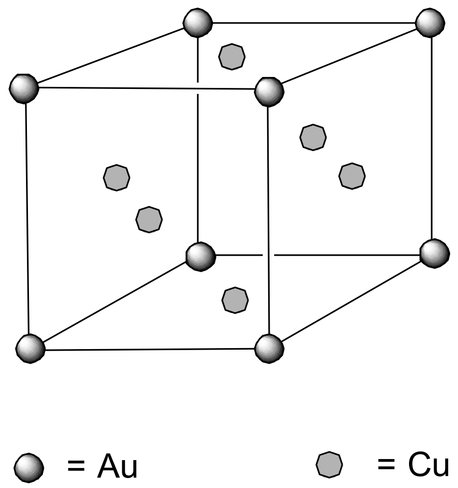
Marks
2

- The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces.



What is the chemical formula of the alloy?

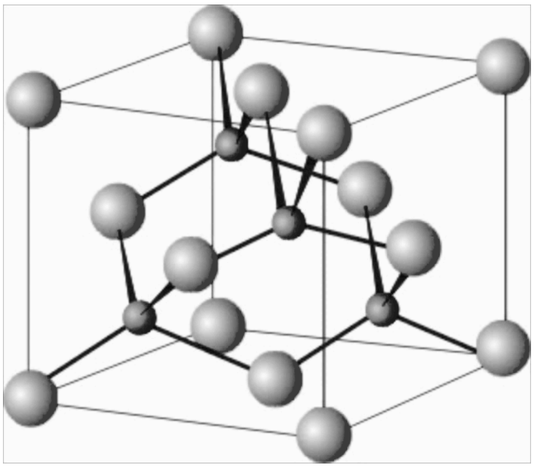
There are 8 Au atoms on the corners: each contributes 1/8 to the unit cell so the net number of Au atoms is 8 × 1/8 = 1.

There are 6 Cu atoms on the faces: each contributes 1/2 to the unit cell so the net number of Cu atoms is 6 × 1/2 = 3.

Answer: **Cu_3Au**

Marks 5

- The cubic form of boron nitride (borazon) is the second-hardest material after diamond and it crystallizes with the structure shown below. The large spheres represent the nitrogen atoms and the smaller spheres represent boron atoms.



From the unit-cell shown above, determine the empirical formula of boron nitride.

There are N atoms on the corners and on the faces of the unit cell:

- **There are 8 N atoms on the corners. These contribute 1/8 to the unit cell giving a total of 8 × 1/8 = 1 N atom.**
- **There are 6 N atoms on the faces. These contribute 1/2 to the unit cell giving a total of 6 × 1/2 = 3 N atoms.**
- **There are a total of 1 + 3 = 4 N atoms in the unit cell.**

There are B atoms inside the unit cell:

- **There are 4 B atoms completely inside the cell. These contribute only to this unit cell giving a total of 4 × 1 = 4 B atoms.**

The formula is therefore B_4N_4 which simplifies to BN.

Answer: **BN**

Determine the oxidation state of the boron atoms.

Nitrogen has an oxidation number of –III (or -3) to complete its octet. To ensure neutrality, boron must be +III (or +3).

Answer: **+III (or +3)**

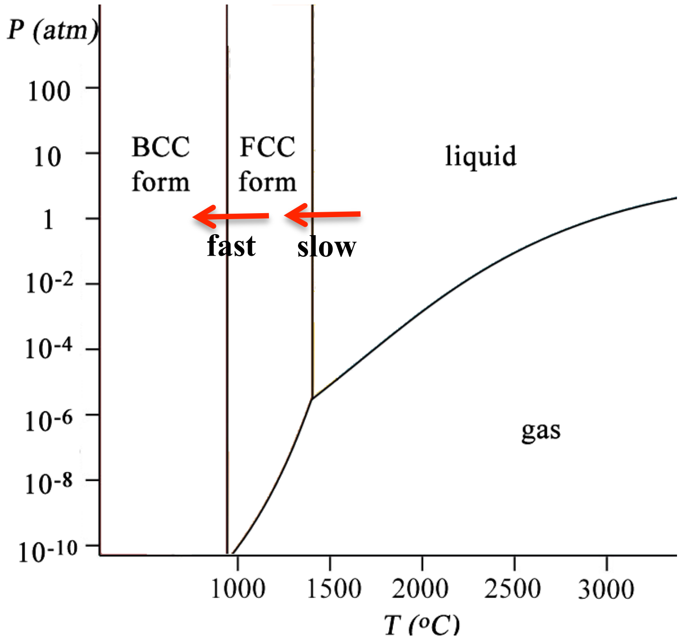
ANSWER CONTINUES ON THE NEXT PAGE

The cubic form of boron nitride is more thermally stable in air than diamond. Provide a reasonable explanation for this observation.

