}\right)_p = -\left(\frac{\partial V_m}{\partial p}\right)_T \times \left(\frac{\partial p}{\partial T}\right)_{V_m} = -\left(\frac{\partial p}{\partial V_m}\right)_T^{-1} \times \left(\frac{\partial p}{\partial T}\right)_{V_m}$$

From the equation of state

$$\left(\frac{\partial p}{\partial V_m}\right)_T = -\frac{RT}{V_m^2} - \frac{2(a+bT)}{V_m^3} = -\frac{V_m RT + 2(a+bT)}{V_m^3}$$

$$\text{and} \quad \left(\frac{\partial p}{\partial T}\right)_{V_m} = \frac{R}{V_m} + \frac{b}{V_m^2} = \frac{RV_m + b}{V_m^2}$$

Substituting

$$\left(\frac{\partial V_m}{\partial T}\right)_p = \left(\frac{V_m^3}{V_m RT + 2(a+bT)}\right) \left(\frac{RV_m + b}{V_m^2}\right) = \frac{RV_m^2 + bV_m}{V_m RT + 2(a+bT)}$$

From the equation of state,  $a + bT = pV_m^2 - RTV_m$

$$\text{Then} \quad \left(\frac{\partial V_m}{\partial T}\right)_p = \frac{RV_m^2 + bV_m}{V_m RT + 2pV_m^2 - 2RTV_m} = \boxed{\frac{RV_m + b}{2pV_m - RT}}$$

$$1C.16 \quad Z = \frac{V_m}{V_m^\circ} \quad [1C.1], \text{ where } V_m^\circ = \text{the molar volume of a perfect gas}$$

From the given equation of state

$$V_m = b + \frac{RT}{p} = b + V_m^\circ$$

For  $V_m = 10b$ , we have  $10b = b + V_m^\circ$ , so  $V_m^\circ = 9b$ .

$$\text{Then } Z = \frac{10b}{9b} = \boxed{\frac{10}{9} = 1.11}$$

1C.18 The virial equation is

$$pV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots\right) \quad [1C.3b]$$

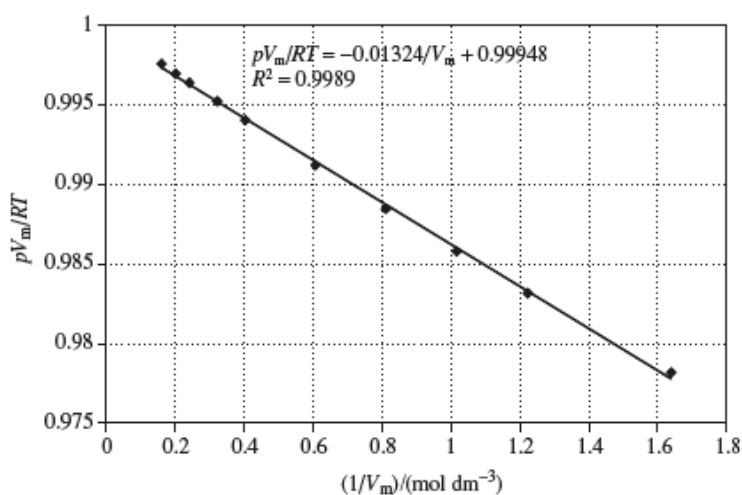
or 
$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

(a) If we assume that the series may be truncated after the  $B$  term, then a plot of  $\frac{pV_m}{RT}$  vs  $\frac{1}{V_m}$

will have  $B$  as its slope and 1 as its y-intercept. Transforming the data gives

$p/\text{MPa}$	$V_m/(\text{dm}^3 \text{ mol}^{-1})$	$(1/V_m)/(\text{mol dm}^{-3})$	$pV_m/RT$
0.4000	6.2208	0.1608	0.9976
0.5000	4.9736	0.2011	0.9970
0.6000	4.1423	0.2414	0.9964
0.8000	3.1031	0.3223	0.9952
1.000	2.4795	0.4033	0.9941
1.500	1.6483	0.6067	0.9912
2.000	1.2328	0.8112	0.9885
2.500	0.98357	1.017	0.9858
3.000	0.81746	1.223	0.9832
4.000	0.60998	1.639	0.9782

