

Topic 1.7: Periodic Trends

Revision Notes · AP Chemistry

UNIT 1 · ATOMIC STRUCTURE AND PROPERTIES

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The One Idea Behind Every Trend

Almost every periodic trend is Coulomb's law wearing different clothes. The attraction between a nucleus and an electron grows with the charges involved and shrinks rapidly as the distance between them grows: $F \propto (q_1 \times q_2) \div r^2$.

For a valence electron, the charge it actually feels is the effective nuclear charge, $Z(\text{eff})$: the full nuclear charge reduced by the shielding of the inner electrons. Core electrons shield well; electrons in the same shell shield each other poorly.

So two questions explain nearly everything in this topic. How strong is the pull on the outer electrons ($Z(\text{eff})$ and charge)? And how far away are they (which shell, and how much shielding)? Answer those, and atomic radius, ionic radius, ionization energy and electronegativity all follow.

Atomic Radius: Across and Down

Across a period, radius decreases. Sodium's atoms are about 186 pm in radius; chlorine's are about 99 pm. Each step right adds a proton and an electron, but the electron joins the same shell and shields poorly, while the proton adds its full charge to the nucleus. $Z(\text{eff})$ climbs, the whole electron cloud is pulled in tighter, and the atom shrinks even though it contains more electrons.

Down a group, radius increases. Lithium is about 152 pm, sodium 186 pm, potassium 227 pm. Each step down starts a new shell. The valence electrons are simply farther from the nucleus, and the extra filled shells shield them more. Distance wins over the larger nuclear charge.

Ionic Radius: Cations Shrink, Anions Swell

Cations are smaller than their parent atoms. A sodium atom is 186 pm; Na^+ is 102 pm. Forming the cation removes the entire outer shell, and the remaining electrons are pulled in by the same nuclear charge spread over fewer electrons, with less electron-electron repulsion pushing them apart.

Anions are larger than their parent atoms. A chlorine atom is 99 pm; Cl^- is 181 pm. The added electron increases repulsion in the same shell while the nuclear charge stays fixed, so the cloud expands.

The isoelectronic series. Species with the same number of electrons are ranked purely by proton count. F^- , Na^+ and Mg^{2+} all have 10 electrons. With 9, 11 and 12 protons respectively, their radii run 133 pm, 102 pm and 72 pm: more protons, same electrons, smaller radius. It is Coulomb's law in its cleanest form.

Ionization Energy

The first ionization energy is the energy needed to remove the outermost electron from a gaseous atom. It measures how tightly that electron is held, so it follows the same two factors: high $Z(\text{eff})$ and small radius mean high ionization energy.

Across a period, ionization energy generally increases (small atoms, strong pull), and **down a group it decreases** (distant, shielded electrons leave easily). Two dips break the smooth rise across a period: boron is lower than beryllium (its outer electron is in the higher, slightly shielded 2p subshell), and oxygen is lower than nitrogen (its fourth 2p electron is paired, and the repulsion in that pair makes it easier to remove).

Successive ionization energies locate the group. Removing electrons one at a time gets steadily harder, then suddenly much harder at one step. Sodium: 496, then 4,562 kJ/mol. The enormous jump after the first electron says the second electron must come from a full inner shell, so sodium has exactly one valence electron. Calcium's jump comes after the second (590, 1,145, then 4,912), and boron's after the third (801, 2,427, 3,660, then 25,026). Find the cliff, count the electrons before it, and you have the group.

Electronegativity and Electron Affinity

Electronegativity is the pull an atom exerts on shared electrons in a bond. It rises across a period (small radius, high $Z(\text{eff})$, the nucleus is close to the bonding pair) and falls down a group. Fluorine,

top right, is the most electronegative element; the pattern mirrors ionization energy because both measure nuclear grip on electrons.

Electron affinity is the energy change when a gaseous atom gains an electron. It generally becomes more exothermic across a period, as the added electron enters a small, high $Z(\text{eff})$ shell. The noble gases are the standing exception: their shells are full, so an extra electron must start a new, distant shell, and the process is not favourable.

Traps That Cost Marks in Topic 1.7

Explaining a trend with the trend. "Radius decreases across a period because atoms get smaller" earns nothing. Every explanation must run through Coulomb's law: name the change in nuclear charge, shielding, shell or distance, then the effect on attraction, then the trend.

Assuming more electrons means a bigger atom. Across a period atoms gain electrons and shrink, because the electrons join the same shell while the nuclear charge grows. Electron count alone never decides size.

Ranking ions by electron count. In an isoelectronic series all species have identical electron counts; the ranking is set by protons alone. Between a cation and an anion that are not isoelectronic, compare shell counts first: losing or filling a shell outweighs everything else.

Putting the ionization energy cliff in the wrong place. The jump appears when the electron being removed comes from the next shell in, i.e. after all valence electrons are gone. For a Group 2 element the cliff is between the second and third ionization energies, and the ratio is typically five to ten times.

Confusing ionization energy with electronegativity. Ionization energy is measured on an isolated gaseous atom and concerns its own electron. Electronegativity exists only in a bond and concerns a shared pair. They trend together but they are different quantities.

Forgetting the two dips. Boron below beryllium, and oxygen below nitrogen, are favourite exam targets precisely because the general trend says the opposite. Both dips have structural reasons (a new subshell, and a paired electron's repulsion), and the reasons are what earn the marks.

Key Relationships to Remember

- Coulomb's law: attraction $\propto (q_1 \times q_2) \div r^2$; effective nuclear charge $Z(\text{eff}) = \text{nuclear charge} - \text{shielding by core electrons}$
- Atomic radius: decreases across a period (rising $Z(\text{eff})$, same shell), increases down a group (new shell, more shielding)
- Cations smaller than parent atoms (outer shell lost); anions larger (extra repulsion, same nuclear charge); in an isoelectronic series radius falls as Z rises
- Ionization energy: increases across a period (dips at boron and oxygen), decreases down a group; the cliff in successive values counts the valence electrons
- Electronegativity: increases across a period, decreases down a group; fluorine highest
- Every trend answer runs: structure change (charge, shell, shielding, distance) $\rightarrow$ attraction change $\rightarrow$ trend

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