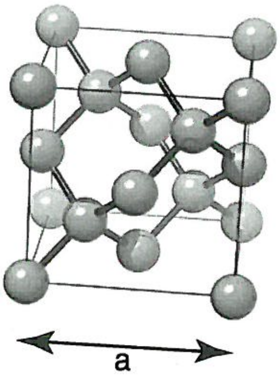
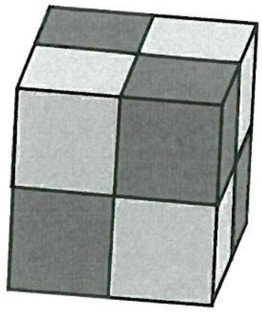
Q1. From the lump of isotopically enriched silicon, a single crystal of silicon-28 was grown. The structure on the left shows the repeating pattern, or unit cell, for silicon. By stacking these cubes together, the structure of the solid is revealed. Atoms that are directly bonded to one another are connected by the bonds (the heavier lines). In the unit cell, silicon atoms are placed with their centres at each corner of the cube, and in the centre of each face. If we divide the unit cell into eight smaller cubes, as shown on the right, there is also one silicon atom right in the middle of every alternate cube (the darker shaded ones).





The length of the cube is **a** pm (1 pm = 1 × 10^{-12} m). The total number of silicon atoms contained within the cube is denoted **n**. The single crystal was fashioned into a perfect sphere of volume **V** cm^3, and mass **m** g. The relative atomic mass of silicon is $\mathbf{A_r}$.

(e) (i) By counting up the contributing fractions, calculate a value for **n**, the number of number of silicon atoms per unit cell.

(ii) Give an expression for the number of atoms in the sphere in terms of **a**, **n**, and **V**. Take care with the units!

(iii) Give an expression for the Avogadro constant in terms of **a**, **n**, **V**, $\mathbf{A_r}$, and **m**.

(f) By considering the atoms within one of the smaller cubes, or otherwise, derive an expression for the Si–Si bond length in terms of distance **a**.

In the experiment, the silicon was isotopically enriched in silicon-28. Analysis of the sample showed the fraction of silicon atoms that were ^{29}Si was 41.2 × 10^{-6} and the fraction that were ^{30}Si was 1.3 × 10^{-6}. The remainder is assumed to be silicon-28.

(g) Given the following accurate masses, determine the relative atomic mass, $\mathbf{A_r}$, for this sample of silicon.

Isotope	^{28}Si	^{29}Si	^{30}Si
Relative isotopic mass	27.97692653	28.97649470	29.97377017

(h) The volume of the sphere, **V**, used in the experiment was 431.059060 cm^3 and its mass, **m**, was 1000.087559 g. The length of the unit cell, **a**, as determined from the crystal structure was 543.0996234 pm. Use these values together with your values for **n** and $\mathbf{A_r}$ to calculate the Avogadro constant to 9 significant figures.

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(e)(i) **calculate n**

$n = (8 \times 1/8) + (6 \times 1/2) + 4 = 8$ ✓✓

2

(ii) **number of atoms in sphere**

n atoms in a^3 pm^3 $\equiv a^3 \times 10^{-36}$ m^3

volume of sphere = V cm^3 $\equiv V \times 10^{-6}$ m^3

atoms in volume V = $\dfrac{V\,n \times 10^{30}}{a^3}$ ✓✓✓

2 marks for expression
3rd mark if with factor of $\times 10^{30}$

3

(iii) **Expression for Avogadro constant**

atoms in m g = $\dfrac{V\,n \times 10^{30}}{a^3}$

atoms in 1 g = $\dfrac{V\,n \times 10^{30}}{ma^3}$

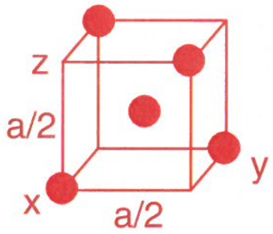
atoms in Ar g = $\dfrac{A_r\,V\,n \times 10^{30}}{m\,a^3}$ ✓✓✓

2 marks for expression
3rd mark if with factor of $\times 10^{30}$

3

leave blank

(f) **Si–Si bond length**



$$xy = \sqrt{\frac{a^2}{4} + \frac{a^2}{4}} = \frac{a}{\sqrt{2}}$$

$$yz = \sqrt{\frac{a^2}{2} + \frac{a^2}{4}} = \frac{\sqrt{3}\,a}{2}$$

yz = twice bond length

Si–Si bond length = $\frac{\sqrt{3}\,a}{4}$ pm (=0.433a pm) ✓✓✓✓

[3 marks if correct but no unit; 2 marks for twice the answer; 1 mark for some Pythagorean working but wrong answer]

4

(g) **A_r for silicon**

$$A_r = (1 - 41.2\times10^{-6} - 1.3\times10^{-6}) \times 27.97692653$$
$$+ (41.2\times10^{-6} \times 28.97649470)$$
$$+ (1.3\times10^{-6} \times 29.97377017)$$

$$= 27.97697031$$ ✓✓

[1 mark for some correct working but wrong answer]

2

(h) **Calculated value for Avogadro constant**

putting values into expression gives

$6.02214096 \times 10^{23}$ ✓

1 mark if this answer. No carry forward.

