
Solids

Answers to worked examples

WE 6.1 Close packing (on p. 263 in *Chemistry*³)

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 6.2 Packing efficiency (on p. 267 in *Chemistry*³)

Show that the packing efficiency of the primitive cubic structure in Figure 6.7(c) (p.265) is 52.4%.

Strategy

Firstly, calculate the number of lattice points in the unit cell based on lattice point sharing where an atom on the corner contributes $\frac{1}{8}$ to the unit cell. Then calculate the volume occupied by this number of atoms considering the atom as a hard sphere

where $\text{volume} = \frac{4}{3}\pi r^3$.

Secondly, find the total volume of the unit cell in terms of the unit cell length. If need be, use Pythagoras's theorem to determine the unit cell length in terms of the radius of the sphere.

Finally, use Equation 6.1 to calculate the packing efficiency (amount of space filled).

Solution

The eight lattice points of a primitive cubic unit cell shown in Figure 6.7(c) are all on corners and shared between eight unit cells. These lattice points all contribute $\frac{1}{8}$ to each cell, so there are $(8 \times \frac{1}{8}) = 1$ lattice points in the unit cell. The total volume of the lattice points in the unit cell is $\frac{4}{3}\rho r^3$.

In a primitive cubic unit cell, the lattice points are in contact with each other along the cell unit edge, which means that the unit cell length, l , is $2r$.

The total volume of the unit cell is l^3 , so:

$$\begin{aligned} l^3 &= (2r)^3 \\ &= 8r^3 \end{aligned}$$

Putting the expressions for the volume of the lattice points and the total volume of the unit cell into Equation 6.1 (p.265) gives:

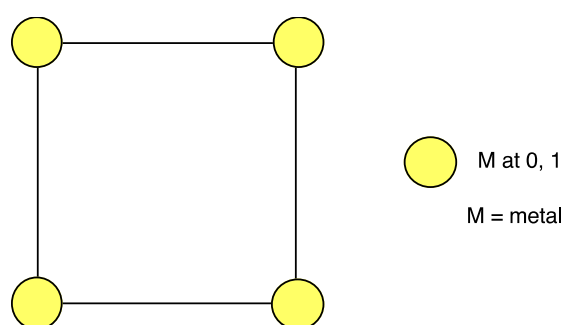
$$\begin{aligned} \text{packing efficiency} &= \frac{\frac{4}{3}\rho r^3}{8r^3} \times 100 \\ &= \frac{\frac{4}{3}\rho}{8} \times 100 \\ &= 52.4\% \end{aligned}$$

WE 6.3 Cell projection diagrams (on p. 270 in *Chemistry*³)

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

Strategy

Using the unit cell for primitive cubic given in Figure 6.7(c) (p.265), 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 6.4 Unit cells and formulae (on p. 285 in *Chemistry*³)**

The unit cell below is for an oxide of rhenium, with the rhenium atoms in green and the oxygen atoms in red. What is the formula of this compound?

Strategy

The formula of any unit cell can be calculated by using the theory of lattice point sharing and producing a formula based on the number of atoms/ions in the unit cell. A lattice point on a corner contributes $\frac{1}{8}$ and on an edge it contributes $\frac{1}{4}$.

Solution

In this unit cell, there are rhenium ions on the corners and oxide ions on each edge. The unit cell consists of a primitive cubic lattice of Re ions with oxide ions on all of the edges. A lattice point on a corner contributes $\frac{1}{8}$ and on an edge it contributes $\frac{1}{4}$.

Atom type	Number of ions in the unit cell	Share of the ion belonging to the unit cell	Total number of ions contributing to the unit cell	Number of ions in the formula
Re	8	$\frac{1}{8}$	$8 \times \frac{1}{8}$	1
O	12	$\frac{1}{4}$	$12 \times \frac{1}{4}$	3

The formula of the compound is therefore ReO_3 .

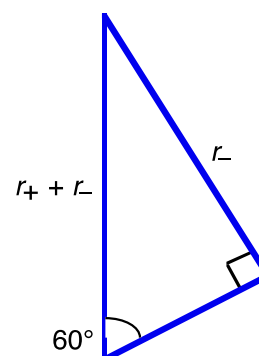
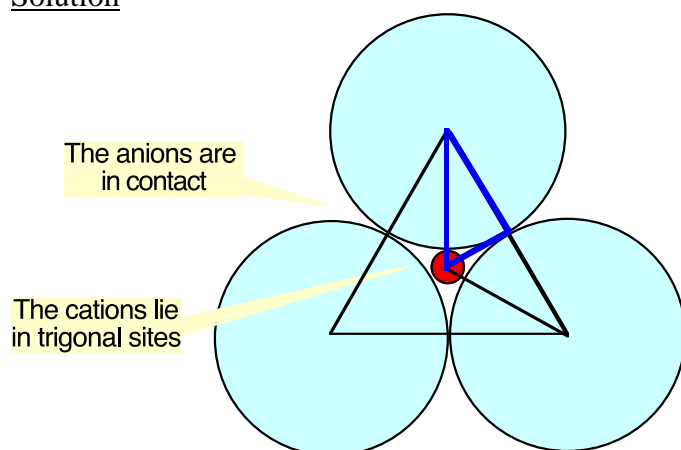
WE 6.5 Limiting radius ratios (on p. 289 in *Chemistry*³)

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 angles (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 6.6 The radius ratio rule (on p. 290 in *Chemistry*³)

Magnesium oxide, MgO, adopts the sodium chloride structure. Does MgO obey the radius ratio rule?

Strategy

Work out r_+/r_- for MgO using the data in Tables 6.4 and 6.5 (p.286). Use Table 6.6 (p.289) to determine what geometry the radius ratio predicts.

