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Topic 1A The perfect gas

1A.1 The molar volume of a substance is, from eqn 1A.9a, the volume of a sample divided by the amount of molecules it contains, $V_m = V/n$. For a perfect gas, the equation of state is given by eqn 1A.5a. Rearranging, and noting that the temperature should be expressed in units of kelvin, and pressure in units of pascal,

$$V_m = \frac{V}{n} = \frac{RT}{p}$$
$$= \frac{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (273.15 + 0.0)\text{K}}{(1.000 \text{ atm}) \times \underbrace{(1.01325 \times 10^5 \text{ Pa atm}^{-1})}_{1 \text{ atm}=1.01325\times10^5 \text{ Pa}}}$$
$$= 22.41 \times 10^{-3} \text{ J Pa}^{-1} \text{ mol}^{-1}$$

The units appear rather strange, until we realise that $1 \text{ Pa} = 1 \text{ J m}^{-3}$, so that

$$V_m = 22.41 \times 10^{-3} \text{ J Pa}^{-1} \text{ mol}^{-1}$$
$$= 22.41 \times 10^{-3} \text{ J (J m}^{-3})^{-1} \text{ mol}^{-1}$$
$$= 22.41 \times 10^{-3} \text{ m}^3\text{mol}^{-1}$$

or, because $10^{-3} \text{ m}^3 = 1 \text{ dm}^3$

$$V_m = \mathbf{22.41 \text{ dm}^3 \text{ mol}^{-1}}$$

1A.2 Using the perfect gas equation of state, eqn 1A.5a,

$$pV = nRT$$

and noting that the amount of carbon dioxide molecules is given by the ratio of the mass to the molar mass, $n = m/M$, then rearranging,

$$p = \frac{nRT}{V} = \frac{(m/M)RT}{V}$$

The molar mass of carbon dioxide is

$$M = \{12.01 + 2 \times (16.00)\} \text{ g mol}^{-1} = 44.01 \text{ g mol}^{-1}$$

so that, substituting,

$$p = \frac{\{(1.22\ \text{g})/(44.01\ \text{g mol}^{-1})\} \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (273.15 + 37)\text{K}}{\underbrace{(500 \times 10^{-3}\ \text{m}^3)}_{1\ \text{dm}^3 = 10^{-3}\ \text{m}^3}}$$

$$= \underbrace{143\ \text{J m}^{-3}}_{1\ \text{J m}^{-3} = 1\ \text{Pa}} = \mathbf{143\ Pa}$$

1A.3 From the combined gas equation, eqn 1A.10, for the change in the pressure, volume and temperature of a fixed amount of gas,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

Rearranging, and remembering to convert the temperature into units of kelvin, the final pressure is

$$p_2 = \frac{p_1 V_1}{T_1} \times \frac{T_2}{V_2} = p_1 \times \frac{V_1}{V_2} \times \frac{T_2}{T_1}$$

$$= (1.00\ \text{bar}) \times \frac{(20.0\ \text{dm}^3)}{(10.0\ \text{dm}^3)} \times \frac{(273.15 + 25)\ \text{K}}{(273.15 + 100)\ \text{K}}$$

$$= \mathbf{1.60\ bar}$$

1A.4 The partial pressure of a component in a gas is defined in terms of the mole fraction of the component and the total pressure through eqn 1A.12, as $p_J = x_J p$. The mole fraction is, in turn, defined through eqn 1A.13a, as $x_J = n_J/n$, where the amount of each gas may be calculated from the ratio of the mass to the molar mass, $n_J = m_J/M_J$. Thus, combining these equations,

$$p_J = x_J p = \frac{n_J}{n} p = \frac{n_J}{n_A + n_B + \cdots} p = \frac{(m_J/M_J)}{(m_A/M_A) + (m_B/M_B) + \cdots} p$$

The molar mass of oxygen, O_2, is

$$M_{O_2} = (2 \times 16.00)\ \text{g mol}^{-1} = 32.00\ \text{g mol}^{-1}$$

and carbon dioxide, CO_2, is

$$M_{CO_2} = \{12.01 + (2 \times 16.00)\}\ \text{g mol}^{-1} = 44.01\ \text{g mol}^{-1}$$

