Solutions Manual for Physical Chemistry

FOURTH EDITION

P. W. Atkins

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Preface to the fourth edition

I have reworked all the solutions in this edition from scratch and in the light of comments received on the earlier editions. I have also adopted, within the constraints of space to which a *Solutions manual* is subject, a slightly more generous style, with more words, more details, a more open layout, and more guidance.

The solutions have been examined in detail by Michael Fuson, of Denison University, Granville, Ohio and by Charles Trapp, of the University of Louisville, Louisville, Kentucky. I am greatly indebted to them both for their good advice, which I have tried to follow, and their detailed comments. If errors remain, they are probably at locations where I ignored what they advised.

Oxford, P.W.A.
April 1990

Contents

PART 1: EQUILIBRIUM

1. The properties of gases

Exercises

1.1 $p_f = \dfrac{V_i}{V_f} \times p_i$ [3]

$V_i = 1.0\ \text{L} = 1000\ \text{cm}^3$, $V_f = 100\ \text{cm}^3$, $p_i = 1.00\ \text{atm}$

$$p_f = \frac{1000\ \text{cm}^3}{100\ \text{cm}^3} \times 1.00\ \text{atm} = 10 \times 1.00\ \text{atm} = \underline{10\ \text{atm}}$$

1.2 (a) Find what pressure a perfect gas exerts from $pV = nRT$. Since the molar mass of Xe is 131 g mol^{-1}, the sample has $n = 1.00$ mol Xe. Therefore, with $p = nRT/V$,

$$p = \frac{1.00\ \text{mol} \times 0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 298.15\ \text{K}}{1.0\ \text{L}} = \underline{24\ \text{atm}}$$

That is, the sample has $p = 24$ atm, not 20 atm.

(b) The van der Waals equation is [11]:

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

For xenon, Table 1.4 gives $a = 4.194\ \text{L}^2\ \text{atm mol}^{-1}$ and $b = 5.105 \times 10^{-2}\ \text{L mol}^{-1}$. Since $n = 1.00$ mol and $V = 1.0$ L,

$$\frac{nRT}{V - nb} = \frac{1.00\ \text{mol} \times 0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 298.15\ \text{K}}{(1.0 - 0.051)\text{L}} = 25.\overline{8}\ \text{atm}$$

$$\frac{an^2}{V^2} = \frac{4.194\ \text{L}^2\ \text{atm mol}^{-1} \times (1.00\ \text{mol})^2}{(1.0\ \text{L})^2} = 4.1\overline{94}\ \text{atm}$$

Therefore,

$$p = 25.\overline{8}\ \text{atm} - 4.1\overline{94}\ \text{atm} = \underline{22\ \text{atm}}$$

1.3 $p_i = \dfrac{V_f}{V_i} \times p_f$ [3]

$V_f = 4.65\ \text{L}$, $V_i = 4.65\ \text{L} + 2.20\ \text{L} = 6.85\ \text{L}$

$p_f = 3.78 \times 10^3\ \text{Torr}$

Therefore

(a) $p_i = \dfrac{4.65\ \text{L}}{6.85\ \text{L}} \times 3.78 \times 10^3\ \text{Torr} = \underline{2.57 \times 10^3\ \text{Torr}}$

(b) Since 1 atm = 760 Torr exactly,

$p_i = 2.57 \times 10^3\ \text{Torr} \times \dfrac{1\ \text{atm}}{760\ \text{Torr}} = \underline{3.38\ \text{atm}}$

1.4 $T_f = \dfrac{V_f}{V_i} \times T_i$ [5]

$V_i = 1.0\ \text{L}$, $V_f = 100\ \text{cm}^3$, $T_i = 298\ \text{K}$

$T_f = \dfrac{100\ \text{cm}^3}{1000\ \text{cm}^3} \times 298\ \text{K} = \underline{30\ \text{K}}$

1.5 $p_f = \dfrac{T_f}{T_i} \times p_i$ [5]

