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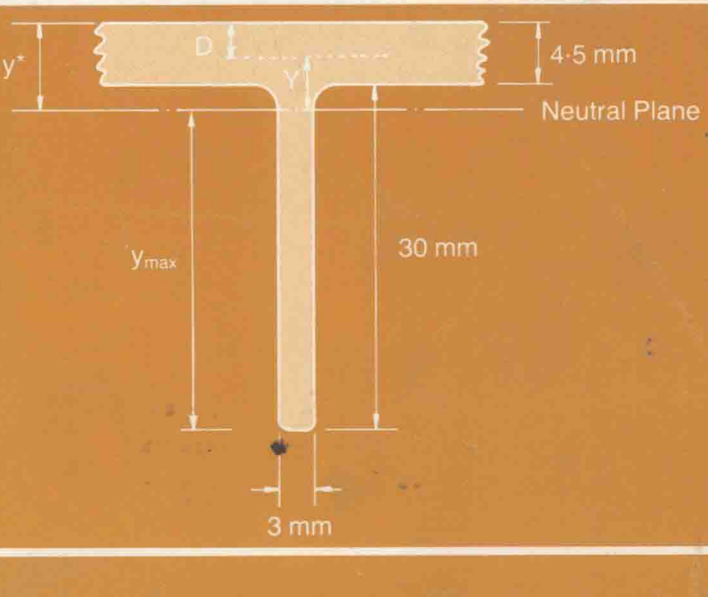
Solutions Manual

to accompany

Principles of Polymer Engineering



OXFORD SCIENCE PUBLICATIONS

Solutions Manual
to accompany
Principles of Polymer Engineering

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Oxford New York Tokyo
OXFORD UNIVERSITY PRESS
1989

Oxford University Press, Walton Street, Oxford OX2 6DP
Oxford New York Toronto
Delhi Bombay Calcutta Madras Karachi
Petaling Jaya Singapore Hong Kong Tokyo
Nairobi Dar es Salaam Cape Town
Melbourne Auckland
and associated companies in
Berlin Ibadan

Oxford is a trade mark of Oxford University Press

Published in the United States
by Oxford University Press, New York

British Library Cataloguing in Publication Data
McCrum, N. G. (Norman Gerard, 1927–)
Solutions manual to accompany principles of polymer engineering.
1. Materials: Polymers
I. Title II. Buckley, C. P. III. Bucknall, C. B.
IIII McCrum, N. G. (Norman Gerard 1927–)
620.1'92
ISBN 0-19-856201-2

Printed in Great Britain
by Bookcraft (Bath) Ltd
Midsomer Norton, Avon.

Authors' Note

In this Manual, we provide detailed solutions to each of the Problems in our textbook *Principles of Polymer Engineering,* published by Oxford University Press in 1988. References in the Manual to *page numbers, Examples, Figures,* and *Problems* relate only to locations in the textbook, and not to the present volume. Where it is necessary to make cross-references to other parts of the present Manual, we specify *Solutions* and not page numbers.

Where appropriate, we have used a subscript asterisk to indicate multiplication, especially where numbers are involved: e.g. $3_*5 = 15$. This usage will be familiar to the majority of readers through computer programming.

Although we have made strenuous efforts to eliminate typing and other errors, some will inevitably remain. As each solution is given in sufficient detail to allow the reader to check the working himself, we hope that any misprints that remain will be easily identified. We would welcome comments from users of both the textbook and the Manual.

Finally, we should like to thank David Bucknall for drawing the diagrams for this Manual.

January 1989

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1
Structure of the molecule

Note: RMM values: H = 1, C = 12, O = 16, F = 19, $C\ell$ = 35.5

Problem 1.1

Method: The monomers shown all form polymers with the repeat unit:

$$-\left[\begin{array}{ccc} H & & X \\ C & - & C \\ H & & Y \end{array}\right]_n-$$

where, for example, in (a) X = H and Y = (C_2H_5).

To calculate the RMM of polymer with degree of polymerisation 1000, we first abbreviate the chemical formula of the repeat unit, then insert RMM values for atoms in the repeat unit, and multiply by 1000.

