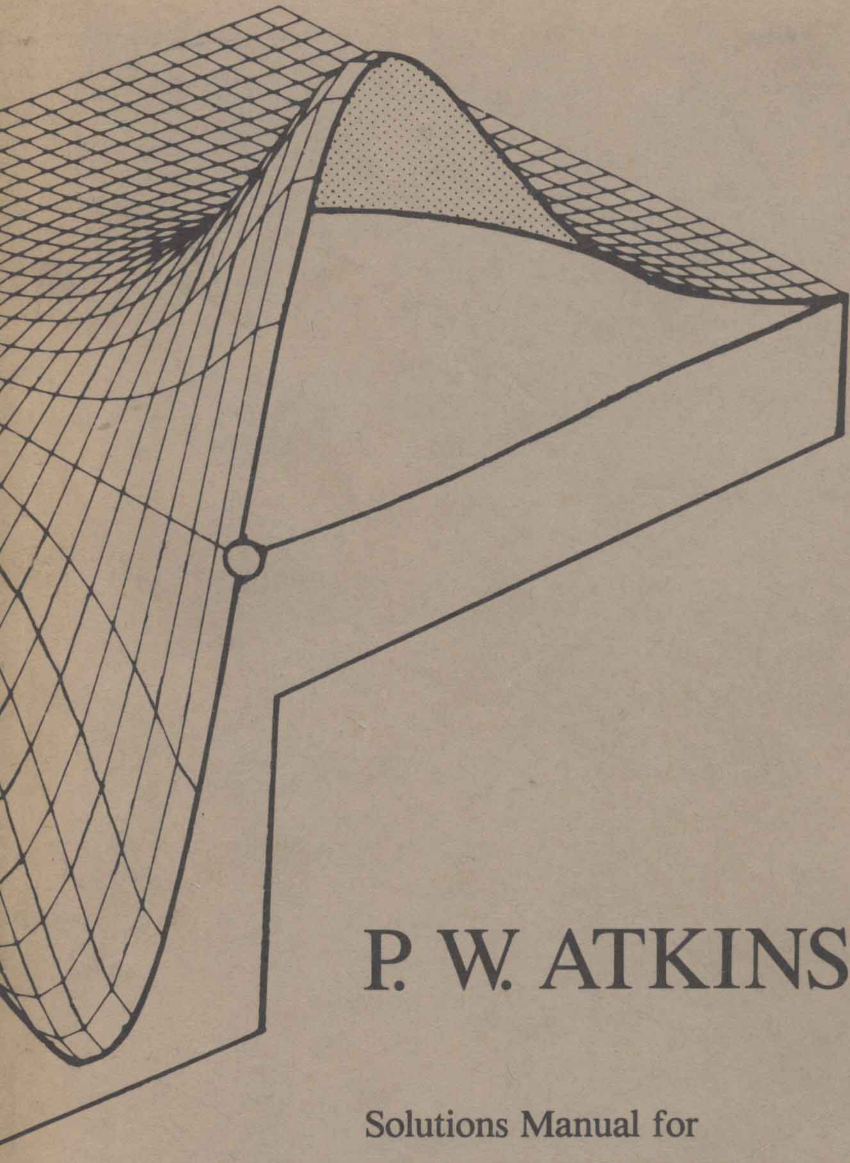

P. W. ATKINS

Solutions Manual for

PHYSICAL CHEMISTRY

Second Edition

Solutions Manual for Physical Chemistry

SECOND EDITION

P. W. Atkins

W. H. Freeman and Company
New York

Printed in the United States of America

ISBN 0-7167-1401-9

4 5 6 7 8 9 0 MP 0 8 9 8 7 6 5 4

Preface to First Edition

The pages that follow give detailed solutions of just about every one of the 1060 problems in the main text. The two or three exceptions are those where the question invites the reader to sit in front of a computer, or simply to sit still and think, or, in one case, to buy sugar. Even in these cases, though, I make suggestions and give advice.

The format is as follows. Steps in the development of an equation or in the development of an argument are elucidated by reference to the main text by a remark in square brackets; for example, [10.2.6] indicates that equation (10.2.6) of the main text has been used. If I refer to a diagram or a table in the main text other than in the present manual, I always add words such as 'of the main text' to avoid confusion.

I would like to acknowledge a great deal of generous help given to me by a number of people during the preparation of this manual. Sean Keating worked hard on checking and improving my solutions instead of working on his doctoral thesis. Five of my undergraduates, Adrian Capel, Peter Coveney, Timothy Parker, Martin Robinson, and Graham Topping, divided up the solutions and spent a lot of time checking them instead of working for an examination. Happily, it seemed to do them the opposite of harm. I owe much gratitude to Cordelle Yoder, who typed, with remarkable speed and precision, the complicated and lengthy text from an almost illegible manuscript, and did so at a distance of about 6000 miles. Perhaps it was better that way. The illustrations are all my own rough sketches but are fairly accurate plots of the actual data.

Oxford, 1978 P.W.A

Preface to Second Edition

In preparing this second edition I have taken into account numerous helpful comments from users of the first. Every solution has been examined in detail, either in order to take into account changes in the data or details of the question, or to present an improved version. There are now 1090 Problems in the text (the extra ones being mainly the result of the new chapter on macromolecules, but there are also deletions in the other chapters and replacements amounting to several dozen overall), and almost all of them are answered here in detail. I have used the same system of reference to pages, equations, and tables of data, and all the references now refer, of course, to the second edition of the main text. I should like to emphasize how grateful I am to all the users of the first edition who took the trouble to write to me.

Oxford P.W.A.
July 1981

Contents

PART 1: EQUILIBRIUM

PART 2: STRUCTURE

PART 3: CHANGE

PART 1: EQUILIBRIUM

1. The properties of gases

1.1 $p_f = (V_i/V_f)p_i$ [1.1.3].

$V_i = 1\ \text{dm}^3 = 1000\ \text{cm}^3$, $V_f = 100\ \text{cm}^3$, $p_i = 1\ \text{atm}$.

$p_f = (1000\ \text{cm}^3/100\ \text{cm}^3) \times (1\ \text{atm}) = 10 \times 1\ \text{atm} = \underline{10\ \text{atm}}$.

1.2 $V_f = (p_i/p_f)V_i$ [1.1.3].

$V_i = 2\ \text{m}^3$, $p_i = 755\ \text{mmHg}$, $p_f =$ (a) 100 mmHg, (b) 10 mmHg.

(a) $V_f = (755\ \text{mmHg}/100\ \text{mmHg}) \times (2\ \text{m}^3) = 7.55 \times 2\ \text{m}^3 = \underline{15.1\ \text{m}^3}$.

