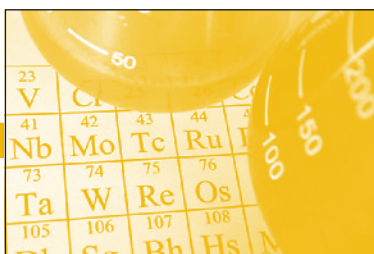


PERIODICITY

3

- 3.1 The periodic table
- 3.2 Physical properties
- 3.3 Chemical Properties
- 13.1 Trends across Period 3 (AHL)
- 13.2 First-row d-block elements (AHL)



TOK Phlogiston and a paradigm shift?

'The early discoverers of the elements allowed chemistry to make great steps with limited apparatus, often derived from the pseudoscience of alchemy. Lavoisier's discovery of oxygen, which overturned the phlogiston theory of heat, could be discussed as an example of a paradigm shift.'

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Fire, and our ability to control it, is one of the major things that has helped us advance beyond other animals. Looking at flames two things are obvious – there is something coming out of the thing that's burning and the process gives out heat and light. Heat seemed part of many natural processes (sunlight and hot-springs), but what could be causing the flame. This is where phlogiston (from the Greek phlogistos, meaning burnt up or flammable) came in – it was the material released when things burnt. There seemed to be less of things after they burnt (compare the ashes that remain to the piece of wood they came from) so it all made sense. The theory is attributed to Johann Becher, a German physician and alchemist, who lived in the middle of the 17th century. It was the accepted theory of combustion for at least a century and so was probably the explanation for combustion in the first edition of Encyclopaedia Britannica in 1768? It is a bit disturbing to reflect on what in the current edition will be considered nonsense a couple of centuries from now!

About a century later however scientists were starting to make more accurate quantitative observations and they noted that some substances (magnesium would be a good example) gained mass when they burnt. It is perhaps interesting to reflect whether previous results to the contrary (i.e. that metals lost weight when they burnt), by such eminent people as Robert Boyle, were a result of poor technique or through wanting the results to fit in with the theory! (Of course you would never "edit" the results of your chemistry experiments to "improve them?") As so often when a paradigm seems to be refuted, some people tried to keep the phlogiston theory alive, even if it meant postulating that it had a negative mass! The real death blow for phlogiston came with the work of Lavoisier in the late 18th century, who produced oxygen and showed that it was necessary for combustion. The discovery of oxygen is variously attributed to Scheele (a German), Priestley (an Englishman) and Lavoisier (a Frenchman) – which you support probably depends on what you feel the word "discover" implies and maybe on where you come from!

3.1 THE PERIODIC TABLE

- 3.1.1 Describe the arrangement of elements in the periodic table in order of increasing atomic number.
- 3.1.2 Distinguish between the terms group and period.
- 3.1.3 Apply the relationship between the electron configuration of elements and their position in the periodic table up to $Z = 20$.
- 3.1.4 Apply the relationship between the number of electrons in the highest occupied energy level for an element and its position in the periodic table.

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The relationship between electronic structure and chemical properties of the elements is one of the key concepts in chemistry. This lies at the heart of the **periodic table** which is a most valuable arrangement of the elements to which chemical properties can be related. The usual form of the periodic table is that shown diagrammatically in Figure 301, but in many places in this chapter (e.g. Figure 302) the “short form” of the periodic table, in which the transition metals are omitted (also shown in Figure 301), is used for clarity.

In the periodic table, the elements are arranged in order of increasing atomic number, reading from left to right, top to bottom (as in reading English). This means that knowing the atomic number, the position of an element can be found by counting down the squares in this way. Try it, using the periodic table in Figure 302, for phosphorus ($Z=15$).

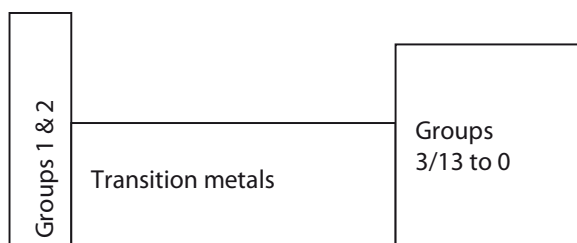
Group →	1	2	3/13	4/14	5/15	6/16	7/17	0
Period								
1	1 H 1							2 He 2
2	3 Li 2,1	4 Be 2,2	5 B 2,3	6 C 2,4	7 N 2,5	8 O 2,6	9 F 2,7	10 Ne 2,8
3	11 Na 2,8,1	12 Mg 2,8,2	13 Al 2,8,3	14 Si 2,8,4	15 P 2,8,5	16 S 2,8,6	17 Cl 2,8,7	18 Ar 2,8,8
4	19 K 2,8,8,1	20 Ca 2,8,8,2						

Figure 302 The first twenty elements in the periodic table and their electronic structures

A group is a vertical column consisting of elements with the same number of electrons in the outer energy level, which gives these elements similar chemical properties. These are numbered above the column and originally they were numbered from 0 to 7, but recently the system has been changed to 0 to 17 to include the d-block elements. This is less ambiguous, though both are shown. It is then found that going across a horizontal row (known as a period) the chemical properties gradually change from those of reactive metals to those of reactive non-metals, with the noble gases in the final group at the far right. Consider this for the first twenty elements shown in Figure 302.

Valence electrons are electrons in the outermost energy level (the highest energy level) of an atom. These are usually the electrons that take part in a chemical reaction and determine the physical and chemical properties of the element. It is therefore not surprising that the position of an element in the periodic table is closely related to its electronic structure, so this can be used as a memory aid. A period is a series of elements arranged according to increasing atomic number, which begins with the first element having one electron in a new main energy level, in which the same electron energy level (or shell) is being filled. Period 1 fills the $n = 1$ level, period 2 the $n = 2$ level etc. Hence the period an element is in gives the number

Usual (long) form of the periodic table



Short form of the periodic table

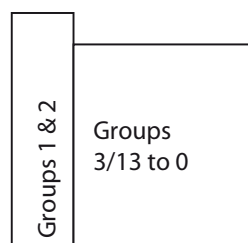


Figure 301 Forms of the periodic table

of energy levels that contain electrons. On the other hand, the group number (or the group number minus 10 in the modern numbering of groups 13 to 17) gives the number of electrons in the valence shell. This is also shown in Figure 302. Phosphorus, for example is in the third period, so it has electrons in the first three energy levels, and in the fifth group, so it has five electrons (or 5-10) in the valence level. Its electronic structure is therefore 2,8,5.

The first element in each period (such as sodium, Na) therefore has only one electron in its outer shell. The elements in this first group are known as the alkali metals. The last but one element in each period (such as chlorine,

Cl) requires one more electron to complete its outer shell. The elements in this last but one group are known as the halogens. The final element in each period (such as argon, Ar) has all its electron shells filled. These elements have little chemical reactivity and are known as the noble gases. Periodicity is the regular repeating of properties according to the arrangement of elements in the periodic table (they occur at regular intervals). It is found that chemical and physical properties of elements show periodicity if the elements are arranged in order of increasing atomic numbers and these are discussed in sections 3.2 and 3.3 respectively.

TOK Risk-taking and science

The predictive power of Mendeleev's periodic table can be seen as an example of a "scientist" as a "risk taker".

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There is no doubt at all that when he proposed his periodic table Mendeleev put his neck on the line. Not only did he predict that there were some elements still to be found, he also made many detailed predictions about their properties, for example his predictions with regard to Germanium (which Mendeleev referred to as eka-silicon) are given below, along with the properties it was found to have after its discovery in 1886, about 15 years after it had been predicted by Mendeleev.

Whether being a risk-taker is a good thing or not is also worth some thought, and probably evolution, through survival of the fittest, is the final arbiter. Having a long tail is obviously a risk for a male peacock when trying to escape from a fox, so do the extra peahens he attracts compensate for this risk? Will he survive long enough to mate with them? In scientific terms it could be argued there is now less risk attached to proposing a new theory than there once was as a result of Karl Popper, a 20th Century Austrian philosopher. Popper said "Our belief in any particular natural law cannot have a safer basis than our unsuccessful critical attempts to refute it.", in other words science progresses by people trying to disprove existing theories. About a century ago it would have been a major disgrace in the scientific world to have had a theory disproved, but now it would be seen as valuable because it stimulated the work that eventually disproved the theory which led (hopefully) to the proposal of a better theory. Now a real risk-taker would set out to disprove the theory of gravity by bungee jumping without the cord!

Property	Mendeleev's prediction	Actual property
Relative atomic mass	72.0	72.6
Density	5.5 g cm ⁻³	5.35 g cm ⁻³
Appearance	Light grey solid	Dark grey solid
Reaction with air	Will react to form a dioxide	Reacts to form GeO ₂
Reaction with water	Reacts only with difficulty	Reacts only if red hot
Reaction with acids	Slight reaction	Does not react with common acids
Reaction with alkalis	No reaction	Does not react with common alkalis
Properties of its oxide	High melting point; density 4.7 g cm ⁻³ ; few acid base reactions	Melts at 1115 °C; density 4.23 g cm ⁻³ ; very weak base
Properties of its chloride	Will form a liquid tetrachloride which boils at under 100 °C	GeCl ₄ is a liquid at room temperature and boils at 84 °C

Exercise 3.1

1. In the periodic table, reading from left to right and top to bottom, the elements are arranged in order of
 - A the number of protons in their nucleus.
 - B the number of neutrons in their nucleus.
 - C increasing relative atomic mass.
 - D increasing mass number.

2. An element has 13 electrons orbiting the nucleus. In which group of the periodic table will it be found?
 - A Group 1
 - B Group 2
 - C Group 3
 - D Group 4

3. Find the element chlorine in the periodic table.
 - a) How many electrons will it have in its outer shell?
 - b) How many fully filled electron shells does it have?
 - c) Give the symbol of another element in the same period as chlorine.
 - d) Give the symbol of another element in the same group as chlorine.
 - e) What name is given to the elements in this group?

3.2 PHYSICAL PROPERTIES

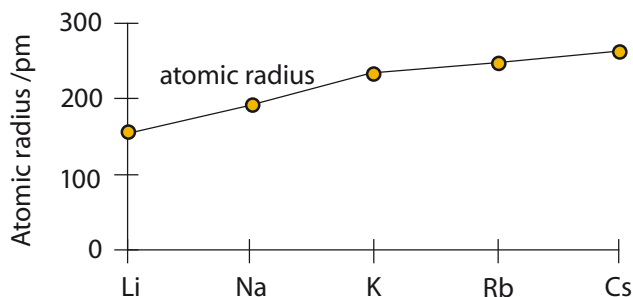
- 3.2.1 Define the terms first ionization energy and electronegativity.
- 3.2.2 Describe and explain the trends in atomic radii, ionic radii, first ionization energies, electronegativities and melting points for the alkali metals ($\text{Li} \rightarrow \text{Cs}$) and the halogens ($\text{F} \rightarrow \text{I}$).
- 3.2.3 Describe and explain the trends in atomic radii, ionic radii, first ionization energies and electronegativities for elements across period 3.
- 3.2.4 Compare the relative electronegativity values of two or more elements based on their positions in the periodic table.

