Properties of Liquids and Solids

Petrucci, Harwood and Herring: Chapter 12

Aims:

To use the ideas of intermolecular forces to:

- –Explain the properties of liquids using intermolecular forces
- –Understand the relation between temperature, pressure and state of matter
- –Introduce the structures of solids

Vaporization of Liquids

- In gases we saw that the speed and kinetic energies of molecules vary, even at the same temperature.
- In the liquid, some molecules will always have sufficient kinetic energy to overcome intermolecular forces and escape into the gaseous state.
- This is vaporization. The enthalpy required for vaporization is the heat of vaporization ΔH_v.

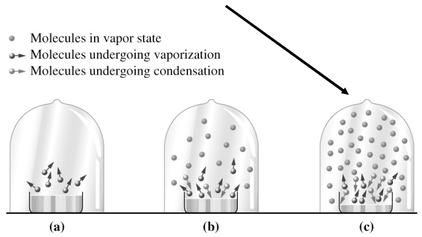
$$\Delta H_v = H_{vapour} - H_{liquid} = - \Delta H_{condensation}$$

Vaporization of Liquids

- Molecules can escape from the liquid into the vapour.
- Gas phase molecules can condense into the liquid.
- An equilibrium is set up between evaporation and condensation.
- The result is that there is constant partial pressure of the vapour called the vapour pressure.
- This will be a strong function of temperature.

Vapor Pressure

$$\text{Liquid} \underset{\text{condensation}}{\overset{\text{vaporization}}{\rightleftharpoons}} \text{Vapor}$$

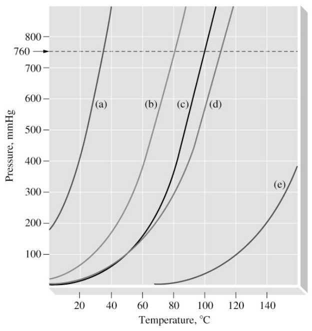


Determining Vapour Pressure

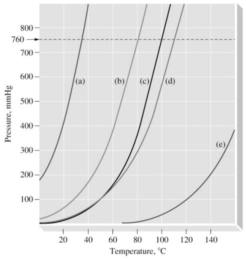
- Vapour pressures usually determined by allowing a liquid to come into equilibrium with its vapour and using the ideal gas law to determine the equilibrium pressure.

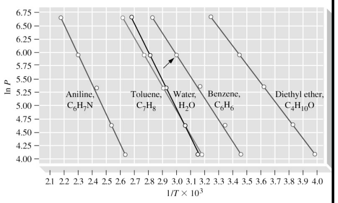
Vapour pressure curves for:

- (a) Diethyl ether, $C_4H_{10}O$;
- (b) benzene, C_6H_6;
- (c) water;
- (d) toluene, C_7H_8;
- (e) aniline, C_6H_7N.



Temperature Dependence of Vapour Pressure





$$\ln(\mathrm{P}) = -\frac{\mathrm{A}}{\mathrm{T}} + \mathrm{B}$$

Temperature Dependence of Vapour Pressure

- From thermodynamics we can show that
  A = $\Delta H_{vap}/R$
- The equation is usually expressed in terms of two temperatures to give the Clausius-Clapeyron equation.

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Boiling and Boiling point

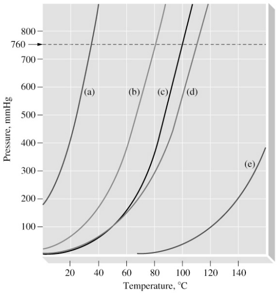
- Suppose vaporization occurs in the bulk liquid.
  - A bubble of vapour forms
- If the vapour pressure is less than the external pressure the bubbles will collapse.
- If the vapour pressure is equal to or greater than the external pressure the bubbles will rise to the surface and escape.
    - This is boiling, and the temperature is the boiling point.
    - The temperature at which the vapor pressure is one atmosphere is the normal boiling point.

What else can we learn here?

At 80° the vapour pressure of water (c) is ~350 torr.

If we force the pressure to be 300 torr, all the liquid will evaporate so we have only vapour.

If we force the pressure to be 500 torr, no evaporation occurs so we have only liquid.

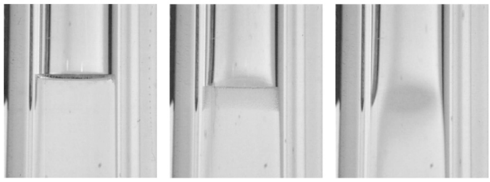


The curve tells us about phases.