(b) $V_f = (755\ \text{mmHg}/10\ \text{mmHg}) \times (2\ \text{m}^3) = 75.5 \times 2\ \text{m}^3 = \underline{151\ \text{m}^3}$.

1.3 $V_f = (p_i/p_f)V_i$ [1.1.3] ; $p_f = \rho g h$ [hydrostatics] $+ 1\ \text{atm}$.

$V_i = 3\ \text{m}^3$, $p_i = 1\ \text{atm}$, $\rho = 1.025\ \text{g cm}^{-3}$, $g = 9.81\ \text{m s}^{-2}$, $h = 50\ \text{m}$

$p_f = (1.025\ \text{g cm}^{-3}) \times (9.81\ \text{m s}^{-2}) \times (50\ \text{m}) + 1\ \text{atm} = 5.03 \times 10^5\ \text{kg m}^{-1}\ \text{s}^{-2} + 1\ \text{atm}$

$= 5.03 \times 10^5\ \text{N m}^{-2} + 1\ \text{atm} = 4.96\ \text{atm} + 1\ \text{atm}$ [end-paper 1] $\approx 6\ \text{atm}$

$V_f = (1\ \text{atm}/6\ \text{atm}) \times (3\ \text{m}^3) = (1/6) \times 3\ \text{m}^3 = \underline{0.5\ \text{m}^3}$.

1.4 External pressure: p_i. Pressure at foot of column: $p_f + \rho g h$.

At equilibrium $p_i = p_f + \rho g h$, or $p_f = p_i - \rho g h$.

$\Delta V/V = (V_f - V_i)/V_i = [(p_i/p_f)V_f - V_i]/V_i = (p_i/p_f) - 1$

$= (p_i - p_f)/p_f = \rho g h/p_f \approx \rho g h/p_i$ $[\rho g h \ll p_i]$.

$\rho g h = (1.0\ \text{g cm}^{-3}) \times (9.81\ \text{m s}^{-2}) \times (15\ \text{cm})$

$= (1.0 \times 10^3\ \text{g m}^{-3}) \times (9.81\ \text{m s}^{-2}) \times (0.15\ \text{m}) = 1.47 \times 10^3\ \text{N m}^{-2}$.

$\Delta V/V = (1.47 \times 10^3\ \text{N m}^{-2})/(1.013 \times 10^5\ \text{N m}^{-2}) = \underline{0.0145, \text{ or } 1.5 \text{ per cent}}$.

1.5 $T_f = (V_f/V_i)T_i$ [1.1.5].

$V_i = 1\ \text{dm}^3$, $V_f = 100\ \text{cm}^3 = 0.1\ \text{dm}^3$, $T_i = 298\ \text{K}$.

$T_f = (0.1\ \text{dm}^3/1.0\ \text{dm}^3) \times (298\ \text{K}) = 0.1 \times (298\ \text{K}) \approx \underline{30\ \text{K}}$.

1.6 $p_f = (I_f/I_i)p_i$ [1.1.6].

Internal pressure = (quoted pressure) + (atmospheric pressure) [$14.0\ \text{lb in}^{-2}$].

$p_i = (24 \text{ lb in}^{-2}) + (14 \text{ lb in}^{-2}) = 38 \text{ lb in}^{-2}$.

$T_i \triangleq -5\ ^\circ\text{C}$, or 268 K; $T_f \triangleq 35\ ^\circ\text{C}$, or 308 K.

$p_i = (308 \text{ K}/268 \text{ K}) \times (38 \text{ lb in}^{-2}) = 43.7 \text{ lb in}^{-2}$.

$p_f(\text{internal}) = (43.7 - 14.0) \text{ lb in}^{-2} = \underline{29.7 \text{ lb in}^{-2}}$.

1.7 Disregard the elasticity of the envelope. $p_iV_i = nRT_i, p_fV_f = nRT_f$ [1.1.1]

$p_iV_i/nRT_i = p_fV_f/nRT_f$, or $p_f = (V_i/V_f)(T_f/T_i)p_i$

$V_f = (4/3)\pi R_f^3$, $V_i = (4/3)\pi R_i^3$, $p_f = (R_i/R_f)^3(T_f/T_i)p_i$.

$R_i = 1$ m, $R_f = 3$ m, $T_i = 298$ K, $T_f \triangleq -20\ ^\circ\text{C}$, or 253 K, $p_i = 1$ atm.

$p_f = (1 \text{ m}/3 \text{ m})^3 \times (253 \text{ K}/298 \text{ K}) \times (1 \text{ atm}) = (\tfrac{1}{3})^3 \times (0.849) \times (1 \text{ atm}) = \underline{0.031 \text{ atm}}$.

1.8 $n = \mathcal{M}/M_m$ [Box 0.1]; $n/V = \mathcal{M}/M_m V = \rho/M_m$ [$\rho = \mathcal{M}/V$].

For a perfect gas, $p = nRT/V = \underline{\rho RT/M_m}$.

For a real gas,

$$p = (nRT/V)\{1 + B'p + \ldots\} = (\rho RT/M_m)\{1 + B'p + \ldots\}$$

$$p/\rho = (RT/M_m) + B'(RT/M_m)p + \ldots$$

Therefore, plot p/ρ against p and expect a straight line with intercept RT/M_m at $p = 0$. Convert p to N m^{-2} using 1 mmHg $\triangleq$ 133.3 N m^{-2} [end-paper 1].

p/mmHg	91.74	188.93	277.3	452.8	639.3	760.0
$p/10^5$ N m^{-2}	0.1223	0.2518	0.3696	0.6036	0.8522	1.0133
ρ/kg m^{-3}	0.2276	0.4695	0.6898	1.1291	1.5983	1.9029
$(p/\rho)/10^5$ m^2 s^{-2}	0.5373	0.5363	0.5358	0.5346	0.5332	0.5325

These points are plotted in Fig. 1.1, and the limiting behavior is confirmed.