1

Total 26

Q2 The rock has a density of 2.7 g cm^{-3} and is found to contain 2.0% by mass of potassium. Furthermore, 1.0% by volume of the rock is water-filled pores. The water from the rock was found to contain 0.0445 cm^3 of ^{40}Ar per cm^3 of water (measured at 0 °C).

(e) (i) Given that 1 mol of gas occupies a volume of 22.4 dm^3 at 0 °C, calculate the number of atoms of ^{40}Ar in 1 cm^3 of water.

(ii) What mass of rock contains this quantity of ^{40}Ar?

(iii) What is the mass of potassium in this quantity of rock?

(iv) Given that only 0.0117% of naturally occurring potassium is ^{40}K, determine the number of atoms of ^{40}K in the mass of rock from part **(ii)**.

The decay constant, λ, of ^{40}K is 5.54×10^{-10} per year. However, only a fraction (0.105) of the decay leads to the formation of ^{40}Ar, the rest leads to the production of ^{40}Ca.

The number of number of atoms of ^{40}Ar formed, $N_{^{40}Ar}$, over a time t years, is related to the number of atoms of ^{40}K remaining, $N_{^{40}K}$, by the following equation:

$$N_{^{40}Ar} = 0.105 \times N_{^{40}K} \times (e^{\lambda t} - 1)$$

(f) Use this equation and your answers to **(e)** to determine the age of the sample of water.

leave blank

2(e)(i) **atoms of ^{40}Ar in 1cm^3 of water:**

1 cm^3 water contains 0.0445 cm^3 of ^{40}Ar

$$= \frac{0.0445 \times 6.022 \times 10^{23}}{22400} = 1.20 \times 10^{18} \text{ atoms}$$ ✓ 1

(e)(ii) **mass of rock:**

since 1.0% by volume of rock is water

100 cm^3 of rock contains 1.0 cm^3 of water = 270 g ✓ 1

(e)(iii) **mass of potassium:**

mass of potassium = 2.0% by mass of rock

= 270 × (2.0 / 100) = 5.4 g 1

(e)(iv) **atoms of ^{40}K:**

moles of potassium in rock = 5.4 / 39.102 = 0.138

moles of ^{40}K is (0.0117 / 100) × 0.138 = 1.62×10^{-5} ✓

∴ number of atoms of ^{40}K = 2

$(5.4/39.102) \times (0.0117/100) \times 6.022 \times 10^{23} = 9.7 \times 10^{18}$ ✓

[if assumed proportion of ^{40}K is 0.0117% by mass, answer comes out as 9.5 × 10^{18} and 1 mark should be given]

(f) **age of sample:**

$$N_{^{40}Ar} = 0.105 \times N_{^{40}K} \times (e^{\lambda t} - 1)$$

rearranging:

$$e^{\lambda t} = \frac{N_{^{40}Ar}}{0.105 \times N_{^{40}K}} + 1 \qquad \therefore t = \frac{1}{\lambda} \times \ln\left(\frac{N_{^{40}Ar}}{0.105 \times N_{^{40}K}} + 1\right)$$ ✓✓ 4

$$\therefore t = \frac{1}{5.54 \times 10^{-10}} \times \ln\left(\frac{1.2 \times 10^{18}}{0.105 \times 9.73 \times 10^{18}} + 1\right) = 1.4 \times 10^{9} \text{ years}$$ ✓✓

= 1.4 billion years

[give 2 marks if equation has been correctly (and usefully) rearranged in some form]

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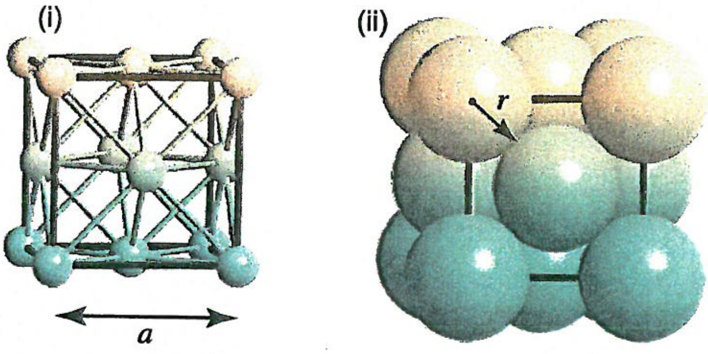
Properties of metallic beryllium

One of the reasons for choosing beryllium for the JWST mirrors was because of its high strength and low density (about 70% that of aluminium). Even though beryllium atoms are the fourth lightest of all the elements, perhaps surprisingly, calcium has the lowest density of the Group 2 elements. The density of an element depends on the mass of the atoms, the size of the atoms, and how well packed together they are.