Solution

$$\frac{r_+}{r_-} = \frac{r(\text{Mg}^{2+})}{r(\text{O}^{2-})} = \frac{72 \text{ pm}}{140 \text{ pm}} = 0.51$$

This is within the range expected for 6-coordination and octahedral geometry. MgO obeys the radius ratio rule.

WE 6.7 Born–Haber cycles (on p. 292 in *Chemistry*³)

Use the data in Figure 6.32 (p.291) and those given below to calculate the lattice enthalpy for CaCl₂.

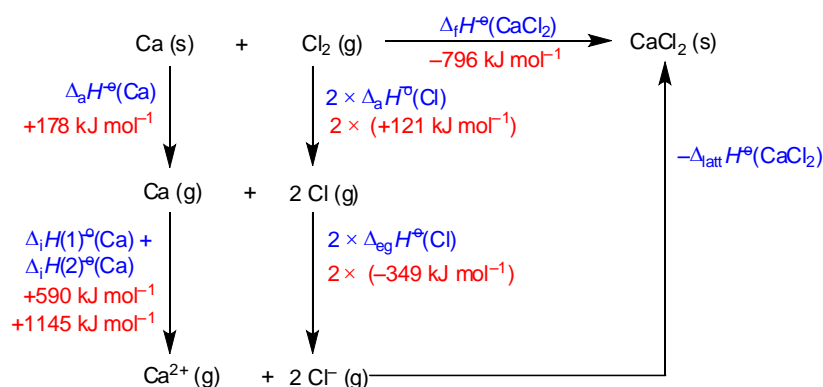
$\Delta_f H^\ominus(\text{CaCl}_2)$	-796 kJ mol^{-1}	$\Delta_i H(1)^\ominus(\text{Ca})$	$+590 \text{ kJ mol}^{-1}$
$\Delta_a H^\ominus(\text{Ca})$	$+178 \text{ kJ mol}^{-1}$	$\Delta_i H(2)^\ominus(\text{Ca})$	$+1145 \text{ kJ mol}^{-1}$

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 6.8 Using the Born–Landé equation (on p. 296 in *Chemistry*³)

Calculate the lattice energy for CsCl given that the closest Cs-Cl distance is 348.1 pm.

Strategy

Use the Born–Landé equation, Equation 6.9 (p.292). Determine the average Born exponent, n , for CsCl from the values for the two ions given in Table 6.8 (p.292). Look up the value of the Madelung constant, A , for CsCl in Table 6.7 (p.292).

Solution

$$\text{Equation 6.10, } D_{\text{latt}} U = \frac{AN_{\text{A}} z_+ z_- e^2}{4\pi\epsilon_0 r} \left(1 - \frac{1}{n} \right)$$

From Table 6.7, A for the CsCl structure = 1.7627.

$n = 12$ for Cs^+ , $n = 9$ for Cl^- , so the average value of $n = 10.5$.

Putting these values into Equation 6.10:

$$\begin{aligned} D_{\text{latt}}U &= \frac{(1.7627) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (1) \times (1) \times (1.602 \times 10^{-19} \text{ C})^2}{4 \times \pi \times (8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}) \times (348.1 \times 10^{-12} \text{ m})} \times \left(1 - \frac{1}{10.5}\right) \\ &= +6.364 \times 10^5 \text{ J mol}^{-1} \\ &= +636.4 \text{ kJ mol}^{-1} \end{aligned}$$

WE 6.9 Using the Kapustinskii equation (on p. 297 in *Chemistry*³)

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

Strategy

Use the Kapustinskii equation, Equation 6.11 (p.297). By using the ionic radius data in Tables 6.4 and 6.5 (p.286), an estimate of the lattice energy can be calculated.

Solution

$$\begin{aligned} \text{Equation 6.11, } D_{\text{latt}}U &= \frac{kvz_+z_-}{r_+ + r_-} \\ D_{\text{latt}}U &= \frac{(107900 \text{ pm kJ mol}^{-1}) \times 2 \times 2 \times 2}{72 \text{ pm} + 140 \text{ pm}} \\ &= +4070 \text{ kJ mol}^{-1} \end{aligned}$$

Answers to boxes

Box 6.1 Nanotubes and nanotechnology (on p. 258 in *Chemistry*³)

The photograph of a nanotube on page 259 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 3.4, p.132).

Box 6.2 Superconductors (on p. 261 in *Chemistry*³)

A major goal of superconductor research is to prepare a material that is superconducting at room temperature. Why would such a materials be important?

Strategy

Consider the effect of resistance on transmitting current using a normal conductor. Relate the energy lost via resistance of a conductor to the energy required to cool a superconductor below the superconducting temperature.

Solution

Such a material would eliminate the need for liquid helium or liquid nitrogen coolants, which are expensive and difficult to handle. The material could, in theory, be used to transmit electricity with no loss of energy.

Box 6.3 CD writers and re-writers (on p. 275 in *Chemistry*³)

Detailed studies on heat-treated samples of Ag–In–Sb–Te alloys suggest several phases are formed, including one that can be described as a face-centred cubic arrangement of tellurium with a 1:1 mixture of silver and antimony occupying the octahedral sites. What is the formula of this phase?

Strategy

Firstly, you need to recognise that the face-centred cubic is the same as cubic close packed. Look at the number of octahedral sites in a ccp structure and see how this relates to the number of atoms.

Solution

A unit cell of the cubic close-packed structure contains four atoms of tellurium and four octahedral sites. Given that silver and antimony both occupy half of the octahedral sites, there are two silver atoms and two antimony atoms for every four tellurium atoms. The formula is therefore AgSbTe_2 .

