
Solids

Answers to worked examples

WE 5.1 Close packing

Is the ABCACABAC structure close packed?

Strategy

Close packing is considered as fitting simple hard spheres together in the spatially most economical way. In this way, one type of layer fits in the depressions created by adjacent layers. Layers of the same type cannot fit together as they would lie directly on top of one another and not fit in the depressions meaning space is wasted.

Solution

The ABACABAC structure is close-packed. Adjacent layers are different so each layer is able to sit in the depressions between the spheres in the layer below.

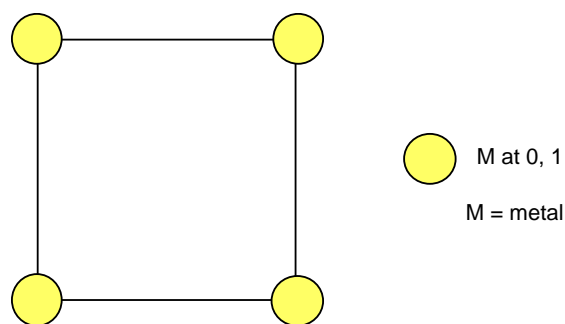
WE 5.3 Cell projection diagrams

Draw a cell projection diagram for the primitive cubic unit cell.

Strategy

Using the unit cell for primitive cubic given in Figure 5.7(c) (p.225), reproduce the unit cell in two dimensions by looking at it from the top (down the z -axis). Work out the z -coordinate for each of the lattice points and show this on your diagram.

Solution



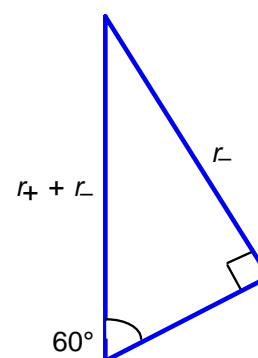
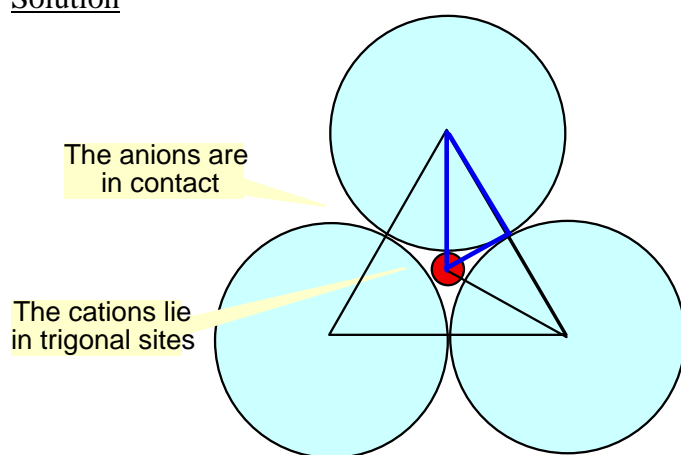
WE 5.5 Limiting radius ratios

What is the limiting radius ratio for the trigonal planar geometry around a positive ion? Comment on its value.

Strategy

Draw out the trigonal planar shape with a small sphere (the cation) at the centre in contact with three larger spheres (the anions) in contact in a triangle. Use trigonometry to relate the distance between the centres of the anions to the distance between the centre of the anion and the cation.

Solution



Close up of the blue triangle, showing the lengths and angle (60° is half of the trigonal planar angle of 120°)

$$\frac{r_+ + r_-}{\sin 90^\circ} = \frac{r_-}{\sin 60^\circ}$$

Since $\sin 90^\circ = 1$, this becomes: $r_+ + r_- = \frac{r_-}{\sin 60^\circ}$

Rearranging to give an expression for r_+

$$r_+ = \frac{r_-}{\sin 60^\circ} - r_-$$

$$= r_- \left(\frac{1}{\sin 60^\circ} - 1 \right)$$

$$\text{Limiting radius ratio} = \frac{r_+}{r_-} = \left(\frac{1}{\sin 60^\circ} - 1 \right) = 0.155$$

The cations need to be very much smaller than the anions to fit into trigonal sites.

WE 5.7 Born–Haber cycles

Use the data in Figure 5.30 (p.251) and those given below to calculate the lattice enthalpy for CaCl_2 .