Hence, for this binary mixture,

$$p_{O_2} = \frac{(m_{O_2}/M_{O_2})}{(m_{O_2}/M_{O_2}) + (m_{CO_2}/M_{CO_2})} p$$

$$= \frac{\{(2.50\ \text{g})/(32.00\ \text{g mol}^{-1})\}}{\{(2.50\ \text{g})/(32.00\ \text{g mol}^{-1})\} + \{(6.43\ \text{g})/(44.01\ \text{g mol}^{-1})\}} \times (88\ \text{kPa})$$

$$= \mathbf{31\ kPa}$$

and

$$p_{CO_2} = \frac{(m_{CO_2}/M_{CO_2})}{(m_{O_2}/M_{O_2}) + (m_{CO_2}/M_{CO_2})} p$$

$$= \frac{\{(6.43\ \text{g})/(44.01\ \text{g mol}^{-1})\}}{\{(2.50\ \text{g})/(32.00\ \text{g mol}^{-1})\} + \{(6.43\ \text{g})/(44.01\ \text{g mol}^{-1})\}} \times (88\ \text{kPa})$$

$$= \mathbf{57\ kPa}$$

Topic 1B   The kinetic model of gases

1B.1   Using eqn 1B.5, the mean speed of the cars is

$$v_{mean} = \left(\frac{8}{3\pi}\right)^{1/2} v_{rms}$$

$$= 0.921 \times (50.2\ \text{km h}^{-1})$$

$$= \mathbf{46.2\ km\ h^{-1}}$$

Alternatively, working from first principles,

$$v_{mean} = \left\{\frac{5 \times (45.0\ \text{km h}^{-1}) + 7 \times (47.0\ \text{km h}^{-1}) + \cdots + 5 \times (57.0\ \text{km h}^{-1})}{5 + 7 + \cdots + 5}\right\}$$

$$= \mathbf{50.0\ km\ h^{-1}}$$

The difference arises because the total number of cars is not sufficiently large for the relationship between the root-mean-square speed and mean speed to be exact.

1B.2   From eqn 1B.7a, the root-mean-square speed is

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

The molar mass of H_2 is

$$M = (2 \times 1.01)\ \text{g mol}^{-1} = 2.02 \times 10^{-3}\ \text{kg mol}^{-1}$$

so that

$$M = \left\{\frac{3 \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (273.15 + 25)\ \text{K}}{(2.02 \times 10^{-3}\ \text{kg mol}^{-1})}\right\}^{1/2}$$

$$= 1920\ (\text{J kg}^{-1})^{1/2} = \mathbf{1920\ m\ s^{-1}}$$

1B.3   The mean speed and root-mean-square speed are related through eqn 1B.5, $v_{mean} = 0.921\ v_{rms}$. This relationship is independent of temperature and so remains constant. Thus, the ratio of the mean speeds must be the same as the ratio of the rms speeds, 0.957.

1B.4   Graham's law of effusion, eqn 1B.9, indicates that at a given pressure and temperature, the rate of effusion of a gas is inversely proportional to the square root

of its molar mass. Thus, the relative rate of effusion of argon atoms and nitrogen molecules is given by

$$\frac{v_{N_2}}{v_{Ar}} = \frac{M_{Ar}^{1/2}}{M_{N_2}^{1/2}} = \left(\frac{M_{Ar}}{M_{N_2}}\right)^{1/2}$$

This ratio refers to the amount of atoms or molecules escaping, rather than the mass, so that the amount of nitrogen escaping is

$$n_{N_2} = \frac{v_{N_2}}{v_{Ar}} \times n_{Ar}$$

Remembering that we may express the amount of a component in terms of the mass and the molar mass, $n_J = m_J/M_J$, then,

$$m_{N_2} = n_{N_2} \times M_{N_2} = \overbrace{\left\{\frac{v_{N_2}}{v_{Ar}} \times n_{Ar}\right\}}^{n_{N_2}} \times M_{N_2}$$

$$= \frac{v_{N_2}}{v_{Ar}} \times \overbrace{\left(\frac{m_{Ar}}{M_{Ar}}\right)}^{n_{Ar}} \times M_{N_2}$$

$$= \left\{\left(\frac{M_{Ar}}{M_{N_2}}\right)^{1/2} \times \left(\frac{M_{N_2}}{M_{Ar}}\right)\right\} \times m_{Ar}$$

$$= \left(\frac{M_{N_2}}{M_{Ar}}\right)^{1/2} \times m_{Ar}$$

$$= \left\{\frac{(2 \times 14.01 \text{ g mol}^{-1})}{39.95 \text{ g mol}^{-1}}\right\}^{1/2} \times (5.0 \text{ g})$$

$$= \mathbf{4.2 \text{ g}}$$

1B.5   For a Cl_2 molecule the collision cross-section is 0.93 nm^2 and the molar mass is $M = 70.90$ g mol^{-1}. Thus, from eqn 1B.12, the collision frequency is

$$z = \frac{2\sigma p}{kT}\left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$= \frac{2 \times (0.93 \times 10^{-18} \text{m}^2) \times \overbrace{(1 \times 10^5 \text{ Pa})}^{1 \text{ bar}=10^5 \text{Pa}}}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (273 + 25) \text{ K}}$$

$$\times \left\{\frac{8 \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (273 + 25) \text{ K}}{\pi \times (70.90 \times 10^{-3} \text{ kg mol}^{-1})}\right\}^{1/2}$$

$$= 10 \times 10^9 \text{ s}^{-1} = \mathbf{10 \text{ ns}^{-1}}$$

which equates to 10 collisions every nanosecond.

