The nuclear atom

COMPOSITION OF ATOMS

The smallest part of an element is an atom. It used to be thought that atoms are indivisible but they can be broken down into many different sub-atomic particles. All atoms, with the exception of hydrogen, are made up of three fundamental sub-atomic particles – protons, neutrons and electrons.

The hydrogen atom, the simplest atom of all, contains just one proton and one electron. The actual mass of a proton is 1.673×10^{-24} g but it is assigned a relative value of 1. The mass of a neutron is virtually identical and also has a relative mass of 1. Compared with a proton and a neutron an electron has negligible mass with a relative mass of only $\frac{1}{2000}$. Neutrons are neutral particles. An electron has a charge of 1.602×10^{-19} coulombs which is assigned a relative value of –1. A proton carries the same charge as an electron but of an opposite sign so has a relative value of +1. All atoms are neutral so must contain equal numbers of protons and electrons.

SUMMARY OF RELATIVE MASS AND CHARGE

Particle	Relative mass	Relative charge
proton	1	+1
neutron	1	0
electron	5×10^{-4}	−1

SIZE AND STRUCTURE OF ATOMS

Atoms have a radius in the order of 10^{-10} m. Almost all of the mass of an atom is concentrated in the nucleus which has a very small radius in the order of 10^{-14} m. All the protons and neutrons (collectively called nucleons) are located in the nucleus. The electrons are to be found in energy levels or shells surrounding the nucleus. Much of the atom is empty space.

SHORTHAND NOTATION FOR AN ATOM OR ION

$${}^{A}_{Z}\mathrm{X}^{n+/n-}$$

MASS NUMBER *A*

Equal to the number of protons and neutrons in the nucleus.

ATOMIC NUMBER *Z*

Equal to the number of protons in the nucleus and to the number of electrons in the atom. The atomic number defines which element the atom belongs to and consequently its position in the periodic table.

CHARGE

Atoms have no charge so n = 0 and this is left blank. However by losing one or more electrons atoms become positive ions, or by gaining one or more electrons atoms form negative ions.

EXAMPLES

Symbol	Atomic number	Mass number	Number of protons	Number of neutrons	Number of electrons
${}^{9}_{4}\mathrm{Be}$	4	9	4	5	4
${}^{40}_{20}\mathrm{Ca}^{2+}$	20	40	20	20	18
${}^{37}_{17}\mathrm{Cl}^{-}$	17	37	17	20	18

ISOTOPES

All atoms of the same element must contain the same number of protons, however they may contain a different number of neutrons. Such atoms are known as isotopes. Chemical properties are related to the number of electrons so isotopes of the same element have identical chemical properties. Since their mass is different their physical properties such as density and boiling point are different.

Examples of isotopes: ${}^{1}_{1}\mathrm{H}$ ${}^{2}_{1}\mathrm{H}$ ${}^{3}_{1}\mathrm{H}$ ${}^{12}_{6}\mathrm{C}$ ${}^{14}_{6}\mathrm{C}$ ${}^{35}_{17}\mathrm{Cl}$ ${}^{37}_{17}\mathrm{Cl}$

RELATIVE ATOMIC MASS

The two isotopes of chlorine occur in the ratio of 3:1. That is, naturally occurring chlorine contains 75% ${}^{35}_{17}\mathrm{Cl}$ and 25% ${}^{37}_{17}\mathrm{Cl}$. The weighted mean molar mass is thus:

$$\frac{(75 \times 35) + (25 \times 37)}{100} = 35.5 \text{ g mol}^{-1}$$

and the relative atomic mass is 35.5. Accurate values to 2 d.p. for all the relative atomic masses of the elements are given in Section 6 of the IB data booklet. These are the values that must be used when performing calculations in the examinations.