Boron and nitrogen have different electronegativities, with N more electronegative than B. This leads to partial δ+ and δ- charges on B and N respectively. These charges give the bonds partial ionic character and this acts to increase the strength of the bonds.

Marks 5

- A simplified phase diagram for iron is shown below, with the solid part divided into the body-centred cubic (BCC) and face-centred cubic (FCC) phases.



Which form of iron is stable at room temperature and pressure?

BCC form

If molten iron is cooled slowly to around 1200 °C and then cooled rapidly to room temperature, the FCC form is obtained. Draw arrows on the phase diagram to indicate this process and explain why it leads to the FCC form as a metastable phase.

The slow cooling leads to the most stable form at 1200 °C – the FCC form. Fast cooling to room temperature does not allow the atoms to re-arrange; they are stuck in the FCC form as considerable re-arrangement is needed to turn this in the BCC form.

The structure is stuck in the FCC arrangement even though BCC is more stable.

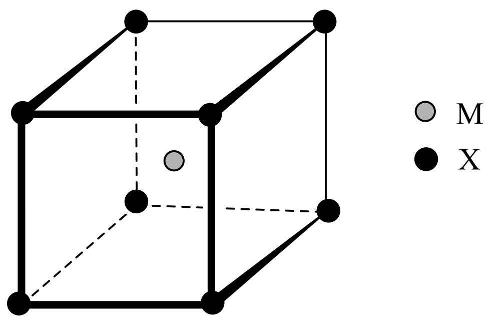
The line dividing the BCC and FCC forms is almost, but not quite vertical. Predict which way this line slopes and explain your answer.

BCC is less dense than FCC – the latter is a close packed structure so has the maximum possible density whereas the former is not closed packed.

Applying pressure will favour the more dense structure as it takes up less space. Increasing pressure therefore favours the FCC structure. The line between BCC and FCC has a negative slope (\). If the system is on the line and the pressure is increased, the system moves into the FCC region.

Marks 2

- The unit cell below has a cation (M) at the centre of the cell and anions (X) at the corners.



What is the formula of the compound?

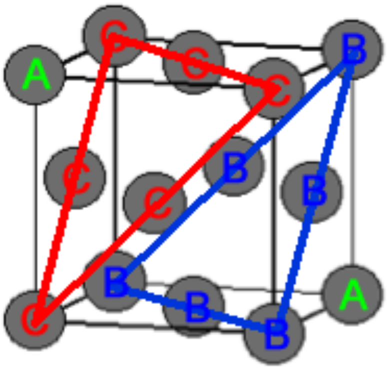
Number of M atoms = 1 (at the centre).
Number of X atoms = 8 × 1/8 (corners) = 1.
Hence, formula = M_1X_1 = MX

What is the coordination number of each type of ion?

Each M is surrounded by the 8 X atoms on the corners: the coordination number of M is 8.
Each X is on the corner of 8 unit cells, each with an M at its centre: the coordination number of X is also 8.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

	Marks
• A face centred cubic (FCC) unit cell has the maximum possible space filling of 74 %. Show the close packed layers, labelling them A, B and C, on the unit cell below.	**3**



How many atoms are in the unit cell?

Atoms on corners: 8 × 1/8 = 1

Atoms on faces: 6 × 1/2 = 3

Total: 1 + 3 = 4

- What are the structural differences between graphite and diamond and how do these differences impact on their physical properties? Mention at least three physical properties.

Marks
3

Diamond is a covalent network solid with each carbon bonded to 4 others in a tetrahedral arrangement. Graphite consists of sheets of sp^2 hybridised carbons, each bonded to 3 others in a trigonal planar arrangement.

Diamond is very hard as each atom is firmly bonded into its place in the crystal. Graphite is very soft and has a greasy feel as the sheets of carbon atoms are free to slide over one another.

Diamond is an insulator. Graphite can conduct a current in the plane of the sheets as the electrons in the unhybridised *p* orbitals are completely delocalised.