Solution:

(a) Repeat unit is (C_4H_8). RMM of (C_4H_8) = $4*12 + 8*1$

Answer = $1000\ (4*12 + 8*1)$ = <u>56,000</u>

(b)	(C_2H_3F)	Answer = $1000\ (2*12+3*1+1*19)$	= <u>46,000</u>
(c)	$(C_2H_2C\ell_2)$	Answer = $1000\ (2*12+2*1+2*35.5)$	= <u>97,000</u>
(d)	(C_4H_8)	Answer = $1000\ (4*12+8*1)$	= <u>56,000</u>
(e)	(C_2H_4O)	Answer = $1000\ (2*12+4*1+1*16)$	= <u>44,000</u>
(f)	$(C_4H_6O_2)$	Answer = $1000\ (4*12+6*1+2*16)$	= <u>86,000</u>

Problem 1.2

Method: We refer to the general formula shown shown in Solution 1.1. When X and Y are dissimilar, polymers can be isotactic or syndiotactic. When X and Y are identical, they cannot.

Solution: **Monomers (a), (b), (e) and (f) can form isotactic and syndiotactic sequences because X and Y differ.**

Problem 1.3

Method: We make or imagine three dimensional models. If two forms of the repeat unit cannot be interconverted by rotation about single bonds, they are stereoisomers.

Solution:

(a) Trans and cis forms are shown in the Answers on *p* 379. Rotation does not occur about a double bond.

(b) No stereoisomerism by the rotation test given above.

(c) No stereoisomerism: the repeat unit is symmetrical.

(d) The five-membered ring does not permit rotation about the horizontal C—C bond shown in the Answer on *p* 379. The two H atoms may be on the same side or opposite sides of the polymer chain.

Problem 1.4

Method: We follow the principles outlined in 1.N.12, noting that isoprene differs from butadiene in having a CH_3 (methyl) group attached to carbon atom number 3, so that the number of permutations possible is greater. We number the carbon atoms in butadiene 1,2,3 and 4, reading from left to right, and use the same convention for the corresponding atoms in isoprene. We use R' and R" to denote the sections of polymer chain on either side of the given isoprene unit. Possible structures are given below.

Solution:

(a) 1,4 addition: *i.e.* R' attached to carbon number 1 and R" attached to carbon number 4. This leaves a double bond between carbons 3 and 4. The structure may be cis (R' and R" on the same side of the double bond) or trans (R' and R" opposed):

```
            Cis                               Trans

R'-CH2        CH2-R"              R'-CH2        CH3
     \       /                         \       /
      C  =  C                           C  =  C
     /       \                         /       \
   H          CH3                     H         CH2-R"
```

The long-chain molecules of natural rubber are composed of cis-polyisoprene units.

(b) 1,2 addition: *i.e.* R' attached to carbon no. 1, and R" attached to carbon no. 2. (see below).

(c) 3,4 addition: *i.e.* R' attached to carbon no. 3 and R" attached to carbon no. 4.

(b)
```
     1     2
R'-CH2-CH-R"
       |
 CH3-C=CH2
     3  4
```

(c)
```
   3          4
R'-C(CH3)-CH2-R"
   |
 H-C=CH2
   2  1
```

If structure (b) is repeated along the chain, the possibility of isotactic and syndiotactic structures arises.

Problem 1.5

The 1-hexene introduces butyl $-(C_4H_9)$ side branches into the polyethylene chain. These hinder crystallisation, thereby **lowering the modulus and density**. The product is called 'linear' low-density polyethylene (LLDPE).

Problem 1.6

In structures (I) and (II) all of the carbon atoms are in the main chain. Addition of hydrogen to the double bonds therefore produces a linear chain of $-CH_2-CH_2-$ units, giving **linear polyethylene** in both cases. Hydrogenation of structure (III) produces ethyl $(-CH_2CH_3)$ side groups. The 8% of structure (III) in case (c) therefore makes the resulting product a **branched polyethylene**.

Problem 1.7

There are three possible main-chain bonds in polycarbonate which could be formed by condensation, with elimination of $HC\ell$: (a) the one between the $-(CH_3)_2C-$ group and the benzene ring; (b) the one between the benzene ring and the oxygen; and (c) the one between the oxygen and the >C=O group.

We can discount (a) because hydrogen attached to either carbon atom would be unreactive. For the same reason, (b) would be possible only if the hydrogen were attached to the oxygen atom. However, in this case the reagent would be carbonic acid (H_2CO_3), a weak and unstable acid made by dissolving CO_2 in water. We are left with option (c). The oxygen atom is electronegative, and would obviously be attached to the hydrogen, leaving the chlorine on the >C=O.