Box 6.5 Self-cleaning windows (on p. 283 in *Chemistry*³)

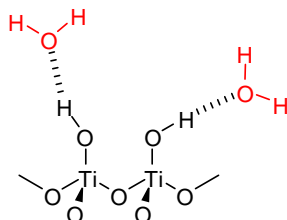
Draw a diagram to show how the TiO_2 surface interacts with water molecules

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 TiO_2 where the protonated surface oxides interact with water molecules spreading them evenly over the surface.

Solution

TiO_2 interactions with water:

**Box 6.6 Determining the Madelung constant (on p. 294 in *Chemistry*³)**

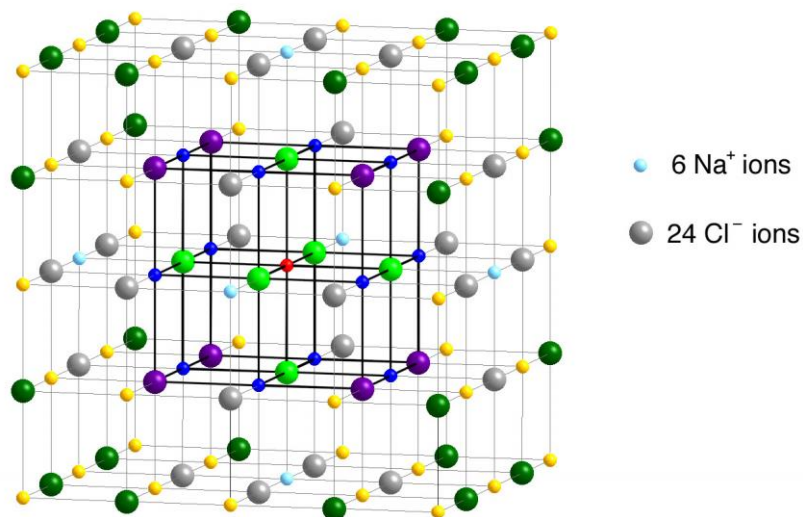
Draw a fragment of the NaCl structure in which a unit cell is extended out from the centre, and use this to identify the next set of closest ions to the central Na^+ ion. Calculate the fourth term in the Madelung constant for NaCl .

Strategy

Extend the diagram shown in Box 6.6 outwards to include the neighbouring unit cells. Determine which of the ions are the fourth closest to the central sodium cation, then use Equation 6.5 (p.293), to calculate the interactions between these ions and the central Na^+ ion.

Solution

The figure below shows the structure of NaCl with the fourth nearest ions shown in pale blue.



The next nearest neighbours to the central Na^+ ion are the Na^+ ions in the centres of the adjacent unit cells. There are six of these and each lies a distance of $2r$ from the central ion. The interaction energy between the central ion and these ions is given by

$$DU_4 = 6 \times \frac{+(1 \times 1)e^2}{4\pi\epsilon_0(2)r} = \frac{6}{2} \times \frac{e^2}{4\pi\epsilon_0 r}$$

Answers to end of chapter questions

1. From the properties in the table below, describe whether each of the elements shown exists as a molecular structure, covalent network structure or a metal.

	T_m / K	T_b / K	Conductivity
Boron	2348	4270	Insulator
Phosphorus (white)	317	554	Insulator
Lead	601	2022	Conductor

Strategy

Look at Table 6.1, which describes the general properties of substances with different types of bonding, and use the information to decide on the types of bonding present in the three elements.

Solution

Boron has a high melting point and boiling point and is an insulator. It has a covalent network structure.

White phosphorus has a low melting point and boiling point and is an insulator. It has a molecular structure.

Lead has a relatively high melting point and boiling point and is a conductor. It is a metal.

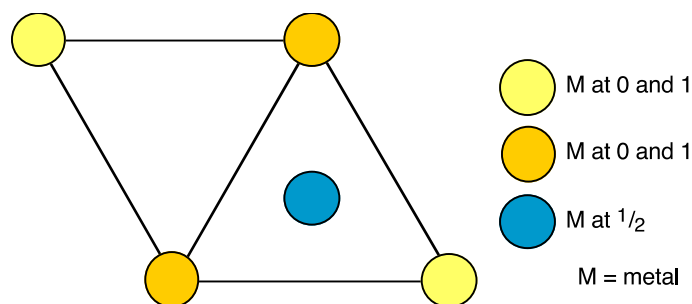
2. Draw the unit cell and a projection diagram for the hexagonal close-packed structure. How many atoms does the unit cell contain? Indicate the positions of the octahedral and tetrahedral sites.

Strategy

Reproduce the unit cell for hcp shown in Figure 6.9(b) (p.266) 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.

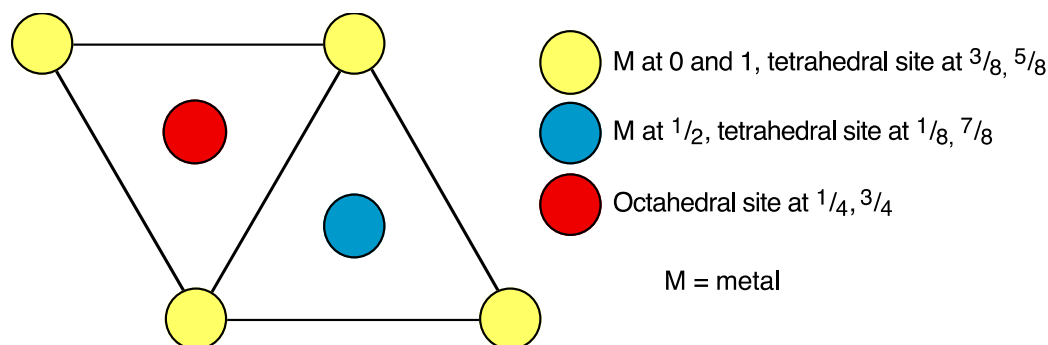
Solution

The hcp unit cell is shown in Figure 6.9(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 $\frac{0 + 0 + 0 + \frac{1}{2}}{4} = \frac{1}{8}$.