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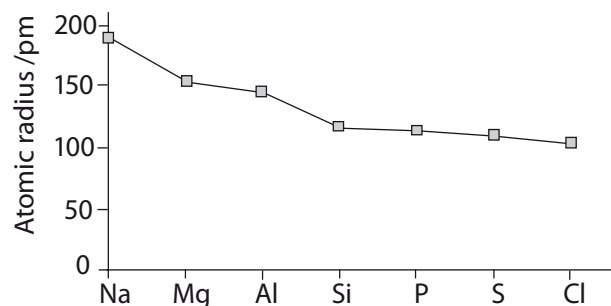
Going down a group of the periodic table, for successive elements there are more energy levels filled with electrons, so the outer electrons are in higher energy levels and farther from the nucleus. The extra charge on the nucleus is approximately cancelled out by additional filled shells of electrons, so the charge acting on the valence electrons (the **Effective Nuclear Charge**) is approximately the same for each element. As a result the valence electrons are further from the nucleus and the radius of the atoms and the ions formed from these atoms, both increase. The electrons are also less strongly attracted by the nucleus so that the **ionisation energy** (the minimum amount of energy required to remove an electron from one mole of gaseous atoms,) and the **electronegativity** (a measure of how strongly the atom attracts the electrons in a covalent bond) both decrease going down the group. These trends are illustrated in Figure 303 using as examples, for atomic and ionic radius, the alkali metals (Group 1), for ionisation energy the noble gases (Group 0) and the halogens (Group 7/17) for electronegativity.

Going across a period of the periodic table, the number of protons in the nucleus and hence the charge on the nucleus increases. This means that going across the period the electrons, which are all in the same energy level, are more strongly attracted and hence move closer to the nucleus causing the atomic and ionic radii (for isoelectronic ions, i.e. those with the same electronic structure) to both decrease. The ionization energy and the

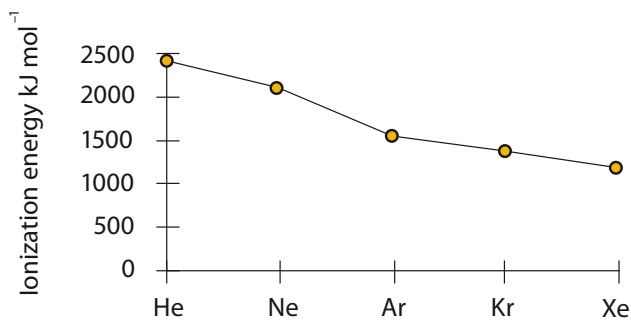
(a) The trend in atomic radius going down Group 1



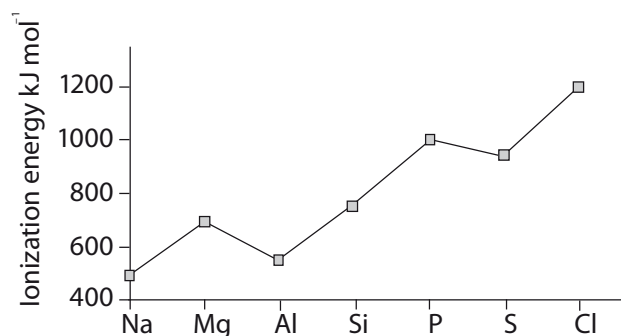
(a) Variation in atomic radius across the third period



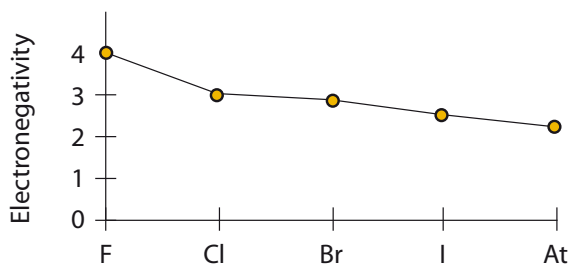
(b) The trend in ionization energy going down Group 0



(b) Variation in ionization energy across the third period



(c) The trend in electronegativity going down Group 17



(c) Variation in electronegativity across the third period

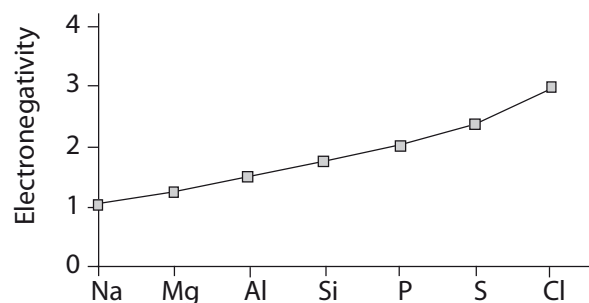


Figure 303 a, b, c Some trends in various atomic properties on going down different groups of the periodic table

Figure 304 a,b,c Variations in some atomic properties on going across the third period of the periodic table

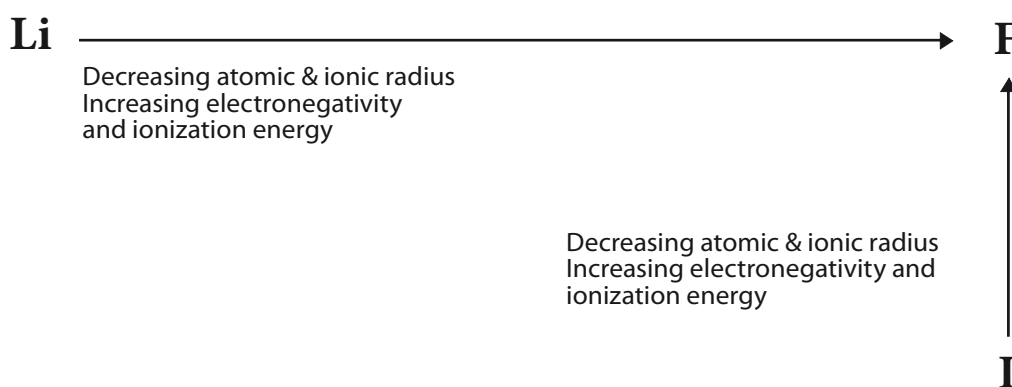


Figure 305 Periodic trends in some atomic properties

electronegativity both increase overall going across the period as the attraction of the nucleus for the electrons increases, although the change in ionization energy is by no means smooth. These trends are illustrated for the chemically reactive elements of period 3 (Na \rightarrow Cl) on the graphs in Figure 304. Note that these variations are much greater than those found within a group.

The overall trends in atomic radius, ionization energy and electronegativity are summarised in Figure 305.

The size of an atom always decreases when it is converted into a positive ion (cation). This may be because the whole of an outer shell of electrons has been lost (e.g. when Cs turns into Cs^+ , see to Figure 306) or because the loss of the electron results in less electron–electron repulsion between the valence electrons (e.g. when Mg turns into Mg^+ , in which 12 protons are now pulling on only 11 electrons).

Conversely the size of an atom always increases when it is converted into a negative ion (anion), because the additional electron results in an increase in repulsion between the valence electrons (e.g. when F turns into F^- , in which 10 electrons repel each other more than the 9 electrons in the F atom, see Figure 306).

Almost every common cation (i.e. positive ion) is smaller than any anion (i.e. negative ion), the converse only being true for the extremities such as Cs^+ and F^- , illustrated in the scale drawings shown in Figure 306. H^- is also quite small.

Physical properties, such as melting point, boiling point and density also depend on the nature of the bonding between the particles of the element. This is dealt with in much greater detail in Chapter 4, which should be read in conjunction with this section. Clear periodicity patterns

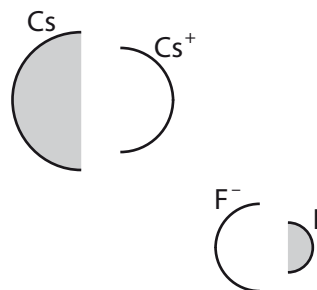


Figure 306 Atom and ion sizes

are visible in a graph of the melting points of the elements against atomic number, shown in Figure 307.

At the left of the period the elements (Li, Na, K) are metallic and going across the period the strength of the metallic bonding increases as there is an increase in nuclear charge. As a result both the number of mobile valence electrons increases and the atomic radius decreases, giving rise to an increase in the melting points (as the metal cations are held closer and more tightly). At the centre of each period (C, Si) giant covalently bonded structures occur in which every atom is joined to all the others by very strong covalent bonds, hence have very high melting points. Following this the melting points suddenly drop (N, P) as the elements here have non-polar, simple molecular structures and only weak **van der Waals' forces** exist between the molecules. Melting points are low, and depend on mass and size of the molecules P_4 , S_8 , and Cl_2 . This is further emphasised with the noble gases (He, Ne, Ar), which exist as single atoms with very weak van der Waals' forces and hence very low melting points. It must be remembered that the melting point is only a measure of the difference in the strength of the forces between particles between the solid and liquid state, rather than a measure of the absolute magnitude of such forces, as boiling point represents.

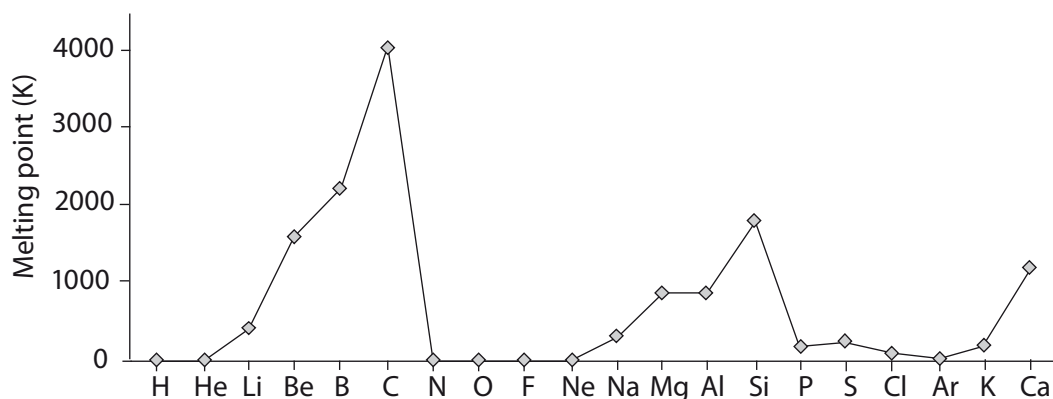



Figure 307 The melting points of the first twenty elements


Element	Na	Mg	Al	Si
Group	1	2	13	14
e ⁻ arrangement	1s ² 2s ² 2p ⁶ 3s ¹ 2.8.1	1s ² 2s ² 2p ⁶ 3s ² 2.8.2	1s ² 2s ² 2p ⁶ 3s ² 3p ¹ 2.8.3	1s ² 2s ² 2p ⁶ 3s ² 3p ² 2.8.4
# Valence e ⁻	1	2	3	4
1 st I.E. (in eV)	5.1	7.6	6.0	8.1
2 nd IE	47.3	15.0	18.8	16.3
3 rd IE	71.7	80.1	28.4	33.5
4 th IE	98.9	109.3	120.0	45.1
5 th IE	139	141	154	167

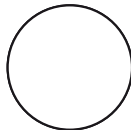
Figure 308 IE data for some elements

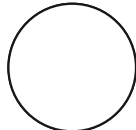
Exercise 3.2

- Which one of the following has the lowest electronegativity?
 - Boron
 - Beryllium
 - Magnesium
 - Carbon
- Which one of the following has the smallest radius?
 - K
 - K⁺
 - Ca
 - Ca²⁺
- The circles below represent the relative sizes of the F⁻, Na⁺, Mg²⁺, K⁺ and ions, but not necessarily in that order. Which one of the following would give them in this order?
 - II, I, III, IV
 - III, I, II, IV
 - I, II, III, IV
 - III, II, I, IV


I


II


III


IV
- Going across a given short period, in which group are you most likely to find the element with the highest melting point?
 - Group 0
 - Group 2
 - Group 4
 - Group 6
- Arrange the following in order of increasing atomic radius
Mg Cs Ca Al Ba
 - For each of the following properties, state how you would expect it to change in the direction indicated and give reasons for the change based on concepts such as nuclear charge, shielding, electron–electron repulsion and atomic/ionic radius.
 - The electronegativity going down a group.
 - The atomic radius going across a period.
 - The radius of an anion compared to its parent atom.
 - The first ionization energy going down a group.
 - The radius of a series of isoelectronic species (i.e. species having the same electronic structure, such as Cl⁻, Ar, Na⁺) with increasing atomic number.