Internal pressure = quoted pressure + atmospheric pressure

$p_i = 24\ \text{lb in}^{-2} + 14.7\ \text{lb in}^{-2} = 38.\overline{7}\ \text{lb in}^{-2}$

$T_i = 268\ \text{K}\ (-5\ ^\circ\text{C})$, $T_f = 308\ \text{K}\ (35\ ^\circ\text{C})$

$p_f = \dfrac{308\ \text{K}}{268\ \text{K}} \times 38.\overline{7}\ \text{lb in}^{-2} = 44.\overline{5}\ \text{lb in}^{-2}$

Therefore

$p(\text{internal}) = 44.\overline{5}\ \text{lb in}^{-2} - 14.7\ \text{lb in}^{-2} = \underline{30\ \text{lb in}^{-2}}$

Complications include the change in volume of the tyre, the change in rigidity of the material from which it is made, and loss of pressure by leaks and diffusion.

1.6 $T_f = \dfrac{V_f}{V_i} \times T_i$ [5]

$V_f = 1.14\ V_i$ (a 14 per cent increase), $T_i = 340\ \text{K}$

Therefore,

$$T_f = \frac{1.14\,V_i}{V_i} \times 340\text{ K} = 1.14 \times 340\text{ K} = \underline{388\text{ K}}$$

1.7 $V_f = \dfrac{p_i}{p_f} \times V_i$ [3]

$V_i = 2.0\text{ m}^3$, $p_i = 755$ Torr, $p_f =$ (a) 100 Torr, (b) 10 Torr

Therefore:

(a) $V_f = \dfrac{755\text{ Torr}}{100\text{ Torr}} \times 2.0\text{ m}^3 = \underline{15\text{ m}^3}$

(b) $V_f = \dfrac{755\text{ Torr}}{10\text{ Torr}} \times 2.0\text{ m}^3 = \underline{1.5 \times 10^2\text{ m}^3}$

1.8 $p = \dfrac{nRT}{V}$ [1]

$$n = \frac{0.255\text{ g}}{20.18\text{ g mol}^{-1}} = 1.26 \times 10^{-2}\text{ mol},\ T = 122\text{ K},\ V = 3.00\text{ L}$$

Therefore,

$$p = \frac{1.26 \times 10^{-2}\text{ mol} \times 0.0821\text{ L atm K}^{-1}\text{ mol}^{-1} \times 122\text{ K}}{3.00\text{ L}} = \underline{4.22 \times 10^{-2}\text{ atm}}$$

1.9 (a) $V = \dfrac{n_J RT}{p_J}$ [7]

$$n(\text{Ne}) = \frac{0.225\text{ g}}{20.18\text{ g mol}^{-1}} = 1.11\bar{5} \times 10^{-2}\text{ mol},\ p(\text{Ne}) = 66.5\text{ Torr},\ T = 300\text{ K}$$

Therefore, since there is only one volume,

$$V = \frac{1.11\bar{5} \times 10^{-2}\text{ mol} \times 62.36\text{ L Torr K}^{-1}\text{ mol}^{-1} \times 300\text{ K}}{66.5\text{ Torr}} = \underline{3.14\text{ L}}$$

(b) $p = \dfrac{nRT}{V}$ [1], $n = n(\text{CH}_4) + n(\text{Ar}) + n(\text{Ne})$

$$n(\text{CH}_4) = \frac{0.320\text{ g}}{16.04\text{ g mol}^{-1}} = 1.99\bar{5} \times 10^{-2}\text{ mol}$$

$$n(\text{Ar}) = \frac{0.175\ \text{g}}{39.95\ \text{g mol}^{-1}} = 4.38\bar{0} \times 10^{-2}\ \text{mol}$$

$$n = (1.99\bar{5} + 4.38\bar{0} + 1.11\bar{5}) \times 10^{-2}\ \text{mol} = 7.49\bar{0} \times 10^{-2}\ \text{mol}$$

