P.W. ATKINS

SOLUTIONS MANUAL FOR PHYSICAL CHEMISTRY

THIRD EDITION

Solutions Manual for Physical Chemistry

THIRD EDITION

P. W. Atkins

with solutions to introductory problems by
J. C. Morrow

Oxford Melbourne Tokyo
OXFORD UNIVERSITY PRESS
1986

Oxford University Press, Walton Street, Oxford OX2 6DP

Oxford New York Toronto
Delhi Bombay Calcutta Madras Karachi
Kuala Lumpur Singapore Hong Kong Tokyo
Nairobi Dar es Salaam Cape Town
Melbourne Auckland

and associated companies in
Beirut Berlin Ibadan Nicosia

Oxford is a trade mark of Oxford University Press

First edition 1978
Second edition 1982
Third edition 1986

British Library Cataloguing in Publication Data

Atkins, P. W.
Solutions manual for Physical chemistry.—3rd ed.
1. Chemistry, Physical and theoretical—Problems, exercises, etc/
I. Title II. Morrow, J. C. III. Atkins, P. W.
Physical chemistry. 3rd ed.
541.3′076 QD456

ISBN 0-19-855193-2

Typeset by Joshua Associates Limited, Oxford
Printed in the United States of America

Solutions Manual for Physical Chemistry

Preface

The following pages give detailed solutions to almost all the approximately 1400 end-of-chapter Problems in the main text, the exceptions being Problems that ask for a computer program. The solutions to the 300 *Introductory Problems* (designated A here and in the text) have been supplied by Professor Morrow.

All the solutions have been reworked during the preparation of this edition, and all my solutions to the new main problems have been checked by Professor Morrow. Moreover, *all* the solutions have been scrutinized for logic, presentation, and numerical accuracy by Michael Golde of the University of Pittsburgh and Juvencio Robles of the University of North Carolina, Chapel Hill, and their suggestions have also resulted in a reformulation and clarification of some of the questions. I am most grateful to them for the huge amount of valuable work they have done, as users of the ***Manual*** will be too, I am sure.

The format is as follows. Equations in the main text are referred to as [10.2.6.], etc. Illustrations in the main text are referred to as 'of the text'. All references relate to the third edition of the text. Although BASIC interprets expressions like $a/b \times c$ as $(a/b) \times c$, the convention here is that $a/b \times c = a/(b \times c)$. All graphs have been plotted with dimensionless coordinates by plotting, for example, the dimensionless quantity p/kPa. As in the main text, in this edition I adopt $1\ \text{M} = 1\ \text{mol dm}^{-3}$ for, even though M is outside SI, its use greatly simplifies the appearance of expressions. As explained in the text, the standard pressure adopted is $p^{\ominus} = 1\ \text{bar} = 10^5\ \text{N m}^{-2}$ exactly. The symbol $\mathcal{T}$ stands for 298.15 K exactly.

I am grateful to everyone who has contributed helpful comments, and would like to single out for thanks Professor L. Epstein of the University of Pittsburgh who made very extensive, detailed, and useful comments. I would also like to record a special word of thanks to the typesetters, who had to cope with an extraordinarily difficult manuscript.

Oxford P. W. A.
1985

Contents

PART 1: EQUILIBRIUM

1. The properties of gases

A1.1 $p_i = p_f V_f / V_i$ [1.1.3]

(a) $p_i = (3.78 \times 10^3\,\text{Torr})\,(4.65\,\text{dm}^3)/(4.65\,\text{dm}^3 + 2.20\,\text{dm}^3) = \underline{2.57 \times 10^3\,\text{Torr.}}$

(b) $p_i = 2.57 \times 10^3\,\text{Torr}/(760\,\text{Torr/atm}) = \underline{3.38\,\text{atm.}}$

A1.2 $T_f = T_i(V_f/V_i)$ [1.1.5]

$= (340\,\text{K})\,(1.18/1) = \underline{401\,\text{K.}}$

A1.3 $p = nRT/V$ [1.1.1]

$= [(0.255/20.2)\text{mol}]\,[8.31\,\text{J K}^{-1}\,\text{mol}^{-1}]\,[122\,\text{K}]\,(3.00 \times 10^{-3}\,\text{m}^3)^{-1}$

$= 4.27 \times 10^3\,\text{Pa}$, or $\underline{4.27\,\text{kPa.}}$

A1.4 (a) $V = n_J RT/p_J$ [1.2.3]

$= [(0.225/20.2)\text{mol}]\,\,[8.31\,\text{J K}^{-1}\,\text{mol}^{-1}]\,[300\,\text{K}]/[(66.5\,\text{Torr})$

$\times\,(133\,\text{Pa/Torr})] = 3.14 \times 10^{-3}\,\text{m}^3$, or $\underline{3.14\,\text{dm}^3.}$

(b) $p_J = n_J RT/V$ [1.2.3]

$= [(0.175/40.0)\text{mol}]\,[8.31\,\text{J K}^{-1}\,\text{mol}^{-1}]\,[300\,\text{K}]/(3.14 \times 10^{-3}\,\text{m}^3)$

$= 3.47 \times 10^3\,\text{Pa}$, or $\underline{3.47\,\text{kPa.}}$

(c) $p = (n_A + n_B + n_C)RT/V$ [1.2.1]

$= [(0.320/16.0)\text{mol} + (0.175/40.0)\text{mol} + (0.225/20.2)\text{mol}]$

$\times\,[8.31\,\text{J K}^{-1}\,\text{mol}^{-1}]\,\,[300\,\text{K}]/(3.14 \times 10^{-3}\,\text{m}^3) = \underline{2.83 \times 10^4\,\text{Pa.}}$

A1.5 $n = pV/RT = (150\,\text{Torr})(133\,\text{Pa/Torr})(10^{-3}\,\text{m}^3)(8.31\,\text{J K}^{-1}\,\text{mol}^{-1})^{-1}$

$\times\,(330\,\text{K})^{-1} = 7.27 \times 10^{-3}\,\text{mol}$, [1.1.1]

$\text{RMM} = 1.23(7.27 \times 10^{-3})^{-1} = \underline{169.}$

A1.6 (a) $V_m(\text{perfect}) = RT/p$ [1.1.1]

$Z = pV_m/RT = [p/RT]\,[0.88(RT/p)] = \underline{0.88.}$ [Section 1.3(a)]

(b) $V_m = 0.88(RT/p) = (0.88)(8.3\,\mathrm{J\,K^{-1}\,mol^{-1}})(250\,\mathrm{K})(15 \times 1.0 \times 10^5\,\mathrm{Pa})^{-1}$

$= 1.2 \times 10^{-3}\,\mathrm{m^3}$ or $\underline{1.2\,\mathrm{dm^3}}$. Attractive forces dominate.

A1.7 $Z = pV_m/RT = 0.86$

$V_m = 0.86(RT/p) = (0.86)(8.3\,\mathrm{J\,K^{-1}\,mol^{-1}})(300\,\mathrm{K})(20 \times 1.0 \times 10^5\,\mathrm{Pa})^{-1}$

$= 1.1 \times 10^{-3}\,\mathrm{m^3\,mol^{-1}}$, or $\underline{1.1\,\mathrm{dm^3\,mol^{-1}}}$.

(a) $V = (1.1\,\mathrm{dm^3\,mol^{-1}})(8.2 \times 10^{-3}\,\mathrm{mol}) = 9.0 \times 10^{-3}\,\mathrm{dm^3}$, or $\underline{9.0\,\mathrm{cm^3}}$.

(b) $B = V_m[(pV_m/RT) - 1] = V_m[Z - 1] = (1.1\,\mathrm{dm^3\,mol^{-1}})(0.86 - 1.00)$

$= \underline{-0.15\,\mathrm{dm^3\,mol^{-1}}}$. [1.3.2]

A1.8 $T_c = (2/3)(2a/3bR)^{\frac{1}{2}} = (2/3)[12p_c(b/R)] = (2/3)(12p_c)(V_{m,c}/3R)$

$= (2/3)(12)(40.0 \times 1.0 \times 10^5\,\mathrm{Pa})(160 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}})$

$\times [(3)(8.3\,\mathrm{J\,K^{-1}\,mol^{-1}})]^{-1}$

$= \underline{206\,\mathrm{K}}$.