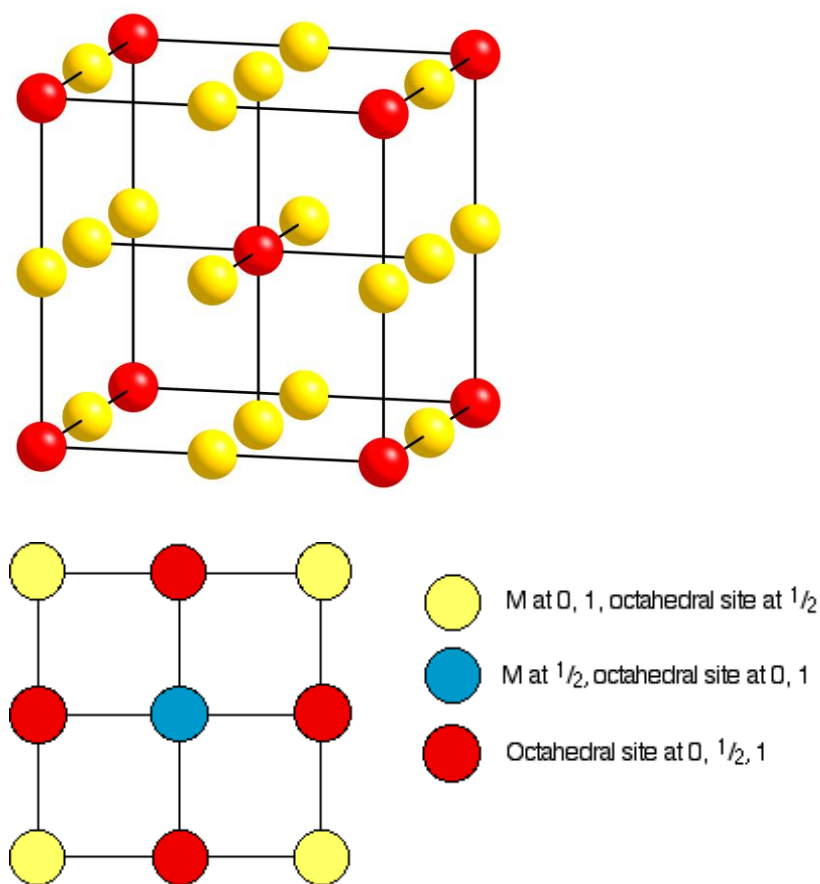
3. The body-centred cubic structure contains octahedral interstitial sites. Draw the unit cell and a cell projection diagram and mark the position of these, verifying the total number of octahedral sites per unit cell is six.

Strategy

The body-centred cubic structure is shown in Figure 6.7(b) (p.265), and the cell projection diagram is shown in Worked example 6.3 (p.270). Octahedral sites are the interstitial sites for which there are six nearest neighbours. When counting the total number of octahedral sites, remember that those on faces contribute $\frac{1}{2}$ to the unit cell, those on the edges contribute $\frac{1}{4}$ and those on vertices contribute $\frac{1}{8}$.

Solution

All of the faces and edges of the unit cell are octahedral sites, and these are shown on the unit cell and cell projection diagram below.



In the unit cell there are $[1 + (\frac{1}{8} \times 8)] = 2$ atoms. There are six faces, each contributing $\frac{1}{2}$ octahedral site, plus 12 edges, each contributing $\frac{1}{4}$ octahedral site.

The total number of octahedral sites is $(6 \times \frac{1}{2}) + (12 \times \frac{1}{4}) = 6$.

4. Nickel adopts the cubic close-packed structure. By considering the contents and the volume of the unit cell, use the data below to estimate the density of nickel (g cm^{-3}).

$$A_r(\text{Ni}) = 58.693, \text{ atomic radius of Ni } 125 \text{ pm.}$$

Strategy

Density is defined as mass per unit volume. If you know the mass and the volume of the unit cell, you can calculate the density of a material. To calculate the mass of the unit cell in grams, you need to know how many nickel atoms are contained in it, multiply this by the relative atomic mass of nickel then divide by the Avogadro constant. To calculate the volume of the unit cell you need to calculate the unit cell length from the atomic radius, then cube this. To calculate the density, divide mass by volume, being careful to ensure the answer is in the correct units.

Solution

In the cubic close-packed structure of nickel there are four atoms in the unit cell. The mass of the unit cell is therefore equal to:

$$\frac{58.693 \text{ g mol}^{-1} \times 4}{6.022 \times 10^{23} \text{ mol}^{-1}} = 3.899 \times 10^{-22} \text{ g}$$

The length of the unit cell can be found using Pythagoras' theorem (see p.267), since

$$\begin{aligned} 2l^2 &= (4r)^2 \\ &= 16r^2 \end{aligned}$$

Rearranging gives $l^2 = 8r^2$, so $l = 8^{1/2}r$

Since the volume of the unit cell is equal to l^3 ,

$$\begin{aligned} \text{volume} &= (8^{1/2}r)^3 = 8^{3/2}r^3 \\ &= 8^{3/2} \times (125 \times 10^{-12} \text{ m})^3 \\ &= 4.419 \times 10^{-29} \text{ m}^3 \end{aligned}$$

Density = mass / volume

$$\begin{aligned} &= (3.899 \times 10^{-22} \text{ g}) / (4.419 \times 10^{-29} \text{ m}^3) \\ &= 8.82 \times 10^6 \text{ g m}^{-3} \\ &= 8.82 \text{ g cm}^{-3} \end{aligned}$$

5. The UK £1 coin is made from a nickel-brass alloy, containing 70% copper, 5.5% nickel and 24.5% zinc. Is this likely to be a substitutional alloy or an interstitial alloy?