Topic 1C Real gases

1C.1   The compression factor is defined by eqn 1C.1a

$$Z = \frac{V_m}{V_m^{perfect}} = \frac{1.12 \times V_m^{perfect}}{V_m^{perfect}} = 1.12$$

The compression factor may also be written as eqn 1C.1b so that, rearranging and noting that 1 atm $= 1.01325 \times 10^5$ Pa,

$$V_m = \frac{ZRT}{p}$$
$$= \frac{(1.12) \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (350 \text{ K})}{(12 \text{ atm}) \times (1.01325 \times 10^5 \text{ Pa atm}^{-1})}$$
$$= 2.7 \times 10^{-3} \text{ J Pa}^{-1}\text{mol}^{-1} = 2.7 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} = \mathbf{2.7\ dm^3\ mol^{-1}}$$

where the units follow because 1 Pa $= 1$ J m^{-3}, and 10^{-3} m$^3 = 1$ dm^3.

The volume of the gas is larger than the volume of a perfect gas under equivalent conditions. This implies that repulsive interactions are dominant, forcing the molecules further apart than expected for a perfect gas.

1C.2   Rearranging the virial equation of state, eqn 1C.3,

$$p = \left(\frac{B}{V_m} + 1\right)\frac{RT}{V_m}$$
$$= \left\{ \frac{\overbrace{(-45.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}^{1 \text{ cm}^3 = 10^{-6}\text{m}^3}}{\underbrace{(1.00 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})}_{1 \text{ dm}^3 = 10^{-3} \text{ m}^3}} + 1 \right\} \times \left\{ \frac{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (573 \text{ K})}{(1.00 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})} \right\}$$
$$= \overbrace{45.5 \times 10^5 \text{ Pa}}^{1 \text{ bar} = 10^5 \text{Pa}} = \mathbf{45.5\ bar}$$

Answers to exercises

Topic 1A The perfect gas

1A.1   We may use the values for the atmospheric pressure expressed in different units to derive conversion factors. Because 1 atm $= 1.01325$ bar $= 101.325$ kPa $= 760$ torr,

(a) a pressure of 108 kPa corresponds to

$$108 \text{ kPa} \times \frac{760 \text{ Torr}}{101.325 \text{ kPa}} = \mathbf{810\ torr}$$

(b) 0.975 bar to

$$0.975 \text{ bar} \times \frac{1 \text{ atm}}{1.01325 \text{ bar}} = \mathbf{0.962\ atm}$$

(c) 22.5 kPa to

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

(d) 770 Torr to

$$770 \text{ Torr} \times \frac{101325 \text{ Pa}}{760 \text{ Torr}} = \mathbf{1.03 \times 10^5 \text{ Pa}}$$

1A.2   Applying the perfect gas equation of state, eqn 1A.5a, and paying particular attention to the units,

$$
\begin{aligned}
p = \frac{nRT}{V} &= \frac{\overbrace{(m/M)}^{n} RT}{V} \\
&= \frac{\{(3.055 \text{ g})/(28.02 \text{ g mol}^{-1})\} \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (273.15 + 32) \text{ K}}{\underbrace{(3.00 \times 10^{-3} \text{ m}^3)}_{1 \text{ dm}^3 = 10^{-3} \text{ m}^3}} \\
&= \underbrace{92 \times 10^3 \text{ J m}^{-3}}_{1 \text{ J m}^{-3} = 1 \text{ Pa}} = 92 \times 10^3 \text{ Pa} = \mathbf{92 \text{ kPa}}
\end{aligned}
$$

1A.3   Applying the perfect gas equation of state, eqn 1A.5a, and expressing the amount of neon in terms of the mass and molar mass,

$$
\begin{aligned}
p = \frac{nRT}{V} &= \frac{\overbrace{(m/M)}^{n} RT}{V} \\
&= \frac{\{(425 \times 10^{-3} \text{ g})/(20.18 \text{ g mol}^{-1})\} \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (77 \text{ K})}{\underbrace{(6.00 \times 10^{-3} \text{ m}^3)}_{1 \text{ dm}^3 = 10^{-3} \text{ m}^3}} \\
&= \underbrace{2.25 \times 10^3 \text{ J m}^{-3}}_{1 \text{ J m}^{-3} = 1 \text{ Pa}} = 2.25 \times 10^3 \text{ Pa} = \mathbf{2.25 \text{ kPa}}
\end{aligned}
$$