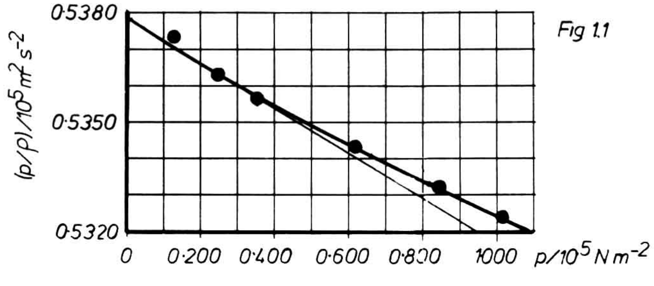

Fig 1.1

The intercept at $p = 0$ is at $(p/\rho)/10^5\ \mathrm{m^2\,s^{-2}} = 0.5379$. Therefore,

$$RT/M_m = 0.5379 \times 10^5\ \mathrm{m^2\,s^{-2}},\ \text{or}\ M_m = RT/(0.5379 \times 10^5\ \mathrm{m^2\,s^{-2}}).$$

$$M_m = \frac{(8.3144\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\ \mathrm{K})}{(0.5379 \times 10^5\ \mathrm{m^2\,s^{-2}})} = 4.609 \times 10^{-2}\ \mathrm{kg\,mol^{-1}}\quad [\mathrm{J} = \mathrm{kg\,m^2\,s^{-2}}]$$

$$= 46.09\ \mathrm{g\,mol^{-1}};\ \underline{M_r = 46.09}.$$

1.9 $n = pV/RT$ [1.1.1], $V = (4/3)\pi R^3$,

$p = 1\ \mathrm{atm} = 1.013 \times 10^5\ \mathrm{N\,m^{-2}}$, $T = 298\ \mathrm{K}$, $R = 3\ \mathrm{m}$,

$V = (4/3)\pi(3.0\ \mathrm{m})^3 = 113.1\ \mathrm{m^3}$, $RT = 2.479\ \mathrm{kJ\,mol^{-1}}$ [end-paper 1].

$$n = \frac{1.013 \times 10^5 \times 113.1}{2.479 \times 10^3} \cdot \frac{\mathrm{N\,m^{-2}\,m^3}}{\mathrm{J\,mol^{-1}}} = \underline{4623\ \mathrm{mol}}\quad [\mathrm{J} = \mathrm{N\,m}]$$

$\mathcal{M} = nM_r\ \mathrm{g\,mol^{-1}}$ [$\mathcal{M}$ = mass of sample] $= (4623\ \mathrm{mol}) \times (2\ \mathrm{g\,mol^{-1}}) = 9246\ \mathrm{g} = 9.2\ \mathrm{kg}$.

Mass of displaced air $= (113.1\ \mathrm{m^3}) \times (1.22\ \mathrm{kg\,m^{-3}}) = 138\ \mathrm{kg}$.

Therefore, payload $= 138\ \mathrm{kg} - 9.2\ \mathrm{kg} = \underline{129\ \mathrm{kg}}$.

For helium, $\mathcal{M} = 4623\ \mathrm{mol} \times (4.0\ \mathrm{g\,mol^{-1}})$ [end-paper 4] $= 18.5\ \mathrm{kg}$.

Therefore, payload $= 138\ \mathrm{kg} - 18.5\ \mathrm{kg} = \underline{120\ \mathrm{kg}}$.

At 30,000 ft, 4.6×10^3 mol of gas occupies a volume

$$V = (nRT/p)\ [1.1.1] = \frac{(4.6 \times 10^3\ \mathrm{mol}) \times (8.31\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (230\ \mathrm{K})}{0.28 \times (1.013 \times 10^5\ \mathrm{N\,m^{-2}})} = 310\ \mathrm{m^3}.$$

Therefore, the mass of displaced air is

$$M_{air} = (310\ \mathrm{m^3}) \times (0.43\ \mathrm{kg\,m^{-3}}) = 133\ \mathrm{kg}$$

and the payload is $133\ \mathrm{kg} - 9\ \mathrm{kg} = \underline{124\ \mathrm{kg}}$ (hydrogen)

or $133\ \mathrm{kg} - 18\ \mathrm{kg} = \underline{115\ \mathrm{kg}}$ (helium).

Whether or not you and your companion can reach that height depends on your combined mass. The combined mass of two 140 lb people is 127 kg. Don't forget to include the mass of the gondola, envelope, sandwiches, etc. Choose an emaciated companion.

In order to inflate the balloon further you would carry extra hydrogen. Suppose, for simplicity, you carried a further 9.2 kg in a compressed state in the same cylinder as before. The payload would then be 120 kg at sea level. If you got to 30,000 ft, and injected the extra 9.2 kg (4.6×10^3 mol) into the indefinitely extensible envelope, you would stretch it to $2 \times 310\ \mathrm{m^3}$, and so displace 266 kg of air, leaving a payload of 248 kg. You will go up. The same conclusion applies to smaller injections of gas.

1.10 $p = \rho RT/M_m$ [Problem 1.8]; $m = M_m/L$ [Box 0.1].

$\rho = \mathcal{M}/V = (33.5 \times 10^{-6}\ \mathrm{kg})/(250 \times 10^{-6}\ \mathrm{m^3}) = 0.134\ \mathrm{kg\,m^{-3}}$.

$$p = 152 \times (133.22\ \mathrm{N\ m^{-2}})\ [\text{end-paper 1}] = 2.026 \times 10^4\ \mathrm{N\ m^{-2}}.$$

$$M_\mathrm{m} = \rho RT/p = \frac{(0.134\ \mathrm{kg\ m^{-3}}) \times (8.3144\ \mathrm{J\ K^{-1}mol^{-1}}) \times (298.15\ \mathrm{K})}{(2.026 \times 10^4\ \mathrm{N\ m^{-2}})}$$

$$= 1.64 \times 10^{-2}\ \mathrm{kg\ J\ mol^{-1}/N\ m} = 1.64 \times 10^{-2}\ \mathrm{kg\ mol^{-1}}\ [\mathrm{J = N\ m}]$$

$$= 16.4\ \mathrm{g\ mol^{-1}};\quad \underline{M_\mathrm{r} = 16.4}.$$

$$m = M_\mathrm{m}/L = (1.64 \times 10^{-2}\ \mathrm{kg\ mol^{-1}})/(6.022 \times 10^{23}\ \mathrm{mol^{-1}}) = \underline{2.72 \times 10^{-26}\ \mathrm{kg}}.$$

1.11 The mass of displaced gas is $V\rho$, where V is the volume of the bulb and ρ the gas density. The balance condition for two gases is $m(\text{bulb}) = V(\text{bulb})\,\rho(1)$, $m(\text{bulb}) = V(\text{bulb})\rho(2)$ and so $\rho(1) = \rho(2)$. But $\rho(X) = M_\mathrm{m}(X)p(X)/kT$ [Problem 1.8], $X = 1, 2$ and so the balance condition is $M_\mathrm{m}(1)p(1) = M_\mathrm{m}(2)p(2)$, or $M_\mathrm{r}(1)p(1) = M_\mathrm{r}(2)p(2)$. Therefore, $M_\mathrm{r}(2) = M_\mathrm{r}(1)[p(1)/p(2)]$. This is valid in the limit of vanishing pressures. In experiment 1, $p(1) = 423.22$ mmHg, $p(2) = 327.10$ mmHg and so $M_\mathrm{r}(2) = 70.014 \times (423.22\ \mathrm{mmHg}/327.10\ \mathrm{mmHg}) = 90.59$. In experiment 2, $p(1) = 427.22$ mHg, $p(2) = 293.22$ mmHg and so $M_\mathrm{r} = 70.014 \times (427.22\ \mathrm{mmHg}/293.22\ \mathrm{mmHg}) = 102.0$. 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, and so we take $\underline{M_\mathrm{r} = 102}$. The molecule $CH_2F \cdot CF_3$ has $M_\mathrm{r} = 102$ [end-paper 4].