$4\pi r^3/3 = (1/3)(V_{m,c})/N_A$ [1.4.3]

$r = [(4 \times 3.14)^{-1}(160 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}})(6.02 \times 10^{23}\,\mathrm{mol^{-1}})^{-1}]^{1/3} = \underline{2.77 \times 10^{-10}\,\mathrm{m}}$.

A1.9 (a) $V_m = RT/p = (8.31\,\mathrm{J\,K^{-1}\,mol^{-1}})(350\,\mathrm{K})(2.30 \times 1.01 \times 10^5\,\mathrm{Pa})^{-1}$

$= 1.25 \times 10^{-2}\,\mathrm{m^3\,mol^{-1}}$, or $\underline{12.5\,\mathrm{dm^3\,mol^{-1}}}$.

(b) $V_m = RT(p + a/V_m^2)^{-1} + b$ [1.4.2] $= (8.31\,\mathrm{J\,K^{-1}\,mol^{-1}})(350\,\mathrm{K})$

$\times [2.30\,\mathrm{atm} + (6.49\,\mathrm{atm\,dm^6\,mol^{-2}})(12.5\,\mathrm{dm^3\,mol^{-1}})^{-2}]^{-1}$

$\times [1.01 \times 10^5\,\mathrm{Pa/atm}]^{-1}[10^3\,\mathrm{dm^3/m^3}] + (5.62 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}})$

$= 12.4\,\mathrm{dm^3\,mol^{-1}}$. Use of $12.4\,\mathrm{dm^3\,mol^{-1}}$ in the attractive term produces:

$V_m = \underline{12.4\,\mathrm{dm^3\,mol^{-1}}}$, and the iteration is stopped. [Table 1.3]

A1.10 (a) $T_B = a/bR = (6.493\,\mathrm{dm^6\,atm\,mol^{-2}})(5.622 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}})^{-1}$

$\times (10^{-3}\,\mathrm{m^3/dm^3})(1.013 \times 10^5\,\mathrm{Pa/atm})(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})^{-1}$

$= \underline{1.407 \times 10^3\,\mathrm{K}}$. [1.4.5, Table 1.3]

(b) $4\pi r^3/3 = b/N_A$ [1.4.3, Table 1.3]

$r = [(4 \times 3.14)^{-1}(3)(5.62 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}})(10^{-3}\,\mathrm{m^3/dm^3})(6.02 \times 10^{23}\,\mathrm{mol^{-1}})^{-1}]^{1/3}$

$= 2.81 \times 10^{-10}\,\mathrm{m}$, or $\underline{0.281\,\mathrm{nm}}$.

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

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

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

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

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

(a) $V_f = (755\ \mathrm{Torr}/100\ \mathrm{Torr}) \times (2\ \mathrm{m}^3) = \underline{15\ \mathrm{m}^3}.$

(b) $V_f = (755\ \mathrm{Torr}/10\ \mathrm{Torr}) \times (2\ \mathrm{m}^3) = \underline{150\ \mathrm{m}^3}.$

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

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

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

$= 5.03 \times 10^5\ \mathrm{N\,m^{-2}} + 1\ \mathrm{atm} = 4.96\ \mathrm{atm} + 1\ \mathrm{atm}$ [end-paper 1] ≈ 6 atm.

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

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 $p_f = p_i - \rho g h$.

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

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

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

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

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

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

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

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

1.6 $p_f = (T_f/T_i)p_i$ [1.1.6].

Internal pressure = (quoted pressure) + (atmospheric pressure) [14.7 lb in^{-2}].

$p_i = (24\ \mathrm{lb\,in^{-2}}) + (14.7\ \mathrm{lb\,in^{-2}}) = 39\ \mathrm{lb\,in^{-2}}.$

$T_i \mathrel{\widehat{=}} -5\ {}^\circ\mathrm{C}$, or 268 K; $T_f \mathrel{\widehat{=}} 35\ {}^\circ\mathrm{C}$, or 308 K.