Answer: **The polymer is made by reacting Bisphenol A $HO(C_6H_4)C(CH_3)_2(C_6H_4)OH$ with phosgene $O{=}CC\ell_2$.**

Problem 1.8

Obviously, the molecule eliminated in this condensation reaction is sodium chloride ($NaC\ell$). The polymer formed is **polysulphone**, structure (XXXV) on *p* 373.

Problem 1.9

Method: We identify the two components as A and B. The weight fraction Ω_A of A is given by:

$$\Omega_A = W_A/(W_A + W_B) = (n_A M_A)/(n_A M_A + n_B M_B)$$

$$\Omega_A = \frac{X_A M_A}{X_A M_A + X_B M_B} = \frac{X_A M_A}{X_A M_A + (1 - X_A) M_B}$$

where W = weight, n = number of moles, M = RMM, and $X_A = n_A/(n_A + n_B)$ = mole fraction of A. Rearranging:

$$X_A = \frac{M_B}{(M_A/\Omega_A) - M_A + M_B}$$

RMM calculations give:

Styrene (C_8H_8)	= 8*12 + 8*1	= 104
Butadiene (C_4H_6)	= 4*12 + 6*1	= 54
Ethylene (C_2H_4)	= 2*12 + 4*1	= 28
Propylene (C_3H_6)	= 3*12 + 6*1	= 42
Acrylonitrile (C_3H_3N)	= 3*12 + 3*1 + 1*14	= 53

Solution:

(a) X_{sty} = 54/[(104/0.25)-104+54] = 0.1475 = **14.75%**

(b) X_{eth} = 42/[(28/0.55)-28+42] = 0.647 = **64.7%**

(c) X_{acr} = 104/[(53/0.235)-53+104] = 0.376 = **37.6%**

(d) X_{acr} = 54/[(53/0.4)-53+54] = 0.404 = **40.4%**

Problem 1.10

A polymer having equal amounts of ethylene and propylene randomly arranged in the chain will be essentially non-crystalline. As the non-crystalline components of both polyethylene and polypropylene become rubbery at temperatures well below 23°C, the random copolymer is a rubbery material. However, there are no double bonds in the structure, and it is therefore difficult to crosslink the rubber by ordinary chemical means. One possibility is to use ionising radiation (*see p* 10). A better solution is to add a third monomer which will copolymerise with ethylene and propylene, and which has two double bonds. One of the double bonds will be needed to incorporate the monomer unit into the copolymer chain. The other will be available **to form crosslinks**. One monomer that is used commercially is dicyclopentadiene.

Problem 1.11

Method: Note that chains will grow until all acid groups have been used up, and all molecules have glycol end groups. The average molecule will then have *n* acid units and *(n + 1)* glycol units. The condensation reaction will produce 2*n* water molecules. See *p* 15.

RMM of H_2O = 2*1 + 1*16 = 18

RMM of glycol ($C_2H_6O_2$) = 2*12 + 6*1 + 2*16 = 62

RMM of acid ($C_8H_6O_4$) = 8*12 + 6*1 + 4*16 = 166

∴ Number average RMM of polyester is given by:

$\overline{M}_n$ = (n+1)*62 + n*166 - 2*n*18

Solution:

(a) (n+1)/n = 1.1 ∴ n = 10

$\overline{M}_n$ = 11*62 + 10*166 - 2*10*18 = **1982**

(b) $(n+1)/n = 1.02 \quad \therefore n = 50$

$$\overline{M}_n = 51*62 + 50*166 - 2*50*18 = \underline{9662}$$

(c) $(n+1)/n = 1 \quad \therefore n = \infty$ and M_n **has no limits**.

Problem 1.12

Method: We follow principles outlined in Solution 1.11. Chain ends are blocked by unreactive CH_3- groups when an average molecule has 100 diamine units, 99 adipic acid units, and 2 acetic acid units, with elimination of 200 water molecules (RMM of H_2O = 18).

