Marks
7
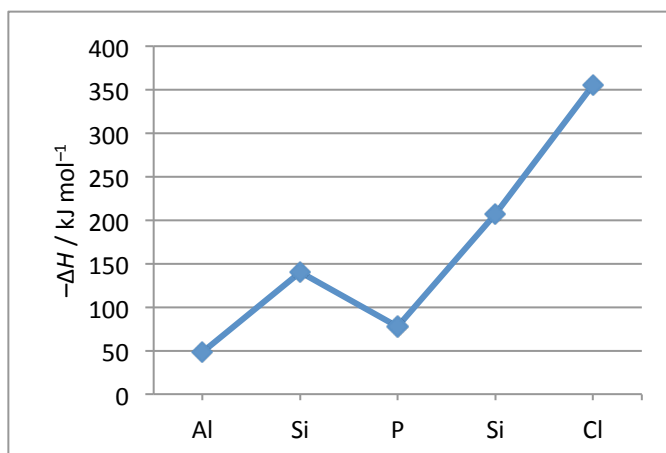
- Electron affinity is the enthalpy change for the reaction   A(g) + e → A⁻(g).
  The graph below shows the trend in electron affinities for a sequence of elements in
  the third row of the Periodic Table.

Give the electron configurations of the following atoms and singly-charged anions.
Use [Ne] to represent core electrons.

Atom	Electron configuration	Ion	Electron configuration
Si	**[Ne] $(3s)^2 (3p)^2$**	Si⁻	**[Ne] $(3s)^2 (3p)^3$**
P	**[Ne] $(3s)^2 (3p)^3$**	P⁻	**[Ne] $(3s)^2 (3p)^4$**
S	**[Ne] $(3s)^2 (3p)^4$**	S⁻	**[Ne] $(3s)^2 (3p)^5$**

Explain why the value for the electron affinity of phosphorus is anomalous.

**The general trend across a row is for the electron affinity to increase, as the
number of protons in the nucleus increases.**

**However, in order to form P⁻, the extra electron must pair up with an existing
electron in one of the *p*-orbitals. The extra repulsion involved leads to the
electron affinity being lower for P than for Si despite the higher nuclear charge.**

What trend would you expect for the electron affinities for Si⁻, P⁻ and S⁻? Explain
your answer.

**The electron affinities of these anions will be much lower than those of the parent
atoms, as adding an electron to an already negatively charged species is much
less favourable.**

**The nuclear charge increase along the series so the electron affinities will
increases: Si⁻ < P⁻ < S⁻. The electron affinity of Si⁻ will also be further decreased
because addition of an electron requires pairing again. However, this will not
affect the order as Si⁻ is already has the lowest electron affinity.**

	Marks 5

• The Periodic Table as arranged by Mendeleev allows us to make predictions about the behaviours of elements based on those around them. Briefly describe why the Periodic Table works.

The Periodic Table groups atoms into:

  • **Groups (columns) based on the number of valence electrons they have, and**
  • **Periods (rows) based on the shell and sub-shell.**

Chemical reactivity is based on the number of valence electrons and the size of the element. Elements in the same group have similar chemical properties as they have the same number of valence electrons. Differences in the reactivity of elements in the same group are due to their size – elements get larger down each group leading to decreased electronegativity.

Silicon and tin have the same structure as diamond. Use the information in the following table to predict the density of tin.

Element	Atomic Mass	Density (g cm^{-3})	Bond length (pm)
Si	28	2.329	233
Sn	118		280

Density depends on the mass and the volume:

   density = mass / volume

The volume of a crystal will increase as the cube of the bond length:

   volume of tin = (280 / 233)^3 × volume of silicon

The mass will increase as the atomic mass increases:

   mass of tin = (118 / 28) × mass of silicon

As the density of silicon is 2.329 g cm^{-3}, the density of tin will therefore be:

   density of tin = density of silicon × (118 / 28) / (280 / 233)^3
   **   = 2.329 g cm^{-3} × (118 / 28) / (280 / 233)^3 = 5.7 g cm^{-3}**

Answer: **5.7 g cm^{-3}**

Explain the trend in the first ionisation energy of these elements.

The first ionisation energy is the energy needed to remove the single electron in the outermost occupied *s* orbital.