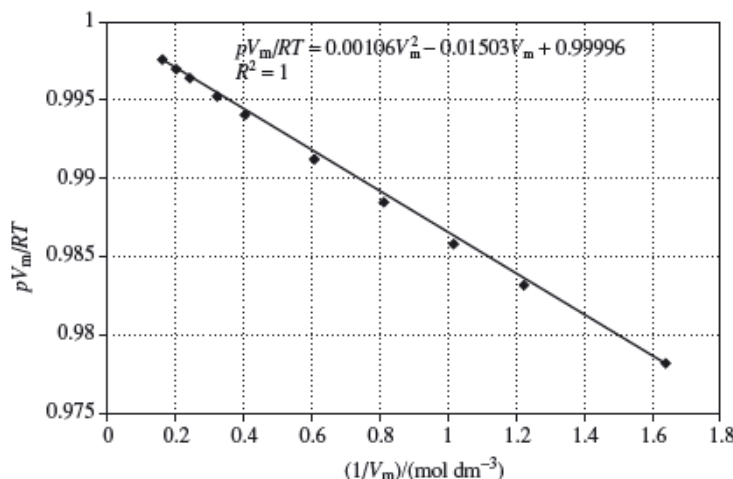
Figure 1C.1(a)



The data are plotted in Figure 1C.1(a). The data fit a straight line reasonably well, and the y-intercept is very close to 1. The regression yields  $B = [-1.324 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}]$ .

(b) A quadratic function fits the data somewhat better (Figure 1C.1(b)) with a slightly better correlation coefficient and a y-intercept closer to 1. This fit implies that truncation of the virial series after the term with  $C$  is more accurate than after just the  $B$  term. The regression then yields

Figure 1C.1(b)



$$B = \boxed{-1.503 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}} \quad \text{and} \quad C = \boxed{-1.06 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2}}$$

**1C.20** The perfect gas equation [1A.5] gives

$$V_m = \frac{RT}{p} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(250 \text{ K})}{150 \times 10^3 \text{ Pa}} = 0.0139 \text{ m}^3 = 13.9 \text{ dm}^3$$

The van der Waals equation [1C.5b] is a cubic equation in  $V_m$ . Cubic equations can be solved analytically. However, this approach is cumbersome, so we proceed as in Example 1C.1. The van der Waals equation is rearranged to the cubic form

$$V_m^3 - \left(b + \frac{RT}{p}\right)V_m^2 + \left(\frac{a}{p}\right)V_m - \frac{ab}{p} = 0$$

$$\text{or} \quad x^3 - \left(b + \frac{RT}{p}\right)x^2 + \left(\frac{a}{p}\right)x - \frac{ab}{p} = 0 \quad \text{with} \quad x = V_m/(\text{dm}^3 \text{ mol}^{-1}).$$

It will be convenient to have the pressure in atm:

$$150 \text{ kPa} \times \frac{1 \text{ atm}}{101.3 \text{ kPa}} = 1.48 \bar{1} \text{ atm}$$

The coefficients in the equation are

$$\begin{aligned} b + \frac{RT}{p} &= (5.42 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}) + \frac{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (250 \text{ K})}{1.48 \bar{1} \text{ atm}} \\ &= (5.42 \times 10^{-2} + 13.8 \bar{5}) \text{ dm}^3 \text{ mol}^{-1} = 13.9 \bar{1} \text{ dm}^3 \text{ mol}^{-1} \end{aligned}$$

$$\frac{a}{p} = \frac{6.260 \text{ dm}^6 \text{ atm mol}^{-2}}{1.48 \bar{1} \text{ atm}} = 4.23 \text{ dm}^6 \text{ mol}^{-2}$$

$$\frac{ab}{p} = \frac{(6.260 \text{ dm}^6 \text{ atm mol}^{-2}) \times (5.42 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})}{1.48 \bar{1} \text{ atm}} = 2.29 \bar{1} \times 10^{-2} \text{ dm}^9 \text{ mol}^{-3}$$

Thus, the equation to be solved is  $x^3 - 13.9 \bar{1}x^2 + 4.23x - (2.29 \bar{1} \times 10^{-2}) = 0$ .

Calculators and computer software for the solution of polynomials are readily available. In this case we find

$$x = 13.6 \text{ and} \quad V_m = \boxed{13.6 \text{ dm}^3 \text{ mol}^{-1}}.$$

Taking the van der Waals result to be more accurate, the error in the perfect-gas value is

$$\frac{13.9 - 13.6}{13.6} \times 100\% = \boxed{2\%}$$