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ENSC 330

Assignment #3

1).

The cubic volume is defined to be 0.478 nm along each edge. Since the unit cell has a cubic configuration, the volume of the unit cell can be determined by the following formula:

$$\left(\frac{volume}{unit\_cell}\right) = side\_1_{unit\_cell} \times side\_2_{unit\_cell} \times side\_3_{unit\_cell}$$

Since each of the sides of the unit cell are defined to be 0.478 nm in length, the volume of the unit cell of CaO can be calculated to be:

$$\left(\frac{volume}{unit\_cell}\right)_{CaO} = 0.478\ nm \times 0.478\ nm \times 0.478\ nm$$

$$\left(\frac{volume}{unit\_cell}\right)_{CaO} = 0.109215352\ nm^3$$

$$\left(\frac{volume}{unit\_cell}\right)_{CaO} = 0.109\ nm^3 \text{ with significant figures applied}$$

The question also states that the cubic volume of CaO contains four Ca^{2+} ions and four O^{2-} ions. The mass of the unit cell contributed by the ions is given by the following formula:

$$\frac{mass}{unit\_cell} = \frac{\left(\frac{ions}{unit\_cell}\right)\left(\frac{mass}{mole}\right)}{\left(\frac{ions}{mole}\right)}$$

Therefore, the contribution to the mass of the unit cell from each of the Ca^{2+} and O^{2-} ions is given by modifying the above formula in the following manner.

$$\left(\frac{mass}{unit\_cell}\right)_{Ca^{2+}} = \frac{\left(\frac{ions}{unit\_cell}\right)_{Ca^{2+}}\left(\frac{mass}{mole}\right)_{Ca^{2+}}}{\left(\frac{ions}{mole}\right)_{Ca^{2+}}}$$

$$\left(\frac{mass}{unit\_cell}\right)_{O^{2-}} = \frac{\left(\frac{ions}{unit\_cell}\right)_{O^{2-}}\left(\frac{mass}{mole}\right)_{O^{2-}}}{\left(\frac{ions}{mole}\right)_{O^{2-}}}$$

The mass of one mole of Ca^{2+} ions is equal to the atomic mass of calcium. The atomic mass of calcium is given as 40.08 g/mol. Similarly, the mass of one mole of O^{2-} ions is equal to the atomic mass of oxygen. The atomic mass of oxygen is given as 15.999 g/mol. The number of atoms or ions in one mole of any element (or the number of molecules in one mole of any compound) is defined to be equal to Avogadro's number (Van Vlack, 1989). Avogadro's number states that a mole of any element possesses 6.02 x 10^{23} atoms or ions of that element (Van Vlack, 1989). Substituting these values into the above equations, we can calculate the contribution to the mass of the CaO unit cell from the Ca^{2+} and O^{2-} ions.

$$\left(\frac{mass}{unit\_cell}\right)_{Ca^{2+}} = \frac{4\left(40.08\ \frac{g}{mol}\right)}{\left(6.022 \times 10^{23}\ \frac{atoms}{mol}\right)}$$

$$\left(\frac{mass}{unit\_cell}\right)_{Ca^{2+}} = 2.662384959 \times 10^{-22}\ g$$

$$\left(\frac{mass}{unit\_cell}\right)_{Ca^{2+}} = 2.662 \times 10^{-22}\ g \text{ with significant figures applied}$$

$$\left(\frac{mass}{unit\_cell}\right)_{O^{2-}} = \frac{4\left(15.999\ \frac{g}{mol}\right)}{\left(6.022 \times 10^{23}\ \frac{atoms}{mol}\right)}$$

$$\left(\frac{mass}{unit\_cell}\right)_{O^{2-}} = 1.062703421 \times 10^{-22}\ g$$

$$\left(\frac{mass}{unit\_cell}\right)_{O^{2-}} = 1.063 \times 10^{-22}\ g \text{ with significant figures applied}$$