They have different appearances (diamond is colourless, graphite is black) due to their different electronic arrangements.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- A binary alloy has a face-centered cubic structure with atoms of element A in the faces and atoms of element B at the corners. What is the formula of the alloy? Explain your reasoning. 1

Atoms on the faces are shared between 2 cells: they contribute ½ to each. There are 6 faces:

number of A atoms = 6 × ½ = 3

Atoms on the corners are shared between 8 cells: they contribute ⅛ to each. There are 8 corners:

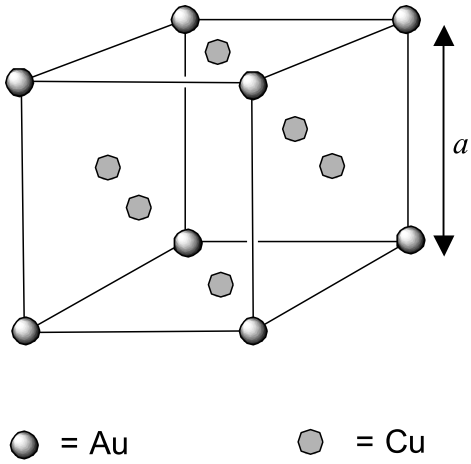
number of B atoms = 8 × ⅛ = 1

The stoichiometry is thus A : B = 3 : 1 so the formula is A_3B.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 5

- The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces. The unit cell dimension (edge length, *a*) for this alloy is 0.36 nm.



What is the chemical formula of the alloy?

There are 8 Au atoms on the corners. Each of these contribute 1/8 to the unit cell:

number of Au atoms = 8 × 1/8 = 1

There are 6 Cu atoms on the face. Each of these contribute 1/2 to the unit cell:

number of Cu atoms = 6 × 1/2 = 3

The ratio of Cu to Au atoms is therefore 3 : 1 and the formula is Cu_3Au.

Answer: **Cu_3Au**

Pure gold is 24 carat, whilst gold alloys consisting of 75 % gold by weight are termed 18 carat gold. What carat gold is this alloy?

The molar mass of Cu_3Au is:

molar mass = (3 × 63.55 (Cu) + 1 × 196.97 (Au)) g mol^{-1} = 387.62 g mol^{-1}.

1 mol of Cu_3Au contains 1 mol of Au, the percentage by weight of gold in Cu_3Au is:

percentage by weight = $\frac{196.97}{387.62}$ × 100 % = 50 %

As a 100 % alloy is 24 carat and a 75% alloy is 18 carat, a 50 % alloy is 12 carat.

Answer: **12 carat**

What is the volume (in cm^3) of the unit cell?

As the unit cell is cubic:

volume = (side length)^3 = a^3 = (0.36 × 10^{-9} m)^3 = 4.7 × 10^{-29} m^3

= 4.7 × 10^{-23} cm^3

Answer: **4.7 × 10^{-23} cm^3**

ANSWER CONTINUES ON THE NEXT PAGE

What is the density (in g cm^{-3}) of the alloy?

From above, the unit cell contains 1 Au atom and 3 Cu atoms:

mass of gold = 196.97 g mol^{-1} / 6.022 × 10^{23} mol^{-1} = 3.271 × 10^{-22} g

mass of copper = 3 × 63.55 g mol^{-1} / 6.022 × 10^{23} mol^{-1} = 3.166 × 10^{-22} g

mass of unit cell = (3.271 × 10^{-22} + 3.166 × 10^{-22}) g = 6.437 × 10^{-22} g

The density is therefore:

density = mass / volume

= 6.437 × 10^{-22} g / 4.7 × 10^{-23} cm^3 = 1.4 × 10^1 g cm^{-3}

Answer: **14 g cm^{-3}**

- Define what is meant by an "allotrope". Give an example of a pair of allotropes involving (i) oxygen and (ii) a pair not involving oxygen. **2**

Allotropes are different structural forms of the same element.

(i) Dioxygen, O_2, and ozone, O_3, are allotropes of oxygen.

(ii) Examples include (a) white and red phosphorus, (b) graphite, diamond and fullerene for carbon and (c) rhombic, monoclinic and amorphous sulfur.