Solution:

From formulae given on *p* 14:

RMM of the diamine ($C_6H_{16}N_2$) = 116

RMM of adipic acid ($C_6H_{10}O_4$) = 146

RMM of acetic acid ($C_2H_4O_2$) = 60

$$\overline{M}_n = 100*116 + 99*146 + 2*60 - 200*18 = \underline{22,574}$$

Problem 1.13

Abstraction of a hydrogen atom from polybutadiene leaves a free radical which will usually have the structure:

```
  H   H   H   H                              H   H   H   H
 -C - C = C - C- ,    which will add        -C - C = C - C-
  H           .       to styrene to give:    H           |
                                                       H C H
                                                         |
                                                       H C C6H5
                                                         .
```

The new free radical will add further styrene units to form a graft copolymer with a polybutadiene backbone and polystyrene side chains. Reaction of the styryl radicals with double bonds in neighbouring polybutadiene chains will also cause crosslinking.

Problem 1.14

(a) The average molecule contains 2*150 styrene units, each of RMM = 104, and 2000 butadiene units, each of RMM = 54. (See Solution 1.9 for RMM values).

$$\therefore \text{Wt fraction styrene units} = \frac{2*150*104}{2*150*104 + 2000*54}$$

$$= \underline{0.224}$$

(b) RMM of single styrene chain = 150*104

Mass of styrene chain $m = 150*104/(6.023*10^{23})$ grams

$m = 150*104/(6.023*10^{26})$ kg

Volume of sphere $V = 4\pi r^3/3 = (4\pi/3)[25*10^{-9}/2]^3$ m^3

Mass of sphere $M = V*\rho = (4\pi/3)[25*10^{-9}/2]^3 *1050$ kg

Number of styrene chains per sphere = M/m = <u>332</u>

Problem 1.15

Method:

$$\overline{M_n} = \frac{\Sigma\, w_i}{\Sigma\, n_i} = \frac{W}{\Sigma\,(w_i/M_i)} \qquad \text{(see eqn 1.3)}$$

$$\overline{M_w} = \frac{\Sigma\, w_i M_i}{W} = \Sigma\, \Phi_i M_i \qquad \text{(see eqn 1.4)}$$

where W = mass of sample = 1 gram, and $\Phi_i = w_i/W$

Solution:

(a) $\Sigma\,(w_i/M_i) = (1/1000)*[(0.10/15) + (0.18/27) + (0.25/39) + (0.17/56) + (0.12/78) + 0.08/104) + (0.06/120) + (0.04/153)]$

$= 2.58484*10^{-5}$

$\overline{M_n} = W/\Sigma(w_i/M_i) = \underline{38{,}687\ g/mol}$

(b) $\overline{M_w} = \Sigma\Phi_i M_i = 1000[0.10*15 + 0.18*27 + 0.25*39 + 0.17*56 + 0.12*78 + 0.08*104 + 0.06*120 + 0.04*153]$

$= \underline{56{,}630\ g/mol}$

Problem 1.16

Method: We modify results given in Solution 1.15:

Solution:

(a) RMM of styrene = 104 (see Solution 1.9)

Adding 0.5 wt.% of styrene gives W = 1.005 g.

Adding an extra term to the series give in (a) above:

$$\Sigma(w_i M_i) = 2.58484*10^{-5} + 0.005/104 = 7.39253*10^{-5}$$

$$\overline{M_n} = W/\Sigma(w_i M_i) = (1.005/7.39253*10^{-5})$$

$$= \underline{13{,}595 \text{ g/mol}}$$

(b) Using result for M_w from Solution 1.15, with an extra term for the styrene monomer, and W = 1.005 g:

$$\overline{M_w} = \Sigma w_i M_i / W = [56{,}630 + 0.005*104]/1.005$$

$$= \underline{56{,}349 \text{ g/mol}}$$

Problem 1.17

The molecule shown on page 29 as $HO(RCOO)_xH$ may also be written as $HORCOO(RCOO)_{x-1}H$, to emphasise the point that it is formed by reaction of (x-1) -OH groups, leaving one unreacted. Since *p* is the fraction of all the -OH groups that have reacted, (1-*p*) is the fraction that have not reacted. Writing P_x as the probability that a given molecule has the structure $HO(RCOO)_xH$:

$$P_x = N_x/N = p^{x-1}(1-p)$$

$$\text{Fraction -OH unreacted} = \frac{\text{current no. of -OH gps}}{\text{original no. of -OH gps}}$$