Therefore, the total mass of the unit cell of CaO can be calculated by summing the mass component of the Ca^{2+} ions and the mass component of the O^{2-} ions. This is determined in the following manner:

$$\left(\frac{mass}{unit\_cell}\right)_{CaO} = \left(\frac{mass}{unit\_cell}\right)_{Ca^{2+}} + \left(\frac{mass}{unit\_cell}\right)_{O^{2-}}$$

$$\left(\frac{mass}{unit\_cell}\right)_{CaO} = 2.662384959 \times 10^{-22}\ g + 1.062703421 \times 10^{-22}\ g$$

$$\left(\frac{mass}{unit\_cell}\right)_{CaO} = 3.725088380 \times 10^{-22}\ g$$

$$\left(\frac{mass}{unit\_cell}\right)_{CaO} = 3.725 \times 10^{-22}\ g \text{ with significant figures applied}$$

The mass/volume of a material is defined to be equal to its density. We can state this relationship in the following manner.

$$density = \left(\frac{mass}{volume} \right)$$

When considering the mass within a unit cell of a material and the volume within a unit cell of a material, a more specific definition of density can be stated.

$$density = \frac{\left(\frac{mass}{unit\_cell} \right)}{\left(\frac{volume}{unit\_cell} \right)}$$

Since we have obtained the values for the mass of a unit cell of CaO and the volume of a unit cell of CaO, we can substitute these values into the above equation to solve for the density of CaO.

$$density_{CaO} = \frac{\left(\frac{mass}{unit\_cell} \right)_{CaO}}{\left(\frac{volume}{unit\_cell} \right)_{CaO}}$$

$$density_{CaO} = \frac{3.7249488 \times 10^{-22}\ g}{0.1092552\ mm^3}$$

$$density_{CaO} = 3.4106949 \times 10^{-21}\ \frac{g}{mm^3}$$

$$density_{CaO} = 3.41 \times 10^{-21}\ \frac{g}{mm^3}$$ with significant figures applied

2).

a).

The mass of a unit cell can be calculated by the following formula.

$$\frac{mass}{unit\_cell} = \frac{\left(\frac{atoms}{unit\_cell} \right)\left(\frac{mass}{mole} \right)}{\left(\frac{atoms}{mole} \right)}$$

The mass of one mole of tin atoms is equal to the atomic mass of tin. The atomic mass of tin is given as 118.69 g/mol. The question states that tin possesses 4 atoms/unit cell. As explained in question #1, the number of atoms or ions in one mole of any element (or the number of molecules in one mole of any compound) is equal to Avogadro's number (Van Vlack, 1989). Avogadro's number states that a mole of any element possesses 6.02 x 10^{23} atoms or ions of that element (Van Vlack, 1989). Using these values in the above equation, we can calculate the mass of a unit cell of tin:

$$\left(\frac{mass}{unit\_cell}\right)_{Tin} = \frac{\left(\frac{atoms}{unit\_cell}\right)_{Tin}\left(\frac{mass}{mole}\right)_{Tin}}{\left(\frac{atoms}{mole}\right)_{Tin}}$$

$$\left(\frac{\quad}{\quad}\right) = \frac{\left(4\ \frac{\quad}{\quad}\right)\left(118.69\ \frac{\quad}{\quad}\right)}{\left(6.022 \times 10^{\quad}\ \frac{\quad}{\quad}\right)}$$

$$\left(\frac{mass}{unit\_cell}\right)_{Tin} = 7.8837548 \times 10^{-22}\ g$$

$$\left(\frac{mass}{unit\_cell}\right)_{Tin} = 7.884 \times 10^{-22}\ g \text{ with significant figures applied}$$

The volume of a unit cell can be calculated by the following formula.

$$\frac{volume}{unit\_cell} = \frac{\left(\frac{mass}{unit\_cell}\right)}{\left(\frac{mass}{volume}\right)}$$

Since the mass/volume of a material is defined to be its density, the above formula can be restated in the following manner.

$$\frac{volume}{unit\_cell} = \frac{\left(\frac{mass}{unit\_cell}\right)}{density}$$

The density of tin is defined to be equal to 7.17 g/cm^3. Thus, using our previous result for the mass in a unit cell of tin, we can use the above formula to calculate the volume of a unit cell of tin.