Marks
3

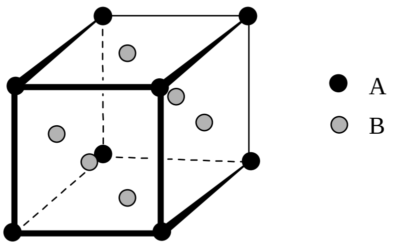
- An alloy is formed by combining elements A and B. The alloy has a face-centred cubic structure, with atoms of A at the corners and atoms of B in the faces. What is the formula of the alloy? Explain your reasoning.

The atoms on the corners are shared between 8 cells: each contributes $^{1}/_{8}$.

The atoms on the faces are shared between 2 cells: each contributes $^{1}/_{2}$.

Thus, there are 8 × $^{1}/_{8}$ A atoms = 1 A atoms and 6 × $^{1}/_{2}$ B atoms = 3 B atoms.

Overall, A: B = 1 : 3 so the formula is AB_3.



Answer: **AB_3**

- Define what is meant by an "allotrope". Give an example of a pair of allotropes involving (i) phosphorus and (ii) a pair not involving phosphorus. 2

Allotropes are different structural forms of the same element.

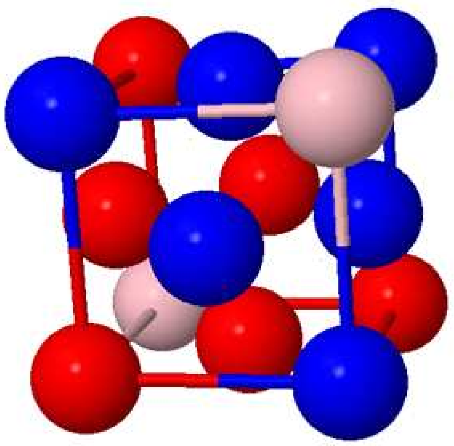
(i) Phosphorus exists as a number of allotropes, including white, red and black phosphorus. The most common forms are white and red phosphorus which are based on P_4 tetrahedra and linked P_4 tetrahedra respectively. Black phosphorus consists of layers of puckered 6-membered rings.

(ii) Other elements showing allotropes include:

- **carbon – diamond, graphite and fullerenes**
- **oxygen – O_2 and O_3 molecules**
- **sulfur – S_n rings with n = 6 – 20.**

Draw the face-centred cubic unit cell. **2**

The face-centred cubic unit cell has one atom on each corner of the cube and one atom on each face. They are no atoms at the centre of the cube.



Marks

- Many elemental metals crystallise in one of three cubic forms, either with a face-centred cubic, a body-centred cubic or a simple cubic unit cell. Explain the main differences and similarities between these different crystalline forms. **3**

All three are based on a cubic unit cell:

- **The simple cubic form has atoms on each corner so that the atoms are stacked directly one on top of the other. As the 8 atoms are shared with eight other cubes, each contributes 1/8 to the cell so that the cell contains 8 × 1/8 = 1 atom. The atoms touch along the edges of the cube.**
- **The body centred cubic form has at an additional atom in the cube centre, giving a total of 2 atoms in the cell. The atoms touch along the cube diagonal.**
- **The face centred cubic form has atoms on each corner and atoms at the centre of each face (with no atom at the centre of the cube). The atoms on the face centres are shared with two other cubes and so contribute 1/2 to the cell. The cell contains 8 × 1/8 (corner) + 6 × 1/2 (face) = 4. The atoms touch along the face diagonals.**
- **The face centred cubic form is the only close packed structure and is the most dense.**
- **In a face centred cubic structure, 74% of the space is occupied. In a body centred cubic, 68% is occupied. In a simple cubic structure, 52% is occupied.**

- Teeth are made from hydroxyapatite, $Ca_5(PO_4)_3OH$. Why does an acidic medium promote tooth decay? Use chemical equations where appropriate. **3**

Hydroxyapatite dissolves in water according to the equation:

$$\mathbf{Ca_5(PO4)_3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)}$$

In a non-acidic medium, the equilibrium lies to the left. In acidic media, H^+ reacts with both PO_4^{3}- and OH^- to form the conjugate acids (HPO_4^{2-} and H_2O, respectively) and this shifts the equilibrium to the right and the tooth dissolves..

How does the fluoridation of drinking water aid the prevention of tooth decay?

Fluoridation can replace OH^- forming $Ca_5(PO_4)_3F(s)$. This is less soluble than hydroxyapatite - it does not react with H^+ to the same extent as OH^-.