1.12 $pV = nRT$ [1.1.1], $V =$ constant.

At $T = T_3^* (= 273.16\ \mathrm{K})$, $p = p_3\ (= 50.2\ \mathrm{mmHg})$.

At a general temperature T, $p(T) = p_3(T/T_3^*)$ [1.1.6]. Therefore,

$$p(274.16\ \mathrm{K}) - p(273.16\ \mathrm{K}) = p_3 \left(\frac{274.16\ \mathrm{K} - 273.16\ \mathrm{K}}{273.16\ \mathrm{K}}\right)$$

$$= p_3/273.16 = (50.2\ \mathrm{mmHg})/273.16 = \underline{0.184\ \mathrm{mmHg}.}$$

For 100 °C:

$$p(373.15\ \mathrm{K}) = (50.2\ \mathrm{mmHg}) \times (373.15\ \mathrm{K}/273.16\ \mathrm{K})$$

$$= 1.366 \times 50.2\ \mathrm{mmHg} = \underline{68.6\ \mathrm{mmHg}}.$$

At 100 °C $p(374.15\ \mathrm{K}) - p(373.15\ \mathrm{K}) = p_3/273.16 = \underline{0.184\ \mathrm{mmHg}}.$

1.13 $n = n(H_2) + n(N_2) = 2\ \mathrm{mol} + 1\ \mathrm{mol} = 3\ \mathrm{mol}.$

$x(H_2) = n(H_2)/n$ [p. 35] $= (2\ \mathrm{mol})/(3\ \mathrm{mol}) = \underline{\tfrac{2}{3}}.$

$x(N_2) = n(N_2)/n = (1\ \mathrm{mol})/(3\ \mathrm{mol}) = \underline{\tfrac{1}{3}}.$

$$p = nRT/V = (3\ \mathrm{mol}) \times (8.3144\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (237.15\ \mathrm{K})/(22.4\ \mathrm{dm^3})$$

$$= 3.04 \times 10^5\ \mathrm{N\ m^{-2}} \mathrel{\widehat{=}} \underline{3.00\ \mathrm{atm}}\ [\text{end-paper 1}].$$

$p(H_2) = x(H_2)p$ [1.2.4] $= \tfrac{2}{3} \times (3\ \mathrm{atm}) = \underline{2\ \mathrm{atm}}.$

$p(N_2) = x(N_2)p = \tfrac{1}{3} \times (3\ \mathrm{atm}) = \underline{1\ \mathrm{atm}}.$

1.14 Draw up the following table based on $H_2 + \frac{1}{3}N_2 \rightarrow \frac{2}{3}NH_3$.

	H_2	N_2	NH_3	
Initially	n_1	n_2	0	
Finally	0	$n_2 - \frac{1}{3}n_1$	$\frac{2}{3}n_1$	
or:	0	$\frac{1}{3}$ mol	$\frac{4}{3}$ mol	[$n_2 = 1$ mol, $n_1 = 2$ mol]
Mole fraction:	0	$\frac{1}{5}$	$\frac{4}{5}$	[total $n = \frac{5}{3}$ mol]

$$p = nRT/V = (\tfrac{5}{3}\,\text{mol}) \times \left\{\frac{(8.3144\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (273.15\ \text{K})}{22.4\ \text{dm}^3}\right\} = \tfrac{5}{3}\ \text{atm}.$$

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

$p(N_2) = x(N_2)p = \frac{1}{5} \times (\frac{5}{3}\,\text{atm}) = \underline{\frac{1}{3}\,\text{atm}}$.

$p(NH_3) = x(NH_3)p = \frac{4}{5} \times (\frac{5}{3}\,\text{atm}) = \underline{\frac{4}{3}\,\text{atm}}$.

1.15 Find what pressure a perfect gas exerts from $p = nRT/V$.

$n = 131\ \text{g}/(131\ \text{g mol}^{-1})$ [end-paper 4] $= 1.00$ mol.

$R = 0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$ [end-paper 2].

$$p = \frac{(1.00\ \text{mol}) \times (0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}) \times (298.15\ \text{K})}{(1.00\ \text{dm}^3)}$$

$$= 0.0821 \times 298.15\ \text{atm} = 24.5\ \text{atm}.$$

Therefore, the sample would exert 24.5 atm, not 20 atm.

1.16 $p = nRT/(V - nb) - an^2/V^2$ [1.4.1a]

$a = 4.194\ \text{dm}^6\ \text{atm mol}^{-2}$, $b = 5.105 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}$ [Table 1.1]

$n = 1.00$ mol [Problem 1.15], $V = 1.00\ \text{dm}^3$

$$nRT/(V - nb) = \frac{(1.00\ \text{mol}) \times (0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}) \times (298.15\ \text{K})}{(1.00\ \text{dm}^3) - (1.00\ \text{mol}) \times (5.105 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1})}$$

$$= \frac{0.0821 \times 298.15\ \text{dm}^3\ \text{atm}}{(1.00 - 0.05)\ \text{dm}^3} = \frac{24.5\ \text{atm}}{0.95} = 25.8\ \text{atm}.$$

$an^2/V^2 = (4.194\ \text{dm}^6\ \text{atm mol}^{-2}) \times (1.00\ \text{mol})^2/(1.00\ \text{dm}^3)^6 = 4.194$ atm.

Therefore $p = 25.8\ \text{atm} - 4.2\ \text{atm} = \underline{21.6\ \text{atm}}$.

1.17 (a) $p = nRT/V$ [1.1.1], (b) $p = nRT/(V - nb) - an^2/V^2$ [1.4.1a].

$a = 4.471\ \text{dm}^6\ \text{atm mol}^{-2}$, $b = 5.714 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1} = 57.14\ \text{cm}^3\ \text{mol}^{-1}$ [Table 1.1].

$RT/V = 1.00 \text{ atm mol}^{-1}$ at 273.15 K and 22.414 dm^3.

(a(i)) $p = (1.00 \text{ mol}) \times (1.00 \text{ atm mol}^{-1}) = \underline{1.00 \text{ atm}}.$

$$(\text{a(ii)})\ p = \frac{(1.00 \text{ mol}) \times (0.0821 \text{ dm}^3 \text{ atm k}^{-1} \text{ mol}^{-1}) \times (1000 \text{ K})}{(0.10 \text{ dm}^3)} \underline{= 821 \text{ atm.}}$$

$$(\text{b(i)})\ nRT/(V - nb) = \frac{(1.00 \text{ mol}) \times (22.41 \text{ dm}^3 \text{ atm mol}^{-1})}{(22.41 \text{ cm}^3) - (5.714 \times 10^{-2} \text{ dm}^3)} = 1.003 \text{ atm.}$$

$$an^2/V^2 = \frac{(4.471 \text{ dm}^6 \text{ atm mol}^{-2}) \times (1.00 \text{ mol})^2}{(22.414 \text{ dm}^3)^2} = 0.009 \text{ atm.}$$

$p = (1.003 - 0.009) \text{ atm} = \underline{0.994 \text{ atm}}.$

$$(\text{b(ii)})\ nRT/(V - nb) = \frac{(1.00 \text{ mol}) \times (82.06 \text{ dm}^3 \text{ atm mol}^{-1})}{(0.10 \text{ dm}^3) - (1.00 \text{ mol}) \times (5.714 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1})}$$

$$= 1915 \text{ atm.}$$

$$an^2/V^2 = \frac{(4.471 \text{ dm}^6 \text{ atm mol}^{-2}) \times (1.00 \text{ mol})^2}{(0.10 \text{ dm}^3)^2} = 447 \text{ atm.}$$

$p = 1915 \text{ atm} - 447 \text{ atm} = \underline{1468 \text{ atm}}.$

1.18 At 25 °C and 1 atm the reduced temperature and pressure of hydrogen are

$T_r = (298.15 \text{ K})/(32.99 \text{ K})$ [Table 1.2, and definition p. 44] $= 9.04$

$p_r = (1 \text{ atm})/(12.77 \text{ atm}) = 0.0783.$

Ammonia, xenon, and helium are in corresponding states when their reduced pressures and temperatures have these values. Hence use $p = p_r p_c$ and $T = T_r T_c$ with $p_r = 0.0783$, $T_r = 9.04$, and the appropriate values (Table 1.2) of p_c and T_c.

(a) Ammonia; $p_c = 111.5$ atm, $T_c = 405.4$ K

hence $\underline{p = 8.73 \text{ atm}, T = 3665 \text{ K}}.$

(b) Xenon; $p_c = 58.0$ atm, $T_c = 289.7$ K

hence $\underline{p = 4.54 \text{ atm}, T = 2619 \text{ K}}.$

(c) Helium; $p_c = 2.26$ atm, $T_c = 5.2$ K

hence $\underline{p = 0.177 \text{ atm}, T = 47.0 \text{ K}}.$

1.19 From [1.4.3] $V_{m,c} = 3b = 3 \times (0.0226 \text{ dm}^3 \text{ mol}^{-1}) = \underline{67.8 \text{ cm}^3 \text{ mol}^{-1}}$

$$p_c = a/27b^2 = \frac{0.751 \text{ atm dm}^6 \text{ mol}^{-2}}{27 \times (0.0226 \text{ dm}^3 \text{ mol}^{-1})^2} = \underline{54.5 \text{ atm}}.$$

$$T_c = 8a/27Rb = \frac{8\times(0.751\ \text{atm dm}^6\ \text{mol}^{-2})}{27\times(0.08206\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1})\times(0.0226\ \text{dm}^3\ \text{mol}^{-1})}$$

$$= 120/\text{K}^{-1} = \underline{120\ \text{K}}.$$

1.20 $b = V_{m,c}/3$ [1.4.3], $a = 3p_c V_{m,c}^2$ [1.4.3]

$V_{m,c} = 98.7\ \text{cm}^3\ \text{mol}^{-1} = 0.0987\ \text{dm}^3\ \text{mol}^{-1}$, $p_c = 45.6\ \text{atm}$

$b = \frac{1}{3}\times(0.0987\ \text{dm}^3\ \text{mol}^{-1}) = \underline{0.0329\ \text{dm}^3\ \text{mol}^{-1}}.$

$a = 3\times(45.6\ \text{atm})\times(0.0987\ \text{dm}^3\ \text{mol}^{-1})^2 = \underline{1.333\ \text{atm dm}^6\ \text{mol}^{-2}}.$

$v_{\text{mol}} \approx b/L$ [p. 40] $= (0.0329\times 10^{-3}\ \text{m}^3\ \text{mol}^{-1})/(6.022\times 10^{23}\ \text{mol}^{-1})$

$= \underline{5.5\times 10^{-29}\ \text{m}^3\ (0.055\ \text{nm}^3,\ 55\ \text{Å}^3)}.$

$$v_{\text{mol}} \approx \tfrac{4}{3}\pi r^3, \text{ whence } r = \left[\frac{3}{4\pi}\times(5.5\times 10^{-29}\ \text{m}^3)\right]^{1/3}$$

$= 2.4\times 10^{-10}\ \text{m or } \underline{r \approx 0.24\ \text{nm}\ (2.4\ \text{Å})}.$

1.21 $V_{m,c} = 2b$ [p. 47], $b \approx (4/3)\pi r^3 L$ so that $r \approx [(3/8\pi)(V_{m,c}/L)]^{1/3}$.

From Table 1.2, $V_{m,c}(\text{He}) = 58\ \text{cm}^3\ \text{mol}^{-1} = 58\times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}$.

$V_{m,c}/L = (58\times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})/(6.022\times 10^{23}\ \text{mol}^{-1})$

$= 9.60\times 10^{-29}\ \text{m}^3.$

Then $r \approx [(3/8\pi)\times(9.60\times 10^{-29}\ \text{m}^3)]^{1/3} = \underline{2.26\times 10^{-10}\ \text{nm} = 226\ \text{pm}}.$

Similarly, $V_{m,c}(\text{Ne}) = 41.7\ \text{cm}^3\ \text{mol}^{-1}$ gives $\underline{r(\text{Ne}) \approx 202\ \text{pm}\ (2.02\ \text{Å})}$

$V_{m,c}(\text{Ar}) = 75.2\ \text{cm}^3\ \text{mol}^{-1}$ gives $\underline{r(\text{Ar}) \approx 246\ \text{pm}\ (2.46\ \text{Å})}.$

$V_{m,c}(\text{Xe}) = 119\ \text{cm}^3\ \text{mol}^{-1}$ gives $\underline{r(\text{Xe}) \approx 287\ \text{pm}\ (2.87\ \text{Å})}.$

1.22 $V_{m,c} = 2b$, $T_c = a/4bR$ [Table 1.4]. Hence $b = \frac{1}{2}V_{m,c}$, $a = 4RT_c b = 2RT_c V_{m,c}$.

