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Anglo-Chinese School (Independent)

Year 5 (2022) IBDP Chemistry HL

TOPIC 3 PERIODICITY (Part 1)

(IBDP syllabus Topic 3)

3.1 Periodic table

- *Essential Idea: The arrangement of the elements in the periodic table helps to predict their electron configuration.*

3.2 Periodic trends

- *Essential Idea: Elements show trends in their physical and chemical properties across periods and down groups.*

3.1 Periodic table

Nature of science:

Obtain evidence for scientific theories by making and testing predictions based on them – scientists organise subjects based on structure and function; the periodic table is a key example of this. Early models of the periodic table from Mendeleev, and later Moseley, allowed for the prediction of properties of elements that had not yet been discovered. (1.9)

Understandings:

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

Applications and skills:

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

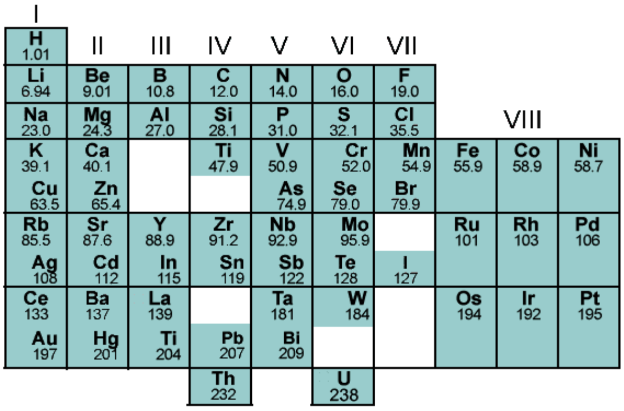
Guidance:

- The terms alkali metals, noble gases, halogens, transition metals, lanthanoids and actinoids should be known.
- The group numbering scheme from group 1 to group 18 as recommended by IUPAC should be used.

Nature of science

Dimitri Mendeleev

Mendeleev:
The Periodic Law by atomic weight, 1869



I	II	III	IV	V	VI	VII	VIII		
H 1.01									
Li 6.94	Be 9.01	B 10.8	C 12.0	N 14.0	O 16.0	F 19.0			
Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5			
K 39.1	Ca 40.1		Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	Fe 55.9	Co 58.9	Ni 58.7
Cu 63.5	Zn 65.4			As 74.9	Se 79.0	Br 79.9			
Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Nb 92.9	Mo 95.9		Ru 101	Rh 103	Pd 106
Ag 108	Cd 112	In 115	Sn 119	Sb 122	Te 128	I 127			
Ce 133	Ba 137	La 139		Ta 181	W 184		Os 194	Ir 192	Pt 195
Au 197	Hg 201	Ti 204	Pb 207	Bi 209					
			Th 232		U 238				

3.1 Periodic trends

Nature of science:

Looking for patterns – the position of an element in the periodic table allows scientists to make accurate predictions of its physical and chemical properties. This gives scientists the ability to synthesize new substances based on the expected reactivity of elements. (3.1)

Understandings:

- Vertical and horizontal trends in the Periodic Table exist for atomic radius, ionic radius, ionisation energy, electron affinity and electronegativity.
- Trends in metallic and non–metallic behaviour are due to the trends above.
- Oxides change from basic through amphoteric and 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 the halogens (group 17).
- Construction of equations to explain the pH changes for the reactions of Na_2O, MgO and P_4O_{10} and the oxides of nitrogen and sulfur with water.

Guidance:

- Only examples of general trends across periods and down groups are required. For ionisation energy the discontinuities in the increase across a period should be covered.
- Group trends should include the treatment of the reactions of alkali metals with water, alkali metals with halogens and halogens with halide ions.

The Periodic Table

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** 1.01																	2 **He** 4.00
2	3 **Li** 6.94	4 **Be** 9.01					Atomic number **Element** Relative atomic mass			Metals	Metalloids	Non-metals	5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
3	11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
4	19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.63	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.90
5	37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.96	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
6	55 **Cs** 132.91	56 **Ba** 137.33	57 † **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	89 ‡ **Ac** (227)	104 **Rf** (267)	105 **Db** (268)	106 **Sg** (269)	107 **Bh** (270)	108 **Hs** (269)	109 **Mt** (278)	110 **Ds** (281)	111 **Rg** (281)	112 **Cn** (285)	113 **Uut** (286)	114 **Uuq** (289)	115 **Uup** (288)	116 **Uuh** (293)	117 **Uus** (294)	118 **Uuo** (294)

†	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.05	71 **Lu** 174.97
‡	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

3.1 Periodic Table

In the **Periodic Table**, elements are arranged in horizontal rows (**periods**) and vertical columns (**groups**) in the order of ***increasing atomic (proton) number, Z***.

3.1.1 Periods

- **Horizontal rows** of elements in the Periodic Table.
- They are labelled using **numerals: 1, 2, 3, 4, 5, 6, 7.**
- **Period number** corresponds to the **principal quantum number,** ***n***, of the highest occupied energy level in the elements of the period.
- Across a period, the chemical properties of the element gradually change from those of reactive **metals to metalloids** and **non–metals** (*except for period 1)*. The thick stepped lines on the periodic table on page 4 of the notes separate the elements into metals on the left, for example, aluminium, and carbon on the right, as a non–metal. However, some of the elements, such as silicon and germanium, have physical and chemical similarities to both metals and non–metals. Chemists classify these elements as **metalloids**. They are poor conductors of electricity and, unlike metals, their conductivity increases with temperature. Some metalloids form amphoteric oxides.

Period 1	**H** $1s^1$							**He** $1s^2$
Period 2	**Li** [He]$2s^1$	**Be** [He]$2s^2$	**B** [He]$2s^22p^1$	**C** [He]$2s^22p^2$	**N** [He]$2s^22p^3$	**O** [He]$2s^22p^4$	**F** [He]$2s^22p^5$	**Ne** [He]$2s^22p^6$
Period 3	**Na** [Ne]$3s^1$	**Mg** [Ne]$3s^2$	**Al** [Ne]$3s^23p^1$	**Si** [Ne]$3s^23p^2$	**P** [Ne]$3s^23p^3$	**S** [Ne]$3s^23p^4$	**Cl** [Ne]$3s^23p^5$	**Ar** [Ne]$3s^23p^6$

3.1.2 Main Group, Transition Elements

- **A group is a vertical column** of elements. They are denoted by **numerals: 1, 2, 3, 4, 5… to 18**
- The **number of valence electrons** (outer–shell electrons) can be found from the group number of the s– and p–block elements.

Group Number IUPAC	**1**	**2**	**13**	**14**	**15**	**16**	**17**	**18**
Electronic Configuration	ns^1	ns^2	$ns^2\ np^1$	$ns^2\ np^2$	$ns^2\ np^3$	$ns^2\ np^4$	$ns^2\ np^5$	$ns^2\ np^6$
Group Name	**Alkali metals**	**Alkaline earth metals**	–	–	**Pnicto–gens**	**Chalco–gens**	**Halo–gens**	**Noble gases**

- **Main Group Elements**: Group 1 (excluding H) and Group 2 and Groups 13 to 18.
- **Transition Elements:** Groups 3 – 11
- **s–block Elements**: Group 1 and 2 and He
- **p–block Elements:** Group 13 to Group 18 (except He)
- **d–block Elements:** Group 3 to 12 (include ^{57}La and ^{89}Ac)
- **f–block Elements:** Elements from Z = 58 to Z = 71 and from Z = 90 to Z =103.
- **Lanthanoids:** Elements from Z = 57 to Z = 71 (many are radioactive)
- **Actinoids:** Elements from Z = 89 to Z = 103.

Exercise 1

1. An atom with the atomic number 15 will be found in

A. group 1.

B. group 13.

C. group 15. √

D. group 17.

2. Which of the following shows the electronic configuration of a noble gas?

A. $1s^2$ √

B. $1s^2 2s^2 2p^4$

C. $1s^2 2s^2 2p^6 3s^2$

D. $1s^2 2s^2 2p^6 3s^2 3p^5$

3. Which of the following determines the order in which the elements are arranged in the modern form of the Periodic Table?

A. relative atomic mass.

B. atomic number. √

C. number of valence electrons.

D. number of neutrons.

4. Consider the element germanium, Ge, in the periodic table.

(a) State in which group of the periodic table germanium belongs.

Group 14

(b) What is the block of elements that germanium belongs to?

p–block

(c) State the number of valence electrons in an atom of germanium.

4 valence electrons

(d) Deduce the full electronic configuration of germanium.

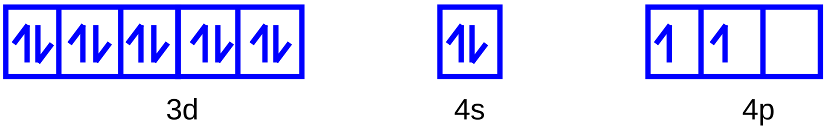
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^2$

(e) Deduce the condensed electron configuration of germanium.

[Ar] $3d^{10}\ 4s^2\ 4p^2$

(f) Draw the orbital diagram (arrow–in–box) for germanium.

[Ar]

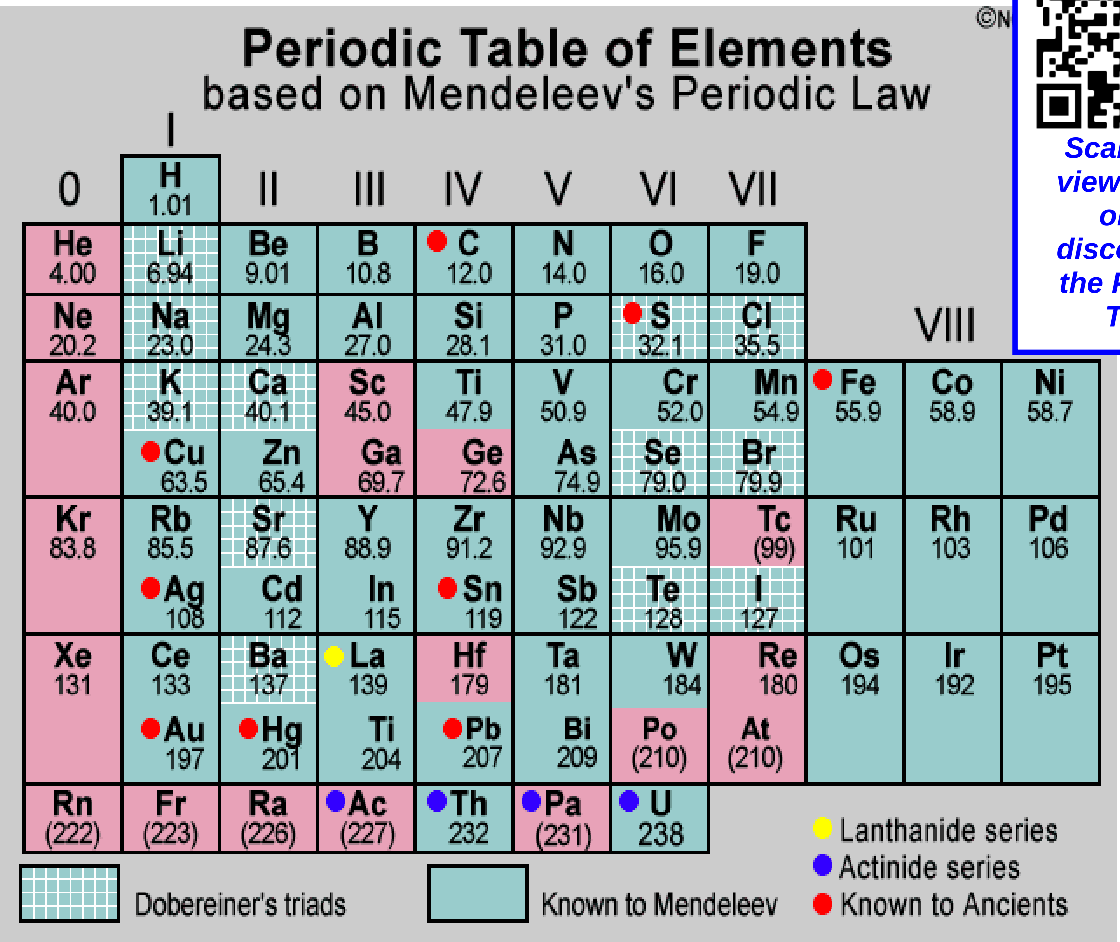


3.2 Periodic Trends

TOK: Risk–taking and science
(Adapted from Chemistry by John Green and Sadru Damji)

The predictive power of Mendeleev’s periodic table can be seen as an example of a “scientist” as a “risk taker” –IBO 2007.
He was inviting other scientists to try and falsify his predictions.

Scan me to view a video on the discovery of the Periodic Table



Periodic Table of Elements
based on Mendeleev's Periodic Law

©N

0	I	II	III	IV	V	VI	VII	VIII		
	H 1.01									
He 4.00	Li 6.94	Be 9.01	B 10.8	🔴 C 12.0	N 14.0	O 16.0	F 19.0			
Ne 20.2	Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	🔴 S 32.1	Cl 35.5			
Ar 40.0	K 39.1 🔴 Cu 63.5	Ca 40.1 Zn 65.4	Sc 45.0 Ga 69.7	Ti 47.9 Ge 72.6	V 50.9 As 74.9	Cr 52.0 Se 79.0	Mn 54.9 Br 79.9	🔴 Fe 55.9	Co 58.9	Ni 58.7
Kr 83.8	Rb 85.5 🔴 Ag 108	Sr 87.6 Cd 112	Y 88.9 In 115	Zr 91.2 🔴 Sn 119	Nb 92.9 Sb 122	Mo 95.9 Te 128	Tc (99) I 127	Ru 101	Rh 103	Pd 106
Xe 131	Ce 133 🔴 Au 197	Ba 137 🔴 Hg 201	🟡 La 139 Ti 204	Hf 179 🔴 Pb 207	Ta 181 Bi 209	W 184 Po (210)	Re 180 At (210)	Os 194	Ir 192	Pt 195
Rn (222)	Fr (223)	Ra (226)	🔵 Ac (227)	🔵 Th 232	🔵 Pa (231)	🔵 U 238				

▦ Dobereiner's triads
🟦 Known to Mendeleev
🟡 Lanthanide series
🔵 Actinide series
🔴 Known to Ancients

Figure 1

About a century ago, it would be a disgrace in the scientific world to have a theory falsified. Surely, Dimitri Mendeleev was taking a risk when he proposed his Periodic Table (Figure 1 – short form) and predicted the properties of some undiscovered elements. He predicted the existence as well as the chemical and physical properties of an element which he named Ekasilicon (Eka means under). This element was discovered 15 years after his prediction and named germanium (Table 1 on the next page).

