

Part 1: Equilibrium



1 The properties of gases

Solutions to exercises

Discussion questions

- E1.1(b)** 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. It 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.
- E1.2(b)** 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 fluids in the so-called supercritical region have both liquid and vapour characteristics. (See Box 6.1 for a more thorough discussion of the supercritical state.)
- E1.3(b)** The van der Waals equation is a cubic equation in the volume, V . Any cubic equation has certain properties, one of which is that there are some values of the coefficients of the variable where the number of real roots passes from three to one. In fact, any equation of state of odd degree higher than 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 (odd) to 1. That is, the multiple values of V converge from n to 1 as $T \rightarrow T_c$. 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.

Numerical exercises

- E1.4(b)** Boyle's law applies.

$$pV = \text{constant} \quad \text{so} \quad p_f V_f = p_i V_i$$
$$p_f = \frac{p_i V_i}{V_f} = \frac{(104 \text{ kPa}) \times (2000 \text{ cm}^3)}{(250 \text{ cm}^3)} = \boxed{832 \text{ kPa}}$$

- E1.5(b)** (a) The perfect gas law 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.

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

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

not 2.0 bar.

(b) The van der Waals equation is

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

$$\text{so } p = \frac{(8.31 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (30 + 273) \text{ K}}{(1.5 \text{ L}/0.626 \text{ mol}) - 3.20 \times 10^{-2} \text{ L mol}^{-1}} - \frac{(1.337 \text{ L}^2 \text{ atm mol}^{-2}) \times (1.013 \text{ bar atm}^{-1})}{(1.5 \text{ L}/0.626 \text{ mol})^2} = \boxed{10.4 \text{ bar}}$$

E1.6(b) (a) Boyle's law applies.

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

$$\text{and } p_i = \frac{p_f V_f}{V_i} = \frac{(1.48 \times 10^3 \text{ Torr}) \times (2.14 \text{ dm}^3)}{(2.14 + 1.80) \text{ dm}^3} = \boxed{8.04 \times 10^2 \text{ Torr}}$$

(b) The original pressure in bar is

$$p_i = (8.04 \times 10^2 \text{ Torr}) \times \left(\frac{1 \text{ atm}}{760 \text{ Torr}} \right) \times \left(\frac{1.013 \text{ bar}}{1 \text{ atm}} \right) = \boxed{1.07 \text{ bar}}$$

E1.7(b) Charles's law applies.

$$V \propto T \quad \text{so} \quad \frac{V_i}{T_i} = \frac{V_f}{T_f}$$

$$\text{and } T_f = \frac{V_f T_i}{V_i} = \frac{(150 \text{ cm}^3) \times (35 + 273) \text{ K}}{500 \text{ cm}^3} = \boxed{92.4 \text{ K}}$$

E1.8(b) The relation between pressure and temperature at constant volume can be derived from the perfect gas law

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

The final pressure, then, ought to be

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

E1.9(b) According to the perfect gas law, one can compute the amount of gas from pressure, temperature, and volume. Once this is done, the mass of the gas can be computed from the amount and the molar mass using

$$pV = nRT$$

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

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

E1.10(b) All gases are perfect in the limit of zero pressure. Therefore the extrapolated value of pV_m/T will give the best value of R .

The molar mass is obtained from $pV = nRT = \frac{m}{M}RT$

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 ρ/p versus p to $p = 0$; the intercept is M/RT .

Draw up the following table

p/atm	$(pV_m/T)/(\text{L atm K}^{-1} \text{ mol}^{-1})$	$(\rho/p)/(\text{g L}^{-1} \text{ atm}^{-1})$
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

From Fig. 1.1(a), $\left(\frac{pV_m}{T}\right)_{p=0} = 0.082\,061\,5 \text{ L atm K}^{-1} \text{ mol}^{-1}$

From Fig. 1.1(b), $\left(\frac{\rho}{p}\right)_{p=0} = 1.42755 \text{ g L}^{-1} \text{ atm}^{-1}$

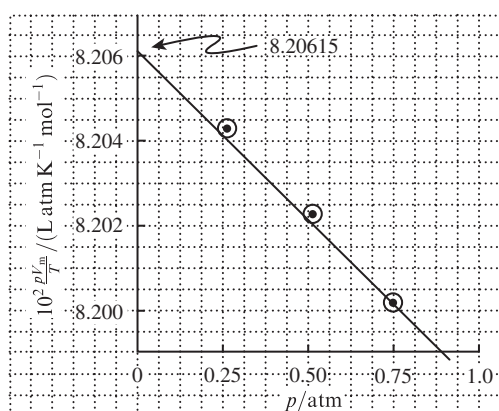


Figure 1.1(a)

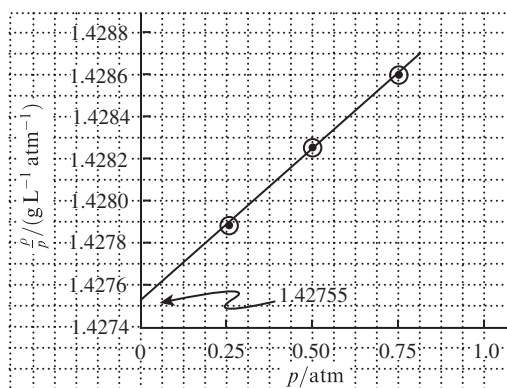


Figure 1.1(b)

$$M = RT \left(\frac{\rho}{p} \right)_{p=0} = (0.0820615 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (273.15 \text{ K}) \times (1.42755 \text{ g L}^{-1} \text{ atm}^{-1})$$

$$= \boxed{31.9987 \text{ g mol}^{-1}}$$

The value obtained for R deviates from the accepted value by 0.005 per cent. The error results from the fact that only three data points are available and that a linear extrapolation was employed. The molar mass, however, agrees exactly with the accepted value, probably because of compensating plotting errors.

