Chem Factsheet

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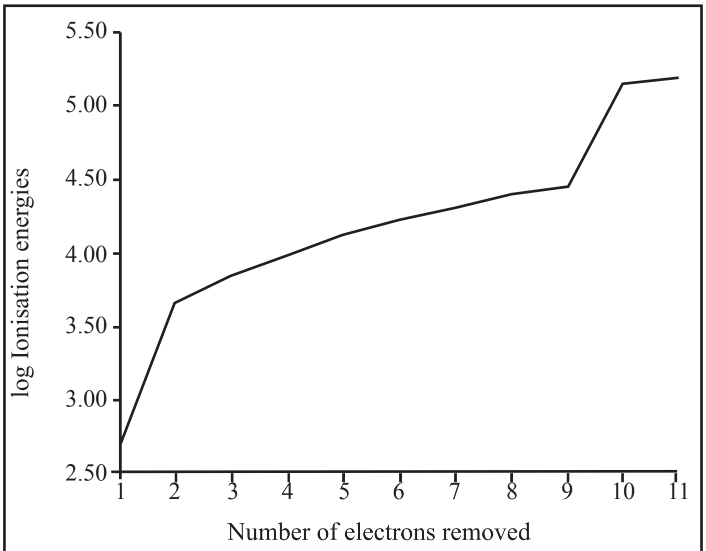
Ionisation Energies: Answering Exam Questions

Investigating variations in successive ionisation energies for a particular element and first ionisation (I_1) values for different elements across the Periodic table gives a lot of information about atomic structure.

A-level exam questions require candidates to:
1. Give definitions of ionisation energies and write corresponding equations.
2. Know the nature of the variations in ionisation energy values and be able to sketch graphs to show the variations.

Variations in the successive ionisation energies of an atom e.g sodium



3. Estimate values of ionisation energies given related data.
4. Assign an element to a group of the Periodic Table using ionisation energy data.
5. Explain why one particular ionisation energy value is smaller or greater than another value.

Definition
The **first ionisation energy (I_1) of an element** is the energy required to remove one electron from each atom in one mole of gaseous atoms to form one mole of gaseous ions, each with a 1+ charge (measured under standard conditions of temperature and pressure)
i.e. $X(g) \rightarrow X^+(g) + e^-$; $\Delta H^{\ominus} = I_1(X)$

e.g.1 $Na(g) \rightarrow Na^+(g) + e^-$; $\Delta H^{\ominus} = I_1(Na) = +496\ kJ\ mol^{-1}$
e.g.2 $Si(g) \rightarrow Si^+(g) + e^-$; $\Delta H^{\ominus} = I_1(Si) = +789\ kJ\ mol^{-1}$
e.g.3 $Cl(g) \rightarrow Cl^+(g) + e^-$; $\Delta H^{\ominus} = I_1(Cl) = +1251\ kJ\ mol^{-1}$
e.g.4 $Ar(g) \rightarrow Ar^+(g) + e^-$; $\Delta H^{\ominus} = I_1(Ar) = +1521\ kJ\ mol^{-1}$

Definition
The **nth ionisation energy (I_n) of an element** is the energy required to remove one electron from each atom / positive ion in one mole of gaseous atoms / positive ions to form one mole of gaseous ions, each with a 1+ extra charge (measured under standard conditions of temperature and pressure)
i.e. $X^{n+}(g) \rightarrow X^{(n+1)+}(g) + e^-$; $\Delta H^{\ominus} = I_n(X)$
[$0 \leq n \leq$ Atomic number of X]

e.g.1 $Na^+(g) \rightarrow Na^{2+}(g) + e^-$; $\Delta H^{\ominus} = I_2(Na) = +4562\ kJ\ mol^{-1}$
e.g.2 $Mg^{4+}(g) \rightarrow Mg^{5+}(g) + e^-$; $\Delta H^{\ominus} = I_5(Mg) = +13630\ kJ\ mol^{-1}$
e.g.3 $Cl^{7+}(g) \rightarrow Cl^{8+}(g) + e^-$; $\Delta H^{\ominus} = I_8(Cl) = +33604\ kJ\ mol^{-1}$
e.g.4 $Li^{2+}(g) \rightarrow Li^{3+}(g) + e^-$; $\Delta H^{\ominus} = I_3(Li) = +11815\ kJ\ mol^{-1}$