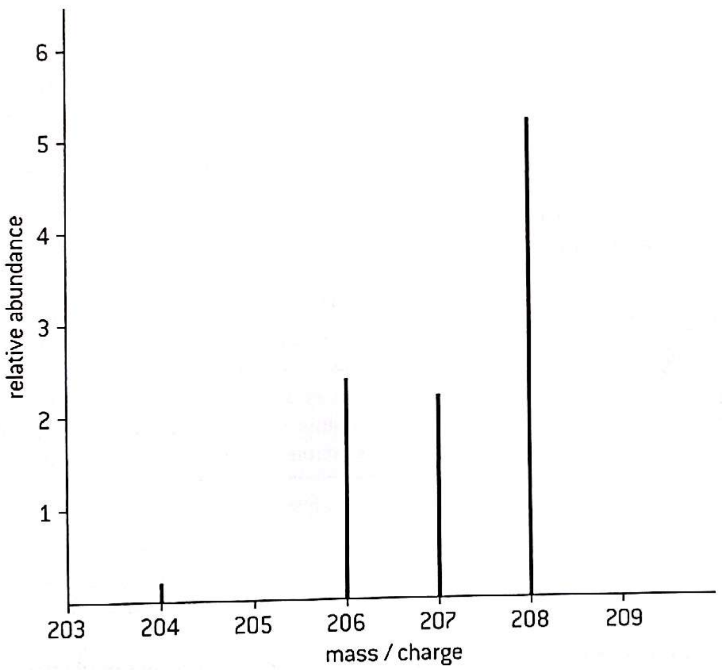
Mass spectrometer and relative atomic mass

MASS SPECTROMETER

Relative atomic masses can be determined using a mass spectrometer. A vaporized sample is injected into the instrument. Atoms of the element are ionized by being bombarded with a stream of high energy electrons in the ionization chamber. In practice the instrument is set so that only ions with a single positive charge are formed. The resulting unipositive ions pass through holes in parallel plates under the influence of an electric field where they are accelerated. The ions are then deflected by an external magnetic field.

The amount of deflection depends both on the mass of the ion and its charge. The smaller the mass and the higher the charge the greater the deflection. Ions with a particular mass/charge ratio are then recorded on a detector which measures both the mass and the relative amounts of all the ions present.

THE MASS SPECTRUM OF NATURALLY OCCURRING LEAD



The relative atomic mass of lead can be calculated from the weighted average:

Isotopic mass	Relative abundance	% relative abundance
204	0.2	2
206	2.4	24
207	2.2	22
208	5.2	52

$$\text{relative atomic mass} = \frac{(2 \times 204) + (24 \times 206) + (22 \times 207) + (52 \times 208)}{100} = 207.2$$

USES OF RADIOACTIVE ISOTOPES

Isotopes have many uses in chemistry and beyond. Many, but by no means all, isotopes of elements are radioactive as the nuclei of these atoms break down spontaneously. When they break down these radioisotopes emit radiation which is dangerous to living things. There are three different forms of radiation. Gamma (γ) radiation is highly penetrating whereas alpha (α) radiation can be stopped by a few centimetres of air and beta (β) radiation by a thin sheet of aluminium. Radioisotopes can occur naturally or be created artificially. Their uses include nuclear power generation, the sterilization of surgical instruments in hospitals, crime detection, finding cracks and stresses in metals and the preservation of food. $^{14}_{6}C$ is used for carbon dating, $^{60}_{27}Co$ is used in radiotherapy and $^{131}_{53}I$ and $^{125}_{53}I$ are used as tracers in medicine for treating and diagnosing illness.