Therefore

$$p = \frac{7.49\bar{0} \times 10^{-2}\ \text{mol} \times 62.36\ \text{L Torr K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{3.13\bar{7}\ \text{L}} = \underline{447\ \text{Torr}}$$

1.10 $n = \frac{pV}{RT}$ [1], $n = \frac{m}{M}$ and $\rho = \frac{m}{V}$

Therefore, $M = \frac{mRT}{pV} = \rho\frac{RT}{p}$

$\rho = 1.23\ \text{g L}^{-1}$, $T = 330\ \text{K}$, $p = 150\ \text{Torr}$

Hence

$$M = \frac{1.23\ \text{g L}^{-1} \times 62.36\ \text{L Torr K}^{-1}\ \text{mol}^{-1} \times 330\ \text{K}}{150\ \text{Torr}} = \underline{169\ \text{g mol}^{-1}}$$

1.11 $M = \rho\frac{RT}{p}$ [Exercise 1.10]

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

$$M = \frac{0.1340\ \text{g L}^{-1} \times 62.36\ \text{L Torr K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}}{152\ \text{Torr}} = \underline{16.4\ \text{g mol}^{-1}}$$

1.12 (a) $p = \frac{nRT}{V}$ [1]

$n = 1.0\ \text{mol}$, $T = 273.15\ \text{K}$ (i) or $100\ \text{K}$ (ii)

$V = 22.414\ \text{L}$ (i) or $100\ \text{cm}^3$ (ii)

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

(ii) $$p = \frac{1.0\ \text{mol} \times 8.206 \times 10^{-2}\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 1000\ \text{K}}{0.100\ \text{L}} = \underline{8.2 \times 10^2\ \text{atm}}$$

(b) $p = \dfrac{nRT}{V-nb} - \dfrac{an^2}{V^2}$ [11]

From Table 1.4, $a = 5.489\ \text{L}^2\ \text{atm mol}^{-2}$ and $b = 6.380 \times 10^{-2}\ \text{L mol}^{-1}$.

Therefore,

(i) $\dfrac{nRT}{V-nb} = \dfrac{1.0\ \text{mol} \times 8.206 \times 10^{-2}\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 273.15\ \text{K}}{(22.414 - 1.0 \times 6.380 \times 10^{-2})\ \text{L}} = 1.00\overline{3}\ \text{atm}$

$\dfrac{an^2}{V^2} = \dfrac{5.489\ \text{L}^2\ \text{atm mol}^{-2} \times (1.0\ \text{mol})^2}{(22.414\ \text{L})^2} = 1.0\overline{9} \times 10^{-2}\ \text{atm}$

and $p = 1.00\overline{3}\ \text{atm} - 1.0\overline{9} \times 10^{-2}\ \text{atm} = 0.992\ \text{atm} = \underline{1.0\ \text{atm}}$

(ii) $\dfrac{nRT}{V-nb} = \dfrac{1.0\ \text{mol} \times 8.206 \times 10^{-2}\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 1000\ \text{K}}{(0.100 - 0.06380)\text{L}} = 2.2\overline{7} \times 10^3\ \text{atm}$

$\dfrac{an^2}{V^2} = \dfrac{5.489\ \text{L}^2\ \text{atm mol}^{-1} \times (1.0\ \text{mol})^2}{(0.100\ \text{L})^2} = 5.4\overline{9} \times 10^2\ \text{atm}$

and $p = 2.2\overline{7} \times 10^3\ \text{atm} - 5.4\overline{9} \times 10^2\ \text{atm} = \underline{1.7 \times 10^3\ \text{atm}}$

1.13 $V_c = 3b$[12a] $= 3 \times 0.0226\ \text{L mol}^{-1} = \underline{6.78 \times 10^{-2}\ \text{L mol}^{-1}}$

$p_c = \dfrac{a}{27b^2}$ [12b] $= \dfrac{0.751\ \text{L}^2\ \text{atm mol}^{-1}}{27 \times (0.0226\ \text{L mol}^{-1})^2} = \underline{54.5\ \text{atm}}$