1A.4   Rearranging the perfect gas equation, eqn 1A.5a,

$$
\begin{aligned}
n = \frac{pV}{RT} &= \frac{(34.5 \times 10^3 \text{ Pa}) \times \overbrace{(300.0 \times 10^{-6} \text{ m}^3)}^{1 \text{ cm}^3 = 10^{-6} \text{m}^3}}{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (273.15 + 14.5) \text{ K}} \\
&= 4.33 \times 10^{-3} \text{ mol} = \mathbf{4.33 \text{ mmol}}
\end{aligned}
$$

1A.5   We may use the difference in mass between the full and empty cylinder to derive an expression for the amount of carbon dioxide molecules present

$$n = m/M = (m_{\text{full}} - m_{\text{empty}})/M$$

Substituting into the perfect gas equation, eqn 1A.5a,

$$
\begin{aligned}
p = \frac{nRT}{V} &= \frac{(m_{\text{full}} - m_{\text{empty}})RT}{MV} \\
&= \frac{\{(1.04 - 0.74) \text{ kg}\} \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times \{(273.15 + 20)\text{K}\}}{(44.01 \times 10^{-3} \text{ kg mol}^{-1}) \times \underbrace{(250 \times 10^{-6} \text{ m}^3)}_{1 \text{ cm}^3 = 10^{-6}\text{m}^3}}
\end{aligned}
$$

$$= 6.6 \times 10^7 \text{ Pa} = \mathbf{660\ bar}$$

1A.6   Boyle's law, eqn 1A.6, states that p is inversely proportional to V at constant temperature, $p \propto 1/V$. It follows from eqn 1A.10, that if temperature is constant,

$$p_1 V_1 = p_2 V_2$$

Thus, denoting the original conditions as p_1 and V_1 and the final conditions as p_2 and V_2,

$$p_2 = \frac{p_1 V_1}{V_2} = \frac{(1.00 \text{ atm}) \times (1.00 \text{ dm}^3)}{\underbrace{(100 \times 10^{-3} \text{ dm}^3)}_{1 \text{ cm}^3 = 10^{-3} \text{dm}^3}} = \mathbf{10.0\ atm}$$

1A.7   For a perfect gas, pressure is proportional to temperature. We may see from eqn 1A.10, that for a fixed volume and amount of gas, the ratio of pressure and temperature remains constant

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Thus, denoting the original conditions as p_1 and T_1 and the final conditions as p_2 and T_2,

$$p_2 = \frac{p_1 T_2}{T_1} = \frac{125 \text{ kPa} \times (273.15 + 700)\text{K}}{(273.15 + 18)\text{K}} = \mathbf{418\ kPa}$$

1A.8   Following the method used in *Exercise* 1A.6,

$$p_2 = \frac{p_1 V_1}{V_2} = \frac{(101 \text{ kPa}) \times (7.20 \text{ dm}^3)}{(4.21 \text{ dm}^3)} = \mathbf{173\ kPa}$$

1A.9   Charles's law, eqn 1A.7, states that volume is proportional to temperature at constant pressure, $V \propto T$. It follows from eqn 1A.10, that if pressure is constant,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Thus, denoting the original conditions as V_1 and T_1 and the final conditions as V_2 and T_2,

$$T_2 = \frac{V_2 T_1}{V_1} = \frac{(0.100 \text{ dm}^3) \times (273.15 + 22.2)\text{K}}{(1.00 \text{ dm}^3)} = 29.5 \text{ K}$$

which is equivalent to

$$\theta = (29.5 - 273.15)\ °\text{C} = \mathbf{-243.6\ °C}$$

1A.10   We may follow the same method as in the previous exercise. If the volume of the sample increases by 25 per cent, then $V_2/V_1 = 1.25$, so that the temperature of the air must be heated to

$$T_2 = \frac{V_2}{V_1}T_1 = 1.25 \times (315\ \text{K}) = \mathbf{394\ K}$$

1A.11   Rearranging eqn 1A.10, which expresses the relationship between the pressure, volume and temperature for a fixed amount of gas

$$V_2 = \frac{p_1V_1}{T_1} \times \frac{T_2}{p_2}$$

(a) Thus, for a pressure of 52 kPa,

$$V_2 = \frac{(104\ \text{kPa}) \times (2.0\ \text{m}^3)}{(273.15 + 21.1)\ \text{K}} \times \frac{(273.15 - 5.0)\ \text{K}}{(52\ \text{kPa})} = \mathbf{3.6\ m^3}$$

(b) and 0.880 kPa,

$$V_2 = \frac{(104\ \text{kPa}) \times (2.0\ \text{m}^3)}{(273.15 + 21.1)\ \text{K}} \times \frac{(273.15 - 52.0)\ \text{K}}{(0.880\ \text{kPa})} = \mathbf{178\ m^3}$$