Strategy

The type of alloy formed depends on the relative sizes of the atoms. If the atoms are markedly different in size, it is possible for the smaller atom to fit on smaller sites within the lattice not normally occupied by the lattice points called interstitial sites. If the two atoms are similar in size, the atom is likely to substitute on a normal lattice point.

Solution

Copper, nickel and zinc have similar atomic radii, so the material is a substitutional alloy.

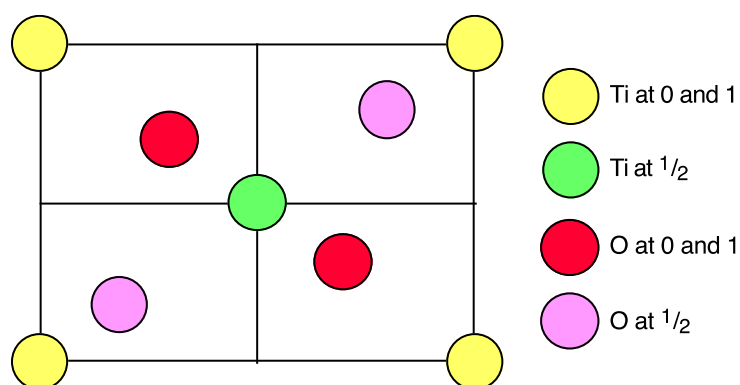
6. Draw the unit cell projection diagram for the rutile structure, shown in Figure 6.26 (p.283).

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:



7. The unit cell for an oxide of copper is shown on page 301. Use the figure to determine the formula of this compound. Draw a cell projection diagram and describe the structure in terms of filling interstitial sites.

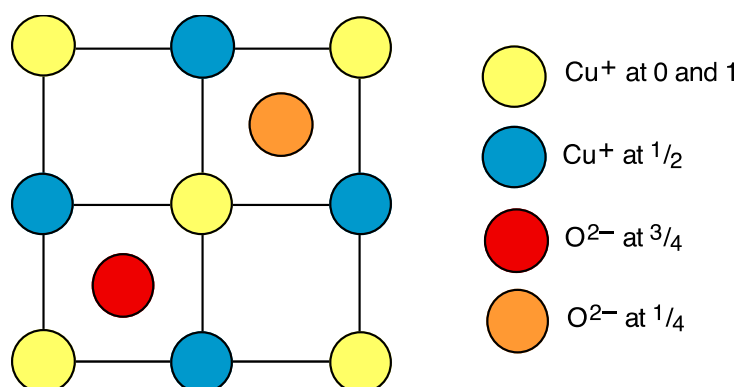
Strategy

Examine the positions of the lattice points and how these points are shared between adjacent unit cells. Investigate the type of hole being filled by determining the coordination number of the lattice point.

Solution

The blue copper cations are forming a face-centred cubic array. The oxide anions are placed on two of the eight tetrahedral holes as far away from each other as possible (to minimize like ion repulsion). From the face-centred cubic lattice, there are 8 ions on the vertices, each contributing $\frac{1}{8}$ to the unit cell, and 6 ions on the faces, each contributing $\frac{1}{2}$ to the unit cell, so the number of copper ions is $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$. The two oxygen anions are fully inside the unit cell. The stoichiometry is therefore 4:2, so the formula is Cu_2O .

Cell projection diagram for Cu_2O :



8. 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 .

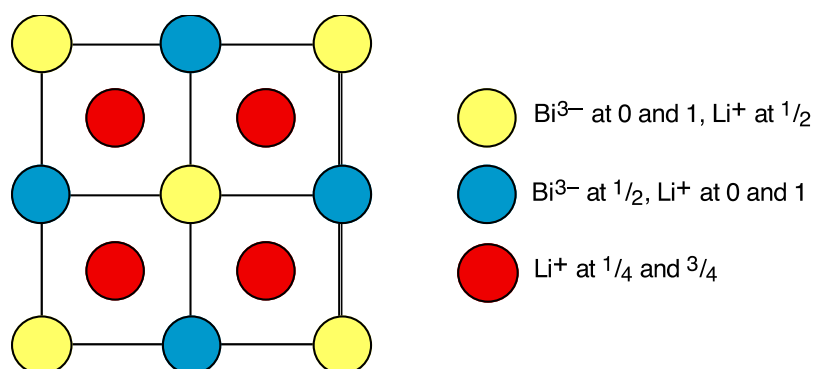
Strategy

Draw a face centred cubic unit cell (Figure 6.7(a) on p.265) 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 :



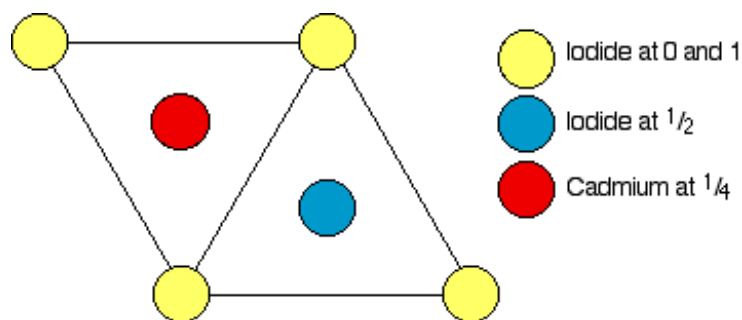
9. Cadmium iodide forms the structure shown in Figure 6.24 (p.281), in which the iodide ions are hexagonally close packed and the Cd^{2+} ions occupy half the octahedral sites. Draw a cell projection diagram for cadmium iodide.