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

$p_f(\text{internal}) = (43.7 - 14.7)\ \text{lb in}^{-2} = \underline{29\ \text{lb in}^{-2}}$.

1.7 Disregard the elasticity of the envelope. $p_i V_i = nRT_i,\ p_f V_f = nRT_f$ [1.1.1]

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

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

$R = 1\ \text{m},\ R_f = 3\ \text{m},\ T_i = 298\ \text{K},\ T_f \,\widehat{=}\, -20\ °\text{C}$, or $253\ \text{K},\ p_i = 1\ \text{atm}$.

$p_f = (1\ \text{m}/3\ \text{m})^3 \times (253\ \text{K}/298\ \text{K}) \times (1\ \text{atm}) = (\tfrac{1}{3})^3 \times (0.849) \times (1\ \text{atm}) = \underline{0.03\ \text{atm}}$.

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

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 $1\ \text{Torr} \,\widehat{=}\, 133.3\ \text{N m}^{-2}$ [end-paper 1].

p/Torr	91.74	188.93	277.3	452.8	639.3	760.0
$p/10^5$ Pa	0.1223	0.2518	0.3696	0.6036	0.8522	1.0131
$\rho/\text{kg m}^{-3}$	0.225	0.456	0.664	1.062	1.468	1.734
$(p/\rho)/10^5\ \text{m}^2\,\text{s}^{-2}$	0.544	0.552	0.557	0.568	0.581	0.584

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

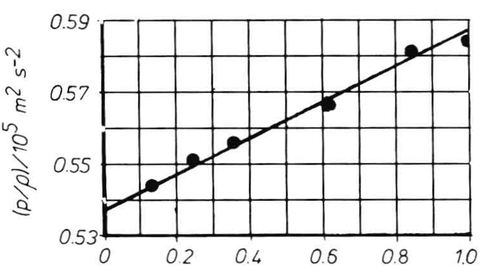

Fig 1.1

The intercept at $p = 0$ is at $(p/\rho)/10^5\ \text{m}^2\,\text{s}^{-2} = 0.540$. Therefore,

$$RT/M_m = 0.540 \times 10^5\ \text{m}^2\,\text{s}^{-2},\ \text{or}\ M_m = RT/(0.540 \times 10^5\ \text{m}^2\,\text{s}^{-2}).$$

$$M_m = \frac{(8.3144\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (298.15\ \mathrm{K})}{0.540 \times 10^5\ \mathrm{m^2\,s^{-2}}} = 4.59 \times 10^{-2}\ \mathrm{kg\,mol^{-1}}\ [\mathrm{J = kg\,m^2\,s^{-2}}]$$

$$= 45.9\ \mathrm{g\,mol^{-1}};\ \underline{M_r = 45.9.}$$

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].

$$n = \frac{1.013 \times 10^5 \times 113.1}{2.479 \times 10^3} \cdot \frac{\mathrm{N\,m^{-2}\,m^3}}{\mathrm{J\,mol^{-1}}} = \underline{4622\ \mathrm{mol}}\quad [\mathrm{J = N\,m}]$$

$M = nM_r\ \mathrm{g\,mol^{-1}}$ [M = mass of sample] $= (4622\ \mathrm{mol}) \times (2\ \mathrm{g\,mol^{-1}}) = 9244\ \mathrm{g} = 9.2\ \mathrm{kg}$.

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, $M = 4622\ \mathrm{mol} \times (4.0\ \mathrm{g\,mol^{-1}})$ [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 $133\ \mathrm{kg} - 18\ \mathrm{kg} = \underline{155\ \mathrm{kg}}$ (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]; $m = M_m/N_A$ [Box 0.1].