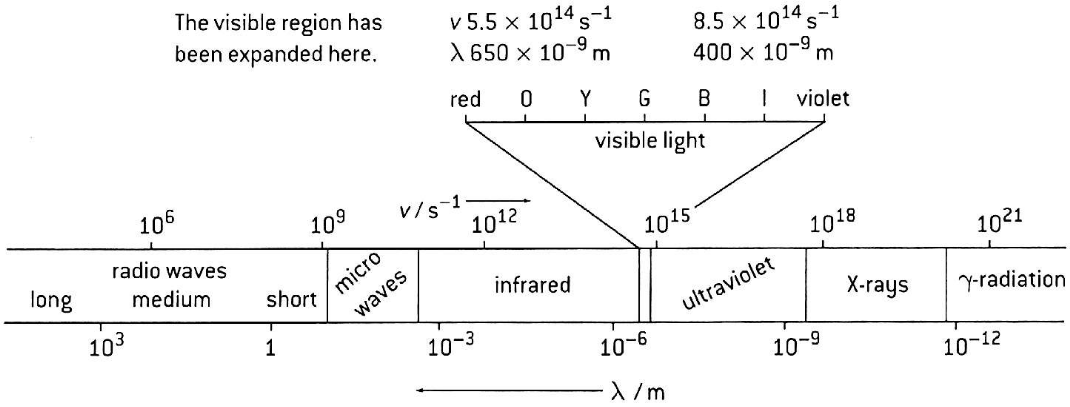
Emission spectra

THE ELECTROMAGNETIC SPECTRUM

Electromagnetic waves can travel through space and, depending on the wavelength, also through matter. The velocity of travel c is related to its wavelength λ and its frequency ν. Velocity is measured in m s^{-1}, wavelength in m and frequency in s^{-1} so it is easy to remember the relationship between them:

$$c = \lambda \times \nu$$
$$(m\ s^{-1})\quad (m)\quad (s^{-1})$$

Electromagnetic radiation is a form of energy. The smaller the wavelength and thus the higher the frequency the more energy the wave possesses. Electromagnetic waves have a wide range of wavelengths ranging from low energy radio waves to high energy γ-radiation. Visible light occupies a very narrow part of the spectrum.

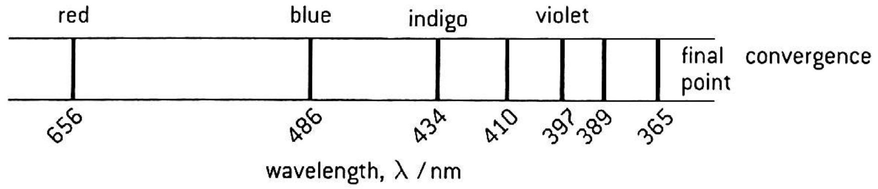


ATOMIC EMISSION SPECTRA

White light is made up of all the colours of the spectrum. When it is passed through a prism a **continuous spectrum** of all the colours can be obtained.

When energy is supplied to individual elements they emit a spectrum which only contains emissions at particular wavelengths. Each element has its own characteristic spectrum known as a **line spectrum** as it is not continuous.

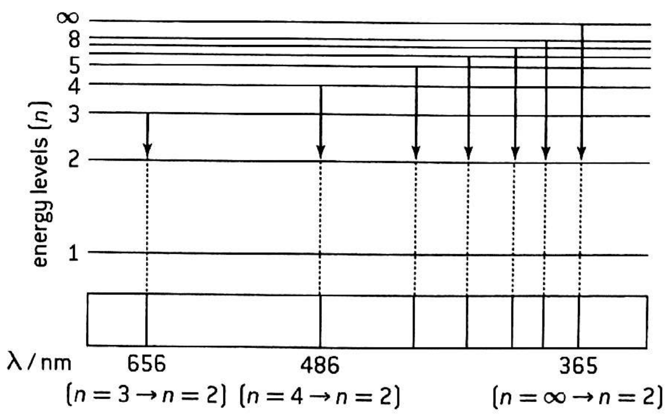
The visible hydrogen spectrum



Note that the spectrum consists of discrete lines and that the lines converge towards the high energy (violet) end of the spectrum. A similar series of lines at even higher energy also occurs in the ultraviolet region of the spectrum and several other series of lines at lower energy can be found in the infrared region of the spectrum.

EXPLANATION OF EMISSION SPECTRA

When energy is supplied to an atom electrons are excited (gain energy) from their lowest (ground) state to an excited state. Electrons can only exist in certain fixed energy levels. When electrons drop from a higher level to a lower level they emit energy. This energy corresponds to a particular wavelength and shows up as a line in the spectrum. When electrons return to the first level ($n = 1$) the series of lines occurs in the ultraviolet region as this involves the largest energy change. The visible region spectrum is formed by electrons dropping back to the $n = 2$ level and the first series in the infrared is due to electrons falling to the $n = 3$ level. The lines in the spectrum converge because the energy levels themselves converge.



