
Solids

6.1 Covalent network structures

- Covalent network structures are infinite structures in which the atoms are linked by covalent bonds.
- Different structural forms of the same *element* are known as allotropes. Graphite, diamond, buckminsterfullerene (C₆₀), nanotubes, and graphene are all allotropes of carbon.
- Different structural forms of the same *compound* are known as polymorphs. Quartz and β -cristobalite are two polymorphs of SiO₂.
- Each different structural form of an element or compound is a different phase. The conversion of one phase to another is called a phase transition.

6.2 Structures based on the packing of spheres


- The most efficient manner in which atoms can pack is called close packing. There are two important types of close packing. Cubic close packing (ccp) has a layer repeat ABCABC . . . and hexagonal close packing (hcp) has a layer repeat of ABABAB . . .
- A unit cell is the smallest possible repeating unit for a structure.
- The cubic close-packed structure is also known as face-centred cubic (fcc).
- Body-centred cubic (bcc) and primitive cubic structures can also be formed, but they have lower packing efficiencies.
- Packing efficiencies for structures can be calculated by dividing the volume of the atoms in a unit cell by the total volume of the unit cell. The value is usually quoted as a percentage.
- Close-packed structures contain octahedral and tetrahedral interstitial sites.
- The density of a substance can be calculated by dividing the total mass of its unit cell by the volume of its unit cell.



For practice questions on these topics, see questions 2–4 at the end of this chapter (p.300).


6.3 Metallic bonding

- The bonding in metals and their conductivity can be explained using band theory, which is derived from molecular orbital theory.
- Alloys are metallic materials containing a mixture of two or more metals, or a metal and a non-metal.
- Substitutional alloys, such as brass, have structures in which the atoms of one element are substituted by those of another.
- Interstitial alloys, such as the austenite phase of steel, have structures in which one element lies in the interstitial sites of another.

 For a practice question on this topic, see question 5 at the end of this chapter (p.300).

6.4 Structures of compounds


- The structures of many binary compounds can be described using a close-packed lattice of one atom or ion, with the other type occupying the octahedral or tetrahedral interstitial sites.
- The NaCl structure has a cubic close-packed array of chloride ions with the Na⁺ ions occupying the octahedral sites whereas the CaF₂ structure has a cubic close-packed array of calcium ions with F⁻ ions occupying the tetrahedral sites.
- Structures can also be based on lattices that are not close packed. An example of this is the structure of CsCl, which consists of a primitive cubic lattice of Cl⁻ ions with Cs⁺ ions in the cubic sites.

 For practice questions on these topics, see questions 6–11 at the end of this chapter (p.301).

6.5 The ionic model


- Coordination numbers and structures of ionic compounds can be predicted using the radius ratio rule, though this is not always reliable as it assumes ions are hard spheres with fixed radii.
- Hess's law enables enthalpy changes to be determined by using Born–Haber cycles.
- The lattice enthalpy for the compound A_xB_y is the enthalpy change for the process

$$A_xB_y(s) \rightarrow x A^{y+}(g) + y B^{x-}(g)$$
- In a Born–Haber cycle, the enthalpy change with the largest magnitude is usually the lattice enthalpy.

 For practice questions on these topics, see questions 12–13 at the end of this chapter (p.301).

6.6 Calculating lattice energy

- Lattice energies can be calculated using the Born–Landé equation.
- Compounds containing polarizable anions and polarizing cations have high covalent character.
- Compounds with a large degree of covalent character have higher lattice energies than anticipated from the Born–Landé equation.
- In the absence of full information, good estimates of lattice energies can be made using the Kapustinskii equation.

 For practice questions on these topics, see questions 14–17 at the end of this chapter (p.301).

6.7 Predicting bond types

- The type of bonding present in a binary compound can be predicted by considering the electronegativities of the elements involved.
- This can be shown on a van Arkel–Ketelaar triangle, which plots the average electronegativity of the elements against the difference in their electronegativities.

 For a practice question on this topic, see question 18 at the end of this chapter (p.301).

Concept review

By the end of this chapter, you should be able to do the following.

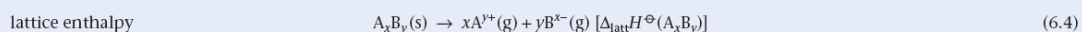
- Use the terms allotrope, polymorph, and unit cell, giving examples of each.
- Understand the differences between cubic close packing (ccp) and hexagonal close packing (hcp).
- Draw unit cells and cell projection diagrams for ccp, hcp, body-centred cubic (bcc), and primitive cubic structures.
- Calculate packing efficiencies and densities.
- Describe the bonding in metals using the free electron model and band theory.
- Describe the structures of binary compounds based on the packing of one type of ion or atom with the other type occupying interstitial sites.
- Predict the limiting radius ratio for different geometries.
- Use the radius ratio rule to predict the structures of ionic compounds.
- Calculate lattice enthalpies using Born–Haber cycles.
- Understand how the Madelung constant can be calculated.
- Calculate lattice energies using the Born–Landé equation and the Kapustinskii equation.
- Predict the type of bonding in a binary compound from the electronegativities of the atoms.

Key equations

packing efficiency	$\text{packing efficiency} = \frac{\text{volume of the atoms in a unit cell}}{\text{total volume of a unit cell}} \times 100$	(6.1)
--------------------	---	-------

radius ratio	$\text{radius ratio} = \frac{r_x}{r_c}$	(6.2)
--------------	---	-------

Density	$\rho = \frac{m}{V}$	(6.3)
---------	----------------------	-------



Born–Landé equation	$\Delta_{\text{lat}}U = \frac{AN_A Z_+ Z_- e^2}{4\pi\epsilon_0 r} \left(1 - \frac{1}{n}\right)$	(6.10)
---------------------	---	--------

Kapustinskii equation	$\Delta_{\text{lat}}U = \frac{kVZ_+Z_-}{r_+ + r_-}$	(6.11)
-----------------------	---	--------