Achievement Standard 91390

Demonstrate understanding of thermochemical principles and the properties of particles and substances

CHEMISTRY

3.4

Externally assessed 5 credits

Essential exam notes

Electron configurations, bonding and periodic trends

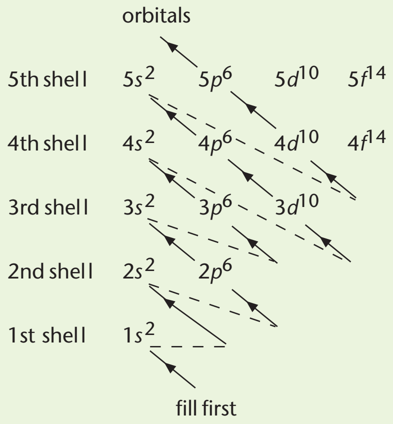
The number of protons (p) determines the **atomic number** and determines what element an atom is. Protons and neutrons (n) have both been given a defined mass of 1 (no units); the sum of p + n for an atom is its **mass number**. Atoms of the same element with different numbers of neutrons are **isotopes**. Electrons are considered to have no mass for the purpose of mass calculations.

One **mole** of an element contains 6.023×10^{23} atoms.

Electrons are arranged around the nucleus of an atom in orbitals within energy levels (electron shells):

- first level has 1*s* orbital only
- second level has 2*s* and 2*p* orbitals
- third level has 3*s*, 3*p* and 3*d* orbitals
- fourth level has 4*s*, 4*p*, 4*d* and 4*f* orbitals.

Aufbau principle – 'electrons fill orbitals from the lowest energy level (1*s*) first and build filling each set of orbitals in turn'.



Example

The 15 electrons on a phosphorus atom fill the 1*s* orbital then the 2*s*, the three 2*p* orbitals, the 3*s* and finish up in the 3*p* orbitals. Its notation is P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

Hund's rule – 'electrons will fill each orbital of a sublevel before pairing'. An atom can have a full energy level, a full orbital, or a half-full orbital (no paired electrons).

When an atom forms an ion, its subshell notation changes to show how its valence electrons are arranged.

Example

When a phosphorus atom gains 3 electrons to form a phosphide ion, it would have the notation P^{3-}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

The first ionisation energy of an element is the energy needed in kJ mol^{-1} to remove one electron from each atom in a mole of the element in its gas state.

- There is a decrease going down a group – the electron being lost is further away from the nucleus and has more shielding from the inner shells of electrons, so it is not held as strongly.
- There is an increase going across a period – the number of protons increases and thus electrons are added in the same energy level and the effective nuclear charge (e.n.c.) acting on the outermost electron is stronger.
- Filling an '*s*' subshell orbital gives extra stability to elements He, Be, Mg, Ca, so their first ionisation energy is above the expected trend.
- Half-filling a '*p*' subshell gives extra stability to elements N and P, which thus have higher than expected values.

Metals form **metallic bonds**, consisting of electrostatic attraction between the lattice of (positive) metal nuclei and the surrounding delocalised electrons (negative).

An increase in the number of valence electrons gives an increase in:

- strength of the metallic bond
- density
- hardness
- melting and boiling points.

Electrons are able to slide past the nuclei and one another to make metals **malleable** ('can be bent'), **ductile** ('can be drawn out into a wire') and **electrically conductive** in the solid and liquid states.

Metals and non-metals react to form **ionic bonds**. Electrons are transferred from the metal and it forms a **cation** (positive ion); the non-metal that receives the electrons forms an **anion** (negative ion). A strong **electrostatic** force of attraction occurs between the oppositely charged ions within a **giant three-dimensional lattice** of the ions in a fixed ratio. Ionic compounds have the following properties:

- greater solubility in polar solvents (e.g. water) than in non-polar solvents
- hard but brittle salts
- conductors of electricity when in solution or molten (liquid)
- high melting and boiling points.

Non-metals form **covalent bonds** with each other by donating one (or more) electron(s) each to a **shared bond pair** of electrons that help make up a full valence electron shell.