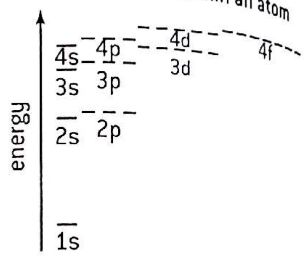
Electronic configuration

TYPES OF ORBITAL

Electrons are found in orbitals. Each orbital can contain a maximum of two electrons each with opposite spins. The first level ($n = 1$) contains just one orbital, called an s orbital. The second level ($n = 2$) contains one s orbital and three p orbitals. The 2p orbitals are all of equal energy but the sub-level made up of these three 2p orbitals is slightly higher in energy than the 2s orbital.

Principal level (shell) n	Number of each type of orbital s	p	d	f	Maximum number of electrons in level ($=2n^2$)
1	1	–	–	–	2
2	1	3	–	–	8
3	1	3	5	–	18
4	1	3	5	7	32

Relative energies of sub-levels within an atom



The relative position of all the sub-levels for the first four main energy levels is shown.

Note that the 4s sub-level is below the 3d sub-level. This explains why the third level is sometimes stated to hold 8 or 18 electrons.

ELECTRONIC CONFIGURATION AND AUFBAU PRINCIPLE

The electronic configuration can be determined by following the aufbau (building up) principle. The orbitals with the lowest energy are filled first. Each orbital can contain a maximum of two electrons. Orbitals within the same sub-shell are filled singly first – this is known as Hund's rule.

e.g.

	H $1s^1$	Li $1s^22s^1$	Na $1s^22s^22p^63s^1$	K $1s^22s^22p^63s^23p^64s^1$
	He $1s^2$	Be $1s^22s^2$	Mg $1s^22s^22p^63s^2$	Ca $1s^22s^22p^63s^23p^64s^2$
		B $1s^22s^22p^1$	Al $1s^22s^22p^63s^23p^1$	Sc $1s^22s^22p^63s^23p^64s^23d^1$
		C $1s^22s^22p^2$	Si $1s^22s^22p^63s^23p^2$	Ti $1s^22s^22p^63s^23p^64s^23d^2$
		N $1s^22s^22p^3$	P $1s^22s^22p^63s^23p^3$	V $1s^22s^22p^63s^23p^64s^23d^3$
		O $1s^22s^22p^4$	S $1s^22s^22p^63s^23p^4$	
		F $1s^22s^22p^5$	Cl $1s^22s^22p^63s^23p^5$	
		Ne $1s^22s^22p^6$	Ar $1s^22s^22p^63s^23p^6$	

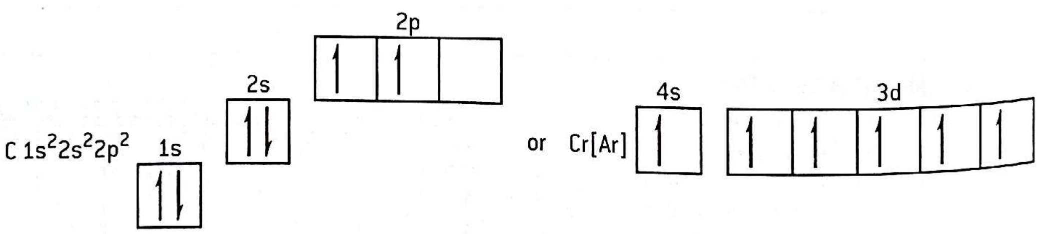
To save writing out all the lower levels the configuration may be shortened by building on the last noble gas configuration. For example, continuing on from titanium, vanadium can be written $[Ar]4s^23d^3$, then Cr $[Ar]4s^13d^5$, Mn $[Ar]4s^23d^5$, Fe $[Ar]4s^23d^6$ etc.