3.3 CHEMICAL PROPERTIES

3.3.1 Discuss the similarities and differences in the chemical properties of elements in the same group.

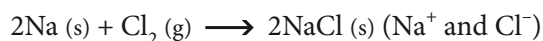
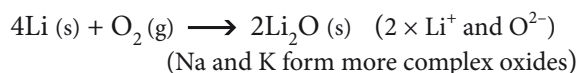
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THE ALKALI METALS

The **alkali metals** Li, Na, K, Rb and Cs (Fr has not been included because of its scarcity and nuclear instability) are soft malleable metals with low melting points and low densities. The low density is a result of the atoms of the alkali metals being the largest atoms in their period of the periodic table, and the softness and low melting points result from the fact that each atom can only contribute one electron to the metallic bonding, so this is less strong than for many other metals. The metals become softer and the melting point decreases (refer to Figure 310) going down the group as the attraction between the nucleus and the outer electrons becomes less, as a result of the increase in the size of the atoms.

Alkali metals are chemically very reactive and tarnish rapidly on exposure to air. The metals all have just one electron in their valence electron shell. This electron is very easily lost and this is the major reason why they are very reactive metals. They always form ions with a single positive charge in their compounds. They combine directly with

reactive non-metals such as oxygen, chlorine, bromine and iodine to form ionically bonded compounds:



Going down the group, as the atomic radius increases, the ionization energy of the elements decreases, the reactivity of the elements increases. This is best illustrated by the reaction of the elements with water. All of the metals react with water to form a solution of the metal hydroxide and hydrogen gas, according to the equation below (M represents the alkali metal):



for example in the case of sodium:



With lithium, the reaction occurs slowly and steadily. In the case of sodium the reaction is vigorous, producing enough heat to melt the sodium which fizzes around on the surface quite vigorously. With potassium the reaction is violent and the heat produced is enough to ignite the hydrogen evolved, which burns with a purple flame. In all cases the solution becomes strongly alkaline owing to the formation of hydroxide ions.

Alkali Metals	₃ Li	₁₁ Na	₁₉ K	₃₇ Rb	₅₅ Cs
Electronic Structure	2,1	2,8,1	2,8,8,1	2,8,8,18,1	2,8,8,18,18,1
Melting Point – K	454	371	336	312	302
Increasing _____ atomic and ionic radius	→				
Decreasing _____ ionization energy	→				
Decreasing _____ electronegativity	→				

Figure 310 Properties of the alkali metals

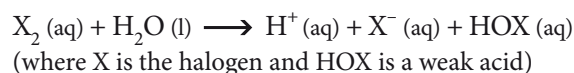
THE HALOGENS

The **halogens** F, Cl, Br and I (At has not been included because of its scarcity and nuclear instability) are very reactive non-metals that occur in the penultimate group of the periodic table, hence they all require just one electron to complete their valence shell.

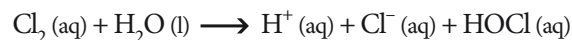
All of the elements exist as diatomic molecules (F_2 , Cl_2 , Br_2 , I_2) in which the atoms are joined by single covalent bonds. Going down the group their state, at room temperature and pressure, changes as the strength of the van der Waals' forces between the molecules increases with molar mass. Fluorine and chlorine are gases, bromine a liquid and iodine a solid that forms a purple vapour on heating. The halogens are all quite electronegative elements. They require just one electron to complete their valence shell, hence they readily gain electrons to form the singly charged halide ions (F^- , Cl^- , Br^- , I^-). The ease with which they gain electrons decreases going down the group, as the electrons gained are further from the nucleus and hence less strongly attracted. This means that, in contrast to the alkali metals, the reactivity of the halogens decreases going down the group.

The halogens are only slightly soluble in water as they are non-polar and hence can only bond by weak van der Waals' forces to the polar water molecules. Concentrated solutions of chlorine have a green tinge and those of bromine darken from yellow through orange to brown as the concentration increases. In non-polar solvents, such as hexane, iodine forms the violet solution that would be expected, but in polar solvents, such as water and ethanol,

the solution is a brown colour. In aqueous solution the halogens dissociate slightly to form an acidic solution:



For example with chlorine:



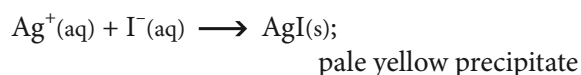
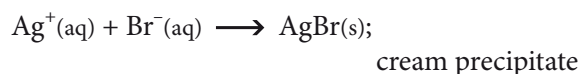
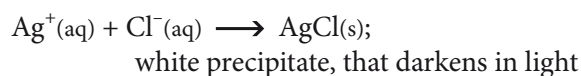
The compound HOX can readily donate its oxygen to other substances, so it acts as an oxidant. Chloric(I) acid ($HOCl$) will, for example, oxidise coloured dyes to colourless products. The second stage of the test for chlorine, in which it turns moist blue litmus paper from blue to red (the acidic solution) and then bleaches it to colourless, depends on this reaction. As a result chloric(I) acid, and its conjugate base the chlorate(I) ion (OCl^-) are used as bleaches (e.g. for paper). They are also toxic to microbes, hence they are used as disinfectants and chlorine is used in water treatment.

The halogens combine with metals to give ionically bonded salts containing the halide ion. These salts are usually white and soluble in water giving colourless solutions. The common insoluble halides are those of lead and silver (though the lead(II) salts are moderately soluble in boiling water). These insoluble salts can be precipitated by adding solutions containing the halide ion to a soluble salt containing the metal ion. Lead(II) iodide (PbI_2) is easily recognised because of its bright yellow colour and this is a convenient test for the iodide ion. The usual test for halide ions is however to add dilute nitric acid (to prevent carbonates etc. giving a precipitate) followed by aqueous silver nitrate to a solution of the unknown substance. The

Halogens	$_9F$	$_{17}Cl$	$_{35}Br$	$_{53}I$
Electronic Structure	2,7	2,8,7	2,8,8,7	2,8,8,18,7
Colour	Pale yellow	Yellow green	Red brown	Black/dark purple
State at room T & P	Gas	Gas	Liquid	Solid
Increasing \longrightarrow atomic and ionic radius				
Decreasing \longrightarrow ionization energy				
Decreasing \longrightarrow electronegativity				

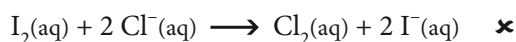
Figure 311 Properties of the halogens

formation of a precipitate (see equation below) indicates that a chloride, bromide or iodide ion is present (note that because AgF is soluble, the fluoride does not give a precipitate). Silver chloride (AgCl) is white, but rapidly darkens through purple to black in sunlight through photodissociation to silver and chlorine. Silver bromide (AgBr) is an off-white (or cream) colour and silver iodide (AgI) a pale yellow.



Both the electronegativity and oxidising power of the halogens decrease going down the group as the size of the atoms increases and the attraction between the nucleus and the electrons becomes less. As a result, going down the group, the elements become less powerful oxidising

agents. This means that a higher halogen will displace a lower halogen from its salts, for example, chlorine will oxidise iodide ions to iodine and this may be detected by the solution changing colour from colourless to brown. A lower halogen cannot however displace a higher halogen from its salts, e.g. iodine will not oxidise chloride ions to chlorine:



The results of displacement reactions of this type, and precipitation reactions with aqueous silver ions, are summarised in Figure 313.

Halide ion Reagent	F^-	Cl^-	Br^-	I^-
Aqueous Ag^+	No reaction	White precipitate (turns black in sunlight) $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl}$	Cream precipitate $\text{Ag}^+ + \text{Br}^- \longrightarrow \text{AgBr}$	Pale yellow precipitate $\text{Ag}^+ + \text{I}^- \longrightarrow \text{AgI}$
Chlorine	No reaction	No reaction	Solution turns yellow then brown $\text{Cl}_2 + 2\text{Br}^- \longrightarrow \text{Br}_2 + 2\text{Cl}^-$	Solution goes yellow then black precipitate $\text{Cl}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Cl}^-$
Bromine	No reaction	No reaction	No reaction	Solution goes yellow then black precipitate $\text{Br}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Br}^-$
Iodine	No reaction	No reaction	No reaction	No reaction

Figure 313 Summary of some reactions of the halide ions

Period 3 elements	Na	Mg	Al	Si	P	S	Cl	Ar
Electronic structure	2,8,1	2,8,2	2,8,3	2,8,4	2,8,5	2,8,6	2,8,7	2,8,8
Boiling point / K	1156	1380	2740	2528	553	718	238	87
Metallic / non-metallic		Metallic		Metalloid		Non-metallic		Inert gas
Decreasing atomic radius \longrightarrow								
Increasing ionisation energy \longrightarrow								
Increasing electronegativity \longrightarrow								
Decreasing metallic character \longrightarrow								
Increasing hydrolysis of chlorides \longrightarrow								
Increasing acidic oxides \longrightarrow								

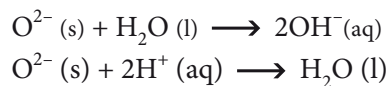
Figure 314 Trends across period 3

3.3.2 Discuss the changes in nature, from ionic to covalent and from basic to acidic, of the oxides across period 3.

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TRENDS IN THE OXIDES OF THE PERIOD 3 ELEMENTS

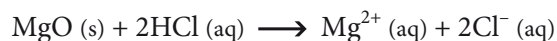
Going across a period of the periodic table, the nature of the elements changes, as shown in Figure 315. At the left hand side the elements (e.g. Na & Mg) have relatively low ionization energies and so they bond to other elements to form ionic compounds in which they have lost their valence electrons and exist as cations. This is typical metallic behaviour. The oxides of these elements are therefore ionic and contain the oxide ion. The oxide ion can form a bond to hydrogen ions and as a result these ionic oxides act as bases dissolving in water to give alkaline solutions and neutralising acids to produce a salt and water:



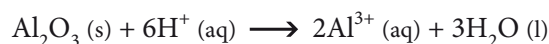
With sodium oxide:



With magnesium oxide: and hydrochloric acid



Aluminium oxide is amphoteric (that is, it will react with and hence dissolve in, both acids and alkalis):



Formula	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇
Ratio of Atoms	2 : 1	2 : 2	2 : 3	2 : 4	2 : 5	2 : 6	2 : 7
Bonding	Ionic	Ionic	Highly polar covalent	Polar covalent	Polar covalent	Polar covalent	Polar covalent
Acid-base Character	Basic	Basic	Amphoteric	Weakly acidic	Acidic	Acidic	Acidic
Other Oxides	Na ₂ O ₂				P ₂ O ₃	SO ₂	ClO ₂ & Cl ₂ O

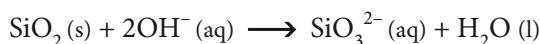
Figure 315 Some properties of the period 3 oxides

It therefore displays the properties of both metallic and non-metallic oxides. Refer to Figure 315.