E1.11(b) The mass density ρ is related to the molar volume V_m by

$$V_m = \frac{M}{\rho}$$

where M is the molar mass. Putting this relation into the perfect gas law 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

$$M = \frac{RT\rho}{p} = \frac{(62.364 \text{ L Torr K}^{-1} \text{ mol}^{-1}) \times [(100 + 273) \text{ K}] \times (0.6388 \text{ g L}^{-1})}{120 \text{ Torr}} = 124 \text{ g mol}^{-1}.$$

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 $\boxed{\text{P}_4}$

E1.12(b) Use the perfect gas equation 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.

$$p = (0.53) \times (2.69 \times 10^3 \text{ Pa}) = 1.43 \times 10^3 \text{ Pa}$$

$$\text{so } n = \frac{(1.43 \times 10^3 \text{ Pa}) \times (250 \text{ m}^3)}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (23 + 273) \text{ K}} = 1.45 \times 10^2 \text{ mol}$$

$$\text{or } m = (1.45 \times 10^2 \text{ mol}) \times (18.0 \text{ g mol}^{-1}) = 2.61 \times 10^3 \text{ g} = \boxed{2.61 \text{ kg}}$$

E1.13(b) (a) The volume occupied by each gas is the same, since each completely fills the container. Thus solving for V from eqn 14 we have (assuming a perfect gas)

$$V = \frac{n_J RT}{p_J} \quad n_{\text{Ne}} = \frac{0.225 \text{ g}}{20.18 \text{ g mol}^{-1}}$$

$$= 1.115 \times 10^{-2} \text{ mol}, \quad p_{\text{Ne}} = 66.5 \text{ Torr}, \quad T = 300 \text{ K}$$

$$V = \frac{(1.115 \times 10^{-2} \text{ mol}) \times (62.36 \text{ L Torr K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{66.5 \text{ Torr}} = 3.137 \text{ L} = \boxed{3.14 \text{ L}}$$

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

$$n_{\text{CH}_4} = \frac{0.320 \text{ g}}{16.04 \text{ g mol}^{-1}} = 1.99\bar{5} \times 10^{-2} \text{ mol} \quad n_{\text{Ar}} = \frac{0.175 \text{ g}}{39.95 \text{ g mol}^{-1}} = 4.38 \times 10^{-3} \text{ mol}$$

$$n = (1.99\bar{5} + 0.438 + 1.11\bar{5}) \times 10^{-2} \text{ mol} = 3.54\bar{8} \times 10^{-2} \text{ mol}$$

$$p = \frac{nRT}{V} [1] = \frac{(3.54\bar{8} \times 10^{-2} \text{ mol}) \times (62.36 \text{ L Torr K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{3.13\bar{7} \text{ L}}$$

$$= \boxed{212 \text{ Torr}}$$

E1.14(b) This is similar to Exercise 1.14(a) with the exception that the density is first calculated.

$$M = \rho \frac{RT}{p} \text{ [Exercise 1.11(a)]}$$

$$\rho = \frac{33.5 \text{ mg}}{250 \text{ mL}} = 0.134\bar{0} \text{ g L}^{-1}, \quad p = 152 \text{ Torr}, \quad T = 298 \text{ K}$$

$$M = \frac{(0.134\bar{0} \text{ g L}^{-1}) \times (62.36 \text{ L Torr K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{152 \text{ Torr}} = \boxed{16.4 \text{ g mol}^{-1}}$$

E1.15(b) This exercise is similar to Exercise 1.15(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.

$$\text{Thus } V = V_0 + \alpha V_0 \theta = V_0 + b\theta, \quad b = \alpha V_0$$

$$\text{At absolute zero, } V = 0, \text{ or } 0 = 20.00 \text{ L} + 0.0741 \text{ L}^\circ\text{C}^{-1} \times \theta(\text{abs. zero})$$

$$\theta(\text{abs. zero}) = -\frac{20.00 \text{ L}}{0.0741 \text{ L}^\circ\text{C}^{-1}} = \boxed{-270^\circ\text{C}}$$

which is close to the accepted value of -273°C .

E1.16(b) (a) $p = \frac{nRT}{V}$
 $n = 1.0 \text{ mol}$
 $T = \text{(i) } 273.15 \text{ K}; \quad \text{(ii) } 500 \text{ K}$
 $V = \text{(i) } 22.414 \text{ L}; \quad \text{(ii) } 150 \text{ cm}^3$

(i) $p = \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.414 \text{ L}}$
 $= \boxed{1.0 \text{ atm}}$

(ii) $p = \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}{0.150 \text{ L}}$
 $= \boxed{270 \text{ atm}} \text{ (2 significant figures)}$

(b) From Table (1.6) for H_2S

$$a = 4.484 \text{ L}^2 \text{ atm mol}^{-1} \quad b = 4.34 \times 10^{-2} \text{ L mol}^{-1}$$

