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CHEM 3420: Physical Chemistry II — Spring 2009

Homework 10 — Solutions

1. (a) To solve for the structure type we need to figure out the indices of the planes given in the pattern. From that we can see what structure we have using the systematic absences (selection rules).

Theta	Sin^2	Normalize	clear fractions	hkl?	check
19.2	0.108	1.00	3	111	0.036
22.25	0.143	1.33	4	200	0.036
32.425	0.288	2.66	8	220	0.036
38.95	0.395	3.65	11	311	0.036
40.925	0.429	3.97	12	222	0.036
49.2	0.573	5.30	16	400	0.036
55.6	0.681	6.29	19	331	0.036

Based on the planes present in the pattern, this structure is FCC.

(b) The lattice constant can be calculated from the interplanar spacings which can be determined from the measured diffraction angles.

$$\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{h^2+k^2+l^2}$$

The final column in the above table (the check) is $\frac{\sin^2\theta}{h^2+k^2+l^2}$, so a can be found from each reflection.

Plane	a
(111)	4.06
(200)	4.07
(220)	4.07
(311)	4.07
(222)	4.08
(400)	4.07
(331)	4.07
Average	4.07

You would not actually take an average if you were doing a real experiment. There are methods for treating the random and systematic error in diffraction patterns that allow you to determine the lattice constant using all the measured reflections.

(c) Since the crystal is FCC, the lattice constant is related to the radius through:

$$4r = \sqrt{2}a$$

$$\boxed{r = 1.44\ \text{Å}}$$

(d) There are four atoms per unit cell, so we can write:

$$\frac{4}{a^3} = \frac{N_a}{V_{molar}}$$

Solving for the molar volume:

$$V_{molar} = \frac{(6.02 \times 10^{23})(4.07 \times 10^{-8}\ cm)^3}{4} = 10.15\ cm^3$$

$$\rho = \frac{66.6\ g/mol}{10.145\ cm^3/mol}$$

$$\boxed{\rho = 6.56\ \text{g/cm}^3}$$

2. (a) We can combine Bragg's Law ($\lambda = 2d\sin\theta$) with the relationship for the interplanar spacing of an FCC crystal ($\frac{1}{d} = \frac{h^2+k^2+l^2}{a^2}$). and solve for a:

$$a = \sqrt{\frac{\lambda^2(h^2+k^2+l^2)}{4\sin^2\theta}}$$

We know the first plane we would see in a diffraction pattern of an FCC crystal is (111):

$$a = \sqrt{\frac{(2.29\ \text{Å})^2(1^2+1^2+1^2)}{4(\sin 33.0°)^2}}$$

Yielding a lattice constant of $a = 3.64$ Å.

(b) Now that we know the lattice constant, we can use Vegard's Law to find the composition of the solid. We are told the relation between composition and lattice constant is linear so we know that we can calculate the slope of the line using any two points and it must be the same regardless of the two points selected. We can set up the following equality:

$$\frac{3.81 - 3.53}{1 - 0} = \frac{3.81 - 3.64}{1 - x}$$

where x is the unknown mole fraction of Rh in the solid associated with the lattice constant calculated in (a). Solving this we get:

$$x = 0.39 \text{ or } 39\% \text{ Rh}$$

(c) This however is not the overall alloy composition, but only the composition of the first solid to form. We now have to construct a tie line connecting the solid curve (the solidus) at 39% Rh to the liquid curve (liquidus). The value of the tie line at the liquidus is the overall alloy composition. In this case, it turns out to be about 20% Rh. (See the figure below of the tie line construction).