TOK: Risk–taking and science

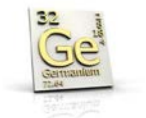


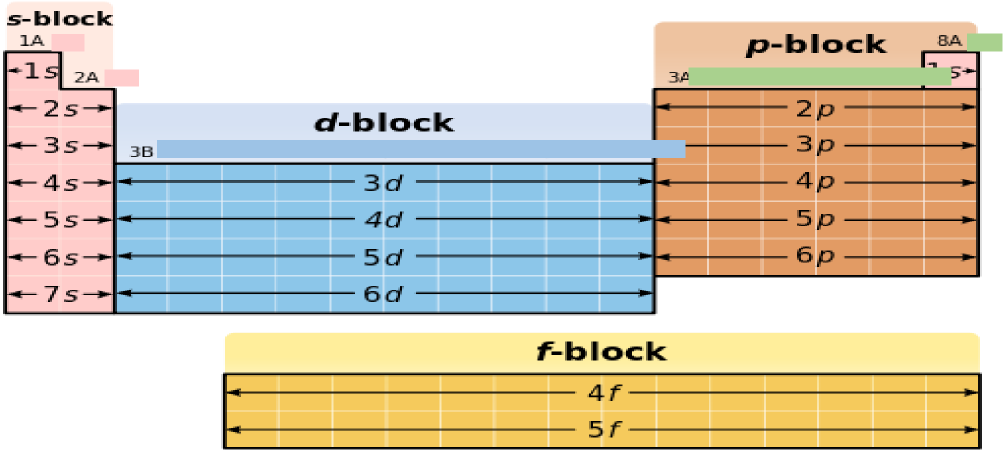
Table 1: A Mendeleev Prediction (1871)

Property	**Predicted properties of *Eka*-silicon(X)**	**Actual Properties of germanium(Ge)**
Atomic weight	72	72.59
Density (g cm^{-3})	5.5	5.35
Specific Heat (J g^{-1}K^{-1})	0.305	0.309
Melting point (^{o}C)	high	937.4
Colour of metal	Dark gray	Gray–white
Formula of oxide	XO_2	GeO_2
Density of oxide (g cm^{-3})	4.7	4.70
Formula of chloride	XCl_4	$GeCl_4$
Density of chloride (g cm^{-3})	1.9	1.84
Boiling point of chloride (^{o}C)	a little under 100	84

The nature of science is such that **a hypothesis (a proposal that explains a particular phenomenon)** has to be tested. This testing is welcomed as it is seen to stimulate further work that may lead to the formulation of new theories that may subsequently replace the hypothesis.

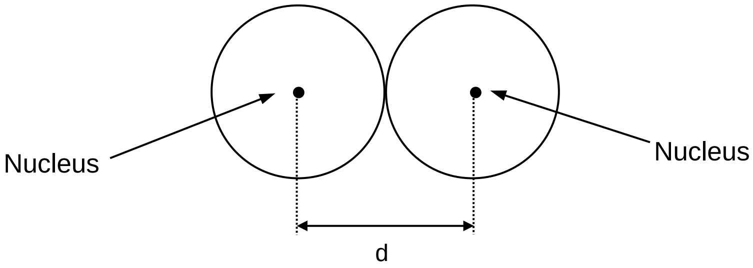
The **repeating pattern of atomic, physical and chemical properties** is known as **periodicity**. Patterns lie at the heart of the Periodic Table and this is a significant tool that allows scientists to make fairly accurate predictions about the behaviour of elements and thus the synthesis of new compounds from elements.

The properties of elements depend on their outer electronic configurations which can be explained through quantum mechanics. This helps us understand many aspects of atomic properties such as atomic radius, ionisation energy, electron affinity and electronegativity.



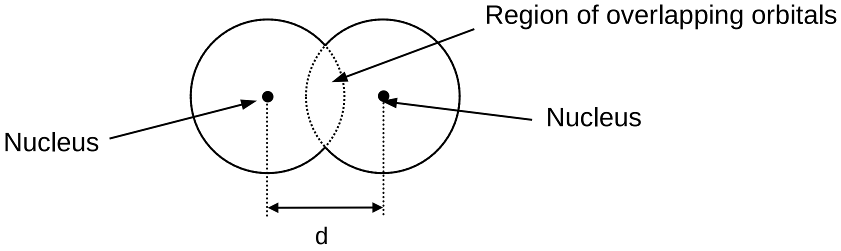
3.2.1 Atomic Radius

The atomic radius of an element is defined as half of the distance between the nuclei of neighbouring atoms in the pure element. If the element is a noble gas, this distance is also known as the non–bonding atomic radius or the van der Waals' radius.



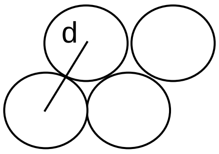
$$\boxed{\text{van der Waals' radius} = \frac{d}{2}}$$

If the element is a non–metal, this distance is the bonding atomic radius and is also known as the **covalent radius**.



$$\boxed{\text{Covalent radius} = \frac{d}{2}}$$

If the element is a metal, this distance is also known as the metallic radius.



$$\boxed{\text{Metallic radius} = \frac{d}{2}}$$

Factors affecting atomic radius

(a) Nuclear charge

- Nuclear charge is the total charge of the protons in the nucleus. This is also the same as the number of protons.
- The greater the number of protons in the nucleus, the greater the electrostatic force of attraction on the electrons, pulling them closer to the nucleus.

(b) Shielding effect by inner electrons

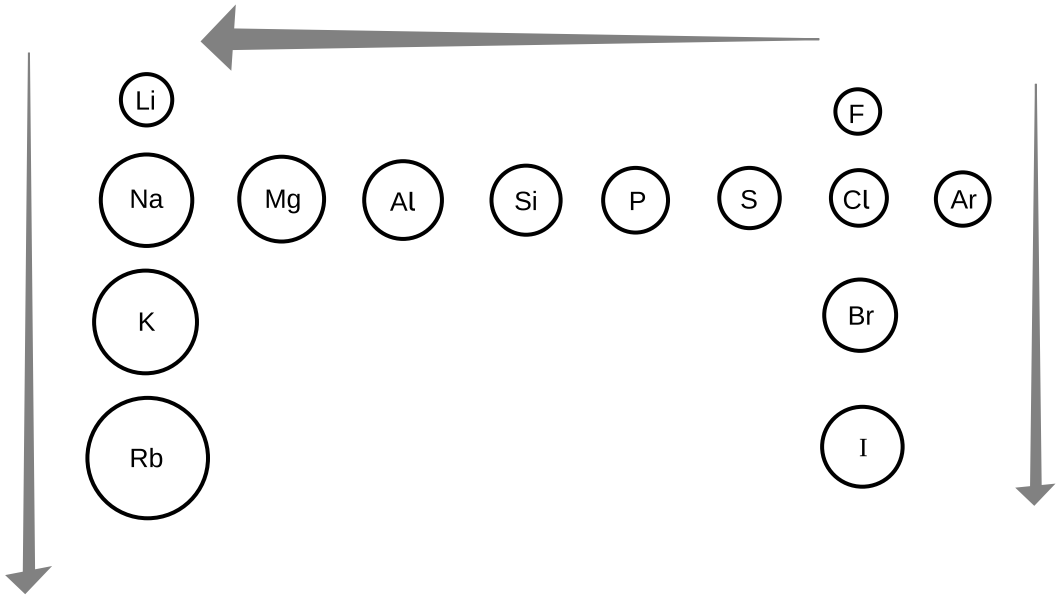
- Electrons in the inner shells repel the valence electrons, giving rise to the shielding effect. Shielding effect is usually given by the number of electrons in the inner quantum shells.
- The core electrons in the inner non–valence energy levels of an atom reduce the positive nuclear charge experienced by a valence electron.
- The greater the shielding effect, the lower electrostatic force of attraction on the valence electrons.

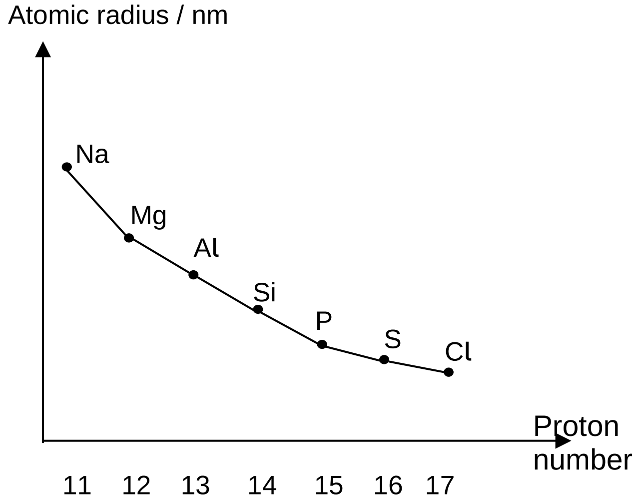
The nuclear charge of an atom serves to attract the electrons towards the nucleus but the shielding effect of the inner core electrons serves to shield the electrostatic forces of attraction of the nucleus on the valence electrons. This balance can be roughly measured by the effective nuclear charge. **Effective nuclear charge (Z_{eff})** is difference between nuclear charge and shielding effect. This gives a measure of the actual nuclear charge experienced by electrons in the valence shell, hence how tightly the electrons are attracted to the nucleus.

3.2.2 Periodic Trends in Atomic Radius

The atomic radii of elements decrease across a period and increases down a group.

Periodic Trends in Atomic Radius





Across a period (from left to right),

- Nuclear charge increases but shielding effect remains relatively constant since the inner quantum shells of electrons remain the same
- Effective nuclear charge increases
- This attracts the valence electrons closer to the nucleus
- Atomic radius decreases

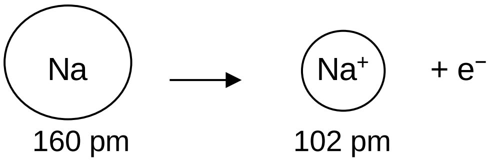
Down a group,

- In each new period the valence electrons enter a new energy level and are further away from the nucleus
- The increased distance reduces the electrostatic attraction between the protons in the nucleus and the valence electrons
- Atomic radius increases

3.2.3 Periodic Trends in Ionic Radius

The radii of cations are always **smaller** than their parent atoms.

For example: Na and Na^+

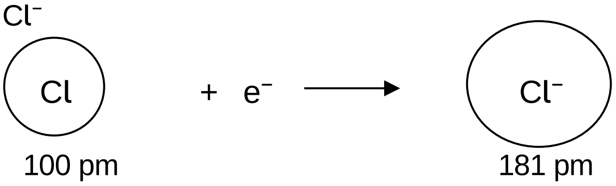


- Number of protons, or nuclear charge, remains the same but there are fewer electrons in the cation.
- Hence, the valence electrons are more strongly attracted to the nucleus.
- Therefore, the **ionic radii of positive ions** are **smaller** than the corresponding atomic radii.

Across the period, the ions contain the **same number of electrons (isoelectronic)**, but an increasing number of protons. Consequently, the proton to electron ratio increases and the outermost electrons are drawn increasingly closer to the nucleus. Hence, the **cationic radius decreases**. Refer to section 9 of the Data booklet.

The radii of anions are always **larger** than their parent atoms.

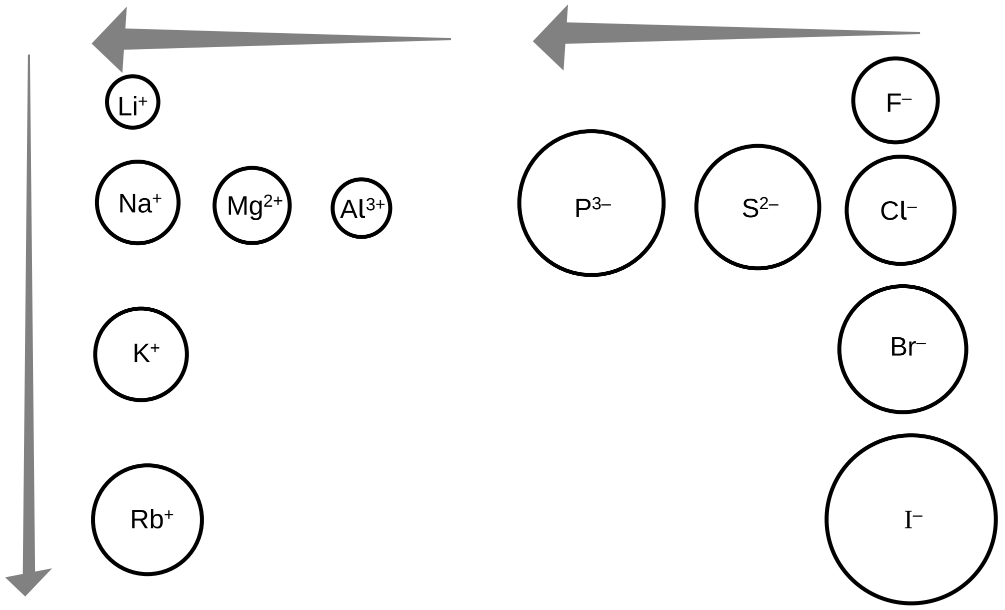
For example: Cl and Cl^-



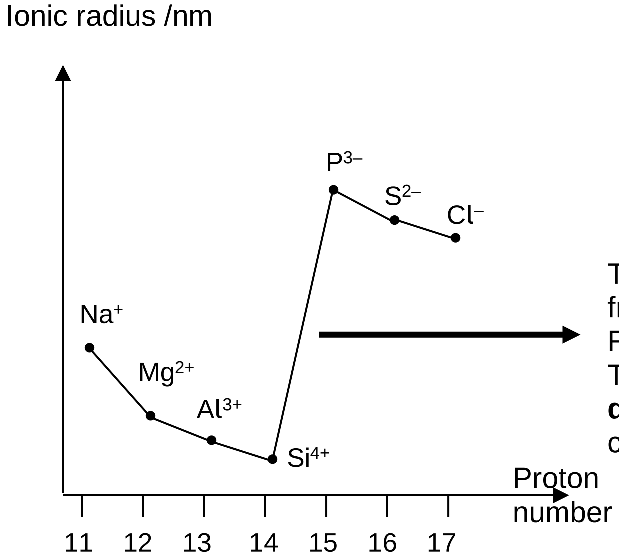
- When one or more electrons are added to an atom, there is **an increase in the repulsion** between the electrons. Hence, the electron cloud increases in size.
- The number of protons, or the nuclear charge, in the ion remains the ***same*** as that of the atom. Hence, the ionic radii of negative ions are **larger** than the corresponding atomic radii.
- **Anions have one more occupied quantum shell of electrons** than the cations, hence, anionic radii are larger than cationic radii within the same period.

