



UK Chemistry Olympiad support resources: crystal unit cells

Introduction

Crystals are solids in which the particles have a regular arrangement held together by forces of attraction. The exact nature of these forces of attraction depends on the type of particles in the crystal. The highly ordered particles form a three dimensional structure known as a crystal lattice.

There are four basic crystal types: ionic, metallic, molecular and macromolecular.

In ionic crystals, such as sodium chloride, the particles are ions held in a lattice structure by strong electrostatic forces of attraction between the oppositely charged ions.

Metallic crystals exist as a lattice of positively charged metal ions surrounded by a sea of delocalised electrons. The lattice of metal ions is held in position by the strong electrostatic force of attraction between the positive metal ion and the delocalised electrons.

Molecular crystals consist of a lattice of simple covalent molecules held in a fixed position by intermolecular forces. Iodine is an example of a molecular crystal in which diatomic iodine, I_2 , molecules are held in position by the Van der Waals forces between the iodine molecules.

Finally, macromolecular crystals consist of atoms covalently bonded together to form one huge three dimensional crystal structure. Examples of macromolecular crystals include diamond and graphite.

Unit cells

A unit cell is the smallest unit that when stacked together repeatedly without any gaps can reproduce the entire crystal.

The unit cell for sodium chloride is shown in figure 1. In figure 1a the green and red spheres represent the centre of the Cl^- and Na^+ ions respectively. Figure 1b provides a more realistic representation with the sodium and chloride ions touching each other along the cell edges.

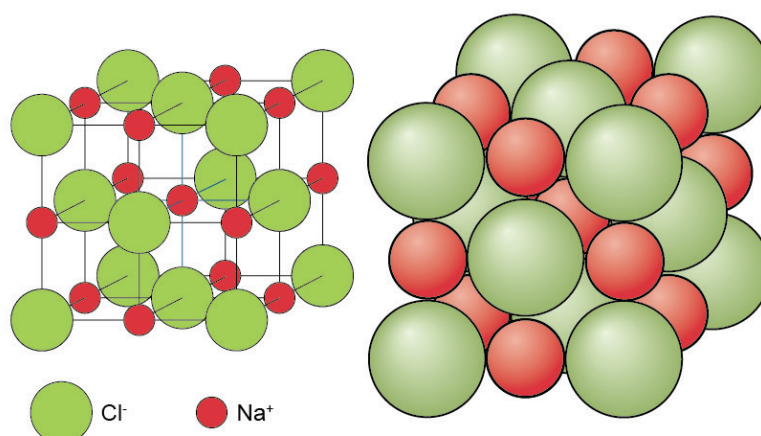


Figure 1a

Figure 1b

Figure 1 Two different representations of the unit cell for sodium chloride



In both these representations of the unit cell it is important to note that the whole particle is not necessarily in the unit cell. A particle at a corner or on a face or an edge is shared by neighbouring unit cells so in a crystal only a fraction of it belongs to the unit cell in question.

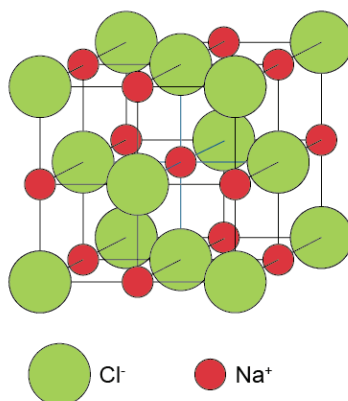
A particle at a corner is shared by eight neighbouring unit cells and hence just $\frac{1}{8}$ of the particle is within the unit cell.

A particle on an edge is shared by four neighbouring unit cells and so $\frac{1}{4}$ of it falls within the unit cell.

A particle on a face is shared by two neighbouring unit cells and so only $\frac{1}{2}$ of it falls within the unit cell.

The total number of particles in a unit cell can therefore be determined by counting the number of particles in each position of the unit cell (at a corner, edge, face or in the body) and multiplying by the fraction of each particle within the unit cell.

Table 1 shows such a calculation for the unit cell of sodium chloride. From the calculation we can see that each unit cell contains 4 Na^+ ions and 4 Cl^- ions and hence the formula of sodium chloride is NaCl and it has no overall charge.