(e) (i) Given the densities of beryllium and calcium are 1.85 and 1.55 g cm^{-3} respectively, calculate their molar volumes, i.e. the volume (in m^3) occupied by 1 mol.

(ii) Given that beryllium and calcium have exactly the same packing efficiencies (the fraction of the structure occupied by atoms), calculate the ratio of their atomic radii, r(Ca) / r(Be).

The unit cell, or repeating unit, for calcium is shown on the right. The structure of metallic calcium is generated by stacking these cubes together. It consists of a regular cube (shown with the dark lines with edge length a), with atoms placed so their centres are at the corners of the cube and in the centre of each face. In (i) the atoms in direct contact with each other are shown connected by the light coloured bonds. In (ii) the atoms are shown in direct contact with their nearest neighbours.



(f) (i) By adding up all the fractional parts of atoms contained within one unit cell, calculate the number of atoms contained in a cube of volume a^3.

(ii) Find an expression for the length, a, and hence volume of the cube in terms of the radius of the atom, r.

(iii) Given the density of calcium is 1.55 g cm^{-3}, calculate the atomic radius of calcium

(e)(i) molar volume of Be

$1.85 \text{ g Be} \equiv 1 \text{ cm}^3 \equiv 10^{-6} \text{ m}^3$

$\therefore 1 \text{ g Be} \equiv \dfrac{10^{-6}}{1.85} \text{ m}^3$

$\therefore 1 \text{ mol Be} \equiv 9.01 \text{ g}$

$\equiv \dfrac{9.01\times10^{-6}}{1.85} \text{ m}^3$

$= 4.87\times10^{-6} \text{ m}^3 \text{ mol}^{-1}$ ✓

molar volume of Ca

$1.55 \text{ g Ca} \equiv 1 \text{ cm}^3 \equiv 10^{-6} \text{ m}^3$

$\therefore 1 \text{ g Ca} \equiv \dfrac{10^{-6}}{1.55} \text{ m}^3$

$\therefore 1 \text{ mol Ca} \equiv 40.08 \text{ g}$

$\equiv \dfrac{40.08\times10^{-6}}{1.55} \text{ m}^3$

$= 2.59\times10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ✓

2

(e)(ii) r **(Ca) /** r **(Be)**

molar volume $\propto$ atomic volume $\propto r^3$

$$\frac{r(\text{Ca})}{r(\text{Be})} = \sqrt[3]{\frac{40.08}{1.55} \times \frac{1.85}{9.01}} = 1.74$$ ✓✓✓

3

[2 marks if inverse i.e. 0.573 ; otherwise zero]

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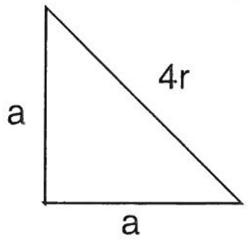
1(f)(i) number of atoms in volume a^3

8 at corners (1/8 each)
+ 6 at faces (1/2 each)
total (8 x 1/8) + (6 x 1/2) = 4 ✓ — 1

(f)(ii) length a

diagonal of cube face = 4r



$2a^2 = 16 r^2$

$a^2 = 8r^2$

$a = 2\sqrt{2}\ r = 2.83\ r$ ✓ — 1

volume of cube

$= (2\sqrt{2})^3 r^3 = 16\sqrt{2}\ r^3 = 22.63\ r^3$ ✓ — 1

(f)(iii) atomic radius of Ca

1.55 g Ca ≡ 1 cm^3 of bulk structure = 10^{-6} m^3

$$\frac{1.55}{40.08} \times 6.022 \times 10^{23} \text{ atoms} \equiv 10^{-6}\ m^3$$

also know 4 atoms in the bulk structure take up $16\sqrt{2}\ r^3\ m^3$

so 4 atoms in $\dfrac{4 \times 40.08 \times 10^{-6}}{1.55 \times 6.022 \times 10^{23}}\ m^3 \equiv 16\sqrt{2}\ r^3\ m^3$

$$r^3 = \frac{4 \times 40.08 \times 10^{-6}}{16\sqrt{2} \times 1.55 \times 6.022 \times 10^{23}}\ m^3 \equiv$$

$$r = \sqrt[3]{\frac{4 \times 40.08 \times 10^{-6}}{16\sqrt{2} \times 1.55 \times 6.022 \times 10^{23}}}\ m = 1.97 \times 10^{-10}\ m$$ ✓✓✓ — 3

or 197 pm

[up to one mark partial credit if a decent attempt]

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