Questions
(a) Write equations for the process corresponding to
(i) $I_3(Si)$ (ii) $I_5(Ar)$ (iii) $I_{12}(Ca)$
(b) Which ionisation energy / energies is / are represented by each of the following equations?
(i) $Br^{4+}(g) \rightarrow Br^{5+}(g) + e^-$
(ii) $Ag^+(g) \rightarrow Ag^{2+}(g) + e^-$
(iii) $Cl^+(g) \rightarrow Cl^{3+}(g) + e^-$

Answers
(a) (i) $Si^{2+}(g) \rightarrow Si^{3+}(g) + e^-$
(ii) $Ar^{4+}(g) \rightarrow Ar^{5+}(g) + e^-$
(iii) $Ca^{11+}(g) \rightarrow Ca^{12+}(g) + e^-$
(b) (i) $I_5(Br)$
(ii) $I_2(Ag)$
(iii) $I_2(Cl) + I_3(Cl)$!

Essentially, ionisation energy values represent the energy required to overcome the net force of attraction between the nuclear (+ve) charge and the outer electron (-ve) that is being removed from the atom or ion.

Reminders
Ionisation energies are related to the force of attraction between the nucleus and the electron being removed by the following variables:
1. The **number of protons in the nucleus** i.e. the nuclear charge. All other factors being equal, as the nuclear charge **increases** the force of attraction, and hence the ionisation energy, will also **increase**.
2. The **distance between the nucleus and the electron being removed**. All other factors being equal, as this **increases**, the force of attraction, and hence the ionisation energy, will **decrease**.
3. The **number of other electrons positioned between the nucleus and the electron being removed**. All other factors being equal, as this **increases** the shielding of the outer electron from the nuclear attraction will increase and the net force of attraction, and hence the ionisation energy, will **decrease**.

Increases in distance have much bigger effects on ionisation energy values than nuclear charge increases. This is because the force of attraction between nucleus and outer electron is inversely proportional to the square of the distance but only directly proportional to the nuclear charge. Consequently a decrease in I_n can occur, even when nuclear charge has increased, because distance and shielding have also increased to outweigh the nuclear charge effect.

***VERY LARGE** decreases in ionisation values suggest large increases in distance from the nucleus and shielding from the nuclear attraction. These are associated with electrons being in more distant **principal** energy levels, rather than more distant sub-levels.*

4. **The number of protons in the nucleus <u>relative</u> to the number of electrons in the particle**. All other factors being equal, as this **ratio increases** as a result of the number of electrons removed increasing and the ion becoming smaller, the ionisation energy will increase.
5. The **spins of the electrons in the highest occupied p sub-level**. If p-electrons are paired (↑↓) by opposite spins, they tend to repel each other causing one of the electrons to be slightly easier to remove than an unpaired electron (↑, ↑↑ or ↑↑↑). This outweighs the effect of the extra proton on going from group 5 to 6.

*When answering the various types of question it is an excellent idea to **write down the atomic number** (number of protons), the **s,p,d-type electron configuration** and the **spins of the electrons** in the highest occupied sub-level of the atom(s) / ion(s) involved. This gives an immediate picture of which factors are constant and which principal energy levels or sub-levels need to be referred to in full answers.*

The latter is not difficult – it comes directly from the Periodic Table provided during the exam! The atomic number is below the symbol of the element and the electron configuration is "read" by working across the periods until the element is reached.

Periods		1	2	3	4	5	6	7	8
			Groups						
1	Z e^-	H 1 $1s^1$							He 2 $1s^2$
2	Z e^-	Li 3 [He]$2s^1$	Be 4 [He]$2s^2$	B 5 $-2s^22p^1$	C 6 $-2s^22p^2$	N 7 $-2s^22p^3$	O 8 $-2s^22p^4$	F 9 $-2s^22p^5$	Ne 10 $-2s^22p^6$
3	Z e^-	Na 11 [Ne]$3s^1$	Mg 12 [Ne]$3s^2$	Al 13 $-3s^23p^1$	Si 14 $-3s^23p^2$	P 15 $-3s^23p^3$	S 16 $-3s^23p^4$	Cl 17 $-3s^23p^5$	Ar 18 $-3s^23p^6$
4	Z e^-	K 19 [Ar]$4s^1$	Ca 20 [Ar]$4s^2$	Ga 31 $-3d^{10}4p^1$	Ge 32 $-3d^{10}4p^2$	As 33 $-3d^{10}4p^3$	Se 34 $-3d^{10}4p^4$	Br 35 $-3d^{10}4p^5$	Kr 36 $-3d^{10}4p^6$

↑

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	CU	Zn
21	22	23	24	25	26	27	28	29	30
[Ca]$3d^1$	[Ca]$3d^2$	[Ca]$3d^3$	[K]$3d^5$	[Ca]$3d^5$	[Ca]$3d^6$	[Ca]$3d^7$	[Ca]$3d^8$	[K]$3d^{10}$	[Ca]$3d^{10}$

Also, remember **unpaired spins are maximised** and s can have only one pair while p sub-levels can have 3 and d sub-levels 5, giving:

s^1	s^2	p^1	p^2	p^3	p^4	p^5	p^6
↑	↑↓	↑	↑↑	↑↑↑	↑↓↑↑	↑↓↑↓↑	↑↓↑↓↑↓

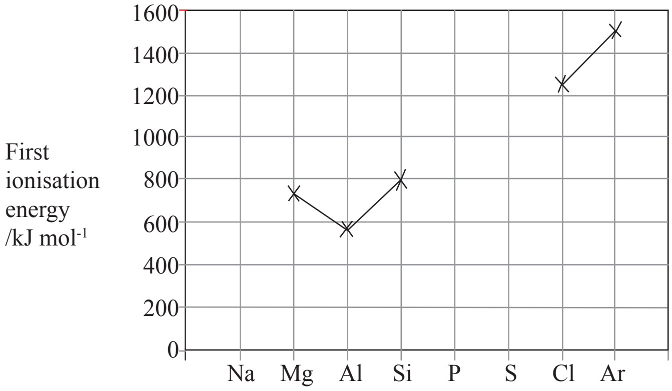
For example

Aluminium atom : 13 ; $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$; ↑
Sodium ion : 11 ; $1s^2\ 2s^2\ 2p^6$; ↑↓ ↑↓ ↑↓
Oxygen atom : 8 ; $1s^2\ 2s^2\ 2p^4$; ↑↓ ↑ ↑

When answering the various types of question, make sure you clearly refer your arguments to a particular atom or ion. Do not refer to "it" because this can be ambiguous since "A" greater than "B" can be confused with "B" less than "A".

Practice Questions

1. The graph below shows the first ionisation energies of some Period 3 elements.



(a) On the diagram, mark the approximate positions of the values of the first ionisation energies for the elements Na, P and S.
(b) Explain the general increase in the values of the first ionisation energies of the elements Na – Ar.
(c) In terms of the electron sub-levels involved, explain the position of aluminium and the position of sulphur in the diagram.

2. (a) Write the electron configuration for the Mg^{2+} ion.
(b) Write an equation to illustrate the process occurring when the second ionisation energy of magnesium is measured.
(c) A Ne atom and a Mg^{2+} ion have the same number of electrons. Give two reasons why the first ionisation energy of neon is lower than the third ionisation energy of magnesium.