$$\left(\frac{volume}{unit\_cell}\right)_{Tin} = \frac{\left(\frac{mass}{unit\_cell}\right)_{Tin}}{density_{Tin}}$$

$$\left(\frac{volume}{unit\_cell}\right)_{Tin} = \frac{7.8837548 \times 10^{-22}\ g}{7.17\ \frac{g}{cm^3}}$$

$$\left(\frac{volume}{unit\_cell}\right)_{Tin} = 1.095854 \times 10^{-22}\ cm^3$$

$$\left(\frac{volume}{unit\_cell}\right)_{Tin} = 1.10 \times 10^{-22}\ cm^3 \text{ with significant figures applied}$$

b).

Tin is tetragonal. This indicates that two sides of its unit cell each have length a. However, the third side, c, of the unit cell is a different length. The question defines the ratio of these two sides in the following manner.

$$\left(\frac{c}{a}\right)_{Tin} = 0.546$$

Rearranging the above equation to solve for the length of side c in the unit cell of tin, we obtain:

$$c_{Tin} = 0.546 \cdot a_{Tin}$$

The volume of tetragonal unit cell is defined to be the product of its three sides. Since two of the sides of the tetragonal unit cell have length a and the other side of the tetragonal unit cell has a length c, this volume can be defined by the following formula.

$$\left(\frac{volume}{unit\_cell}\right) = side\_1_{unit\_cell} \times side\_2_{unit\_cell} \times side\_3_{unit\_cell}$$

$$\left(\frac{volume}{unit\_cell}\right)_{Tetragonal} = a \times a \times c$$

Applying the above equation which relates the lengths a and c for the unit cell of tin, we can obtain an expression for the volume of a unit cell of tin.

$$\left(\frac{volume}{unit\_cell}\right)_{Tin} = a_{Tin} \times a_{Tin} \times c_{Tin}$$

$$\left(\frac{volume}{unit\_cell}\right)_{Tin} = a_{Tin} \times a_{Tin} \times 0.546 \cdot a_{Tin}$$

$$\left(\frac{volume}{unit\_cell}\right)_{Tin} = 0.546 \cdot a_{Tin}^3$$

We can rearrange this equation to solve for a:

$$a_{Sn} = \left(\frac{\left(\frac{volume}{unit\_cell} \right)_{Sn}}{0.546} \right)^{\frac{1}{3}}$$

In part a, we obtained a numerical value for the volume of a unit cell of tin. Thus, we can substitute that numerical value into the above equation and solve for the length of a in a unit cell of tin.

$$a_{Sn} = \left(\frac{1.09548054 \times 10^{-22}\ cm^3}{0.546} \right)^{\frac{1}{3}}$$

$$a_{Sn} = 5.864748392 \times 10^{-8}\ cm$$

$$a_{Sn} = 5.86 \times 10^{-8}\ cm \text{ with significant figures applied}$$

This value for a in a unit cell of tin can be substituted into the above expression which relates the lengths of a and c in a unit cell of tin. The value of c in a unit cell of tin can then be determined.

$$c_{Sn} = 0.546 \cdot a_{Sn}$$
$$c_{Sn} = 0.546 \cdot 5.864748392 \times 10^{-8}\ cm$$
$$c_{Sn} = 3.200863736 \times 10^{-8}\ cm$$
$$c_{Sn} = 3.20 \times 10^{-8}\ cm \text{ with significant figures applied}$$

3).

The plane under investigation in this question has a Miller index of (1 1 1). The Miller indices are defined to be “the reciprocals of the three intercepts that the plane makes with each of the axes, cleared of fractions and common multipliers” (Van Vlack, 1989). Therefore, a given Miller index represents a set of parallel planes. The (1 1 1) plane intercepts the x-axis at (a,0,0), intercepts the y-axis at (0,a,0), and intercepts the z-axis at (0,0,a), where a is any number. This is depicted in the following diagram of the (1,1,1) plane:

We know that this (1 1 1) plane must pass through the centre of the unit cell. The centre of the unit cell is given as the point p = (0.5,0.5,0.5). Therefore, the (1 1 1) plane we are concerned with must contain the point p = (0.5,0.5,0.5).