As you go down the group, the principal quantum number increases and the distance between the nucleus and the orbital increases. The coulombic attraction between nucleus and electron therefore decreases and less energy is required to remove the electron.

Marks
6

- The electron affinity is negative if energy is released upon addition of an electron. If it is positive, the resultant anion is unstable. Explain why beryllium has a positive electron affinity, while that of fluorine is highly negative.

An additional electron in Be will have to go into a 2*p* orbital, which has a planar node through the nucleus and thus does not feel nuclear charge. Consequently this leads to a higher energy system.

In F, the high nuclear charge and small atom offset the above effect and the extra electron is tightly bound.

Why is the ionisation potential of oxygen slightly smaller than nitrogen, despite being further across the period?

The electron removed from O (1s^2 2s^2 2p^4) is the one in the 2*p* orbital with 2 electrons in it. This electronic repulsion offsets the greater nuclear charge of O compared to N.

How is this related to the slightly positive electron affinity of nitrogen?

The electron affinity of N is Δ*H* for the process 2p^3 → 2p^4.

The ionisation potential for O is Δ*H* for the process 2p^4 → 2p^3.

The only difference (apart from the direction of the reaction) is the nuclear charge on the atom.

| | | | | | | Marks |

- Explain the trends in electron affinities for the first 5 elements of the second row of the periodic table, in terms of their electronic configurations.

  i.e. Discuss the trend in ΔH for the following reaction: $A(g) + e^- \rightarrow A^-(g)$

Marks 3

Element	Li	Be	B	C	N
ΔH (in kJ mol^{-1})	−60	+241	−27	−122	+8

The electron configuration of Li is [He] $2s^1$ - it has a single unpaired electron in its outer shell. There is space in the $2s$ orbital for another electron so a higher energy orbital does not to be occupied. The nuclear charge of Li holds onto the extra electron sufficiently to compensate for the extra electron – electron repulsion that occurs. Adding an extra electron is favourable and so ΔH is negative.

The electron configuration of Be is [He] $2s^2$ - it has a filled $2s$ orbital. Any an extra electron would have to go into the $2p$ orbital. This has a higher energy and occupation of it is energetically unfavourable, despite the higher nuclear charge of Be compared to Li.

The electron configuration of B is [He] $2s^2 2p^1$ - it has a single unpaired electron in its $2p$ orbital. The extra electron is being added to the same subshell. The extra proton in the B nucleus means that an electron is favourable compared to the situation in Be. As the extra electron can have a spin parallel with the other $2p$ electron, the additional electron – electron repulsion is minimal.

The electron configuration of C is [He] $2s^2 2p^2$. It has 2 unpaired electrons in its $2p$ orbitals. The extra electron is being added to the same subshell. The extra proton in the C nucleus means that an electron is even more favourable compared to the situation in B. As the extra electron can have a spin parallel with the other $2p$ electrons, the additional electron – electron repulsion is minimal.

The electron configuration of N is [He] $2s^2 2p^3$ - it has 3 unpaired electrons in its $2p$ orbitals. An additional electron has to pair its spin with one of these electrons and this leads to a large increase in electron – electron repulsion. Because of this, ΔH is positive.

- Briefly explain the following concepts and their electronic origins.

2

(a) paramagnetism

Paramagnetism is the property of any substance that is attracted by a magnetic field. It is occurs to the presence of unpaired electrons. Paramagnets lose their magnetism when the magnetic field is removed.

(b) polar bond

If the electron density in a covalent bond is not shared equally between the 2 atoms, a polar bond is formed. This occurs when the 2 atoms have different electronegativities.

<div style="text-align:right">Marks
3</div>

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The electron configuration of Be is [He] $2s^2$ - it has a filled $2s$ orbital. Any an extra electron would have to go into the $2p$ orbital. This has a higher energy and occupation of it is energetically unfavourable, despite the higher nuclear charge of Be compared to Li.

The electron configuration of B is [He] $2s^2\,2p^1$ - it has a single unpaired electron in its $2p$ orbital. The extra electron is being added to the same subshell. The extra proton in the B nucleus means that an electron is favourable compared to the situation in Be. As the extra electron can have a spin parallel with the other $2p$ electron, the additional electron – electron repulsion is minimal.