Strategy

Reproduce the unit cell for CdI_2 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 CdI_2 :



10. A mixed oxidation state oxide of iron has a structure based on a cubic close-packed arrangement of oxide ions with Fe^{2+} ions in one-eighth of the tetrahedral sites and Fe^{3+} ions in half of the octahedral sites. What is the formula of the compound?

Strategy

Work out the number of oxide ions in the cubic close-packed unit cell. Determine the total number of octahedral and tetrahedral sites, and use the fractions given in the question to work out how many Fe^{2+} and Fe^{3+} ions are present.

Solution

The cubic close-packed structure has four oxide ions in the unit cell, along with four octahedral sites and eight tetrahedral sites. One-eighth of the tetrahedral sites contain Fe^{2+} , meaning $\frac{1}{8} \times 8 = 1 \text{ Fe}^{2+}$ ion per unit cell. Half of the octahedral sites contain Fe^{3+} meaning $\frac{1}{2} \times 4 = 2 \text{ Fe}^{3+}$ ions per unit cell. The overall formula is therefore $(\text{Fe}^{\text{II}})(\text{Fe}^{\text{III}})_2\text{O}_4$, or more simply Fe_3O_4 .

11. Molybdenum sulfide, MoS_2 , has a structure containing hexagonal layers of sulfide ions in a AABBAABB arrangement with molybdenum ions occupying interstitial sites between layers of the same type (*i.e.* AA or BB), as shown on page 301.
- Is the structure of MoS_2 based on close packing?
 - What are the coordination numbers and coordination geometries of the cations and anions?
 - Suggest a reason why MoS_2 can be used as a solid lubricant.

Strategy

Examine the structure of MoS₂ on page 301, recognising that the molybdenum atoms are shown in brown and the sulfur atoms are shown in yellow.

Solution

- (a) The structure contains sulfur atoms that are lying directly above other sulfur atoms. This means that the structure cannot be close packed.
- (b) From the figure, each sulfur atom has three nearest neighbours, so it has a coordination number of 3. It is in a trigonal pyramidal geometry. Each molybdenum atom has six nearest neighbours, so it has a coordination number of 6. It is in a trigonal prismatic geometry.
- (c) There are only weak interactions between the A and B layers, so it is easy for the layers to slip against each other along these planes.

12. Do the following compounds obey the radius ratio rule? The observed structure is given in square brackets:

- (a) copper(I) chloride [sphalerite structure]
 (b) thallium(I) chloride [caesium chloride structure]
 (c) caesium iodide [caesium chloride structure]
 (d) potassium fluoride [sodium chloride structure]
 (e) zinc sulfide [sphalerite structure]

Strategy

Work out r_+/r_- for each compound using the data in Tables 6.4 and 6.5 (p.286). Use the radius ratio rule predictions in Table 6.6 (p.289) to investigate whether these compounds obey the radius ratio rule.

Solution

	r_+/r_-	Radius ratio rule prediction	Observed structure	Rule succeeds or fails?
(a)	$77 \text{ pm} / 181 \text{ pm} = 0.43$	6-coordination (octahedral geometry)	Zinc blende structure. Both ions have tetrahedral geometry.	Fails (but close to borderline).

(b)	150 pm / 181 pm = 0.83	8-coordination (cubic geometry)	CsCl structure. Both ions have cubic geometry.	Succeeds
(c)	167 pm / 220 pm = 0.76	8-coordination (cubic geometry)	CsCl structure. Both ions have cubic geometry.	Succeeds
(d)	138 pm / 133 pm = 1.04	12-coordination (cuboctahedral geometry).	NaCl structure. Both ions have octahedral geometry.	Fails.
(e)	74 pm / 184 pm = 0.40	4-coordination (tetrahedral geometry)	Sphalerite structure. Both ions have tetrahedral geometry.	Succeeds

12. Construct a Born–Haber cycle for the formation of MgO(s) from Mg(s) and O₂(g) and use the information below to calculate the lattice enthalpy of MgO.

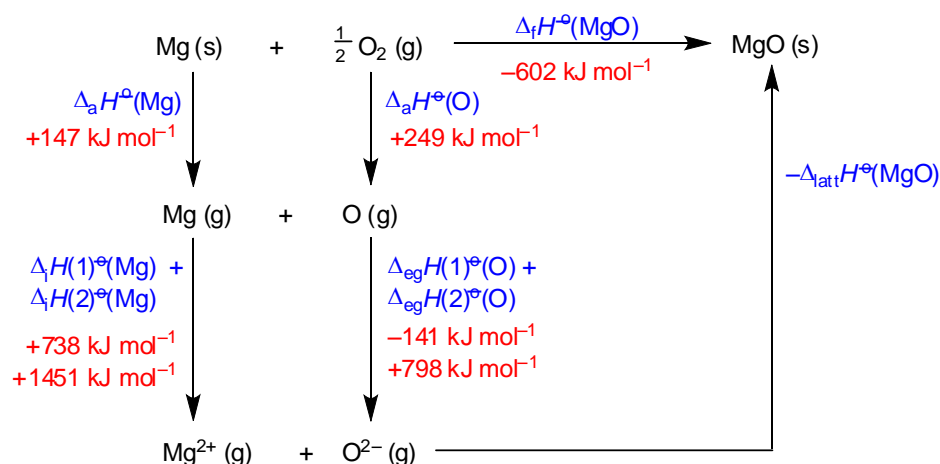
$\Delta_f H^\ominus(\text{MgO})$	-602 kJ mol^{-1}
$\Delta_i H(1)^\ominus(\text{Mg})$	$+738 \text{ kJ mol}^{-1}$
$\Delta_i H(2)^\ominus(\text{Mg})$	$+1451 \text{ kJ mol}^{-1}$
$\Delta_a H^\ominus(\text{Mg})$	$+147 \text{ kJ mol}^{-1}$
$\Delta_a H^\ominus(\text{O})$	$+249 \text{ kJ mol}^{-1}$
$\Delta_{\text{eg}}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

Strategy

Use the data to construct a Born–Haber cycle being careful to use only half a mole of O₂ in the cycle as MgO only contains one oxide ion. Use these data to calculate the lattice enthalpy.