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

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

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

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

$$= 16.4\,\mathrm{g\,mol^{-1}};\ \underline{M_r = 16.4.}$$

$m = M_m/N_A = (1.64 \times 10^{-2}\,\mathrm{kg\,mol^{-1}})/(6.022 \times 10^{23}\,\mathrm{mol^{-1}}) = \underline{2.7 \times 10^{-26}\,\mathrm{kg}.}$

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 $\rho(X) = M_m(X)p(X)/kT$ [Problem 1.8], $X = 1, 2$ and so the balance condition is $M_m(1)p(1) = M_m(2)p(2)$, or $M_r(1)p(1) = M_r(2)p(2)$. Therefore, $M_r(2) = M_r(1)[p(1)/p(2)]$. This is valid in the limit of vanishing pressures. In experiment 1, $p(1) = 423.22$ Torr, $p(2) = 327.10$ Torr and so $M_r(2) = 70.014 \times (423.22\,\text{Torr}/327.10\,\text{Torr}) = 90.59$. In experiment 2, $p(1) = 427.22$ Torr, $p(2) = 293.22$ Torr and so $M_r = 70.014 \times (427.22\,\text{Torr}/293.22\,\text{Torr}) = 102.0$. 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 $\underline{M_r = 102.}$ The molecule CH_2FCF_3 has $M_r = 102$ [end-paper 4].

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

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

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

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

$$= p_3/273.16 = (50.2\,\text{Torr})/273.16 = \underline{0.184\,\text{Torr}.}$$

For 100 °C:

$$p(373.15\,\mathrm{K}) = (50.2\,\text{Torr}) \times (373.15\,\mathrm{K}/273.16\,\mathrm{K})$$

$$= 1.366 \times 50.2\,\text{Torr} = \underline{68.6\,\text{Torr}.}$$

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

1.13 $n = n(H_2) + n(N_2) = 2.0\,\mathrm{mol} + 1.0\,\mathrm{mol} = 3.0\,\mathrm{mol}$.

$x(H_2) = n(H_2)/n$ [Section 1.2(a)] $= (2.0\,\mathrm{mol})/(3.0\,\mathrm{mol}) = \underline{0.67.}$

$x(N_2) = n(N_2)/n = (1.0\,\mathrm{mol})/(3.0\,\mathrm{mol}) = \underline{0.33.}$

$p = nRT/V = (3.0\,\mathrm{mol}) \times (8.3144\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (273.15\,\mathrm{K})/(22.4\,\mathrm{dm^3})$

$$= 3.0 \times 10^5\,\mathrm{N\,m^{-2}} \mathrel{\hat{=}} \underline{3.0\,\mathrm{atm}}\ \text{[end-paper 1]}.$$

$p(H_2) = x(H_2)p$ [1.2.4] $= 0.67 \times (3.0\,\text{atm}) = \underline{2.0\,\text{atm}}$.

$p(N_2) = x(N_2)p = 0.33 \times (3.0\,\text{atm}) = \underline{1.0\,\text{atm}}$.

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	0.33 mol	1.33 mol	[$n_1 = 2.0$ mol, $n_2 = 1.0$ mol]
Mole fraction:	0	0.20	0.80	[total $n = 1.66$ mol]

$$p = nRT/V = (1.66\,\text{mol}) \times \left\{\frac{(8.3144\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (273.15\,\text{K})}{22.4\,\text{dm}^3}\right\} = 1.66\,\text{atm}.$$

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

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

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

1.15 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].

$$p = \frac{(1.00\,\text{mol}) \times (0.0821\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})}{(1.0\,\text{dm}^3)} = 24\,\text{atm}.$$

Therefore, the sample would exert 24 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 1.3],

$n = 1.00$ mol [Problem 1.15], $V = 1.0\,\text{dm}^3$.

$$nRT/(V - nb) = \frac{(1.00\,\text{mol}) \times (0.0821\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})}{(1.0\,\text{dm}^3) - (1.00\,\text{mol}) \times (5.105 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1})}$$

$$= \frac{0.0821 \times 298.15\,\text{dm}^3\,\text{atm}}{(1.0 - 0.05)\,\text{dm}^3} = \frac{24.5\,\text{atm}}{0.95} = 26\,\text{atm}.$$

$an^2/V^2 = (4.194\ \text{dm}^6\ \text{atm mol}^{-2}) \times (1.00\ \text{mol})^2/(1.0\ \text{dm}^3)^6 = 4.2\ \text{atm}.$

Therefore $p = 26\ \text{atm} - 4.2\ \text{atm} = \underline{22\ \text{atm}.}$

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 1.3].