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

$$\begin{aligned}
 \text{(i)} \quad p &= \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.414 \text{ L} - (1.0 \text{ mol}) \times (4.34 \times 10^{-2} \text{ L mol}^{-1}) - \frac{(4.484 \text{ L}^2 \text{ atm mol}^{-1}) \times (1.0 \text{ mol})^2}{(22.414 \text{ L})^2}} \\
 &= \boxed{0.99 \text{ atm}} \\
 \text{(ii)} \quad p &= \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}{0.150 \text{ L} - (1.0 \text{ mol}) \times (4.34 \times 10^{-2} \text{ L mol}^{-1}) - \frac{(4.484 \text{ L}^2 \text{ atm mol}^{-1}) \times (1.0 \text{ mol})^2}{(0.150 \text{ L})^2}} \\
 &= 185.6 \text{ atm} \approx \boxed{190 \text{ atm}} \text{ (2 significant figures).}
 \end{aligned}$$

E1.17(b) The critical constants of a van der Waals gas are

$$V_c = 3b = 3(0.0436 \text{ L mol}^{-1}) = \boxed{0.131 \text{ L mol}^{-1}}$$

$$p_c = \frac{a}{27b^2} = \frac{1.32 \text{ atm L}^2 \text{ mol}^{-2}}{27(0.0436 \text{ L mol}^{-1})^2} = \boxed{25.7 \text{ atm}}$$

$$\text{and } T_c = \frac{8a}{27Rb} = \frac{8(1.32 \text{ atm L}^2 \text{ mol}^{-2})}{27(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (0.0436 \text{ L mol}^{-1})} = \boxed{109 \text{ K}}$$

E1.18(b) The compression factor is

$$Z = \frac{pV_m}{RT} = \frac{V_m}{V_{m,\text{perfect}}}$$

(a) Because $V_m = V_{m,\text{perfect}} + 0.12 V_{m,\text{perfect}} = (1.12)V_{m,\text{perfect}}$, we have $Z = \boxed{1.12}$

Repulsive forces dominate.

(b) The molar volume is

$$\begin{aligned}
 V &= (1.12)V_{m,\text{perfect}} = (1.12) \times \left(\frac{RT}{p} \right) \\
 V &= (1.12) \times \left(\frac{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (350 \text{ K})}{12 \text{ atm}} \right) = \boxed{2.7 \text{ L mol}^{-1}}
 \end{aligned}$$

E1.19(b) (a)
$$V_m^o = \frac{RT}{p} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{(200 \text{ bar}) \times (10^5 \text{ Pa bar}^{-1})} = 1.24 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} = \boxed{0.124 \text{ L mol}^{-1}}$$

(b) The van der Waals equation is a cubic equation in V_m . The most direct way of obtaining the molar volume would be to solve the cubic analytically. However, this approach is cumbersome, so we proceed as in Example 1.6. The van der Waals equation is rearranged to the cubic form

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

with $x = V_m/(\text{L mol}^{-1})$.

The coefficients in the equation are evaluated as

$$b + \frac{RT}{p} = (3.183 \times 10^{-2} \text{ L mol}^{-1}) + \frac{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{(200 \text{ bar}) \times (1.013 \text{ atm bar}^{-1})}$$

$$= (3.183 \times 10^{-2} + 0.120\bar{8}) \text{ L mol}^{-1} = 0.152\bar{6} \text{ L mol}^{-1}$$

$$\frac{a}{p} = \frac{1.360 \text{ L}^2 \text{ atm mol}^{-2}}{(200 \text{ bar}) \times (1.013 \text{ atm bar}^{-1})} = 6.71 \times 10^{-3} (\text{L mol}^{-1})^2$$

$$\frac{ab}{p} = \frac{(1.360 \text{ L}^2 \text{ atm mol}^{-2}) \times (3.183 \times 10^{-2} \text{ L mol}^{-1})}{(200 \text{ bar}) \times (1.013 \text{ atm bar}^{-1})} = 2.13\bar{7} \times 10^{-4} (\text{L mol}^{-1})^3$$

Thus, the equation to be solved is $x^3 - 0.152\bar{6}x^2 + (6.71 \times 10^{-3})x - (2.13\bar{7} \times 10^{-4}) = 0$.

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

$$x = 0.112 \quad \text{or} \quad V_m = \boxed{0.112 \text{ L mol}^{-1}}$$

The difference is about 15 per cent.

E1.20(b) (a) $V_m = \frac{M}{\rho} = \frac{18.015 \text{ g mol}^{-1}}{0.5678 \text{ g L}^{-1}} = \boxed{31.72\bar{8} \text{ L mol}^{-1}}$

$$Z = \frac{pV_m}{RT} = \frac{(1.00 \text{ bar}) \times (31.72\bar{8} \text{ L mol}^{-1})}{(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (383 \text{ K})} = \boxed{0.996\bar{3}}$$

(b) Using $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$ and substituting into the expression for Z above we get

$$Z = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$$

$$= \frac{31.72\bar{8} \text{ L mol}^{-1}}{31.72\bar{8} \text{ L mol}^{-1} - 0.03049 \text{ L mol}^{-1}}$$

$$- \frac{5.464 \text{ L}^2 \text{ atm mol}^{-2}}{(31.72\bar{8} \text{ L mol}^{-1}) \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (383 \text{ K})}$$

$$= \boxed{0.995\bar{4}}$$

Comment. Both values of Z are very close to the perfect gas value of 1.000, indicating that water vapour is essentially perfect at 1.00 bar pressure.