$$(1 - p) = N/N_o$$

$$\therefore\ N_x = Np^{(x-1)}(1 - p) = N_o p^{(x-1)}(1 - p)^2$$

Wt. fraction of polymer molecules having x (RCOO) units = w_x/W

$$\therefore \quad W_x = w_x/W = mxN_x/mN_o = xN_x/N_o$$

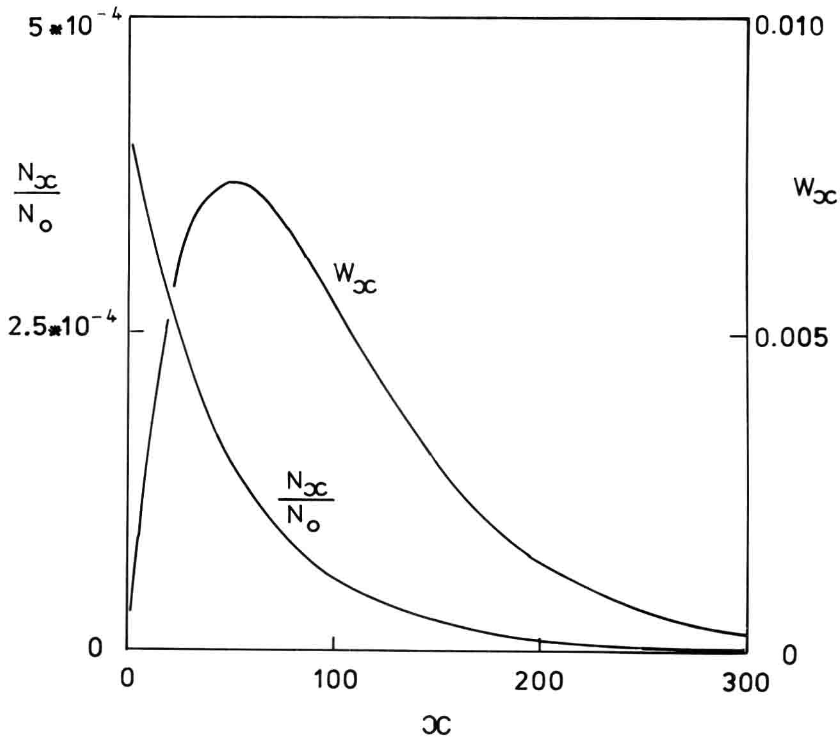
where m is the mass of the monomer molecule. The change in mass due to loss of H_2O is neglected here. Substituting for N_x/N_o from above:

$$W_x = xp^{x-1}(1 - p)^2$$

When $p = 0.98$, $(1 - p)^2 = 0.02^2 = 4*10^{-4}$

and $W_x = 4*10^{-4}*x*(0.98)^{x-1}$

Plots of N_x/N_o and W_x against x, obtained by inserting values of x between 1 and 300 into the above equations, are shown below:



2
Structure of polymeric solids

Problem 2.1

Method: Mass of unit cell $m = M/N_A$ grams $= M/1000*N_A$ kg

where M = RMM of groups in unit cell

and N_A = Avogadro's number

$1/1000*N_A = 1.6603*10^{-27}$

Volume of unit cell $v = A*B*C\ (pm)^3 = A*B*C*10^{-36}\ m^3$

where A, B and C are the magnitudes of the vectors

$\therefore$ Density $\rho = m/v = (M/A*B*C)*1.6603*10^9\ kg/m^3$

Solution:

(a) Cell contains C_4H_8. RMM = 4*12 + 8*1 = 56

$\rho = 56*1.6603*10^9/(736*492*254)$ = <u>1011 kg/m³</u>

(b) $C_8H_{12}Cl_4$. RMM = 8*12 + 12 + 4*35.5 = 250

$\rho = 250*1.6603*10^9/(1040*530*510)$ = <u>1477 kg/m³</u>

(c) $C_4H_6F_2$. RMM = 4*12 + 6 + 2*19 = 92

$\rho = 92*1.6603*10^9/(857*495*252)$ = <u>1429 kg/m³</u>

(d) $C_4H_4F_4$. RMM = 4*12 + 4 + 4*19 = 128

$\rho = 128*1.6603*10^9/(847*470*256)$ = <u>2085 kg/m³</u>

(e) $8[C_5H_8]$. RMM = 8*(5*12 + 8] = 544

$\rho = 520*1.6603*10^9/(1246*886*810)$ = <u>1010 kg/m³</u>

Problem 2.2

Method: As Solution 2.1, except that the volume of the unit cell is now given by $A*B*C*\sin\beta$, because the component of c normal to the plane **ab** is $C*\sin\beta$.