By definition, a normal vector to a plane is any vector which begins at a point in the plane and has a direction that is perpendicular (or orthogonal) to the surface of the plane (The Vector Equation of a Plane, 2003). Any (1 1 1) plane must be parallel to any other (1 1 1) plane, so they must all have the same normal vector. In other words, any vector beginning at a point on the (1 1 1) plane and having a direction that is perpendicular to the surface of the plane will, regardless of how the plane is shifted, still begin at a point on the (1 1 1) plane and have a direction that is perpendicular to the surface of the plane.

To construct a normal vector to a plane, we can consider the position vectors of three points on the plane (The Vector Equation of a Plane, 2003). Let us call these points b, c, and d. We know that the (1 1 1) plane contains the points:

$$b = \langle a,0,0 \rangle$$

$$c = \langle 0,a,0 \rangle$$

$$d = \langle 0,0,a \rangle$$

Using the definition of vectors, we can create vectors that connect these points (The Vector Equation of a Plane, 2003). From linear algebra, any of these vectors must lie on our (1 1 1) plane (The Vector Equation of a Plane, 2003). For example, consider the following two vectors, **E** and **F**:

$$\vec{E} = c - b$$
$$\vec{E} = (0,a,0) - (a,0,0)$$
$$\vec{E} = \langle -a, a, 0 \rangle$$

$$\vec{F} = d - b$$
$$\vec{F} = (0,0,a) - (a,0,0)$$
$$\vec{F} = \langle -a, 0, a \rangle$$

Since both of these vectors must lie in our (1 1 1) plane, if we take the cross-product of the two vectors, this will yield the normal vector to the (1 1 1) plane (The Vector Equation of a Plane, 2003). This is performed in the following calculation (Cross product, 2003):

$$\hat{n} = \vec{E} \times \vec{F}$$
$$\vec{n} = (-a,a,0) \times (-a,0,a)$$
$$\times \quad n = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ -a & a & 0 \\ -a & 0 & a \end{vmatrix}$$
$$\hat{n} = \langle a^2 - 0 \rangle \cdot \hat{i} - \langle -a^2 - 0 \rangle \cdot \hat{j} + (0 - (-a^2)) \cdot \hat{k}$$
$$\hat{n} = \langle a^2 \rangle \cdot \hat{i} + \langle a^2 \rangle \cdot \hat{j} + (a^2) \cdot \hat{k}$$
$$\hat{n} = \langle a^2, a^2, a^2 \rangle$$

where **n** is the normal vector to the (1 1 1) plane.

Therefore, any vector of the form (a^2,a^2,a^2) will act as a normal vector to the (1 1 1) plane.

Vector algebra also demonstrates that, if we know the normal vector, **n**, of a plane and a point, p, on the plane, any other point, r, that lies on the plane must satisfy the following equation (The Vector Equation of a Plane, 2003):

$$(r - p) \cdot n = 0$$

Therefore, we can substitute the values p = (0.5,0.5,0.5), **n** = (a^2,a^2,a^2), and r = (x_1,y_1,z_1), where each of x_1, y_1, and z_1 can be any number, into the above equation. This produces the following relationship (Dot Product, 2003):

$$(x_1, y_1, z_1 - 0.5,0.5,0.5) \cdot (a^2, a^2, a^2) = 0$$
$$(x_1 - 0.5, y_1 - 0.5, z_1 - 0.5) \cdot (a^2, a^2, a^2) = 0$$
$$(x_1 - 0.5)\,a^2 + (y_1 - 0.5)\,a^2 + (z_1 - 0.5)\,a^2 = 0$$