$T_c = \dfrac{8a}{27Rb}$ [12c] $= \dfrac{8 \times 0.751\ \text{L}^2\ \text{atm mol}^{-1}}{27 \times 8.206 \times 10^{-2}\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 0.0226\ \text{L mol}^{-1}}$

$= \underline{120\ \text{K}}$

1.14 $Z = \dfrac{pV_m}{RT}$ [9]; for a perfect gas $V_m^0 = RT/p$. Since the molar volume is 12 per cent smaller than that of a perfect gas,

$V_m = 0.88\ V_m^0 = 0.88\dfrac{RT}{p}$

Therefore,

(a) $Z = \dfrac{p}{RT} \times 0.88\dfrac{RT}{p} = \underline{0.88}$

(b) $V_m = \dfrac{ZRT}{p} = \dfrac{0.88 \times 8.206 \times 10^{-2}\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{20\ \text{atm}} = \underline{1.1\ \text{L}}$

Since $V_m < V_m^0$, attractive forces dominate

1.15 $Z = \dfrac{pV_m}{RT}$ [9], implying that $V_m = \dfrac{ZRT}{p}$

Since $Z = 0.86$, $T = 300$ K, $p = 20$ atm,

$$V_m = \frac{0.86 \times 8.206 \times 10^{-2}\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{20\ \text{atm}} = 1.0\overline{59}\ \text{L mol}^{-1}$$

(a) $V = nV_m = 8.2 \times 10^{-3}\ \text{mol} \times 1.0\overline{59}\ \text{L mol}^{-1}$

$= \underline{8.7\ \text{mL}}$

(b) $B = V_m\left(\dfrac{pV_m}{RT} - 1\right)$ [10b] $= V_m(Z-1)$

$= 1.0\overline{59}\ \text{L mol}^{-1} \times (0.86 - 1) = \underline{-0.15\ \text{L mol}^{-1}}$

1.16 $n = n(H_2) + n(N_2) = 2.0\ \text{mol} + 1.0\ \text{mol} = 3.0\ \text{mol}$

(a) $x(H_2) = \dfrac{2.0\ \text{mol}}{3.0\ \text{mol}} = \underline{0.67}$

$x(N_2) = \dfrac{1.0\ \text{mol}}{3.0\ \text{mol}} = \underline{0.33}$

(b) $p_J = n_J \dfrac{RT}{V}$ [7]

$$\frac{RT}{V} = \frac{8.206 \times 10^{-2}\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 273.15\ \text{K}}{22.4\ \text{L}} = 1.00\ \text{atm mol}^{-1}$$

$p(H_2) = 2.0\ \text{mol} \times 1.00\ \text{atm mol}^{-1} = \underline{2.0\ \text{atm}}$

$p(N_2) = 1.0\ \text{mol} \times 1.00\ \text{atm mol}^{-1} = \underline{1.0\ \text{atm}}$

(c) $p = p(H_2) + p(N_2)$ [7]

$= 2.0\ \text{atm} + 1.0\ \text{atm} = \underline{3.0\ \text{atm}}$

1.17 $b = \frac{1}{3}V_c$ [12a, $V_c = 98.7\ \text{cm}^3\ \text{mol}^{-1}$]

$= \frac{1}{3} \times 98.7\ \text{cm}^3\ \text{mol}^{-1} = \underline{32.9\ \text{cm}^3\ \text{mol}^{-1}}$

$a = 27b^2p_c = 3V_c^2p_c$ [12b, $p_c = 45.6\ \text{atm}$]

$= 3 \times (98.7 \times 10^{-3}\ \text{L mol}^{-1})^2 \times 45.6\ \text{atm} = \underline{1.33\ \text{L}^2\ \text{atm mol}^{-2}}$