E1.21(b) The molar volume is obtained by solving $Z = \frac{pV_m}{RT}$ [1.20b], for V_m , which yields

$$V_m = \frac{ZRT}{p} = \frac{(0.86) \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{20 \text{ atm}} = 1.05\bar{9} \text{ L mol}^{-1}$$

(a) Then, $V = nV_m = (8.2 \times 10^{-3} \text{ mol}) \times (1.05\bar{9} \text{ L mol}^{-1}) = 8.7 \times 10^{-3} \text{ L} = \boxed{8.7 \text{ mL}}$

- (b) An approximate value of B can be obtained from eqn 1.22 by truncation of the series expansion after the second term, B/V_m , in the series. Then,

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

$$= (1.059 \text{ L mol}^{-1}) \times (0.86 - 1) = \boxed{-0.15 \text{ L mol}^{-1}}$$

- E1.22(b)** (a) Mole fractions are

$$x_N = \frac{n_N}{n_{\text{total}}} = \frac{2.5 \text{ mol}}{(2.5 + 1.5) \text{ mol}} = \boxed{0.63}$$

Similarly, $x_H = \boxed{0.37}$

- (c) According to the perfect gas law

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

so $p_{\text{total}} = \frac{n_{\text{total}} RT}{V}$

$$= \frac{(4.0 \text{ mol}) \times (0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (273.15 \text{ K})}{22.4 \text{ L}} = \boxed{4.0 \text{ atm}}$$

- (b) The partial pressures are

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

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

- E1.23(b)** The critical volume of a van der Waals gas is

$$V_c = 3b$$

$$\text{so } b = \frac{1}{3} V_c = \frac{1}{3} (148 \text{ cm}^3 \text{ mol}^{-1}) = 49.3 \text{ cm}^3 \text{ mol}^{-1} = \boxed{0.0493 \text{ L mol}^{-1}}$$

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

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

$$r = \frac{1}{2} \left(\frac{3(49.3 \text{ cm}^3 \text{ mol}^{-1})}{4\pi(6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 1.94 \times 10^{-8} \text{ cm} = \boxed{1.94 \times 10^{-10} \text{ m}}$$

The critical pressure is

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

$$\text{so } a = 27p_c b^2 = 27(48.20 \text{ atm}) \times (0.0493 \text{ L mol}^{-1})^2 = \boxed{3.16 \text{ L}^2 \text{ atm mol}^{-2}}$$

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

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

According to the constants we have already determined, T_c should be

$$T_c = \frac{8(3.16 \text{ L}^2 \text{ atm mol}^{-2})}{27(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (0.0493 \text{ L mol}^{-1})} = 231 \text{ K}$$

However, the reported T_c is 305.4 K, suggesting our computed a/b is about 25 per cent lower than it should be.

- E1.24(b)** (a) The Boyle temperature is the temperature at which $\lim_{V_m \rightarrow \infty} \frac{dZ}{d(1/V_m)}$ vanishes. According to the van der Waals equation

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

$$\begin{aligned} \text{so } \frac{dZ}{d(1/V_m)} &= \left(\frac{dZ}{dV_m}\right) \times \left(\frac{dV_m}{d(1/V_m)}\right) \\ &= -V_m^2 \left(\frac{dZ}{dV_m}\right) = -V_m^2 \left(\frac{-V_m}{(V_m - b)^2} + \frac{1}{V_m - b} + \frac{a}{V_m^2 RT}\right) \\ &= \frac{V_m^2 b}{(V_m - b)^2} - \frac{a}{RT} \end{aligned}$$

In the limit of large molar volume, we have

$$\lim_{V_m \rightarrow \infty} \frac{dZ}{d(1/V_m)} = b - \frac{a}{RT} = 0 \quad \text{so} \quad \frac{a}{RT} = b$$

$$\text{and } T = \frac{a}{Rb} = \frac{(4.484 \text{ L}^2 \text{ atm mol}^{-2})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (0.0434 \text{ L mol}^{-1})} = \boxed{1259 \text{ K}}$$

- (b) 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); the Avogadro constant times the volume is the molar excluded volume b

$$\begin{aligned} b &= N_A \left(\frac{4\pi(2r^3)}{3}\right) \quad \text{so} \quad r = \frac{1}{2} \left(\frac{3b}{4\pi N_A}\right)^{1/3} \\ r &= \frac{1}{2} \left(\frac{3(0.0434 \text{ dm}^3 \text{ mol}^{-1})}{4\pi(6.022 \times 10^{23} \text{ mol}^{-1})}\right)^{1/3} = 1.286 \times 10^{-9} \text{ dm} = 1.29 \times 10^{-10} \text{ m} = \boxed{0.129 \text{ nm}} \end{aligned}$$

- E1.25(b)** States that have the same reduced pressure, temperature, and volume are said to correspond. The reduced pressure and temperature for N_2 at 1.0 atm and 25°C are

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

The corresponding states are

(a) For H₂S

$$p = p_r p_c = (0.030) \times (88.3 \text{ atm}) = \boxed{2.6 \text{ atm}}$$

$$T = T_r T_c = (2.36) \times (373.2 \text{ K}) = \boxed{881 \text{ K}}$$

(Critical constants of H₂S obtained from *Handbook of Chemistry and Physics*.)

(b) For CO₂

$$p = p_r p_c = (0.030) \times (72.85 \text{ atm}) = \boxed{2.2 \text{ atm}}$$

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

(c) For Ar

$$p = p_r p_c = (0.030) \times (48.00 \text{ atm}) = \boxed{1.4 \text{ atm}}$$

$$T = T_r T_c = (2.36) \times (150.72 \text{ K}) = \boxed{356 \text{ K}}$$

E1.26(b) The van der Waals equation 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

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

Solutions to problems

Solutions to numerical problems

P1.2

Identifying p_{ex} in the equation $p = p_{\text{ex}} + \rho gh$ [1.4] as the pressure at the top of the straw and p as the atmospheric pressure on the liquid, the pressure difference is

$$p - p_{\text{ex}} = \rho gh = (1.0 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (0.15 \text{ m})$$

$$= \boxed{1.5 \times 10^3 \text{ Pa}} \quad (= 1.5 \times 10^{-2} \text{ atm})$$

P1.4

$pV = nRT$ [1.12] implies that, with n constant, $\frac{p_f V_f}{T_f} = \frac{p_i V_i}{T_i}$

Solving for p_f , the pressure at its maximum altitude, yields $p_f = \frac{V_i}{V_f} \times \frac{T_f}{T_i} \times p_i$

Substituting $V_i = \frac{4}{3}\pi r_i^3$ and $V_f = \frac{4}{3}\pi r_f^3$

$$p_f = \left(\frac{(4/3)\pi r_i^3}{(4/3)\pi r_f^3} \right) \times \frac{T_f}{T_i} \times p_i = \left(\frac{r_i}{r_f} \right)^3 \times \frac{T_f}{T_i} \times p_i$$

$$= \left(\frac{1.0 \text{ m}}{3.0 \text{ m}} \right)^3 \times \left(\frac{253 \text{ K}}{293 \text{ K}} \right) \times (1.0 \text{ atm}) = \boxed{3.2 \times 10^{-2} \text{ atm}}$$

P1.6 The value of absolute zero can be expressed in terms of α by using the requirement that the volume of a perfect gas becomes zero at the absolute zero of temperature. Hence

$$0 = V_0[1 + \alpha\theta(\text{abs. zero})]$$

$$\text{Then } \theta(\text{abs. zero}) = -\frac{1}{\alpha}$$

All gases become perfect in the limit of zero pressure, so the best value of α and, hence, $\theta(\text{abs. zero})$ is obtained by extrapolating α to zero pressure. This is done in Fig. 1.2. Using the extrapolated value, $\alpha = 3.6637 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$, or

$$\theta(\text{abs. zero}) = -\frac{1}{3.6637 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}} = \boxed{-272.95^\circ\text{C}}$$

which is close to the accepted value of -273.15°C .

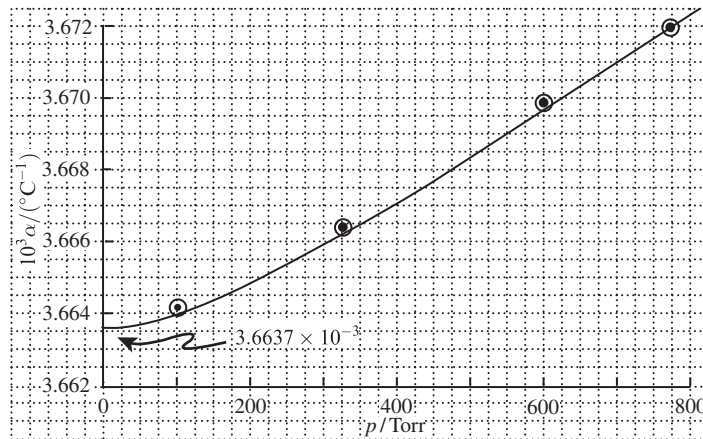


Figure 1.2

P1.7 The mass of displaced gas is ρV , where V is the volume of the bulb and ρ is the density of the gas. The balance condition for the two gases is $m(\text{bulb}) = \rho V(\text{bulb})$, $m(\text{bulb}) = \rho' V(\text{bulb})$

which implies that $\rho = \rho'$. Because [Problem 1.5] $\rho = \frac{pM}{RT}$

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; hence

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

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

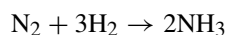
$$M' = \frac{427.22 \text{ Torr}}{293.22 \text{ Torr}} \times 70.014 \text{ g mol}^{-1} = 102.0 \text{ g mol}^{-1}$$

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; it may be safe to conclude that

$M \approx 102 \text{ g mol}^{-1}$. The molecules CH_2FCF_3 or CHF_2CHF_2 have $M \approx 102 \text{ g mol}^{-1}$.

P1.9

We assume that no H_2 remains after the reaction has gone to completion. The balanced equation is



We can draw up the following table

	N_2	H_2	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

$$p = \frac{nRT}{V} = (1.66 \text{ mol}) \times \left(\frac{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (273.15 \text{ K})}{22.4 \text{ L}} \right) = \boxed{1.66 \text{ atm}}$$

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

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

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

P1.10

(a) $V_m = \frac{RT}{p} = \frac{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (350 \text{ K})}{2.30 \text{ atm}} = \boxed{12.5 \text{ L mol}^{-1}}$

(b) From $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$ [1.25b], we obtain $V_m = \frac{RT}{\left(p + \frac{a}{V_m^2}\right)} + b$ [rearrange 1.25b]

Then, with a and b from Table 1.6

$$\begin{aligned} V_m &\approx \frac{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (350 \text{ K})}{(2.30 \text{ atm}) + \left(\frac{6.260 \text{ L}^2 \text{ atm mol}^{-2}}{(12.5 \text{ L mol}^{-1})^2}\right)} + (5.42 \times 10^{-2} \text{ L mol}^{-1}) \\ &\approx \frac{28.72 \text{ L mol}^{-1}}{2.34} + (5.42 \times 10^{-2} \text{ L mol}^{-1}) \approx \boxed{12.3 \text{ L mol}^{-1}} \end{aligned}$$

Substitution of 12.3 L mol^{-1} into the denominator of the first expression again results in $V_m = 12.3 \text{ L mol}^{-1}$, so the cycle of approximation may be terminated.