Although any point on the plane must satisfy this relationship, we are concerned with the axial intercepts of the plane. This corresponds to the points (a,0,0), (0,a,0), and (0,0,a). Let us consider the first of these points, (a,0,0). For r = (a,0,0), the above equation becomes:

$$(a - 0.5)\,a^2 + (0 - 0.5)\,a^2 + (0 - 0.5)\,a^2 = 0$$
$$(a - 0.5)\,a^2 + (-0.5)\,a^2 + (-0.5)\,a^2 = 0$$
$$a^3 - 1.5a^2 = 0$$
$$a - 1.5\,a^2 = 0$$

which implies:

$$a - 1.5 = 0$$
or
$$a^2 = 0$$

These expressions imply the solutions:

$$a = 1.5$$
and
$$a = 0$$
and
$$a = 0$$

Either of the a = 0 solutions would make each of our axial intercepts equal to (0,0,0), which would not allow the plane to pass through p = (0.5,0.5,0.5). Therefore, a=1.5 must be the correct answer. This implies that the three axial intercepts are at:

$$(1.5,0,0)$$
$$(0,1.5,0)$$
$$(0,0,1.5)$$

A final sketch of the plane is as follows:

4). The plane that includes the points (0,0,0) and (1,0,1) and (1,0.5,0.5) has been sketched in the following diagram:

Note that these points represent the coefficients of the point locations in terms of the unit cell dimensions (Van Vlack, 1989). They do not represent the absolute positions of the points (Van Vlack, 1989). Thus, these point coefficients can be multiplied by the side length, a, of the unit cell in order to obtain the absolute locations of each of the points (Van Vlack, 1989). This is why the symbol a is used to denote the lengths of the sides of the unit cell in the above diagram, as well as in each of the following diagrams. Note also that this question has been answered on the assumption that the unit cell structure under consideration is cubic. A non-cubic unit cell structure would yield precisely the same point coefficients for the axial intercepts (and thus the same Miller indices) (Van Vlack, 1989). However, the side lengths would not all be equal to a. This would cause the absolute locations of each of the axial intercepts to be different (Van Vlack, 1989).

This plane passes through the origin. However, the origin can be shifted. The Miller index of the plane will depend on where the origin is shifted. However, the Miller index that is obtained from shifting the origin in one direction will be equivalent to any other Miller index that is obtained from shifting the origin in any other direction. This is because all the Miller indices obtained through this technique of shifting the origin will represent parallel (and equivalent) planes (Van Vlack, 1989).

Let us consider the situation of shifting the origin one unit in the positive x-direction. The plane in question has been resketched below with the origin shifted one unit in the positive x-direction.

The plane now includes the points (-1,0,0), (0,0,1), and (0,0.5,0.5). From these points, we can see that the intercept with the x-axis is –1, and the intercept with the z-axis is 1. Note again that these intercept numbers

represent the coefficients of the intercepts' positions in terms of the unit cell dimensions, rather than the absolute locations of the intercepts (Van Vlack, 1989). The absolute distance from the new origin to the intercept with the x-axis is therefore equal to -1a. The absolute distance from the new origin to the intercept with the z-axis is equal to 1a. To determine the location of the intercept with the y-axis, consider a vector on the plane that intercepts the y-axis. From vector algebra, we know that any two points on the plane will define a vector that lies on the plane (The Vector Equation of a Plane, 2003). Therefore, let us consider the vector **v** that connects the two points (0,0,1) and (0,0.5,0.5). This vector can be defined as the difference between the two points:

$$\hat{v} = \langle 0,0,1 \rangle - \langle 0,0.5,0.5 \rangle$$
$$\hat{v} = \langle 0,-0.5,0.5 \rangle$$

Any scalar multiple of this vector will yield a parallel vector (Young-Hoo, 1998). Therefore, any scalar multiple of the vector **v** can be defined as:

$$s \cdot \hat{v} = s \cdot \langle 0,-0.5,0.5 \rangle$$
$$s \cdot \hat{v} = \langle 0,-0.5s,0.5s \rangle$$

where s is a scalar multiplier.