1A.12   Applying the perfect gas equation of state, eqn 1A.5a, and expressing the amount of gas in terms of the mass, m, and molar mass, M,

$$V = \frac{nRT}{p} = \frac{(m/M)RT}{Mp} = \frac{mRT}{Mp}$$

$$= \frac{\overbrace{(250 \times 10^3\ \text{kg})}^{\text{mass of SO}_2} \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (273.15 + 800)\text{K}}{(64.06 \times 10^{-3}\text{kg mol}^{-1}) \times \underbrace{(1.01325 \times 10^5\ \text{Pa})}_{\text{1 atm} = 1.01325 \times 10^5\ \text{Pa}}}$$

$$= \mathbf{3.4 \times 10^5\ m^3}$$

1A.13   Mole fraction is defined through eqn 1A.13a. Thus, expressing the amount of each substance in terms of the molar mass and total mass,

$$x_J = \frac{n_J}{n}$$

$$= \frac{(m_J/M)}{(m_J/M) + \cdots}$$

The molar mass of benzene is $M_B = 78.11\ \text{g mol}^{-1}$ and of toluene is $M_T = 92.14\ \text{g mol}^{-1}$. Thus, the mole fraction of benzene is

$$x_B = \frac{(56\ \text{g}/78.11\ \text{g mol}^{-1})}{(56\ \text{g}/78.11\ \text{g mol}^{-1}) + (120\ \text{g}/92.14\ \text{g mol}^{-1})}$$

$$= \mathbf{0.355}$$

and of toluene is

$$x_B = \frac{(120\ \text{g}/92.14\ \text{g mol}^{-1})}{(56\ \text{g}/78.11\ \text{g mol}^{-1}) + (120\ \text{g}/92.14\ \text{g mol}^{-1})}$$
$$= 0.645$$

A quick check confirms that $x_B + x_T = 1$.

1A.14   (a) We may consider partial pressure as the pressure that a component of a gaseous mixture would exert if it alone occupied the container. Thus, considering the partial presure of nitrogen, and using the perfect gas equation of state to express the total volume in terms of the pressure, temperature and amount of nitrogen gas,

$$V = \frac{n_{N_2} RT}{p_{N_2}} = \frac{(m_{N_2}/M_{N_2})RT}{p_{N_2}}$$
$$= \frac{\{(225 \times 10^{-3}\text{g})/(28.02\ \text{g mol}^{-1})\} \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (300\ \text{K})}{(15.2 \times 10^3\ \text{Pa})}$$
$$= 1.32 \times 10^{-3}\text{m}^3$$

(b) The partial pressure of nitrogen is, however, defined in terms of the mole fraction and total pressure, through eqn 1A.12. Thus, rearranging and expressing the amount of the each component in terms of the mass and molar mass

$$p = \frac{p_{N_2}}{x_{N_2}} = \frac{p_{N_2}}{(n_{N_2}/n)} = \frac{\overbrace{(n_{CH_4} + n_{Ar} + n_{N_2})}^{\text{total amount of gas},n}\, p_{N_2}}{n_{N_2}}$$
$$= \frac{\{\overbrace{(m_{CH_4}/M_{CH_4})}^{n_{CH_4}} + \overbrace{(m_{Ar}/M_{Ar})}^{n_{Ar}} + \overbrace{(m_{N_2}/M_{N_2})}^{n_{N_2}}\}p_{N_2}}{n_{N_2}}$$
$$= \frac{\left\{\left(\frac{320 \times 10^{-3}\text{g}}{16.05\ \text{g mol}^{-1}}\right) + \left(\frac{175 \times 10^{-3}\text{g}}{39.95\ \text{g mol}^{-1}}\right) + \left(\frac{225 \times 10^{-3}\text{g}}{28.02\ \text{g mol}^{-1}}\right)\right\} \times 15.2 \times 10^3\ \text{Pa}}{\left(\frac{225 \times 10^{-3}\text{g}}{28.02\ \text{g mol}^{-1}}\right)}$$
$$= 61.2 \times 10^3\ \text{Pa}$$

Topic 1B The kinetic model of gases

1B.1   The root-mean-square speed of molecules is given by eqn 1B.7a.

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

(a) Thus, for N_2

$$v_{\text{rms}} = \left\{\frac{3 \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (273\ \text{K})}{(28.02 \times 10^{-3}\ \text{kg mol}^{-1})}\right\}^{1/2} = \mathbf{493\ m\ s^{-1}}$$

(b) and for H_2O,

$$v_{rms} = \left\{ \frac{3 \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (273 \text{ K})}{(18.02 \times 10^{-3} \text{ kg mol}^{-1})} \right\}^{1/2} = \textbf{615 m s}^{-1}$$