Answers

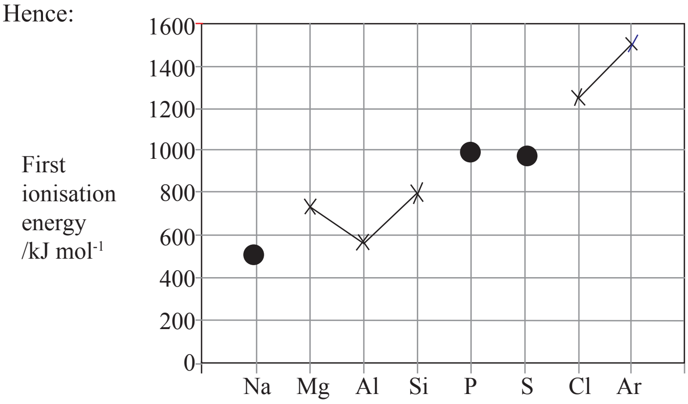
1. (a) Na atom : **11** ; $1s^2\,2s^2\,2p^6\,3s^1$; ↑
Mg atom : **12** ; $1s^2\,2s^2\,2p^6\,3s^2$; ↑↓)

The significant difference is the **number of protons**.
For Na this is less than for Mg causing sodium's ionisation energy to be **lower** than magnesium.

Si atom : **14** ; $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$; ↑↑
P atom : **15** ; $1s^2\,2s^2\,2p^6\,3s^2\,3p^3$; ↑↑↑
The significant difference is the **number of protons**. For Si this is less than for P causing phosphorus's ionisation energy to be **higher** than silicon.

P atom : **15** ; $1s^2\,2s^2\,2p^6\,3s^2\,3p^3$; ↑↑↑
S atom : **16** ; $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$; ↑↓↑↑)
The significant difference is the **spin pairing of the p electrons in S**. Even though S has one more proton than P, the repulsions between the paired electrons (↑↓) cause sulphur's ionisation energy to be **lower** than phosphorus.

Hence:



(b) From Na to Ar the constantly changing factor is the increasing number of nuclear protons. With the outer electrons being in the same principal energy level (3rd) with similar shielding, the increasing number of protons generally causes an increasingly strong force of attraction between the nucleus and the electron being removed.

(c) Mg atom : **12** ; $1s^2\,2s^2\,2p^6\,3s^2$; ↑↓
Al atom : **13** ; $1s^2\,2s^2\,2p^6\,3s^2\,3p^1$; ↑
Aluminium is lower than magnesium because, even though Al has an extra proton, the force of attraction between the nucleus and the electron being removed is weaker because the outer electron of Al is in a slightly more distant and more shielded 3p sub-level rather than a 3s sub-level.

P atom : **15** ; $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$; ↑↑↑
S atom : **16** ; $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$; ↑↓↑↑
P and S have the same number of occupied sub-levels and therefore similar shielding. Sulphur is lower than magnesium because, even though S has an extra proton, the force of attraction between the nucleus and the electron being removed is weaker because the outer electron of S is paired by spin (↑↓↑↑) whereas those in P are all unpaired (↑↑↑). The pair repel each other making it slightly easier to remove one of them.

2 (a) Mg(12) is $1s^2\,2s^2\,2p^6\,3s^2$ → since 2 e- removed,
Mg^{2+} is $\mathbf{1s^2\,2s^2\,2p^6}$.

(b) Second e- is being removed hence start with Mg^+.
Remember states of matter.
→ $\mathbf{Mg^+(g) \rightarrow Mg^{2+}(g) + e^-}$

(c) Mg^{2+} ion : **12** ; $1s^2\,2s^2\,2p^6$; ↑↓↑↓↑↓
Ne atom : **10** ; $1s^2\,2s^2\,2p^6$; ↑↓↑↓↑↓)

The number of sub-levels and spin patterns are the same but the **outer e- of the Mg ion are much closer to the nucleus** (because 12 protons pull only 10e- much closer to the nucleus than 10 protons pulling in 10e- in neon) <u>and</u> the **number of attracting protons acting on the outer e- is greater** for the Mg ion (12 > 10).

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