Note that the electron configurations of the transition metals show two irregularities. When there is the possibility of the d sub-level becoming half-full or completely full it takes precedence over completely filling the 4s level first so chromium has the configuration $[Ar]4s^13d^5$ (rather than $[Ar]4s^23d^4$) and copper has the configuration $[Ar]4s^13d^{10}$ (rather than $[Ar]4s^23d^9$). When transition metals form ions the 4s electrons are removed first so Fe^{2+} has the configuration $[Ar]3d^6$. The IB requires that you can write the configuration for any element or ion up to krypton ($Z = 36$). The full electronic configuration for krypton is $1s^22s^22p^63s^23p^64s^23d^{10}4p^6$ or it can be shortened to $[Ar]4s^23d^{10}4p^6$.

(When writing electronic configurations check that for a neutral atom the sum of the superscripts adds up to the atomic number of the element.)

Sometimes boxes are used to represent orbitals so the number of unpaired electrons can easily be seen,

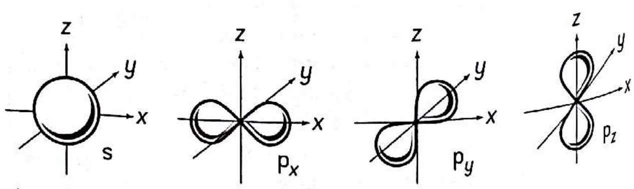
e.g.



SHAPES OF ORBITALS

An electron has the properties of both a particle and a wave. Heisenberg's uncertainty principle states that it is impossible to know the exact position of an electron at a precise moment in time. An orbital describes the three-dimensional shape where there is a high probability that the electron will be located.

s orbitals are spherical and the three p orbitals are orthogonal (at right angles) to each other.



Evidence from ionization energies

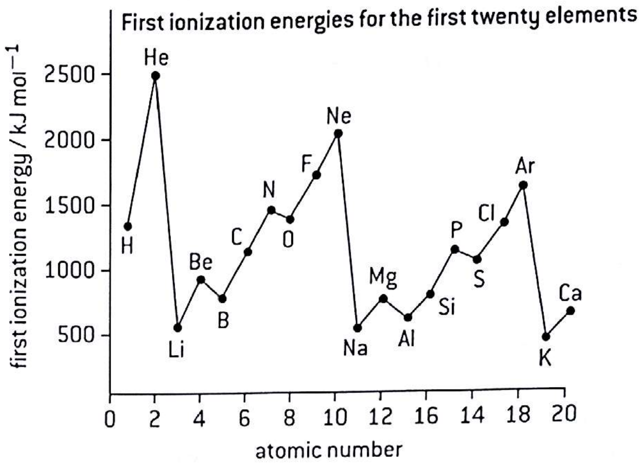
EVIDENCE FROM IONIZATION ENERGIES

The first ionization energy of an element is defined as the energy required to remove one electron from an atom in its gaseous state. It is measured in kJ mol^{-1}.

$$X(g) \rightarrow X^+(g) + e^-$$

A graph of first ionization energies plotted against atomic number shows a repeating pattern.

It can be seen that the highest value is for helium, an atom that contains two protons and two electrons. The two electrons are in the lowest level and are held tightly by the two protons. For lithium it is relatively easy to remove an electron, which suggests that the third electron in lithium is in a higher energy level than the first two. The value then generally increases until element 10, neon, is reached before it drops sharply for sodium. This graph provides evidence that the levels can contain different numbers of electrons before they become full.



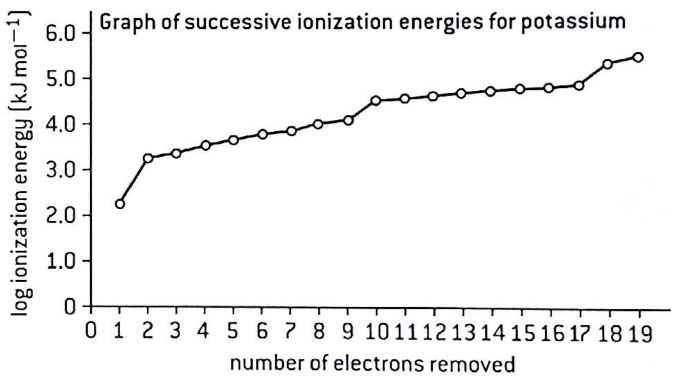
Electrons with opposite spins tend to repel each other. When orbitals of the same energy (degenerate) are filled the electrons will go singly into each orbital first before they pair up to minimize repulsion. This explains why there is a regular increase in the first ionization energies going from B to N as the three 2p orbitals each gain one electron. Then there is a slight decrease between N and O as one of the 2p orbitals gains a second electron before a regular increase again.