- **Across the period**, the **anionic radius decreases** as the proton to electron ratio increases. Refer to section 9 of the Data Booklet.

Periodic Trends in Ionic Radius



Note:
The data for silicon ions are calculated values. Silicon does not form simple ions as it has a tendency to form covalent bonds.



There is a sharp increase in ionic radius from Si^{4+} to P^{3-}.
Reason:
The **anions have one more occupied quantum shell of electrons** than the cations.

3.2.4 Ionisation Energy

The **first ionisation energy** ,1st I.E., is defined as the **minimum energy** required in **removing one mole of valence electrons** from **one mole of gaseous atoms** to form **1 mole of singly positively charge gaseous ion**.

For example first I.E. of sodium, $Na\ (g) \rightarrow Na^{+}\ (g) + e^{-}$ 1st I.E. = +496 kJ mol^{-1}

Ionisation energy values are always positive (endothermic process) as energy is always required to overcome the electrostatic attraction between the electron to be removed and the protons in the nucleus.

3.2.5 Periodic Trends in Ionisation Energy

First ionisation energy generally increases across a period and decreases down a group.

Factors affecting ionisation energies

- **Across a period: effective nuclear charge**
- **Down a group: atomic radii**

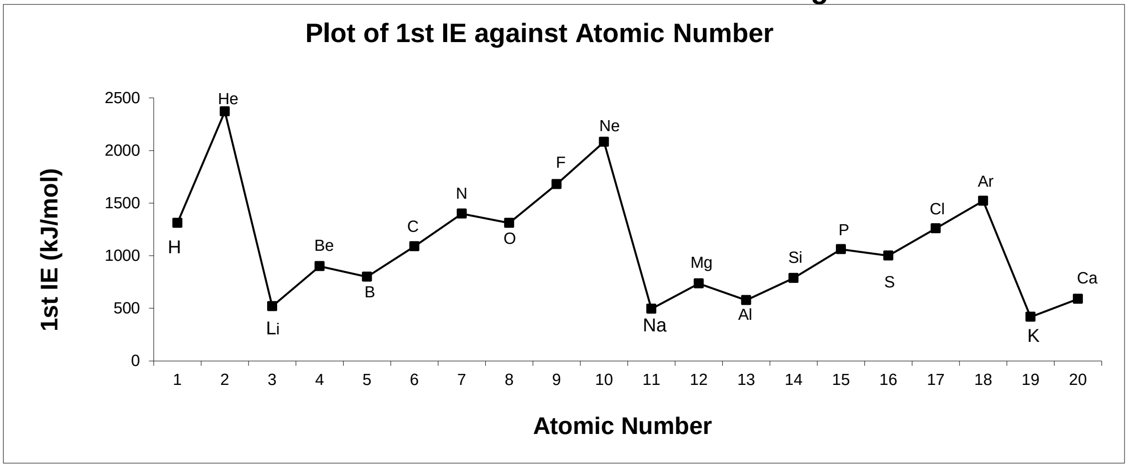
Across a period (from left to right),

- There is an **increase** in effective nuclear charge, Z_{eff}. This is because nuclear charge increases but shielding effect remains relatively constant since the inner quantum shells of electrons remain the same.
- The valence electrons are drawn closer to the nucleus, so the electrostatic attractions between the valence electrons and the nuclei increase.
- More energy is required to remove a valence electron from the gaseous atom.

Down a group,

- The number of filled quantum shells increases and the size of the atoms increase.
- The valence electrons occupy energy levels that are increasingly further from the nucleus.
- This increased distance reduces the electrostatic attractions between the protons in the nuclei and the valence electrons.
- Hence the electrostatic forces of attraction of the nucleus for the valence electrons decreases and less energy is required to remove them.

Periodic Trends in First Ionisation Energies



For periods 2 and 3,

- The group 13 element has a **lower first ionisation energy** than the group 2 element.
- The group 16 element has a **lower first ionisation energy** than the group 15 element.

Example 1:

Boron has **lower first ionisation energy** (+801 kJ mol^{-1}) than that of **beryllium** (+900 kJ mol^{-1}).
The electronic configuration of beryllium and boron atoms**:**

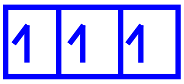
Be : $1s^2 2s^2$
B : $1s^2 2s^2 2p^1$

It is because less energy is required to remove a 2p electron in the boron atom than a 2s electron in the beryllium atom as the 2p sub–level is of higher energy than the 2s sub–level and the 2p electron is further from the nucleus. The 2p electron also experiences shielding by the 2s electrons. As a result, the 2p electron experiences a weaker electrostatic force of attraction from the nucleus.

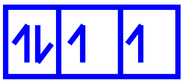
Example 2:

Oxygen has a **lower first ionisation energy** (+1314 kJ mol^{-1}) than that of **nitrogen** (+1402 kJ mol^{-1})**.**

N : $1s^2 2s^2 2p^3$



O : $1s^2 2s^2 2p^4$



It is because in an oxygen atom, there are two electrons occupying the same 2p orbital and this gives rise to inter–electronic repulsion. Thus, less energy is required to remove a paired 2p electron from an oxygen atom compared to the energy required to remove an unpaired 2p electron from a nitrogen atom.

3.2.6 Electronegativity

Electronegativity is defined as the relative attraction that an atom has for the shared pair of electrons in a covalent bond.

Electronegativity cannot be directly measured and must be calculated from other atomic or molecular properties. The most commonly used method of calculation is that originally proposed by an American scientist, Linus Pauling, in 1932. This gives a dimensionless quantity commonly referred to as the **Pauling scale**, on a relative scale running from around 0.7 to 4.0 (hydrogen = 2.2).

Highly electronegative elements are **fluorine (F)**, **oxygen (O)** and **chlorine (Cl) and nitrogen (N)**.

Fluorine, with a value of 4.0, is the most electronegative element. Why do you think this is so?

3.2.7 Periodic Trends in Electronegativity

Electronegativity generally increases across a period and decreases down a group.

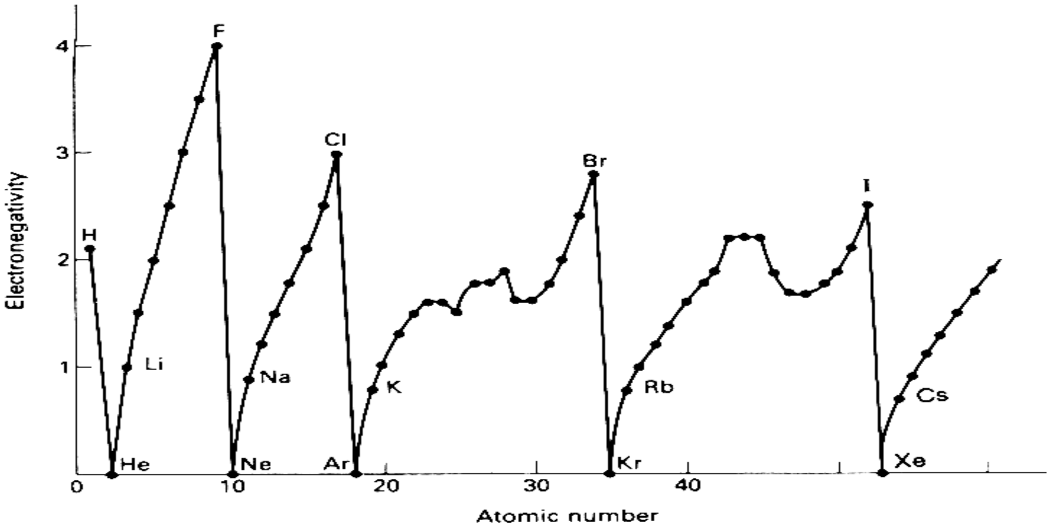
Across a period (from left to right),

- The atoms get smaller, resulting in decreased distance between bonding electrons and the nuclei.
- Nuclear charge increases but shielding effect remains relatively constant since the inner quantum shells of electrons remain the same.
- Effective nuclear charge increases.
- As a result, electrostatic attraction between the bonding electrons and the nuclei increases.
- Therefore, **electronegativity increases**.

Down a group,

- The atoms get larger, resulting in increased distance between bonding electrons and the nuclei.
- This increase in distance results in a decrease in electrostatic attraction between the bonding electrons and the nuclei of the atoms.
- Therefore, **electronegativity decreases**.

Periodic Trends in Electronegativity

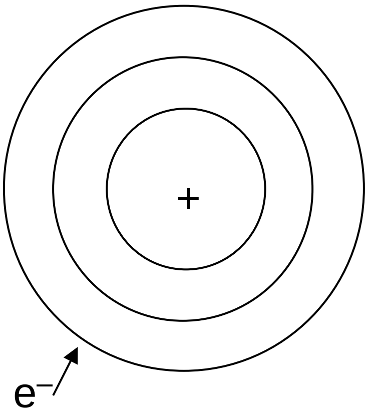


3.2.8 Electron Affinity

The **first electron affinity**, 1st E.A., is the enthalpy change when **one mole of gaseous atoms** acquires one mole of electrons to form **one mole of singly negatively charged gaseous ions**.

For example: $S(g) + e^- \rightarrow S^-(g)$ 1st E.A. = −200 kJ mol^{-1}

Note: The **first electron affinity** is **exothermic for most elements**.



Explanation:

- As the electron is added to the atom, there will be electrostatic attraction between the protons in the nucleus and the incoming electron.
- Energy is released when the nucleus attracts the electron which is in the outer shell (similar to bond forming).

3.2.9 Periodic Trends in Electron Affinity

Patterns of first electron affinity vary by group, so first electron affinity values do not show the same clear trends.

In general, down a group,

- Atomic radius increases
- Decrease in the attraction between the nucleus and the added electron as the electron is brought to a shell which is further from the nucleus.
- Therefore, **electron affinity becomes less exothermic**.

Going down group 17 the first electron affinity becomes less exothermic i.e. less negative (with the exception of fluorine). Group 17 elements have the most negative first E.A. values.

	1st E.A. / kJ mol^{-1}
$F (g) + e^- \rightarrow F^- (g)$	−328
$Cl (g) + e^- \rightarrow Cl^- (g)$	−349
$Br (g) + e^- \rightarrow Br^- (g)$	−325
$I (g) + e^- \rightarrow I^- (g)$	−295

Question: Why is the first electron affinity of fluorine less exothermic than chlorine?
Hint: electron–electron repulsion.

Across a period, first electron affinity generally becomes more exothermic i.e. more negative (with some exceptions).

Across a period (from left to right),

- Increase in effective nuclear charge
- Decrease in atomic radius
  Hence, the added electron will be more strongly attracted by the nucleus. Therefore, the first **electron affinity becomes more exothermic**.

	1st E.A. / kJ mol^{-1}
$B (g) + e^- \rightarrow B^- (g)$	−27
$C (g) + e^- \rightarrow C^- (g)$	−122
$N (g) + e^- \rightarrow N^- (g)$	(exception > 0)
$O (g) + e^- \rightarrow O^- (g)$	−141
$F (g) + e^- \rightarrow F^- (g)$	−328

Nitrogen has a less exothermic first electron affinity than oxygen because of its electronic configuration. Nitrogen has three unpaired electrons in the 2p sublevel. When an electron is added to a nitrogen atom, the incoming electron “pairs up” with an electron in the p–orbital. This introduces an extra repulsion component that is not present in oxygen. **Energy needs to be supplied to overcome the inter–electronic repulsion between the paired electrons**. Hence, the process is less exothermic than expected.

The nuclear charges of fluorine and oxygen are larger than nitrogen. There is a stronger electrostatic force of attraction between the nucleus and the incoming electron. The energy released when the nucleus attracts an electron is larger than the energy taken in to overcome inter–electronic repulsion. Hence for fluorine and oxygen the first electron affinity values are exothermic.

Second electron affinity

The **second electron affinity**, 2nd E.A., is the enthalpy change when **one mole of singly negatively charged gaseous ions** acquires one mole of electrons to form **one mole of doubly negatively charged gaseous ions**.

For example: $M^{-}(g) + e^{-} \rightarrow M^{2-}(g)$ 2nd E.A. = positive ($kJ\ mol^{-1}$)

It is **always positive** since the electron is now being added to a negative ion (anion). Energy needs to be supplied to overcome the repulsion between the two negatively charged species.

Examples:

$O(g) + e^{-} \rightarrow O^{-}(g)$	1st E.A. = −141 $kJ\ mol^{-1}$
$O^{-}(g) + e^{-} \rightarrow O^{2-}(g)$	2nd E.A. = +798 $kJ\ mol^{-1}$
$S(g) + e^{-} \rightarrow S^{-}(g)$	1st E.A. = −200 $kJ\ mol^{-1}$
$S^{-}(g) + e^{-} \rightarrow S^{2-}(g)$	2nd E.A. = +640 $kJ\ mol^{-1}$

3.2.10 Melting Points

The normal melting point is the temperature at which a pure solid is in equilibrium with its pure liquid at one atmospheric pressure.