	Number of ions	
	Na^+	Cl^-
at 8 corners	-	$8 \times \frac{1}{8} = 1$
on 12 edges	$12 \times \frac{1}{4} = 3$	-
on 6 faces	-	$6 \times \frac{1}{2} = 3$
in the body of the cell	1	-
Total	4	4

Table 1 Calculation to determine total number of particles in a unit cell of sodium chloride

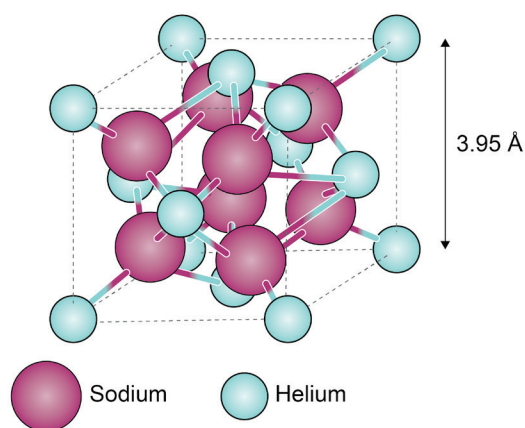
Knowing the numbers of each particle within a unit cell it is then possible to calculate other properties of the crystal.



Worked example: UK Chemistry Olympiad 2018 paper 1 question 5

Helium is very unreactive, with a full outer shell and the highest ionisation energy of any element. Last year a collaboration between 17 researchers across the globe suggested that compound **X** (a compound of helium and sodium) had been formed under an extreme pressure of 300 GPa.

The unit cell of a crystal is determined by X-ray crystallography and shows the arrangement of the atoms in the crystal. Stacking the unit cells together generates the bulk structure.



The unit cell of compound **X** is represented in the diagram above, with helium atoms positioned at the corners and at the centres of the faces of the unit cell, and sodium atoms positioned cubically within the unit cell. Some of the atoms are contained completely within the boundaries of a single Unit cell, whilst for atoms centred on the corners, edges or faces, only a fraction of the atom is contained within a single unit cell.

(c)

By considering the number of fractions of atoms within one unit cell, count the total numbers of sodium and helium atoms within one unit cell.

(d)

What is the formula of compound **X**?

(e)

Use your answer in part (c) and the dimensions of the unit cell to calculate the density of compound **X** in g cm^{-3} .



Answers to worked example

(c)

By looking at the diagram of the unit cell, first determine the number of each atom at the corners, edge, faces and in the body of the unit cell. Multiply by the fraction of each atom within the unit cell to determine the total number of sodium and helium atoms in one unit cell.

	Number of atoms	
	Na	He
at 8 corners	-	$8 \times \frac{1}{8} = 1$
on 12 edges	-	-
on 6 faces	-	$6 \times \frac{1}{2} = 3$
in the body of the cell	8	-
Total	8	4

(d)

From (c) we know that each unit cell of **X** contains eight Na and four He atoms.

Therefore the formula of the compound is Na_8He_4 which simplifies to Na_2He .

(e)

A unit cell is the smallest unit that when stacked together repeatedly without any gaps can reproduce the entire crystal. Therefore the density of compound **X** is the same as the density of the unit cell.

This question is therefore asking us to calculate the density of the unit cell.

To do this we need to know that:

$$\text{density / g cm}^{-3} = \frac{\text{mass / g}}{\text{volume / cm}^3}$$

TOP TIP Use the units of density of g cm^{-3} to help you remember the formula.

To calculate the mass of the unit cell in g:

Each unit cell contains eight Na atoms and four He atoms.

To find the mass of these atoms we use the fact that the relative atomic mass of an element measured in grams contains 1 mole or 6.02×10^{23} atoms of that element.

Therefore the mass of a single atom can be calculated by dividing an element's relative atomic mass in grams (its molar mass) by 6.02×10^{23} .

$$\text{Mass of 8 Na atoms} = 8 \times \frac{22.99 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 3.055 \times 10^{-22} \text{ g}$$

$$\text{Mass of 4 He atoms} = 4 \times \frac{4.003 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 2.660 \times 10^{-23} \text{ g}$$

$$\text{Total mass} = 3.321 \times 10^{-22} \text{ g}$$

To calculate the volume of the unit cell in cm^3 :

The unit cell in the question is a cube.