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

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

$$\text{(a(ii))}\ p = \frac{(1.00\ \text{mol}) \times (0.0821\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}) \times (1000\ \text{K})}{(0.100\ \text{dm}^3)} = \underline{821\ \text{atm}.}$$

$$\text{(b(i))}\ nRT/(V-nb) = \frac{(1.00\ \text{mol}) \times (22.414\ \text{dm}^3\ \text{atm mol}^{-1})}{(22.414\ \text{dm}^3) - (5.714 \times 10^{-2}\ \text{dm}^3)} = 1.003\ \text{atm}.$$

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

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

$$\text{(b(ii))}\ nRT/(V-nb) = \frac{(1.00\ \text{mol}) \times (82.06\ \text{dm}^3\ \text{atm mol}^{-1})}{(0.100\ \text{dm}^3) - (1.00\ \text{mol}) \times (5.714 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1})}$$

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

$$an^2/V^2 = \frac{(4.471\ \text{dm}^6\ \text{atm mol}^{-2}) \times (1.00\ \text{mol})^2}{(0.100\ \text{dm}^3)^2} = 447\ \text{atm}.$$

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

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

$T_r = (298.15\ \text{K})/(33.23\ \text{K})$ [Table 1.2, and eqn. (1.4.6)] $= 8.97$,

$p_r = (1\ \text{atm})/(12.8\ \text{atm}) = 0.0781$.

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 $p_r = 0.0781$. $T_r = 8.97$, and the appropriate values (Table 1.2) of p_c and T_c.

(a) Ammonia; $p_c = 111.3\ \text{atm}$, $T_c = 405.5\ \text{K}$

hence $\underline{p = 8.69\ \text{atm},\ T = 3640\ \text{K}.}$

(b) Xenon; $p_c = 58.0\ \text{atm}$, $T_c = 289.8\ \text{K}$

hence $\underline{p = 4.53\ \text{atm},\ T = 2600\ \text{K}.}$

(c) Helium; $p_c = 2.26$ atm, $T_c = 5.21$ K

hence $\underline{p = 0.177 \text{ atm}, T = 46.7 \text{ K}}$.

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]

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

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

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

$v_{mol} \approx b/N_A$ [Section 1.4(a)] $= (0.0329 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})/(6.022 \times 10^{23} \text{ mol}^{-1})$

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

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

$$\text{whence } r = \left[\frac{3}{4\pi} \times (5.5 \times 10^{-29} \text{ m}^3)\right]^{1/3} = 2.4 \times 10^{-10} \text{ m or } \underline{r \approx 0.24 \text{ nm}}.$$

1.21 $V_{m,c} = 2b$ [Box 1.1], $b \approx (4/3)\pi r^3 N_A$ so that $r \approx [(3/8\pi)(V_{m,c}/N_A)]^{1/3}$.

From Table 1.2, $V_{m,c}(\text{He}) = 57.8 \text{ cm}^3 \text{ mol}^{-1} = 57.8 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$.

$V_{m,c}/N_A = (57.8 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})/(6.022 \times 10^{23} \text{ mol}^{-1})$

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

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

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

$V_{m,c}(\text{Ar}) = 75.3 \text{ cm}^3 \text{ mol}^{-1}$ gives $\underline{r(\text{Ar}) \approx 246 \text{ pm}}$.

$V_{m,c}(\text{Xe}) = 118.8 \text{ cm}^3 \text{ mol}^{-1}$ gives $\underline{r(\text{Xe}) \approx 287 \text{ pm}}$.

1.22 $V_{m,c} = 2b$, $T_c = a/4bR$ [Box 1.1]. Hence $b = \frac{1}{2} V_{m,c}$, $a = 4RT_c b = 2RT_c V_{m,c}$.

$V_{m,c} = 118.8 \text{ cm}^3 \text{ mol}^{-1}$; $\underline{b = 59.4 \text{ cm}^3 \text{ mol}^{-1}}$. $T_c = 289.75$ K;

$a = 2 \times (0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (289.75 \text{ K}) \times (0.1188 \text{ dm}^3 \text{ mol}^{-1})$

$= \underline{5.65 \text{ dm}^6 \text{ atm mol}^{-2}}$; hence $p = 20.6$ atm [Dieterici equation, Box 1.1].