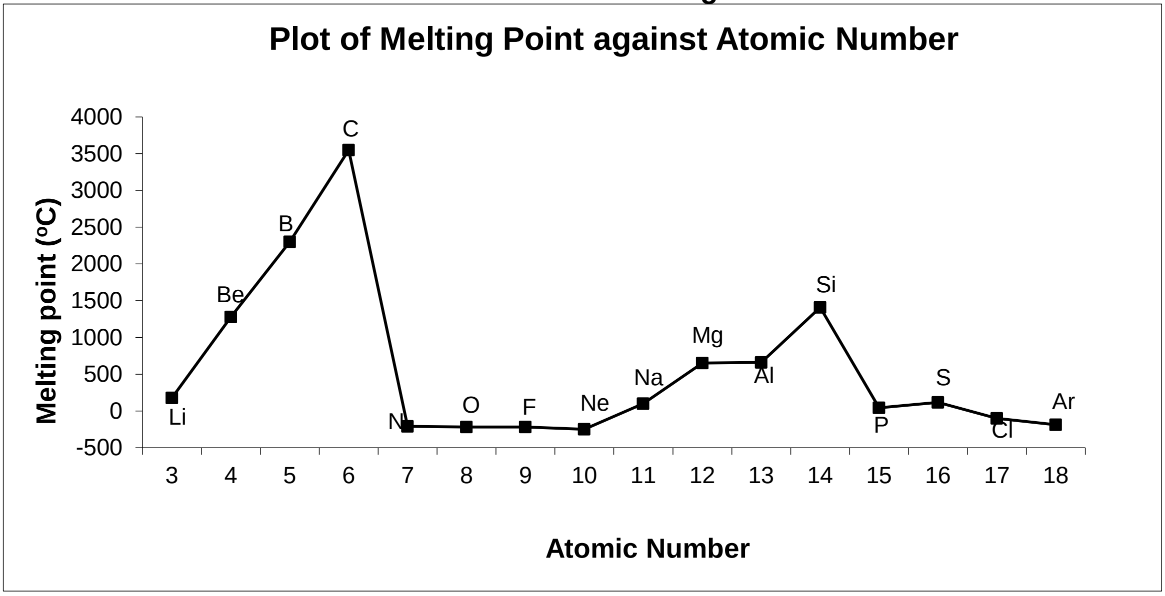
Melting involves overcoming the forces of attraction between ions, atoms or molecules in different types of solids. If the forces of attraction between the particles are strong, the melting point is high; if the forces are weak, the melting point is low.

Melting point depends on both the **structure (packing)** and the **electrostatic forces of attraction between the particles.**

Summary of Structure and Bonding for Period 2 and Period 3 Elements

Elements	**Structure**	**Bonding**
Li Be **Na Mg Al**	Giant metallic	Metallic bonds between cations and sea of delocalised electrons.
B C **Si**	Giant molecular	Covalent bonds throughout the entire giant 3–D network structure
C_{60} N_2 O_2 F_2 **P_4 S_8 Cl_2**	Simple molecular	Instantaneous dipole–induced dipole (London (dispersion)) forces between molecules
Ne **Ar**	Monoatomic	Instantaneous dipole–induced dipole (London (dispersion)) forces between atoms

Periodic Trends in Melting Points



3.2.11 Periodic Trends in Melting Points

Across a period, the melting point **rises through the metals and the metalloids** and **drops abruptly for the non–metals**.

Na to Al

- Due to **giant metallic structure**
- Melting point **increases from Na to Al** because the **metallic bond strength increases** from Na to Al.
- The **increase in the metallic bond strength** is due to:
    - decrease in metallic radius,
    - increase in the number of electrons donated per atom to the mobile sea of electrons.
- This results in an increase in the charge density of cations upon across the period.
- As a result the electrostatic attraction between the cations in the metallic lattice and the delocalised electrons in the metallic lattice increases.
- More energy is required to break the stronger metallic bond as we from Na to Al.

Si

- Higher melting point than sodium, magnesium and aluminium.
- Due to **giant molecular structure/ giant 3–D network**.
- Its high melting point is due to energy required to overcome **many strong covalent bonds** in the entire structure.

P to Ar

- Low melting point.
- Due to **simple molecular structures**, e.g. P_4, S_8, Cl_2 and Ar.
- These molecules / atoms are attracted to each other by **instantaneous dipole – induced dipole (London (dispersion)) forces**. Thus, less thermal energy is required to overcome the forces of attraction between them.

Element	**P_4**	**S_8**	**Cl_2**	**Ar**
M_r	**123.88**	**256.48**	**70.90**	**39.95**
Melting point/ ºC	44	119	–101	–189

- As the relative molecular mass increases the **instantaneous dipole – induced dipole (London (dispersion)) forces** between the molecules also increase as the electron clouds of the molecules increases in size and hence in polarisability.
- More energy is required to overcome the increasing strength of the **instantaneous dipole – induced dipole (London (dispersion)) forces** down the group.
- Therefore, the melting points decreases in the following order: $S_8 > P_4 > Cl_2 >$ Ar

Noble Gases

The elements in Group 18 were once called the inert gases (‘inert’ meaning unreactive). However, since a few compounds of these elements have been prepared, they are now termed the noble gases.

The melting and boiling points of the noble gases are very low because the **instantaneous dipole – induced dipole (London (dispersion))** forces are weak. Down the group, the melting points and boiling points increase because there are more electrons that are easily polarized.

3.2.12 Properties of Elements in Group 1 and Group 17

The physical and chemical properties of group 1 and group 17 will be discussed.

Melting Point and Boiling Point

Group 1 (alkali metals)

Group 1 elements	Li	Na	K	Rb	Cs
Melting point / ºC	180	98	63	39	28

Down group 1,

- Melting point decreases.
- The strength of the metallic bond decreases as the cations in the metallic lattice increase in size down the group.
- This results in a decrease in the charge density of cations upon descending the group. As a result the electrostatic attraction between the cations in the metallic lattice and the delocalised electrons in the metallic lattice decreases
- Less energy is required to break the weaker metallic bond as we go down group 1.

Group 17 (halogens)

Group 17 elements	F_2	Cl_2	Br_2	I_2	At_2
Melting point / ºC	−220	−101	−7	−114	302
Boiling point / ºC	−188	−35	59	184	337

Down group 17

- Melting point and boiling point increases.
- The increase in electron cloud size of the molecules increases in size and increases polarizability, hence increasing the strength of **intermolecular instantaneous dipole – induced dipole (London (dispersion)) forces**
- More energy is required to overcome the increasing strength of the **instantaneous dipole – induced dipole (London (dispersion))** forces down the group.

Group 1 The Alkali Metals

Alkali metals	Li	Na	K	Rb	Cs
Electron Configuration	[He] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$
Down the group: increasing atomic and ionic radius					
Down the group: decreasing first ionisation energy					
Down the group: decreasing electronegativity					
Down the group: increasing reactivity					

- Soft, malleable metals
- Low melting point metals relative to transition metals
- Highly reactive metals
- Good reducing agents (by losing an electron)

Reaction of the Alkali Metal with Water and Halogens

Alkali metals react with water to form an **alkaline solution** and **hydrogen gas**. Reactivity increases down the group. Lithium floats and reacts quietly. Sodium immediately reacts with water and darts around on the surface. The heat generated from the reaction between potassium and water is sufficient to ignite the hydrogen gas; a lilac flame is observed.

$$2K\,(s) \;+\; 2H_2O\,(l) \;\rightarrow\; 2KOH\,(aq) \;+\; H_2\,(g)$$

They all react with reactive non–metals (e.g. halogens) to form **ionic compounds**.

Sodium burns in a gas jar of chlorine gas to form white fumes of sodium chloride.

$$Na\,(s) \;+\; Cl_2\,(g) \;\rightarrow\; 2NaCl\,(s)$$

Scan me to view a video on the physical properties of Group 1 metals

Scan me to view a video on the reaction between Group 1 metals and water

Group 17 The Halogens

Fluorine is the most reactive non-metallic element known. The halogens react with metals by gaining one electron to form X^- ion or by forming covalent compounds with non–metals.

Halogens	F_2	Cl_2	Br_2	I_2
Electron Configuration	[He] $2s^2\ 2p^5$	[Ne] $3s^2\ 3p^5$	[Ar] $4s^2\ 4p^5$	[Xe] $5s^2\ 5p^5$
Colour	Pale yellow	Yellow - green	Red - orange	Grey-black, shiny
Physical state at 25 °C, 1 atm	gas	gas	liquid	Solid (sublimes – purple vapour)
Down the group: increasing atomic and ionic radius →				
Down the group: decreasing first ionisation energy →				
Down the group: decreasing electronegativity →				
Down the group: decreasing reactivity →				
Down the group: decreasing oxidising strength →				

- Electronegative elements, diatomic molecules
- Highly reactive non–metals
- Good oxidising agents

Reaction of the Halogens with Alkali Metals

The halogens combine with alkali metals to form salts containing the halide ion. These salts are ionic compounds, white / colourless and soluble in water giving colourless, neutral solutions.

The presence of halide ions in solution can be detected by adding silver nitrate solution. The silver ions react with the halide ions to form a precipitate of the silver halide. The silver halides can be distinguished by their colour. The silver halides, when exposed to UV or sunlight, rapidly decomposes to silver (grey).

$$Ag^+(aq) + \mathbf{X}^-(aq) \rightarrow Ag\mathbf{X}(s)$$

X = Cl , Br or I [AgCl white; AgBr cream; AgI yellow]

Displacement Reactions of Chlorine, Bromine and Iodine

The oxidising strength of the halogens decreases down the group as the radii of the atom increases and the electrostatic attraction between the protons in the nucleus and electrons decreases. This means chlorine has the strongest affinity for electrons and will remove electrons from bromide and iodide ions. Hence, it displaces bromine and iodine from their salts, e.g. chlorine water reacts with a solution of potassium iodide to give iodine. The ionic equation for the reaction is given below. These reactions are **redox reactions** and refer to the standard electrode potentials in Topic 9, Oxidation and Reduction.

$$Cl_2\,(aq) \;+\; 2I^-\,(aq) \;\rightarrow\; \underset{\text{brown}}{I_2\,(aq)} \;+\; 2Cl^-\,(aq)$$

Summary of Reactions of the Halide Ions

Reagent	KCl (aq)	KBr (aq)	KI (aq)
Aqueous Ag^+	White precipitate	Cream precipitate	Pale yellow precipitate
Cl_2	No reaction	Solution turns yellow, then brown	Solution turns yellow, then brown, with black precipitate
Br_2	No reaction	No reaction	Solution turns yellow, then brown, with black precipitate
I_2	No reaction	No reaction	No reaction

Scan me to view a video on the displacement reactions

Exercise 2

1. Which of the following element is most electronegative?

A. magnesium

B. potassium

C. fluorine √

D. chlorine

2. Which property increases with increasing atomic number for both the alkali metals and the halogens?

A. atomic radius √

B. electronegativity

C. ionisation energy

D. melting point

3. Which of the following has the lowest first ionisation energy?

A. Li

B. Mg

C. Na √

D. Al

4. The reactivity of the halogens decreases in the order

A. chlorine, bromine, iodine. √

B. bromine, iodine, chlorine.

C. bromine, chlorine, iodine.

D. chlorine, iodine, bromine.

5. Which of the following is true of the alkali metals?

A. They have a high density.

B. They form covalent compounds.

C. They react with water to form a colourless solution. √

D. They form amphoteric oxides.

6. Which property generally decreases across the period 3 elements?

A. atomic number

B. electronegativity

C. atomic radius √

D. melting points

7. For each of the following state the general trend and explain using atomic properties such as nuclear charge and shielding effect.

(a) The change of atomic radius across a period.

Atomic radii decrease.

The increasing nuclear charge and the relatively small increase in shielding effect by the inner shells of electrons cause the valence electrons to be strongly attracted to the nucleus.

(b) The radius of a cation compared to its parent atom.

Cationic radius is smaller than the parent atom.

The cation and the parent atom have the same nuclear charge but the cation has fewer electrons than protons so the electrostatic attraction between the nucleus and the valence electrons is greater.

(c) The electronegativity going down a group.

Electronegativity decreases down the group.

Atomic radius increases, with extra shell of electrons, the electrons involved in bonding are further from the nucleus.

(d) The first ionisation energy going down a group.

First ionisation energies decrease.

The valence electrons are further away from the nucleus because of increased atomic radius so the valence electron requires less energy to remove.

8. How does the oxidising strength of the halogens vary down the group? Explain the trend.

Going down the group, the oxidising strength decreases.

As atomic radius increases, the electrostatic attraction between the protons and the added electron decreases, hence oxidising strength decreases.

9. Describe what you will see if chlorine gas is bubbled through a solution of potassium bromide. Write the ionic equation with state symbols for the reaction.

Colourless solution turns reddish-orange. $Cl_2 (aq) + 2Br^- (aq) \rightarrow Br_2 (aq) + 2Cl^-(aq)$

3.2.13 Oxides of Period 3 Elements

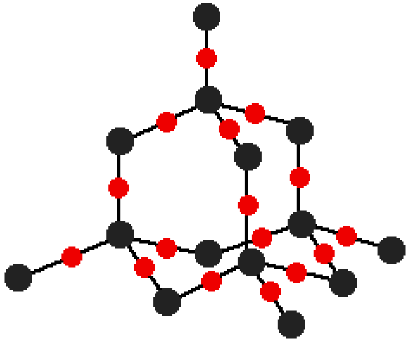
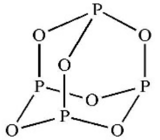
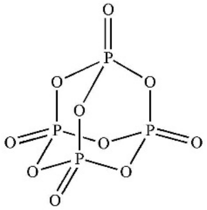
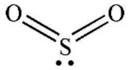
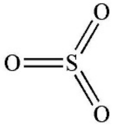
An oxide is formed when the element combines with oxygen usually with heating. The bonding of the oxides changes from **ionic to covalent across the period** because the **electronegativity difference** between the element and oxygen **decreases**.

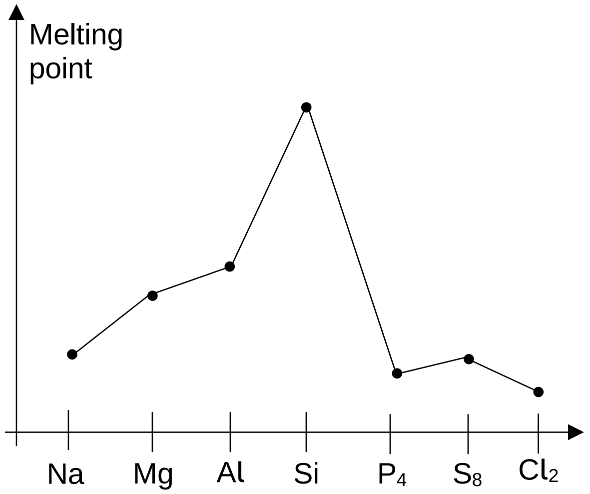
The oxides of sodium, magnesium and aluminium exist as **giant ionic lattice structures**. They have **high melting points** as the **ionic bonds** present in the crystal lattice **are strong**. As MgO has a more endothermic lattice energy than Na_2O, it has a stronger ionic bond strength and hence, a higher melting point than Na_2O. As Al_2O_3 has some extent of covalent character, it has a lower melting point than MgO.

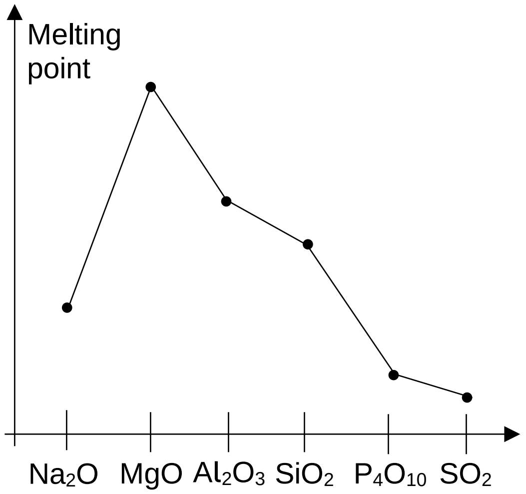
SiO_2 has a **giant molecular structure**. It also has a **high melting point**, as the numerous strong **silicon–oxygen covalent bond** must be broken as the oxide melts.

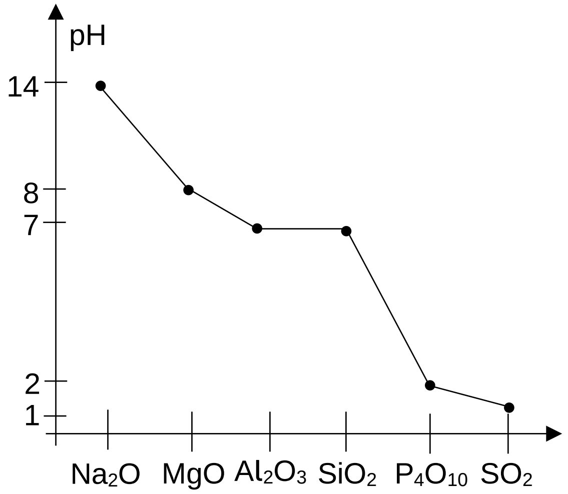
The oxides of phosphorous and sulfur have **simple molecular structures**. Their melting points are low relative to that of the earlier elements (exist as solids, liquids and gases at standard conditions) as the instantaneous dipole–induced dipole (London (dispersion)) forces holding the molecules together require little energy to overcome. P_4O_6 / P_4O_{10} has a higher melting point than SO_2 / SO_3 as it has a larger electron cloud. Hence, P_4O_6 / P_4O_{10}'s electron cloud is more polarisable. More energy is required to overcome the stronger instantaneous dipole–induced dipole forces.

Expansion of the octet structure is possible in phosphorous and sulfur because of the energetically accessible 3d orbitals available for accommodating the extra electrons. Thus, **expansion of the octet** is only possible for **elements from the third period onwards** because elements in the first and second period do not possess any **energetically accessible d orbitals** in their valence shell.

Formula of oxides	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_4O_6 / P_4O_{10}**	**SO_2 / SO_3**
Structure	Giant ionic lattice structure	Giant ionic lattice structure	Giant ionic lattice with partial covalent character	 Giant molecular structure	  Simple molecular structure	  Simple molecular structure
Oxidation numbers	+1	+2	+3	+4	+3 / +5	+4 / +6
Melting point/°C	1132	2900	2040	1610	24 / 580	-75 / 17
Boiling point /°C	1950	3600	2980	2230	175 / sublimes	-10 / 45







As the non–metallic character of elements increases across the period, so will the nature of the bonding in the oxides and their acid-base characters. The **ionic oxides are basic** and the **covalent oxides are acidic**. Aluminium oxide is **ionic with covalent character**, so its oxide is **amphoteric**.

- The **Na_2O** and **MgO** are **ionic, basic oxides**. Na_2O reacts to give an aqueous solution of sodium hydroxide.

  Na_2O (s) + H_2O (l) → $2Na^+$ (aq) + $2OH^-$ (aq) pH ≈ 13–14

  MgO is not soluble in water, due to its high lattice energy but reacts with it to give magnesium hydroxide which is sparingly soluble. The $Mg(OH)_2$ formed dissolves to a small extent to give hydroxide ions in water.

  MgO (s) + H_2O (l) → $Mg(OH)_2$ (s)
  $Mg(OH)_2$ (s) ⇌ Mg^{2+} (aq) + $2OH^-$ (aq) pH ≈ 8–9

- **Al_2O_3** is **an ionic compound with partial covalent character**. It does <u>not</u> dissolve in water, due to its high lattice energy. However, it will react with both acids and strong bases to form salts, hence an **amphoteric oxide**.

  Reaction with acids: Al_2O_3 (s) + 6HCl (aq) → $2AlCl_3$ (aq) + $3H_2O$ (l)
  Reaction with bases: Al_2O_3 (s) + 2NaOH (aq) + $3H_2O$ (l) → $2NaAl(OH)_4$ (aq)

- **Silicon oxide** does <u>not</u> dissolve in water.
  However, it is an acidic oxide as it forms sodium silicate(IV) with hot concentrated sodium hydroxide.

  SiO_2 (s) + 2NaOH (aq) → Na_2SiO_3 (aq) + H_2O (l)

- The **oxides of phosphorus and sulfur** are simple covalent molecules and therefore **acidic**. They react with water to form acidic solutions (pH ≈ 1–2).

P_4O_6 (s) + $6H_2O$ (l) → $4H_3PO_3$ (aq)	phosphorous acid or phosphoric(III) acid
P_4O_{10} (s) + $6H_2O$ (l) → $4H_3PO_4$ (aq)	phosphoric acid or phosphoric(V) acid
SO_2 (g) + H_2O (l) → H_2SO_3 (aq)	sulfurous acid or sulfuric(IV) acid
SO_3 (l) + H_2O (l) → H_2SO_4 (aq)	sulfuric acid or sulfuric(VI) acid

- Nitrogen forms many oxides ranging from N_2O, NO_x to N_2O_5. Of importance to the impact on the environment is NO, nitrogen monoxide and NO_2, nitrogen dioxide. NO is a neutral gas and it is virtually insoluble in water. NO is oxidised in the atmosphere to NO_2, an acidic oxide which reacts with water to form nitric acid which is responsible for acid deposition (Discussed in topic 8 acids and bases).

  $2NO_2$ (g) + H_2O (l) → HNO_2 (aq) + HNO_3 (aq)

Summary (Sections 3.1 – 3.2)

1. In the Periodic Table, the elements are arranged in order of increasing atomic (proton) number.
2. There are four blocks in the Periodic Table, s, p, d and f and this arrangement of the elements is according to their electronic configurations.
3. The chemical properties of elements are largely determined by the electrons in the outer (valence) shell.
4. Elements with similar chemical properties are placed under each other, in a vertical column termed **groups**. Members of the same group have the same number of electrons in their outer shells.
5. By IUPAC recommendations, the groups in the periodic table are numbered 1 to 18.
6. Members of Group 1 are alkali metals, Group 2 alkali earth metals, Group 17 the halogens and Group 18 the noble gases. Groups 2 and 13 are separated by the transition elements.
7. The horizontal row in the Periodic table is called the **period** number, *n*, which is the outer energy level that is occupied by electrons.
8. The elements of period 2 and 3 changes from metallic to metalloids and non–metallic across the period.
9. The covalent bond radius or bonding atomic radius is defined as half the inter–nuclear distance between two identical atoms joined by a single covalent bond.
10. The atomic radius become smaller across a period as the nuclear charge pulls the electrons closer to the nucleus. Down a group, the atomic radius increases.
11. The radii of cations are smaller than their parent atoms. The radii of anions are larger than their parent atoms.
12. The first ionisation energy of an atom is the energy required to remove completely a mole of electrons from a mole of gaseous atoms in its ground state.
13. First ionisation energy generally increases across a period and decreases down a group.
14. In general, second ionisation energy is always greater than the first ionisation energy.
15. The electronegativity (Pauling scale) is a measure of an atom's ability to attract a shared pair of electrons in a covalent bond.
16. Electronegativity increases across a period and up a group (bottom to top).
17. First electron affinity is the enthalpy change when one mole of gaseous atoms acquires one mole of electrons to form one mole of negatively charged gaseous ions.
18. Elements in Group 1, the alkali metals have an outermost electronic configuration ns^1. They are soft metals with low density and low melting point. They form M^+ cations.
    - They have relatively low first ionisation energies.
    - They are strong reducing agents.
    - Reactivity increases down the group which correlates with decrease in first ionisation energies, due to increasing distance between the nucleus and the valence electron.
    - Key reactions of group 1 metals, M:
        - with water, $2M (s) + 2H_2O (l) \rightarrow 2MOH (aq) + H_2 (g)$
        - with halogens, $2M (s) + X_2 (g) \rightarrow 2MX (s)$
        - with oxygen (heating), $2M(s) + O_2 \rightarrow M_2O(s)$

19. Group 17 Chemistry – The halogens are reactive non–metals and they form X^- ions.
    - They have high electronegativity values and are oxidising agents.
    - Reactivity decreases down the group which correlates with a decrease in first electron affinity due to increasing distance between the nucleus and the incoming electron.
    - Key reactions of group 17 elements
        - Displacement reactions X_2 (aq) + $2Y^-$ (aq) → X^- (aq) + Y_2 (aq), X is a more reactive halogen than Y.
        - Precipitation reactions: X^- (aq) + Ag^+ (aq) → AgX (s)

20. All the elements in Period 3 except chlorine and argon, combine directly with oxygen to form oxides. The oxides of the elements in the third periods change across the periods from being ionic and basic (reacting with acids) to being covalent and acidic (reacting with bases).

Element	Na	Mg	Al	Si	P	S
Formula of oxide	Na_2O (s)	MgO (s)	Al_2O_3 (s)	SiO_2 (s)	P_4O_{10} (s) / P_4O_6 (s)	SO_3 (l) / SO_2 (g) +6 / +4
Oxidation no.	+1	+2	+3	+4	+5 / +3	
Bonding and structure	Giant ionic lattice structure		Giant ionic lattice with partial covalent character	Giant molecular structure	Simple molecular structure	
Acid/base nature	basic		amphoteric	acidic		
Electrical conductivity	conducts when molten/ aqueous		conducts when molten	does not conduct		
Solubility of oxide in water and pH of solution	NaOH (aq) alkaline solution pH ≈ 13–14	$Mg(OH)_2$ (aq) sparingly soluble, alkaline solution pH ≈ 8–9	Insoluble in water		React with water to form acidic solutions. pH ≈ 1–2	

Recommended reading materials

1. Bylikin Sergey; Horner; Murphy; Tarcy *Chemistry Course Companion 2014 Edn.* Oxford University Press ; pp 67-92
2. Steve Owen, *Chemistry for the IB Diploma 2nd Edn.* Cambridge University Press; pp 85-115
3. Talbot, C.;Harwood, R.; Coates, C. *Chemistry for IB Diploma.* Hodder Education; London, 2010; pp 71-92

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Anglo–Chinese School (Independent)

Year 5 (2022) IBDP Chemistry HL

TOPIC 3 PERIODICITY (Part 2)

(IBDP syllabus Topic 13)

13.1 First–row d–block elements

- *Essential Idea: The transition elements have characteristic properties; these properties are related to their all having incomplete d sublevels.*

13.2 Coloured complexes

- *Essential Idea: 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 may 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.*

13.1 First Row d–block Elements

Collectively, the elements in groups 3 to 12 inclusive of La and Ac are referred to as the d–block elements. For the first row d–block elements in the fourth period, from scandium to zinc, the 3d sub–level is being filled.

A transition element is defined as an element that forms **at least one stable ion with a partially filled d sub–level**.

Zinc is a d–block element but not a transition element. The only ion it forms is the +2 ion. Zn^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ has a completely filled d sub–level. IUPAC included scandium as a transition element, but this is controversial. In almost every compound of scandium, the oxidation number is +3 (no d electrons). However, it forms a couple of compounds (ScH_2 and $CsScCl_3$) with oxidation number of +2 but the chemical bonding in these compounds is more complicated and does not necessarily contain a +2 ion.

For the IB syllabus, elements **^{21}Sc to ^{29}Cu** are first row **transition elements**.

Element	**Symbol**	**Atomic No.**	**Electronic Configuration**						
				3d					**4s**
Scandium	Sc	21	[Ar]	↑					↑↓
Titanium	Ti	22	[Ar]	↑	↑				↑↓
Vanadium	V	23	[Ar]	↑	↑	↑			↑↓
*Chromium	Cr	24	[Ar]	↑	↑	↑	↑	↑	↑
Manganese	Mn	25	[Ar]	↑	↑	↑	↑	↑	↑↓
Iron	Fe	26	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Cobalt	Co	27	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Nickel	Ni	28	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
*Copper	Cu	29	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zinc	Zn	30	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

**The electronic configurations of chromium and copper are anomalies (refer to Topic 2 Atomic Structure)*

There appears to be a certain measure of stability associated with a full d^{10} sub–level and a half–filled d^5 sub–level. What would you expect to be the electron configurations of molybdenum and silver atoms? Are there exceptions? Examine tungsten, W.

13.1.1 Characteristics and Properties of Transition Elements

The electronic configurations of the d–block elements shape their chemistry and properties.

The characteristics and properties of transition metals include:

- high densities, melting and boiling points
- form compounds with different oxidation states
- their compounds and ions are often coloured
- used as catalysts for industrial processes
- form complex ions and complexes with ligands
- magnetic properties which depend on their oxidation states and coordination number
- salt solutions of transition metals are slightly acidic

Members of the first row transition elements are all hard and dense metals with **very similar physical properties** due to the **relatively small difference in effective nuclear charge**.

A. Atomic and Ionic Radius

From Sc to Cu,

- Slight decrease in atomic and ionic radii.
- **Generally, the change in metallic radii is small compared to the decrease across elements in Period 2 and 3**.

Reason:

- Across the period, nuclear charge increases but each ‘additional’ electron enters the inner 3d sub–level.
- The inner 3d sub–level electrons provide a more effective shield between the nucleus and the outer 4s electrons, hence almost nullifying the influence of an added proton in the nucleus.
- **The ionic radius of M^{2+} is much smaller than the metallic radius M.**
- With the loss of the 4s electrons, the nuclear charge will attract the remaining electrons more strongly.

Element, M	^{21}**Sc**	^{22}**Ti**	^{23}**V**	^{24}**Cr**	^{25}**Mn**	^{26}**Fe**	^{27}**Co**	^{28}**Ni**	^{29}**Cu**
Atomic Radii x10^{-12} m	159	148	144	130	129	124	118	117	122
Ionic Radii M^{2+} x10^{-12} m	75	86	79	62	83	61	65	69	77

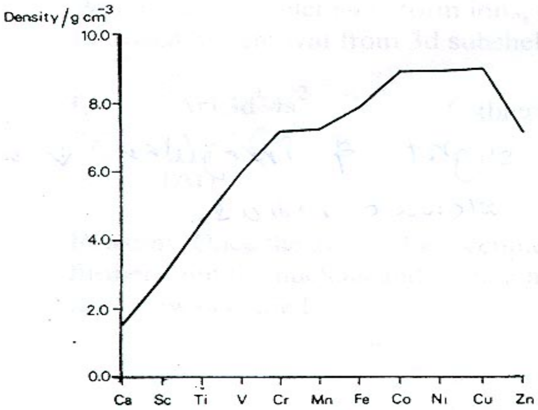
B. Density

From Sc to Cu,

- Gradual increase in density (d–block metals are much denser than s–block metals).

Reason:

- Across the period, relative atomic mass increases.
- Atomic volume decreases due to the **small decrease in metallic radius and the 'closely packed' structures**. Although the decrease in metallic radius is small across the period, the effect is magnified in the volume because volume, V is proportional to the cube of the radius, r ($V \propto r^3$).



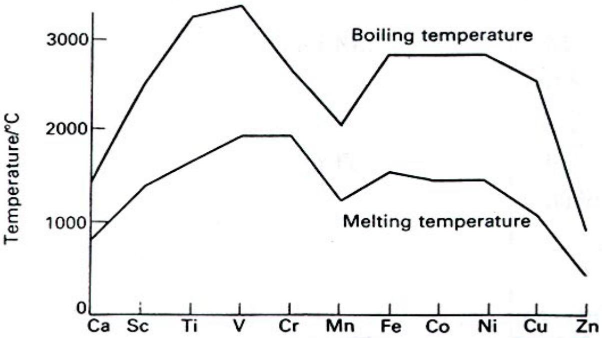
C. Melting and Boiling Points

From Sc to Cu,

- All the elements have a melting point over 1000 °C, in contrast to the s–block elements.

Reason:

- Strong metallic bonding due to the availability of both 3d and 4s electrons for delocalisation.
- Small metallic radius and hence strong electrostatic attraction of the protons in the nucleus for the delocalised electrons.



The relatively low melting point of manganese is due to the stability of the half–filled 3d sub–level which lowers the availability of valence electrons for delocalisation. Hence, this result in weaker metallic bonding and less energy required for melting.

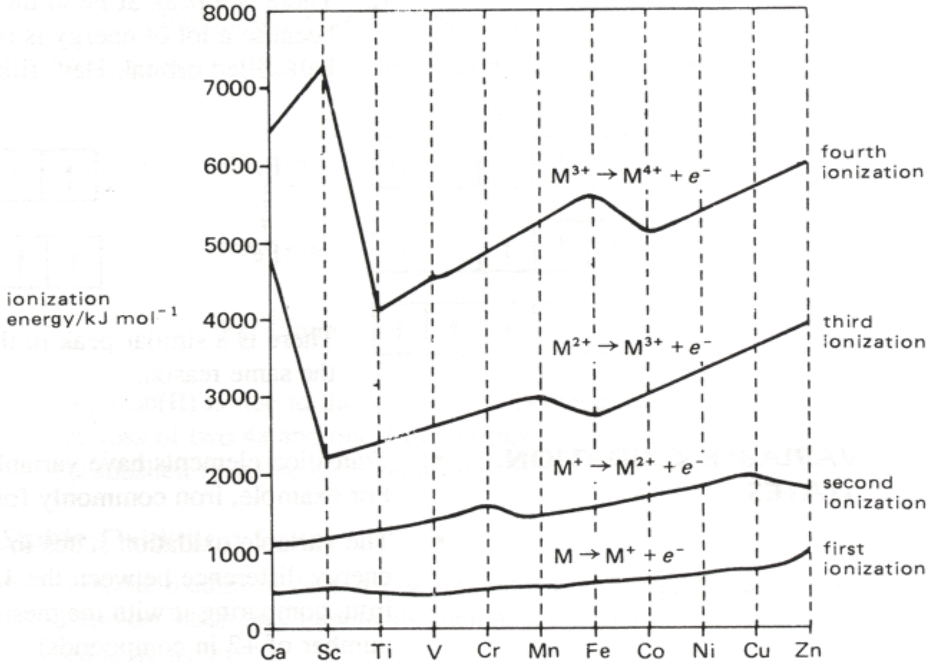
D. Ionisation Energy

From Sc to Zn,

- There is a small increase in both the 1st and 2nd IE but a greater increase in the 3rd and 4th IE.

Reason:

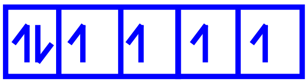
- For **1st IE and 2nd IE**, the removal of **4s** electrons is involved. The **shielding effect by the inner 3d electrons causes a minimal increase in the effective nuclear charge**.
- For **3rd IE and 4th IE**, the removal of electrons from the d sub–level electrons is involved. The **remaining d electrons provides poor shielding effect.** This causes a **significant increase in the effective nuclear charge**.

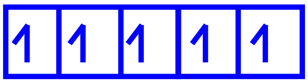


Anomalies:

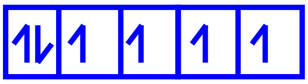
- The lower than expected values of 3rd IE for iron and 4th IE for cobalt is due to the successive electron being removed is paired in the 3d orbital.

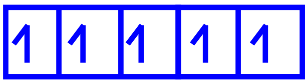
3rd IE of Fe: Fe^{2+} (g) → Fe^{3+} (g) + e
[Ar] $3d^6$ [Ar] $3d^5$





4th IE of Co: Co^{3+} (g) → Co^{4+} (g) + e
[Ar] $3d^6$ [Ar] $3d^5$





- This gives rise to inter–electronic repulsion. Thus, less energy is required to remove a paired 3d electron from an iron and cobalt ion.

13.1.2 Variable Oxidation States and Successive Ionisation Energies

The transition metals form **cations** by the loss of electrons. All the first row transition metals show an oxidation number of **+2**. In most cases, the formation of the +2 ion corresponds to the **loss of the two electrons in the 4s sub–level**.

Electrons are **removed from the 4s sub–level** first, followed by removal from the 3d sub–level.

Examples:				
	Fe	[Ar] $3d^6\ 4s^2$	Cu	[Ar] $3d^{10}\ 4s^1$
	Fe^{2+}	[Ar] $3d^6$	Cu^+	[Ar] $3d^{10}$
	Fe^{3+}	[Ar] $3d^5$	Cu^{2+}	[Ar] $3d^9$

When the 3d sub–level is being filled, the electrons in that level penetrate more efficiently than the 4s electrons as the 3d sub–level are of a smaller principal quantum number. These electrons in the 3d sub–level shield the nucleus and repel the electrons in the 4s sub–level, raising the energy of the 4s sub–level.

When the atoms are ionised, the 3d orbitals become significantly more stabilised and the +2 and +3 oxidation states all have $3d^n$ configurations.

Metal	Oxidation State		
	0	+2	+3
Ti	[Ar] $3d^2\ 4s^2$	[Ar] $3d^2$	[Ar] $3d^1$
V	[Ar] $3d^3\ 4s^2$	[Ar] $3d^3$	[Ar] $3d^2$
Cr	[Ar] $3d^5\ 4s^1$	[Ar] $3d^4$	[Ar] $3d^3$
Mn	[Ar] $3d^5\ 4s^2$	[Ar] $3d^5$	[Ar] $3d^4$
Fe	[Ar] $3d^6\ 4s^2$	[Ar] $3d^6$	[Ar] $3d^5$
Co	[Ar] $3d^7\ 4s^2$	[Ar] $3d^7$	[Ar] $3d^6$
Ni	[Ar] $3d^8\ 4s^2$	[Ar] $3d^8$	[Ar] $3d^7$
Cu	[Ar] $3d^{10}\ 4s^1$	[Ar] $3d^9$	[Ar] $3d^8$

Electronic configuration of the first row transition metals oxidation states +2 and +3

The transition elements exhibit a variety of oxidation states like +2 and +3. This is due to the **4s and 3d sub–levels are close in energy and there are no 'big jumps' in the successive ionisation energies** when the 4s and 3d electrons are removed.

The successive ionisation energies of magnesium and iron are shown in the table below. When magnesium forms an ionic compound, the energy released during lattice formation (ionic bonding) is much greater than the energy required to form the ions, Mg^{2+}. However, this lattice enthalpy is not able to supply the energy required to remove the 3rd and 4th electrons from magnesium.

Element	1st IE / kJ mol^{-1}	2nd IE / kJ mol^{-1}	3rd IE / kJ mol^{-1}	4th / IE kJ mol^{-1}
Magnesium	736	1450	7740	10500
Iron	762	1560	2960	5400

Successive ionisation energies of magnesium and iron

For simplicity, the number of electrons lost will depend on these factors such as lattice enthalpy, ionisation energy and hydration enthalpy (refer to Topic 5, Energetics, Born Haber cycle).

For the transition metals electrons are not removed to give the nearest noble gas electron configuration unlike the s–block metals.

^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{25}Mn	^{26}Fe	^{27}Co	^{28}Ni	^{29}Cu	^{30}Zn
(+1)	(+1)	(+1)	(+1)	(+1)	(+1)	(+1)	(+1)	+1	
(+2)	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	(+3)	(+3)	
	+4	+4		+4					
		+5							
			+6	+6					
				+7					

Note: The *uncommon* oxidation states are in brackets, ( ).

TOK: Ions with high oxidation number

Manganese in the manganate(VII) ion, MnO_4^-, has an oxidation number of +7. This implies the presence of Mn^{7+}. It must be remembered that the oxidation state of an atom does not represent the 'real' charge on that atom. This is particularly true of high oxidation states, where the ionisation energy required to produce a highly charged positive ion is far greater than the energies available in chemical reactions (from lattice formation and hydration). The manganese in the manganate(VII) ion form polar coordinate bonds with oxygen ligands which are much more electronegative. The assignment of electrons between atoms in calculating an oxidation state is purely a set of useful but artificial beliefs for the understanding of many chemical reactions. Oxidation numbers are not 'real' – they are simply mathematical constructs and a method for keeping track of electrons.

Talbot, C.; Harwood, R.; Coates, C. Chemistry for IB Diploma. Hodder Education: London, 2010.

13.1.3 Magnetic Properties of Transition Elements

Paramagnetism is caused by **unpaired electrons** and paramagnetic substances are **attracted by a magnetic field**.

Diamagnetism is caused by **paired electrons** and diamagnetic substances are **repelled slightly by a magnetic field**.

All substances have paired electrons and so all substances exhibit diamagnetism. However, the diamagnetic effect is much smaller than the paramagnetic effect and so, if there are any unpaired electrons present; the paramagnetic effect is predominant and will be attracted by the magnetic field.

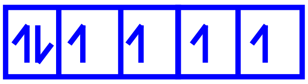
The **more unpaired electrons, the greater the paramagnetism** (magnetic moment) of the substance.

All the first row transition metals have unpaired electrons and show paramagnetism. In addition, iron, cobalt and nickel show a stronger form of magnetism known as ferromagnetism.

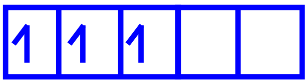
If you consider Fe^{2+} and Cr^{3+} transition metal ions, both will exhibit paramagnetic properties. Because Fe^{2+} has four unpaired electrons while Cr^{3+} has only three, iron(II) compounds are more paramagnetic.

Electronic configuration of Fe^{2+} and Cr^{3+}:

Fe^{2+}: [Ar] $3d^6$



Cr^{3+}: [Ar] $3d^3$

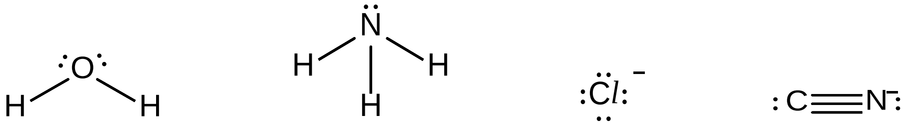


13.1.4 Complex Ions

A **d–block metal complex ion** consists of a **central metal ion closely bonded by coordinate covalent bonds to a cluster of molecules or negative ions (anions) called ligands**.

Ligands are negative ions or molecules and they must have **at least one lone (non–bonding) pair of electrons** which it uses to form a **coordinate covalent bond with the central metal ion.**

The figure below shows some examples of common ligands, H_2O, NH_3, CN^-, Cl^-. They share the lone pair of electrons with the empty orbitals in the central metal ion to form a complex ion.



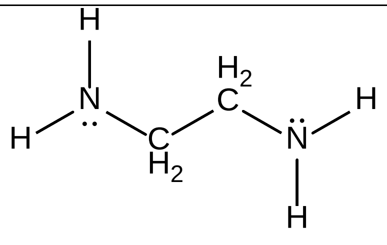
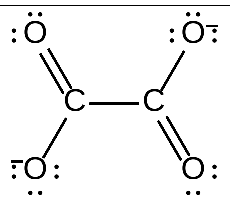
Ligands are classified according to the number of coordinate bonds it can form with the metal ion.

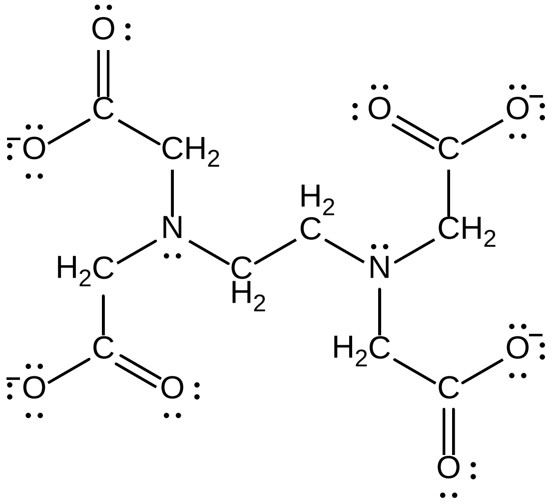
Coordination number is the number of coordinate bonds formed between the ligands and the transition metal ion.

Transition metal ions can form complexes because

- Relatively high charge density of the cation allows it to attract the lone pair of electrons from ligands.
- Availability of energetically accessible empty orbitals (3d, 4s or 4p) to accept the lone pair of electrons from ligands.

Classification of ligands according to the number of coordinate covalent bonds it can form to the central metal atom / ion (Section 16 of Data Booklet):

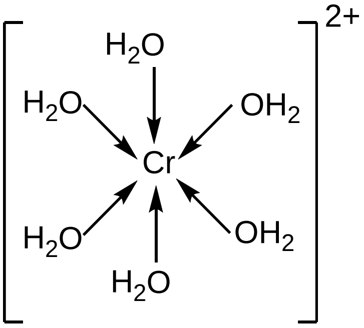
Ligand Type	Examples	
Monodentate (one coordinate bond)	I^-, Br^-, S^{2-}, Cl^-, F^-, OH^-, H_2O, SCN^-, NH_3, CN^-, CO	
Bidentate (two coordinate bonds)	 Ethylenediamine (en)	 Ethanedioate (oxalate) ion

Hexadentate (six coordinate bonds)	 EDTA (ethanediaminetetraethanoic acid)

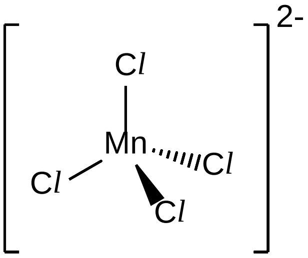
In the +2 and +3 oxidation states, the metal complexes in aqueous solutions are usually four– or six–coordinate and are generally similar with respect to their chemical properties and reaction stoichiometries.

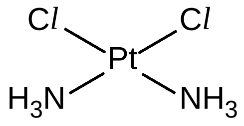
$[Ni(CN)_4]^{2-}$	coordination number = 4	(Four monodentate ligands)
$[Co(NH_3)_6]^{3+}$	coordination number = 6	(Six monodentate ligands)
$[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$	coordination number = 6	(Three bidentate ligands)

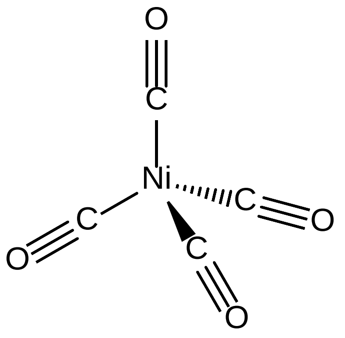
All first row transition elements, except titanium, form an octahedral complex ion with the formula $[M(H_2O)_6]^{2+}$ in aqueous solution. Representations of the structure of $[M(H_2O)_6]^{2+}$ ion is shown in the figure below.

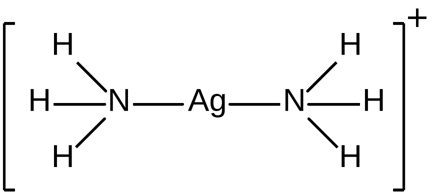


Complex ions can have various shapes depending on the number of ligands. For example, complexes containing four ligands may be tetrahedral or less commonly square planar. However, the shapes cannot be worked out using the old Valence Bond theory (by Linus Pauling in 1930s) and has been superseded by a number of other bonding theories including Crystal Field theory and Ligand Field theory based on the MO, molecular orbital theory.









Ligand exchange reactions.

A **stronger ligand can replace a weaker ligand** from a cation complex in a ligand exchange reaction.

Example of ligand exchange:

$$\mathrm{M}\mathbf{L}_6 + \mathbf{Y} \rightleftharpoons \mathrm{M}\mathbf{L}_5\mathbf{Y} + \mathbf{L}$$

- Ligand **Y** is a stronger ligand than ligand **L**.
- $\mathrm{M}\mathbf{L}_5\mathbf{Y}$ is a more stable complex than $\mathrm{M}\mathbf{L}_6$.

For example, when concentrated HCl is added to a solution containing Cu^{2+} (aq) ions, the solution turns green.

$$\underset{\text{Blue}}{[Cu(H_2O)_6]^{2+}}\ (aq) + 4Cl^-\ (aq) \rightleftharpoons \underset{\text{Yellow}}{[CuCl_4]^{2-}}\ (aq) + 6H_2O\ (l)$$

- Stronger Cl^- ligands replaces weaker H_2O ligands in the blue $[Cu(H_2O)_6]^{2+}$ complex in a ligand exchange reaction to form yellow $[CuCl_4]^{2-}$ complex ion.

- Presence of both complex ions give solution a resultant green colour.

In another example, when potassium thiocyanate solution, KSCN is added to a solution containing Fe^{3+} ions, a colour change is observed.

$$\underset{\text{pale yellow}}{[Fe(H_2O)_6]^{3+}} \text{ (aq)} + SCN^- \text{ (aq)} \rightleftharpoons \underset{\text{blood red}}{[Fe(H_2O)_5(SCN)]^{2+}} \text{ (aq)} + H_2O \text{ (l)}$$

- Stronger SCN^- ligand replaces one of the weaker H_2O ligands in the yellow $[Fe(H_2O)_6]^{2+}$ complex in a ligand exchange reaction to form blood red $[Fe(H_2O)_5(SCN)]^{2+}$ complex ion.

There are many examples in which a compound that is insoluble in water is 'dissolved' by conversion into a complex.

For example, when dilute ammonia is gradually added to a solution containing Cu^{2+} (aq) ions a pale blue precipitate is formed, which dissolves on adding more dilute ammonia.

The above transformation can be explained as such:

When small amounts of ammonia is added gradually,

$$[Cu(H_2O)_6]^{2+} \text{ (aq)} + \underset{\text{(from } NH_3\text{)}}{2OH^- \text{ (aq)}} \rightleftharpoons \underset{\text{pale blue ppt}}{Cu(OH)_2 \text{ (s)}} + 6H_2O \text{ (l)} \qquad \text{– (1)}$$

- A pale blue precipitate of $Cu(OH)_2$ is formed.

In excess ammonia,

- Both NH_3 and OH^- compete to combine with $[Cu(H_2O)_6]^{2+}$.
- Stronger NH_3 ligands replace H_2O ligands in a ligand exchange reaction to form a deep blue complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

$$[Cu(H_2O)_6]^{2+} \text{ (aq)} + 4NH_3 \text{ (aq)} \rightleftharpoons \underset{\text{deep blue complex}}{[Cu(NH_3)_4(H_2O)_2]^{2+} \text{ (aq)}} + 4H_2O \text{ (l)} \qquad \text{– (2)}$$

- As concentration of $[Cu(H_2O)_6]^{2+}$ is decreased, position of equilibrium for equation (1) shifts to the left.
- Pale blue precipitate of $Cu(OH)_2$ dissolves to give a deep blue solution.

Naming complex ions and complexes

Complex ions are named according to the following rules:

- The prefixes di(2), tetra(4) and hexa(6) are used to indicate the number of monodentate ligands.
- The type of ligand(s) present is indicated by names: e.g. NH_3 (ammine), Cl^- (chloro), H_2O (aqua), CN^- (cyano), CO (carbonyl), $C_2O_4^{2-}$ (oxalato), OH^- (hydroxo) and S^{2-} sulfide ion (thio).
- If the complex ion has a positive charge, then the name of the complex ion ends with the d–block metal ion and its oxidation state as a Roman numeral. For example, $[Cu(H_2O)_6]^{2+}$ is the hexaaquacopper(II) ion.
- If the complex has a negative charge, then the same name ends with a shortened name or the Latin name of the element followed by –ate. For example, $[CoCl_4]^{2-}$ is tetrachlorocobaltate(II) ion.
- Complexes are named with the positive ion (cation) first. For example, $K_2[Co(NH_3)_2Cl_4]$ is named as the potassium diamminetetrachlorocobaltate(II) ion.
- The prefixes bis and tris are used to indicate the number of polydentate ligands present. For example, $[CrCl_2(en)_2]_2SO_4$, dichlorobis(ethylenediammine)chromium (III) sulfate.

Deducing the total charge of the complex ion

The total or net charge on a complex depends upon the number of ligands, their charge and the oxidation state of the central transition metal ion to which the ligands are bonded. The total or net charge on a complex ion can be deduced from its composition and the oxidation state of the central cation. The oxidation state of the central can be deduced from the formula and charge of the complex.

Example:
Platinum(II) can form a complex ion with one ammonia and three chloride ligands. What is the overall charge and formula of the complex ion?

Platinum(II) has a charge of 2+, ammonia is a neutral ligand and the chloride ion has a charge of 1−.
The formula of the complex ion is **$[Pt(NH_3)Cl_3]^-$**.

Isomerism in complex ions

Where a square planar complex ion contains two different ligands, it can exist as two isomers in which there is a different arrangement of the ligands. This is termed cis–trans isomerism referring to the relative positions of the two ligands.

Cis means same side, but trans means opposite side. The structure of the cis– and trans–complex $[PtCl_2(NH_3)_2]$, diamminedichloroplatinum(II) is shown in the figure below. Find out which one has been used in chemotherapy to treat certain types of cancer.

cis–isomer trans–isomer

Octahedral isomers containing a bidentate ligand can form a pair of complexes that are mirror images of each other. These molecules are known as enantiomers or optical isomers which is a form of stereoisomerism (refer to Topic 10, Organic Chemistry).

13.1.5 Catalytic Activity

A catalyst is a substance that **increases the rate of a chemical reaction without being chemically changed at the end of the reaction**. The catalyst provides an **alternative pathway with a lower activation energy**, which results in a greater proportion of particles having energy greater than the activation energy. This results in an increase in the frequency of effective collisions between them (refer to Topic 6 Chemical Kinetics).

The table below illustrates the difference between **heterogeneous** and **homogeneous** catalysts:

Type of Catalyst	**Physical State**	**Catalytic Ability**
Heterogeneous	**Different** from reactants	Availability of **partially filled 3d orbitals** Ability to co–ordinate with other molecules or ions
Homogeneous	**Same** as reactants	Ability to **vary oxidation states**

The table below shows some examples of transition metal elements and their compounds functioning as heterogeneous catalysts:

Reaction Catalysed	**Heterogeneous Catalyst**
Contact Process $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$	V_2O_5, Vanadium(V) oxide
Haber Process $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$	Fe or Fe_2O_3
Decomposition of Hydrogen Peroxide $2H_2O_2 \rightarrow 2H_2O + O_2$	MnO_2, Manganese(IV) oxide
Hydrogenation of Alkenes $C_nH_{2n} + H_2 \rightarrow CnH_{2n+2}$	Ni
Manufacture of Polyethene $nCH_2{=}CH_2 \rightarrow n{-}[CH_2{-}CH_2]{-}$	Ziegler–Natta catalyst – titanium compounds E.g. $TiCl_3$ with $Al(C_2H_5)_3$
Manufacture of Nitric Acid from Ammonia $4NH_3\ (g) + 5O_2\ (g) \rightarrow 4NO\ (g) + 6H_2O\ (g)$ –catalysed $2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$ $3NO_2\ (g) + H_2O\ (l) \rightarrow 2HNO_3\ (aq) + NO\ (g)$	Pt
Catalytic Converters in Motor Cars	Pt, Pd, Rh

Scan me to view a video on how heterogeneous catalysts work

Scan me to view a video on how homogeneous catalysts work

13.1.6 Acidic Behaviour of Salts of Transition Metal

Hydration:

$$FeCl_3\ (aq) + 6\ H_2O\ (l) \rightarrow [Fe(H_2O)_6]^{3+}\ (aq) + 3\ Cl^-\ (aq)$$

Hydrolysis:

$$[Fe(H_2O)_6]^{3+}\ (aq) + H_2O\ (l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}\ (aq) + H_3O^+\ (aq)$$

The very high charge density of the Fe^{3+} ion enables it to polarize the electron cloud of its surrounding water molecules, weakening and breaking the O–H bond which results in the release of a proton.

13.2 Coloured Complexes

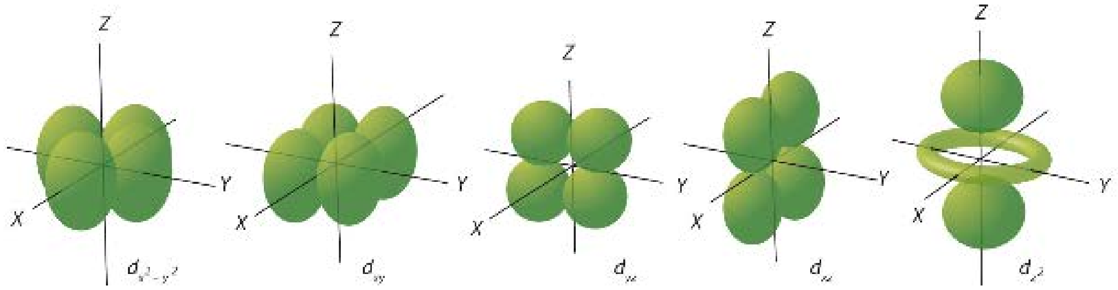
Most d–block metal compounds are coloured both in solution and in solid state. The colours of many but not all these compounds are due to light absorbed when an electron transition takes place between split d–orbitals.

Oxidation Number	+2	+3	+4	+5
Ti		$[Ti(H_2O)_6]^{3+}$ violet	$[Ti(H_2O)_6]^{4+}$ colourless	
V	$[V(H_2O)_6]^{2+}$ violet	$[V(H_2O)_6]^{3+}$ green	$[VO(H_2O)_5]^{2+}$ blue	$[VO_2(H_2O)_4]^{+}$ yellow
Cr	$[Cr(H_2O)_6]^{2+}$ sky blue	$[Cr(H_2O)_6]^{3+}$ green $[Cr(NH_3)_6]^{3+}$ yellow		
Mn	$[Mn(H_2O)_6]^{2+}$ pale pink	$[Mn(H_2O)_6]^{3+}$ red		MnO_4^{3-} blue
Fe	$[Fe(H_2O)_6]^{2+}$ pale green $[Fe(CN)_6]^{4-}$ Yellow	$[Fe(H_2O)_6]^{3+}$ Yellow $[FeSCN(H_2O)_5]^{2+}$ Blood-red $[Fe(CN)_6]^{3-}$ orange red		
Co	$[Co(H_2O)_6]^{2+}$ pink $[Co(NH_3)_6]^{2+}$ pale brown $[CoCl_4]^{2-}$ blue	$[Co(NH_3)_6]^{3+}$ dark brown		
Ni	$[Ni(H_2O)_6]^{2+}$ green $[Ni(NH_3)_6]^{2+}$ blue $[Ni(CN)_4]^{2-}$ yellow			
Cu	$[Cu(H_2O)_6]^{2+}$ blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$ Deep blue / violet $[CuCl_4]^{2-}$ yellow			

Note: You are not required to memorise the colours of complex ions.

13.2.1 Crystal Field Theory

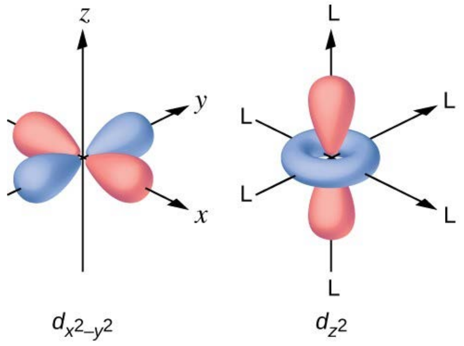
In a gaseous transition metal atom, the five d–orbitals are degenerate (i.e. identical energies).



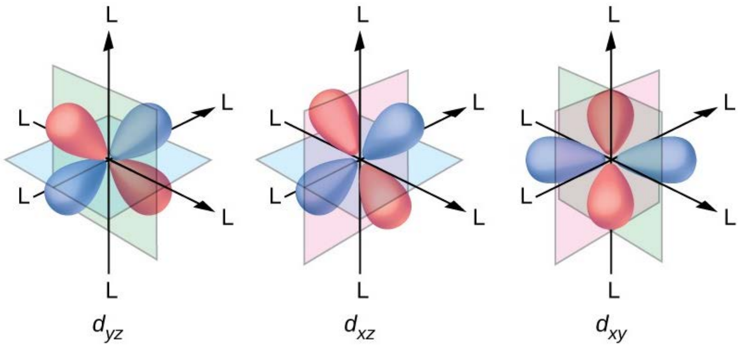
These 3d orbitals play the major role in the electronic structure of first row transition elements, thereby determining in large part the structures of the compounds, the complexes, the magnetic properties and the colours. This relationship between the d–orbitals and the physical and chemical properties can be rationalised by the Ligand Field Theory. This theory was derived from an electrostatic model known as the Crystal Field Theory (CFT). CFT is based on what happens to the energy levels of free metal ions when they are placed in the electrostatic field caused by anions.

This electrostatic field is termed 'crystal field', where the central metal ion and the ligands are assumed to be point charges. Hence, the ligands will repel the electrons associated with the central metal ion. Consequently, the d–orbitals reorganise in order to conserve overall energy as the d–orbitals have different shapes and spatial arrangements.

In complexes, the 3d sub–levels are oriented differently due to the presence of ligands. The 3d electrons close to a ligand will be repelled and have higher energy. Conversely, 3d electrons that are further away from the ligand will have lower energy.



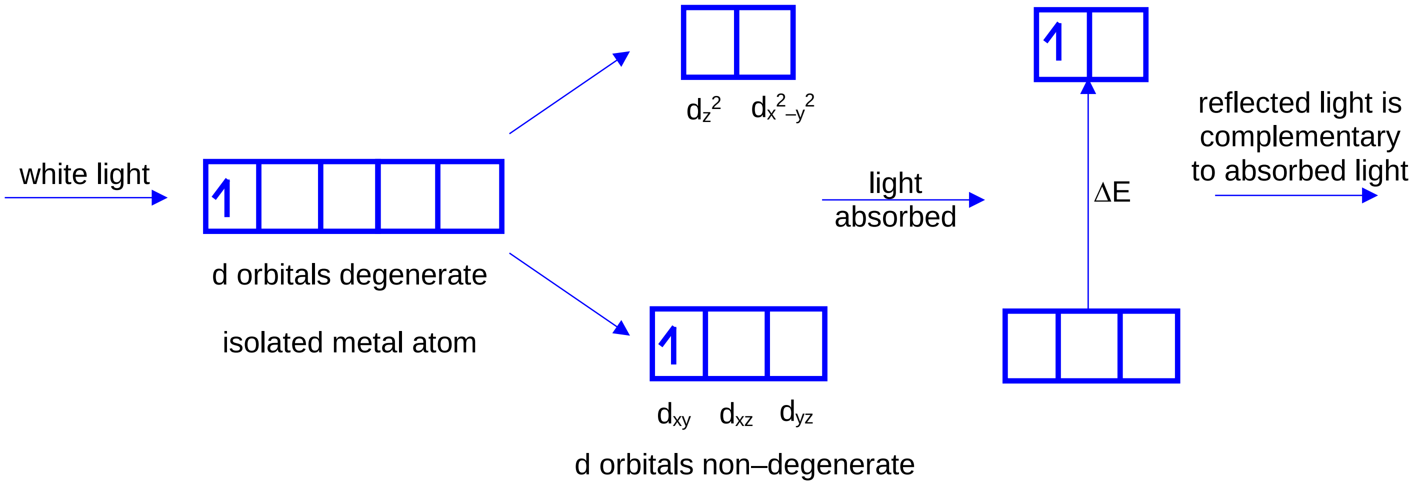
For d_{z^2} and $d_{x^2-y^2}$ orbitals, there is a head–on approach by the ligands. These orbitals have their lobes pointing at the ligands along the x, y and z axes respectively, hence they experience greater repulsion from the ligands.



The other 3 d–orbitals experienced less repulsion since their lobes do not point at the ligands along the axes.

The **3d sub–level is now 'split' into two energy levels**. Octahedral complexes are very common and the splitting of the d sub–levels with an energy gap between them, ΔE.

Example:
Consider the octahedral complex $[Ti(H_2O)_6]^{3+}$ which is violet.



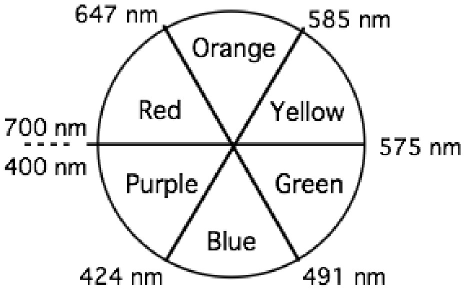
The **Planck's equation** can give an approximate value of the **energy gap**,
$\Delta E = hv$
h = Planck's constant = 6.63×10^{-34} J s
v = frequency of light in Hz (s^{-1})

A transition metal ion has partially filled d orbitals. In a transition metal complex, the **d orbitals are split into two groups** due to the ability of the ligands to split them into the energy levels as shown above. This effect is known as **d orbital splitting**.

The **energy gap, ΔE**, between the non–degenerate sub–levels **corresponds to the wavelength of light in the visible region** of the electromagnetic spectrum.

When a d–electron absorbs this light, it will be promoted from the lower energy level to the higher energy level termed, **d–d electron transition**. Hence yellow–green light is absorbed and the colour of the hydrated titanium(III) ions appears violet.

In other words, the wavelength of light energy not absorbed will be the colour of the complex which is the complementary colour. These colours are opposite each other in a colour wheel (found in Section 17 of IB Data Booklet).



The following factors influence the ΔE, the energy gap or the magnitude of the 3d sub–level splitting and hence the colour of complexes.

- the 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 metal ion.

  Ligands interact more effectively with the d orbitals of ions with a higher nuclear charge. A more effective interaction will result in a greater extent of d orbital splitting, leading to a larger energy gap. Hence, a smaller wavelength of light from the visible region of the electromagnetic spectrum will be absorbed. The complementary colour observed will be of a longer wavelength.

- the number of d electrons

  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 states of the metal.

  For example, $[Fe(H_2O)_6]^{2+}$ absorbs violet light and appears to be green while $[Fe(H_2O)_6]^{3+}$ appears to be yellow.

- the nature of the ligand

  Ligands of greater charge density interact more effectively with the d orbitals of ions with a higher nuclear charge. A more effective interaction will result in a greater extent of d orbital splitting, leading to a larger energy gap. Hence, a smaller wavelength of light from the visible region of the electromagnetic spectrum will be absorbed. The complementary colour observed will be of a longer wavelength.

  The common ligands are arranged in the order of increasing splitting they produced between the two sets of d-orbitals in an octahedral complex in the spectrochemical series. A stronger field ligand for example, CN^- has a greater splitting power than a weaker field ligand, Cl^-.

  The spectrochemical series shown below, is also found in Section15 of the IB Data Booklet.

Ligand	I^-	Br^-	S^{2-}	Cl^-	F^-	OH^-	H_2O	SCN^-	NH_3	CN^-	CO
λ_{max}	Longest wavelength	wavelength increasing ←									Shortest wavelength
ΔE	Weakest field	ΔE increasing →									Strongest field

- the geometry of the complex

  The geometry of the complex ion can affect the splitting in energy of the d orbitals as this depends on the relative orientation of the ligands and the d orbitals.

Note:
The CFT has its weaknesses as it does not consider the covalent bonding between the ligands and the central metal cation. For example, the MO theory addresses some of the limitations of the CFT.

The dichromate(VI) ion, orange, the chromate(VI) ion, yellow and the manganate(VII) ion are intensely coloured but they do not have any d electrons. They are coloured by a different mechanism known as electron transfer.

Exercise 13.1

1. Which is a characteristic property of transition metals?

A. They are colourless.

B. They are powerful oxidants.

C. They form complex ions. √

D. They exhibit one oxidation number in their compounds.

2. Which ion is colourless?

A. $[Cu(NH_3)_4]^{2+}$

B. $[Zn(H_2O)_4]^{2+}$ √

C. $[CuCl_4]^{2-}$

D. $[Fe(H_2O)_6]^{3+}$

3. Which compound will be diamagnetic?

A. $CrCl_3$

B. $TiCl_4$ √

C. $CuCl_2$

D. VCl_2

4. The cyanide ion (CN^-) can form two complex ions with iron ions. The formulae of these are $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$.

(a) What shape would you expect these to have?

Octahedral

(b) What is the oxidation state of the iron in the two complex ions?

+2 in $[Fe(CN)_6]^{4-}$ and +3 in $[Fe(CN)_6]^{3-}$

(c) What feature of CN^- allows it to form complex ions with transition metals?

The presence of a lone pair on the C of the $C\equiv N^-$ ligand allows complex formation.

5. Give the formulae of the complex ion(s) or oxyanion(s) of the first row of d-block elements corresponding to each of the following:

(a) A blue solution that turns green then yellow then concentrated hydrochloric acid is added.

$[Cu(H_2O)_6]^{2+}$ changing to $[CuCl_4]^{2-}$

(b) The ion formed when excess aqueous ammonia is added to aqueous copper(II) sulfate.

$[Cu(NH_3)_4]^{2+}$

(c) An orange solution that turns yellow when alkali is added to it.

$Cr_2O_7^{2-}$ changing to CrO_4^{2-}

Summary (Sections 13.1 and 13.2)

1. The first row d–block elements are scandium to zinc.
2. d–block elements have electron configurations that feature an outer pair of 4s electrons, within which there is a partially or totally filled 3d sub–level. Copper and chromium atoms adopt $3d^5\ 4s^1$ and $3d^{10}\ 4s^1$ configurations to reflect the stability of half–filled and full 3d sub–levels.
3. A transition metal is a d–block metal which has at least one of its ions with a partly filled d sub–level. (This definition excludes zinc as a transition metal).
4. The elements scandium to copper show features associated with transition metals, that is variable stable oxidation states, moderate chemical reactivity, complexes, paramagnetism and coloured ions (in solution and the solid state).
5. The magnetic moment of a first row transition metal is related to the number of unpaired electrons.
6. The elements of the 3d block have relatively high melting and boiling points.
7. The first ionization energies increase only slightly across the row from scandium to zinc, as the 4s electrons are being removed which are shielded from the nuclear attraction by the inner 3d electrons.
8. Most of the transition metals form M^{2+} cations by the loss of the 4s electrons, and some form M^{3+} ions as well.
9. Their simple cations have a strong tendency to form complex ions with anions or molecules with lone (non–bonding) pairs (known as ligands) that can form coordinate (covalent) bonds.
10. The ions of the 3d block elements often form complex ions by receiving 12 electrons from six ligands and forming coordinate covalent bonds. These complex ions have an octahedral shape.
11. Four–coordinate complexes can be tetrahedral or square planar; two coordinate complexes are linear.
12. The number of coordinate bonds formed between the ligands and the transition metal ion is called the coordination number of a complex ion. For the first row d–block complexes, 4 and 6 are the most common coordination numbers.
13. Monodentate ligands coordinate through one donor atom, whereas polydentate ligands coordinate through more than one donor atom, giving rise to chelates.
14. Structural isomers and enantiomers are possible for coordination complexes.
15. Higher oxidation states of d–block metals in the middle of the row involve the formation of polar covalent bonds. They are often oxidising agents.
16. Many transition metals and their compounds are important catalysts in industrial processes.
17. d–orbitals have the same energy or degenerate in an isolated atom but split into two sub–levels in a complex ion. d^0 and d^{10} cations are colourless.
18. Crystal Field theory is a simple electrostatic model of bonding in coordination complexes that regards the ligands as point charges. Electrostatic attraction between the transition metal cation and the ligands holds the complex ion together.
19. In an octahedral complex, the d orbitals are split into two sets, with three orbitals stabilised (the lower set) and two orbitals destabilized (the higher set). The crystal field splitting energy, ΔE is the energy gap between these sets.
20. The ranking of ligands based on the magnitude of ΔE, energy gap is called the spectrochemical series.
21. Ligands with large values of ΔE are called strong field ligands, and those with small values of ΔE are called weak field ligands.
22. Ligand Field theory is a bonding model of transition metal complexes based on Molecular Orbital theory.
23. Valence Bond theory assumes that coordination compound contains metal ions, in which ligands form coordinate bonds. Empty atomic orbitals of the metal are involved in the bonding.

24. Ligands replacement or substitution reactions occur when one ligand replaces another. Polydentate ligands, such as EDTA, form very stable complexes.
25. d–block complex ions are coloured. The electric field of ligands cause the d–orbitals in the metal ion to split so that d–d transitions of electrons occur, and the energy absorbed correspond to a photon in the visible region of the electromagnetic spectrum.
26. The colour observed for a complex ion is complementary to the colour of the light absorbed for the d–d transition.

Recommended reading materials

1. Bylikin Sergey; Horner; Murphy; Tarcy *Chemistry Course Companion 2014 Edn.* Oxford University Press ; pp 67-92
2. Steve Owen, *Chemistry for the IB Diploma 2nd Edn.* Cambridge University Press; pp 85-115
3. Talbot, C.;Harwood, R.; Coates, C. *Chemistry for IB Diploma.* Hodder Education; London, 2010; pp 71-92