As b is approximately the volume occupied per mole of particles

$$v_{mol} \approx \frac{b}{N_A} = \frac{32.9 \times 10^{-6}\ m^3\ mol^{-1}}{6.022 \times 10^{23}\ mol^{-1}} = 5.46 \times 10^{-29}\ m^3$$

Then, with $v_{mol} = \frac{4}{3}\pi r^3$,

$$r \approx \left(\frac{3}{4\pi} \times 5.46 \times 10^{-29}\ m^3\right)^{1/3} = \underline{0.24\ nm}$$

1.18 (a) $T_B = \dfrac{a}{bR}$ [14]

From Table 1.4, $a = 6.493\ L^2\ atm\ mol^{-2}$, $b = 5.622 \times 10^{-2}\ L\ mol^{-1}$. Therefore,

$$T_B = \frac{6.493\ L^2\ atm\ mol^{-2}}{5.622 \times 10^{-2}\ L\ mol^{-1} \times 8.206 \times 10^{-2}\ L\ atm\ K^{-1}\ mol^{-1}} = \underline{1.4 \times 10^3\ K}$$

(b) As in Example 1.17, $v_{mol} \approx \dfrac{b}{N_A} = \dfrac{5.622 \times 10^{-5}\ m^3\ mol^{-1}}{6.022 \times 10^{23}\ mol^{-1}} = 9.3 \times 10^{-29}\ m^3$

$$r \approx \left(\frac{3}{4\pi} \times 9.3 \times 10^{-29}\ m^3\right)^{1/3} = \underline{0.28\ nm}$$

1.19 At 25 °C and 10 atm, the reduced temperature and pressure [Section 1.5] of hydrogen are

$$T_r = \frac{298\ K}{33.23\ K} = 8.96\bar{8} \quad [T_c = 33.23\ K, \text{ Table 1.3}]$$

$$p_r = \frac{1.0\ atm}{12.8\ atm} = 0.078\bar{1} \quad [p_c = 12.8\ atm, \text{ Table 1.3}]$$

Hence, the gases named will be in corresponding states at $T = 8.96\bar{8} \times T_c$ and at $p = 0.078\bar{1} \times p_r$.

(a) For ammonia, $T_c = 405.5\ K$ and $p_c = 111.3\ atm$ [Table 1.3], so

$T = 8.96\bar{8} \times 405.5\ K = \underline{3.64 \times 10^3\ K}$

$p = 0.078\bar{1} \times 111.3\ atm = \underline{8.7\ atm}$

(b) For xenon, $T_c = 289.75\ K$ and $p_c = 58.0\ atm$, so

$T = 8.96\bar{8} \times 289.75\ K = \underline{2.60 \times 10^3\ K}$

$p = 0.078\overline{1} \times 58.0 \text{ atm} = \underline{4.5 \text{ atm}}$

(c) For helium, $T_c = 5.21$ K and $p_c = 2.26$ atm, so

$T = 8.96\overline{8} \times 5.21 \text{ K} = \underline{46.7 \text{ K}}$

$p = 0.078\overline{1} \times 2.26 \text{ atm} = \underline{0.18 \text{ atm}}$

Problems

1.1 $V_f = \dfrac{p_i}{p_f} \times V_i$ [3] and $p = \rho g h$ [Example 1.2]

Total pressure: $p_i = 1.0$ atm

$$p_f = 1.0 \text{ atm} + \rho g h$$

$\rho g h = 1.025 \times 10^3 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2} \times 50 \text{ m} = 5.03\overline{3} \times 10^5 \text{ Pa}$

Hence, $p_f = 1.0\overline{1} \times 10^5 \text{ Pa} + 5.03\overline{3} \times 10^5 \text{ Pa} = 6.04\overline{4} \times 10^5 \text{ Pa}$

$$V_f = \frac{1.0\overline{1} \times 10^5 \text{ Pa}}{6.04\overline{4} \times 10^5 \text{ Pa}} \times 3 \text{ m}^3 = \underline{0.5 \text{ m}^3}$$

