



3.2 Periodic trends

Understandings:

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

Guidance

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

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

Applications and skills:

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

Guidance

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

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

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

Henri Poincaré,
1854–1912

Do you agree with this description of science?

TOK

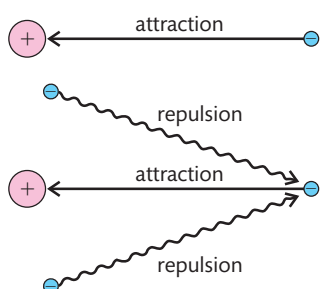


Figure 3.2 An electron in the hydrogen atom experiences the full attraction of the nuclear charge, but in a many-electron atom the attraction for the nucleus is reduced as the outer electron is repelled by inner electrons.

Physical properties

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

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

Effective nuclear charge

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

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

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



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

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

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

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

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

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

Atomic radius

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

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

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



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

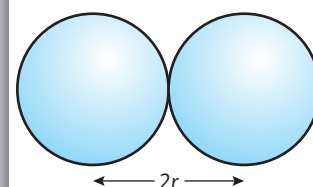


Figure 3.3 The atomic radius r is measured as half the distance between neighbouring nuclei.

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



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

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

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

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

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

Ionic radius

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

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

Five trends can be identified.

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

Worked example

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

O²⁻, F⁻, Ne, Na⁺, and Mg²⁺.

Solution

The ions and the Ne atom have 10 electrons and the electron configuration $1s^2 2s^2 2p^6$.

The nuclear charges increase with atomic number:

O: $Z = +8$

F: $Z = +9$

Ne: $Z = +10$

Na: $Z = +11$

Mg: $Z = +12$

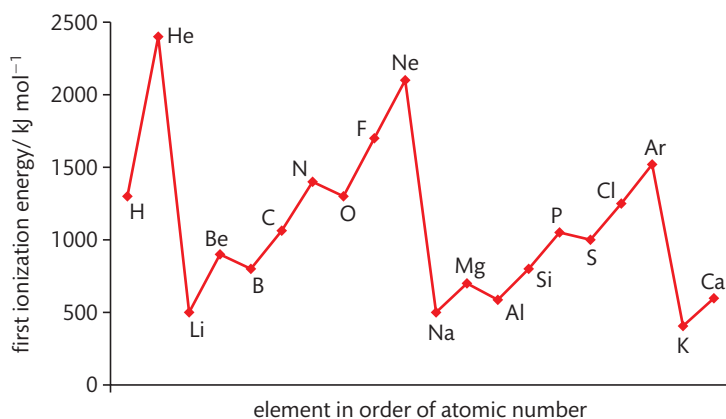
The increase in nuclear charge results in increased attraction between the nucleus and the outer electrons. The ionic radii decrease as the atomic number increases.

Exercises

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

Ionization energies

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



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

Figure 3.4 First ionization energies of the first 20 elements.

Two general trends can be identified from Figure 3.4.

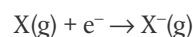
- Ionization energies increase across a period. The increase in effective nuclear charge causes an increase in the attraction between the outer electrons and the nucleus and makes the electrons more difficult to remove.
- Ionization energies decrease down a group. The electron removed is from the energy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

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

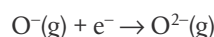
The trend in ionization energy is the reverse of the trend in atomic radii. Both trends are an indication of the attraction between the nucleus and the outer electrons.

Electron affinity

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



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



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

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

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

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

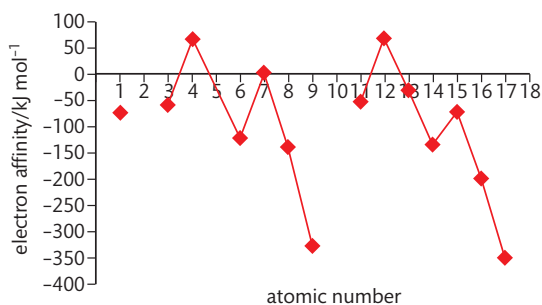


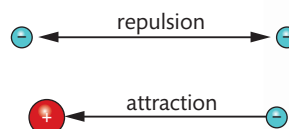
Figure 3.5 The electron affinities of the first 18 elements. Note there are no values assigned to the noble gases.

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



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

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



Electronegativity

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

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

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

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

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

Metals have lower ionization energies and electronegativities than non-metals

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

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

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

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

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