P1.13 (a) Since $B'(T_B) = 0$ at the Boyle temperature (section 1.3b): $B'(T_B) = a + b e^{-c/T_B^2} = 0$

$$\text{Solving for } T_B: T_B = \sqrt{\frac{-c}{\ln\left(\frac{-a}{b}\right)}} = \sqrt{\frac{-(1131 \text{ K}^2)}{\ln\left[\frac{-(-0.1993 \text{ bar}^{-1})}{(0.2002 \text{ bar}^{-1})}\right]}} = 501.0 \text{ K}$$

(b) Perfect Gas Equation: $V_m(p, T) = \frac{RT}{p}$

$$V_m(50 \text{ bar}, 298.15 \text{ K}) = \frac{0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1} (298.15 \text{ K})}{50 \text{ bar}} = 0.496 \text{ L mol}^{-1}$$

$$V_m(50 \text{ bar}, 373.15 \text{ K}) = \frac{0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1} (373.15 \text{ K})}{50 \text{ bar}} = 0.621 \text{ L mol}^{-1}$$

Virial Equation (eqn 1.21 to first order): $V_m(p, T) = \frac{RT}{p} (1 + B'(T)p) = V_{\text{perfect}} (1 + B'(T)p)$

$$B'(T) = a + b e^{-\frac{c}{T^2}}$$

$$B'(298.15 \text{ K}) = -0.1993 \text{ bar}^{-1} + 0.2002 \text{ bar}^{-1} e^{-\frac{1131 \text{ K}^2}{(298.15 \text{ K})^2}} = -0.00163 \text{ bar}^{-1}$$

$$B'(373.15 \text{ K}) = -0.1993 \text{ bar}^{-1} + 0.2002 \text{ bar}^{-1} e^{-\frac{1131 \text{ K}^2}{(373.15 \text{ K})^2}} = -0.000720 \text{ bar}^{-1}$$

$$V_m(50 \text{ bar}, 298.15 \text{ K}) = 0.496 \text{ L mol}^{-1} (1 - 0.00163 \text{ bar}^{-1} 50 \text{ bar}) = 0.456 \text{ L mol}^{-1}$$

$$V_m(50 \text{ bar}, 373.15 \text{ K}) = 0.621 \text{ L mol}^{-1} (1 - 0.000720 \text{ bar}^{-1} 50 \text{ bar}) = 0.599 \text{ L mol}^{-1}$$

The perfect gas law predicts a molar volume that is 9% too large at 298 K and 4% too large at 373 K. The negative value of the second virial coefficient at both temperatures indicates the dominance of very weak intermolecular attractive forces over repulsive forces.

P1.15 From Table 1.6 $T_c = \left(\frac{2}{3}\right) \times \left(\frac{2a}{3bR}\right)^{1/2}$, $p_c = \left(\frac{1}{12}\right) \times \left(\frac{2aR}{3b^3}\right)^{1/2}$

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

$$\begin{aligned} T_c &= \left(\frac{2}{3}\right) \times \left(\frac{12bp_c}{R}\right) = \left(\frac{8}{3}\right) \times \left(\frac{p_c V_c}{R}\right) \\ &= \left(\frac{8}{3}\right) \times \left(\frac{(40 \text{ atm}) \times (160 \times 10^{-3} \text{ L mol}^{-1})}{8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}}\right) = \boxed{210 \text{ K}} \end{aligned}$$

$$v_{\text{mol}} = \frac{b}{N_A} = \left(\frac{1}{3}\right) \times \left(\frac{V_c}{N_A}\right) = \frac{160 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}{(3) \times (6.022 \times 10^{23} \text{ mol}^{-1})} = 8.86 \times 10^{-29} \text{ m}^3$$

$$v_{\text{mol}} = \frac{4\pi}{3} r^3$$

$$r = \left(\frac{3}{4\pi} \times (8.86 \times 10^{-29} \text{ m}^3)\right)^{1/3} = \boxed{0.28 \text{ nm}}$$

P1.16 $V_c = 2b, \quad T_c = \frac{a}{4bR}$ [Table 1.6]

Hence, with V_c and T_c from Table 1.5, $b = \frac{1}{2}V_c = \frac{1}{2} \times (118.8 \text{ cm}^3 \text{ mol}^{-1}) = \boxed{59.4 \text{ cm}^3 \text{ mol}^{-1}}$

$$\begin{aligned} a &= 4bRT_c = 2RT_cV_c \\ &= (2) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (289.75 \text{ K}) \times (118.8 \times 10^{-3} \text{ L mol}^{-1}) \\ &= \boxed{5.649 \text{ L}^2 \text{ atm mol}^{-2}} \end{aligned}$$

