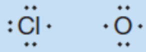
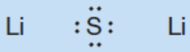
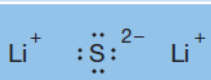
<u>**Covalent molecular and ionic substances**</u>

DRAWING ELECTRON-DOT STRUCTURES

	Example: Li and S	Example: O and Cl
1 Determine the number of valence electrons on the atom of each element (by using group number or by counting along the relevant period of the Periodic Table, ignoring transition elements) and draw this number of dots around the symbol for each element.		
2 Decide how many electrons each atom needs to gain or lose to obtain a noble gas configuration.	Li needs to lose one *e*– (to become like He). S needs to gain two *e*– (to become like Ar).	O needs to gain two *e*– (to become like Ne). Cl needs to gain one *e*– (to become like Ar).
3 Decide whether the compound will be ionic or covalent: if one atom wants to gain electrons while the other wants to lose, the compound will be ionic; if both want to gain electrons then the compound will be covalent	Compound will be ionic.	Compound will be covalent.
4 **For an ionic compound**		
a Work out the number of atoms of each type that must combine so that the total number of electrons lost equals the total number gained.	Need two Lis for each S (so total number of *e*⁻s lost and gained is two).	
b Draw the atomic symbols with the electrons transferred.		
c Put the appropriate charges on the symbols; each electron lost produces one positive charge and each electron gained produces one negative charge. You now have the electron-dot structure for the compound.		
d If asked for it, write the formula for the compound.	Li_2S	
5 **For a covalent compound**		
a Work out the number of atoms of each type needed for all the atoms to obtain noble gas configuration.[a]		To gain the required two *e*⁻s O needs to share electrons with *two* Cls; but Cl only needs to share with *one* O so we need *two* Cls for each *one* O.
b Pair up electrons to give each atom a noble gas configuration. This is the required electron-dot structure.		
c If a structural formula is required, draw it by using a dash for each shared pair of electrons (each covalent bond).		Cl—O—Cl
d If a molecular formula is required, write it.		Cl_2O

IONIC EQUATIONS WITH ELECTRON-DOT STRUCTURES

We can represent the formation of ions from metal and non-metal atoms by using equations involving electron-dot structures. For *sodium* and *chloride* ions:

$$\mathrm{Na}\cdot \longrightarrow \mathrm{Na}^+ + e^-$$

$$:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot + e^- \longrightarrow :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^-$$

where e^- and $\cdot$ each represent an electron. For the formation of the compound sodium chloride we can add these equations together to get:

$$\mathrm{Na}\cdot + :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot \longrightarrow \mathrm{Na}^+ + :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^- \quad \text{(the formula is NaCl)}$$

Similar equations for the formation of sulfide and magnesium icons are:

$$\cdot\underset{\cdot\cdot}{\ddot{\mathrm{S}}}\cdot + 2e^- \longrightarrow :\underset{\cdot\cdot}{\ddot{\mathrm{S}}}:^{2-}$$

$$\mathrm{Mg}: \longrightarrow \mathrm{Mg}^{2+} + 2e^-$$

To make equations for the formation of sodium sulfide and magnesium chloride, the appropriate ion-formation equations are added (after doubling one equation in each pair in order to balance out the electrons):

$$2(\mathrm{Na}\cdot) + \cdot\underset{\cdot\cdot}{\ddot{\mathrm{S}}}\cdot \longrightarrow 2\mathrm{Na}^+ + :\underset{\cdot\cdot}{\ddot{\mathrm{S}}}:^{2-} \quad \text{(the formula is } Na_2S\text{)}$$

$$\mathrm{Mg}: + 2(:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot) \longrightarrow \mathrm{Mg}^{2+} + 2(:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^-) \quad \text{(the formula is } MgCl_2\text{)}$$

EXERCISES

24 Draw electron-dot diagrams and give molecular formulae for the covalent molecules formed between:

- **a** hydrogen and iodine
- **b** two bromine atoms
- ***c** nitrogen and hydrogen
- ***d** sulfur and fluorine

25 Explain why:

- **a** the compound formed between fluorine and oxygen is F_2O and not FO_2 or FO
- ***b** ammonia is NH_3 and not NH_2 or NH_4

26 Decide the formula you would expect, and give your reasons, for the compound formed between:

- **a** sulfur and chlorine
- **b** hydrogen and iodine
- ***c** silicon and hydrogen
- ***d** phosphorus and fluorine

27 **a** Draw electron-dot structures for the bromide ion and the oxide ion.