$V_{m,c} = 119\ \text{cm}^3\ \text{mol}^{-1}$; $b = 59.5\ \text{cm}^3\ \text{mol}^{-1}$.

$T_c = 289.7\ \text{K}$; $a = 2\times(0.08206\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1})\times(289.7\ \text{K})\times(0.119\ \text{dm}^3\ \text{mol}^{-1})$

$= \underline{5.66\ \text{dm}^3\ \text{atm mol}^{-2}}.$

1.23 $p = RT/(V_m - b) - a/V_m^2$ [Table 1.4] $= (RT/V_m)\left\{\dfrac{1}{1-(b/V_m)}\right\} - a/V_m^2.$

Use $\dfrac{1}{1-x} = 1 + x + x^2 + \ldots$ with $x = b/V_m$.

$$\text{Then } p = (RT/V_m)\{1 + (b/V_m) + (b/V_m)^2 + \ldots\} - a/V_m^2$$

$$= (RT/V_m)\{1 + [b - (a/RT)]/V_m + (b/V_m)^2 + \ldots\}.$$

Compare with

$p = (RT/V_m)\{1 + B(T)/V_m + C(T)/V_m^2 + \ldots\}$ [Table 1.4].

Then $B(T) = b - a/RT$, $C(T) = b^2$.

1.24 $p = \{RT/(V_m - b)\}\exp(-a/RTV_m)$ [Table 1.4].

Use $1/(1-x) = 1 + x + x^2 + \ldots$, $e^y = 1 + y + \dfrac{1}{2!}y^2 + \ldots$ and then collect coefficients of power of $1/V_m$.

$$\begin{aligned} p &= (RT/V_m)\left[\frac{1}{1-(b/V_m)}\right]\exp(-a/RTV_m) \\ &= (RT/V_m)\{1 + (b/V_m) + (b/V_m)^2 + \ldots\}\{1 - (a/RTV_m) + \tfrac{1}{2}(a/RTV_m)^2 + \ldots\} \\ &= (RT/V_m)\{1 + [b - (a/RT)](1/V_m) + [b^2 - (ab/RT) + \\ &\quad + (a^2/2R^2T^2)](1/V_m)^2 + \ldots\}. \end{aligned}$$

Compare with $p = (RT/V_m)\{1 + B(T)/V_m + C(T)/V_m^2 + \ldots\}$.

Then $B(T) = b - a/RT$, $C(T) = b^2 - (ab/RT) + (a^2/2R^2T^2)$.

1.25 For a van der Waals gas $B = b - a/RT$, $C = b^2$ [Problem 1.23], hence $b = \sqrt{C}$, $a = (b - B)RT$. Then use $p_c = a/27b^2$, $V_{m,c} = 3b$, $T_c = 8a/27Rb$.

$B(T) = -21.7\ \text{cm}^3\ \text{mol}^{-1}$, $C(T) = 1200\ \text{cm}^6\ \text{mol}^{-2}$.

Therefore $b = 34.6\ \text{cm}^3\ \text{mol}^{-1}$,

$$\begin{aligned} a &= \{34.6\ \text{cm}^3\ \text{mol}^{-1} - (-21.7\ \text{cm}^3\ \text{mol}^{-1})\}\{(0.0821\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (273\ \text{K})\} \\ &= (56.3\ \text{cm}^3\ \text{mol}^{-1}) \times (22.4\ \text{dm}^3\ \text{atm}\ \text{mol}^{-1}) \\ &= 1260\ \text{cm}^3\ \text{dm}^3\ \text{atm}\ \text{mol}^{-2} = 1.26\ \text{dm}^6\ \text{atm}\ \text{mol}^{-2}. \end{aligned}$$

Then $p_c = (1.26\ \text{dm}^6\ \text{atm}\ \text{mol}^{-2})/27(34.6 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1})^2 = \underline{39.0\ \text{atm}}$.

$V_{m,c} = 3 \times (34.6\ \text{cm}^3\ \text{mol}^{-1}) = \underline{104\ \text{cm}^3\ \text{mol}^{-1}}$.

$$T_c = \frac{8 \times (1.26\ \text{dm}^6\ \text{atm}\ \text{mol}^{-2})}{27 \times (0.0821\ \text{dm}^3\ \text{atm}\ \text{K}^{-1}\ \text{mol}^{-1}) \times (34.6 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1})} = \underline{131\ \text{K}}.$$

For a Dieterici gas, $B = b - a/RT$, $C = b^2 - (ab/RT) + (a^2/2R^2T^2)$ [Problem 1.24]. Hence $C - \frac{1}{2}B^2 = \frac{1}{2}b^2$, so that $b = \sqrt{(2C - B^2)}$ and $a = (b - B)RT$. Then use $p_c = a/4e^2b^2$, $V_{m,c} = 2b$, $T_c = a/4bR$.

$b = \sqrt{\{2400\ \text{cm}^6\ \text{mol}^{-2} - (-21.7\ \text{cm}^3\ \text{mol}^{-1})^2\}} = \underline{43.9\ \text{cm}^3\ \text{mol}^{-1}}$.

$$\begin{aligned} a &= \{43.9\ \text{cm}^3\ \text{mol}^{-1} - (-21.7\ \text{cm}^3\ \text{mol}^{-1})\} \times \{22.4\ \text{dm}^3\ \text{atm}\ \text{mol}^{-1}\} \\ &= 1470\ \text{cm}^3\ \text{dm}^3\ \text{mol}^{-2}\ \text{atm} = \underline{1.47\ \text{dm}^3\ \text{atm}\ \text{mol}^{-2}}. \end{aligned}$$

$p_c = (1.47\ \text{dm}^3\ \text{atm}\ \text{mol}^{-2})/4e^2(43.9 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1})^2 = \underline{25.8\ \text{atm}}$.