What if there is no external pressure?

- If the liquid is heated in a sealed container the pressure will just continue to rise.
- The density of the vapour will rise and eventually it will be the same as the liquid
  - The distinction between the vapour and liquid disappears
  - There is no meniscus
  - This is the critical point

Critical point



About 10 °C below T_c

About 1 °C below T_c

Critical temp T_c

There is no distinction between liquid and vapour. We must talk about a fluid.

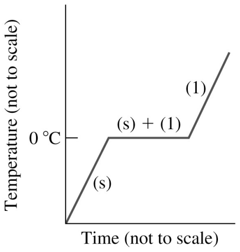
Properties of solids

- In solids the intermolecular forces are large enough that the molecules are held in place.
- There is a temperature at which enough energy is provided to overcome these forces and the solid melts.
- This is the melting point or freezing point.
- The enthalpy for this process is the heat of fusion.

$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H_{fus} = H_{liquid} - H_{solid}$

Properties of Solids

- We can determine the melting point from a heating curve.
- This gives the temperature and shows that the temperature remains constant while there are two phases present.



Properties of Solids

- The reverse is a cooling curve.
- There is "overshoot" in the cooling.
  - This is supercooling and arises because the liquid needs something to crystallize on.

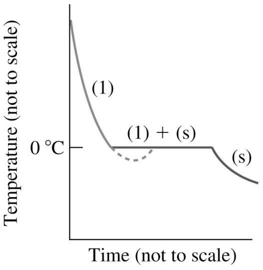


Fig. 13-14

Sublimation

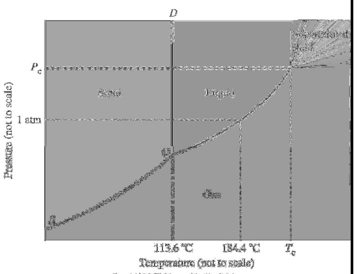
- Solids are generally not volatile as liquids at a given temperature.
- The direct passage of molecules from the solid to the vapour is called sublimation.
- We can obtain vapour pressure curves for sublimation.

Phase diagrams

- A phase diagram is a plot (usually pressure as a function of temperature) that summarizes information about the phases of a compound.

Phase Diagram for Iodine

- The diagram shows the phases as a function of pressure and temperature.
- WATCH OUT
  - The pressure here is the pressure of the compound.



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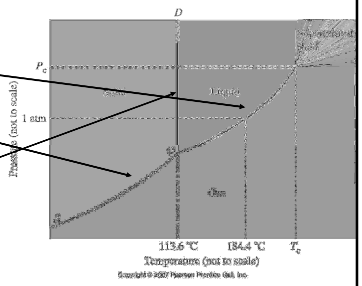
Phase Diagram for Iodine

- Vapour pressure curve

•Sublimation curve

•fusion curve



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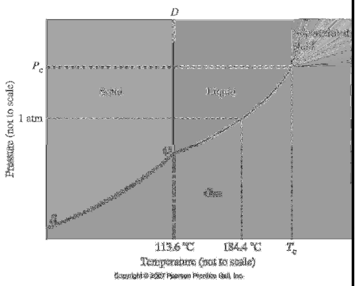
Phase Diagram for Iodine

- The critical point (***C***) is shown as the end of the vapour pressure line.
- The triple point (***O***) shows the only conditions where three phases exist in equilibrium.



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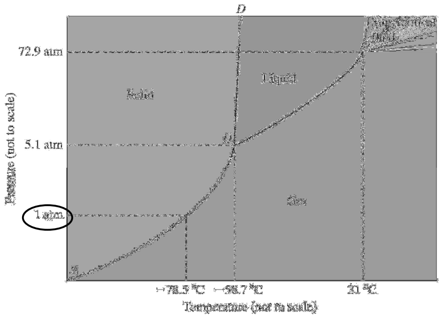
Phase Diagram for CO_2