By applying the principles of vector algebra, we can determine the point at which this vector intersects the y-axis. Any point on the y-axis, p_y, is defined by:

$$p_y = \langle 0, y_1, 0 \rangle$$

where y_1 is the y component of the point p_y, and can be any number. Let us consider the relationship between point p_y and the point (0,0,1). The scalar-multiplied vector s**v**, point p_y, and the point (0,0,1) all lie in the y-z plane. We can therefore define the scalar-multiplied vector s**v** as the difference between the point p_y and the point (0,0,1):

$$s \cdot \hat{v} = \langle 0,0,1 \rangle - \langle 0, y_1, 0 \rangle$$

Since we have already determined the value of s•**v** in a previous calculation, we can substitute this value into the above equation.

$$\langle 0,-0.5s,0.5s \rangle = \langle 0,0,1 \rangle - \langle 0, y_1, 0 \rangle$$

This equation can now be rearranged to solve for y_1 in the following fashion:

$$\langle 0, y_1, 0 \rangle = \langle 0,0,1 \rangle - \langle 0,-0.5s,0.5s \rangle$$
$$\langle 0, y_1, 0 \rangle = \langle 0,0.5s,1-0.5s \rangle$$

The x, y and z components on the left side of the above equation must be equal to the x, y and z components on the right side of the equation. The equation therefore yields the following three relationships:

$$0 = 0$$
$$y_1 = 0.5s$$
$$0 = 1 - 0.5s$$

The last of the above three relationships can be rearranged to solve for s.

$$0.5s = 1$$
$$s = 2$$

Substituting this value of s into the previous relationship for y_1 allows us to solve for y_1:

$$y_1 = 0.5s$$
$$y_1 = 0.5(2)$$
$$y_1 = 1$$

This indicates that the plane under consideration must intersect the y-axis at the point (0,1,0). As a result, the intercept with the y-axis is 1. Note again that this intercept number represents the coefficient of the intercept's position in terms of the unit cell dimensions, rather than the absolute position of the intercept (Van Vlack, 1989). The absolute distance from the new origin to the intercept with the y-axis is therefore equal to 1a. In summary, therefore, the coefficients of the three axial intercepts occur at the points:

$$-1,0,0$$
$$0,1,0$$
$$0,0,1$$

The absolute locations of the three axial intercepts occur at the points:

$$-1a,0,0$$
$$0,1a,0$$
$$0,0,1a$$

In question #3 above, we had defined the Miller indices to be "the reciprocals of the three intercepts that the plane makes with each of the axes, cleared of fractions and common multipliers" (Van Vlack, 1989). This indicates that the Miller Indices of the plane in question are:

(1/-1 1/1 1/1)

$(\overline{1}\ 1\ 1)$

This plane is again displayed in the following sketch:

5). Chain addition polymerization is a highly exothermic process because heat is volumetrically created with the addition of each monomer to the polymer (Polymerization Processes, 2003) - a pi-bond in the monomer converts into a sigma-bond in the polymer – typically resulting in the generation of 8 to 20 kcal/mol (Polymers, 2003). Heat removal normally occurs by transferring heat through the wall of the reactor - which requires at least one dimension of the reactor to be small - or through solvent or gas transport media, or by monomer evaporation and condensation, so the reactor and processes should be very well designed, controlled and monitored (Polymerization Processes, 2003) because explosions and fires can result if process control is lost and if polymerization occurs when not desired (Polymerization, 2002). Additionally, excess heat energy can cause polymers to be converted back into monomers (Polymerization Processes, 2003).

References:

Cross product. 2003. http://www.physics.uoguelph.ca/tutorials/torque/Q.torque.cross.html.

Dot Product. 2003. http://freespace.virgin.net/hugo.elias/routines/r_dot.htm.

Kosek, J. November 22, 1999. Catalytic Polymerization Processes. http://www.vscht.cz/obsah/english/research/appl_research/jkk_polymer.html.

Polymers. 2003. http://www.cem.msu.edu/~reusch/VirtualText/polymers.htm.

Polymerization. July 7, 2002. http://www.ilpi.com/msds/ref/polymer.html.

Polymerization Processes. 2003. http://www.mse.ufl.edu/~cbeat/EMA_3066/Polymerization_Process_A-F.doc.

The Vector Equation of a Plane. 2003. http://members.tripod.com/~Paul_Kirby/vector/Vplane.html.

Van Vlack, L.H. 1989. Elements of Material Science and Engineering, Sixth Edition. Addison-Wesley Publishing Company, Reading, Massachusetts.

Young-Hoo K. 1998. Vector. http://kwon3d.com/theory/vect/vector.html.