The strong force of attraction of the positive nuclei to the shared bond pair is greater than the repelling effect of the two positive nuclei.

- Bond strength **decreases** down a group – the bond pair becomes further from the nucleus and shielding from inner electron shells increases.
- Double bonds are shorter and stronger than single bonds.
- Electrons in a covalent bond between different atoms will be **shared unequally** due to a difference in each atom's **electronegativity** (measure of an atom's attraction for a bond pair of electrons). The uneven distribution of the electrons creates a **polar covalent** bond between the atoms and a **permanent dipole** across the bond.

Polar covalent bonds in a molecule create a dipole across the entire molecule unless they cancel each other out because they are arranged symmetrically.

Intermolecular forces involve weak forces of attraction between molecules.

- **Temporary dipole-dipole** attractions or **dispersion forces** – temporary uneven distribution of electrons around an atom/molecule repel electrons in a nearby atom/molecule **inducing** a small dipole in both – more likely to occur in larger atoms/molecules that contain more electrons.
- **Permanent dipole-dipole** attractions – occur between the opposite ends of molecules with a permanent dipole across the molecule. The more polar the molecule, the stronger the attraction.
- **Hydrogen bonds** are the **strongest** attraction force (but are still only about 10% of the strength of a covalent bond). A molecule must contain a hydrogen atom bonded to a fluorine, oxygen or nitrogen atom. This bond has a very large dipole that is attracted to the opposite end of the same bond on a nearby molecule (e.g. water has a much higher melting and boiling point than molecules of similar size and polarity).

The periodic table

- Atomic number increases across a period – number of protons increases.
- Atoms get smaller across a period – effective nuclear charge experienced by electrons in the same shell increases, pulling them in closer.
- Atoms get larger down a group – number of electron levels (shells) increases; effective nuclear charge is shielded from outer electrons by inner electrons.
- Ions formed by elements on the left are smaller than their atoms because they have lost electrons to empty an energy level (shell).
- Ions formed by elements on the right are larger than their atoms because they have gained electrons so there is increased repulsion between valence electrons.

Transition metals

Transition metals are elements in groups 3–12 (**d block**). They always lose the 4s electrons first when forming ions.

- Chromium has greater stability with half-filled 4s and 3d orbitals.
- Copper has greater stability with half-filled 4s and full 3d orbitals.

Atom	Electron configuration of atom	Common oxidation states	Most common ions	Electron configuration of most common ion(s)	Colour of most common hydrated ion(s)
Sc	$[Ar]3d^1 4s^2$	3	Sc^{3+}	[Ar]	colourless
Ti	$[Ar]3d^2 4s^2$	3, 4	Ti^{3+}	$[Ar]3d^1$	violet
V	$[Ar]3d^3 4s^2$	3, 5	V^{3+}	$[Ar]3d^2$	green
Cr	$[Ar]3d^5 4s^1$	3, 6	Cr^{3+}	$[Ar]3d^3$	violet
Mn	$[Ar]3d^5 4s^2$	2, 4, 7	Mn^{2+}	$[Ar]3d^5$	pale pink
Fe	$[Ar]3d^6 4s^2$	2, 3	Fe^{2+} Fe^{3+}	$[Ar]3d^6$ $[Ar]3d^5$	pale green yellow-orange
Co	$[Ar]3d^7 4s^2$	2, 3	Co^{2+}	$[Ar]3d^7$	pink
Ni	$[Ar]3d^8 4s^2$	2	Ni^{2+}	$[Ar]3d^8$	blue-green
Cu	$[Ar]3d^{10} 4s^1$	1, 2	Cu^+ Cu^{2+}	$[Ar]3d^{10}$ $[Ar]3d^9$	colourless blue
Zn	$[Ar]3d^{10} 4s^2$	2	Zn^{2+}	$[Ar]3d^{10}$	colourless

Other properties

Transition metals have **variable oxidation states** – due to having spare 3d electrons they can share (e.g. chromium +3 and +6; manganese +2, +4; copper +1 and +2).

Transition metals form **coloured ions** – incomplete d orbital electrons absorb light of different wavelengths; colours seen are wavelengths not absorbed.