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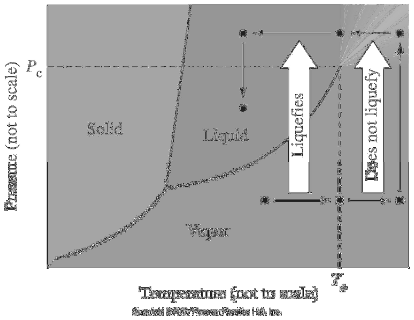
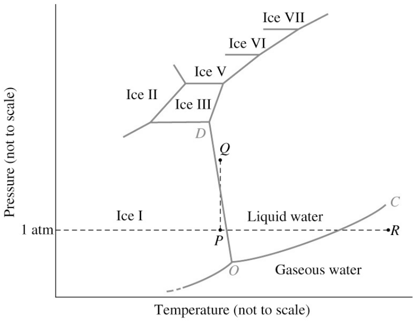
Critical point and supercritical fluid



Phase Diagram for H_2O

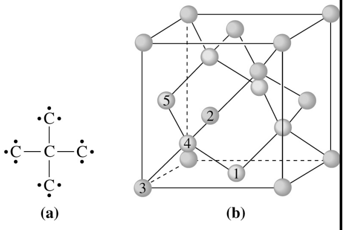


Chemical bonds as intermolecular forces

- Intermolecular forces are weak compared with the σ and π bonds between atoms.
  - As the dispersive forces increase (molecules get bigger/heavier) the molecules exist as:
    - gases
    - liquids
    - solids
- In a few cases there are real covalent bonds between molecules (network covalent solids).

Network covalent solids: Diamond

- The Lewis structure suggests the carbon is tetrahedral. This points to sp^3 hybridization.
- Each atom is bonded to four others.
- Atoms 1, 2, 3 and 5 form a tetrahedron with atom 4 at the centre.

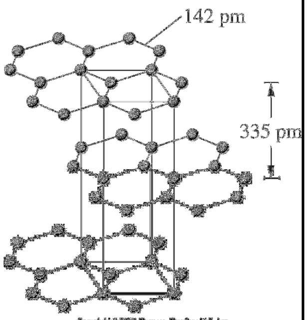


Network covalent solids: Silicon carbide

- Substituting silicon atoms for half the carbon atoms gives silicon carbide.
- Both diamond and silicon carbide are extremely hard.
- They do not conduct electricity.
- They melt or sublime at very high T.
  - SiC sublimes at 2700 °C
  - diamond melts above 3500 °C.

Network covalent solids: Graphite

- This bonding involves the orbital set $sp^2 + p$.
- The three sp^2 orbitals are in a plane at angles of 120°.
- The p orbital is above and below the plane and provides the bonding between planes.
- Bonding within layers is strong, but between layers is much weaker.



Graphite

- Because bonding between layers is weak, the layers can glide over one another rather easily so it is a good lubricant.
- The p electrons can migrate through the planes of carbon atoms so graphite conducts electricity.

Ionic solids

- Starting point:
  - We can assess how difficult it is to break up an ionic crystal into its ions by determining the lattice energy of a crystal.
  - The lattice energy is the energy given off when gas phase ions come together to form one mole of a solid ionic compound.

Lattice energy

- This is determined using Hess’s law (known as the Born-Fajans-Haber cycle).

Enthalpy diagram for the formation of NaCl(s)

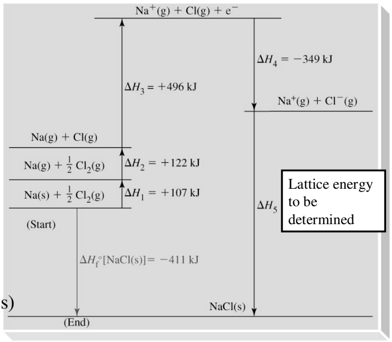
$Na(s) \rightarrow Na(g)$

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$

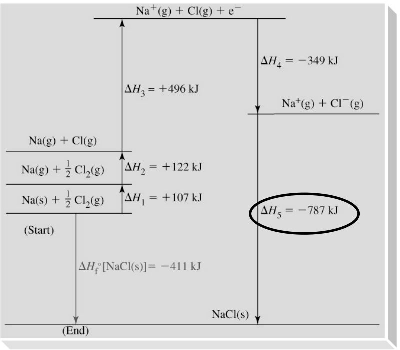
$Na(g) \rightarrow Na^+(g) + e^-$

$Cl(g) + e^- \rightarrow Cl^-(g)$

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$



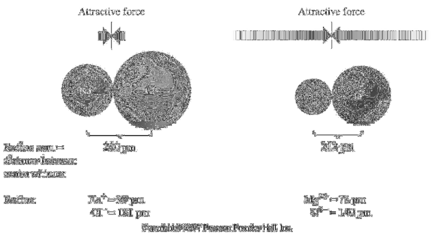
Enthalpy diagram for the formation of NaCl(s)



Interionic Forces

- The attractive force increases with increased charge on the ions and with decreased ionic sizes.