- ***b** In a very small number of compounds nitrogen exists as the nitride ion. Draw an electron-dot structure for this ion.
- **c** Draw electron-dot structures for barium and caesium atoms and the ions they form.

28 Draw electron-dot diagrams (in the form of equations) that show the formation (from atoms)

a of the following ions:

i Ca^{2+} **ii** O^{2-} **iii** Al^{3+} **iv** F^-

b of the following compounds:

i calcium oxide **ii** aluminium fluoride

Answers:

24 a  HI **b**  Br_2

25 a O (2, 6) needs to gain two electrons; F (2, 7) needs to gain one. To satisfy both drives two F atoms combine with one O atom:

For FO and FO_2 at least one atom would have only 7 electrons and so would not be stable:

26 a SCl_2; S needs to gain 2 electrons, Cl needs to gain 1, so we need two Cls for each S.

b HI; each atom needs to gain just 1 electron.

27 a $:\ddot{\underset{..}{Br}}:^-$ $:\ddot{\underset{..}{O}}:^{2-}$

c *Atoms*: Ba: Cs· *Ions*: Ba^{2+} Cs^+

28 a **i** Ca: ⟶ Ca^{2+} + $2e^-$

ii $\cdot\ddot{\underset{..}{O}}\cdot$ + $2e^-$ ⟶ $:\ddot{\underset{..}{O}}:$

b **i** Ca: + $\cdot\ddot{\underset{..}{O}}\cdot$ ⟶ Ca^{2+} + $:\ddot{\underset{..}{O}}:^{2-}$

Contrasting properties of covalent molecular and ionic substances

Ionic substances	Covalent molecular substances
solids at room temperature	at room temperature, generally *gases* (N_2, SO_2, NH_3) or *liquids* (H_2O, CCl_4, methanol CH_3OH); a few are solids (I_2, PCl_5, CBr_4)
high melting points (typically above 400°C) and *high boiling points* (typically over 1000°C)	*low melting points* (generally below 200°C) and *low boiling points* (generally below 400°C)
hard and brittle	when solid they are *soft*
as solids *they do **not** conduct electricity*	pure covalent substances *do not conduct electricity* either as solids or as liquids
when molten or when in aqueous solution *they **do** conduct electricity*.	In aqueous solution *do not conduct electricity* (unless they actually react with water to form ions)

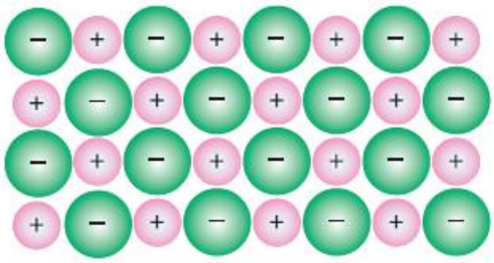
• ***explain the relationship between the properties of conductivity and hardness and the structure of ionic, covalent molecular and covalent network compounds***

• ***describe ionic compounds in terms of repeating three dimensional lattices of ions***

Properties of ionic substances

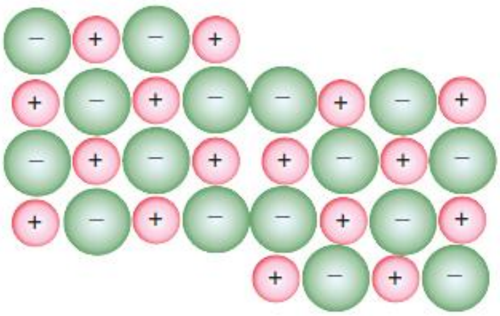
Melting an ionic solid means breaking up the orderly arrangement of ions. As the electrostatic forces between ions are strong, much energy (and therefore a high temperature) is needed to do this. Boiling an ionic substance means producing a vapour that consists of well-separated ion pairs. This requires an even greater amount of energy and so an even higher temperature is needed.

(a)



Ionic substances consist of orderly arrays of positive and negative ions:
(a) a two-dimensional array of ions,

The strong electrostatic attraction between pairs of ions makes ionic substances hard. If the orderly array of ions is disturbed by applying a strong force, then ions of the same charge come close together.



Ionic substances are brittle because distorting the crystal brings like charges together and they repel one another: this causes the crystal to break

They then repel each other and this causes the crystal to shatter. This means that ionic crystals are brittle.

Solid ionic compounds do not conduct electricity because in the solid the ions are tightly bound into an orderly array and so are unable to move towards a charged electrode. However when ionic substances melt, the orderly arrangement of ions is broken up and the ions can move about relatively freely. They can then migrate towards a charged electrode; so molten ionic substances conduct electricity.

Similarly, when ionic substances are dissolved in water, the crystals are completely broken up and the solutions consist of individual ions moving randomly about through the water.

These freely moving ions can migrate towards oppositely charged electrodes; so solutions of ionic substances conduct electricity.

• ***explain why the formula for an ionic compound is an empirical formula***

Empirical formulae

The empirical formula of a compound represents its atomic or ionic composition expressed as a simple whole number ratio.

Examples:

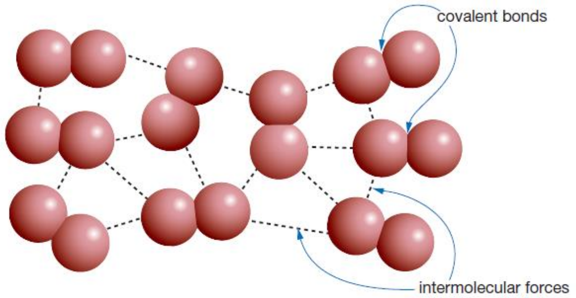
1. Ethane is a covalent molecular compound with the molecular formula C2H6. Its molecules are composed of two atoms of carbon bonded to six atoms of hydrogen. The C : H ratio of 2 : 6 is not the simplest ratio.
The simplest ratio is 1 : 3, so the empirical formula of ethane is CH3.

2. Benzene is also a covalent molecular compound. Its molecular formula is C6H6. The C : H ratio of 6 : 6 is not the simplest ratio. The simplest ratio of atoms is 1 : 1, so the empirical formula of benzene is CH.

Ionic compounds however, have their lattices continuous three dimensions, and there are no discrete molecules as in molecular compounds. The simplest repeating unit of the crystal is called the *unit cell*.
The simplest ratio of ions can be determined for the unit cell. This simple ratio is the empirical formula of the ionic compound.

Properties of covalent molecular substances

While the bonding forces holding atoms together within a covalent molecule are very strong, the forces between one molecule and its neighbours are quite weak. These weak forces between pairs of molecules are called **intermolecular forces**.



In liquid bromine there are weak intermolecular forces (dotted lines) between each bromine molecule and its neighbours. Boiling overcomes these relatively weak forces; it does not break the strong covalent bonds holding pairs of bromine atoms together as molecules

There is a strong covalent bond holding the two bromine atoms together within each bromine molecule, Br_2. There are only weak intermolecular forces (the dotted lines) between pairs of bromine molecules.

Boiling involves separating molecules from one another. This means that boiling overcomes intermolecular forces: it does not break any covalent bonds. Because the intermolecular forces holding the bromine molecules to one another in the liquid are weak, bromine has a relatively low boiling point of 58°C; that is, not much energy is required. Similarly in solid bromine, the intermolecular forces holding the molecules to one another are relatively weak (compared with covalent bonds). Melting just involves disrupting the orderly arrangement of molecules; that is, melting, like boiling, only overcomes weak intermolecular forces. Therefore bromine has a relatively low melting point (–7°C).

Bromine is typical of all covalent molecular substances; there are only weak forces holding the molecules to one another and so they have low melting and boiling points.

However the strength of the intermolecular forces does vary from one molecular compound to another. We find that:

the stronger the intermolecular forces in molecular compounds, the higher are the melting and boiling points.

Because these weak intermolecular forces are easily overcome, it is easy to distort a solid covalent molecular substance. This means that such solids are soft.
Because covalent molecules are neutral species, they cannot conduct electricity either as pure substances or in solution (for example iodine, sucrose or urea in water).

EXERCISES

29 Phosphorus trichloride is a liquid with a boiling point of 74°C; it does not conduct electricity. Calcium chloride is a solid with a melting point of 772°C; when molten it conducts electricity. Explain, in terms of bonding, why these two compounds have such different properties.

30 The boiling points of the fluorides of the elements of Period 2 of the Periodic Table are: LiF (1720°C), BeF_2 (1175°C), BF_3 (–101°C), CF_4 (–128°C), NF_3 (–120°C), OF_2 (–145°C) and F_2 (–188°C). Explain why the boiling points of lithium and beryllium fluorides are so much higher than the others.

Answers:

29 PCl_3 is covalent, $CaCl_2$ is ionic.
30 They are ionic compounds whereas the others are covalent.

• ***identify common elements that exist as molecules or as covalent lattices***

COVALENT NETWORK SOLIDS

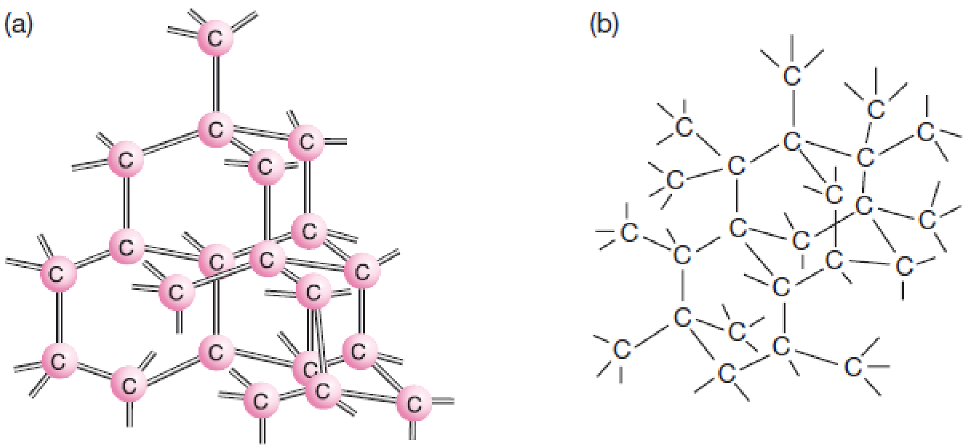
Covalent network solids are solids in which the covalent bonding extends indefinitely throughout the whole crystal.

Covalent network solids are sometimes called **covalent lattice solids** or just **covalent lattices**.

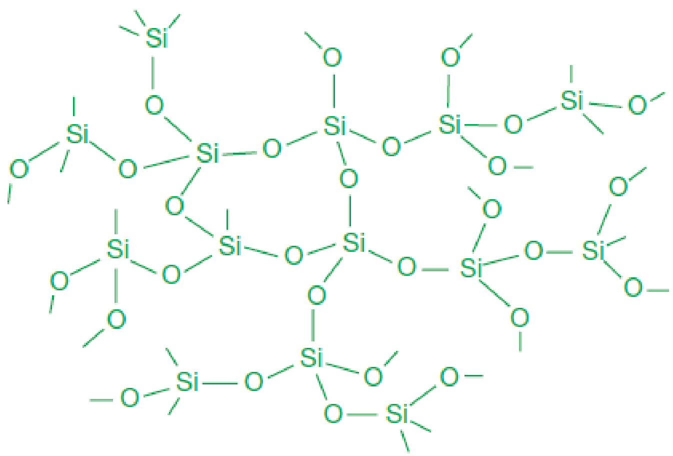
The word **lattice** is used to mean an infinite orderly array of particles. Ionic solids are sometimes called **ionic lattices**.

Carbon in the form of diamond is an example of a covalent network solid. As we expect from the Periodic Table, each carbon atom is covalently bonded to four other atoms, and since we are talking about an element it can only be to four other carbon atoms.

(a) is an exploded view of part of the crystal, showing atoms as spheres and using lines to represent the covalent bonds. The lines have no physical reality: in the actual diamond crystal the atoms are overlapping one another. (b) is the structure chemists usually draw for diamond: each dash or line represents a covalent bond. Literally billions of atoms are bonded together in this way to form what we call a covalent network solid.



The structure of diamond



The structure of silica,

Silica (silicon dioxide or quartz, SiO2) is another example. From the Periodic Table we see that silicon wants to form four covalent bonds while oxygen wants to form two. Therefore in silica each silicon atom is covalently bonded to four oxygen atoms, and each oxygen atom is bonded to two silicon atoms to form an infinite network of covalent bonds.

Covalent lattices have extremely high melting points, typically well above 1000°C (diamond > 3550°C, silica 1700°C).

Elements as covalent molecules or covalent lattices

Several elements exist as covalent molecules:

- H_2, F_2, Cl_2, O_2 and N_2 are diatomic gases.
- Br_2 is a diatomic liquid while I_2 is a diatomic solid.

- Phosphorus and sulfur exist as covalent P4 and S8 molecules respectively.

Some other elements exist as covalent lattices:

- Carbon exists as diamond which is a three-dimensional lattice and as graphite which is a two-dimensional lattice.
- The semi-metals B, Si, Ge, As, Sb and Te closely approximate to covalent lattices though their bonding electrons are not as firmly localised as in diamond.

We have already seen that the noble gases (He, Ne, Ar, Kr, Xe, Rn) exist as monatomic molecules; that is, without any chemical bonding at all.

The majority of the elements, however, display metallic bonding.

Covalent network solids in the Earth

Many substances in the lithosphere are covalent network solids:

- Sand and quartz are silicon dioxide.
- Some gemstones (amethyst and citrine) are silicon dioxide with traces of impurities which provide the colour, while others (emerald, aquamarine, topaz and garnet) are silicates or alumino-silicates which are covalent lattices with some ionic bits incorporated.
- Mica, talc and asbestos are also silicate lattices.
- Clays and zeolites are alumino-silicate lattices, again with some ionic portions.

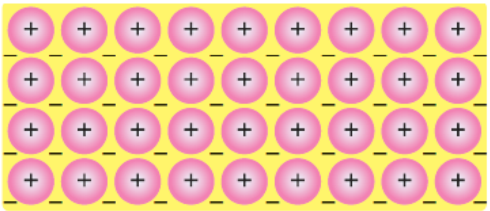
• ***describe metals as three dimensional lattices of ions in a sea of electrons***

METALLIC BONDING

Metals, with the exception of mercury, are solids at room temperature. Most have relatively high melting points and are fairly hard. They are all good conductors of electricity.

These properties arise because a metal consists of an orderly three-dimensional array of positive ions held together by a mobile 'sea' of **delocalised electrons**. The valence electrons break away from their atoms, leaving behind positive ions. These free electrons, called delocalised because they no longer belong to particular atoms, move randomly through the lattice and, by being shared by numerous positive ions, provide the chemical bonding that holds the crystal together.

metallic bond: a strong attractive force that holds metal ions in their crystal lattice; the attraction between metal ions and the sea of mobile electrons



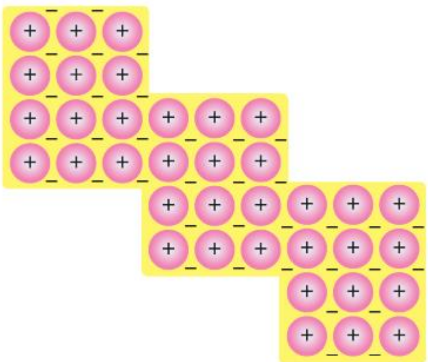
A metal is a three-dimensional lattice of positive ions immersed in a 'sea' of delocalised electrons. For clarity just a two-dimensional 'slice' is shown here

It is the ability of these delocalised electrons to move freely through the lattice that causes metals to be good conductors of electricity. Electric current through a metallic wire is a flow of electrons.

Metals can be bent, rolled into sheets, and drawn into rods and wires. These processes are possible because when the orderly array of positive ions is sheared, the mobile electrons are able to adjust to the new arrangement of positive ions and again provide the 'glue' to hold the whole assembly together.

This contrasts with ionic or covalent lattices; when these are sheared they shatter.

Ionic and covalent lattices are hard but brittle. Metals (generally) are also hard but by contrast they are malleable (able to be rolled into sheets) and ductile (able to be drawn into wires).



The mobile electrons are able to hold the positive ions of metals together even when the metal is distorted. This explains the malleability and ductility of metals

• describe the physical properties used to classify compounds as ionic, covalent molecular or covalent network

SOLIDS SUMMARISED

Types of solids and their properties

	MOLECULAR SOLIDS	LATTICE SOLIDS: metallic	LATTICE SOLIDS: ionic	LATTICE SOLIDS: covalent network[a]
melting and boiling points	low	variable	high	high
conduct electricity?	no	yes	as solid, no molten, yes	no
hardness and/or workability	soft	variable hardness; malleable and ductile	hard and brittle	hard and brittle
forces holding particles together in the solid	intermolecular	delocalised electrons (metallic bonding)	electrostatic	covalent bonding throughout the crystal

[a] *sometimes called covalent lattice solids*

EXERCISES

32 Silicon dioxide and carbon dioxide have similar formulae, SiO_2 and CO_2, yet one is an extremely hard solid while the other is a gas at room temperature. Explain why they are so different.

***33** The melting points and electrical conductivities of seven elements are as follows:

Element	A	B	C	D	E	F	G
Melting point (°C)	113	650	3550	1280	2030	1083	44
Conductivity[a]	10^{-20}	23	10^{-17}	29	10^{-10}	58	10^{-15}

[a] *of a 1 metre cube in megohm*$^{-1}$.

a Which elements are metals?
b Which elements are made up of discrete small covalent molecules?
c Which elements are covalent lattices?
d Explain why each of these three classes of elements has the properties given in the table.

Answers:

32 CO_2 exists as small discrete molecules with only weak intermolecular forces between any one molecule and its neighbours. SiO_2 is a covalent lattice with strong covalent bonding extending throughout the whole crystal.