$V_{\mathrm{m,c}} = 2 \times (43.9\ \mathrm{cm^3\ mol^{-1}}) = \underline{87.8\ \mathrm{cm^3\ mol^{-1}}}.$

$T_{\mathrm{c}} = (1.47\ \mathrm{dm^3\ atm\ mol^{-2}})/4 \times (43.9 \times 10^{-3}\ \mathrm{dm^3\ atm\ mol^{-1}})$

$\quad \times (0.0821\ \mathrm{dm^3\ atm\ K^{-1}\ mol^{-1}}) = \underline{102\ \mathrm{K}}.$

1.26 For critical behaviour, show that there is a point of inflection [p. 43] and find the critical constants.

$$p = RT/V_{\mathrm{m}} - B/V_{\mathrm{m}}^2 + C/V_{\mathrm{m}}^3$$

$$\left.\begin{aligned} \mathrm{d}p/\mathrm{d}V_{\mathrm{m}} &= -RT/V_{\mathrm{m}}^2 + 2B/V_{\mathrm{m}}^3 - 3C/V_{\mathrm{m}}^4 = 0 \\ \mathrm{d}^2p/\mathrm{d}V_{\mathrm{m}}^2 &= 2RT/V_{\mathrm{m}}^3 - 6B/V_{\mathrm{m}}^4 + 12C/V_{\mathrm{m}}^5 = 0 \end{aligned}\right\} \text{at } p_{\mathrm{c}}, V_{\mathrm{m,c}}, T_{\mathrm{c}}.$$

$$\left.\begin{aligned} -RT_{\mathrm{c}}V_{\mathrm{m,c}}^2 + 2BV_{\mathrm{m,c}} - 3C &= 0 \\ RT_{\mathrm{c}}V_{\mathrm{m,c}}^2 - 3BV_{\mathrm{m,c}} + 6C &= 0 \end{aligned}\right\}$$

which solve to $\underline{V_{\mathrm{m,c}} = 3C/B,\ T_{\mathrm{c}} = B^2/3RC.}$

Use the equation of state to find p_{c}:

$p_{\mathrm{c}} = RT_{\mathrm{c}}/V_{\mathrm{m,c}} - B/V_{\mathrm{m,c}}^2 + C/V_{\mathrm{m,c}}^3$

$\quad = R(B^2/3RC)/(3C/B) - B/(3C/B)^2 + C/(3C/B)^3 = \underline{B^3/27C^2.}$

$Z_{\mathrm{c}} = p_{\mathrm{c}}V_{\mathrm{m,c}}/RT_{\mathrm{c}} = (B^3/27C^2)\,(3C/B)/R(B^2/3RC) = \underline{\tfrac{1}{3}}.$

1.27 $pV_{\mathrm{m}}/RT = 1 + B'p + C'p^2 + \dots$ [1.3.1]

$pV_{\mathrm{m}}/RT = 1 + B/V_{\mathrm{m}} + C/V_{\mathrm{m}}^2 + \dots$ [1.3.2].

Equating the two expressions for pV_{m}/RT gives

$B'p + C'p^2 + \dots = B/V_{\mathrm{m}} + C/V_{\mathrm{m}}^2 + \dots$

Therefore $B'pV_{\mathrm{m}} + C'pV_{\mathrm{m}}^2 + \dots = B + C/V_{\mathrm{m}} \dots$

Replace pV_{m} by $RT\{1 + (B/V_{\mathrm{m}}) + \dots\}$ and equate coefficients of powers of $1/V_{\mathrm{m}}$.

$B'RT\{1 + (B/V_{\mathrm{m}}) + \dots\} + (C'/V_{\mathrm{m}})\,(RT)^2\ \{1 + (B/V_{\mathrm{m}}) + \dots\}^2 = B + C/V_{\mathrm{m}} + \dots$

or $B'RT + (BB'RT + C'R^2T^2)/V_{\mathrm{m}} + \dots = B + C/V_{\mathrm{m}} + \dots$

Therefore $B'RT = B$, implying $\underline{B' = B/RT.}$

Also $BB'RT + C'R^2T^2 = C$, or $B^2 + C'R^2T^2 = C$, implying $\underline{C' = (C - B^2)/R^2T^2.}$

1.28 At $T = T_{\mathrm{B}}, B' = 0$ [p. 38]. $B' = B/RT$ [Problem 1.27] $= (b - a/RT)/RT$ [Problem 1.23]. Therefore, $b - a/RT_{\mathrm{B}} = 0$, or $\underline{T_{\mathrm{B}} = a/Rb.}$

At $T = T_{\mathrm{B}}, Z = pV/RT_{\mathrm{B}} = (1/RT_{\mathrm{B}})RT_{\mathrm{B}}\ \{1 + B'(T_{\mathrm{B}})p + C'(T_{\mathrm{B}})p^2 + \dots\}$

$\quad = 1 + C'(T_{\mathrm{B}})p^2 + \dots \approx 1$ if $C'p^2 \ll 1$.

Therefore, xenon has $Z \approx 1$ at $T \approx T_\mathrm{B} \approx a/Rb$.

$$T_\mathrm{B}(\mathrm{Xe}) \approx \frac{4.194\ \mathrm{dm^6\ atm\ mol^{-1}}}{(0.08206\ \mathrm{dm^3\ atm\ K^{-1}\ mol^{-1}}) \times (0.05105\ \mathrm{dm^3\ mol^{-1}})} = \underline{1001\ \mathrm{K}}.$$

1.29 (a) $T_\mathrm{B} = a/Rb$ [Problem 1.28] ; $T_\mathrm{c} = 27bR/8a$ [Table 1.4].

$T_{\mathrm{B,r}} = T_\mathrm{B}/T_\mathrm{c} = (a/Rb)/(27bR/8a) = 27/8 = \underline{3.375}$

(b) For a Dieterici gas, $B = b - a/RT$ [Problem 1.24], hence $B' = (b - a/RT)/RT$ [Problem 1.27] $= 0$ when $b = a/RT$. Therefore, $T_\mathrm{B} = a/Rb$. Since $T_\mathrm{c} = a/4bR$ [Table 1.4],