LE= -787 kJ mol^{-1} LE = -3795 kJ mol^{-1}



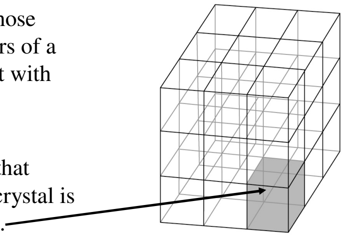
Interionic Forces

- For most ionic compounds, lattice energies so large that:
  - ions do not readily detach themselves from the crystal and pass into the gaseous state.
  - Ionic solids do not sublime at ordinary temperatures.
- The higher the lattice energy of an ionic compound, the higher is its melting point.

Crystal Structures

- In crystals we observe a regularity in shape.
  - This is due to an underlying regular pattern in the arrangement of atoms, ions, or molecules.
  - We will look at some arrangements of atoms/ions in crystal structures.
  - Understanding the structure at the molecular (ionic) level can explain the macroscopic properties.

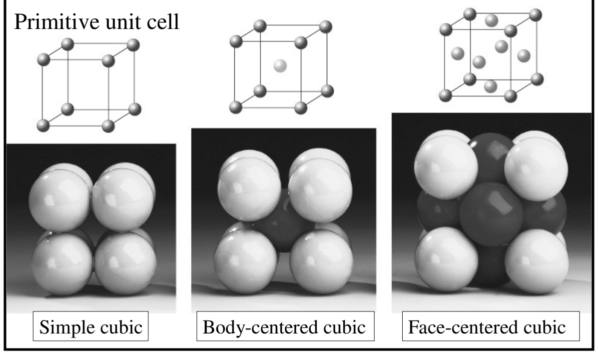
Crystal Structures



- We will concentrate on cubic structures, those atoms at the corners of a cube. We will start with neutral atoms.
- The smallest unit that repeats itself in a crystal is called the unit cell.

Unit cells in the cubic crystal system

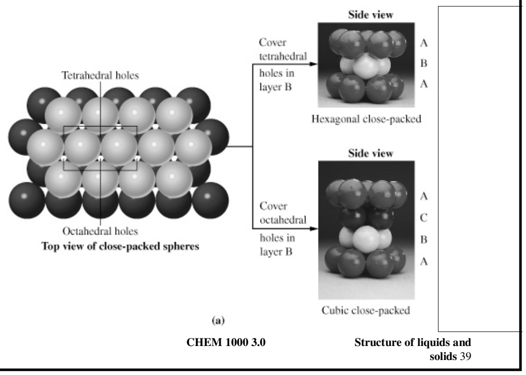
Primitive unit cell



Closest Packed Structures

- Spheres will arrange themselves to minimize the space between them.
- This is called close packing.
- We will look at the possible closest packing then try to relate it to the unit cell.

Closest Packed Structures

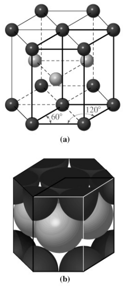


Closest Packed Structures (continued)

The cubic close-packed structure has a face-centered cubic unit cell.

Closest Packed Structures (continued)

The hexagonal close-packed structure does not have a cubic unit cell.



Descriptor of the packing

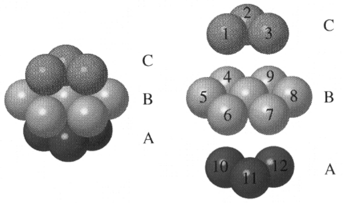
- We commonly use the coordination number and the number of atoms in a unit cell to describe the crystal structure.

Coordination number

- The number of atoms with which a given atom is in contact.
- For a body centered cubic, the central atom is in contact with the corner atoms. Hence the coordination number is 8.

Body-centered cubic

Coordination number



ccp

- The coordination number is 12 for the cubic close packed, or face centered cubic structure.

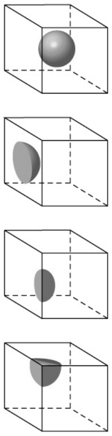
Closest Packed Structures

- The best examples of crystal structures based on the closest packing of spheres are found among the metals.