1B.2   The mean speed is, from eqn 1B.7b

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

Hence, for He atoms, with a molar mass of $M = 4.00$ g mol^{-1},

$$v_{mean}(79 \text{ K}) = \left\{ \frac{8 \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (79 \text{ K})}{\pi \times (4.00 \times 10^{-3} \text{ kg mol}^{-1})} \right\}^{1/2}$$

$$= \textbf{647 m s}^{-1}$$

$$v_{mean}(315 \text{ K}) = \left\{ \frac{8 \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (315 \text{ K})}{\pi \times (4.00 \times 10^{-3} \text{ kg mol}^{-1})} \right\}^{1/2}$$

$$= 1.29 \times 10^3 \text{ m s}^{-1} = \textbf{1.29 km s}^{-1}$$

$$v_{mean}(1500 \text{ K}) = \left\{ \frac{8 \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (1500 \text{ K})}{\pi \times (4.00 \times 10^{-3} \text{ kg mol}^{-1})} \right\}^{1/2}$$

$$= 2.82 \times 10^3 \text{ m s}^{-1} = \textbf{2.82 km s}^{-1}$$

and for methane molecules, with a molar mass of $M = 16.04$ g mol^{-1}

$$v_{mean}(79 \text{ K}) = \left\{ \frac{8 \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (79 \text{ K})}{\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1})} \right\}^{1/2}$$

$$= \textbf{323 m s}^{-1}$$

$$v_{mean}(315 \text{ K}) = \left\{ \frac{8 \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (315 \text{ K})}{\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1})} \right\}^{1/2}$$

$$= \textbf{645 m s}^{-1}$$

$$v_{mean}(1500 \text{ K}) = \left\{ \frac{8 \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (1500 \text{ K})}{\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1})} \right\}^{1/2}$$

$$= 1.41 \times 10^3 \text{ m s}^{-1} = \textbf{1.41 km s}^{-1}$$

1B.3   According to Graham's law, eqn 1B.9, the rate of effusion is inversely proportional to the square root of the molar mass. Thus, the relative rate at which the hydrogen and carbon monoxide leak from the cylinder is

$$\frac{v_{H_2}}{v_{CO}} = \left(\frac{M_{CO}}{M_{H_2}} \right)^{1/2}$$

$$= \left(\frac{28.01 \text{ g mol}^{-1}}{2.02 \text{ g mol}^{-1}} \right)^{1/2} = \textbf{3.72}$$

1B.4   The number of molecules escaping per second depends, according to Graham's law of effusion, on the molar mass through eqn 1B.9

$$v \propto \frac{1}{M^{1/2}}$$

Thus, the relative number of molecules escaping in a given time period is

$$\frac{n_{N_2}}{n_{CO_2}} = \left(\frac{M_{CO_2}}{M_{N_2}}\right)^{1/2}$$

The amount of molecules is related to the mass and molar mass, $n = m/M$, so that

$$n_{N_2} = \left(\frac{M_{CO_2}}{M_{N_2}}\right)^{1/2} n_{CO_2}$$

$$= \left(\frac{M_{CO_2}}{M_{N_2}}\right)^{1/2} \left(\frac{m_{CO_2}}{M_{CO_2}}\right)$$

and therefore

$$m_{N_2} = n_{N_2} M_{N_2}$$

$$= \overbrace{\left(\frac{M_{CO_2}}{M_{N_2}}\right)^{1/2} \left(\frac{m_{CO_2}}{M_{CO_2}}\right)}^{n_{N_2}} M_{N_2}$$

$$= \left(\frac{M_{N_2}}{M_{CO_2}}\right)^{1/2} m_{CO_2}$$

Substituting

$$m_{N_2} = \left(\frac{28.01 \text{ g mol}^{-1}}{44.01 \text{ g mol}^{-1}}\right)^{1/2} \times 1.0 \text{ g} = \textbf{0.80 g}$$

In the same way,

$$m_{He} = \left(\frac{4.00 \text{ g mol}^{-1}}{44.01 \text{ g mol}^{-1}}\right)^{1/2} \times 1.0 \text{ g} = \textbf{0.30 g}$$

1B.5   The volume of a spherical vessel of diameter d is

$$V = (4/3)\pi(d/2)^3 = \pi d^3/6$$

so that, rearranging,

$$d = (6V/\pi)^{1/3}$$

The mean free path of a molecule is given by eqn 1B.10

$$\lambda = \frac{kT}{2^{1/2}\sigma p}$$

Equating these two quantities and rearranging for pressure,

$$p = \frac{kT}{2^{1/2}\sigma(6V/\pi)^{1/3}}$$

$$= \frac{(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (273.15 + 25)\text{K}}{2^{1/2} \times \underbrace{(0.36 \times 10^{-18}\text{m}^2)}_{1\ \text{nm}^2 = 10^{-18}\text{m}^2} \times \{6 \times \underbrace{(1.0 \times 10^{-3}\text{m}^3)}_{1\ \text{dm}^3 = 10^{-3}\text{m}^3}/\pi\}^{1/3}}$$

$$= \underbrace{0.065\ \text{J m}^{-3}}_{1\ \text{J m}^{-3} = 1\ \text{Pa}} = \textbf{65 mPa}$$