Solution

Born-Haber cycle for MgO:



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

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

- 14.** Use the Born–Landé equation to calculate the lattice energy of KF, which adopts the sodium chloride structure with a K–F distance of 268.4 pm.

Strategy

Use the Born–Landé equation (Equation 6.10 on p.295), with the Madelung constant for NaCl (see Table 6.7 on p.294) to calculate the lattice energy. Be careful to convert the K–F distance into metres before using the equation.

Solution

$$\text{Equation 6.10, } D_{\text{latt}} U = \frac{AN_A z_+ z_- e^2}{4\pi\epsilon_0 r} \left(1 - \frac{1}{n}\right)$$

For the NaCl structure $A = 1.7476$ (Table 6.7). The Born exponent, n , for K^+ is 9, whereas that for F^- is 7 (Table 6.8) so the average value of n is 8.

Substituting into Equation 6.10,

$$D_{\text{latt}}U = \frac{(1.7476) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (1) \times (1) \times (1.6022 \times 10^{-19} \text{ C})^2 \left(1 - \frac{1}{8}\right)}{4 \times \rho \times (8.8542 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}) \times (268.4 \times 10^{-12} \text{ m})}$$

$$= +7.916 \times 10^5 \text{ J mol}^{-1}$$

$$= +791.6 \text{ kJ mol}^{-1}$$

- 15.** Use the Kapustinskii equation and the data in Tables 6.4 and 6.5 (p.286) to estimate the lattice energies for KF, KCl and KBr. Suggest a reason for the trend you observe.

Strategy

Use the Kapustinskii equation (Equation 6.11 on p.297) 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 6.11, $D_{\text{latt}}U = \frac{kvz_+z_-}{r_+ + r_-}$

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

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

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

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

- 16.** Use the Kapustinskii equation and the data in Tables 6.4, 6.5 (p.286) and 6.9 (p.297) to estimate the lattice energies for CaCl₂ and CaSO₄.

Strategy

Using the Kapustinskii equation, Equation 6.11, to calculate the lattice energies

Solution

$$\text{Equation 6.11, } D_{\text{latt}}U = \frac{kvz_+z_-}{r_+ + r_-}$$

$$\text{For CaCl}_2, D_{\text{latt}}U = \frac{(107900 \text{ pm kJ mol}^{-1}) \times 3 \times 2 \times 1}{100 \text{ pm} + 181 \text{ pm}} = +2300 \text{ kJ mol}^{-1}$$

$$\text{For CaSO}_4, D_{\text{latt}}U = \frac{(107900 \text{ pm kJ mol}^{-1}) \times 2 \times 2 \times 2}{100 \text{ pm} + 230 \text{ pm}} = +2620 \text{ kJ mol}^{-1}$$

17. Use the data below to construct Born-Haber cycles for lithium chloride and silver chloride, and from those work out the lattice enthalpies for both compounds. Use the ionic radii for Li^+ , Ag^+ and Cl^- given in Tables 6.4 and 6.5 (p. 286) to estimate the lattice energies for lithium chloride and silver chloride using the Kapustinskii equation. Compare the values you have obtained from these two approaches, and comment on the differences between them.

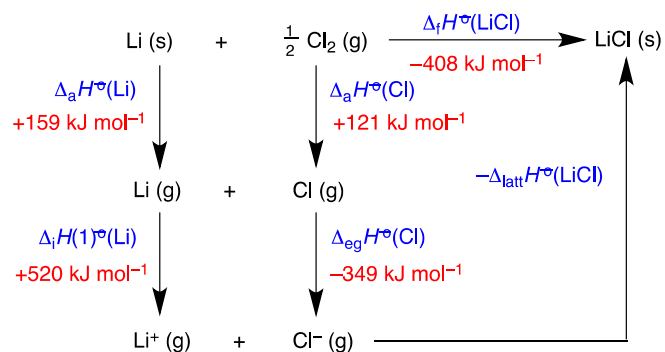
$$\begin{aligned} \Delta H_{\text{a}}^{\circ}(\text{Li}) \ 159 \text{ kJ mol}^{-1}, \Delta H_{\text{a}}^{\circ}(\text{Ag}) \ 285 \text{ kJ mol}^{-1}, \Delta H_{\text{a}}^{\circ}(\text{Cl}) \ 121 \text{ kJ mol}^{-1} \\ \Delta H_{\text{i}(1)}^{\circ}(\text{Li}) \ 520 \text{ kJ mol}^{-1}, \Delta H_{\text{i}(1)}^{\circ}(\text{Ag}) \ 731 \text{ kJ mol}^{-1}, \Delta H_{\text{eg}(1)}^{\circ}(\text{Cl}) \ -349 \text{ kJ mol}^{-1} \\ \Delta H_{\text{f}}^{\circ}(\text{LiCl}) \ -408 \text{ kJ mol}^{-1}, \Delta H_{\text{f}}^{\circ}(\text{AgCl}) \ -127 \text{ kJ mol}^{-1} \end{aligned}$$

Strategy

Use the data to construct Born-Haber cycles for LiCl and AgCl, and use these to calculate the lattice enthalpies. Use the Kapustinskii equation (Equation 6.11) to calculate lattice energies. Comment on how close the two values for each compound are.