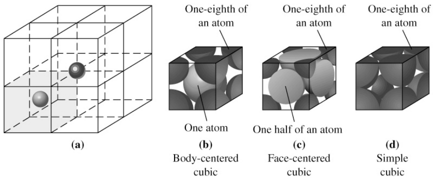
TABLE 12.6 Some Features of Crystal Structures in Metals

	Coordination Number	Number of Atoms per Unit Cell	Examples
Hexagonal closest packed (hcp)	12	2	Cd, Mg, Ti, Zn
Face-centered cubic (fcc)	12	4	Al, Cu, Pb, Ag
Body-centered cubic (bcc)	8	2	Fe, K, Na, W

Atoms per unit cell



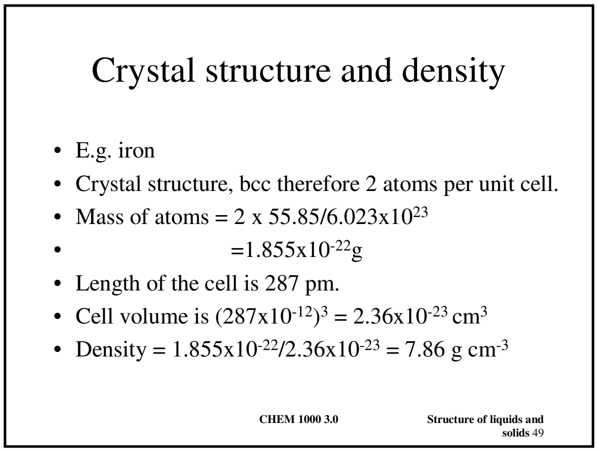
- Not every atom in a unit cell is only in that cell. It can be in more.
- We can determine the actual number in a unit cell by considering what fraction of each atom is in the cell.



- In the fcc unit cell, the corner atoms account for 1/8 × 8 = 1 atom, and those in the center of the faces for ½ × 6 = 3 atoms. For a total of 4 atoms.
- The simple cubic unit cell contains 1 atom per unit cell.
- The bcc contains 2 atoms per unit cell.

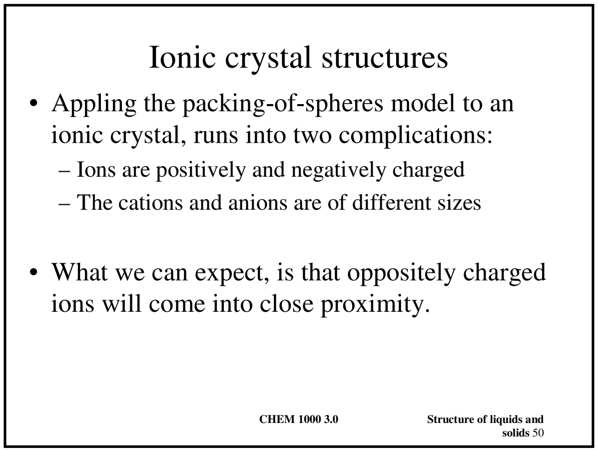
Crystal structure and density

- We can check/understand the crystal structure by predicting a density.
- We know the number of atoms in a unit cell so we can determine its mass.
- We know the size of the unit cell so we can get its volume.
- Density = mass/volume



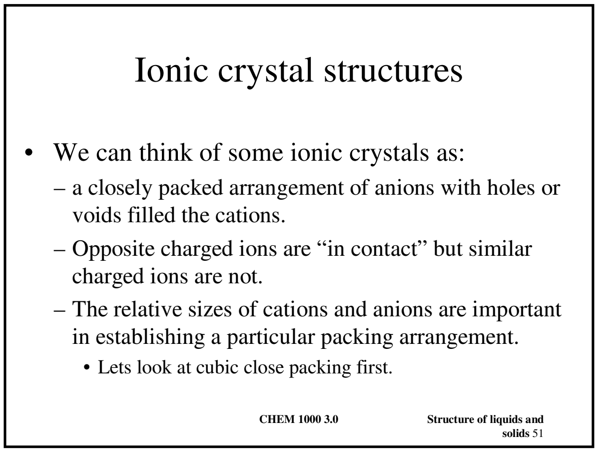
Crystal structure and density

- E.g. iron
- Crystal structure, bcc therefore 2 atoms per unit cell.
- Mass of atoms = 2 x 55.85/6.023x10^{23}
- =1.855x10^{-22}g
- Length of the cell is 287 pm.
- Cell volume is (287x10^{-12})^3 = 2.36x10^{-23} cm^3
- Density = 1.855x10^{-22}/2.36x10^{-23} = 7.86 g cm^{-3}



Ionic crystal structures

- Appling the packing-of-spheres model to an ionic crystal, runs into two complications:
  - Ions are positively and negatively charged
  - The cations and anions are of different sizes
- What we can expect, is that oppositely charged ions will come into close proximity.