Hence

$$\begin{aligned} p &= \frac{RT}{V_m - b} e^{-a/RTV_m} = \frac{nRT}{V - nb} e^{-na/RTV} \\ &= \frac{(1.0 \text{ mol}) \times (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(1.0 \text{ L}) - (1.0 \text{ mol}) \times (59.4 \times 10^{-3} \text{ L mol}^{-1})} \\ &\quad \times \exp\left(\frac{-(1.0 \text{ mol}) \times (5.649 \text{ L}^2 \text{ atm mol}^{-2})}{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (1.0 \text{ L}^2 \text{ atm mol}^{-1})}\right) \\ &= 26.0 \text{ atm} \times e^{-0.231} = \boxed{21 \text{ atm}} \end{aligned}$$

Solutions to theoretical problems

P1.18 This expansion has already been given in the solutions to Exercise 1.24(a) and Problem 1.17; the result is

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

Compare this expansion with $p = \frac{RT}{V_m} \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$ [1.22]

and hence find $\boxed{B = b - \frac{a}{RT}}$ and $\boxed{C = b^2}$

Since $C = 1200 \text{ cm}^6 \text{ mol}^{-2}$, $b = C^{1/2} = \boxed{34.6 \text{ cm}^3 \text{ mol}^{-1}}$

$$\begin{aligned} a &= RT(b - B) = (8.206 \times 10^{-2}) \times (273 \text{ L atm mol}^{-1}) \times (34.6 + 21.7) \text{ cm}^3 \text{ mol}^{-1} \\ &= (22.40 \text{ L atm mol}^{-1}) \times (56.3 \times 10^{-3} \text{ L mol}^{-1}) = \boxed{1.26 \text{ L}^2 \text{ atm mol}^{-2}} \end{aligned}$$

P1.22 For a real gas we may use the virial expansion in terms of p [1.21]

$$p = \frac{nRT}{V} (1 + B'p + \dots) = \rho \frac{RT}{M} (1 + B'p + \dots)$$

which rearranges to $\frac{p}{\rho} = \frac{RT}{M} + \frac{RTB'}{M}p + \dots$

Therefore, the limiting slope of a plot of $\frac{p}{\rho}$ against p is $\frac{B'RT}{M}$. From Fig. 1.2 in the *Student's Solutions Manual*, the limiting slope is

$$\frac{B'RT}{M} = \frac{(4.41 - 5.27) \times 10^4 \text{ m}^2 \text{ s}^{-2}}{(10.132 - 1.223) \times 10^4 \text{ Pa}} = -9.7 \times 10^{-2} \text{ kg}^{-1} \text{ m}^3$$

From Fig. 1.2, $\frac{RT}{M} = 5.39 \times 10^4 \text{ m}^2 \text{ s}^{-2}$; hence

$$B' = -\frac{9.7 \times 10^{-2} \text{ kg}^{-1} \text{ m}^3}{5.39 \times 10^4 \text{ m}^2 \text{ s}^{-2}} = -1.80 \times 10^{-6} \text{ Pa}^{-1}$$

$$B' = (-1.80 \times 10^{-6} \text{ Pa}^{-1}) \times (1.0133 \times 10^5 \text{ Pa atm}^{-1}) = \boxed{-0.182 \text{ atm}^{-1}}$$

$$B = RTB' \text{ [Problem 1.21]}$$

$$= (8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (-0.182 \text{ atm}^{-1})$$

$$= \boxed{-4.4 \text{ L mol}^{-1}}$$

P1.23 Write $V_m = f(T, p)$; 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

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

From the equation of state

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

Substituting

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

From the equation of state $\frac{(a+bT)}{V_m^2} = p - \frac{RT}{V_m}$

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

P1.25 $Z = \frac{V_m}{V_m^0}$, where V_m^0 = the molar volume of a perfect gas

From the given equation of state

$$V_m = b + \frac{RT}{p} = b + V_m^0 \quad \text{then } Z = \frac{b + V_m^0}{V_m^0} = 1 + \frac{b}{V_m^0}$$

For $V_m = 10b$, $10b = b + V_m^0$ or $V_m^0 = 9b$

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

P1.27 The two masses represent the same volume of gas under identical conditions, and therefore, the same number of molecules (Avogadro's principle) and moles, n . Thus, the masses can be expressed as

$$nM_N = 2.2990 \text{ g}$$

for 'chemical nitrogen' and

$$n_{\text{Ar}}M_{\text{Ar}} + n_N M_N = n[x_{\text{Ar}}M_{\text{Ar}} + (1 - x_{\text{Ar}})M_N] = 2.3102 \text{ g}$$

for 'atmospheric nitrogen'. Dividing the latter expression by the former yields

$$\frac{x_{\text{Ar}}M_{\text{Ar}}}{M_N} + (1 - x_{\text{Ar}}) = \frac{2.3102}{2.2990} \quad \text{so} \quad x_{\text{Ar}} \left(\frac{M_{\text{Ar}}}{M_N} - 1 \right) = \frac{2.3102}{2.2990} - 1$$

$$\text{and } x_{\text{Ar}} = \frac{\frac{2.3102}{2.2990} - 1}{\frac{M_{\text{Ar}}}{M_N} - 1} = \frac{\frac{2.3102}{2.2990} - 1}{\frac{39.95 \text{ g mol}^{-1}}{28.013 \text{ g mol}^{-1}} - 1} = \boxed{0.011}$$

Comment. This value for the mole fraction of argon in air is close to the modern value.