1.2 External pressure is p_i and pressure at foot of column is $p_f + \rho g h$. At equilibrium the two pressures are the same, so

$$p_f - p_i = \rho g h$$
$$= 1.0 \times 10^3 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2} \times 0.15 \text{ m}$$
$$= \underline{1.5 \times 10^3 \text{ Pa}} \ (= 1.5 \times 10^{-2} \text{ atm})$$

1.3 $pV = nRT$ [1] implies that, with n constant,

$$\frac{p_f V_f}{T_f} = \frac{p_i V_i}{T_i}$$

or

$$p_f = \frac{V_i}{V_f} \times \frac{T_f}{T_i} \times p_i = \left(\frac{r_i}{r_f}\right)^3 \times \frac{T_f}{T_i} \times p_i \quad [\text{since } V = \tfrac{4}{3}\pi r^3]$$

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

1.4 $n = \dfrac{pV}{RT}$ and $n = \dfrac{m}{M}$, hence $\rho = \dfrac{m}{V} = \dfrac{Mp}{RT}$

That is, $p = \rho\dfrac{RT}{M}$, or $\dfrac{p}{\rho} = \dfrac{RT}{M}$

For a real gas

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

which rearranges to

$$\frac{p}{\rho} = \frac{RT}{M} + \frac{RTB'}{M}p + \cdots$$

Therefore, plot p/ρ against p and expect a straight line with intercept RT/M at $p = 0$. Draw up the following table:

p/Torr	91.74	188.93	277.3	452.8	639.3	760.0
$\rho/(\text{kg m}^{-3})$	0.225	0.456	0.664	1.062	1.468	1.734
$(p/\rho)/(10^5\,\text{m}^2\,\text{s}^{-3})$	0.544	0.552	0.557	0.568	0.581	0.584

The points are plotted in Fig. 1.1, and the limiting behaviour is confirmed

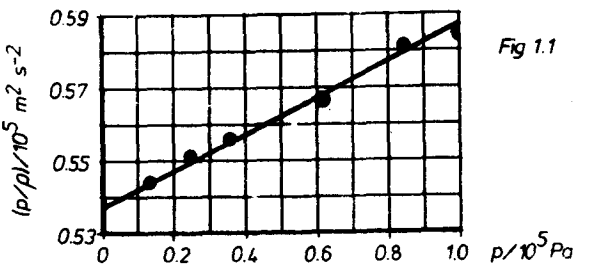

Fig 1.1

The intercept at $p = 0$ is at

$$\frac{p}{\rho}\Big/(10^5\,\text{m}^2\,\text{s}^{-2}) = 0.540, \text{ or } p/\rho = 0.540 \times 10^5\,\text{m}^2\,\text{s}^{-2}$$

Therefore,

$$M = \frac{RT}{0.540 \times 10^5\,\text{m}^2\,\text{s}^{-2}}$$

$$= \frac{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298.15\ \text{K}}{0.540 \times 10^5\ \text{m}^2\ \text{s}^{-2}}$$

$$= 4.59 \times 10^{-2}\ \text{kg mol}^{-1} = \underline{45.9\ \text{g mol}^{-1}}$$

1.5 $n = \dfrac{pV}{RT}$ [1], $V = \dfrac{4\pi}{3} r^3 = \dfrac{4\pi}{3} \times (3.0\text{m})^3 = 11\bar{3}\ \text{m}^3$

$p = 1.0$ atm, $T = 298$ K

(a) $n = \dfrac{1.0\ \text{atm} \times 11\bar{3} \times 10^3\ \text{L}}{8.206 \times 10^{-2}\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}} = \underline{4.6\bar{2} \times 10^3\ \text{mol}}$

(b) $m(\text{H}_2) = nM(\text{H}_2) = 4.6\bar{2} \times 10^3\ \text{mol} \times 2.02\ \text{g mol}^{-1} = 9.3\bar{3} \times 10^3\ \text{g}$

Mass of displaced air $= 11\bar{3}\ \text{m}^3 \times 1.22\ \text{kg m}^{-3} = 1.3\bar{8} \times 10^2\ \text{kg}$