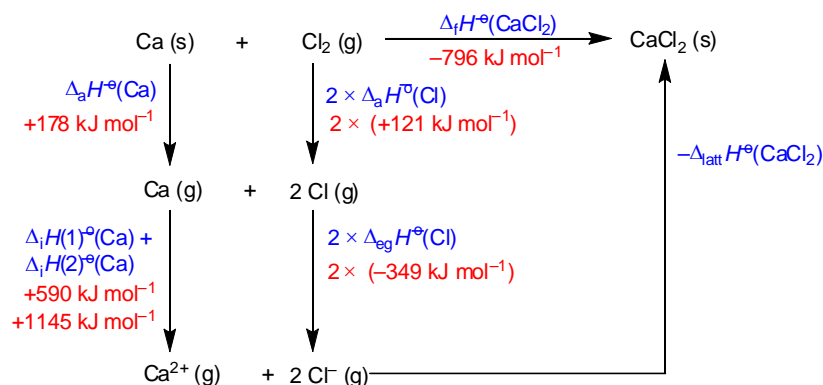


Strategy

Use the data to draw a Born–Haber cycle for the formation of CaCl_2 . Be careful to check the signs of the individual quantities when putting the data into the expressions.

Solution

Born–Haber cycle for the formation of CaCl_2 :



$$\Delta_f H^\circ(\text{CaCl}_2) = \Delta_a H^\circ(\text{Ca}) + \Delta_i H(1)^\circ(\text{Ca}) + \Delta_i H(2)^\circ(\text{Ca}) + 2\Delta_a H^\circ(\text{Cl}) + 2\Delta_{\text{eg}} H^\circ(\text{Cl}) - \Delta_{\text{latt}} H^\circ(\text{CaCl}_2)$$

$$\begin{aligned} \Delta_{\text{latt}} H^\circ(\text{CaCl}_2) &= -\Delta_f H^\circ(\text{CaCl}_2) + \Delta_a H^\circ(\text{Ca}) + \Delta_i H(1)^\circ(\text{Ca}) + \Delta_i H(2)^\circ(\text{Ca}) + 2\Delta_a H^\circ(\text{Cl}) + \\ &\quad 2\Delta_{\text{eg}} H^\circ(\text{Cl}) \\ &= -(-796 \text{ kJ mol}^{-1}) + 178 \text{ kJ mol}^{-1} + 590 \text{ kJ mol}^{-1} + 1145 \text{ kJ mol}^{-1} + (2 \\ &\quad \times 121 \text{ kJ mol}^{-1}) + (2 \times -349 \text{ kJ mol}^{-1}) \\ &= +2253 \text{ kJ mol}^{-1} \end{aligned}$$

WE 5.9 Using the Kapustinskii equation

Use the Kapustinskii equation to estimate the lattice energy for MgO.

Strategy

Use the Kapustinskii equation, Equation 5.10 (p.257). By using the ionic radius data in Tables 5.5 and 5.6 (p.246), an estimate of the lattice energy can be calculated.

Solution

$$\text{Equation 5.10, } \Delta_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$$

$$\begin{aligned} \Delta_{\text{latt}} U &= \frac{(107900 \text{ pm kJ mol}^{-1}) \times 2 \times 2 \times 2}{72 \text{ pm} + 140 \text{ pm}} \\ &= +4070 \text{ kJ mol}^{-1} \end{aligned}$$

Answers to boxes**Box 5.1 Nanotubes and nanotechnology**

The photograph of a nanotube on page 219 was obtained using a form of electron microscopy. Suggest why it is not possible to see nanotubes using a conventional optical microscope.

Strategy

Consider the size of the nanotube in relation to the wavelength of visible light.

Solution

You can only see something if its size is of the same order of magnitude or greater than the wavelength of the light used. The shortest wavelength of visible light has a wavelength of 390 nm, which is over ten times larger than the diameter of a nanotube. Electron microscopy can be used as the wavelength associated with an electron is much smaller (see Section 2.4, p.92).

Box 5.3 CD writers and re-writers

What are the key requirements needed for a material such as the Ag-In-Sb-Te alloy to be used in a CD-RW?

Strategy

What properties are necessary for the material to be able to retain information and how are these data recorded. Note: the terminology 'burning a CD' may give clues to the properties required.

Solution

The material needs to have two phases with different optical properties. The phase formed at high temperature needs to remain unaltered on cooling to room temperature even though it is less stable than the original phase, but must be convertible to this phase on mild heating.

Box 5.5 Self-cleaning windows

Draw a diagram to show how the TiO₂ surface interacts with water molecules

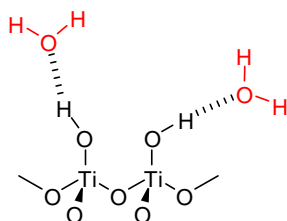
Strategy

Glass is hydrophobic and repels water meaning water streams down normal windows concentrating the dirt in certain channels. This is a contrast to the TiO₂ where the

protonated surface oxides interact with water molecules spreading them evenly over the surface.