1.23 $p = RT/(V_m - b) - a/V_m^2$ [Box 1.1] $= (RT/V_m)\left\{\dfrac{1}{1-(b/V_m)}\right\} - a/V_m^2$.

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

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

$p = (RT/V_m)\{1 + B/V_m + C/V_m^2 + \ldots\}$ [Box 1.1].

Then $\underline{B = b - a/RT, C = b^2.}$

1.24 $p = \{RT/(V_m - b)\}\exp(-a/RTV_m)$ [Box 1.1].

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

$$p = (RT/V_m)\left[\frac{1}{1-(b/V_m)}\right]\exp(-a/RTV_m)$$

$= (RT/V_m)\{1 + (b/V_m) + (b/V_m)^2 + \ldots\}\{1 - (a/RTV_m) + \tfrac{1}{2}(a/RTV_m)^2 + \ldots\}$

$= (RT/V_m)\{1 + [b - (a/RT)]\,(1/V_m) + [b^2 - (ab/RT) +$

$+ (a^2/2R^2T^2)]\,(1/V_m)^2 + \ldots\}$.

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

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

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 $p_c = a/27b^2$, $V_{m,c} = 3b$, $T_c = 8a/27\,Rb$.

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

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

$a = \{34.6\ \text{cm}^3\,\text{mol}^{-1} - (-21.7\ \text{cm}^3\,\text{mol}^{-1})\}\{(0.0821\ \text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (273\ \text{K})\}$

$= (56.3\ \text{cm}^3\,\text{mol}^{-1}) \times (22.4\ \text{dm}^3\,\text{atm}\,\text{mol}^{-1})$

$= 1260\ \text{cm}^3\,\text{dm}^3\,\text{atm}\,\text{mol}^{-2} = 1.26\ \text{dm}^6\,\text{atm}\,\text{mol}^{-2}$.

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

$p_c = a/4e^2b^2$, $V_{m,c} = 2b$, $T_c = a/4bR$.

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

$a = \{43.9\ \text{cm}^3\ \text{mol}^{-1} - (-21.7\ \text{cm}^3\ \text{mol}^{-1})\} \times \{22.4\ \text{dm}^3\ \text{atm}\ \text{mol}^{-1}\}$

$= 1470\ \text{cm}^3\ \text{dm}^3\ \text{mol}^{-2}\ \text{atm} = 1.47\ \text{dm}^3\ \text{atm}\ \text{mol}^{-2}.$

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

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

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

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

1.26 For critical behavior, show that there is a point of inflection with zero slope [Section 1.4(b)] and find the critical constants.

$$p = RT/V_m - B/V_m^2 + C/V_m^3$$

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

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

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

Use the equation of state to find p_c:

$p_c = RT_c/V_{m,c} - B/V_{m,c}^2 + C/V_{m,c}^3$

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

$Z_c = p_cV_{m,c}/RT_c = (B^3/27C^2)(3C/B)/R(B^2/3RC) = \underline{\tfrac{1}{3}}.$

1.27 $pV_m/RT = 1 + B'p + C'p^2 + \ldots$ [1.3.1]

$pV_m/RT = 1 + B/V_m + C/V_m^2 + \ldots$ [1.3.2].

Equating the two expressions for pV_m/RT gives

$B'p + C'p^2 + \ldots = B/V_m + C/V_m^2 + \ldots$

Therefore $B'pV_m + C'pV_m^2 + \ldots = B + C/V_m \ldots$

Replace pV_m by $RT\{1 + (B/V_m) + \ldots\}$ and equate coefficients of powers of $1/V_m$.

$B'RT\{1 + (B/V_m) + \ldots\} + (C'/V_m)(RT)^2\{1 + (B/V_m) + \ldots\}^2 = B + C/V_m + \ldots$

or $B'RT + (BB'RT + C'R^2T^2)/V_m + \ldots = B + C/V_m + \ldots$

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 $\underline{C' = (C - B^2)/R^2T^2}.$