The electron configuration of C is [He] $2s^2\,2p^2$. It has 2 unpaired electrons in its $2p$ orbitals. The extra electron is being added to the same subshell. The extra proton in the C nucleus means that an electron is even more favourable compared to the situation in B. As the extra electron can have a spin parallel with the other $2p$ electrons, the additional electron – electron repulsion is minimal.

The electron configuration of N is [He] $2s^2\,2p^3$ - it has 3 unpaired electrons in its $2p$ orbitals. An additional electron has to pair its spin with one of these electrons and this leads to a large increase in electron – electron repulsion. Because of this, ΔH is positive.

- The graph shows the first ionisation energies for second row elements of the periodic table.
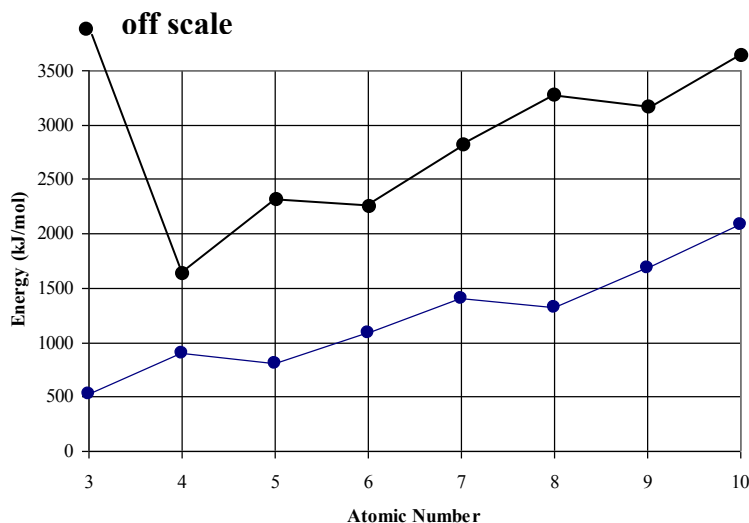
Explain the general trend and both anomalies.

The general trend of an *increase* in ionisation energy across the period is due to the increase in effective nuclear charge (Z_{eff}). The electrons feel a greater pull from the nucleus as Z_{eff} increases. This leads to a decrease in the size of the atom and an increase in the energy required to remove an electron.

First anomaly - the *decrease* in ionisation energy in going from Be (at. no. 4) to B (at. no. 5). Be has an electron configuration of [He] $2s^2$ while B has a configuration of [He] $2s^2 2p^1$. Due to shielding in a multi-electron atom, the $2p$ orbital is higher in energy than the $2s$ orbital and thus any electron in the $2p$ orbital is held less tightly than those in the $2s$ orbital. B therefore has a lower ionisation energy than Be, despite having a higher nuclear charge.

Second anomaly - another (slight) drop in ionisation energy going form N (at. no. 7) to O (at. no. 8). There are only three p orbitals, so the next electron to go into one of the p orbitals must pair up. Paired electrons in the same orbital suffer higher electron – electron repulsion so O has a lower ionisation energy than N, despite having a higher nuclear charge.

On the above graph, plot your estimates of the second ionisation energies for the second row elements. Make sure your graph clearly shows the general trends.

See figure above.

The second ionisation of Li is > 7000 kJ mol^{-1} as a core electron is ionised. The second ionisations of the other elements follow the same trends as the first ionisations (for exactly the same reasons), but displaced one atomic number to the right and at a slightly higher energy (as Z_{eff} is greater).

	Marks
• Explain why, in general, there is a decrease in atomic radius from left to right across the second row of the periodic table (lithium to neon), but an abrupt increase in radius on going to the next row.	**4**

Across the period, the number of protons and the number of electrons increases. This leads to a greater pull from the nucleus and greater electron – electron repulsion. Because electrons are good at avoiding each other, the *net* effect is an increase in the effective nuclear charge, Z_{eff}.

The effective nuclear charge (Z_{eff}) increases going from left to right across the period. The electrons feel a greater pull from the nucleus as Z_{eff} increases as they are all being added to the same $n = 2$ orbital. This leads to a decrease in the size of the atom across the period.

When the 11th electron is added for Na, it goes into the $n = 3$ shell. The higher n quantum number leads to a much larger average radius and a big increase in the radius of the atom going from Ne to Na.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY