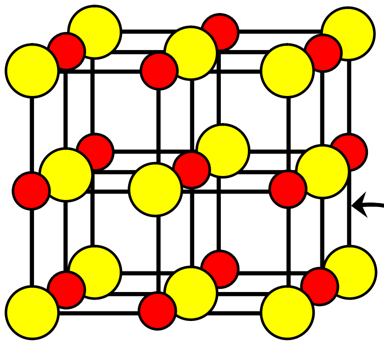
Bonding in Elements and Compounds

- Structure of solids, liquids and gases
- Types of bonding between atoms and molecules
  - **Ionic**
    - Many compounds between metals & non-metals (salts), e.g. NaCl, $MgCl_2$, $MgSO_4$
  - **Covalent**
    - **Giant molecular**
      - Covalent bonds hold all the atoms or molecules together in a giant molecule, e.g. diamond (C), quartz (SiO2), silicon (Si), silicon carbide (SiC)
    - **Simple molecular**
      - Covalent bonds between atoms within each molecule, weak intermolecular forces between molecules, e.g sulphur (S_8), H_2O, halogens (F_2, Cl_2, Br_2, I_2)
  - **Metallic**
    - Metals and alloys, e.g. sodium, magnesium, iron, steel, copper, zinc, tin, brass, bronze

Intermolecular Forces (weak)

- instantaneous dipole – induced dipole attractions (van der Waal's)
  - monoatomic
    - Nobel gases (He, Ne, Ar, Xe, Kr)
  - simple molecular covalent
    - Elements, e.g. halogens, sulphur (S_8)
- permanent dipole – permanent dipole attractions (van der Waal's)
  - simple molecular covalent
    - Compounds, e.g. HCl(g), H_2S
- hydrogen-bonds
  - H-{O, N, F} e.g. H_2O, NH_3, HF, CH_3COOH, CH_3CH_2OH

Ionic Bonding



Above: the giant ionic lattice of NaCl – which spheres represent the sodium ions (large or small)?

•An ionic bond is the force of electrostatic attraction between positively charged ions (cations) and negatively charged ions (anions).

•Unlike charges attract, like charges repel.

•Many compounds of metals and non-metals are ionic (why?) and all Group I and Group II metal / non-metal compounds are ionic, e.g. NaCl, $MgCl_2$, $CaSO_4$, KNO_3.

Note: the sticks in this diagram DO NOT represent the ionic bonds since ionic bonds act in all directions!

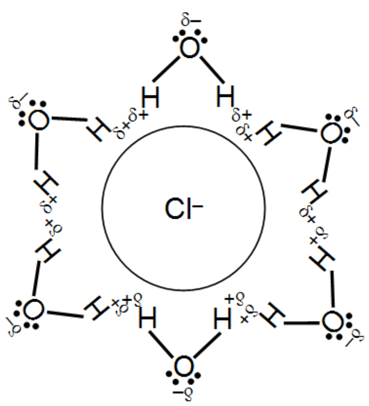
Physical Properties of Ionic Compounds:

•Hardness: ionic bonds are strong and rigid and so ionic compounds tend to be hard, high melting point solids.

•Brittleness: unlike metallic bonds, ionic bonds are rigid and so break suddenly when enough force is applied – ionic solids tend to be brittle.

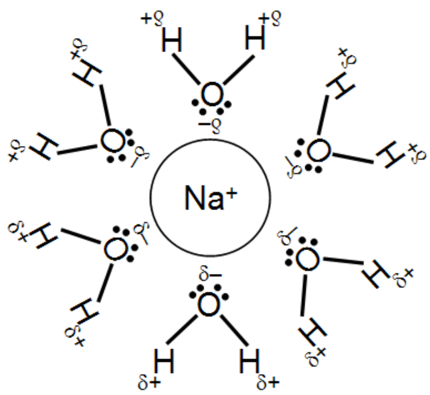
•Electrical conductivity: to conduct electricity we need mobile charge carriers. In metals these are the delocalised electrons. In ionic solids the ions are held in a rigid ionic lattice and are not free to move, so ionic solids are poor conductors of electricity. However, when molten (fused) ionic solids do conduct electricity.

•Solubility: so long as the ionic bonds are not too strong, ionic solids dissolve in water (and other polar solvents) since polar water molecules surround the ions and partially screen the ionic attraction, ripping them from the lattice:



Attraction between ions and the charges on water molecules causes them to become surrounded by shells of water molecules, called solvation shells.

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



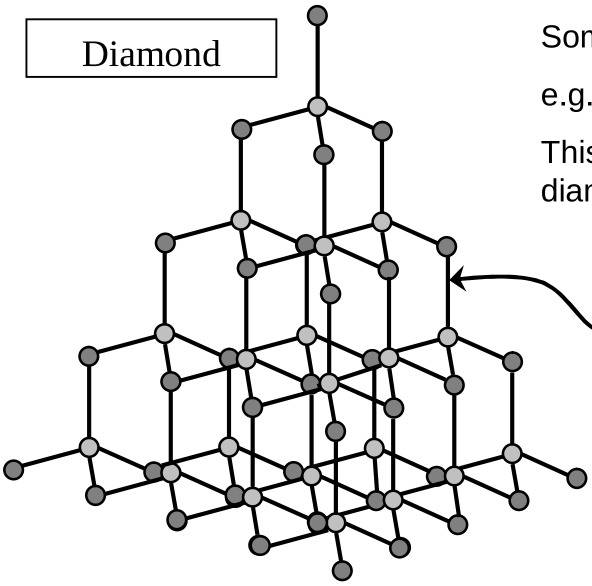
•Conductivity in solution: although the solvation shells partially screen the electric charge of the ions, enough charge remains to enable the ions in solution to conduct electricity, since ions in solution are mobile charge carriers. The positive ions move toward the negative electrode (cathode) and are called cations; negative ions move toward the positive electrode and are called anions.

Covalent Compounds

Giant covalent molecules / lattices

•All the atoms are bonded together into a giant molecule.

•Some elements, e.g. diamond (carbon), silicon – both have the 'diamond' structure:



Some compounds also have the 'diamond' structure:

e.g. quartz (SiO_2, crystalline silica / silicon dioxide)

This lattice can extend indefinitely – a single crystal of diamond or quartz is a single giant molecule!

These lines do represent covalent bonds, each formed by one pair of shared electrons.

Physical Properties of Giant Covalent Substances

•Poor electrical conductivity: the atoms are neutral and held together by rigid covalent bonds and the electrons are not free to move, so these materials are poor electrical conductors and are insulators.

•Hardness and strength: covalent bonds are strong, in diamond each carbon makes 4 covalent bonds with neighbouring atoms, to break diamond all these bonds must be broken – diamond is very hard and strong (but brittle, since the bonds are rigid and sufficient force will snap them suddenly). Diamond is one of the hardest known materials and makes excellent drills (e.g. oil drills).

•High melting / boiling points: To vapourise diamond, each of the 4 strong covalent bonds around each atom must be broken – this takes a lot of heat energy! Diamond: m.p = 3500ºC (at high pressure, more at atmospheric pressure!)

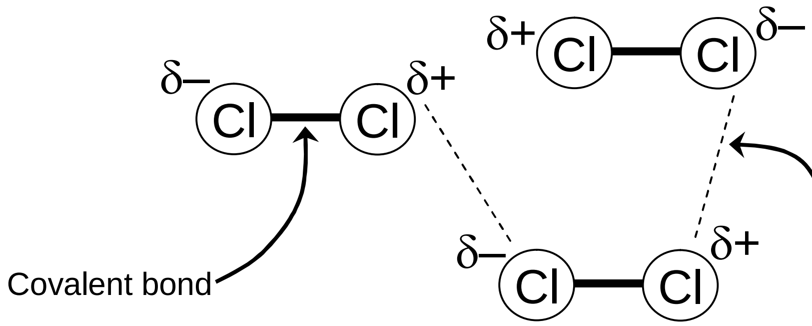
•Insolubility: The atoms are neutral and so water is not attracted to the atoms and water molecules can not rip them away from the lattice – diamond is totally insoluble in water!

Simple Molecular Covalent Substances

These materials are made up of simple discrete molecules, not giant molecules like diamond.

E.g. halogens, sulphur, hydrogen halides, water.

Covalent bonds exist between the atoms within the molecules, weak intermolecular forces between molecules.

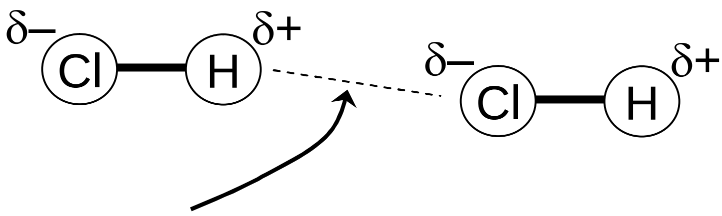


1. Instaneous dipole - induced dipole attractions

Chlorine gas comprises diatomic molecules, Cl_2, which can temporarily require bond dipoles (δ^+-δ^-) weak forces of electric attraction occur between opposite dipoles on neighbouring molecules.

Instantaneous-induced dipole-dipole attractions are transient and constantly form and break as the molecules in chlorine gas move around (due to thermal motion).

Weak intermolecular force of the van der Waal's instantaneous-induced dipole type.



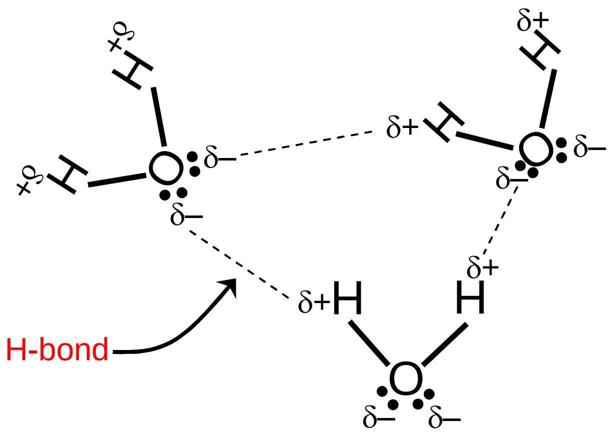
Weak intermolecular force of the van der Waal's permanent-permanent dipole type – stronger than instaneous-induced dipole attractions, which are also present.

2. Permanent dipole - permanent dipole attractions

In hydrogen halides, like hydrogen chloride gas, there are permanent bond dipoles (due to the difference in electronegativity between H and Cl) in addition to induced dipoles = stronger bond dipoles.

HCl is odd in that it breaks up into ions in aqueous solution, forming hydrochloric acid:

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

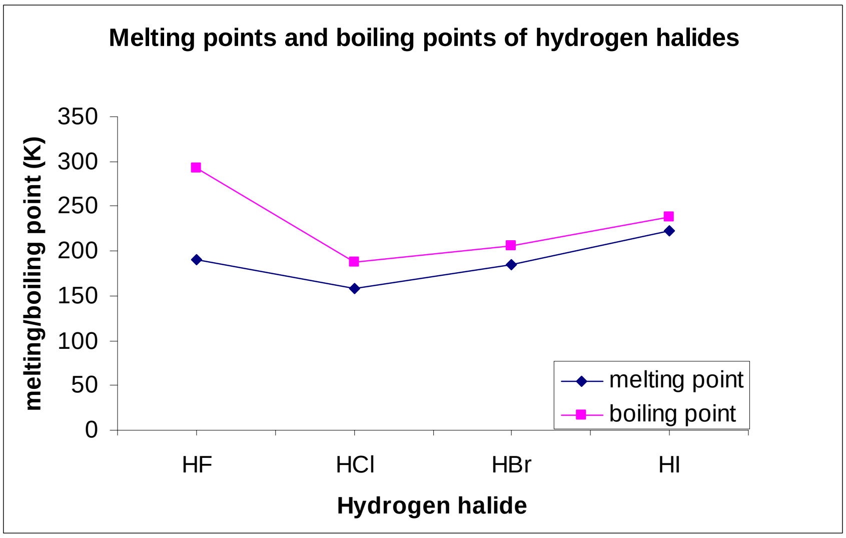


3. H-bonds (hydrogen bonds):

- When H is covalently bonded to O, N or F, the difference in electronegativity is great and the bond is highly polarised.
- This produces especially strong permanent-permanet dipole attractions called hydrogen-bonds.
- Strength: H-bonds > permanent-permanent dipole > instantaneous-induced dipole attractions.

Properties of Simple Molecular covalent compounds

Q.1 How can we explain the trends in melting and boiling points in the Group 7 halides shown below?



Explanation:

The molecular mass of the hydrogen halides increases from HF to HI, which will increase the strength of van der Waal's forces and so increase the heat energy needed to separate the molecules and so raise the m.p. from HF to HI. However, HF has a much higher m.p. due to additional stronger H-bonds between the molecules.

Properties of simple molecular compounds:

•Low melting / boiling points: intermolecular forces are weak, so it is easy to separate the molecules by supplying heat, which increases the thermal motion of the molecules until their movements break the forces between them. Many are gases or liquids at room temp.

•Effect of molecular mass: as molecular mass increases, so does the strength of the intermolecular forces (higher mass = more electrons to polarise = larger polarisation = stronger forces of attraction). Thus iodine (I_2) is a solid (which sublimes easily however), whilst Br_2 is a liquid, Cl_2 a gas. Sulphur, S_8 is a solid. As molecular mass increases, it also takes more heat energy to make the molecules vibrate faster.

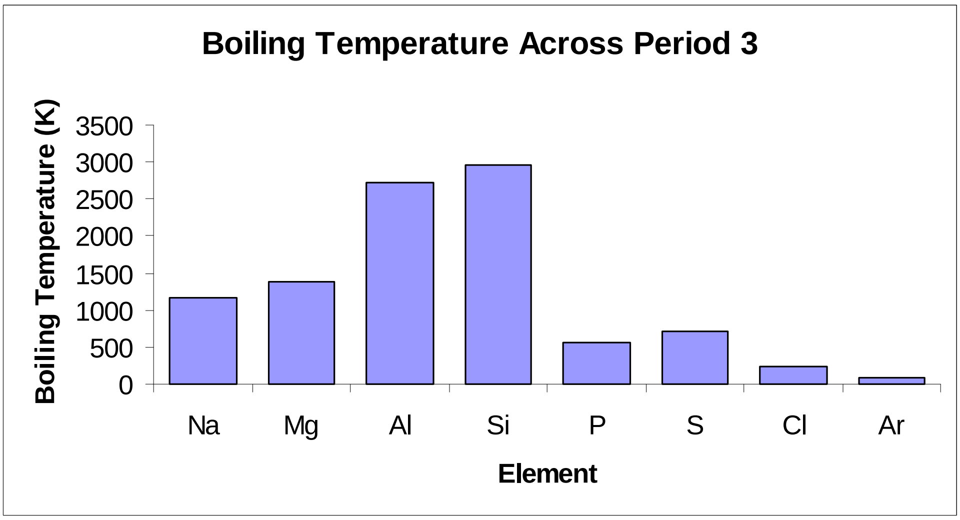
•H-bonds are stronger: H-bonds are usually about 10x stronger than the other intermolecular forces (but 0.1 the strength of a covalent bond). Thus compounds with H-bonding have higher melting / boiling points.

Remember: instantaneous dipole – induced dipole attractions occur between ALL types of molecules in all substances and also between atoms in noble gases and are the WEAKEST of the intermolecular forces.

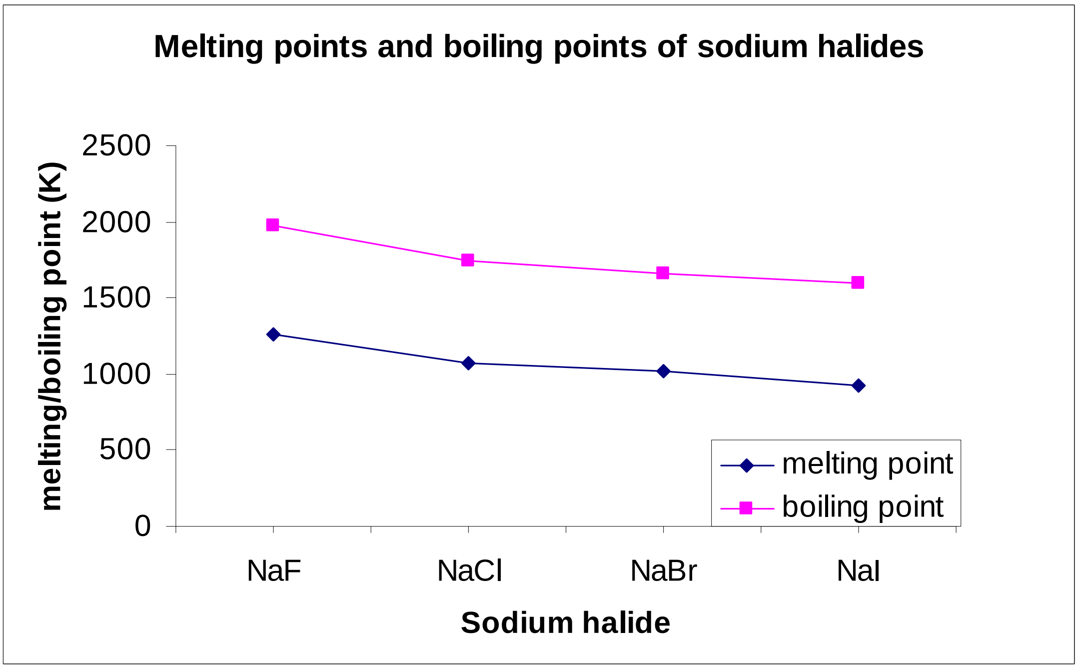
Decreasing order of bond strength:

covalent/metallic/ionic > H-bonds > permanent–permanent dipole > instaneous-induced dipole

Q.2 Explain the trends in boiling point across Period 3 (shown below) by referring to the structure of each element and the chemical bonding within it.



Q.2 Explain the trends in boiling point for the sodium halides (shown below) by referring to the strength of chemical bonding within each.



Q.3 Why are oxygen and nitrogen gases at room temperature? Which would you expect to have the higher boiling point and why?

Answers:

Q.1 Across Period 3, the boiling point (b.p.) increases from sodium to aluminium, since the number of valence electrons contributing to metallic bonding increases from 1 for Na, 2 for Mg and 3 for Al. These valence electrons are delocalised into the ‘electron sea’ surrounding the remaining positively charged ions. It is the Coulomb (electrostatic) attraction between the positively charged ions and the negatively charged delocalised electrons which holds the metal atoms together. As more electrons contribute to the delocalised pool, these electrostatic forces or metallic bonds strengthen and so more heat (kinetic) energy is needed to separate the atoms and the b.p. is higher.

Silicon forms giant covalent molecules in which each Si atom is covalently bonded to 4 other Si atoms. Covalent bonds are strong (comparable to metallic bonds) and as each Si atom forms 4 of them all 4 bonds must be broken to separate the atoms and Si has a very high b.p., even higher than that of Al.

B.p. drops when we reach phosphorous, since P typically forms simple covalent molecules, P_4, with the atoms within each molecule held together by strong covalent bonds, but with the molecules held together by fairly weak van der Waal’s forces of the weaker instantaneous-induced dipole type. White phosphorous is a white waxy solid – the presence of 4 atoms in each molecule makes the van der waal’s forces moderatly strong. Sulphur is also simple molecular and typically forms S_8 molecules held together by instantaneous-induced dipole attractions as in P_4, but with 8 atoms contributing more electrons, enabling the molecules to form stronger dipoles and more and stronger van der Waal’s ‘bonds’. Thus S has a low b.p. but higher than that of P.

Cl only forms diatomic Cl_2 molecules. This makes the van der Waal’s forces between the molecules much weaker than in P and S and Cl has a very low b.p. and forms a gas at r.t.p. (room temperature and pressure). Argon is monatomic and only very weak van der Waal’s forces (due to temporary induced dipoles) exist between the atoms, giving Ar the lowest b.p. in the period.

Q.2.

Although the molecular mass increases from NaF to NaI, the m.p. and b.p. drops from NaF to NaI and so cannot be explained using inertia or van der Waal’s forces. The sodium halides are held together by ionic bonds. Shorter ionic bonds tend to be stronger as the electrostatic forces of attraction are stronger at closer range. The halide ions increase in size from fluoride, F^- to iodide, I^-. This means that in NaI the ions cannot pack as closely togeher as they can in NaF and the bonds are longer in NaI. Thus, NaI has the weakest bonds of all the sodium halides and so requires less energy to separate the ions and so has lower melting and boiling points.

Q.3.

Oxygen and nitrogen form the diatomic molecules, O_2 and N_2, in which pairs of atoms are held together by strong covalent bonds, but the forces between the molecules are of the weaker van der Waal’s type due to instantaneous-induced dipoles. As these molecules are diatomic they have fewer electrons to contribute to these intermolecular forces which are thus especially weak and it takes little energy to separate the molecules and we would expect both to be ghases at r.t.p. However, O has a higher atomic mass than N and so has more electrons to contribute to intermolecular bonding and so should have stronger forces and a higher b.p.

Metallic Bonding

•Occurs in elemental metals and alloys and some non-metals like graphite.

•Depends on the valence electrons – those ‘spare electrons’ that tend to detach when a metal atom ionises. Group 1 metals have 1 valence electron, Group 2 metals have 2.

•Sodium has only one valence electron and a melting point of 97.7°C and is a soft metal.

•Magnesium has 2 valence electrons and a m.p. = 650°C and is quite hard.

•Iron has 3 valence electrons and a m.p. = 1538°C and is a hard metal.

•Tungsten has 6 valence electrons and a m.p. = 3422°C.

Metal	Valence electrons	Melting / boiling point (°C)	Hardness
Sodium (Na)	1	97.7 / 883	Soft (easily cut with a knife)
Magnesium (Mg)	2	650 / 1091	Quite hard (can be cut with a knife with difficulty)
Iron (Fe)	3	1538 / 2862	Hard
Hafnium (Hf)	4	2233 / 4603	Hard
Tantalum (Ta)	5	3017 / 5458	Hard
Tungsten (W)	6	3422 / 5555	Very hard

Did you know? Tungsten carbide is the hardest metal alloy available (it is an alloy of tungsten and carbon). Steel is iron carbide (an alloy of iron and carbon). Adding small amounts of carbon hardens many metals.

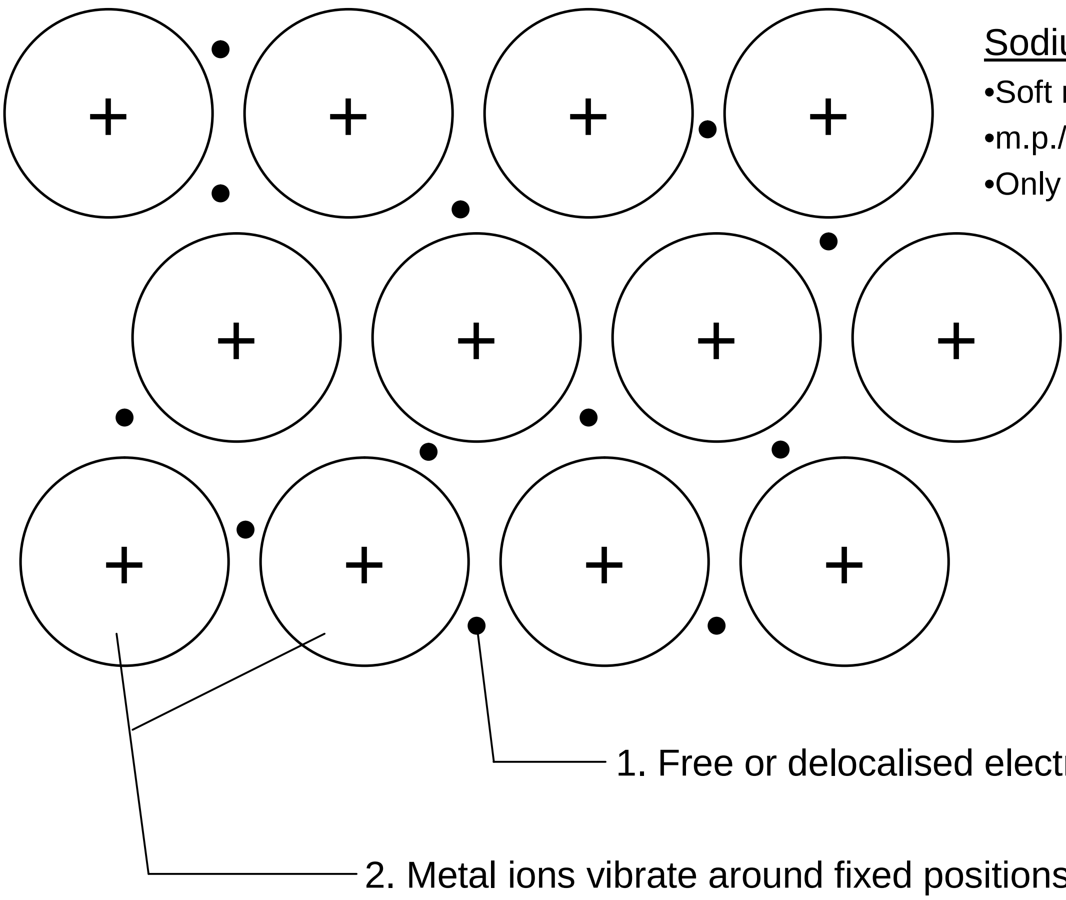
Physical Properties of Metals:

1. Conductivity: the delocalised electrons in metals are free to move within the metal and when electrodes are connected across a block of metal, these electrons move away from the negative electrode toward the positive electrode, carrying electric current with them. The electrons also conduct heat. Metals are good conductors of electricity and heat. Silver is the best electrically conducting metal.
2. Ductility and malleability: the delocalised electrons act like a ‘liquid glue’ and the metal atoms are free to move past one another without breaking the metal – metals are ductile (can be drawn into wires) and malleable (can be beaten into shape).
3. Hardness and density: metallic bonds are strong so metals are hard and most have high melting / boiling points. The atoms are closely packed (like oranges in a box) and so metals have high density. Osmium (Os) is the densest, lithium (Li) the least dense
4. Metallic lustre: the delocalised electrons are good at reflecting (or re-emittinG) light that strikes the metal surface and so metals are shiny (lustrous).

Metallic Bonding

<u>Sodium</u> (Na)

- Soft metal
- m.p./b.p. = 97.7 / 883 ºC
- Only one valence electron



<u>Tungsten</u> (W)

- Very hard metal
- m.p./b.p. = 3422 / 5555ºC
- Six valence electron