

## Homework CH1

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.)

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

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

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

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,  $n = n_{\text{CH}_4} + n_{\text{Ar}} + n_{\text{Ne}}$ .

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

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

$$\text{and} \quad p = \frac{nRT}{V} = \frac{3.55 \times 10^{-2} \text{ mol} \times 8.3145 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{3.14 \times 10^{-3} \text{ m}^3} \\ = \boxed{2.82 \times 10^4 \text{ Pa}} = \boxed{28.2 \text{ kPa}}$$

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

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

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

According to the perfect gas law

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

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

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

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

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

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

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

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

(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

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

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

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

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

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,  $\text{H}_2$ ).

**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  $b = 0.0434 \text{ dm}^3 \text{ mol}^{-1}$ .

$$\text{(i)} \quad P = \frac{(1.0 \text{ mol}) \times (0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (273.15 \text{ K})}{22.414 \text{ dm}^3 - (1.0 \text{ mol}) \times (4.34 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})} - \frac{(4.484 \text{ dm}^6 \text{ atm mol}^{-2}) \times (1.0 \text{ mol})^2}{(22.414 \text{ dm}^3)^2} = \boxed{0.99 \text{ atm}}$$

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

**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

$$\begin{aligned}
 V_m &= (1.12)V_m^\circ = (1.12) \times \left( \frac{RT}{p} \right) \\
 &= (1.12) \times \left( \frac{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (350 \text{ K})}{12 \text{ atm}} \right) = \boxed{2.7 \text{ dm}^3 \text{ mol}^{-1}}
 \end{aligned}$$

Since  $V_m > V_m^\circ$  repulsive forces dominate.

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

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

(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

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

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

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

$$\begin{aligned}
 b + \frac{RT}{p} &= (3.183 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}) + \frac{(0.08206 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})}{197.4 \text{ atm}} \\
 &= (3.183 \times 10^{-2} + 0.1239) \text{ dm}^3 \text{ mol}^{-1} = 0.1558 \text{ dm}^3 \text{ mol}^{-1}
 \end{aligned}$$

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

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

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.8(b)** States that have the same reduced pressure, temperature, and volume [1C.8] are said to correspond. The reduced pressure and temperature for N<sub>2</sub> at 1.0 atm and 25°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 H<sub>2</sub>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 CO<sub>2</sub>

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

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

(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  $b$

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

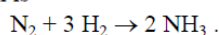
$$= \boxed{1.3 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}}$$

The compression factor is

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

## Problem

**1A.6** We assume that no H<sub>2</sub> remains after the reaction has gone to completion. The balanced equation is



We can draw up the following table

	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>	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

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

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

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

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

**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

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

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

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

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

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

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