1B.6   The mean free path of a molecule is given by eqn 1B.10

$$\lambda = \frac{kT}{2^{1/2}\sigma p}$$

$$= \frac{(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (217\ \text{K})}{2^{1/2} \times \underbrace{(0.43 \times 10^{-18}\text{m}^2)}_{1\ \text{nm}^2 = 10^{-18}\text{m}^2} \times \underbrace{(0.050\ \text{atm} \times 1.01325 \times 10^5\ \text{Pa atm}^{-1})}_{1\ \text{atm} = 1.01325 \times 10^5\ \text{Pa}}}$$

$$= 0.97 \times 10^{-6}\ \text{m} = \textbf{0.97 μm}$$

The collisional frequency is given by eqn 1B 12, so that

$$z = \frac{2\sigma p}{kT}\left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$= \frac{2 \times (0.43 \times 10^{-18}\text{m}^2)}{(1.381 \times 10^{-23}\text{J K}^{-1}) \times (217\ \text{K})} \times \left\{\frac{8 \times (8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (217\ \text{K})}{\pi \times (28.02 \times 10^{-3}\ \text{kg mol}^{-1})}\right\}^{1/2}$$

$$= 120 \times 10^3\ \text{s}^{-1}$$

The number of collisions in 1 s is therefore

$$N = z\delta t$$

$$= 120 \times 10^3\ \text{s}^{-1} \times 1\text{s}$$

$$= \textbf{120} \times \textbf{10}^\textbf{3}$$

1B.7   The number of collisions made by an atom or molecule is given by the product of the collision frequency z and the time interval δt. Expressing the collision frequency in terms of the temperature and pressure using eqn 1B.12 and taking the collision cross-section from Table 1B.1, the number of collisions in 1 s at a pressure of 10 bar $= 10^6$ Pa and temperature of $(273.15 + 25)$ K = 298 K is

$$N = z\delta t$$

$$= \frac{2\sigma p}{kT}\left(\frac{8RT}{\pi m_{\text{Ar}}}\right)^{1/2}\delta t$$

$$= \frac{2\sigma p}{kT}\left(\frac{8kT}{\pi m_{\text{Ar}}}\right)^{1/2}\delta t$$

$$= 2\sigma p\left(\frac{8}{\pi m_{\text{Ar}}kT}\right)^{1/2}\delta t$$

The atomic mass is $39.95 m_u = 39.95 \times (1.602 \times 10^{-27}\ \text{kg})$, so that

$$z = 2 \times (0.36 \times 10^{-18}\ \text{m}^2) \times (10^6\ \text{Pa})$$

$$\times \left\{ \frac{8}{\pi \times \underbrace{39.95 \times (1.602 \times 10^{-27}\ \text{kg})}_{m_{\text{Ar}}} \times (1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (298\ \text{K})} \right\}^{1/2}$$

$$\times (1\ \text{s})$$

$$= \mathbf{7.0 \times 10^{10}}$$

The number of collisions is directly proportional to the pressure, so that, for a pressure of 100 kPa, which is one tenth of that used above,

$$N = \mathbf{7.0 \times 10^{8}}$$

and for a pressure of 1 Pa, which is a factor of 10^{-6} of the original pressure,

$$N = \mathbf{7.0 \times 10^{4}}$$

1B.8   The mean free path of an atom or molecule is given by eqn 1B.10. Thus, manipulating the equation and recognising that we may use the perfect gas law, eqn 1A.5, to replace some terms

$$\lambda = \frac{kT}{2^{1/2}\sigma p} = \frac{(R/N_A)T}{2^{1/2}\sigma p} = \frac{RT}{p} \times \frac{1}{2^{1/2}N_A\sigma} = \frac{V}{n} \times \frac{1}{2^{1/2}N_A\sigma} = \frac{V}{2^{1/2}nN_A\sigma}$$

Thus, the mean free path is directly proportional to the volume of the container for a fixed amount of gas and is not dependent upon temperature.

1B.9   The mean free path of an atom or molecule is given by eqn 1B.10. Thus, assuming that air may be represented by nitrogen molecules, N_2, and using the value for the collision cross section from Table 1B.1, at 10 bar,

$$\lambda = \frac{kT}{2^{1/2}\sigma p}$$

$$= \frac{(1.381 \times 10^{-23}\ \text{J K}^{-1}) \times (298\ \text{K})}{2^{1/2} \times (0.43 \times 10^{-18}\ \text{m}^2) \times (10\ \text{bar} \times 10^5\ \text{Pa bar}^{-1})}$$

$$= 6.8 \times 10^{-9}\ \text{m} = \mathbf{6.8\ nm}$$

The mean free path is inversely proportional to pressure. Thus, for a pressure of 103 kPa, which is approximately one tenth of the pressure above, the mean free path will be ten times the original result

$$\lambda = \mathbf{68\ nm}$$

In the same way, at a pressure of 1.0 Pa, which is 10^{-6} times lower than in the original calculation, the mean free path will be 10^6 times greater

$$\lambda = 6.8 \times 10^{-3}\ \text{m} = \mathbf{6.8\ mm}$$

Topic 1C Real gases

1C.1   From the definition of the compression factor, eqn 1C.1b, and being careful to convert the quantities to SI base units

$$
\begin{aligned}
Z_c &= \frac{p_c V_{m,c}}{RT_c} \\
&= \frac{\{(111.3 \text{ atm}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1})\} \times (72.5 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (405.5 \text{ K})} \\
&= \mathbf{0.242}
\end{aligned}
$$

The compression factor $Z_c < 1$, indicating that attractive interactions must be dominant at the critical point.

1C.2   The compression factor at the critical point is given by eqn 1C.1b

$$
Z_c = \frac{p_c V_{m,c}}{RT_c}
$$

Thus, for methane, CH_4,

$$
\begin{aligned}
Z_c &= \frac{\{(45.6 \text{ atm}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1})\} \times (98.7 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (190.6 \text{ K})} \\
&= \mathbf{0.288}
\end{aligned}
$$

for ethane, C_2H_6,

$$
\begin{aligned}
Z_c &= \frac{\{(48.6 \text{ atm}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1})\} \times (260 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (562.7 \text{ K})} \\
&= \mathbf{0.274}
\end{aligned}
$$

and for propane, C_3H_8,

$$
\begin{aligned}
Z_c &= \frac{\{(41.9 \text{ atm}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1})\} \times (200 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (369.8 \text{ K})} \\
&= \mathbf{0.276}
\end{aligned}
$$

The values for the compression factors are remarkably similar. We may derive expressions for the critical parameters in terms of the van der Waals parameters a and b. These relationships are given in the caption to Figure 1C.6 as $p_c = a/27b^2$, $V_c = 3b$ and $T_c = 8a/27Rb$. Substituting,

$$
\begin{aligned}
Z_c &= \frac{p_c V_c}{RT_c} \\
&= \frac{(a/27b^2) \times (3b)}{R \times (8a/27Rb)} \\
&= 3/8 = 0.375
\end{aligned}
$$

Thus, van der Waals theory predicts that the value of the compression factor should be the same for all gases at the critical point, although the data do show that the actual value differs somewhat from that observed.

1C.3   Applying the virial equation of state, eqn 1C.3, and truncating after the second term in the expansion, for 1.00 mol of methane, confined to a volume of 1.00 dm³ at 273 K, the pressure is

$$p = \frac{nRT}{V}\left(1 + \frac{nB}{V} + \cdots\right)$$

$$= \frac{(1.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (273 \text{ K})}{(1.00 \times 10^{-3}\text{m}^3)}$$

$$\times \left\{1 + \frac{(1.00 \text{ mol}) \times (-53.6 \times 10^{-6} \text{ m}^3\text{mol}^{-1})}{(1.00 \times 10^{-3}\text{m}^3)}\right\}$$

$$= 2.15 \times 10^6 \text{ Pa} = \mathbf{2.15 \text{ MPa}}$$

which is only 95 per cent of the value of a perfect gas under the same conditions. This implies that attractive interactions between the molecules dominate at this temperature.

1C.4   Rearranging the truncated virial equation of state

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

and noting that a pressure of 10 bar is equivalent to 10^6 Pa, and a molar volume of 3.90 dm³ mol⁻¹ is equal to 3.90×10^{-3} m³ mol⁻¹, the value of the second virial coffeicient is

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

$$= \left(\frac{(10^6 \text{ Pa}) \times (3.90 \times 10^{-3} \text{ m}^3\text{mol}^{-1})}{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (273.15 + 200)\text{K}} - 1\right) \times (3.90 \times 10^{-3} \text{ m}^3\text{mol}^{-1})$$

$$= \mathbf{-3.37 \times 10^{-5} \text{ m}^3\text{mol}^{-1}}$$

1C.5   Rearranging the truncated form of the virial equation of state, and substituting the definition of the compression factor, eqn 1C.1b

$$B' = \frac{Z - 1}{p}$$

$$= \frac{(pV_m/RT) - 1}{p}$$

$$= \frac{V_m}{RT} - \frac{1}{p}$$

$$= \left\{\frac{(5.53 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})}{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (647.4 \text{ K})}\right\}$$

$$- \left\{\frac{1}{(218.3 \text{ atm}) \times (1.01325 \times 10^5 \text{ Pa atm}^{-1})}\right\}$$

$$= \mathbf{-3.49 \times 10^{-8} \text{ Pa}^{-1}}$$

The value of the second virial coefficient is negative, indicating that for water at the critical point, attractive interactions dominate.