Moving towards the middle of the periodic table the ionization energy becomes too great for cation formation and the elements tend towards non-metallic behaviour. In this region the elements (e.g. C and Si) bond by means of covalent bonds. Carbon dioxide reacts reversibly with water to form a weakly acidic solution

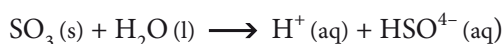
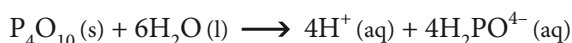


Silicon dioxide has little acid-base activity, but it does show weakly acidic properties by slowly dissolving in hot concentrated alkalis to form silicates.



At the far right of the period the elements (except for the noble gases) continue to be able to form covalent bonds by sharing electrons with other non-metals, but gaining an additional electron also becomes energetically feasible. This means that these elements (e.g. S and Cl) also have the option of combining with metals to form ionic compounds in which they exist as anions (e.g. S²⁻ and Cl⁻).

The oxides of these elements react completely when dissolved in water to form acidic solutions. For example phosphorus(V) oxide reacts to form a solution of phosphoric(V) acid a weak acid and sulfur trioxide reacts to form a solution of sulfuric acid, a strong acid:



These trends in the properties of the compounds of the elements on going across the third period are discussed in considerably more detail in the next section.

Exercise 3.3

- The reactivity of the alkali metals increases in the order
 - Na, K, Li
 - K, Na, Li
 - Li, Na, K
 - Li, K, Na
- An aqueous solution of chlorine acts as a bleach. This is because the solution
 - acts as an oxidant and converts the coloured dye to a colourless product.
 - acts as a base and converts the coloured dye to a colourless product.
 - acts as a reductant and converts the coloured dye to a colourless product.
 - acts as an acid and converts the coloured dye to a colourless product.
- Going down the halogen group the state of the elements, at room temperature and pressure, changes from gas to liquid to solid. The reason for this is that
 - the strength of the bonds between the atoms increases.
 - the strength of the forces between the molecules increases.
 - the polarity of the molecules increases.
 - the electronegativity of the atoms decreases.

4. On going across a period of the periodic table, the elements tend to become less metallic in character. Which one of the following is not an indication of this trend?
- There is an overall increase in molar mass.
 - There is an increase in electronegativity.
 - There is an overall increase in ionization energy.
 - There is a change in bond type from ionic to covalent.
5. Which one of the following is not true of the alkali metals?
- They have a high density.
 - They form ionic compounds.
 - Their chlorides dissolve in water to form neutral solutions.
 - Their oxides dissolve in water to form alkaline solutions.
6. a) Write a balanced equation for the reaction of sodium with water.
 b) What would be seen as this reaction occurred?
 c) To what class of chemical reactions does this belong?
 d) Describe how the change in the character of this reaction can be used to compare the reactivity of sodium with those of lithium and potassium.
7. Give the colours of the following:
- Iodine vapour.
 - The precipitate initially formed when aqueous barium chloride reacts with aqueous silver nitrate.
 - The colour this changes to when exposed to sunlight for a long time.
 - The colour of the solution when chlorine is bubbled through aqueous sodium bromide.
 - The precipitate formed by the reaction of aqueous solutions of lead(II) nitrate and potassium iodide.
8. When aqueous silver nitrate is added to a colourless aqueous bromide solution, in the presence of excess nitric acid, an off-white precipitate forms. The experimenter assumes that this shows the presence of bromide ions in the solution.
- If this is the case, write a balanced ionic equation for the formation of the precipitate.
- A colleague suggests that this would also be the expected result if the solution had contained a mixture of chloride and iodide ions.
- How could the experimenter test his colleague's hypothesis? Describe what s/he should do, and give the results you would expect for both the bromide ion and the mixture of chloride and iodide ions. Write balanced equations for any reactions that you describe.
9. For each of the following pairs, state whether a reaction would or would not occur on mixing, explaining your reasoning. In cases where a reaction does occur, write an ionic equation for the reaction and state any colour change you would expect to see.
- chlorine and aqueous sodium bromide.
 - bromine and aqueous potassium fluoride.
 - bromine and aqueous calcium iodide.
 - iodine and aqueous magnesium bromide.
10. Properties of the elements and their compounds often show regular variations with respect to their position in the periodic table.
- Describe the general trend in acid-base character of the oxides of the elements in the third period (Na to Ar). Give one example each of an acidic oxide and a basic oxide and show with equations how these oxides react with water.
 - How does the oxidising strength of the halogens vary down the group? Account for this trend.
 - How does the reducing strength (i.e. the ability to donate electrons) of the alkali metals vary down the group? Account for this trend.

HIGHER LEVEL

13.1 TRENDS
ACROSS PERIOD 3 (AHL)

13.1.1 Explain the physical states (under standard conditions) and the electrical conductivity (in the molten state) of the chlorides and oxides of the elements in period 3 in terms of their bonding and structure.

13.1.2 Describe the reactions of chlorine and the chlorides referred to in 13.1.1 with water.

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The position of the elements in the periodic table is related to the type of chemical bonding that occurs in their compounds, which in turn has an effect on the formulas and properties of the compounds. The physical properties that result from different types of chemical bonding are more fully discussed in chapter 4 and this should be referred to when reading this section.

OXIDES OF PERIOD 3

As the number of valence electrons increases, going across the period there is a steady increase in the number of electrons available for bond formation and hence in the number of oxygen atoms that each element bonds to. The formulas of the highest oxides of the period 3 elements display distinct periodicity, with each successive element bonding to an extra half oxygen – Na_2O , MgO , Al_2O_3 , SiO_2 , P_4O_{10} (equivalent to P_2O_5), SO_3 , Cl_2O_7 . (see Figure 315 & 316) Often at the right of the periodic table more than one oxide exists and these contain the element in different oxidation states. For example phosphorus can form phosphorus(III) oxide (P_4O_6 ; P in a +3 oxidation state) as well as phosphorus(V) oxide (P_4O_{10} ; P in a +5 oxidation state). Similarly sulfur forms sulfur dioxide (SO_2 ; +4 state) as well as sulfur trioxide (SO_3 ; +6 state), whereas chlorine forms dichlorine monoxide (Cl_2O ; +1 state) and the explosive chlorine dioxide (ClO_2 ; +4 state), as well as dichlorine heptoxide (Cl_2O_7 ; +7 state).

The oxides of the elements on the left of the periodic table (Na and Mg) are ionically bonded and hence are solids with high melting and boiling points. In the centre of the periodic table silicon dioxide exists as a giant covalent lattice in which each atom is joined to all the others by

strong covalent bonds. As a result it is a solid with very high melting and boiling points. To the right of the period, molecular covalent bonding occurs, so that the compounds are gases, liquids or low melting point solids as a result of the relatively weak forces that exist between the molecules. The molten oxides of the first two elements (sodium and magnesium) can conduct owing to the presence of mobile ions in the liquid, but the oxides of the non-metals do not conduct in the liquid state. Aluminium oxide shows characteristics of both ionic and covalent bonding. It has an exceptionally high melting point and is a poor conductor of electricity in the liquid phase.

The acid-base properties of the oxides of period 3 were described in the previous section.

CHLORIDES OF PERIOD 3

The formulas of the highest chlorides of the period 3 elements also display a marked periodicity, though this is not as complete as that displayed by the oxides (see Figure 316). Going across the period each element bonds to one more chlorine – NaCl , MgCl_2 , AlCl_3 (more correctly written as Al_2Cl_6 in its gaseous state), SiCl_4 and PCl_5 . Once again at the right hand side other chlorides exist in which the element has a different oxidation state, for example PCl_3 (P in a +3 state) exists as well as PCl_5 (P in a +5 state).

The chlorides of metals, such as sodium chloride and magnesium chloride, are ionically bonded, crystalline solids with high melting points. When added to water these chlorides dissolve without chemical reaction, to give solutions in which the component ions can behave independently.



Even though aluminium is a metal the behaviour of many of its compounds, especially when anhydrous, is more typical of non-metals. This is a result of the small size and high charge of the ion that aluminium forms. Aluminium chloride for example, although a solid, sublimes at the surprisingly low temperature of 178°C to give a vapour consisting mainly of Al_2Cl_6 molecules. When added to water, anhydrous aluminium chloride undergoes vigorous hydrolysis (that is splitting by the action of water) in which the bonds between aluminium and chlorine are broken and a strongly acidic solution is formed.



Even hydrated aluminium chloride produces quite acidic solutions owing to the dissociation of the water molecules associated with the small, highly charged, Al^{3+} ion.

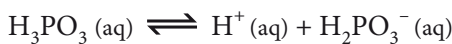
The giant covalent structure, found for the oxides of the elements in the middle of the period, is not generally found for the chlorides because chlorine usually forms only one bond, making an extended lattice impossible. The chlorides of non-metals, such as silicon tetrachloride and the chlorides of phosphorus, all have molecular covalent structures. As a result of the weak forces between their molecules these compounds have low melting and boiling points. When added to water a hydrolysis reaction occurs, in which the bonds between the element and chlorine are replaced by bonds between the element and oxygen. The result is an acidic solution containing hydrogen ions, chloride ions and the oxide, or an oxyacid of the element. For example with silicon tetrachloride:



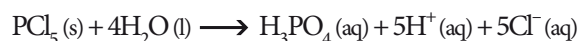
In the case of the chlorides of phosphorus, such as phosphorus trichloride (or phosphorus(III) chloride), the oxyacid formed also dissociates:



$\text{P}(\text{OH})_3$ or H_3PO_3 is phosphoric(III) acid; a weak acid that partially dissociates as shown:



Similarly with phosphorus pentachloride (or phosphorus(V) chloride),



H_3PO_4 is phosphoric(V) acid; a strong acid that fully dissociates as shown below.



Chlorine itself (Cl_2), which may be regarded as “chlorine chloride”, fits in with this pattern of behaviour, being a molecular covalent substance that reacts with water in an analogous hydrolysis reaction.

Because of the presence of mobile ions, sodium and magnesium chlorides conduct electricity when molten or in aqueous solution. The chlorides of the remaining elements of period 3 do not conduct electricity in the molten state, as would be expected for molecular covalent compounds. In aqueous solution however they do conduct electricity because of the ions formed in the chemical reactions above.