Solution

TiO₂ interactions with water:



Answers to end of chapter questions

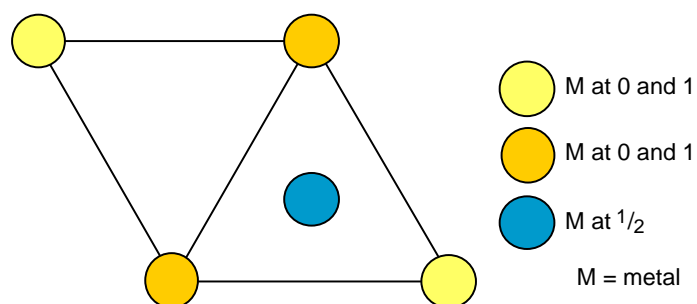
1. Draw the unit cell and a projection diagram for the hexagonal close-packed structure. How many atoms does the unit cell contain? Indicate the positions of the octahedral and tetrahedral sites.

Strategy

Reproduce the unit cell for hcp shown in Figure 5.9(b) (p.226) in two dimensions by looking at it from the top (down the z -axis). Work out the z -coordinate for each of the atoms and show this on your diagram.

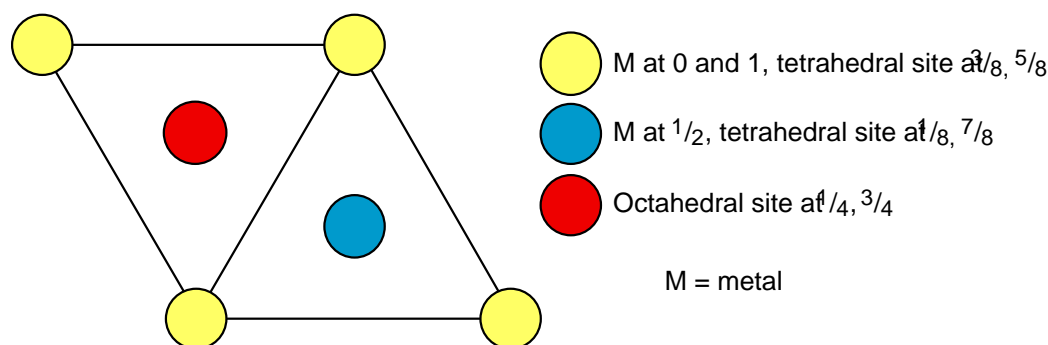
Solution

The hcp unit cell is shown in Figure 5.9(b) and the cell projection diagram is shown below.



The vertex atoms are shared between 8 unit cells, but do not contribute equally to all of them. Those shown in orange in the cell projection diagram contribute $\frac{1}{6}$ to the unit cell, whereas those shown in yellow contribute only $\frac{1}{12}$. The atom in blue is fully within the unit cell. This means there are $(\frac{1}{6} \times 4) + (\frac{1}{12} \times 4) + (1 \times 1) = 2$ atoms in the unit cell.

The positions of the octahedral and tetrahedral sites are shown on the figure below. To work out the z -coordinate for a tetrahedral site you need to take into account the z -coordinates of the four atoms it lies between. So, for a tetrahedral site between three atoms with a z -coordinate of 0 and one with a z -coordinate of $\frac{1}{2}$, the tetrahedral site has a z -coordinate of $\frac{0 + 0 + 0 + \frac{1}{2}}{4} = \frac{1}{8}$.



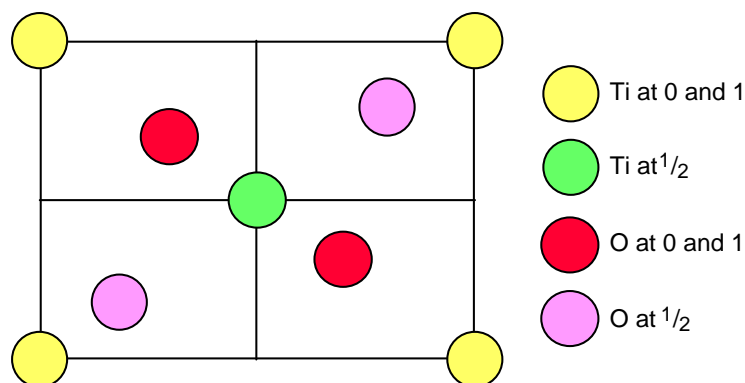
3. Draw the unit cell projection diagram for the rutile structure, shown in Figure 5.26 (p.243).

Strategy

Reproduce the unit cell for rutile in two dimensions by looking at it from the top (down the z -axis). Work out the z -coordinate for each of the atoms and show this on your diagram.

Solution

Cell projection diagram for rutile:



5. Lithium bismuthide (Li_3Bi) adopts a structure based on a cubic close-packed lattice of Bi^{3-} anions with Li^+ cations occupying the octahedral and tetrahedral sites. Draw a cell projection diagram for Li_3Bi .

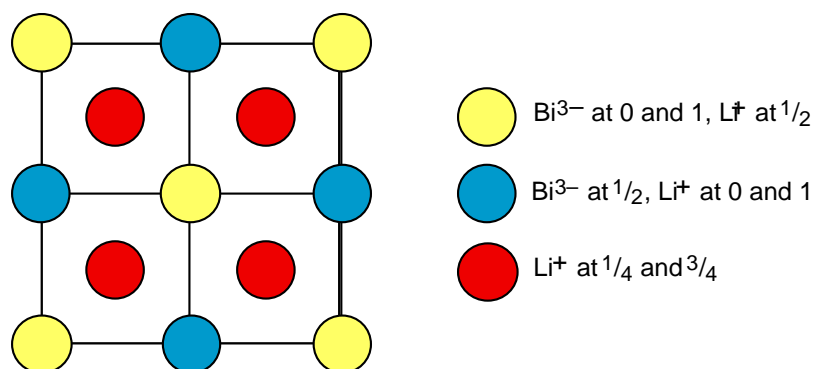
Strategy

Draw a face centred cubic unit cell (Figure 5.7(a) on p.225) of bismuth anions and fill both the tetrahedral and octahedral holes with the lithium cations.

Solution

In the ccp structure, Bi^{3-} ions are present on the vertices (the yellow spheres on the corners at coordinates 0 and 1) and the centres of the faces (the yellow sphere in the centre at coordinates 0 and 1 and the blue spheres at coordinate $\frac{1}{2}$). Li^+ ions occupy the octahedral sites (the yellow spheres on the corners and the centre at coordinate $\frac{1}{2}$ and the blue spheres at coordinates 0 and 1). Li^+ ions also occupy the tetrahedral sites (the red spheres at coordinates $\frac{1}{4}$ and $\frac{3}{4}$).

Cell projection diagram for Li_3Bi :



7. Construct a Born–Haber cycle for the formation of $\text{MgO}(\text{s})$ from its elements in their standard states and use the information given to calculate the lattice enthalpy of MgO .

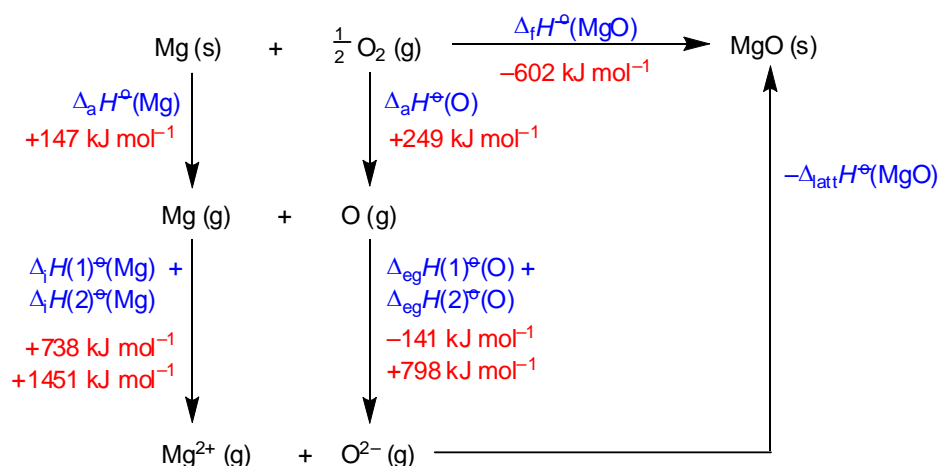
$\Delta_f H^\circ(\text{MgO})$	-602 kJ mol^{-1}
$\Delta_i H(1)^\circ(\text{Mg})$	$+738 \text{ kJ mol}^{-1}$
$\Delta_i H(2)^\circ(\text{Mg})$	$+1451 \text{ kJ mol}^{-1}$
$\Delta_a H^\circ(\text{Mg})$	$+147 \text{ kJ mol}^{-1}$
$\Delta_a H^\circ(\text{O})$	$+249 \text{ kJ mol}^{-1}$
$\Delta_{\text{cg}} H(1)^\circ(\text{O})$	-141 kJ mol^{-1}
$\Delta_{\text{cg}} H(2)^\circ(\text{O})$	$+798 \text{ kJ mol}^{-1}$

Strategy

Use the data to construct a Born–Haber cycle being careful to use only half a mole of O_2 in the cycle as MgO only contains one oxide ion. Use these data to calculate the lattice enthalpy.

Solution

Born-Haber cycle for MgO :



$$\Delta_f H^\ominus(\text{MgO}) = \Delta_a H^\ominus(\text{Mg}) + \Delta_i H(1)^\ominus(\text{Mg}) + \Delta_i H(2)^\ominus(\text{Mg}) + \Delta_a H^\ominus(\text{O}) + \Delta_{\text{eg}} H(1)^\ominus(\text{O}) + \Delta_{\text{eg}} H(2)^\ominus(\text{O}) - \Delta_{\text{latt}} H^\ominus(\text{MgO})$$

$$\begin{aligned} \Delta_{\text{latt}} H^\ominus(\text{MgO}) &= -\Delta_f H^\ominus(\text{MgO}) + \Delta_a H^\ominus(\text{Mg}) + \Delta_i H(1)^\ominus(\text{Mg}) + \Delta_i H(2)^\ominus(\text{Mg}) + \Delta_a H^\ominus(\text{O}) + \\ &\quad \Delta_{\text{eg}} H(1)^\ominus(\text{O}) + \Delta_{\text{eg}} H(2)^\ominus(\text{O}) \\ &= -(-602 \text{ kJ mol}^{-1}) + 147 \text{ kJ mol}^{-1} + 738 \text{ kJ mol}^{-1} + 1451 \text{ kJ mol}^{-1} + \\ &\quad 249 \text{ kJ mol}^{-1} + (-141 \text{ kJ mol}^{-1}) + 798 \text{ kJ mol}^{-1} \\ &= +3844 \text{ kJ mol}^{-1} \end{aligned}$$

9. Use the Kapustinskii equation and the data in Tables 5.5 and 5.6 (p.246) to estimate the lattice energies for KF, KCl and KBr. Suggest a reason for the trend you observe.

Strategy

Use the Kapustinskii equation (Equation 5.10 on p.257) to calculate the lattice energies for the three potassium halides and look for a reason for the trend in the values. For example, consider the effect of increasing number of electrons on the ionic character of the halide.

Solution

Equation 5.10, $\Delta_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$

$$\text{For KF, } \Delta_{\text{latt}}U = \frac{(107900 \text{ pm kJ mol}^{-1}) \times 2 \times 1 \times 1}{138 \text{ pm} + 133 \text{ pm}} = +796 \text{ kJ mol}^{-1}$$

$$\text{For KCl, } \Delta_{\text{latt}}U = \frac{(107900 \text{ pm kJ mol}^{-1}) \times 2 \times 1 \times 1}{138 \text{ pm} + 181 \text{ pm}} = +676 \text{ kJ mol}^{-1}$$

$$\text{For KBr, } \Delta_{\text{latt}}U = \frac{(107900 \text{ pm kJ mol}^{-1}) \times 2 \times 1 \times 1}{138 \text{ pm} + 196 \text{ pm}} = +646 \text{ kJ mol}^{-1}$$

As the anions get larger, the ionic separation increases, electrostatic attraction decreases and the lattice energy decreases.

- 11.** Predict the type of bonding in KF and PbI₂ using the bond type triangle in Figure 5.31 (p.258).

Strategy

The ionic character of a bond is controlled by the difference in electronegativity of the elements involved. The greater the difference, the more likely it is to be ionic in character. Elements which are considered soft acid and bases (see Chapter 6 on p.263) have more covalency in their bonding, e.g heavy elements or those with poorly screened charges (*d* and *f* elements).

Solution

Electronegativities are given in Figure 3.6 (p138). $\chi(\text{K}) = 0.82$ and $\chi(\text{F}) = 3.98$, so for KF $\bar{\chi} = 2.40$ and $\Delta\chi = 3.16$. This is close to the ionic corner of the triangle. $\chi(\text{Pb}) = 1.8$ and $\chi(\text{I}) = 2.66$, so for PbI₂ $\bar{\chi} = 2.23$ and $\Delta\chi = 0.86$. This suggests PbI₂ has considerable covalent character which is not surprising considering the low oxidation state and size of the species involved.