Solution:

(a) $12[C_3H_6]$ RMM = 12*(3*12 + 6) = 504

$\rho = 504*1.66*10^9/(666*2078*650*\sin 99.6^o)$ = **943 kg/m³**

(b) $8[C_6H_{11}NO]$ = 8*(6*12 + 11 + 14 + 16) = 904

$\rho = 904*1.66*10^9/(956*1724*801*\sin 67.5)$ = **1231 kg/m³**

Problem 2.3

Method: As Solutions 2.1 and 2.2, but now we must evaluate the scalar triple product $\underset{\sim}{a}.(\underset{\sim}{b} \times \underset{\sim}{c})$ to obtain v.

Let $\underset{\sim}{i}$, $\underset{\sim}{j}$ and $\underset{\sim}{k}$ represent unit vectors in the x, y and z directions. Let $\underset{\sim}{a}$ lie along the x axis, and $\underset{\sim}{b}$ be in the x-y plane. We can then write:

$\underset{\sim}{a} = \underset{\sim}{i}*A_x = \underset{\sim}{i}*A$

$\underset{\sim}{b} = \underset{\sim}{i}*B_x + \underset{\sim}{j}*B_y = \underset{\sim}{i}*B*\cos\gamma + \underset{\sim}{j}*B*\sin\gamma$

$\underset{\sim}{c} = \underset{\sim}{i}*C_x + \underset{\sim}{j}*C_y + \underset{\sim}{k}*C_z = \underset{\sim}{i}*C*\cos\beta + \underset{\sim}{j}*C_y + \underset{\sim}{k}*C_z$

Since $B_z = 0$ (*see* above), scalar product $\underset{\sim}{b}.\underset{\sim}{c}$ gives:

$\underset{\sim}{b}.\underset{\sim}{c} = B_x*C_x + B_y*C_y$

$= (B*\cos\gamma)*(C*\cos\beta) + (B*\sin\gamma)*C_y$

also $\underset{\sim}{b}.\underset{\sim}{c} = B*C*\cos\alpha$

$\therefore \quad C_y/C = (\cos\alpha - \cos\beta*\cos\gamma)/\sin\gamma$

But $C^2 = C_x{}^2 + C_y{}^2 + C_z{}^2$

and $C_x = C*\cos\beta$

$\therefore \quad (C_z/C)^2 = 1 - \cos^2\beta - [(\cos\alpha - \cos\beta\ \cos\gamma)/\sin\gamma]^2$

$\therefore$ Volume $v = A_x*B_y*C_z$

$= A*B*\sin\gamma*C*(C_z/C)$ pm³

Solution:

(a) $(C_z/C)^2 = 1 - \cos^2 77 - \left[\frac{\cos 48.5 - \cos 77 \cos 63.5}{\sin 63.5}\right]^2$

$= (0.7448)^2$

$v = 490*540*1720*\sin 63.5*0.7448 \quad pm^3$

$= 3.03*10^8 \quad pm^3$

Cell atoms are $C_{12}H_{22}O_2N_2$

RMM = 12*12 + 22 + 2*16 + 2*14 = 226

$\rho = 226*1.66*10^9/3.03*10^8$ = **1238 kg/m³**

(b) $(C_z/C)^2 = 1 - \cos^2 118 - \left[\frac{\cos 98.5 - \cos 118 \cos 112}{\sin 112}\right]^2$

$= [0.811]^2$

$v = 456*596*1075*\sin 112*0.811 \quad pm^3$

$= 2.197*10^8 \quad pm^3$

Cell atoms are $C_{10}H_8O_4$

RMM = 10*12 + 8 + 4*16 = 192

$\rho = 192*1.66*10^9/2.197*10^8$ = **1451 kg/m³**

Problem 2.4

Method Angle $\theta = \sin^{-1}(n\lambda/2d)$

The planes are specified by their Miller indices, which are based on units of one cell edge length. The indices give the reciprocals of the intercepts of the plane on the a, b and c axes. Thus, as shown in the diagram, the (110) plane meets the a axis at distance a/1 = 736 pm (*see* Problem 2.1 for data), the b axis at distance b/1 = 492 pm, and the c axis at c/0 = infinity (*i.e.* it is parallel to the c axis). For a fuller explanation of Miller indices, see any book on physical metallurgy or crystallography.