



03

Periodicity



Essential ideas

3.1 The arrangement of elements in the Periodic Table helps to predict their electron configuration.

3.2 Elements show trends in their physical and chemical properties across periods and down groups.

13.1 The transition elements have characteristic properties; these properties are related to their all having incomplete d sub-levels.

13.2 d orbitals have the same energy in an isolated atom, but split into two sub-levels in a complex ion. The electric field of ligands cause the d orbitals in complex ions to split so that the energy of an electron transition between them corresponds to a photon of visible light.

Water being dripped into a dish containing potassium metal. Potassium reacts violently and exothermically with water, producing potassium hydroxide and hydrogen gas. The reaction is explosive because the generated heat causes the hydrogen to ignite.

The Periodic Table is the ‘map’ of chemistry; it suggests new avenues of research for the professional chemist and is a guide for students – as it disentangles a mass of observations and reveals hidden order. Chemistry is not the study of a random collection of elements, but of the trends and patterns in their chemical and physical properties.

The Periodic Table is a remarkable demonstration of the order of the subject. It was first proposed in 1869 by the Russian chemist Dmitri Mendeleev. Previous attempts had been made to impose order on the then known 62 elements, but Mendeleev had the insight to realize that each element has its allotted place, so he left gaps where no known elements fitted into certain positions. As a scientific idea it was extremely powerful as it made predictions about the unknown elements that fitted these gaps, predictions which could be tested. When these elements were later discovered, the agreement between the predicted properties and the actual properties was remarkable.



Mendeleev grouped the known elements into families, leaving gaps corresponding to elements that should exist but which had not yet been discovered.

TOK

What is the role of imagination and creativity in the sciences? To what extent might the formulation of a hypothesis be comparable to imagining and creating a work of art?

TOK

Which attributes of the IB Learner Profile are demonstrated by Mendeleev’s work on the Periodic Table?

Typische Elemente			K = 39	Rb = 85	Cs = 133	—	—
H = 1	Li = 7	Na = 23	Ca = 40	Sr = 87	Ba = 137	—	—
	Be = 9,4	Mg = 24	—	? Yt = 88?	? Di = 138?	Er = 178?	—
	B = 11	Al = 27,3	Ti = 48?	Zr = 90	Ce = 140?	? La = 180?	Tb = 231
	C = 12	Si = 28	V = 51	Nb = 94	—	Ta = 182	—
	N = 14	P = 31	Cr = 52	Mo = 96	—	W = 184	U = 240
	O = 16	S = 32	Mn = 55	—	—	—	—
	F = 19	Cl = 35,5	Fe = 56	Ru = 104	—	Os = 195?	—
			Co = 59	Rh = 104	—	Ir = 197	—
			Ni = 59	Pd = 106	—	Pt = 198?	—
			Cu = 63	Ag = 108	—	Au = 199?	—
			Zn = 65	Cd = 112	—	Hg = 200	—
			—	In = 113	—	Tl = 204	—
			—	Sn = 118	—	Pb = 207	—
			As = 75	Sb = 122	—	Bi = 208	—
			Se = 78	Te = 125?	—	—	—
			Br = 80	J = 127	—	—	—

Mendeleev’s Periodic Table of 1869. The noble gas elements had not been discovered. Reading from top to bottom and left to right, the first four gaps were waiting for scandium (1879), gallium (1875), germanium (1886) and technetium (1937).

Mendeleev had no knowledge of the structure of the atom, which we discussed in Chapter 2. With the benefit of hindsight it is clear that the periodicity of the elements is a direct consequence of the periodicity of the electron configurations within the atom.

The position of an element in the Periodic Table is based on the sub-level of the highest-energy electron in the ground-state atom.

3.1 The Periodic Table

Understandings:

- The Periodic Table is arranged into four blocks associated with the four sub-levels: s, p, d, and f.
- The Periodic Table consists of groups (vertical columns) and periods (horizontal rows).

Guidance

The group numbering scheme from group 1 to group 18, as recommended by IUPAC, should be used.

- The period number (n) is the outer energy level that is occupied by electrons.
- The number of the principal energy level and the number of the valence electrons in an atom can be deduced from its position on the Periodic Table.
- The Periodic Table shows the positions of metals, non-metals and metalloids.

Guidance

The terms alkali metals, halogens, noble gases, transition metals, lanthanoids and actinoids should be known.

Applications and skills:

- Deduction of the electron configuration of an atom from the element's position on the Periodic Table, and vice versa.

Mendeleev is said to have made his discovery after a dream. When he awoke he set out his chart in virtually its final form. He enjoyed playing a form of patience (solitaire) and wrote the properties of each element on cards which he arranged into rows and columns.



Periods and groups

If you have visited a large supermarket you will appreciate the importance of a classification system. Similar products are grouped together to help you find what you want. In the same way, a chemist knows what type of element to find in different parts of the Periodic Table. The elements are placed in order of increasing atomic number (Z), which we now know is a fundamental property of the element – the number of protons in the nucleus of its atoms. As there are no gaps in the sequence of atomic numbers we can be confident that the search for new elements in nature is over.

The only way to extend the Periodic Table is by making elements artificially. Today there are over 110 elements recognized by the International Union of Pure and Applied Chemistry (IUPAC). The columns of the table are called **groups** and the rows **periods**.

In the IB data booklet Periodic Table the main groups are numbered from 1 to 18.

As discussed in Chapter 2, the position of an element is related to the electron configuration of its atoms.

Elements whose valence electrons occupy an s sub-level make up the **s block**, elements with valence electrons in p orbitals make up the **p block**, and the **d block** and **f block** are similarly made up of elements with outer electrons in d and f orbitals. The element sodium, for example, is in Period 3 as it has three occupied principal energy levels, and is in Group 1 of the s block as there is one electron in the valence energy level $[\text{Ne}] 3s^1$. Bromine is in Period 5 and in Group 17 of the p block as it has seven electrons in the fifth principal energy level, and seventeen more electrons than the previous noble gas, argon: $[\text{Ar}] 4d^{10}5s^25p^5$ (Figure 3.1).

IUPAC is an international, non-governmental body with a membership made up of chemists which has the aim of fostering worldwide communication in chemistry.



s^1 s^2 d^1 d^2 d^3 d^{5s^1} d^5 d^6 d^7 d^8 d^{10s^1} d^{10} p^1 p^2 p^3 p^4 p^5 p^6
 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

1	H hydrogen 1																	He helium 2																														
2	Li lithium 3	Be beryllium 4											B boron 5	C carbon 6	N nitrogen 7	O oxygen 8	F fluorine 9	Ne neon 10																														
3	Na sodium 11	Mg magnesium 12											Al aluminium 13	Si silicon 14	P phosphorus 15	S sulfur 16	Cl chlorine 17	Ar argon 18																														
4	K potassium 19	Ca calcium 20	Sc scandium 21	Ti titanium 22	V vanadium 23	Cr chromium 24	Mn manganese 25	Fe iron 26	Co cobalt 27	Ni nickel 28	Cu copper 29	Zn zinc 30	Ga gallium 31	Ge germanium 32	As arsenic 33	Se selenium 34	Br bromine 35	Kr krypton 36																														
5	Rb rubidium 37	Sr strontium 38	Y yttrium 39	Zr zirconium 40	Nb niobium 41	Mo molybdenum 42	Tc technetium 43	Ru ruthenium 44	Rh rhodium 45	Pd palladium 46	Ag silver 47	Cd cadmium 48	In indium 49	Sn tin 50	Sb antimony 51	Te tellurium 52	I iodine 53	Xe xenon 54																														
6	Cs caesium 55	Ba barium 56	57-71 see below	Hf hafnium 72	Ta tantalum 73	W tungsten 74	Re rhenium 75	Os osmium 76	Ir iridium 77	Pt platinum 78	Au gold 79	Hg mercury 80	Tl thallium 81	Pb lead 82	Bi bismuth 83	Po polonium 84	At astatine 85	Rn radon 86																														
7	Fr francium 87	Ra radium 88	89-103 see below	Rf rutherfordium 104	Db dubnium 105	Sg seaborgium 106	Bh bohrium 107	Hs hassium 108	Mt meitnerium 109	Ds darmstadtium 110	Rg roentgenium 111	Cp copernicium 112	Uut ununtrium 113	Fl flerovium 114	Uup ununpentium 115	Lv livermorium 116	Uus ununseptium 117	Uuo ununoctium 118																														
<table border="1"> <tr> <td>La lanthanum 57</td> <td>Ce cerium 58</td> <td>Pr praseodymium 59</td> <td>Nd neodymium 60</td> <td>Pm promethium 61</td> <td>Sm samarium 62</td> <td>Eu europium 63</td> <td>Gd gadolinium 64</td> <td>Tb terbium 65</td> <td>Dy dysprosium 66</td> <td>Ho holmium 67</td> <td>Er erbium 68</td> <td>Tm thulium 69</td> <td>Yb ytterbium 70</td> <td>Lu lutetium 71</td> </tr> <tr> <td>Ac actinium 89</td> <td>Th thorium 90</td> <td>Pa protactinium 91</td> <td>U uranium 92</td> <td>Np neptunium 93</td> <td>Pu plutonium 94</td> <td>Am americium 95</td> <td>Cm curium 96</td> <td>Bk berkelium 97</td> <td>Cf californium 98</td> <td>Es einsteinium 99</td> <td>Fm fermium 100</td> <td>Md mendelevium 101</td> <td>No nobelium 102</td> <td>Lr lawrencium 103</td> </tr> </table>																			La lanthanum 57	Ce cerium 58	Pr praseodymium 59	Nd neodymium 60	Pm promethium 61	Sm samarium 62	Eu europium 63	Gd gadolinium 64	Tb terbium 65	Dy dysprosium 66	Ho holmium 67	Er erbium 68	Tm thulium 69	Yb ytterbium 70	Lu lutetium 71	Ac actinium 89	Th thorium 90	Pa protactinium 91	U uranium 92	Np neptunium 93	Pu plutonium 94	Am americium 95	Cm curium 96	Bk berkelium 97	Cf californium 98	Es einsteinium 99	Fm fermium 100	Md mendelevium 101	No nobelium 102	Lr lawrencium 103
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Figure 3.1 The Periodic Table. The rows are called periods. The period number gives the number of occupied electron principal energy levels. The columns in the Periodic Table are called groups. The colours show the blocks formed by the elements with their outer electrons in the same electron sub-level: s block (blue), d block (yellow), p block (red), f block (green). It is these outer electrons that determine an element's chemical properties.

The discovery of the elements was an international endeavour. This is illustrated by some of their names. Some derive from the place where they were made, some derive from the origins of their discoverers, and some derive from the geographical origins of the minerals from which they were first isolated. The Periodic Table of chemical elements hangs in front of chemistry classrooms and in science laboratories throughout the world.



The rows in the Periodic Table are called periods. The period number gives the number of occupied electron principal energy levels. The columns in the Periodic Table are called groups.

Worked example

How many electrons are in the outer shell of iodine?

Solution

Find the element in the Periodic Table. It is Period 5, so has the noble gas core of Kr, with electrons added to 5s, then 4d, and then 5p.

As it is Group 17 it has the configuration: $[\text{Kr}] 5s^2 4d^{10} 5p^5$ or $[\text{Kr}] 4d^{10} 5s^2 5p^5$ and so has seven electrons in its valence energy level.

CHALLENGE YOURSELF

- Four elements derive their name from a small town called Ytterby, just outside Stockholm, Sweden. Try to find their names.

Exercises

- Use the IB Periodic Table to identify the position of the following elements:

	Element	Period	Group
(a)	helium		
(b)	chlorine		
(c)	barium		
(d)	francium		

- Phosphorus is in Period 3 and Group 15 of the Periodic Table.
 - Distinguish between the terms 'period' and 'group'.
 - State the electron configuration of phosphorus and relate it to its position in the Periodic Table.
- How many valence (outer shell) electrons are present in the atoms of the element with atomic number 51?

The lanthanides with scandium and yttrium are sometimes called rare earth metals. They are not, however, that rare. Cerium for example is the 26th most abundant element in the earth's crust.



Non-metallic elements. Clockwise from top left, they are sulfur (S), bromine (Br), phosphorus (P), iodine (I) and carbon (C). Non-metals are generally poor conductors of both heat and electricity.

Graphite, an allotrope of carbon, is unusual in that it is a non-metal that does conduct electricity.

CHALLENGE YOURSELF

- 2 How many elements in the IB Periodic Table are liquids and how many are gases?

Metals and non-metals



metals found at the extreme right-hand side in Group 18. Metallic elements are found on the left-hand side of the table in the s block, in the central d block, and the island of the f block. The alkali metals, for example, are a reactive group of metals in Group 1 of the s block. The lanthanoids and actinoids are metals which make up the first and second row of the f block.

The metalloid elements have the characteristics of both metals and non-metals. Their physical properties and appearance most resemble the metals, although chemically they have more in common with the non-metals. In the Periodic Table the metalloid elements silicon, germanium, arsenic, antimony, tellurium, and polonium form a diagonal staircase between the metals and non-metals.

One of the key features of the Periodic Table is that the metals, metalloids, and non-metals occupy different regions. The non-metals are found on the upper right-hand side of the p block.

The **halogens**, for example, are a reactive group of non-metals in Group 17 and the **noble gases** are a very unreactive family of non-



◀ Silicon is a metalloid. There is enough silicon in this piece to make many hundreds of computers.

▶ Europium (Eu), is one of the lanthanoids. It is a hard silvery-white metallic element and is used in television screens and fluorescent light bulbs.



CHALLENGE YOURSELF

- 3 Distinguish between the terms 'metalloid' and 'semiconductor'.



The element europium is used in the security marking of euro notes and other banknotes. When placed in UV radiation europium compounds fluoresce, making the security markers visible.



The lanthanoids and actinoids both make up the f block of the Periodic Table.

CHALLENGE YOURSELF

- 4 State the electron configuration of europium.

Exercises

- 4 Which of the following elements is a metalloid?
A calcium **B** manganese **C** germanium **D** magnesium
- 5 Which of the following materials is the best conductor of electricity in the solid state?
A silicon **B** graphite **C** phosphorus **D** antimony
- 6 Which of the following properties is used to arrange the elements in the modern Periodic Table?
A relative atomic mass **B** number of valence electrons
C atomic number **D** effective nuclear charge

NATURE OF SCIENCE

Scientists attempt to discover relationships by looking for patterns, trends, and discrepancies. Classification is an important aspect of scientific work. In the 18th century, Antoine Lavoisier tried to bring order to the confusing number of elements by classifying the elements into groups such as gases, non-metals, and metals. Some classification systems are, however, more useful than others and classifications based on quantitative data are more useful than those on qualitative data. The publication of 1858 by Stanislao Cannizzaro of a list of atomic masses allowed the elements to be placed in some sort of order.

One of the first attempts to classify the elements was made by Johann Döbereiner (1780–1849) who organized the elements into groups of three or 'triads' with similar properties (such as lithium, sodium, and potassium), where the average mass of the first and third element equalled the mass of the second. This pattern is approximately true for several triads of elements. The average relative mass of lithium and potassium, the first and third elements in a triad, for example = $(6.94 + 39.10)/2 = 23.02$ which is very close to the relative atomic mass of sodium (22.99), the second element in the triad.

In 1862 Alexandre de Chancourtois wrote a list of the elements on a tape and wound it in a spiral and noticed that chemically similar elements formed vertical groups.

John Newlands developed this idea and noted that many similar elements occur in intervals, rather like the seven notes in a musical scale. His law of octaves stated that any given element will be similar in its properties to the eighth element following it in the table.

Mendeleyev recognized that the breakdown in the periodicity of Newlands' octaves was due to the table's incomplete nature as some elements were yet to be discovered. Mendeleyev left gaps for these elements to ensure that periodicity was maintained, and predicted the physical and chemical properties of these missing elements. This was a key step in the scientific process as his precise predictions could be confirmed or falsified with the discovery of the new elements.

The discovery of elements such as gallium and germanium confirmed Mendeleyev's ideas. One advantage of Mendeleyev's table over previous attempts was that it exhibited similarities not only in small units such as the triads, but showed similarities in an entire network of vertical, horizontal, and diagonal relationships.

Mendeleyev did not propose an explanation for his periodic law. This had to await the discovery of the electron by Thomson in 1897 and the work of Rutherford and Bohr at the beginning of the 20th century.

'Theories' and 'laws' are terms which have a special meaning in science and it is important to distinguish these from their everyday use. Scientific laws are descriptive, normative statements derived from observations of regular patterns of behaviour. They do not necessarily explain a phenomenon. Newlands' law of octaves and Mendeleyev's periodic law, for example, tell us that there is pattern in the properties of the elements but they do not attempt to explain these patterns.



TOK

The patterns observed in the evolution of the Periodic Table were as a result of inductive reasoning. What do these patterns illustrate about the problems of induction? Is induction ever a reliable source for knowledge?



The development of the Periodic Table took many years and involved scientists from different countries building upon the foundations of each other's work and ideas.

3.2 Periodic trends

Understandings:

- Vertical and horizontal trends in the Periodic Table exist for atomic radius, ionic radius, ionization energy, electron affinity, and electronegativity.

Guidance

Only examples of general trends across periods and down groups are required. For ionization energy the discontinuities in the increase across a period should be covered.

- Trends in metallic and non-metallic behaviour are due to the trends above.
- Oxides change from basic through amphoteric to acidic across a period.

Applications and skills:

- Prediction and explanation of the metallic and non-metallic behaviour of an element based on its position in the Periodic Table.
- Discussion of the similarities and differences in the properties of elements in the same group, with reference to alkali metals (Group 1) and halogens (Group 17).

Guidance

Group trends should include the treatment of the reactions of alkali metals with water, alkali metals with halogens and halogens with halide ions.

- Construction of equations to explain the pH changes for reactions of Na_2O , MgO , P_4O_{10} , and the oxides of nitrogen and sulfur with water.

'Science is built of facts the way a house is built of bricks: but an accumulation of facts is no more science than a pile of bricks is a house.'

Henri Poincaré,
1854–1912

Do you agree with this description of science?

TOK

Physical properties

The elements in the Periodic Table are arranged to show how the properties of the elements repeat periodically. This **periodicity** of the elements is reflected in their physical properties. The atomic and ionic radii, electronegativity, and ionization energy are of particular interest as they explain the periodicity of the chemical properties.

The concept of effective nuclear charge is helpful in explaining trends in both physical and chemical properties.

Effective nuclear charge

The **nuclear charge** of the atom is given by the atomic number and so increases by one between successive elements in the table, as a proton is added to the nucleus. The outer electrons which determine many of the physical and chemical properties of the atom do not, however, experience the full attraction of this charge as they are **shielded** from the nucleus and repelled by the inner electrons. The presence of the inner electrons reduces the attraction of the nucleus for the outer electrons (Figure 3.2). The **effective charge** 'experienced' by the outer electrons is less than the full nuclear charge.

Consider, for example, a sodium atom. The nuclear charge is given by the atomic number of element ($Z = 11$). The outer electron in the $3s$ orbital is, however, shielded from these 11 protons by the 10 electrons in the first and second principal energy levels ($1s^2 2s^2 2p^6$).

Consider the first four elements in Period 3, as shown in the table on page 103.

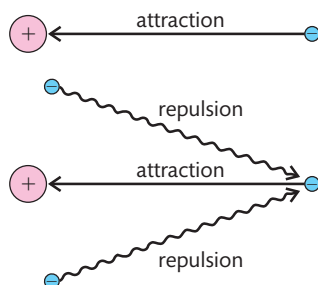


Figure 3.2 An electron in the hydrogen atom experiences the full attraction of the nuclear charge, but in a many-electron atom the attraction for the nucleus is reduced as the outer electron is repelled by inner electrons.

Element	Na	Mg	Al	Si
Nuclear charge	11	12	13	14
Electron configuration	[Ne] 3s ¹	[Ne] 3s ²	[Ne] 3s ² 3p ¹	[Ne] 3s ² 3p ²
Effective nuclear charge	≈ 11 – 10 ≈ +1	≈ 12 – 10 ≈ +2	≈ 13 – 10 ≈ +3	≈ 14 – 10 ≈ +4

As the period is crossed from left to right, one proton is added to the nucleus and one electron is added to the valence electron energy level. The effective charge increases with the nuclear charge as there is no change in the number of inner electrons, as all the atoms have a noble gas structure of 10 electrons ([Ne] = 1s²2s²2p⁶).

If we assume that the noble gas core is completely shielding, then the 10 inner electrons of the neon core make the effective nuclear charge 10 less than the nuclear charge.

The changes down a group can be illustrated by considering the elements in Group 1, as shown in the table below:

Element	Nuclear charge	Electron configuration
Li	3	1s ² 2s ¹
Na	11	1s ² 2s ² 2p ⁶ 3s ¹
K	19	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹

As we descend the group, the increase in the nuclear charge is largely offset by the increase in the number of inner electrons; both increase by eight between successive elements in the group. The effective nuclear charge experienced by the outer electrons remains approximately +1 down the group.

Atomic radius

The concept of atomic radius is not as straightforward as you may think. We saw in the last chapter that electrons occupy atomic orbitals, which give a probability description of the electrons' locations, but do not have sharp boundaries. The atomic radius r is measured as half the distance between neighbouring nuclei (Figure 3.3). For many purposes, however, it can be considered as the distance from the nucleus to the outermost electrons of the Bohr atom.

Table 8 in the IB data booklet shows that atomic radii increase down a group and decrease across a period. To explain the trend down a group consider, for example, the Group 1 elements – as shown in the table below.

Element	Period	No. of occupied principal energy levels	Atomic radius/10 ⁻¹² m
Li	2	2	152
Na	3	3	186
K	4	4	231
Rb	5	5	244
Cs	6	6	262



The effective nuclear charge experienced by an atom's outer electrons increases with the group number of the element. It increases across a period but remains approximately the same down a group.

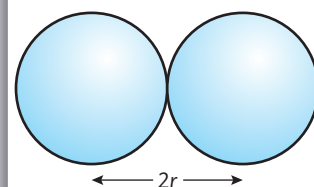


Figure 3.3 The atomic radius r is measured as half the distance between neighbouring nuclei.

The atomic radii of the noble gases are not given in Table 8 of the IB data booklet. Their inter-nuclei distances are difficult to measure as noble gases do not generally bond to other atoms.



The atomic radii increase down a group, as the number of occupied electron shells (given by the period number) increases.

The trend across a period is illustrated by the Period 3 elements, as shown below.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic radius/ 10^{-12} m	186	160	143	117	110	104	99	–

All these elements have three occupied principal energy levels. The attraction between the nucleus and the outer electrons increases as the nuclear charge increases so there is a general decrease in atomic radii across the period.

The decrease in radii across a period is quite significant; a chlorine atom, for example, has a radius that is about half that of a sodium atom.

Ionic radius

The atomic and ionic radii of the Period 3 elements are shown in the table below.

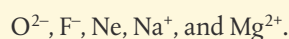
Element	Na	Mg	Al	Si	P	S	Cl
Atomic radius/ 10^{-12} m	186	160	143	117	110	104	99
Ionic radius/ 10^{-12} m	98 (Na ⁺)	65 (Mg ²⁺)	45 (Al ³⁺)	42 (Si ⁴⁺); 271 (Si ⁴⁻)	212 (P ³⁻)	190 (S ²⁻)	181 (Cl ⁻)

Five trends can be identified.

- Positive ions are smaller than their parent atoms. The formation of positive ions involves the loss of the outer shell. The Na⁺ ion, for example, is formed by the removal of the 3s electron from the Na atom.
- Negative ions are larger than their parent atoms. The formation of negative ions involves the addition of electrons into the outer shell. Cl⁻ is formed by the addition of an electron into the 3p sub-shell. The increased electron repulsion between the electrons in the outer principal energy level causes the electrons to move further apart and so increases the radius of the outer shell.
- The ionic radii decrease from Groups 1 to 14 for the positive ions. The ions Na⁺, Mg²⁺, Al³⁺, and Si⁴⁺ all have the same electron configuration (1s²2s²2p⁶). The decrease in ionic radius is due to the increase in nuclear charge with atomic number across the period. The increased attraction between the nucleus and the electrons pulls the outer shell closer to the nucleus.
- The ionic radii decrease from Groups 14 to 17 for the negative ions. The ions Si⁴⁻, P³⁻, S²⁻ and Cl⁻ have the same electron configuration (1s²2s²2p⁶3s²3p⁶). The decrease in ionic radius is due to the increase in nuclear charge across the period, as explained above. The positive ions are smaller than the negative ions, as the former have only two occupied electron principal energy levels and the latter have three. This explains the big difference between the ionic radii of the Si⁴⁺ and Si⁴⁻ ions and the discontinuity in the middle of the table.
- The ionic radii increase down a group as the number of electron energy levels increases.

Worked example

Describe and explain the trend in radii of the following atoms and ions:



Solution

The ions and the Ne atom have 10 electrons and the electron configuration $1s^22s^22p^6$.

The nuclear charges increase with atomic number:

O: $Z = +8$

F: $Z = +9$

Ne: $Z = +10$

Na: $Z = +11$

Mg: $Z = +12$

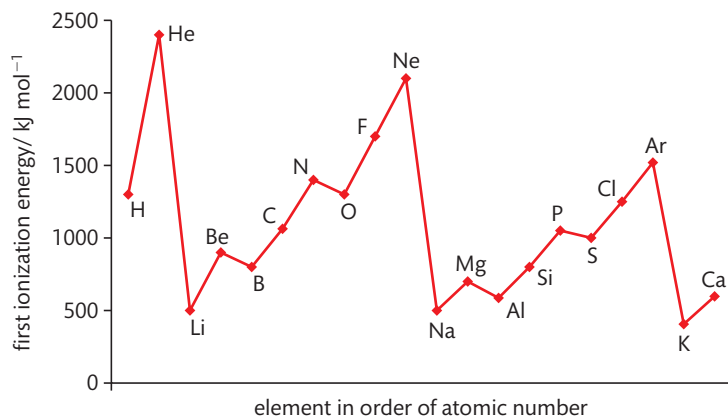
The increase in nuclear charge results in increased attraction between the nucleus and the outer electrons. The ionic radii decrease as the atomic number increases.

Exercises

- 7 (a) Explain what is meant by the atomic radius of an element.
- (b) The atomic radii of the elements are found in Table 9 of the IB data booklet.
 - (i) Explain why no values for ionic radii are given for the noble gases.
 - (ii) Describe and explain the trend in atomic radii across the Period 3 elements.
- 8 Si^{4+} has an ionic radius of 4.2×10^{-11} m and Si^{4-} has an ionic radius of 2.71×10^{-10} m. Explain the large difference in size between the Si^{4+} and Si^{4-} ions.

Ionization energies

First ionization energies are a measure of the attraction between the nucleus and the outer electrons. They were defined in Chapter 2 (page 73), where they provided evidence for the electron configuration of the atoms of different elements (Figure 3.4).



Two general trends can be identified from Figure 3.4.

- Ionization energies increase across a period. The increase in effective nuclear charge causes an increase in the attraction between the outer electrons and the nucleus and makes the electrons more difficult to remove.
- Ionization energies decrease down a group. The electron removed is from the energy level furthest from the nucleus. Although the nuclear charges increase, the effective nuclear charge is about the same, owing to shielding of the inner electrons, and so the increased distance between the electron and the nucleus reduces the attraction between them.



The first ionization energy of an element is the energy required to remove one mole of electrons from one mole of gaseous atoms in their ground state.

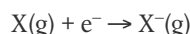
Figure 3.4 First ionization energies of the first 20 elements.

The small departures from these trends provide evidence for division of energy levels into sub-levels, as discussed in Chapter 2 (page 90). Thus, the Group 13 elements, with the electron configuration ns^2np^1 , have lower first ionization energies than Group 2 elements, with the configuration ns^2 , as p orbitals have higher energy than s orbitals. The drop between Groups 15 and 16 occurs as the electron removed from a Group 16 element, unlike a Group 15 element, is taken from a doubly occupied p orbital. This electron is easier to remove as it is repelled by its partner.

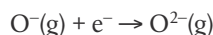
The trend in ionization energy is the reverse of the trend in atomic radii. Both trends are an indication of the attraction between the nucleus and the outer electrons.

Electron affinity

The first **electron affinity** of an element ($\Delta H_{\text{ea}}^\ominus$) is the energy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous ions:



Values are tabulated in Table 8 of the IB data booklet. The noble gases do not generally form negatively charged ions so electron affinity values are not available for these elements. As the added electron is attracted to the positively charged nucleus the process is generally exothermic. The second and third electron affinities are defined similarly. The second electron affinity for oxygen, for example, corresponds to the change:



This process is endothermic as the added electron is repelled by the negatively charged oxide (O^-) ion, and energy needs to be available for this to occur.

The electron affinities of the first 18 elements are shown below. The pattern in electron affinities is related to that observed with first ionization energy but generally displaced to the right by one and inverted. The minimum values for electron affinities occur for the Group 17 elements whereas the values for ionization energy reach a maximum for Group 18.

Electron affinities can be thought of as the negative of first ionization energy of the anion.

- The Group 17 elements have incomplete outer energy levels and a high effective nuclear charge of approximately +7 and so attract electrons the most.
- The Group 1 metals have the lowest effective nuclear charge of approximately +1 and so attract the extra electron the least.

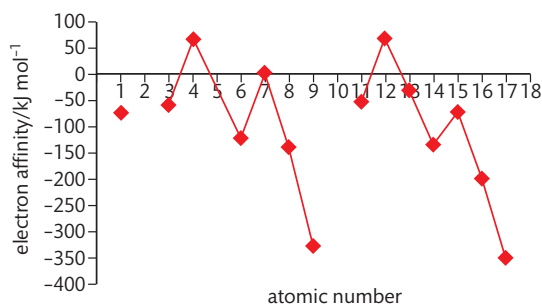
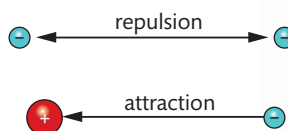


Figure 3.5 The electron affinities of the first 18 elements. Note there are no values assigned to the noble gases.

The electron affinities reach a maximum for Group 2 and Group 5 elements. Group 2 elements have an electron configuration ns^2 , so the added electron must be placed into

a 2p orbital which is further from the nucleus and so experiences reduced electrostatic attraction due to shielding from electrons in the ns orbital. The value for beryllium is actually endothermic as there is electrostatic repulsion between the electrons of the Be atom and the added electron. The electrons in the 1s and 2s orbitals of Be also shield the added electron from the positively charged nucleus.

Group 15 elements have the configuration $ns^2np_x^1p_y^1p_z^1$ so the added electron must occupy a p orbital that is already singly occupied: the attraction between the electron and atom is less than expected as there is increased inter-electron repulsion. The value is only just exothermic for nitrogen.



Electronegativity

The **electronegativity** of an element is a measure of the ability of its atoms to attract electrons in a covalent bond (see Chapter 4). It is related to ionization energy as it is also a measure of the attraction between the nucleus and its outer electrons – in this case *bonding electrons*.

An element with a high electronegativity has strong electron pulling power and an element with a low electronegativity has weak pulling power. The concept was originally devised by the American chemist Linus Pauling and his values are given in the IB data booklet (Section 8). The general trends are the same as those for ionization energy.

- Electronegativity increases from left to right across a period owing to the increase in nuclear charge, resulting in an increased attraction between the nucleus and the bond electrons.
- Electronegativity decreases down a group. The bonding electrons are furthest from the nucleus and so there is reduced attraction.

The most electronegative element is on the top right of the Periodic Table and the least electronegative element on the bottom left. As the concept does not apply to the Group 18 elements, which do not form covalent bonds, Pauling assigned the highest value of 4.0 to fluorine and the lowest value of 0.7 to caesium.

Although the general trends in ionization energy and electronegativity are the same, they are distinct properties. Ionization energies can be measured directly and are a property of gaseous atoms. Elements with high electronegativities have the most exothermic electron affinities, but again care should be taken to avoid confusion between the terms. Electron affinities are properties of isolated gaseous atoms whereas electronegativity is a property of an atom in a molecule. Electronegativity values are derived indirectly from experimental bond energy data.

Metals have lower ionization energies and electronegativities than non-metals

The ability of metals to conduct electricity is due to the availability of their valence electrons to move away from the atomic nucleus. This can be related to their low ionization energies and electronegativities. There is a transition from metal to metalloid and non-metal from left to right as these properties increase. The diagonal band of metalloids which divides the metals from the non-metals can also be related to the similar electronegativities of these elements.

The electron affinity of an atom is the energy change that occurs when one mole of electrons is added to one mole of gaseous atoms.

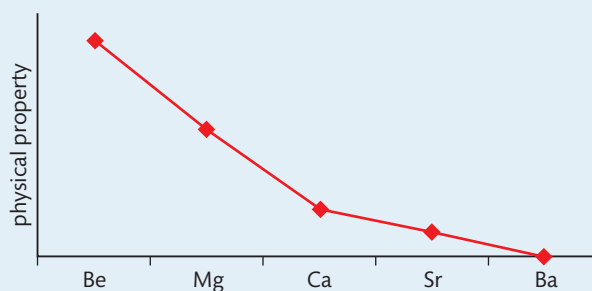
Figure 3.6 Energy is needed to bring two particles of the same charge closer together as they repel each other: this is an endothermic process. Particles of the opposite charge attract each other. They will spontaneously move closer together: it is an exothermic process.

Electronegativity is the ability of an atom to attract electrons in a covalent bond.

Linus Pauling has the unique distinction of winning two *unshared* Nobel Prizes – one for Chemistry in 1954 and one for Peace in 1962. His Chemistry Prize was for improving our understanding of the chemical bond and his Peace Prize was for his campaign against nuclear weapons testing.

Exercises

- 9 Which of the following is a property of gaseous atoms?
- I ionization energy
II electron affinity
III electronegativity
- A I and II B I and III C II and III D I, II, and III
- 10 Which of the following changes is endothermic?
- I $\text{Ca(g)} \rightarrow \text{Ca}^+(\text{g}) + \text{e}^-$
II $\text{I(g)} + \text{e}^- \rightarrow \text{I}^-(\text{g})$
III $\text{O}^- + \text{e}^- \rightarrow \text{O}^{2-}(\text{g})$
- A I and II B I and III C II and III D I, II, and III
- 11 Identify the element which is likely to have an electronegativity value most similar to that of lithium?
- A beryllium B sodium C magnesium D hydrogen
- 12 The graph represents the variation of a property of the Group 2 elements.



Identify the property.

- A ionic radius B atomic radius C neutron/proton ratio
D first ionization energy
- 13 Atomic radii and ionic radii are found in the IB data booklet.
Explain why:
- (a) the potassium ion is much smaller than the potassium atom.
(b) there is a large increase in ionic radius from silicon (Si^{4+}) to phosphorus (P^{3-}).
(c) the ionic radius of Na^+ is less than that of F^- .

Melting points

Comparisons between melting points of different elements are more complex as they depend on both the type of bonding and the structure (Chapter 4). Trends down Groups 1 and 17 can, however, be explained simply, as the elements within each group bond in similar ways. Trends in melting points down Group 1 and Group 17 are shown in the table below.

Element	Melting point / K	Element	Melting point / K
Li	454	F_2	54
Na	371	Cl_2	172
K	337	Br_2	266
Rb	312	I_2	387
Cs	302	At_2	575

Melting points decrease down Group 1. The elements have metallic structures which are held together by attractive forces between **delocalized** outer electrons and the positively charged ions. This attraction decreases with distance.

Melting points increase down Group 17. The elements have molecular structures which are held together by London (dispersion) forces. These increase with the number of electrons in the molecule. This is explained more fully in Chapter 4.

Melting points generally rise across a period and reach a maximum at Group 14. They then fall to reach a minimum at Group 18. In Period 3, for example, the bonding changes from metallic (Na, Mg, and Al) to giant covalent (Si) to weak van der Waals' attraction between simple molecules (P_4 , S_8 , Cl_2) and single atoms (Ar) (Figure 3.7). All the Period 3 elements are solids at room temperature except chlorine and argon.

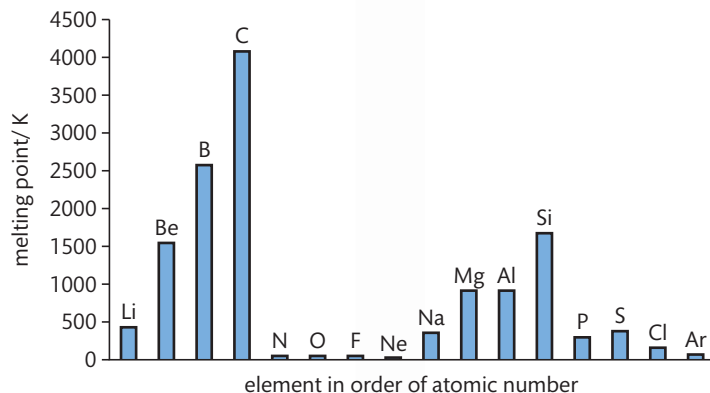
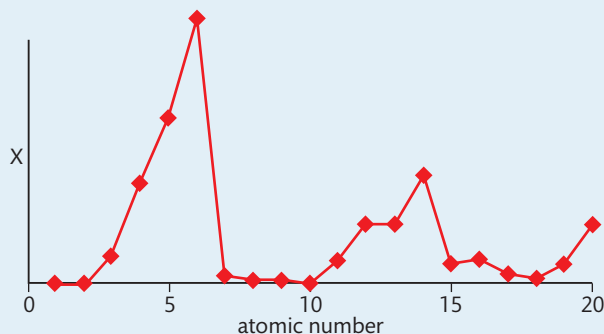


Figure 3.7 The melting points show a periodic pattern as the bonding changes from metallic, to giant covalent, to simple molecular.

Exercises

- 14** Explain why sulfur has a higher melting point than phosphorus.
- 15** Which physical property generally increases down a group but decreases from left to right across a period?
- A** melting point **B** electronegativity **C** ionization energy **D** atomic radius
- 16** The elements in the Periodic Table are arranged in order of increasing:
- A** relative atomic mass
B ionic radii
C nuclear charge
D ionization energy
- 17** What is the order of decreasing radii for the species Cl , Cl^+ , and Cl^- ?
- 18** Which one of the following elements has the highest electronegativity?
- A** Be **B** Cl **C** Ca **D** Br
- 19** Which properties of the Period 3 elements increase from sodium to argon:
- A** nuclear charge and atomic radius
B atomic radius and electronegativity
C nuclear charge and electronegativity
D nuclear charge, atomic radius, and electronegativity
- 20** The following graph shows the variation of a physical property, X, of the first 20 elements in the Periodic Table with the atomic number.



Identify the property X.

- A** atomic radius **B** first ionization energy
C ionic radius **D** melting point

TOK

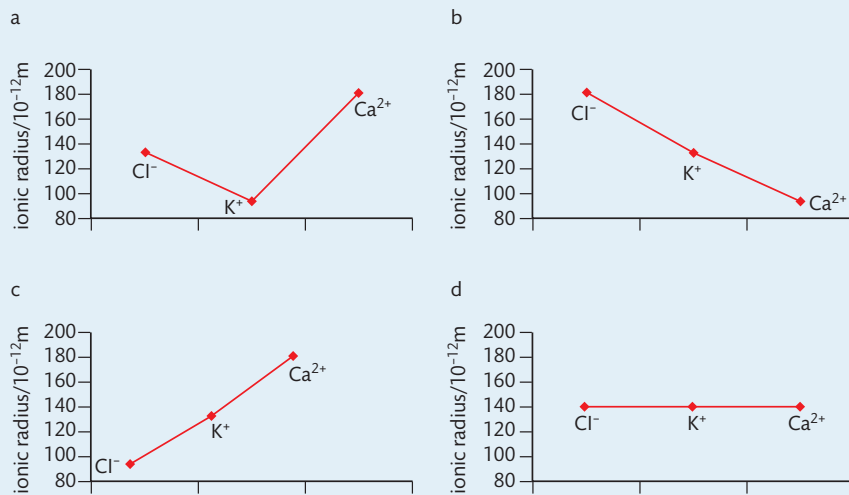
No one knows how high the atomic number of the elements will go, but it is expected that all new elements will fit into the current scheme. Could there ever be an 'end' to science? Could we reach a point where everything important in a scientific sense is known?

The structure of the Periodic Table was first discovered by observing patterns in the chemical and physical properties of the elements. We now realize that it is determined by the electron configuration of the elements. What roles did inductive and deductive reasoning play in the development of the Periodic Table? What role does inductive and deductive reasoning have in science in general?

TOK

Exercises

21 Identify the graph which shows the correct ionic radii for the isoelectronic ions Cl^- , K^+ , and Ca^{2+} ?



NATURE OF SCIENCE

Although Mendeleev is given most of the credit for arranging the elements into a Periodic Table in 1869, the periodicity in the physical properties was independently demonstrated the same year by the German chemist Lothar Meyer. Meyer plotted a range of physical properties against relative atomic mass. The graph of density against relative atomic mass is shown in Figure 3.8. Elements in the same group occur at similar points on the curve. The noble gases, for example, are all near the minimum points in the curve.

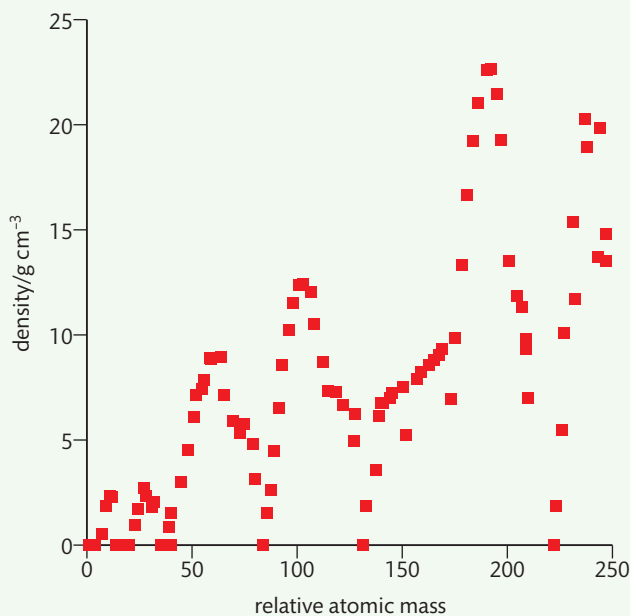


Figure 3.8 The relationship between relative atomic mass and density.

Many scientific laws and theories have often been developed independently by different scientists working in different countries. This illustrates the objective nature of science.

Chemical properties

The chemical properties of an element are determined by the electron configuration of its atoms. Elements of the same group have similar chemical properties as they have the same number of valence electrons in their outer energy level. The alkali metals in Group 1, for example, all have one electron in their outer shell and the halogens in Group 17 have seven outer electrons. The trends in their chemical properties can be accounted for by the trends in their properties discussed earlier.

Group 18: the noble gases

To understand the reactivity of the elements it is instructive to consider Group 18, which contains the least reactive elements – the noble gases. This chemically aloof family of elements was only discovered at the end of the 19th century after Mendeleev first published his table.

- They are colourless gases.
- They are monatomic: they exist as single atoms.
- They are very unreactive.

Their lack of reactivity can be explained by the inability of their atoms to lose or gain electrons. They do not generally form positive ions as they have the highest ionization energies. They do not form negative ions as extra electrons would have to be added to an empty outer energy level shell where they would experience a negligible effective nuclear force, with the protons shielded by an equal number of inner electrons. With the exception of helium, they have complete valence energy levels with eight electrons; a **stable octet**. Helium has a complete principal first energy level with two electrons.

The reactivity of elements in other groups can be explained by their unstable incomplete electron energy levels. They lose or gain electrons so as to achieve the electron configuration of their nearest noble gas.

- Elements in Groups 1, 2, and 13 lose electrons to adopt the arrangement of the nearest noble gas with a lower atomic number. They are generally metals.
- Elements in Groups 15 to 17 gain electrons to adopt the electron configuration of the nearest noble gas on their right in the Periodic Table. They are generally non-metals.
- The metalloids in the middle of the table show intermediate properties.

Group 1: the alkali metals

All the elements are silvery metals and are too reactive to be found in nature. They are usually stored in oil to prevent contact with air and water. The properties of the first three elements are summarized in the table below.

Physical properties	Chemical properties
<ul style="list-style-type: none">• They are good conductors of electricity and heat.• They have low densities.• They have grey shiny surfaces when freshly cut with a knife.	<ul style="list-style-type: none">• They are very reactive metals.• They form ionic compounds with non-metals.



Chemical properties of an element are largely determined by the number of valence electrons in their outer energy level.



NATURE OF SCIENCE

The electron arrangement description of the atom is sufficient to explain the chemical properties of elements in the s and p blocks. We will follow Occam's razor and use this simple but incomplete model. The principle of Occam's razor is often used as a guide to developing a scientific theory. The theory should be as simple as possible while maximizing explanatory power.



What characteristics must an explanation possess to be considered 'good' within the natural sciences? What is the difference between explanations in the different areas of knowledge?



Group 18 used to be called the 'inert gases' as it was thought that they were completely unreactive. No compounds of helium or neon have ever been found. The first compound of xenon was made in 1962 and compounds of krypton and argon have now been prepared. The most reactive element in the group has the lowest ionization energy as reactions involve the withdrawal of electrons from the parent atom.



▲ Lithium is a soft reactive metal. When freshly cut, it has a metallic lustre. However, it rapidly reacts with oxygen in the air, giving it a dark oxide coat.

It has been estimated that at any one time there are only 17 francium atoms on the Earth.



▲ Sodium is softer and more reactive than lithium.



▲ Potassium is softer and more reactive than sodium.

They form single charged ions, M^+ , with the stable octet of the noble gases when they react. Their low ionization energies give an indication of the ease with which the outer electron is lost. Reactivity increases down the group as the elements with higher atomic number have the lowest ionization energies. Their ability to conduct electricity and heat is also due to the mobility of their outer electron.

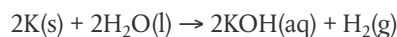
Reaction with water

The alkali metals react with water to produce hydrogen and the metal hydroxide. When you drop a piece of one of the first three elements into a small beaker containing distilled water, the following happens.

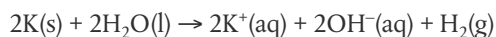
- Lithium floats and reacts slowly. It releases hydrogen but keeps its shape.
- Sodium reacts with a vigorous release of hydrogen. The heat produced is sufficient to melt the unreacted metal, which forms a small ball that moves around on the water surface.
- Potassium reacts even more vigorously to produce sufficient heat to ignite the hydrogen produced. It produces a lilac coloured flame and moves excitedly on the water surface.

The metals are called alkali metals because the resulting solution is alkaline owing to the presence of the hydroxide ion formed.

For example, with potassium:



As KOH is an ionic compound (Chapter 4) which dissociates in water, it is more appropriate to write the equation as:



The reaction becomes more vigorous as the group is descended. The most reactive element, caesium, has the lowest ionization energy and so forms positive ions most readily.



▲ Potassium reacting with water. The heat generated causes the hydrogen to ignite.

Note that the metal hydroxide is produced when Group 1 elements are added to water. A common mistake is to give the oxide as the product.

Observations must be something that can be observed. You cannot usually identify chemicals by simple observations. If you are asked to describe what you would see, saying 'a gas was produced' would gain more marks than 'hydrogen was produced'.



Exercises

- 22** State two observations you could make during the reaction between sodium and water. Give an equation for the reaction.

23 Which property increases down Group 1 from lithium to caesium?

- A** electronegativity **B** first ionization energy **C** melting point
D chemical reactivity

Group 17: the halogens

The Group 17 elements exist as diatomic molecules, X_2 . Their physical and chemical properties are summarized in the table below.

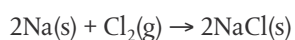
Physical properties	Chemical properties
<ul style="list-style-type: none">• They are coloured.• They show a gradual change from gases (F_2 and Cl_2), to liquid (Br_2), and solids (I_2 and At_2).	<ul style="list-style-type: none">• They are very reactive non-metals. Reactivity decreases down the group.• They form ionic compounds with metals and covalent compounds with other non-metals.



The trend in reactivity can be explained by their readiness to accept electrons, as illustrated by their very exothermic electron affinities discussed earlier. The nuclei have a high effective charge, of approximately +7, and so exert a strong pull on any electron from other atoms. This electron can then occupy the outer energy level of the halogen atom and complete a stable octet. The attraction is greatest for the smallest atom fluorine, which is the most reactive non-metal in the Periodic Table. Reactivity decreases down the group as the atomic radius increases and the attraction for outer electrons decreases.

Reaction with Group 1 metals

The halogens react with the Group 1 metals to form ionic **halides**. The halogen atom gains one electron from the Group 1 element to form a halide ion X^- . The resulting ions both have the stable octet of the noble gases. For example:



The electrostatic force of attraction between the oppositely charged Na^+ and Cl^- ions bonds the ions together. The outer electron moves like a harpoon from the sodium to the chlorine. Once the transfer is complete the ions are pulled together by the mutual attraction of their opposite charges (Figure 3.9).



The names of diatomic elements all end in *-ine* or *-gen*.



Group 1 and Group 17 are on opposite sides of the Periodic Table and show opposite trends in their reactivities and melting points.



From left to right: chlorine (Cl_2), bromine (Br_2), and iodine (I_2). These are toxic and reactive non-metals. Chlorine is a green gas at room temperature. Bromine is a dark liquid, although it readily produces a brown vapour. Iodine is a crystalline solid.



Two halogens are named by their colours: *chloros* means 'yellowish green' and *ioeides* is 'violet' in Greek. One is named by its smell: '*bromos*' is the Greek word for 'stench'.



Chlorine was used as a chemical weapon during World War I. Should scientists be held morally responsible for the applications of their discoveries?



The electron involved in the bonding of sodium is described as a harpoon. How useful are similes and metaphors in the sciences? Does the language we use in the sciences have a descriptive or interpretive function?

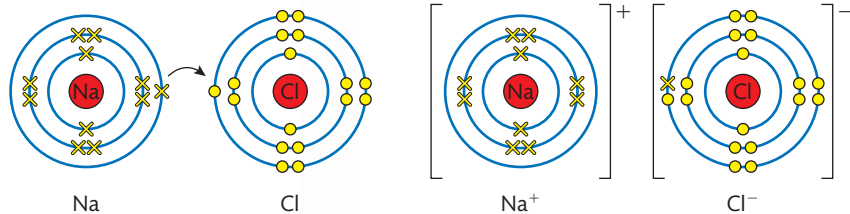
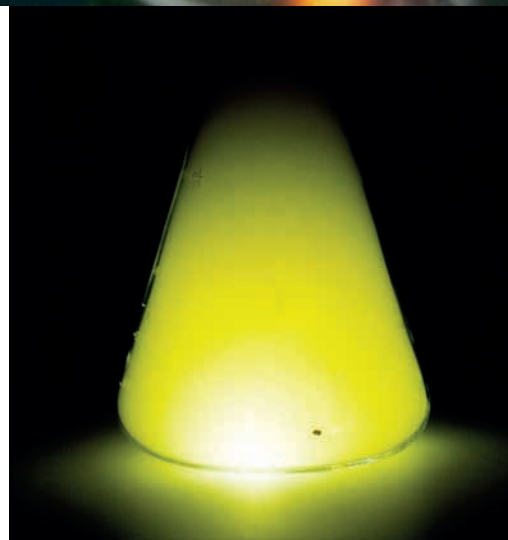


Figure 3.9 The high effective charge of the chlorine nucleus pulls the outer electron from the sodium atom. Once the transfer is complete the ions are pulled together by electrostatic attraction.

Sodium reacting with chlorine to form sodium chloride (NaCl, table salt). The violent reaction is exothermic and releases much heat.



When chlorine water is added to the colourless potassium bromide solution, bromine (yellow/orange) is formed. Bromine is displaced from solution by the more reactive chlorine.

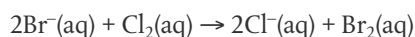
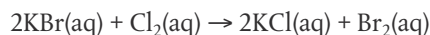
The more reactive halogen displaces the ions of the less reactive halogen from its compounds.



The most vigorous reaction occurs between the elements which are furthest apart in the Periodic Table: the most reactive alkali metal, francium, at the bottom of Group 1, with the most reactive halogen, fluorine, at the top of Group 17.

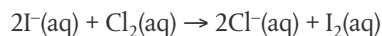
Displacement reactions

The relative reactivity of the elements can also be seen by placing them in direct competition for an extra electron. When chlorine is bubbled through a solution of potassium bromide the solution changes from colourless to orange owing to the production of bromine:

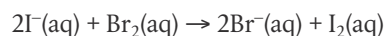


A chlorine nucleus has a stronger attraction for an electron than a bromine nucleus because of its smaller atomic radius and so takes the electron from the bromide ion. The chlorine has gained an electron and so forms the chloride ion, Cl^- . The bromide ion loses an electron to form bromine.

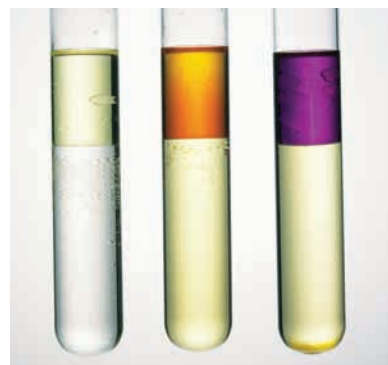
Other reactions are:



The colour changes from colourless to dark orange/brown owing to the formation of iodine.



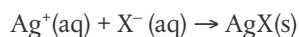
The colour darkens owing to the formation of iodine. To distinguish between bromine and iodine more effectively, the final solution can be shaken with a hydrocarbon solvent. Iodine forms a violet solution and bromine a dark orange solution as shown in the photo.



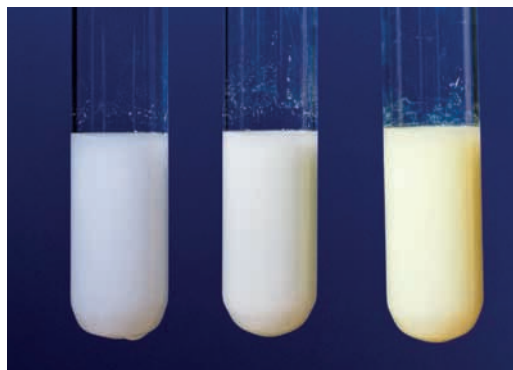
Solutions of chlorine (left), bromine (middle), and iodine (right) in water (lower part) and cyclohexane (upper part). Chlorine dissolves in water, but the halogens are generally more soluble in non-polar solvents like cyclohexane.

The halides

The halogens form insoluble salts with silver. Adding a solution containing the halide to a solution containing silver ions produces a **precipitate** that is useful in identifying the halide ion.



This is shown in this photo.



Silver halide precipitates formed by reacting silver nitrate (AgNO_3) with solutions of the halides. From left to right, these are silver chloride (AgCl), silver bromide (AgBr), and silver iodide (AgI).

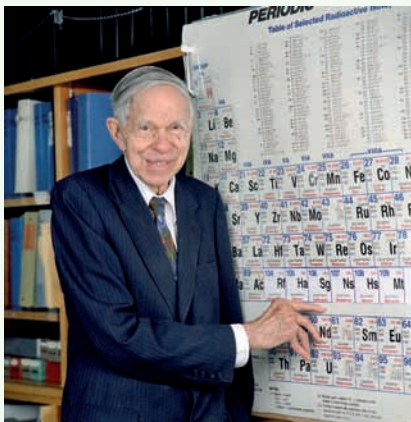
Exercises

- 24** How do the reactivities of the alkali metals and the halogens vary down the group?
- 25** Which property of the halogens increases from fluorine to iodine?
- A** ionic charge **C** melting point of the element
B electronegativity **D** chemical reactivity with metals
- 26** Which pair of elements reacts most readily?
- A** $\text{Li} + \text{Br}_2$ **B** $\text{Li} + \text{Cl}_2$ **C** $\text{K} + \text{Br}_2$ **D** $\text{K} + \text{Cl}_2$
- 27** Chlorine is a greenish-yellow gas, bromine is a dark red liquid, and iodine is a dark grey solid. Identify the property which most directly causes these differences in volatility.
- A** the halogen-halogen bond energy
B the number of neutrons in the nucleus of the halogen atom
C the number of outer electrons in the halogen atom
D the number of electrons in the halogen molecule
- 28** A paper published in April 2010 by Yu. Ts. Oganessian and others claims the synthesis of isotopes of a new element with atomic number 117. One of the isotopes is ${}^{293}_{117}\text{Uus}$. Which of the following statements is correct?
- A** the nucleus of the atom has a relative charge of +117
B ${}^{293}_{117}\text{Uus}$ has a mass number of 117
C there are 262 neutrons in ${}^{293}_{117}\text{Uus}$
D the atomic number is $293 - 117$

NATURE OF SCIENCE

Element 117 would be a new halogen. Whereas the discovery of the early elements involved the practical steps of extraction and isolation often performed by one individual, later elements are made by teams of scientists working together. New elements are as much invented as discovered, but their existence provides further knowledge about the natural world. The first synthetic elements were the transuranics. They are radioactive elements which are heavier than uranium, the heaviest natural element.

Claims that a new halogen, element 117, had been made were first made in April 2010 but these findings have yet to be confirmed. Scientists publish their own results in scientific journals after their work has been reviewed by several experts working in the same field. This process is called peer review. If the element turns out to have the properties predicted of a halogen below astatine, it will provide more evidence to support our model of the atom and the Periodic Table.



Glenn Seaborg (1912–1999) pointing to the element seaborgium (Sg). Seaborg discovered the transuranic element plutonium (Pu) in 1940. Seaborg also discovered americium (Am) and seven other transuranics. He won the 1951 Nobel Prize in Chemistry.

TOK

How can the production of artificial elements give us more knowledge of the natural world?



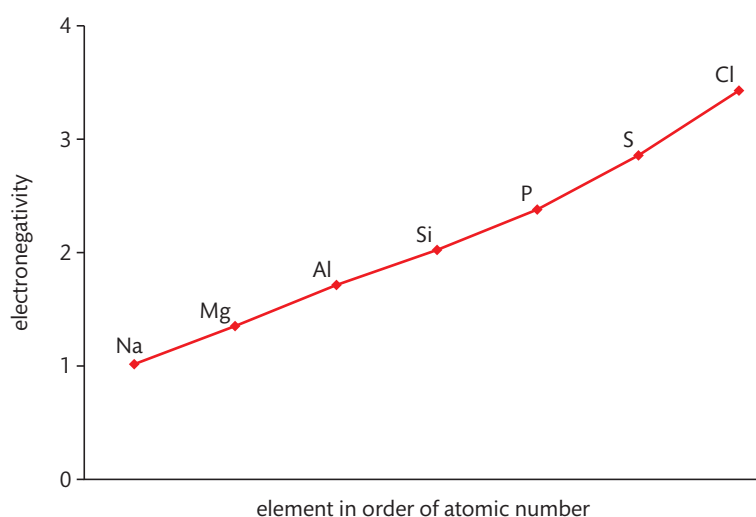
Cut and polished slices of agate. Agate is a variety of quartz (silicon dioxide). The colours are formed by impurities and the concentric bands are formed as successive layers of the oxide precipitate out of solution during formation of the agate.

Figure 3.10 Electronegativities increase across the period and approach 3.4, the value for oxygen.

Bonding of the Period 3 oxides

The transition from metallic to non-metallic character is illustrated by the bonding of the Period 3 oxides. Ionic compounds are generally formed between metal and non-metal elements and so the oxides of elements Na to Al have **giant ionic** structures. Covalent compounds are formed between non-metals, so the oxides of phosphorus, sulfur, and chlorine are **molecular covalent**. The oxide of silicon, which is a metalloid, has a **giant covalent** structure.

The ionic character of a compound depends on the *difference* in electronegativity between its elements. Oxygen has an electronegativity of 3.4, so the ionic character of the oxides decreases from left to right, as the electronegativity values of the Period 3 elements approach this value (Figure 3.10).



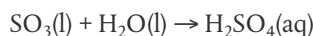
The oxides become more ionic down a group as the electronegativity decreases.

The conductivity of the molten oxides gives an experimental measure of their ionic character, as is shown in the table below. They only conduct electricity in the liquid state, when the ions are free to move.

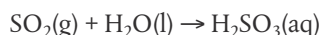
Note that the maximum oxidation number of a Period 3 element is related to the group number. It is +1 for elements in Group 1, +2 for elements in Group 2, +3 for elements in Group 13, +4 for elements in Group 14, and so on. Oxidation numbers are discussed in Chapter 9.

Formula of oxide	Na ₂ O(s)	MgO(s)	Al ₂ O ₃ (s)	SiO ₂ (s)	P ₄ O ₁₀ (s)/ P ₄ O ₆ (s)	SO ₃ (l)/ SO ₂ (g)	Cl ₂ O ₇ (l)/ Cl ₂ O(g)
Oxidation number	+1	+2	+3	+4	+5/+3	+6/+4	+7/+1
Electrical conductivity in molten state	high	high	high	very low	none	none	none
Structure	giant ionic			giant covalent	molecular covalent		

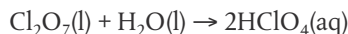
Sulfur trioxide reacts with water to produce sulfuric(VI) acid:



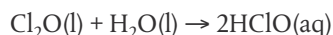
Sulfur dioxide reacts with water to produce sulfuric(IV) acid:



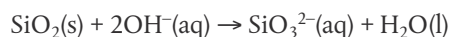
Dichlorine heptoxide (Cl_2O_7) reacts with water to produce chloric(VII) acid (HClO_4):



Dichlorine monoxide (Cl_2O) reacts with water to produce chloric(I) acid (HClO):



Silicon dioxide does not react with water, but reacts with concentrated alkalis to form silicates:

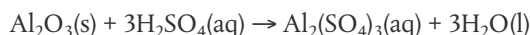
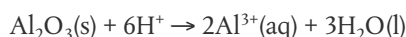


The Periodic Table has been called the most elegant classification chart ever devised. Is it a description or an explanation of periodic trends? Do other unifying systems exist in other areas of knowledge? To what extent do the classification systems we use affect the knowledge we obtain?

TOK

Amphoteric oxides

Aluminium oxide does not affect the pH when it is added to water as it is essentially insoluble. It has amphoteric properties, however, as it shows both acid and base behaviour. For example, it behaves as a base as it reacts with sulfuric acid:



and behaves as an acid when it reacts with alkalis such as sodium hydroxide:



Exercises

- 29** An oxide of a Period 3 element is a solid at room temperature and forms a basic oxide. Identify the element.
- A** Mg **B** Al **C** P **D** S
- 30** Which pair of elements has the most similar chemical properties?
- A** N and S **B** N and P **C** P and Cl **D** N and Cl
- 31** Identify the oxide which forms an acidic solution when added to water.
- A** $\text{Na}_2\text{O}(\text{s})$ **B** $\text{MgO}(\text{s})$ **C** $\text{SiO}_2(\text{s})$ **D** $\text{SO}_3(\text{g})$
- 32 (a)** Use the data below to identify the state of the four oxides listed under standard conditions.

Oxides	Melting point / K	Boiling point / K
MgO	3125	3873
SiO_2 (quartz)	1883	2503
P_4O_{10}	297	448
SO_2	200	263

- (b)** Explain the difference in melting points by referring to the bonding and structure in each case.
- (c)** The oxides are added to separate samples of pure water. State whether the resulting liquid is acidic, neutral, or alkaline. Describe all chemical reactions by giving chemical equations.
- (d)** Use chemical equations to describe the reactions of aluminium oxide with:
- (i)** hydrochloric acid
- (ii)** sodium hydroxide
- 33** Describe the acid–base character of the oxides of the Period 3 elements Na to Ar. For sodium oxide and sulfur trioxide, write balanced equations to illustrate their acid–base character.

High melting points are associated with ionic or covalent giant structures, low melting points with molecular covalent structures.

Make sure that you understand all the chemical equations presented in this topic. You could be expected to reproduce them under exam conditions.

13.1 First-row d-block elements

Understandings:

- Transition elements have variable oxidation numbers, form complex ions with ligands, have coloured compounds, and display catalytic and magnetic properties.

Guidance

Common oxidation numbers of the transition metal ions are listed in the IB Data booklet in sections 9 and 14.

- Zn is not considered to be a transition element as it does not form ions with incomplete d orbitals.
- Transition elements show an oxidation number of +2 when the s electrons are removed.

Applications and skills:

- Explanation of the ability of transition metals to form variable oxidation states from successive ionization energies.
- Explanation of the nature of the coordinate bond within a complex ion.
- Deduction of the total charge given the formula of the ion and ligands present.
- Explanation of the magnetic properties in transition metals in terms of unpaired electrons.

The elements of the d block have properties which have allowed us to advance technologically throughout the ages. To many people, a typical metal is a transition metal of the d block. We use the strength of iron and its alloy steel to construct buildings and machines, the electrical conductivity and low reactivity of copper to direct the flow of electricity and water, and we treasure gold and silver because of their appearance and rarity.

The ten elements of the first row of the d-block elements from Sc to Zn show a 'lull' in the periodic patterns we have seen in elements of the s and p blocks. The 10 d-block elements have similar physical and chemical properties.

TOK

The medical symbols for female and male originate from the alchemical symbols for copper and iron. What role has the pseudoscience of alchemy played in the development of modern science?

Transition elements have characteristic properties

Electron configuration

The similarity in the properties of first row d-block elements is illustrated by the relatively small range in atomic radii (Figure 3.11).

To understand the trend in atomic radii it is instructive to consider the electron configuration of the elements, summarized in the table on page 120. The unusual electron configurations of chromium (Cr) and copper (Cu) are due to the stability of the half-filled and filled 3d sub-level respectively. This is discussed on page 82.

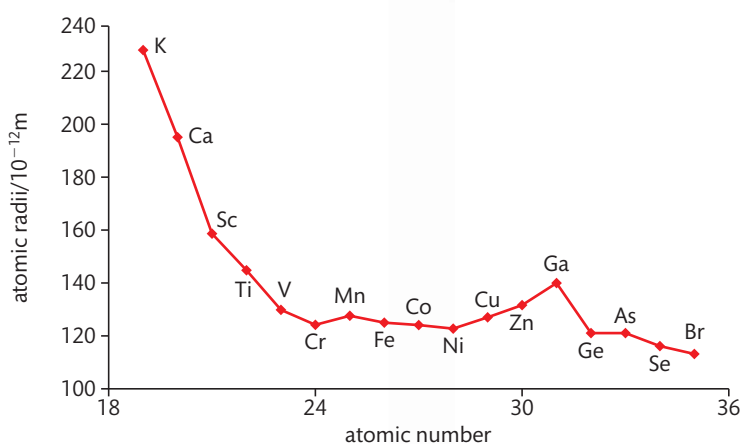


Figure 3.11 Atomic radii across Period 4.

Element	Core	3d					4s
Sc	[Ar]	↑					↑↓
Ti	[Ar]	↑	↑				↑↓
V	[Ar]	↑	↑	↑			↑↓
Cr	[Ar]	↑	↑	↑	↑	↑	↑
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

The relatively small decrease in atomic radii across the d block is due to the correspondingly small increase in effective nuclear charge experienced by the outer 4s electrons. The increase in nuclear charge due to the added proton is largely offset by the addition of an electron in an *inner* 3d sub-level. This similarity in atomic radii explains the ability of the transition metals to form alloys: the atoms of one d-block metal can be replaced by atoms of another without too much disruption of the solid structure. The small increase in effective nuclear charge also accounts for the small range in first ionization energies across the first transition series. As discussed in Chapter 2 (page 83), it is the 4s electrons which are removed first when the atom is ionized.

Exercises

34 State the electron configuration of the following metal ions by filling in the boxes below. Use arrows to represent the electron spin.

Ion	3d					4s
Sc ³⁺						
Ti ³⁺						
Ni ²⁺						
Zn ²⁺						

Physical properties

The transition elements are all metals with the following general physical properties:

- high electrical and thermal conductivity
- high melting point
- malleable – they are easily beaten into shape
- high tensile strength – they can hold large loads without breaking
- ductile – they can be easily drawn into wires
- iron, cobalt, and nickel are ferromagnetic.

These properties can be explained in terms of the strong metallic bonding found in the elements. As the 3d electrons and 4s electrons are close in energy, they are all involved in bonding, and form part of the delocalized sea of electrons which holds the metal

lattice together (Chapter 4). This large number of delocalized electrons accounts for the strength of the metallic bond and the high electrical conductivity. The smaller atomic radii of the d-block metals compared to their s-block neighbours also account, in part, for their higher densities.

The magnetic properties of the transition metal elements and compounds are discussed in more detail later.

Chemical properties

The chemical properties of the transition metals are very different from those of the s-block metals. Transition metals:

- form compounds with more than one oxidation number
- form a variety of complex ions
- form coloured compounds
- act as catalysts when either elements or compounds.

These properties are discussed in more detail later in the chapter.



Zinc is not a transition metal

The absence of zinc (Zn) from the collection of coloured ions in the photo above is significant. Zinc compounds do not generally form coloured solutions. Zinc is a d-block element but not a transition metal as it does not display the characteristic properties listed earlier; it shows only the +2 oxidation state in its compounds. The reason for its exceptional behaviour can be traced to the electronic configuration of its atom and the Zn^{2+} ion – the d sub-level is complete in both species (see the table on page 122). The electron configuration of the transition metal ions Ti^{2+} and Cu^{2+} are included for comparison. $\text{Sc}^{3+}(\text{aq})$ is also colourless in aqueous solution as it has no d electrons, but it is a transition metal as its atom has an incomplete d sub-shell, and the Sc^{2+} ion, although not common, does exist with a single d electron.



The properties and uses of the transition metals make them important commodities on the international stock exchange. The mining and extraction of these elements is an important industrial process in the economic development of some countries.

Transition element ions are coloured in aqueous solutions. From left to right the transition metal ions are: $\text{Ti}^{2+}(\text{aq})$, $\text{V}^{3+}(\text{aq})$, $\text{VO}^{2+}(\text{aq})$, $\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$, $\text{Mn}^{2+}(\text{aq})$, $\text{MnO}_4^{-}(\text{aq})$, $\text{Fe}^{3+}(\text{aq})$, $\text{Co}^{2+}(\text{aq})$, $\text{Ni}^{2+}(\text{aq})$, and $\text{Cu}^{2+}(\text{aq})$.



Transition metals are element whose atoms have an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell.

Ion	Core	3d					4s
Sc ³⁺	[Ar]						
Ti ²⁺	[Ar]	↑	↑				
Cu ²⁺	[Ar]	↑↓	↑↓	↑↓	↑↓	↑	
Zn ²⁺	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	

Explanation of variable oxidation number of transition elements

One of the key features of transition metal chemistry is the wide range of oxidation numbers that the metals display in their compounds. This should be contrasted with the s-block metals, which show only the oxidation state corresponding to their group number in their compounds. Calcium, for example, only shows the +2 state whereas titanium shows the +4, +3, and +2 states (Figure 3.12). The difference in behaviour can be related to patterns in successive ionization energies.

Element	Electron configuration
Ca	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ²
Ti	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ² 4s ²

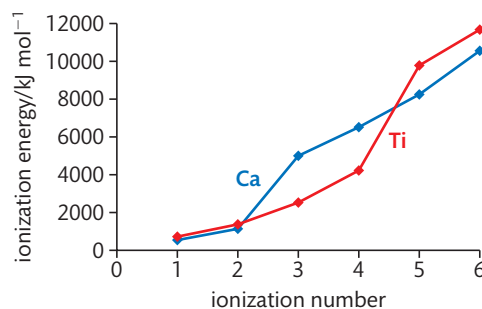


Figure 3.12 Successive ionization energies for Ca and Ti.

The Ca³⁺ ion is energetically unstable because there is a large jump in ionization energy as the third electron is removed from the inner 3p orbital. The increase in successive energies for titanium is more gradual as the 3d and 4s orbitals are close in energy. Titanium shows the +2, +3, and +4 oxidation states. A large jump occurs between the fourth and fifth ionization energies, as the inner 3p electron is removed, so titanium does not form the +5 state.

The oxidation states of the d block elements are summarized below. The more common oxidation states are highlighted in blue.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
+2	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

The oxidation states of vanadium and manganese can be investigated experimentally.





Chromium chloride CrCl_3 (violet) and chromium nitrate $\text{Cr}(\text{NO}_3)_3$ (green) illustrate chromium in the oxidation state +3. In potassium chromate K_2CrO_4 (yellow) and potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ (orange) chromium has an oxidation state of +6.

The following points are important and should be noted.

- All the transition metals show both the +2 and +3 oxidation states. The M^{3+} ion is the stable state for the elements from scandium to chromium, but the M^{2+} state is more common for the later elements. The increased nuclear charge of the later elements makes it more difficult to remove a third electron.
- The maximum oxidation state of the elements increases in steps of +1 and reaches a maximum at manganese. These states correspond to the use of both the 4s and 3d electrons in bonding. Thereafter, the maximum oxidation state decreases in steps of -1.
- Oxidation states above +3 generally show covalent character. Ions of higher charge have such a large charge density that they polarize negative ions and increase the covalent character of the compound (see Figure 3.13).
- Compounds with higher oxidation states tend to be oxidizing agents. The use of potassium dichromate(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$), for example, in the oxidation of alcohols is discussed in Chapter 10.

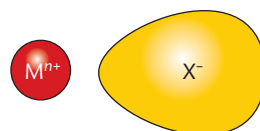


Figure 3.13 The high charge density of the transition metal ions M^{n+} pulls the weakly held outer electrons of the X^- ion. This polarization of negative ions increases the covalent character of the compounds of the transition metal ions with oxidation number greater than +3.

Exercises

- 35** Identify the property/properties which are characteristic of an element found in the d block of the Periodic Table.
- A** all the compounds of the element are ionic
B the element exhibits a variety of oxidation states and colours in its compounds
C the element has a low melting point
D the element is a good conductor of heat and electricity
- 36** Identify the oxidation number which is the most common among the first-row transition elements.
- A** +1 **B** +2 **C** +4 **D** +6
- 37** An element has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$. Which oxidation state(s) would this element show?
- A** +2 and +3 only **B** +2 and +5 only **C** +3 and +5 only **D** +2, +3, +4, and +5
- 38** (a) State the full electron configuration of zinc (Zn).
 (b) State the full electron configuration of Zn^{2+} .
 (c) Explain why zinc is not classed as a transition metal.
- 39** State the oxidation states shown by calcium and chromium, and explain the difference in their behaviour.



NATURE OF SCIENCE

Science involves the investigation of patterns and trends. The d block elements follow certain patterns of behaviour, but scandium, zinc, chromium, and copper show significant discrepancies. Scientific knowledge is provisional and continues to evolve; scandium is sometimes classed as a transition element due to the rarity of the +2 oxidation state, but this is now considered to be incorrect.

Complex ions

Full details of how to carry out this experiment with a worksheet are available online.



Figure 3.14 The complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. The water molecules are ligands as they form coordinate bonds to the central ion.

A coordinate bond uses a lone pair of electrons to form a covalent bond.



A ligand is a species that uses a lone pair of electrons to form a coordinate bond with a metal ion.



The word 'ligand' is derived from *ligandus*, the Latin word for 'bound'.

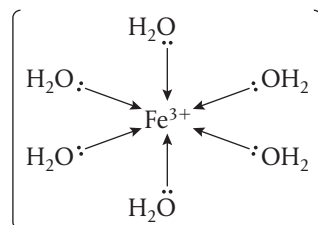


Figure 3.15 Shapes and coordination numbers of some complex ions.

A solution of pale blue copper(II) sulfate contains $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (left). The yellow $[\text{CuCl}_4]^{2-}$ complex, formed when concentrated hydrochloric acid is added (centre) gives a vivid green colour in the presence of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. The dark blue $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ complex is formed when ammonia is added.

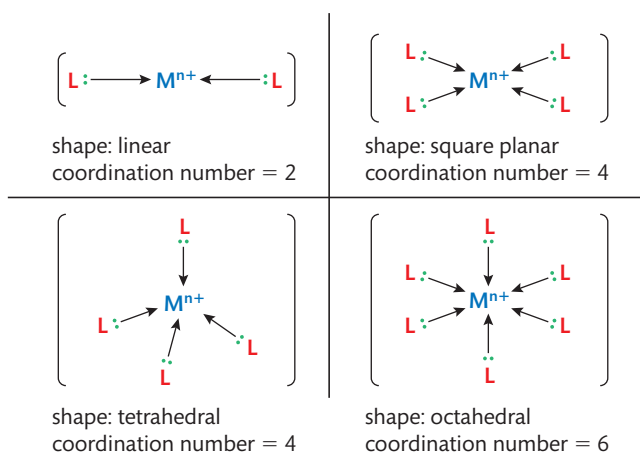
Complex ions

Transition metal ions in solution have a high charge density and attract water molecules which form coordinate bonds with the positive ions to form a **complex ion**.



More generally a complex is formed when a central ion is surrounded by molecules or ions which possess a lone pair of electrons. These surrounding species (**ligands**), are attached via a coordinate bond. All ligands have at least one atom with a lone pair of electrons which is used to form a coordinate bond with the central metal ion.

The number of coordinate bonds from the ligands to the central ion is called the **coordination number**. The shapes of some complex ions and their coordination numbers are shown in Figure 3.15.



In aqueous solution, water molecules generally act as ligands but these can be replaced in a process known as ligand exchange. As complexes often have distinctive colours they can be used in qualitative analysis.



Beakers showing the colour change in a test for the iron(III) ion. The complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ on the left has an orange colour. This reacts with the colourless potassium thiocyanate solution (centre) to form a distinctive blood-red colour (right); one of the water ligands (H_2O) is replaced with a thiocyanate ion (SCN^-). The resulting complex ion has a formula $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$.

Some examples of complex ions are shown in the table below.

Complex	Ligand	Coordination number	Oxidation number of central ion	Shape
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	H_2O	6	+3	octahedral
$[\text{Co}(\text{NH}_3)_6]^{3+}$	NH_3	6	+3	octahedral
$[\text{CuCl}_4]^{2-}$	Cl^-	4	+2	tetrahedral
$[\text{Fe}(\text{CN})_6]^{3-}$	CN^-	6	+3	octahedral
$[\text{Ag}(\text{NH}_3)_2]^+$	NH_3	2	+1	linear
MnO_4^-	O^{2-}	4	+7	tetrahedral
$\text{Ni}(\text{CO})_4$	CO	4	0	tetrahedral
$\text{PtCl}_2(\text{NH}_3)_2$	Cl^- and NH_3	4	+2	square planar

Polydentate ligands act as chelating agents

Some species have more than one lone pair available to form a coordinate bond with the central transition ion. EDTA^{4-} (old name ethylenediaminetetraacetic acid) is an example of a polydentate ligand as it has six atoms (two nitrogen atoms and four oxygen atoms) with lone pairs available to form coordinate bonds.

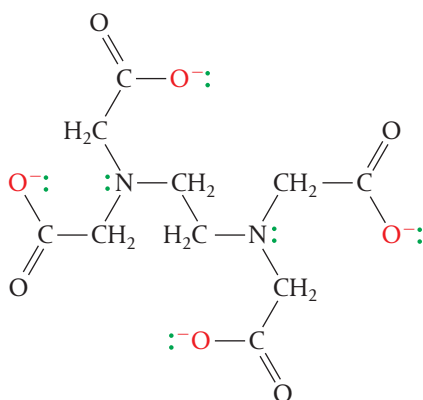


Figure 3.16 The polydentate ligand EDTA^{4-} can take the place of six monodentate ligands as it has six lone pairs available.

A chelate is a complex containing at least one polydentate ligand. The name is derived from the Greek word for *claw*.



EDTA⁴⁻ is thus equivalent to six monodentate ligands and is described as a hexadentate (six-toothed) ligand. It can occupy all the octahedral sites and grip the central ion in a six-pronged claw called a **chelate**.

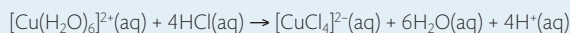
Chelates are very important in foods and all biological systems. EDTA⁴⁻ forms chelates with many metal ions and is widely used as a food additive as it removes transition ions from solution and so inhibits enzyme-catalysed oxidation reactions.

Exercises

40 Identify the species which cannot act as a ligand:

- A** H₂O **B** CO **C** CH₄ **D** Cl⁻

41 Consider the reaction below:



Which of the following is acting as a ligand?

- A** H⁺ only **B** H⁺ and Cl⁻ only **C** H₂O and Cl⁻ only **D** H⁺, H₂O, and Cl⁻

42 The colour and formulas of some coordination compounds of hydrated forms of chromium(III) chloride are listed in this table.

	I	II	III
Formula	[Cr(H ₂ O) ₆]Cl ₃	[CrCl(H ₂ O) ₅]Cl ₂ ·H ₂ O	[CrCl ₂ (H ₂ O) ₄]Cl·2H ₂ O
Colour	purple	blue-green	green

What are the charges on each of the complex ions?

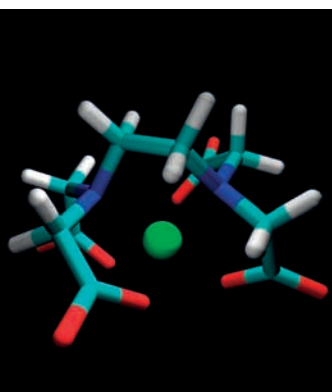
	I	II	III
A	0	0	0
B	+	2+	3+
C	2+	3+	+
D	3+	2+	+

43 Identify the feature which is an essential characteristic of all ligands.

- A** a negative charge
B an electronegative atom
C the presence of a non-bonding pair of electrons
D the presence of two or more atoms

44 Elements with atomic number 21 to 30 are Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn.

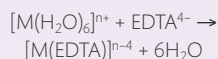
- (a) Identify which of the d-block elements is not considered to be a transition metal.
 (b) Deduce the oxidation state of the transition metal in the following species.
 (i) Fe₃O₄
 (ii) MnO₄⁻
 (iii) CrO₄²⁻
 (iv) [Fe(CN)₆]⁴⁻



Computer graphic of a molecule of the chelating agent ethyldiaminetetraacetic acid surrounding a magnesium ion (Mg, green sphere). The atoms (tubes) of the molecule are colour-coded: carbon (light blue), nitrogen (dark blue), hydrogen (white) and oxygen (red). EDTA is used to preserve DNA (deoxyribonucleic acid) samples by removing the magnesium ions that aid the degradation of DNA. It is also used to detoxify patients suffering from heavy metal poisoning (chelation therapy).

CHALLENGE YOURSELF

5 Assuming the transition metal ion, Mⁿ⁺, is originally surrounded by water molecules, the ligand replacement reaction can be represented as:



Predict the entropy change for this reaction and explain the stability of the chelate formed.

Transition metals and their ions are important catalysts

The use of the transition elements in construction was discussed earlier. The use of the metals and their compounds as catalysts is also of economic importance. A catalyst is a substance which alters the rate of reaction, by providing an alternative reaction pathway with a lower activation energy (see Chapter 6).

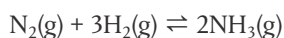
Catalysts play an essential role in the chemical industry as they allow chemical processes to proceed at an economical rate.

Transition metals and their ions as heterogeneous catalysts

In **heterogeneous** catalysis, the catalyst is in a different state from the reactants. The ability of transition metals to use their 3d and 4s electrons to form weak bonds to reactant molecules makes them effective heterogeneous catalysts as they provide a surface for the reactant molecules to come together with the correct orientation.

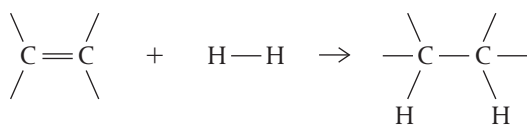
Examples of transition metals as heterogeneous catalysts include the following.

- Iron (Fe) in the Haber process:



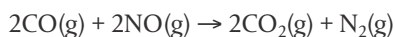
Ammonia (NH_3) is the raw material for a large number of other useful chemical products such as fertilizers, plastics, drugs, and explosives.

- Nickel (Ni) in the conversion of alkenes to alkanes:



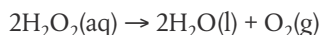
This reaction allows unsaturated vegetable oils with a carbon–carbon double bond to be converted to margarine.

- Palladium (Pd) and platinum (Pt) in catalytic converters:

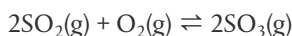


This reaction removes harmful primary pollutants from a car's exhaust gases.

- MnO_2 in the decomposition of hydrogen peroxide:



- V_2O_5 in the Contact process:



Sulfur trioxide (SO_3) is used in the production of sulfuric acid, the manufacturing world's most important chemical.

Heterogeneous catalysis is generally preferred in industrial processes as the catalyst can be easily removed by filtration from the reaction mixture after use.

Ions of transition metals as homogeneous catalysts

Homogeneous catalysts are in the same state of matter as the reactants. The ability of transition metals to show variable oxidation states allows them to be particularly effective homogeneous catalysts in redox reactions. As many of the enzyme-catalysed cell reactions in the body involve transition metals as homogeneous catalysis, they are of fundamental biological importance. Examples include the following.

- Fe^{2+} in heme: oxygen is transported through the bloodstream by forming a weak bond with the heme group of hemoglobin. This group contains a central Fe^{2+} ion surrounded by four nitrogen atoms. The O_2 – Fe^{2+} bond is easily broken when the oxygen needs to be released.
- Co^{3+} in vitamin B_{12} . Part of the vitamin B_{12} molecule consists of an octahedral Co^{3+} complex. Five of the sites are occupied by

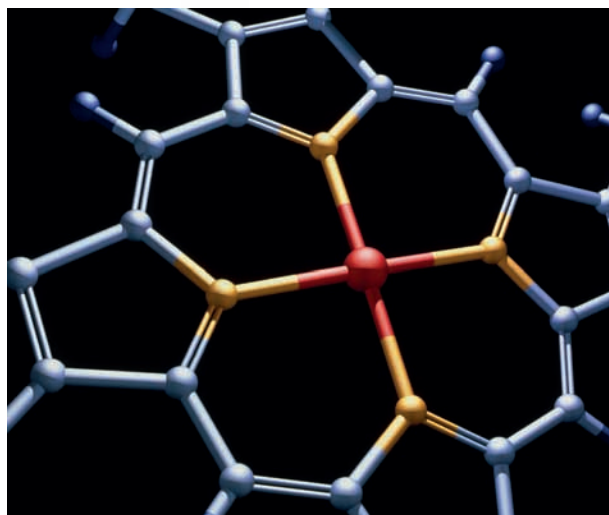


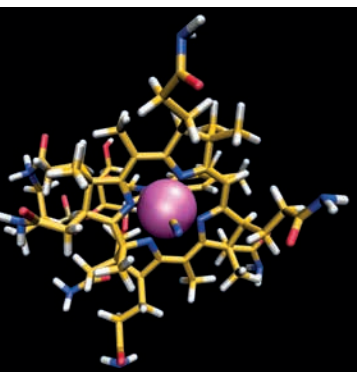
More details of heterogeneous and homogeneous catalysis are discussed in Chapter 12.



The action of transition metal catalysis such as manganese (IV) oxide in the decomposition of hydrogen peroxide, and cobalt chloride in the decomposition of potassium sodium tartrate.

The molecular structure of a heme group of the blood protein hemoglobin, which carries oxygen and carbon dioxide around the body. The Fe^{2+} (red) ion is bonded to four nitrogen atoms (yellow). The flat group of four rings around the Fe^{2+} ion gives oxygen easy access to the iron from above, allowing binding and release without any chemical change.





Vitamin B₁₂. The central Co³⁺ (purple) is coordinated to five nitrogen atoms (blue).

The term 'magnetic' derives from the mineral magnetite, which has been widely used as a compass because of its magnetic properties. The origins of the term 'ferromagnetism' derive from iron's magnetic properties.



nitrogen atoms, leaving the sixth site available for biological activity. Vitamin B₁₂ is needed for the production of red blood cells and for a healthy nervous system.

As homogeneous catalysts mix effectively with the reactants, they work under the mild conditions of the human body.

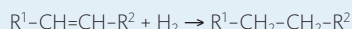
Exercises

45 Study the structure of heme shown in the picture on page 127.

- What is the oxidation state of the central iron ion?
- What is the geometry of the nitrogen atoms around the central iron ion?
- Explain why the complex is ideally suited to carry oxygen around the body

46 Name the catalyst in each of the following processes:

- The hydrogenation of vegetable oils to form margarine:



- The manufacture of sulfuric acid in the Contact process.
 - The removal of carbon monoxide and nitrogen monoxide from exhaust emissions.
- 47
- Distinguish between homogeneous catalysis and heterogeneous catalysis.
 - Explain why the transition metals make effective heterogeneous catalysts.
 - Explain why heterogeneous catalysts are generally used in industrial processes.

The magnetic properties of the transition metals and their compounds

Every spinning electron in an atom or molecule can behave as a tiny magnet. Electrons with opposite spins behave like minute bar magnets with opposing orientation and so have no net magnetic effect. Most substances have paired electrons that pair up and so are non-magnetic. Some transition metals and their compounds are unusual in having some electrons that remain unpaired, which when aligned lead to magnetic properties.

Substances can be distinguished by their response to externally applied magnetic fields

Materials are classified as diamagnetic, paramagnetic, or ferromagnetic based on their behaviour when placed in an external magnetic field.

- **Diamagnetism** is a property of all materials and produces a very weak opposition to an applied magnetic field.
- **Paramagnetism**, which only occurs with substances which have unpaired electrons, is stronger than diamagnetism. It produces magnetization proportional to the applied field and in the same direction.
- **Ferromagnetism** is the largest effect, producing magnetizations sometimes orders of magnitude greater than the applied field.

Most materials are diamagnetic as the orbital motion of their electrons produces magnetic fields which oppose any external field. Paramagnetism is a property of single atoms or ions with unpaired spinning electrons, whereas ferromagnetism only occurs if there is long range ordering of the unpaired electrons.

Iron, cobalt, and nickel are ferromagnetic

Iron, nickel, and cobalt are ferromagnetic; the unpaired d electrons in large numbers of atoms line up with parallel spins in regions called **domains**. Although these domains

are generally randomly oriented with respect to each other, they can become more ordered if exposed to an external magnetic field. The magnetism remains after the external magnetic field is removed, as the domains remain aligned due to the long range interaction between the unpaired electrons in the different atoms.

Transition metals and their complexes show paramagnetic properties

Transition metal complexes with unpaired electrons show paramagnetic properties as they are pulled into a magnetic field. Paramagnetic and diamagnetic complexes can be distinguished using the experimental arrangement in Figure 3.17. The sample to be tested, shown in green, is placed in an electromagnet. When the field is turned on paramagnetic materials are attracted into the magnetic field of the electromagnet and so will move downwards causing the blue counterweight to move up; the sample appears to have increased in mass. Diamagnetic materials will move out of the field in the opposite direction and so will appear to have reduced in mass.

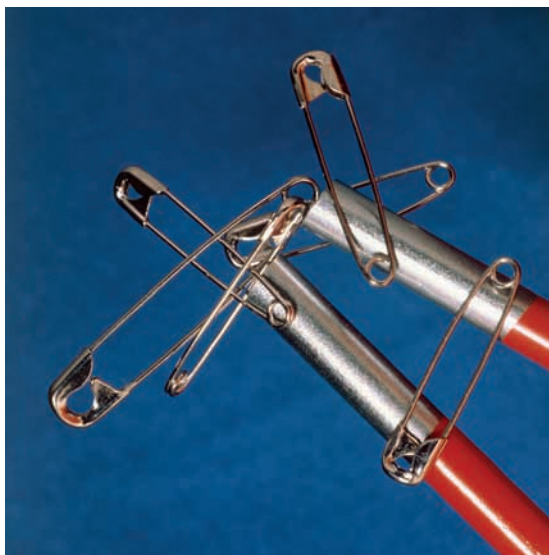
Paramagnetism increases with the number of unpaired electrons so generally increases from left to right across the Periodic Table, reaches a maximum at chromium, and decreases. Zinc has no unpaired electrons and so is diamagnetic.

The presence of electron spin was first demonstrated in the Stern–Gerlach experiment. A beam of silver atoms divided into two as it travelled through an electromagnetic field. Atoms with the unpaired electron spinning \uparrow moved in the opposite direction to those atoms with electrons spinning \downarrow .

The action at a distance of invisible magnetic forces mystified early thinkers, who drew parallels between magnetism and other areas of human experiences – such as infection and love. Remnants of this confusion are reflected in our language; the French word for ‘magnet’ is *aimant*. Language allows knowledge to be passed on to others and to be accumulated over time for future generations. This is how knowledge is ‘shared’, but outdated ideas and theories can be communicated in the same way. How does the vocabulary we use help and hinder the pursuit of knowledge?

Exercises

- 48 Which of the following elements would be expected to be paramagnetic?
A Ca **B** Zn **C** He **D** Mn
- 49 Which of the elements is the most paramagnetic?
A Sc **B** Ti **C** V **D** Cr
- 50 Explain why chromium is the most paramagnetic element in the first transition series and why zinc is diamagnetic.



A horseshoe magnet holding some safety-pins. Magnetic objects have the capability to retain a certain amount of magnetization once exposed to an external magnetic field. Domains in the crystalline structure of these metals are small regions, 0.1–1 mm across, in which the magnetic moment of each atom has the same direction. When an external field is applied all the domains are lined up with the field, providing the high magnetization.

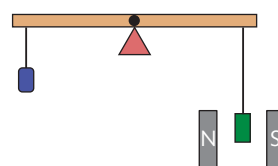


Figure 3.17 Diamagnetic and paramagnetic materials will move in different directions in the field produced by an electromagnet. The sample, shown in green, will appear to increase in mass when the field is turned on if it is paramagnetic, and will appear to decrease in mass if it is diamagnetic.



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Magnetism was used in navigation by the Chinese long before it was explained scientifically. Historically, technology emerged before science. Materials were often used practically long before there was an understanding of why they possessed their properties.

In today's world the reverse is often the case, with scientific understanding leading to technological developments, which in turn drive further developments in scientific ideas.



13.2 Coloured complexes

Understandings:

- The d sub-level splits into two sets of orbitals of different energy in a complex ion.
- Complexes of d-block elements are coloured, as light is absorbed when an electron is excited between the d orbitals.
- The colour absorbed is complementary to the colour observed.

Guidance

The relation between the colour observed and absorbed is illustrated by the colour wheel in the IB Data booklet in section 17.

Applications and skills:

- Explanation of the effect of the identity of the metal ion, the oxidation number of the metal, and the identity of the ligand on the colour of transition metal ion complexes.

Guidance

Students are not expected to recall the colour of specific complex ions.

- Explanation of the effect of different ligands on the splitting of the d orbitals in transition metal complexes and colour observed using the spectrochemical series.

Guidance

The spectrochemical series is given in the IB data booklet in section 15. A list of polydentate ligands is given in the data booklet in section 16. Students are not expected to know the different splitting patterns and their relation to the coordination number. Only the splitting of the 3-d orbitals in an octahedral crystal field is required.

The colours of complex ions can be experimentally investigated.



The colour of transition metal ions (shown in the table below) can be related to the presence of partially filled d orbitals. The ion Sc^{3+} is colourless because the 3d sub-level is empty; Zn^{2+} is colourless because the 3d sub-level is full.

Ion	Electron configuration	Colour
Sc^{3+}	[Ar]	colourless
Ti^{3+}	[Ar] 3d ¹	violet
V^{3+}	[Ar] 3d ²	green
Cr^{3+}	[Ar] 3d ³	violet
Mn^{2+}	[Ar] 3d ⁵	pink
Fe^{3+}	[Ar] 3d ⁵	yellow
Fe^{2+}	[Ar] 3d ⁶	green
Co^{2+}	[Ar] 3d ⁷	pink
Ni^{2+}	[Ar] 3d ⁸	green
Cu^{2+}	[Ar] 3d ⁹	blue
Zn^{2+}	[Ar] 3d ¹⁰	colourless

The visible spectrum

The visible spectrum ranges from 400 nm to about 700 nm. The colour we see depends on wavelength.

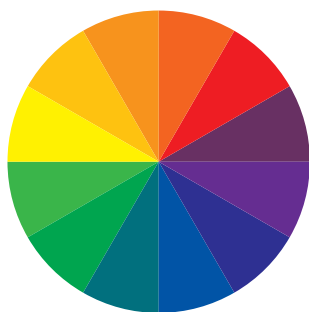


Figure 3.18 The colour wheel. There is a colour wheel in section 17 of the IB Data booklet.

Colour	Wavelength range / nm
Red	630–700
Orange	590–630
Yellow	560–590
Green	490–560
Blue	450–490
Violet	400–450

The colour of a substance is determined by which colour(s) of light it absorbs and which colour(s) it transmits or reflects (the complementary colour(s)). Copper sulfate, for example, appears turquoise because it absorbs orange light. Orange and turquoise are complementary colours; they are opposite each other in the colour wheel (Figure 3.18).

Transition metals appear coloured because they absorb visible light

As discussed in Chapter 2, white light is composed of all the colours of the visible spectrum. Transition metal compounds appear coloured because their ions absorb some of these colours. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, for example, appears yellow because it absorbs light in the blue region of the spectrum (Figures 3.19 and 3.20).

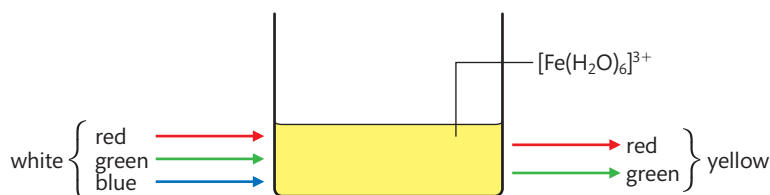


Figure 3.19 Complementary colours. Yellow light (a mixture of red and green light) added to blue light makes white light. White light changes to yellow when the blue is removed.

Figure 3.20 The ion Fe^{3+} appears yellow because it absorbs blue light. Yellow is the complementary colour to blue.

Transition metals absorb light because the d orbitals split into two sub-levels

The d orbitals in an isolated transition metal atom are said to be degenerate as they all have the same energy. However, in the electric field produced by the ligand's lone pair of electrons, they split into two sub-levels. Consider, for example, the octahedral complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ with the water molecules placed along the x-, y-, and z-axes (Figure 3.21).

When light passes through a solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, one 3d electron is excited from the lower to the higher energy sub-level (Figure 3.22). A photon of green light is absorbed and light of the complementary colour (purple) is transmitted, which accounts for the purple colour of a solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

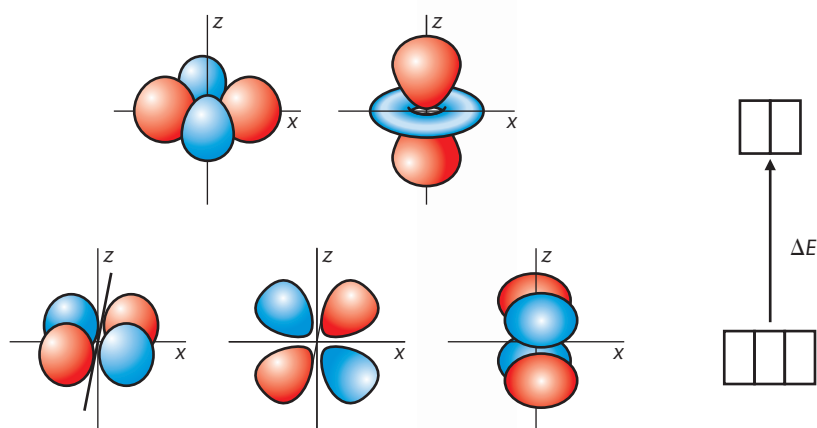


Figure 3.21 An electron in a d orbital orientated along the bond axis has a higher energy than an electron in one of the three orbitals which point between the axes.



The energy separation between the orbitals is ΔE and hence the colour of the complex depends on the following factors:

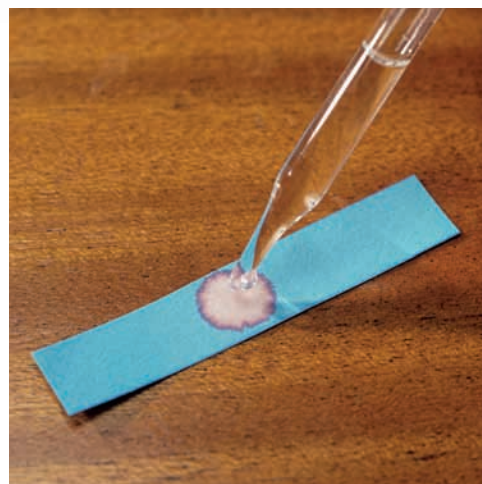
- the nuclear charge and the identity of the central metal ion;
- the charge density of the ligand;
- the geometry of the complex ion (the electric field created by the ligand's lone pair of electrons depends on the geometry of the complex ion);
- the number of d electrons present and hence the oxidation number of the central ion.

Figure 3.22 Green light of energy $h\nu$ excites an electron from a d orbital of lower energy to a d orbital of higher energy. The transmitted light is purple.

Cobalt chloride paper is used to indicate the presence of water. The colour changes from blue to pink as the ligands change from Cl^- ions to H_2O molecules.

$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (on the left) is pale pink and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (on the right) is yellow/brown. Both have the same electron configuration. The manganate ion, MnO_4^- (in the centre) shows manganese in a +7 oxidation state. It has a distinctive intense purple colour.

Each of these factors is discussed in turn below.



Exercises

- 51** Explain why the two cobalt complex ions $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$ are different colours.



Don't confuse the colour of transition metal ions, produced as a result of light being absorbed as electrons jump between the split d sub-levels, with the emission of colour produced when excited electrons return to the ground state.

The colour depends on the nuclear charge and identity of the central metal ion

The strength of the coordinate bond between the ligand and the central metal ion depends on the electrostatic attraction between the lone pair of electrons and the nuclear charge of the central ion. Ligands interact more effectively with the d orbitals of ions with a higher nuclear charge. For example, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ both have the same electron configuration but the iron nucleus has a higher nuclear charge and so has a stronger interaction with the water ligands. Manganese(II) compounds are pale pink in aqueous solution as the ions absorb in the green region of the visible spectrum of light, whereas iron(III) compounds are yellow/brown as they absorb higher energy light in the blue region of the spectrum.

Charge density of the ligand

The spectrum of the copper complex formed when four of the water molecule ligands are replaced by four ammonia molecules is shown in Figure 3.23. The $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex absorbs the shorter wavelength yellow light, therefore the complex has a deep blue colour. Ammonia has a greater charge density than water and so produces a larger split in the d orbitals. The higher charge density of the ammonia compared to water also explains their relative base strengths.



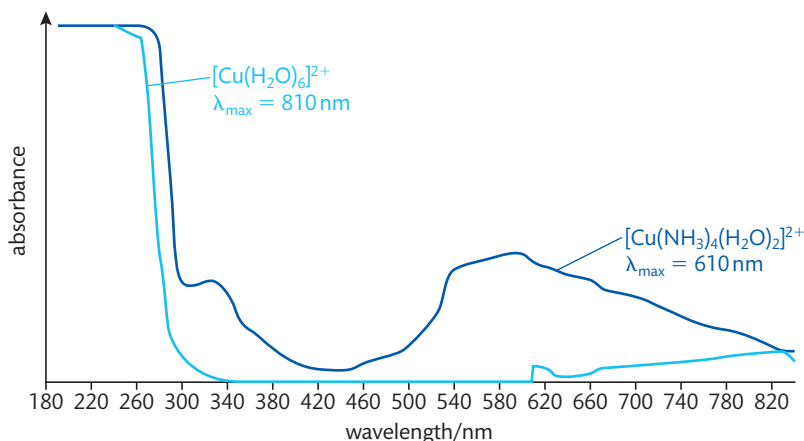


Figure 3.23 The electronic UV-vis absorption spectrum of some copper complexes. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ absorbs light in the orange region of the spectrum and so appears turquoise. $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ absorbs light in the yellow region of the spectrum and so appears dark blue.

The **spectrochemical series** arranges the ligands according to the energy separation, ΔE , between the two sets of d orbitals. The wavelength at which maximum absorbance occurs, λ_{max} , decreases with the charge density of the ligand, as shown in the table below. The large iodide ion, which has the lowest charge density, repels the d electrons the least and so produces a small splitting. The smaller chloride ion, with a relatively high charge density, has a larger splitting. The large splitting of the CN^- ion and carbon monoxide is more complex and is partly due to the presence of π bonding in the ligand; electrons in the p orbitals on the carbon atoms can interact with the d orbitals of the transition metal. The spectrochemical series is given in section 15 of the IB Data booklet.

Ligand	I^-	Br^-	S^{2-}	Cl^-	H_2O	OH^-	NH_3	CN^-	CO
λ_{max}	longest wavelength	← wavelength increasing →							shortest wavelength
ΔE	weakest field	← ΔE increasing →							strongest field

Geometry of the complex

The change of the colour in the cobalt complex in the photo on the right is also in part due to the change in coordination number and geometry of the complex ion. The splitting in energy of the d orbitals depends on the relative orientation of the ligand and the d orbitals.

Number of d electrons and oxidation state of the central metal ion

The strength of the interaction between the ligand and the central metal ion and the amount of electron repulsion between the ligand and the d electrons depends on the number of d electrons and hence the oxidation state of the metal. For example, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ absorbs violet light and so appears green/yellow, whereas $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ absorbs blue light and appears orange/brown.

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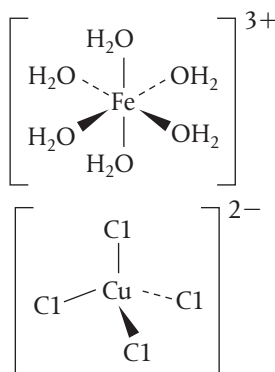
The colour of transition metal complexes can be explained through the use of models and theories based on how electrons are distributed in d orbitals. A detailed understanding needs a consideration of the three-dimensional symmetry of the complex ions. The ability to visualize the three-dimensional arrangement of atoms and ions is a key skill of the chemist.



▲ The pink solution (left) contains the complex ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. If concentrated hydrochloric acid is added (centre), a blue colour is seen. The chloride ions of the acid displace the water in the cobalt complex, forming a new complex ion, $[\text{CoCl}_4]^{2-}$, with a characteristic blue colour. Adding water (right) reverses the reaction.

CHALLENGE YOURSELF

- 6 Explain why the absorption spectra of gaseous atoms are made up from a series of lines, whereas complex ions produce broad absorption bands.



Emeralds are green due to trace amounts of chromium.

Worked example

State the formula and the shape of the complex ion formed in the following reactions.

- Some iron metal is dissolved in sulfuric acid and then left exposed to air until a yellow solution is formed.
- Concentrated hydrochloric acid is added to aqueous copper sulfate solution to form a yellow solution.
- A small volume of sodium chloride is added to aqueous silver nitrate solution. The white precipitate dissolves to form a colourless solution when ammonia solution is added.

Solution

- (a) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

The oxidation state is +3 as the complex is left exposed to air.

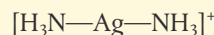
The shape is octahedral as the coordination number = 6 (see left).

- (b) The complex $[\text{CuCl}_4]^{2-}$ is yellow.

The shape is tetrahedral as the coordination number = 4 (see left).

- (c) $\text{NaCl}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$

The complex $[\text{Ag}(\text{NH}_3)_2]^+$ is linear as the coordination number is 2.



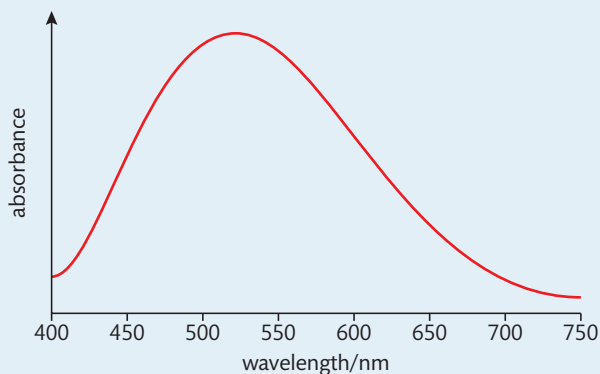
Exercises

- 52 The colour of transition metal complexes depends on several factors.

- Suggest why the colour of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is different from the colour of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.
- Suggest why the colour of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is different from the colour of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.
- Suggest why the colour of $[\text{Fe}(\text{NH}_3)_6]^{2+}$ is different from the colour of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

- 53 Explain why $\text{Fe}^{2+}(\text{aq})$ is coloured and can behave as a reducing agent, whereas $\text{Zn}^{2+}(\text{aq})$ is not coloured and does not behave as a reducing agent.

- 54 The absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is shown below. Use the colour wheel to suggest a colour for the complex.



- 55 (a) Draw a diagram to show how the electrons are arranged in Fe^{2+} when it is present in the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion.

- (b) Predict whether the splitting of the d orbitals in $[\text{Fe}(\text{CN})_6]^{4-}$ would be less than or greater than the splitting in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.

- 56 (a) Explain why $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ have different colours.

- (b) Explain why $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ have different colours.

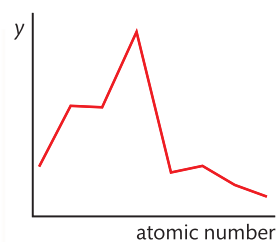
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Colour is a trans-disciplinary subject that is of interest to the artist and the scientist alike. Science looks for the hidden structures and processes at smaller dimensions to explain observable phenomena. The poet John Keats criticised Newton for destroying the poetry of the rainbow by reducing it to the colours of a prism, but an explanation of colour in terms of electron transitions and molecular symmetries adds to our appreciation and understanding of the natural world.

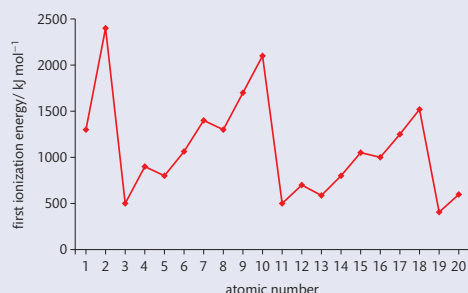
Practice questions

- Which property generally decreases across Period 3?
A atomic number **B** electronegativity **C** atomic radius
D first ionization energy
- Which statements about Period 3 are correct?
I The electronegativity of the elements increases across Period 3.
II The atomic radii of the elements decreases across Period 3.
III The oxides of the elements change from acidic to basic across Period 3.
A I and II only **B** I and III only **C** II and III only **D** I, II, and III
- Which property decreases down Group 17 in the Periodic Table?
A melting point **B** electronegativity **C** atomic radius **D** ionic radius
- Which oxides produce an acidic solution when added to water?
I P_4O_{10}
II MgO
III SO_3
A I and II only **B** I and III only **C** II and III only **D** I, II, and III
- The x-axis of the graph on the right represents the atomic number of the elements in Period 3. Which variable could represent the y-axis?
A melting point **B** electronegativity **C** ionic radius **D** atomic radius
- Which is the best definition of *electronegativity*?
A Electronegativity is the energy required for a gaseous atom to gain an electron.
B Electronegativity is the attraction of an atom for a bonding pair of electrons.
C Electronegativity is the attraction between the nucleus and the valence electrons of an atom.
D Electronegativity is the ability of an atom to attract electrons from another atom.
- What happens when sodium is added to water?
I a gas is evolved
II the temperature of the water increases
III a clear, colourless solution is formed
A I and II only **B** I and III only **C** II and III only **D** I, II, and III
- What are the products of the reaction between chlorine and water?
A O_2 , H_2 , and HCl **B** H_2 and OCl_2 **C** HCl and $HOCl$ **D** $HOCl$, H_2 , and Cl_2
- Which statements are correct for the complex ion $[CuCl_4]^{2-}$?
I The oxidation number of Cu in the complex ion is +2.
II The coordination number of the copper ion is 4.
III Chloride ions are behaving as ligands.
A I and II only **B** I and III only **C** II and III only **D** I, II, and III



- 10 In which complexes does iron have an oxidation number of +3?
I $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
II $[\text{Fe}(\text{H}_2\text{O})_5(\text{CN})]^{2+}$
III $[\text{Fe}(\text{CN})_6]^{3-}$
A I and II only **B** I and III only **C** II and III only **D** I, II, and III
- 11 Which transition element, or compound of a transition element, is used as a catalyst in the Contact process?
A Fe **B** MnO_2 **C** V_2O_5 **D** Ni
- 12 Which process is responsible for the colour of a transition metal complex?
A the absorption of light when electrons move between s orbitals and d orbitals
B the emission of light when electrons move between s orbitals and d orbitals
C the absorption of light when electrons move between different d orbitals
D the emission of light when electrons move between different d orbitals
- 13 (a) Define the term *first ionization energy*. (2)
(b) Explain why the first ionization energy of magnesium is higher than that of sodium. (2)
(Total 4 marks)
- 14 Samples of sodium oxide and sulfur trioxide are added to separate beakers of water. Deduce the equation for each reaction and identify each oxide as acidic, basic, or neutral.
(Total 3 marks)
- 15 Describe and explain what you will see if chlorine gas is bubbled through a solution of
(a) potassium iodide (2)
(b) potassium fluoride (1)
(Total 3 marks)
- 16 The Periodic Table shows the relationship between electron configuration and the properties of elements and is a valuable tool for making predictions in chemistry.
(a) Identify the property used to arrange the elements in the Periodic Table. (1)
(b) Outline two reasons why electronegativity increases across Period 3 in the Periodic Table and one reason why noble gases are not assigned electronegativity values. (3)
(Total 4 marks)
- 17 (a) Outline two reasons why a sodium ion has a smaller radius than a sodium atom. (2)
(b) Explain why the ionic radius of P^{3-} is greater than the ionic radius of Si^{4+} . (2)
(Total 4 marks)
- 18 Sodium oxide, Na_2O , is a white solid with a high melting point.
(a) Explain why solid sodium oxide is a non-conductor of electricity. (1)
(b) Molten sodium oxide is a good conductor of electricity. State the half-equation for the reaction occurring at the positive electrode during the electrolysis of molten sodium oxide. (1)
(c) (i) State the acid/base nature of sodium oxide. (1)
(ii) State the equation for the reaction of sodium oxide with water. (1)
(Total 4 marks)

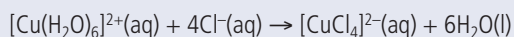
- 19 The graph below of the first ionization energy plotted against atomic number for the first 20 elements shows periodicity.



- (a) Define the term *first ionization energy* and state what is meant by the term *periodicity*. (2)
- (b) State the electron configuration of argon and explain why the noble gases, helium, neon, and argon, show the highest first ionization energies for their respective periods. (3)
- (c) A graph of atomic radius plotted against atomic number shows that the atomic radius decreases across a period. Explain why chlorine has a smaller atomic radius than sodium. (1)
- (d) Explain why a sulfide ion, S^{2-} , is larger than a chloride ion, Cl^- . (1)
- (e) Explain why the melting points of the Group 1 metals (Li to Cs) decrease down the group whereas the melting points of the Group 17 elements (F to I) increase down the group. (3)

(Total 10 marks)

- 20 When concentrated hydrochloric acid is added to a solution containing hydrated copper(II) ions, the colour of the solution changes from light blue to green. The equation for the reaction is:



- (a) Explain what the square brackets around the copper containing species represent. (1)
- (b) Explain why the $[Cu(H_2O)_6]^{2+}$ ion is coloured and why the $[CuCl_4]^{2-}$ ion has a different colour. (2)

(Total 3 marks)



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