Transition metals form **complex ions** – a central metal cation is bonded to a fixed number of **ligands** (small molecules (e.g. H_2O, NH_3) or ions (e.g. Cl^-, CN^-) with lone pairs of electrons that can datively bond to the metal cation). Ligands often change the colour absorption of a transition metal.

The pH of complex ions with water molecules is acidic as one of the waters acts as a proton donor:

$$[Fe(H_2O)_6]^{3+}(aq) \rightarrow [Fe(H_2O)_5OH]^{2+}(aq) + H^+(aq)$$

Chromium(VI) exists as **yellow** chromate in alkaline solutions and **orange** dichromate in acidic solutions:

$$\underset{\text{yellow}}{2CrO_4^{2-}(aq)} + 2H^+ \rightarrow \underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + H_2O(\ell)$$

NCEA practice

Questions
Electron configurations, bonding and periodic trends

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Question One: Electrons and molecules

a. Complete the table.

Symbol	Electron configuration
Se	
V	
V^{3+}	

b. Discuss the data for each of the following pairs of particles.

i.

Atom	Electronegativity
O	3.44
Se	2.55

ii.

Atom or ion	Radius/pm
Cl	99
Cl^-	181

iii.

Atom	First ionisation energy / kJ mol^{-1}
Li	526
Cl	1 257

Achievement Standard 91392

Demonstrate understanding of equilibrium principles in aqueous systems

CHEMISTRY

3.6

Externally assessed 5 credits

Essential exam notes

Solubility calculations

When an ionic salt dissolves (**solute**) into a **solvent**, it **dissociates** into a **solution** of the ions in that salt. The bonds within the solute and between the solvent particles are broken endothermically, and bonds form between the solute ions and the solvent particles exothermically. The overall change in energy is the **enthalpy of solution** ($\Delta_{sol}H$) and dissolving will only occur if this is exothermic (negative) or very slightly endothermic.

A solution may have:

- **Colligative properties** – the amount of moles of particles in solution can raise its boiling point by 0.5 °C per mole and lower its freezing point by 1.86 °C per mole.
- **Conductivity** – a solution with free ions is called an **electrolyte**. A substance that dissociates completely releases lots of ions, so it is a strong electrolyte. Pure water is a poor electrolyte.
- **pH** – if the substance dissociating releases H^+ ions, these react with H_2O to form H_3O^+ which lowers the pH. If OH^- is released, the pH is raised. pH = 7 when the numbers of moles of H^+ and OH^- ions are equal at 1×10^{-7} mol L^{-1}.
- **Species in solution** – a dissolving substance may react with the water molecules or just associate with them. A reaction with water is called a **hydrolysis reaction**.
  Sucrose dissolving in water is a physical process only: $C_{12}H_{22}O_{11}(s) \rightarrow C_{12}H_{22}O_{11}(aq)$
  Sulfur trioxide dissolves by a hydrolysis reaction with the water molecule and produces H^+ ions from the water particles; $SO_3(g) + H_2O(\ell) \rightarrow SO_4^{2-}(aq) + 2H^+(aq)$
- **Composition concentrations** – water has the concentration of 55.55 mol L^{-1}; the concentrations of all other species depend on the amount dissolved and the mole ratio of the ions (don't forget the very small amount of H^+ and OH^- ions in a neutral solution).

When enough of a sparingly soluble salt is added to a solution so that no more will dissolve, it is **saturated** and an equilibrium is established between the undissolved salt and the ions in solution.

- The **solubility** of the salt is the amount that has dissolved (in mol L^{-1} or g L^{-1}).
- The **ionic product** (**IP**) or **reaction quotient** (**Q**) is the concentration of the ions, to the power of their mole ratios, multiplied together.
- The **solubility constant** or **solubility product** (**K_s**) is the equilibrium constant with no units.

K_s expressions for common ionic salts

AB type compound

• Cation : anion ratio	1 : 1
• Equilibrium expression	$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$
• K_s expression	$K_s(AB) = [A^+]\,[B^-]$
• Example	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$
	$K_s(CaSO_4) = [Ca^{2+}]\,[SO_4^{2-}]$

- Concentration of each ion in solution at equilibrium is the same as the concentration of the salt (e.g. in a 1.5×10^{-5} mol L^{-1} solution of $CaSO_4$, $[Ca^{2+}]$ and $[SO_4^{2-}]$ will also be 1.5×10^{-5} mol L^{-1}).
- If $x = [A^+]$, $[B^-] = x$, $K_s = x^2$; i.e. K_s can be determined by squaring the molar solubility of the compound and $x = \sqrt{K_s(AB)}$.

A_2B type compound

• Cation : anion ratio	2 : 1
• Equilibrium expression	$A_2B(s) \rightleftharpoons 2A^+(aq) + B^{2-}(aq)$
• K_s expression	$K_s(A_2B) = [A^+]^2 [B^{2-}]$
• Example	$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$ $K_s(Ag_2SO_4) = [Ag^+]^2 [SO_4^{2-}]$

In a 1.5×10^{-5} mol L^{-1} solution of Ag_2SO_4, $[SO_4^{2-}]$ will be 1.5×10^{-5} mol L^{-1} but $[Ag^+]$ will be 3×10^{-5} mol L^{-1}.
If x mol of A_2B dissolves per litre of solution:
$[A^+] = 2x$ mol L^{-1}
$[B^{2-}] = x$ mol L^{-1}
$K_s = (2x)^2 \times x = 4x^3$ and $x = \sqrt[3]{\frac{K_s}{4}}$

AB_2 type compound

• Cation : anion ratio	1 : 2
• Equilibrium expression	$AB_2(s) \rightleftharpoons A^{2+}(aq) + 2B^-(aq)$
• K_s expression	$K_s(AB_2) = [A^{2+}] [B^-]^2$
• Example	$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$ $K_s(Ca(OH)_2) = [Ca^{2+}] [OH^-]^2$

In a 1.5×10^{-5} mol L^{-1} solution of $Ca(OH)_2$, $[Ca^{2+}]$ will be 1.5×10^{-5} mol L^{-1} but $[OH^-]$ will be 3×10^{-5} mol L^{-1}.
If x mol of AB_2 dissolves per litre of solution:
$[A^{2+}] = x$ mol L^{-1}
$[B^-] = 2x$ mol L^{-1}
$K_s = x \times (2x)^2 = 4x^3$ and $x = \sqrt[3]{\frac{K_s}{4}}$

Ionic product

The **ionic product** (**IP**) for a particular dissolving reaction can be calculated and compared with the K_s:

- $IP > K_s$ – salt will precipitate out of solution.
- $IP = K_s$ – solution is saturated and at equilibrium so no more solute will dissolve.
- $IP < K_s$ – solution is unsaturated, no precipitation will occur, more solute can be dissolved.

Common ion effect

If there is more than one source of an ion in a particular solution, a **common ion effect** changes the solubility of the solute. The new concentration of the common ion must be calculated (remember the volume may have changed) for use in finding the IP of the salt.

If the common ion is H^+ or OH^- and the solute contains an ion that is a weak acid or base, then **pH effect** can change the solubility of a solute.

$pH = -\log[H^+]$ therefore $[H^+] = 10^{-pH}$ and $[H^+][OH^-] = 1 \times 10^{-14}$

The total concentration for either ion (remember the volume may have changed) can be calculated.

NCEA practice

Questions
Solubility calculations

Question One: Silver's solubility

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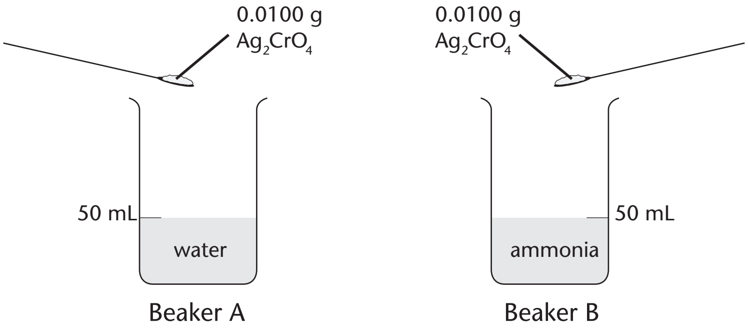
In an experiment, a saturated solution was made by dissolving 1.44×10^{-3} g of Ag_2CrO_4 in water, and making it up to a volume of 50.0 mL. $M(Ag_2CrO_4) = 332$ g mol^{-1}

a. Write the K_s expression for $Ag_2CrO_4(s)$.

b. **i.** Calculate the solubility of $Ag_2CrO_4(s)$, and hence give the $[Ag^+]$ and $[CrO_4^{2-}]$ in the solution.

ii. Determine the $K_s(Ag_2CrO_4)$.

c. In another experiment, 0.0100 g of Ag_2CrO_4 in beaker A was made up to a volume of 50.0 mL with water. In beaker B, 0.0100 g of Ag_2CrO_4 was made up to a volume of 50.0 mL with 0.100 mol L^{-1} ammonia solution.



Compare and contrast the solubility of Ag_2CrO_4 in beaker A and beaker B. No calculations are necessary.

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Question Two: Iron solubility

Iron(II) hydroxide, $Fe(OH)_2$, has a K_s of 4.10×10^{-15} at 25 °C.

a. **i.** Write the equation for $Fe(OH)_2$ dissolving in water.

ii. Write the expression for $K_s(Fe(OH)_2)$.

b. Calculate the solubility (in mol L^{-1}) of iron(II) hydroxide in water at 25 °C.

c. **i.** Determine whether a precipitate of iron(III) hydroxide, $Fe(OH)_3$, will form when $Fe(NO_3)_3$ is dissolved in water. $[Fe(NO_3)_3] = 1.05 \times 10^{-4}$ mol L^{-1}.

Assume the pH of the water is 7.

$K_s(Fe(OH)_3) = 2.00 \times 10^{-39}$

ii. Discuss the effect of decreasing the pH of the water on the solubility of $Fe(OH)_3$.

Answers and explanations

Achievement Standard 91390 (Chemistry 3.4): Demonstrate understanding of thermochemical principles and the properties of particles and substances

3.4 Electron configurations, bonding and periodic trends

Question One: Electrons and molecules

p. 4

a. Se: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$

V: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$

V^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^2$

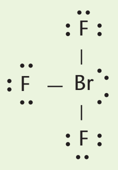
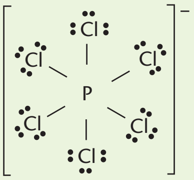
> You can follow the pattern of electron filling by using the periodic table (see page **vii.**). Remember that transition metals lose their 4*s* electrons first when forming ions.

b. i. Electronegativity is a measure of an atom's attraction to bonding electrons. Se has a lower electronegativity than O because the bonded electrons are in a higher valence level. Thus they are further from the attraction of the nucleus's charge and subject to shielding from inner electrons.

ii. Cl^- ion has a larger radius than the Cl atom because Cl^- has an additional electron in the outer energy level which increases the repulsions occurring with the surrounding valence electrons compared with the Cl atom's outer electrons. This has the effect of expanding and increasing the radius.

iii. The 1st ionisation energy (I.E.) is the energy required to remove one electron from a mol of gaseous atoms. Cl has a higher 1st I.E. than Li as Cl has more protons in its nucleus (i.e. is further across to the right of the periodic table than is Li), causing a stronger electrostatic attraction to the outer electron, which requires more energy to remove it. In Cl, although the outer (seven) electrons experience more shielding from inner electrons than does the (single) outer Li electron – Cl is on a lower row of the periodic table (i.e. Cl is in row 3 c.f. Li in row 2) – this increase in shielding is not enough to compensate for the increased nuclear charge.

c. i.

Molecule	BrF_3	PCl_6^-
Lewis diagram		
Name of shape	T-shaped	Octahedral

ii. SF_4 has 5 regions of negative charge surrounding the central S atom, which repel each other in three-dimensional space. Only 4 of these regions of negative charge are bonded, so SF_4 is a see-saw (or distorted tetrahedral) shape. SF_4 has polar bonds between the S and F atoms due to a difference in electronegativity causing the bonding electrons to be unequally shared. The SF_4 molecule's see-saw shape is unsymmetrical for bonding regions – thus the polar bonds are not cancelled and cause the molecule overall to be polar.

XeF_4 has 6 regions of negative charge surrounding the central Xe atom. XeF_4 only has 4 of these regions of negative charge bonded; thus forms a square planar shape. XeF_4 also has polar bonds between the Xe and F atoms, but the molecule is symmetrical so the effect of the polar bonds is cancelled to leave the overall molecule non-polar.

> It is important to know all the various shapes that can be formed from up to 6 regions of charge – you can then link the shapes formed to the polarity of a molecule.

(**A** – two from a. correct and either one of b. i., ii., iii. and c. i. or ii. with limited explanation; **M** – a. all correct and full discussion for one of b. and c. ii. with one molecule explained completely; **E** – **M** with two fully correct of b. and full discussion for c. ii.)

Question Two: Copper and germanium

p. 6

a. Ge: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6\ 4p^2$

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$

Cu^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^{10}$

> $4s^0$ can be absent, i.e. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

> Take extra care to ensure the configuration of an ion is correct.

Transition metals lose their 4*s* electrons first; so, for the Cu^+ ion, it still has complete 3*d* orbitals.

b. The colour of transition metals is due to having incomplete *d*-orbital electrons that are able to be excited to higher energy levels by absorbing some colour wavelengths of light from the white spectrum. Copper has the ability to have an incomplete *d*-orbital arrangement of [Ar] $4s^2\ 3d^{10}$ in some compounds, so these compounds are coloured. Copper also can have the compete *d*-orbital arrangement of [Ar] $4s^1\ 3d^{10}$, which is not coloured because there are no unpaired *d*-orbital electrons.

c. Ge: 128

Cu: 123

Cu^+: 77

Cu is a transition metal which means it will have a smaller radius than most other elements of the fourth period. This is because when moving across the period, the transition metal electrons are filling lower energy 3*d* orbitals. Moving across the period from Cu to Ge, there is an increase in the number of protons in the nucleus, which creates a greater attraction to the outermost electrons and reduces the radius of the atoms.

The ions of metals have smaller radii than their atomic radii because the atom has lost an energy level to become an ion –

Answers

in the case of Cu$^+$, the 4*s*. A cation also has more protons than electrons in the nucleus, which causes a greater attraction on the remaining electrons and draws them closer. Thus Cu$^+$ is smaller than Cu, and Cu is smaller than Ge.

> This is a hard question because it deviates from the usual rule that moving across a period reduces atomic radii, as the transition metals are an exception. Ensure that you show your understanding of the link between the attractions of protons in the nucleus and the position of the outer electrons on atomic radii.

(**A** – two from a. correct and either b. or c. with limited explanation; **M** – a. all correct and full discussion for b. or c.; **E** – **M** with full discussion for both b. and c.)

Question Three: Electrons and radii

p.7

a. Fe: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$
Al: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
Al^{3+}: $1s^2\ 2s^2\ 2p^6$
Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$

> Take extra care to ensure the configuration of an ion is correct.

b. Larger radius: Al

Justification: The Al^{3+} ion has no electrons in the third energy level so its radius only extends to the outer electron in the second energy level which is drawn closer by the nuclear charge. Thus the Al atom with its radius extending out an additional energy level is larger than its ion.

c. i. $\mathrm{Li}(g) \rightarrow \mathrm{Li}^+(g) + e^-$

> Note that this occurs in the gaseous state.

ii. The ionisation energy (I.E.) trend moving from Li across elements in the same period is that of a general increase. This is due to additional protons causing an increase on the effective nuclear charge (e.n.c.) acting on the same energy level electrons which requires more energy to be overcome to remove an electron.

Between Li and Na atoms there is a decrease in I.E., as moving down the same group the outer electrons are held in a higher energy level, which are further from the protons in the nucleus and thus require less energy to remove.

B is lower than expected as its outer electron is a lone 2p orbital electron. This requires less energy to remove as, once removed, the B atom gains some stability from having the residual full 2s orbital.

O ($1s^2$, $2s^2$, $2p^4$) is also lower than expected as losing an outer electron allows O to form a more stable orbital configuration of three half-filled p orbitals ($2p^4 \rightarrow 2p^3$). Thus less energy is required to remove this electron than expected.

> I.E. of electrons in higher energy levels can also be affected by shielding/interference of the proton attraction by inner-level electrons of an atom.

(**A** – three from a. correct and either b. with limited explanation or c. i. or general trend in c. ii. stated; **M** – a. fully correct, b. with mostly correct explanation and c. with partial discussion; **E** – **M** with full discussion of required parts of the graph in c.)

Question Four: Calcium, chromium and manganese

p.8

a. Ca: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$
Mn^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ (4s^0)$

> The Cr atom rearranges its 4s and 3d electrons to gain the stability of two half-filled orbital levels.

b. Calcium only has 2*s* orbital electrons in its outer shell, which it loses to form a +2 oxidation state – whereas manganese also has partially filled *d* orbitals in its outer energy level, so can lose different numbers of electrons and cause several different oxidation states.

> Variable oxidation states due to varying amounts of *d* electrons is a feature of transition metals.

c. Ca: 197 pm
Ca^{2+}: 99 pm
Mn: 137 pm

The Ca^{2+} ion is the smallest as a result of having lost electrons to empty its outer energy level. The valence electrons are in an energy level closer to the nucleus with same nuclear charge as Ca. This creates a higher e.n.c. on the remaining electrons; radius is therefore smaller.

The Mn is smaller than the Ca as atomic radii decrease moving across a period. This is due to an increasing number of protons causing a higher e.n.c. acting on electrons in the same energy level, which draws them closer. Mn is bigger than the Ca^{2+} ion as its outermost electrons are in a higher energy level.

This means the Ca atom has the largest radius of the three.

(**A** – two correct in a., understanding of *d* electrons in b. or two sizes correct in c.; **M** – all of a. and b. correct, and one radius explained correctly in c.; **E** – as for **M** with all radii sizes correctly explained in c.)

Question Five: Atoms and electrons

p.9

a. Ca^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$
Fe^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ (4s^0)$

> Transition metals lose their 4s electrons first as they become ions.

b. i. Br and Ca are on the same row of the periodic table, but Br has more protons to increase the effective nuclear charge (e.n.c.) acting on the same energy level electrons. Thus it requires more energy to remove an outermost electron from Br than from Ca, making the ionisation energy of Br higher.

ii. The Br$^-$ ion's radius is larger than the Br atom's radius because Br$^-$ has an extra electron in its valence shell with increased repulsion between these electrons causing the electrons to move further apart and increase the radius.

The I atom's radius is larger than the Br atom's radius because it has one extra energy level of electrons. These electrons are further away from the I nucleus and they also experience more shielding from the protons by inner shell electrons, so a lower e.n.c. Therefore, valence shell electrons are not held as close and thus the radius is greater for I than for Br atoms.

> The general trend going across and up the periodic table is an increase in 1st ionisation energy and a decrease in atomic radius.

(**A** – two correct from a., b. i. or ii. partly correct; **M** – **A** plus one of b. i. or ii. fully answered; **E** – all correct, minor error allowed in b. i. or ii.)

Question Six: Atoms, ions and their properties

p.10

a. i. $\mathrm{H}^+ < \mathrm{H} < \mathrm{H}^-$

ii. H$^+$ is a nucleus without any electron energy levels, so is the smallest. H$^-$ is the biggest, because the extra electron causes a greater distribution of the attraction from the proton in the nucleus, thus both the electrons present are able to move further from the nucleus and the radius increases.

b. Sc: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$
Br$^-$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$
Mn^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ (4s^0)$

> Always take care to check if you are writing an electron configuration for an atom or an ion.

c. i. Br atom also has more protons and they are acting on the extra electrons that are in the same energy level. This means there is a stronger electrostatic attraction between nucleus and valence electrons, which draws these outer