$T_{\mathrm{B,r}} = (a/Rb)/(a/4bR) = \underline{4}.$

1.30 $p/\rho = (RT/M_\mathrm{m}) + (B'RT/M_\mathrm{m})p + \ldots$ [Problem 1.8]. A plot of p/ρ against p therefore has a limiting slope $B'RT/M_\mathrm{m}$. Write $(p/\rho)/(10^5\ \mathrm{m^2\ s^{-2}}) = (RT/M_\mathrm{m})/(10^5\ \mathrm{m^2\ s^{-2}}) + \{(B'RT/M_\mathrm{m})/(10^5\ \mathrm{m^2\ s^{-2}})\}\ (p/10^5\ \mathrm{Nm^{-2}})\ (10^5\ \mathrm{Nm^{-2}})$ and so a plot of $(p/\rho)/(10^5\ \mathrm{m^2\ s^{-2}})$ against $(p/10^5\ \mathrm{Nm^{-2}})$, as in Fig. 1.1, has a (dimensionless) slope equal to $\{B'RT/M_\mathrm{m})/(10^5\ \mathrm{m^2\ s^{-2}})\} \times (10^5\ \mathrm{Nm^{-2}}) = (B'RT/M_\mathrm{m})\ \mathrm{Nm^{-4}\ s^2}$.

$$\text{From Fig. 1.1, limiting slope} \approx \frac{0.5325 - 0.5379}{0.93} = -0.0058.$$

Therefore $(B'RT/M_\mathrm{m})\ \mathrm{N\ m^{-4}\ s^2} = -0.0058$, $RT/M_\mathrm{m} = 0.5379 \times 10^5\ \mathrm{m^2\ s^{-2}}$

$$B' = \frac{-0.0058}{(RT/M_\mathrm{m})\ \mathrm{N\ m^{-4}\ s^2}} = \frac{-0.0058}{0.5379 \times 10^5\ \mathrm{m^{-2}\ N}} = -1.08 \times 10^{-7}\ \mathrm{N^{-1}\ m^2}.$$

$$B = B'RT\ \text{[Problem 1.27]} = (-1.08 \times 10^{-7}\ \mathrm{N^{-1}\ m^2}) \times (8.3144\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (300\ \mathrm{K})$$

$$= -2.69 \times 10^{-4}\ \mathrm{J\ N^{-1}\ m^2\ mol^{-1}} = -2.69 \times 10^{-4}\ \mathrm{m^3\ mol^{-1}} = \underline{-0.269\ \mathrm{dm^3\ mol^{-1}}}$$

1.31 Consider a slab of fluid of area A, thickness $\mathrm{d}h$, density ρ. Its mass is $\rho A\,\mathrm{d}h$. The force downwards is $\rho Ag\mathrm{d}h$. The force per unit area is $\rho Ag\mathrm{d}h/A = \rho g\mathrm{d}h$. This is the difference of the pressures at the bottom and top of the slab. Therefore, if h is measured vertically, $\mathrm{d}p = -\rho g\mathrm{d}h$ ($\mathrm{d}p/\mathrm{d}h$ is negative: pressure decreases as height increases). For a perfect gas $\rho = (M_\mathrm{m}/RT)p$ [Problem 1.8] ; therefore $\mathrm{d}p = -(M_\mathrm{m}/RT)\,gp\mathrm{d}h$ or $\mathrm{d}p/p = -(M_\mathrm{m}/RT)\,g\mathrm{d}h$. If $p = p_0$ at $h = 0$ and $p = p(h)$ at a height h, this integrates to $\ln[p(h)/p_0] = -(M_\mathrm{m}g/RT)h$ or $\underline{p(h) = p_0 \exp\{(-M_\mathrm{m}g/RT)h\}}$.

1.32 $p_0 = 1\ \mathrm{atm}$, $M_\mathrm{m} \approx 30\ \mathrm{g\ mol^{-1}}$.

$$M_\mathrm{m}g/RT = \frac{(30\ \mathrm{g\ mol^{-1}}) \times (9.81\ \mathrm{ms^{-2}})}{(2.48 \times 10^3\ \mathrm{J\ mol^{-1}})} = 1.19 \times 10^{-4}\ \mathrm{m^{-1}}.$$

(a) $h = 15\text{ cm} = 0.15\text{ m}$

$p = p_0 \exp(-0.15 \times 1.19 \times 10^{-4}) = \underline{0.999\,98\, p_0}.$

(b) $h = 1350\text{ ft} \,\widehat{=}\, 411\text{ m}$

$p(411\text{ m}) = p_0 \exp(-411 \times 1.19 \times 10^{-4}) = 0.952\, p_0.$

Therefore, if $p_0 = 1.0$ atm, $p(411\text{ m}) = \underline{0.95\text{ atm}}.$

1.33 Each component of an ideal gas behaves independently, and so for the component J of molar mass $M_{\text{J,m}}$

$p_{\text{J}}(h) = p_{0\text{J}} \exp\{-M_{\text{J,m}}g/RT)h\}.$

From p. 35, partial pressures at sea level ($p = 1$ atm) are $p_0(N_2) = 0.782$ atm, $p_0(O_2) = 0.208$, $p_0(\text{Ar}) = 0.009$ atm, $p_0(CO_2) = 0.003$ atm, $M_r(N_2) = 28$ $M_r(O_2) = 32$, $M_r(\text{Ar}) = 40$, $M_r(CO_2) = 44$.

$$M_{\text{J,m}}g/RT = (M_{\text{J,r}}\text{ g mol}^{-1}) \times (9.81\text{ m s}^{-2})/(2.437 \times 10^3\text{ J mol}^{-1})$$
$$= 4.02 \times 10^{-6} M_{\text{J,r}}\text{ m}^{-1}.$$

Hence, draw up the following table using the appropriate values of M_r and h.

$h =$		1350 ft	29000 ft	100 km
$\widehat{=}$		411 m	8840 m	10^5 m
$p_{\text{J}}(h)$/atm =	N_2	0.747	0.289	1.10×10^{-5}
$[x_{\text{J}}(h)]$ =		[0.784]	[0.807]	[0.953]
	O_2	0.198	0.067	5.41×10^{-7}
		[0.208]	[0.187]	[0.047]
	Ar	0.008	0.002	9.3×10^{-10}
		[0.008]	[0.006]	$[8.1 \times 10^{-5}]$
	CO_2	0.0003	6×10^{-5}	6.2×10^{-12}
		[0.0003]	$[1.7 \times 10^{-4}]$	$[5.4 \times 10^{-7}]$.

Mole fractions were computed from $x_{\text{J}} = p_{\text{J}}/p$, $p = p(N_2) + p(O_2) + \ldots.$

1.34 $Nx \exp(-m'gh/KT)$, $m' = m' = v(\rho_{\text{solute}} - \rho_{\text{solvent}})$

$\ln N = \text{const.} - (m'g/kT)h$. Hence, plot $\ln N$ against h; the slope is $m'g/kT$. Draw up the following Table:

h/mm	0	0.05	0.07	0.09	0.10	0.15	0.20
$\ln N$	6.91	5.99	5.63	5.25	5.08	4.09	3.22