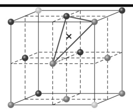


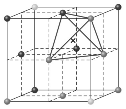
Ionic crystal structures

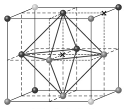
- We can think of some ionic crystals as:
  - a closely packed arrangement of anions with holes or voids filled the cations.
  - Opposite charged ions are “in contact” but similar charged ions are not.
  - The relative sizes of cations and anions are important in establishing a particular packing arrangement.
    - Lets look at cubic close packing first.

Ionic crystal structures

- The anion adopts the cubic closest packed structure (FCC) and the cation fits in one of the holes between the close-packed spheres.
- There are three kinds of holes each of a different size.


(a) Trigonal hole


(b) Tetrahedral hole


(c) Octahedral hole

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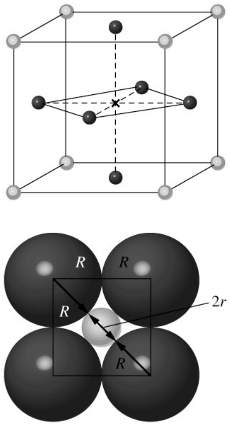
Possible size of a cation

- •Take the octahedral hole
- •If the anion has radius R and the cation radius r
- •The maximum possible value for r without distorting the anions can be obtained from geometry



Possible size of a cation

$$(2R)^2 + (2R)^2 = (2R + 2r)^2$$

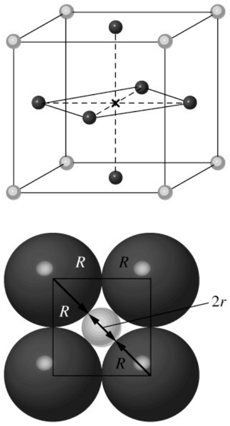
$$\Rightarrow r = 0.414R$$

Similarly for terahedral holes

r = 0.225R

For trigonal holes

r = 0.155R



Holes geometry and ionic radius

- To get bigger holes the crystal structure needs to be simple cubic arrangement which has a hole size of r = 0.732R.

Holes geometry and ionic radius

- So what really happens?
  - A cation that is a bit bigger than the hole size will displace the anions. This actually helps stability as it reduces the interaction between the anions.
  - e.g. if a cation is to occupy a tetrahedral hole the ion should be bigger than the tetrahedral hole, but smaller than the octahedral hole.

The Radius-Ratio Rule

The following table provides guidelines for the ionic structures expected for various cation/anion radius ratios:

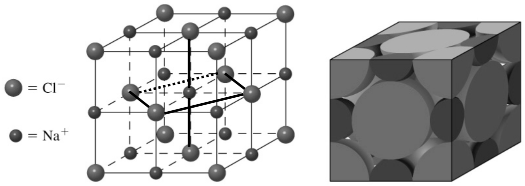
	hole occupied by cation
$0.155 < r^+/R^- < 0.225$	trigonal (hole r=0.155R)
$0.225 < r^+/R^- < 0.414$	tetrahedral (hole r=0.225R)
$0.414 < r^+/R^- < 0.732$	octahedral (hole r=0.414R)
$0.732 < r^+/R^-$	cubic (hole r=0.732R)

Example NaCl (Cl^- in FCC)

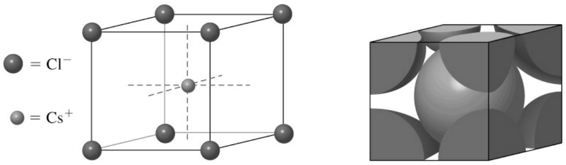
- Radius ratio $r_{Na+}/R_{Cl-} = 0.55$
  - Expect Na^+ in an octahedral hole
- Unit cell contains $1+1/4*12 = 4\ Na^+$

  $6*1/2 + 8*1/8 = 4\ Cl^-$

  The chemical formula is right



Example CsCl (Cl^- in simple cubic)



- $r_{Cs+}/R_{Cl-} = 0.934$, so cubic makes sense
- The unit cell contains 1 Cs^+ and $8 \times (1/8) = 1\ Cl^-$ corresponding to the formula CsCl.