Therefore, the payload is $138\ \text{kg} - 9.3\bar{3}\ \text{kg} = \underline{12\bar{9}\ \text{kg}}$

(c) For helium, $m = nM(\text{He}) = 4.6\bar{2} \times 10^3\ \text{mol} \times 4.00\ \text{g mol}^{-1} = 18\ \text{kg}$

The payload is now $13\bar{8}\ \text{kg} - 18\ \text{kg} = \underline{120\ \text{kg}}$

1.6 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 $\rho = \rho'$. however, because [Problem 1.4]

$$\rho = \frac{pM}{RT}$$

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 molecule CH_2FCF_3 has $M \approx 102 \text{ g mol}^{-1}$.

1.7 At constant volume, $p = \frac{T}{T_3} \times p_3$ where T_3 and p_3 are the temperature and pressure of the triple point. Therefore,

(a) $$p_{274.16\text{ K}} - p_{273.16\text{ K}} = \left(\frac{274.16 \text{ K}}{273.16 \text{ K}} - 1\right) p_3$$

$$= \frac{1}{273.16} \times p_3 = \frac{1}{273.16} \times 50.2 \text{ Torr} = \underline{0.184 \text{ Torr}}$$

(b) For 100 °C (373 K)

$$p = \frac{373 \text{ K}}{273.16 \text{ K}} \times 50.2 \text{ Torr} = \underline{68.6 \text{ Torr}}$$

(c) $$p_{374\text{ K}} - p_{373\text{ K}} = \left(\frac{374 \text{ K}}{373 \text{ K}} - 1\right) p_{373\text{ K}} = \frac{68.6 \text{ Torr}}{373} = \underline{0.184 \text{ Torr}}$$

1.8 Draw up the following table, which is based on the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

	N_2	H_2	NH_3	Total
Initial amounts	n	n'	0	$n + n'$
Final amounts	$n - \frac{1}{3}n'$	0	$\frac{2}{3}n'$	$n + \frac{1}{3}n'$
Specifically	0.33 mol	0	1.33 mol	1.66 mol
Mole fractions	0.20	0	0.80	1.00

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

$= \underline{1.66 \text{ atm}}$

$p(H_2) = x(H_2)p = \underline{0}$

$p(N_2) = x(N_2)p = 0.20 \times 1.66 \text{ atm} = \underline{0.33 \text{ atm}}$

$p(NH_3) = x(NH_3)p = 0.80 \times 1.66 \text{ atm} = \underline{1.33 \text{ atm}}$

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

$= \underline{12.5 \text{ L mol}^{-1}}$

(b) From $p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$ [11b], we obtain $V_m = \dfrac{RT}{p + \dfrac{a}{V_m^2}} + b$ [rearrange 11b]

Then, with a and b from Table 1.4,

$$V_m \approx \frac{8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1} \times 350 \text{ K}}{2.30 \text{ atm} + \dfrac{6.493 \text{ L}^2 \text{ atm mol}^{-2}}{(12.5 \text{ L mol}^{-1})^2}} + 5.622 \times 10^{-2} \text{ L mol}^{-1}$$

$$\approx \frac{28.7\bar{2} \text{ L mol}^{-1}}{2.34} + 5.622 \times 10^{-2} \text{ L mol}^{-1}$$

$\approx \underline{12.3 \text{ L mol}^{-1}}$

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

1.10 $T_c = \dfrac{2}{3}\left(\dfrac{2a}{3bR}\right)^{1/2} = \dfrac{2}{3} \times \dfrac{12 p_c b}{R}$ [Table 1.5]

$$= \frac{8}{3} \times \frac{p_c V_c}{R}$$

$$= \frac{8}{3} \times \frac{40 \text{ atm} \times 160 \times 10^{-3} \text{ L mol}^{-1}}{8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}} = \underline{21\bar{0} \text{ K}}$$

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

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