P1.29

$$Z = \frac{pV_m}{RT} = \left(\frac{T_c}{T} \right) \times \left(\frac{p}{p_c} \right) \times \left(\frac{p_c V_m}{RT_c} \right) = \frac{p_r V_r'}{T_r} \quad [1.20b, 1.28]$$

$$= \frac{V_r'}{T_r} \left\{ \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \right\} \quad [1.29]$$

$$\text{But } V_r = \frac{V}{V_c} = \frac{RT_c}{p_c V_c} \times \left(\frac{p_c V}{RT_c} \right) = \frac{8}{3} \frac{p_c V}{RT_c} [1.27] = \frac{8}{3} V_r'$$

$$\text{Therefore } Z = \frac{V_r'}{T_r} \left\{ \frac{8T_r}{3 \left(\frac{8V_r'}{3} \right) - 1} - \frac{3}{\left(\frac{8V_r'}{3} \right)^2} \right\}$$

$$= \frac{V_r'}{T_r} \left\{ \frac{T_r}{V_r' - 1/8} - \frac{27}{64(V_r')^2} \right\}$$

$$= V_r' \left\{ \frac{1}{V_r' - 1/8} - \frac{27}{64T_r(V_r')^2} \right\}$$

$$\boxed{Z = \frac{V_r'}{V_r' - 1/8} - \frac{27}{64T_r V_r'}} \quad (2)$$

To derive the alternative form, solve eqn 1 for V_r' , substitute the result into eqn 2, and simplify into polynomial form.

$$V_r' = \frac{ZT_r}{p_r}$$

$$Z = \frac{ZT_r/p_r}{\frac{ZT_r}{p_r} - \frac{1}{8}} - \frac{27}{64T_r} \left(\frac{p_r}{ZT_r} \right)$$

$$= \frac{8ZT_r}{8ZT_r - p_r} - \frac{27p_r}{64ZT_r^2}$$

$$= \frac{512T_r^3 Z^2 - 27p_r \times (8T_r Z - p_r)}{64T_r^2 \times (8ZT_r - p_r)Z}$$

$$64T_r^2 (8ZT_r - p_r)Z^2 = 512T_r^3 Z^2 - 216T_r p_r Z + 27p_r^2$$

$$512T_r^3 Z^3 - (64T_r^2 p_r + 512T_r^3) Z^2 + 216T_r p_r Z - 27p_r^2 = 0$$

$$\boxed{Z^3 - \left(\frac{p_r}{8T_r} + 1\right)Z^2 + \frac{27p_r}{64T_r^2}Z - \frac{27p_r^2}{512T_r^3} = 0} \quad (3)$$

At $T_r = 1.2$ and $p_r = 3$ eqn 3 predicts that Z is the root of

$$Z^3 - \left(\frac{3}{8(1.2)} + 1\right)Z^2 + \frac{27(3)}{64(1.2)^2}Z - \frac{27(3)^2}{512(1.2)^3} = 0$$

$$Z^3 - 1.3125Z^2 + 0.8789Z - 0.2747 = 0$$

The real root is $\boxed{Z = 0.611}$ and this prediction is independent of the specific gas.

Figure 1.27 indicates that the experimental result for the listed gases is closer to 0.55.

Solutions to applications

P1.31 Refer to Fig. 1.3.

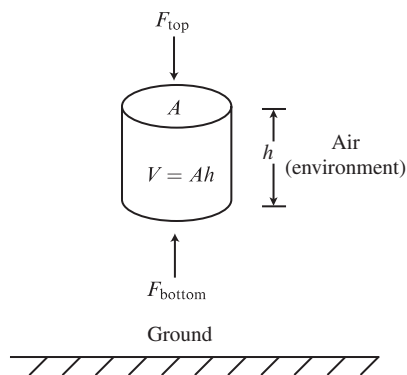


Figure 1.3

The buoyant force on the cylinder is

$$F_{\text{buoy}} = F_{\text{bottom}} - F_{\text{top}}$$

$$= A(p_{\text{bottom}} - p_{\text{top}})$$

according to the barometric formula.

$$p_{\text{top}} = p_{\text{bottom}} e^{-Mgh/RT}$$

where M is the molar mass of the environment (air). Since h is small, the exponential can be expanded in a Taylor series around $h = 0$ ($e^{-x} = 1 - x + \frac{1}{2!}x^2 + \dots$). Keeping the first-order term only yields

$$p_{\text{top}} = p_{\text{bottom}} \left(1 - \frac{Mgh}{RT}\right)$$

The buoyant force becomes

$$\begin{aligned} F_{\text{buoy}} &= Ap_{\text{bottom}} \left(1 - 1 + \frac{Mgh}{RT} \right) = Ah \left(\frac{p_{\text{bottom}}M}{RT} \right) g \\ &= \left(\frac{p_{\text{bottom}}VM}{RT} \right) g = nMg \quad \left[n = \frac{p_{\text{bottom}}V}{RT} \right] \end{aligned}$$

n is the number of moles of the environment (air) displaced by the balloon, and $nM = m$, the mass of the displaced environment. Thus $F_{\text{buoy}} = mg$. The net force is the difference between the buoyant force and the weight of the balloon. Thus

$$F_{\text{net}} = mg - m_{\text{balloon}}g = (m - m_{\text{balloon}})g$$

This is Archimedes' principle.