The length of one face is given in Ångströms (Å).



Therefore, to calculate the volume in cm^3 first we must convert 3.95 \AA into cm

$$1 \text{ \AA} = 1 \times 10^{-10} \text{ m or } 1 \times 10^{-8} \text{ cm.}$$

And hence, $3.95 \text{ \AA} = 3.95 \times 10^{-8} \text{ cm}$

Therefore, the volume of the unit cell in cm^3 is

$$(3.95 \times 10^{-8} \text{ cm})^3 = 6.163 \times 10^{-23} \text{ cm}^3$$

To calculate the density of compound **X**:

Substitute the values of the mass and volume into the equation for density to calculate the density of compound **X**:

$$\text{density / g cm}^3 = \frac{3.321 \times 10^{-22} \text{ g}}{6.163 \times 10^{-23} \text{ cm}^3} = 5.39 \text{ g cm}^3$$

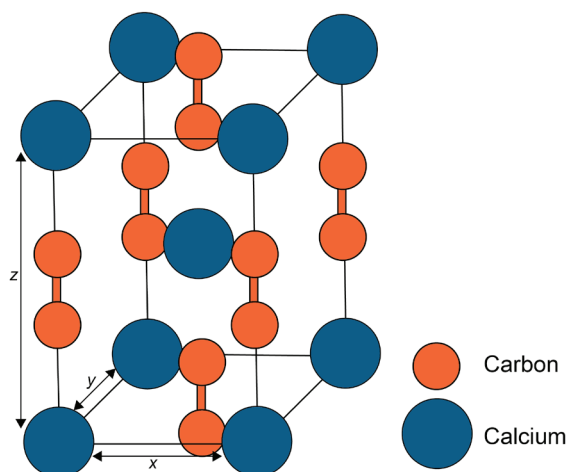
TOP TIP If you are uncertain about converting from \AA into cm directly, first convert into m and then into cm . Since $100 \text{ cm} = 1 \text{ m}$ multiply by 100 to convert m into cm .

TOP TIP In extended calculations keep intermediate values on your calculator. Only round to the appropriate number of significant figures in the final answer.

Now you have a go: UK Chemistry Olympiad 2020 round 1 question 1

The diagram shows the unit cell of calcium carbide. Calcium is positioned at the corners and centre of the unit cell.

Some of the atoms are completely contained within the boundaries of a single unit cell. Only a fraction of atoms centred on corners, edges, or faces are contained within a single unit cell.



(d)

By considering the number of fractions of atoms within one unit cell, count the net numbers of calcium and carbon atoms within one unit cell.

The density of calcium carbide is 2.20 g cm^{-3} and the values of x and y are both 3.88 \AA .

(e)

Calculate the value of z in \AA .

When you're done, turn over to check your answers.



Answers to UK Chemistry Olympiad 2020 round 1 question 1

(d)	2 calcium atoms and 4 carbon atoms. <i>1 mark for each correct answer.</i>
(e)	Molar volume of $\text{CaC}_2 = 64.1 \text{ g mol}^{-1} / 2.20 \text{ g cm}^{-3} = 29.14 \text{ cm}^3 = 2.914 \times 10^{-5} \text{ m}^3$ <i>One mark for correct molar volume in m^3.</i> Volume of CaC_2 unit cell = $2 \times 2.914 \times 10^{-5} \text{ m}^3 / 6.02 \times 10^{23} \text{ mol}^{-1}$ <i>One mark for correct molar volume in m^3 or in \AA^3.</i> Length of side $z = \sqrt[3]{9.68 \times 10^{-29} \text{ m}^3 / (3.88 \times 10^{-10} \text{ m})^2} = 6.43 \times 10^{-10} \text{ m} = 6.43 \text{ \AA}$ <i>One mark</i> <i>Correct answer scores three marks regardless of working.</i>

Further challenge

Challenge your understanding further with UK [Chemistry Olympiad 2010 round 1](#) question 6.

Worked answers explaining each step can be found in this UK Chemistry Olympiad Bite
<https://edu.rsc.org/resources/chemistry-olympiad-bites-question-6-2010/1061.article>