Solution

For LiCl, using a Born-Haber cycle:

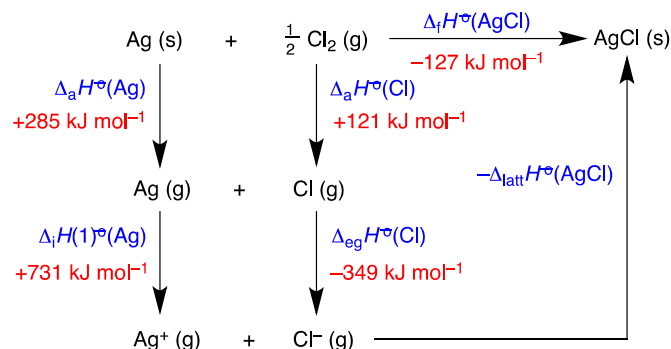


So, $\Delta_f H^\ominus(\text{LiCl}) = \Delta_a H^\ominus(\text{Li}) + \Delta_i H(1)^\ominus(\text{Li}) + \Delta_a H^\ominus(\text{Cl}) + \Delta_{\text{eg}} H(1)^\ominus(\text{Cl}) - \Delta_{\text{latt}} H^\ominus(\text{LiCl})$

By rearranging this equation, you can obtain an expression for the lattice enthalpy for LiCl

$$\begin{aligned}\Delta_{\text{latt}} H^\ominus(\text{LiCl}) &= -\Delta_f H^\ominus(\text{LiCl}) + \Delta_a H^\ominus(\text{Li}) + \Delta_i H(1)^\ominus(\text{Li}) + \Delta_a H^\ominus(\text{Cl}) + \Delta_{\text{eg}} H(1)^\ominus(\text{Cl}) \\ &= -(-408 \text{ kJ mol}^{-1}) + (+159 \text{ kJ mol}^{-1}) + (+520 \text{ kJ mol}^{-1}) + (+121 \\ &\quad \text{kJ mol}^{-1}) + (-349 \text{ kJ mol}^{-1}) \\ &= 859 \text{ kJ mol}^{-1}.\end{aligned}$$

For AgCl, using a Born-Haber cycle:



So, $\Delta_f H^\ominus(\text{AgCl}) = \Delta_a H^\ominus(\text{Ag}) + \Delta_i H(1)^\ominus(\text{Ag}) + \Delta_a H^\ominus(\text{Cl}) + \Delta_{\text{eg}} H(1)^\ominus(\text{Cl}) - \Delta_{\text{latt}} H^\ominus(\text{AgCl})$

By rearranging this equation, you can obtain an expression for the lattice enthalpy for AgCl

$$\begin{aligned}\Delta_{\text{latt}} H^\ominus(\text{AgCl}) &= -\Delta_f H^\ominus(\text{AgCl}) + \Delta_a H^\ominus(\text{Ag}) + \Delta_i H(1)^\ominus(\text{Ag}) + \Delta_a H^\ominus(\text{Cl}) + \\ &\quad \Delta_{\text{eg}} H(1)^\ominus(\text{Cl}) \\ &= -(-127 \text{ kJ mol}^{-1}) + (+285 \text{ kJ mol}^{-1}) + (+731 \text{ kJ mol}^{-1}) + (+121 \\ &\quad \text{kJ mol}^{-1}) + (-349 \text{ kJ mol}^{-1}) \\ &= 915 \text{ kJ mol}^{-1}.\end{aligned}$$

For LiCl, using the Kapustinskii equation.

$$\Delta_{\text{latt}}U = \frac{kVz_+z_-}{r_+ + r_-} \quad \text{with } k = 107\,900 \text{ pm kJ mol}^{-1}$$

$$\begin{aligned} \Delta_{\text{latt}}U &= \frac{107\,900 \text{ pm kJ mol}^{-1} \times 2 \times 1 \times 1}{76 \text{ pm} + 181 \text{ pm}} \\ &= 840 \text{ kJ mol}^{-1}. \end{aligned}$$

This is quite close to the value obtained from the Born-Haber cycle, suggesting that LiCl can be described well by the ionic model.

For AgCl, using the Kapustinskii equation.

$$\Delta_{\text{latt}}U = \frac{kVz_+z_-}{r_+ + r_-} \quad \text{with } k = 107\,900 \text{ pm kJ mol}^{-1}$$

$$\begin{aligned} \Delta_{\text{latt}}U &= \frac{107\,900 \text{ pm kJ mol}^{-1} \times 2 \times 1 \times 1}{129 \text{ pm} + 181 \text{ pm}} \\ &= 696 \text{ kJ mol}^{-1}. \end{aligned}$$

This is much lower than the value obtained from the Born-Haber cycle, suggesting there are significant covalent interactions for AgCl.

- 18.** Draw a van Arkel-Ketelaar triangle, and use the electronegativities of the elements to estimate the positions of KF and PbI₂. Use this to estimate the type of bonding in the two compounds.

Strategy

Draw a van Arkel-Ketelaar triangle as shown in Figure 6.34 (p.298). For each compound, work out the average electronegativity of the two elements and the difference in electronegativity between the elements. Use these values to place each compound on the triangle.

Solution

Electronegativities are given in Figure 4.6 (p.178). $\chi(\text{K}) = 0.82$ 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 PbI_2 $\bar{\chi} = 2.23$ and $\Delta\chi = 0.86$. This is lower down in the triangle, closer to the covalent corner. This suggests PbI_2 has considerable covalent character which is consistent with the low oxidation state and size of the species involved.