The trends in the properties of the elements, chlorides and oxides of the elements from sodium to chlorine are summarised in Figure 316.

Element	Na	Mg	Al	Si	P	S	Cl
Bonding	Metallic			Giant covalent	Molecular covalent		
Chloride							
Formula	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₅ PCl ₃	Complex	Cl ₂
Bonding	Ionic		Intermediate	Molecular covalent			
Oxide							
Formula	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀ P ₄ O ₆	SO ₃ SO ₂	Cl ₂ O ₇ Cl ₂ O
Bonding	Ionic		Intermediate	Giant covalent	Molecular covalent		
Acid/base properties	Sol. basic	Insol. basic	Amphoteric	Insol. acidic	Soluble acidic		

Figure 316 The period 3 elements, their chlorides and their oxides

Exercise 13.1

1. Going across the third period of the periodic table, there is a steady change in the formulae of the oxides formed. Which one of the following oxides is not an example of this trend?

- A Al_2O_3
 B Na_2O
 C SO_2
 D P_4O_{10}

2. Hydrolysis is a reaction in which

- A water adds on to a molecule.
 B water splits up a molecule.
 C water is a product.
 D water acts as a catalyst.

3. a) When sodium chloride is added to water the resulting solution is a good electrical conductor. The same is true of the solution formed when phosphorus trichloride is added to water, but for slightly different reasons. Explain this behaviour, writing equations for any reactions involved.

- b) Given a sample of the two solutions produced by adding these two chlorides to water describe, giving the results that would be observed,

- i a test to show that both contained the chloride ion.
 ii a test that would tell which solution was formed from which chloride.

4. The oxides of the elements in the third period show a trend in acid-base properties going across the period. Choose specific examples of three oxides, one basic, one amphoteric and one acidic, then use these examples to illustrate this trend, writing balanced equations for any chemical reactions involved.

5. There is a trend in the chemical character of the elements in the third period (Na to Ar). Describe this briefly with respect to the bonding present in the element and its chloride. Explain these in terms of trends that occur in atomic properties such as nuclear charge, ionization energy and electronegativity.

13.2 FIRST ROW D-BLOCK ELEMENTS (AHL)

13.2.1 List the characteristic properties of transition elements.

13.2.2 Identify why Sc and Zn are not considered to be transition elements.

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The **d-block elements** are those that occur in the central block of the periodic table, i.e the groups headed by the elements scandium to zinc, in which the d-subshell of an atom is being filled with electrons. A subset of these elements, known as the **transition elements**, are those in which the element has a partially filled d-sublevel in one of its common oxidation states.

The elements of the d-block are all dense, hard metallic elements. The electronic structures differ by the addition of one more d-electrons for each successive element, but note the two exceptional electronic structures of chromium and copper. In these elements there is only one electron present in the 4s sublevel, with the 'missing' electron being present in the 3d sublevel so as to gain the additional stability associated with a half filled and fully filled d-sublevel respectively. This again shows how similar in energy the 3d and 4s sublevels are.

Since the 3d electrons quite effectively shield the outer 4s electrons, the first ionization energy remains relatively constant. As a result the d-block elements have many similar chemical and physical characteristics. The ease with which the 3d electrons are lost decreases as the nuclear charge increases, resulting in a trend from the maximum oxidation state being the most stable at the start of the series to the +2 oxidation state being the most stable at the end. As a result of their partially filled d-sublevel, the transition metals have certain properties in common, which are not generally shared by other metals (including Sc and Zn), some of these are:

- a variety of stable oxidation states
- the ability to form complex ions
- the formation of coloured ions
- catalytic activity

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic structure	[Ar] 3d ¹ 4s ²	[Ar] 3d ² 4s ²	[Ar] 3d ³ 4s ²	[Ar] 3d ⁵ 4s ¹	[Ar] 3d ⁵ 4s ²	[Ar] 3d ⁶ 4s ²	[Ar] 3d ⁷ 4s ²	[Ar] 3d ⁸ 4s ²	[Ar] 3d ¹⁰ 4s ¹	[Ar] 3d ¹⁰ 4s ²
Decreasing stability of maximum oxidation state →										
Increasing stability of +2 oxidation state →										

Figure 318 Electronic structure and oxidation state stability of the d-block elements (first row)

13.2.3 Explain the existence of variable oxidation number in ions of transition elements.

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VARIABLE OXIDATION STATES

The **s-block metals**, such as sodium and calcium, have s-electrons that are easily lost, but the ionization energies for the inner electrons are so high that these are never lost in chemical reactions, as shown in Figure 319 for calcium. For this reason they always have the same oxidation states in their compounds +1 for group 1 and +2 for group 2. Transition metals have slightly higher effective nuclear charges and so their first ionization energies are a little higher, but there is no sudden increase in successive ionization energies in the same way as there is with the s-block elements (until all the 3d and 4s electrons have been lost), as can be seen for chromium in Figure 319. This is because the 3d and 4s electrons have similar energies. The oxidation state of transition metals therefore depends on how strongly oxidising the environment is, which depends on the presence of species that readily gain electrons.

It can be seen by referring to Table 320, that one of the most commonly found oxidation states of transition metals is the +2 state which corresponds to the loss of the two 4s electrons. This is a very stable state on the right of the d-block where the high nuclear charge increases the difference in energy between the 3d and 4s electrons, but becomes an increasingly powerful reductant going to the left. Ti^{2+} , for example, does not exist in aqueous solution because it reduces water to hydrogen. The second commonly found oxidation state, going as far as manganese, is that which corresponds to the loss of all the 3d and 4s valence electrons (+3 for Sc; +4 for Ti etc.). These are stable on the left of the d-block, but become increasingly powerful oxidants going across the period as the energy required to produce these states becomes quite high (see Fig. 319). The highest oxidation states usually occur as oxoanions, such as dichromate(VI) ($\text{Cr}_2\text{O}_7^{2-}$) and permanganate (also referred to as manganate(VII); (MnO_4^-)). There are also a few other commonly encountered states, such as Cr^{3+} and Fe^{3+} , which do not fit into this pattern. These common oxidation states are summarised in Table 320.

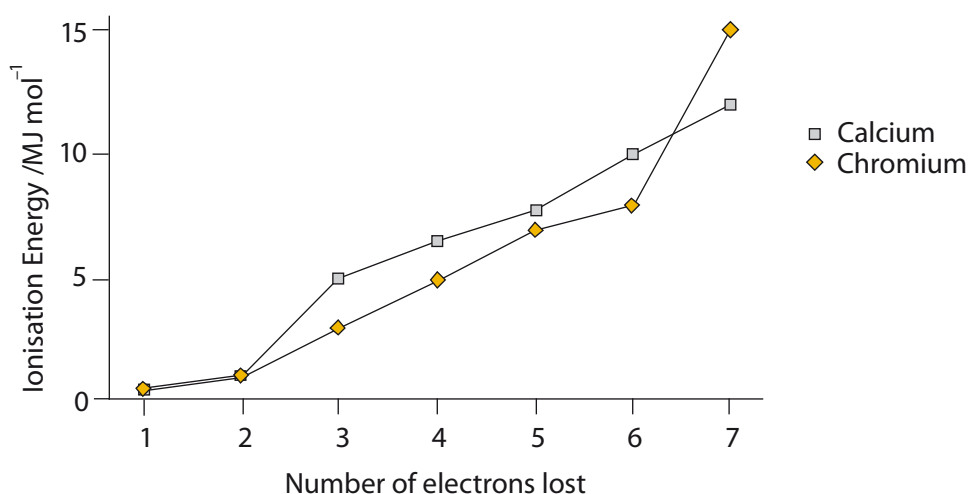


Figure 319 The successive ionisation energies of calcium and chromium

TOK The historical development of the Periodic Table

Although the periodic table, in its modern form, is organised in terms of atomic numbers and electronic structure, it originated from a study of the periodicity of chemical properties. No sooner had theoretical chemistry been put on a sound footing in the early 18th century by the recognition of the elements as fundamental building blocks, through the work of Boyle, Lavoisier and Dalton, and the determination of the relative atomic masses of these, especially by Berzelius and Cannizzaro, than chemists started to notice that certain elements had very similar chemical properties. Döbereiner noticed that if three elements had similar chemical properties then one element often had a relative atomic mass approximately mid-way between the other two. Examples of this are Li (7), Na (23), K (39) and Cl (35), Br (80), I (127). Döbereiner named these groups 'triads'. Newlands then noticed that every eighth element, when placed in order of increasing relative atomic mass, showed similar chemical properties and referred to these as 'octaves'. The examples given above fit in with this as do many others (note the noble gases had not been discovered at this date). There were however still many anomalies, for example copper was in the same group as sodium and potassium!

The name most closely associated with the periodic table is undoubtedly that of Mendeléeu. He extended and rearranged Newland's table, separating groups into two subgroups that gave better correspondence with chemical properties. Another innovation was that he left gaps in the table to improve the fit, and predicted that elements would be discovered to fit these gaps. The early ones correspond to the elements we now know as scandium, gallium and germanium. Mendeléeu gave detailed predictions of the physical and chemical properties that he expected these undiscovered elements to have and his predictions proved to be remarkably accurate – a classic example of scientific methodology in action. Mendeléeu's periodic table is shown in Table 17 below with his gaps marked by stars (*):

The modern periodic table is similar to that of Mendeléeu, except that the elements have been re-ordered according to atomic number (otherwise argon would be classified as an alkali metal!), the noble gases have been added and the d- and f-block metals have been collected together as separate groups in the centre of the table.

Series	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
1	H							
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	*	Ti	V	Cr	Mn	Fe,Co,Ni
5	Cu	Zn	*	*	As	Se	Br	
6	Rb	Sr	Y	Zr	Nb	Mo	*	Ru,Rh,Pd
7	Ag	Cd	In	Sn	Sb	Te	I	
8	Cs	Ba	Dy	Ce	*	*	*	
9	*	*	*	*	*	*	*	
10	*	*	Er	La	Ta	W	*	Os,Ir,Pt
11	Au	Hg	Tl	Pb	Bi	*	*	
12	*	*	*	Th	*	U		

Figure 317 Mendeléeu's Periodic Table

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
+7					MnO_4^-				
+6				CrO_4^{2-} $\text{Cr}_2\text{O}_7^{2-}$	MnO_4^{2-}				
+5			VO_2^+ VO_3^-						
+4		Ti^{4+}	VO^{2+}		MnO_2				
+3	Sc^{3+}	Ti^{3+}	V^{3+}	Cr^{3+}		Fe^{3+}			
+2			V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
+1									Cu^+
<p>Increasing stability of +2 state \longrightarrow</p> <p>\longleftarrow Increasing stability of maximum state</p>									

Figure 320 Common oxidation states of the d-block elements

Note that the variety of oxidation states increases to a maximum at manganese and in the second half of the d-block far fewer oxidation states are found because the greater nuclear charge causes an increase in the ionization energies of the 3d electrons. The stability of the half-filled and fully filled 3d level (encountered before in the unusual electronic structures of Cr and Cu) also affects the stability of oxidation states. In manganese the +2 state, which has a half filled shell ($[\text{Ar}]3d^5$), is much more stable than the +3 ($[\text{Ar}]3d^4$) state and the +4 ($[\text{Ar}]3d^3$) state (usually only encountered as manganese(IV) oxide, MnO_2), which are therefore quite strong oxidants. With iron however the reverse is true because it is the +3 state that has the half filled shell ($[\text{Ar}]3d^5$) and the +2 state ($[\text{Ar}]3d^6$) is quite strongly reducing. In copper, the existence of the +1 state is due to the stability of the filled shell ($[\text{Ar}]3d^{10}$). Note that because the Cu^+ ion has a full 3d sub-shell, like Zn^{2+} , its compounds are not coloured.

13.2.4 Define the term 'ligand'.

13.2.5 Describe and explain the formation of complexes of d-block elements.

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THE FORMATION OF COMPLEX IONS

The ions of d-block metals and those in the lower section of the p-block (such as lead) have low energy unfilled d- and p-orbitals. These orbitals can accept a lone pair of electrons from species, known as ligands, to form a dative bond between the ligand and the metal ion. For example an ammonia molecule can donate its non-bonding electron pair to a copper(II) ion.

	Complex Ion	Charge on Complex Ion	Oxidation State of Metal Ion	Similar to
$[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2+	+2	CaCl_2
$[\text{K}_2(\text{CuCl}_4)]$	$(\text{CuCl}_4)^{2-}$	2-	+2	K_2SO_4

Figure 322 Two compounds of complex ions

This behaviour, in which one species donates an electron pair whilst another accepts it, is **Lewis acid–base** behaviour. Species which contain ligands bonded to a central metal ion are known as complex ions, a common example being the deep blue complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ formed when excess aqueous ammonia is added to a solution of a copper(II) salt. Note that the complex ion is written in square brackets. The charge is the sum of the charge on the central metal ion and the charges on the ligands. For example the charge on the $[\text{CoCl}_4]^{2-}$ ion is the sum of the +2 charge on the cobalt and the four –1 charges on the chloride ions (+2 – 4 = –2).

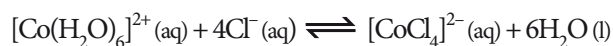
Ligands are species that can donate a pair of non-bonding electrons to the central metal ion in the complex; the most common examples are water, ammonia, chloride ion and cyanide ion. Most complex ions have either six ligands arranged octahedrally around the central atom (usually found with water and ammonia ligands), or four ligands arranged tetrahedrally (usually found with chloride ion

ligands), though some examples of linear complex ions with a two ligands are found. These are illustrated in Figure 321.

The number of ligands around the central ion is known as the coordination number of the complex ion, hence the coordination number of the metal ion in the ammine is 2, in the chloroanion is 4 and in the aqua ion is 6. The term “coordination number” also has a similar use in describing crystal structures.

Complex ions can have either a positive charge (\therefore cations) or a negative charge (\therefore anions) and hence form salts with ions of the opposite charge as illustrated in Figure 322 above. Both complexes are water soluble and conduct electricity in aqueous solution. Some complex ions are however neutral because the charge on the metal ion and the ligands cancel. An example would be $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. Being uncharged this is almost insoluble and behaves as a molecular species. With aqueous silver nitrate it does not form a precipitate showing that in the complex ion the chloride ions are strongly bonded to the central metal ion and are not free to react with the silver ions (see also the chromium(III) species in Figure 324).

The formation of complex ions stabilises certain oxidation states and hence affects the E° value of the related redox system. For example the value for the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}/[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ couple is +0.77 V, whereas that for the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ couple is +0.36V, in other words the presence of the cyanide ligand stabilises the iron(III) state. The formation of a complex ion can also have a major effect on the colour of a metal ion in solution. Aqueous cobalt(II) salts, for example contain the hexaaquacobalt(II) ion, which is a pink colour. If concentrated hydrochloric acid is added to this, the solution turns blue owing to the formation of the tetrachlorocobalt(II) ion:



Pink

Blue

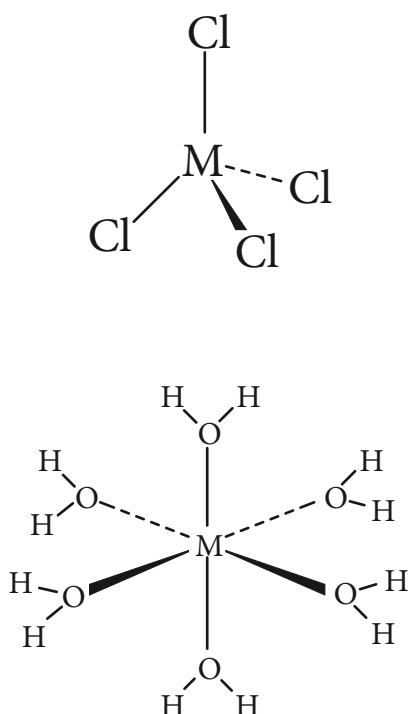


Figure 321 Tetrahedral and octahedral complex ions

This is an example of a ligand exchange reaction. For most transition metal ions, such as cobalt(II) and copper(II)

Metal ion	Water Octahedral	Ammonia Octahedral/Sq. planar	Chloride ion Tetrahedral
Cobalt(II)	Pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	Straw $[\text{Co}(\text{NH}_3)_6]^{2+}$	Blue $[\text{CoCl}_4]^{2-}$
Nickel(II)	Green $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	Blue $[\text{Ni}(\text{NH}_3)_6]^{2+}$	Yellow-green $[\text{NiCl}_4]^{2-}$
Copper(II)	Blue $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Deep blue $[\text{Cu}(\text{NH}_3)_4]^{2+}$	Yellow $[\text{CuCl}_4]^{2-}$

Figure 323 Some common complex ions and their colours

ligand replacement takes place freely in aqueous solution, but for others, such as chromium(III) and cobalt(III) there is a significant activation energy barrier to this, hence the complex ion is unusually stable, as for example the chromium(III) complex ions given in Figure 324.

Some examples of common complex ions and their colours are given Figure 323.

ISOMERISM IN COMPLEX IONS

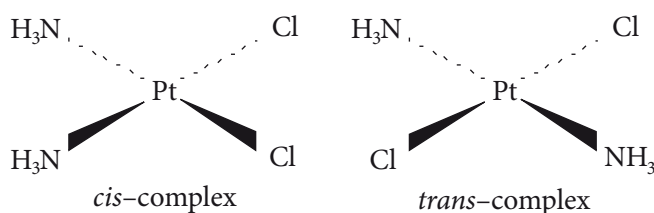
Complex ions exhibit many types of **isomerism** analogous to those found with organic compounds. Firstly there is formula isomerism (analogous to structural isomerism) associated with which species are acting as ligands and hence directly bonded to the metal ion. There are for example three forms of chromium(III) chloride hexahydrate that vary in the way the chloride ions are bonded. Because the bonding of the ligand to the metal ion is very stable in this case, the number of chloride ions present as free chloride ions can be found by titration with aqueous silver nitrate. These isomers are summarised in Figure 324 below:

Formula	Colour	Amount of chloride precipitated by $\text{Ag}^+(\text{aq})$
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+\text{Cl}^- \cdot 2\text{H}_2\text{O}$	Dark green	1 mol
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}(\text{Cl}^-)_2 \cdot \text{H}_2\text{O}$	Light green	2 mol
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{Cl}^-)_3$	Grey-blue	3 mol

Figure 324 Isomers of hydrated chromium(III) chloride hexahydrate

Stereoisomerism also occurs in complex ions. The simplest examples of geometric isomerism occurs in square planar transition metal complexes such as $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ (note that as it contains Pt^{2+} , this is an electrically neutral complex), which exists in both *cis*- and *trans*- forms:

Geometric isomerism can also occur in six coordinate octahedral complexes such as $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ depending

Figure 325 *cis*- and *trans*- forms

on whether the two chloride ligands occupy adjacent (*cis*) or opposite (*trans*) sites.

The ligands considered up to now can only form one bond to the metal ion, they are monodentate ligands. With bidentate ligands (i.e. those that can form two rather than one bond to a metal ion) such as diaminoethane

($\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ shown as $\text{N}-\text{N}$ below) non-superimposable mirror image forms can occur, giving rise to enantiomerism. An example is the complex ion $[\text{Co}(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2)_3]^{3+}$, shown below:

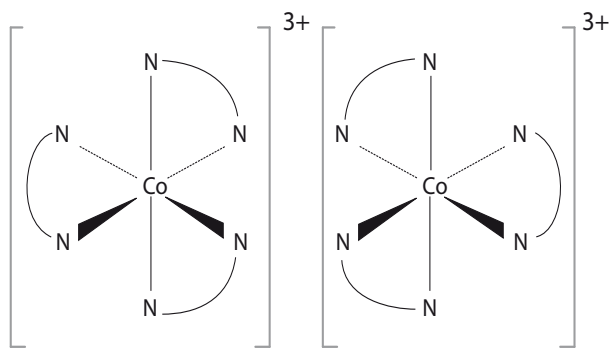


Figure 326 The two enantiomers of the complex ion $[\text{Co}(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2)_3]^{3+}$

13.2.6 Explain why some complexes of d-block elements are coloured.

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In the case of most copper(II) compounds, red and yellow light are absorbed so that they look a blue-green colour, that is, we see the transmitted light which is the complementary colour of the absorbed light. The exact shade depends slightly on the species surrounding the copper, so that the hexaaquacopper(II) ion is light blue but the tetraamminecopper(II) ion is dark blue.

If there are no electrons in the d-orbitals, as is the case for Sc^{3+} and Ti^{4+} , then there are no d-electrons to move and the compounds are colourless. If the d-orbitals are all completely filled, as is the case with Zn^{2+} , then there are no vacant orbitals for the electrons to move into and again the compounds are colourless.

13.2.7 State examples of the catalytic action of transition elements and their compounds.

13.2.8 Outline the economic significance of catalysts in the Contact and Haber processes.

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COLOURED IONS

In an isolated atom all of the d-orbitals have exactly the same energy, but if an atom or ion is surrounded by charged ions or polar molecules, the effect of the electric field from these has a different effect on the various d-orbitals. Because of their symmetry the orbitals are often split up into two different groups. For octahedral complex ions three orbitals are at low energy and two orbitals at higher energy. The difference in energy between these two groups of orbitals varies slightly with the nature of the species surrounding the metal ion, but the frequency of the light corresponding to this (linked by the formula $\Delta E = h.f$) occurs in the visible region. This means that when white light passes through a compound of a transition metal, light of a particular frequency is absorbed and an electron is promoted from a lower energy orbital to a higher energy orbital, as shown in the Figure 327 below.

The light that passes through therefore appears coloured because some of the frequencies have been absorbed.

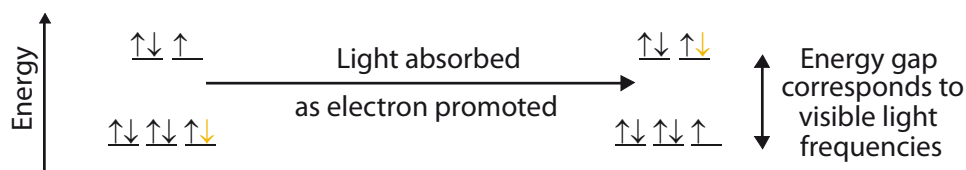


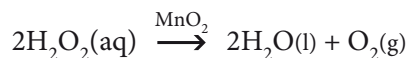
Figure 327 The interaction between transition metal ions and light

CATALYTIC ACTIVITY

The catalytic behaviours of **transition metals** and their ions are mainly caused by a combination of two properties already mentioned. Firstly they form complex ions with species that can donate lone pairs of electrons. This results in close contact between the different ligands, as well as between the metal and the ligand. Secondly transition metal ions have a wide variety of relatively stable oxidation states, so they can readily gain and lose electrons in redox reactions.

d-block element catalysts can either be heterogeneous or homogeneous, though the former are more common. Many enzymes involved in catalysing redox reactions also contain transition metal ions near the active site (refer to Chapter 13). In a heterogeneous catalyst the surface of the metal or compound provides an active surface on which the reaction can occur with a reduced activation energy. A common example of heterogeneous catalysis is

manganese(IV) oxide which catalyses the decomposition of hydrogen peroxide to water and oxygen.



Another example is nickel catalysing the reaction between hydrogen and an alkene to produce an alkane.

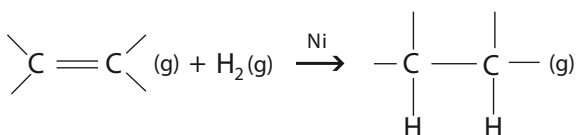
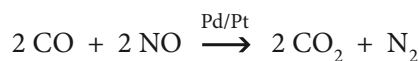


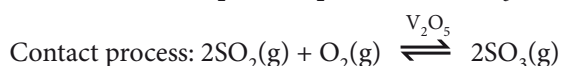
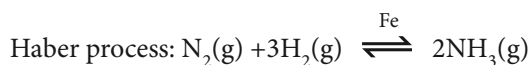
Figure 328 Production of an alkane

Here bonding to the metal surface not only brings the molecules into close contact, but also electrons from the bonds are used to bond to the metal atoms. This weakens the bonds in the molecules and lowers the activation energy.

Platinum and palladium are found in the catalytic converters fitted to the exhaust systems of cars to reduce the emission of pollutants such as carbon monoxide and oxides of nitrogen, e.g.



Many other important industrial catalysts involve transition metals, such as iron in the **Haber process** and vanadium(V) oxide in the **Contact process**.

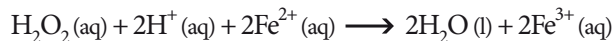


The economic importance of the chemical industry rests on the food, clothes, medicines and the great variety of consumer articles that it produces. One of the signs of the economic development of a country is the state of its chemical industry because the chemical industry can take essentially simple and often cheap raw materials and turn them into much more valuable products. For example, the Haber process which exploits the 'free' supply of nitrogen (it still costs money to extract the nitrogen) from the atmosphere and converts it into ammonia and then into explosives upon which wars and conflicts have become dependent (the commercialization of this process likely prolonged World War I by at least one year). It is also vital in the production of fertilizers that are now vital for our supply of food. Nitrogen is an element vital for plant growth, so the major use of ammonia is in the manufacture of fertilizers such as ammonium salts and urea. It is also

used in the manufacture of nitrogen containing polymers such as nylon.

Sulfuric acid is considered the "king of chemicals" and is relatively easy to produce. Sulfuric acid has numerous uses in the chemical industry – indeed the tonnage of it used annually gives a good indication of the extent of a country's chemical industry. These uses include manufacture of fertilizers (especially converting insoluble phosphate rock to soluble 'superphosphate'), polymers, detergents, paints and pigments. It is also widely used in the petrochemicals industry and in the industrial processing of metals. One of its minor, though possibly most familiar uses, is as the electrolyte in automobile batteries.

In homogeneous catalysis, the catalyst is in the same phase as the reactants. In these reactions a particular metal ion is oxidised in one stage and then reformed by being reduced in a second stage. A good example is the role of iron(II)/(III) in catalysing the slow reaction between acidified hydrogen peroxide and iodide ions. The iron(II) is oxidised by the peroxide to iron(III).



This is then reduced by the iodide ions to reform iron(II).



These reactions occur more rapidly than the direct reaction because they both have lower activation energies than the direct reaction.

Examples of enzymes containing transition metals include the presence of iron in heme, the active part of haemoglobin responsible for carrying oxygen in the blood, and of cobalt in vitamin B12 which is vital factor in the production of red blood cells as well as having other functions. The structures of these two enzymes are given in Figures 329 and 330.

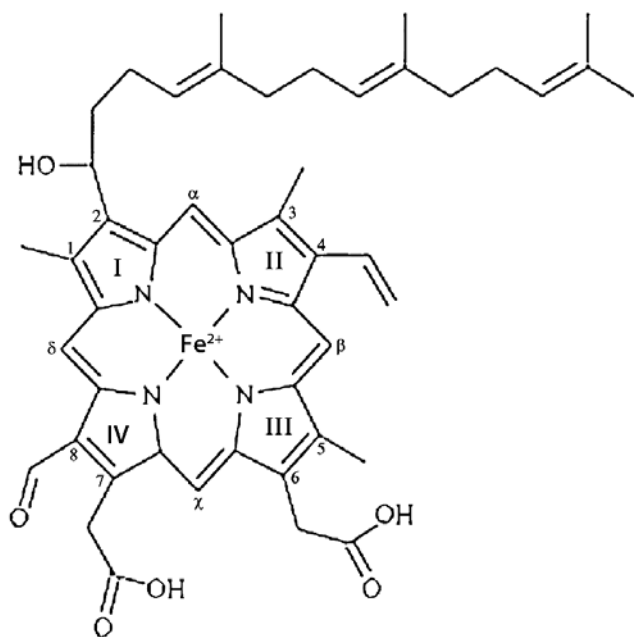


Figure 329 The structure of a heme group from cytochrome oxidase

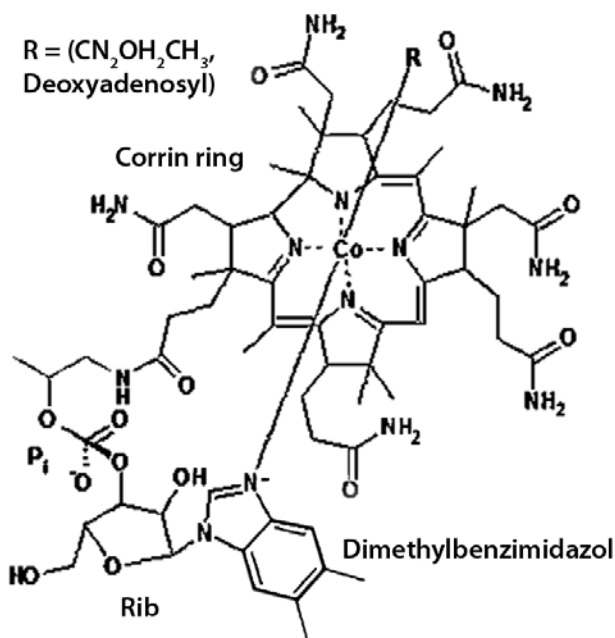


Figure 330 The structure of Vitamin B12

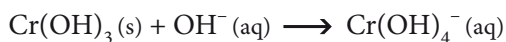
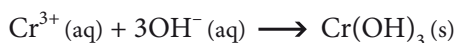
EXTENSION

THE CHEMISTRY OF INDIVIDUAL TRANSITION METAL ELEMENTS

Titanium has an electronic structure $[\text{Ar}] 3d^2 4s^2$. Titanium is actually a component of a number of quite common minerals. It is however relatively difficult to extract from these, hence the high price of the metal. Nevertheless because of its low density, high strength and corrosion resistance it finds widespread use in the aerospace industry. Its most common oxidation state in compounds is the +4 state and, as titanium dioxide (found naturally as rutile), it finds widespread use as a white pigment in paint and cosmetic products. The easily hydrolysed tetrachloride is employed as a catalyst in the Ziegler-Natta polymerisation of alkenes. Titanium(III) ions, produced by reducing titanium(IV) compounds with zinc, are powerful reductants in aqueous solution and titanium(II) is so powerfully reducing it will reduce water to hydrogen.

Vanadium has an electronic structure $[\text{Ar}] 3d^3 4s^2$ and can exist in a variety of oxidation states from +2 to +5, the higher ones existing as various oxy-ions. For example vanadium(V) can exist as VO_2^+ and VO_3^- , as well as the more familiar vanadium(V) oxide (V_2O_5 , used as a catalyst in the Contact process). If zinc is added to an acidic solution of the yellow vanadate(V) ion (VO_3^-) a notable series of colour changes take place as it is reduced firstly to blue vanadium(IV), then to green vanadium(III) and finally to the lavender coloured vanadium(II). These lower oxidation states are gradually more powerful reductants.

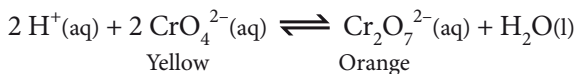
Chromium has an electronic structure $[\text{Ar}] 3d^5 4s^1$ (n.b. like copper an exception in only having one 4s electron). Its common oxidation states are +3 and +6. Compounds of chromium(III), such as chromium(III) oxide, Cr_2O_3 , and the hexaqua chromium(III) ion, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, are usually a dark green colour. Dark green chromium(III) hydroxide is precipitated when aqueous alkali is added to solutions of chromium(III) salts. Like aluminium hydroxide, it is amphoteric and redissolves in high concentrations of hydroxide ions to give a dark green solution containing the chromate(III) ion (also called chromite):



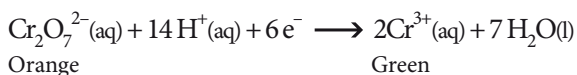
The common compounds of chromium(VI) are the dark red-brown oxide, CrO_3 , which in many ways resembles SO_3 , as well as the yellow chromate(VI), CrO_4^{2-} , and orange dichromate(VI), $\text{Cr}_2\text{O}_7^{2-}$, ions derived from it.



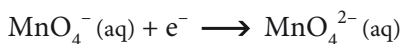
The chromate(VI) and dichromate(VI) ions are in an acid–base equilibrium. If acid is added to the yellow chromate, then the equilibrium shifts to the right to give the orange dichromate. This change can be reversed by adding an alkali:



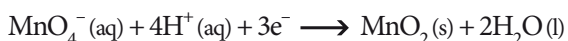
The dichromate(VI) ion is a strong oxidant in acidic solution, being reduced to the green chromium(III) ion:



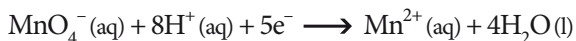
Manganese has an electronic structure $[\text{Ar}] 3\text{d}^5 4\text{s}^2$. Its common oxidation states are +2, +4, +6 and +7. The most common manganese(VII) compound is the permanganate ion (or manganate(VII) ion), MnO_4^- , which has a very intense purple colour. It is a very powerful oxidant and the other common oxidation states can be formed by its reduction under various conditions, depending on the pH at which the reaction occurs. In very strongly alkaline conditions, the dark green manganate(VI) ion is the product:



In approximately neutral solution, a brown precipitate of manganese(IV) oxide forms:



In acidic solution the almost colourless (in concentrated solution, very pale pink) manganese(II) ion is the product. This reaction is frequently used in titrations to determine the concentrations of easily oxidised species, such as SO_3^{2-} and Fe^{2+} .



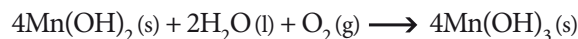
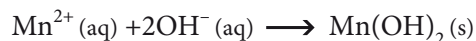
Manganese(IV) oxide is itself a powerful oxidant, for example oxidising concentrated hydrochloric acid to chlorine:



It is most commonly encountered because of its ability to catalyse the decomposition of hydrogen peroxide.

When aqueous alkali is added to solutions of manganese(II) salts a flesh coloured precipitate of manganese(II) hydroxide is formed. This rapidly darkens in the presence of air as

manganese(II) hydroxide is oxidised to manganese(III) hydroxide by oxygen in aqueous solution:

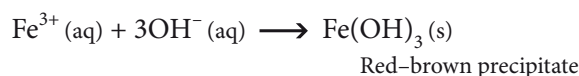
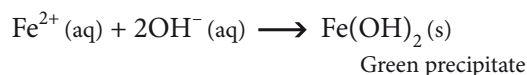


Iron has an electronic structure $[\text{Ar}] 3\text{d}^6 4\text{s}^2$. Its two common oxidation states are +2 and +3. Iron(II) compounds are usually pale green in colour. Iron(III) compounds usually vary from yellow to brown in colour. The two oxidation states are readily interconverted ($E^\ominus = 0.77\text{ V}$) so that iron(II) acts as a mild reductant and iron(III) as a mild oxidant:



Oxygen in the air will oxidise iron(II) to iron(III), the higher the pH the faster the reaction. As a result iron(II) compounds are often contaminated with traces of iron(III).

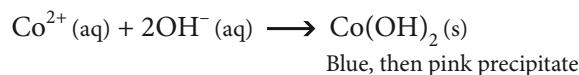
The oxidation state of iron in aqueous solution can be readily detected by adding aqueous alkali until a precipitate of the hydroxide forms. Iron(II) hydroxide is green, though it turns brown on standing as a result of aerial oxidation (similar to that of manganese(II) hydroxide above though the reaction is rather slower), and iron(III) hydroxide is red–brown:



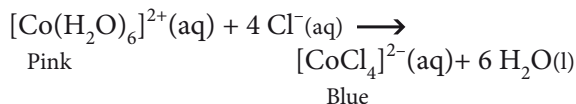
When thiocyanate (SCN^-) ions are added to a solution of an iron(III) compound an intense blood–red coloured complex ion is formed. Iron(II) salts, if pure, give no reaction. The major reaction is that shown below, though further ligand exchange is possible and the precise product will depend on the concentration of thiocyanate ions.



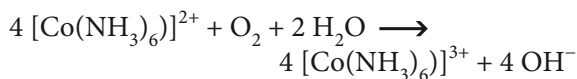
Cobalt has an electronic structure $[\text{Ar}] 3\text{d}^7 4\text{s}^2$ and is used in a variety of steels. Its most stable oxidation state is the +2 state, which in dilute aqueous solution exists as the pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion. Adding aqueous alkali to its solutions precipitates out the hydroxide, which though initially blue, slowly changes to a pink colour:



When concentrated hydrochloric acid is added to solutions containing the hexaaqua cobalt(II) ion the colour gradually changes from pink through shades of purple, eventually yielding the deep blue tetrachloro ion:

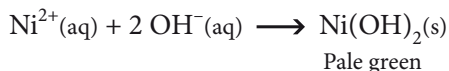


The cobalt(III) state also exists but it is generally a powerful oxidant, oxidising water to oxygen in aqueous solution. Ammonia ligands however stabilise the cobalt(III) state so that when aqueous ammonia is added to cobalt(II) compounds the straw coloured solution, formed when the initial green precipitate redissolves, gradually darkens as dissolved oxygen oxidises the cobalt(II) hexammine complex to the cobalt(III) hexammine complex.

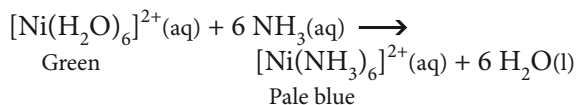


In the presence of chloride ions it is also possible to produce an interesting variety of isomers, similar to those given in Figure 324 for complex ions containing chromium(III) with chloride and water ligands, that are kinetically stable to ligand exchange reactions.

Nickel has an electronic structure $[\text{Ar}] 3d^8 4s^2$ and its only significant oxidation state is the +2 state formed by the loss of the two 4s electrons. The metal is widely used in a variety of steels and in alloys used to make coins. Nickel(II) compounds are generally pale green and in aqueous solution exist as the green hexaaqua ion, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. This precipitates out the pale green nickel(II) hydroxide when aqueous alkali is added:

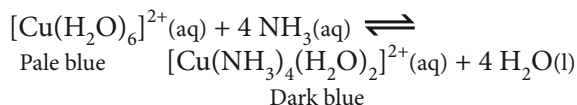
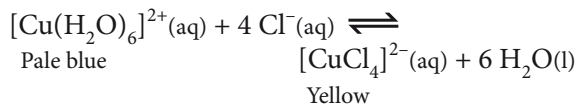


If ammonia is added the initial precipitate readily redissolves to form a pale blue solution containing the hexaammine complex:

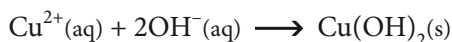


Copper has an electronic structure $[\text{Ar}] 3d^{10} 4s^1$ (again note that this is an exception, having only one 4s-electron). The most common oxidation state of copper is the copper(II) state. Copper(II) compounds are usually blue coloured though some, such as the carbonate, are green and both copper(II) oxide and copper(II) sulfide are black. Most copper(II) compounds are water soluble forming the pale blue hexaaquacopper(II) ion, but this is readily converted

into other complex ions. Adding concentrated hydrochloric acid produces the yellow tetrachlorocopper(II) anion. Adding aqueous ammonia, initially produces a pale blue precipitate of copper(II) hydroxide, but this readily redissolves in excess of the reagent to give a dark blue solution containing the tetraamminecopper(II) cation:



The reaction to precipitate blue copper(II) hydroxide also occurs when other aqueous alkalis are added to solutions of copper(II) salts:

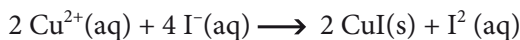


Copper can also exist in a +1 oxidation state. This state has a completely filled d-subshell (like Ag^+ and Zn^{2+}), so that most of its compounds are colourless. The ion is unstable in aqueous solution forming copper metal and copper(II) ions:

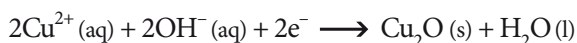


Note that in this reaction the copper(I) is simultaneously oxidised and reduced. Reactions of this type are known as disproportionation reactions.

Insoluble copper(I) salts are stable however, the most common being copper(I) iodide, which is a white solid formed by the reduction of copper(II) compounds with iodide ions. The iodine, formed at the same time, can be removed by adding excess aqueous thiosulfate.



Copper(I) oxide is a red-brown solid that is formed when copper(II) compounds are reduced under alkaline conditions, for example in Fehling's solution where tartrate ions complex the copper(II) ions to prevent copper(II) hydroxide precipitating:



Transition metals form a number of relatively small highly charged ions, such as Cr^{3+} and Fe^{3+} . In aqueous solution the water ligands of these hydrated ions dissociate to make the solution acidic, in a similar way to Al^{3+} .



Exercise

- The oxidation state that occurs for the greatest number of first row transition metals is
 - +1
 - +2
 - +3
 - +4
- The high oxidation states of transition metals are
 - usually found to the right hand side of the transition series.
 - usually found to involve simple ions.
 - usually powerful oxidants.
 - usually colourless.
- Transition metal ions are frequently coloured because
 - they absorb infrared radiation and re-emit it as visible light.
 - of the vibrations of the ligands surrounding them.
 - of the movement of electrons between d-orbitals.
 - light causes them to spontaneously change their oxidation state.
- The colour of the complex ion formed between cobalt(II) ions and excess chloride ions is
 - green.
 - yellow.
 - pink.
 - blue.
- Which one of the following elements is not classified as a transition metal?
 - Cu
 - Zn
 - Mn
 - Ti
- Explain briefly why
 - Potassium always occurs as a +1 ion in its compounds and calcium as a + 2 ion, but compounds of manganese are known in which the oxidation state of the manganese varies from +2 to +7.
 - There is a slight change in the shade of green of an aqueous solution of nickel(II) sulfate, when concentrated hydrochloric acid is added.
 - Ammonia forms complex ions with cobalt(II) ions, but methane does not.
- Describe what would be seen during the following:
 - A few drops of aqueous ammonia are added to aqueous copper(II) sulfate and then a large excess is added.
 - Sulfur dioxide gas (a strong reducing agent) is bubbled through acidified potassium dichromate(VI).
 - Aqueous iron(II) sulfate is warmed with excess aqueous hydrogen peroxide and then aqueous sodium hydroxide is added to the product.
 - Solid manganese(IV) oxide is added to aqueous hydrogen peroxide.
- Catalysts containing transition metals or their compounds, are important in many industrial processes. Choose **two** examples of this and in each case:
 - Name the catalyst.
 - Write a balanced equation for the reaction that it catalyses.

Explain the difference between homogeneous and heterogeneous catalysis and state which category your chosen examples belong to.
- Give the formulae of the complex ion(s) or oxyanion(s) of the first row of d-block elements (Sc to Zn) corresponding to each of the following:
 - A blue solution that turns green then yellow when concentrated hydrochloric acid is added.
 - The ion formed when excess aqueous ammonia is added to aqueous copper(II) sulfate.
 - A blue solution that turns pink when water is added to it.
 - An orange solution that turns yellow when alkali is added to it.

- e) A purple solution that goes dark green when concentrated alkali and a reductant are added.
10. The cyanide ion (CN^-) can form two complex ions with iron ions. The formulae of these are $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$.
- What shape would you expect these to have?
 - What is the oxidation state of the iron in the two complex ions?
 - What feature of CN^- allows it to form complex ions with transition metals?
11. Account for the following observations:
- Ti^{2+} will reduce water to hydrogen, but Ca^{2+} will not.
 - V^{3+} compounds are coloured but Sc^{3+} compounds are not.
 - V^{3+} can act as both an oxidising agent and a reducing agent, whilst Sc^{3+} is neither.
 - Cu^+ has colourless compounds but Cu^{2+} compounds are coloured.
 - $\text{Co}(\text{NH}_3)_3\text{Cl}_3$ exists in a number of isomeric forms.
12. The complex ion $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$ is octahedral and exists as two different geometric isomers.
- Draw these isomers so as to illustrate how the geometric isomerism arises.

One of these two isomers can also exist in two enantiomeric forms.

- Draw these isomers so as to illustrate how the enantiomerism arises and explain why. enantiomers of the other geometric isomer do not occur.
- Name a vitamin that contains cobalt and state a metabolic function of this vitamin.