EVIDENCE FOR SUB-LEVELS

The graph already shown above was for the first ionization energy for the first 20 elements. Successive ionization energies for the same element can also be measured, e.g. the second ionization energy is given by:

$$X^+(g) \rightarrow X^{2+}(g) + e^-$$

As more electrons are removed the pull of the protons holds the remaining electrons more tightly so increasingly more energy is required to remove them, hence a logarithmic scale is usually used. A graph of the successive ionization energies for potassium also provides evidence of the number of electrons in each main level.



By looking to see where the first 'large jump' occurs in successive ionization energies one can determine the number of valence electrons (and hence the group in the periodic table to which the element belongs).

If the graph for first ionization energies is examined more closely then it can be seen that the graph does not increase regularly. This provides evidence that the main levels are split into sub-levels.

IONIZATION ENERGIES FROM EMISSION SPECTRA

It can be seen from the emission spectrum of hydrogen that the energy levels converge. Hydrogen contains just one electron, which will be in the lowest energy level in its ground state. If sufficient energy is supplied it can be promoted to the infinite level – that is it has been removed from the atom and the atom has become ionized to form the H^+ ion. This amount of energy corresponds to the energy it would emit if it fell back from $n = \infty$ to $n = 1$ which produces a line in the ultraviolet region of the spectrum at a wavelength of 91.2 nm. We can use this value to calculate the energy involved. Wavelength and frequency are related by the expression $c = \lambda\nu$ where c is the velocity of light. Energy and frequency are related by the expression $E = h\nu$ where h is Planck's constant and has the value 6.63×10^{-34} J s.

The energy to remove one electron $= h\nu = \dfrac{hc}{\lambda} = \dfrac{6.63 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{91.2 \times 10^{-9}\ \text{m}} = 2.18 \times 10^{-18}$ J

For one mole of electrons we need to multiply by Avogadro's constant (6.02×10^{23}) to give 1.312×10^{6} J mol^{-1} or 1312 kJ mol^{-1}. This value is exactly the same as the experimentally determined value for the first ionization energy of hydrogen.

MULTIPLE CHOICE QUESTIONS – ATOMIC STRUCTURE

1. Which of the following particles contain more neutrons than electrons?

   I. $^{1}_{1}H^{+}$ II. $^{79}_{35}Br^{-}$ III. $^{23}_{11}Na^{+}$

   A. I and II only C. II and III only

   B. I and III only D. I, II and III

2. Which one of the following sets represents a pair of isotopes?

   A. $^{31}_{15}P$ and $^{32}_{15}P$ C. Diamond and C_{60}

   B. $^{24}_{12}Mg$ and $^{24}_{12}Mg^{2+}$ D. $^{40}_{18}Ar$ and $^{40}_{20}Ca$

3. Which species contains 16 protons, 17 neutrons and 18 electrons?

   A. $^{32}S^{-}$ C. $^{34}S^{-}$

   B. $^{33}S^{2-}$ D. $^{35}S^{2-}$

4. Which quantities are the same for all atoms of chlorine?

   I. Number of protons

   II. Number of electrons

   III. Number of neutrons

   A. I and II only C. II and III only

   B. I and III only D. I, II and III

5. A sample of zinc has the following composition:

Isotope	% abundance
^{64}Zn	55
^{66}Zn	40
^{68}Zn	5

   What is the relative atomic mass of the zinc in this sample?

   A. 64.5 C. 65.9

   B. 65.0 D. 66.4

6. In the electromagnetic spectrum, which will have the shortest wavelength **and** the greatest energy?

	Shortest wavelength	Greatest energy
A.	ultraviolet	ultraviolet
B.	infrared	infrared
C.	ultraviolet	infrared
D.	infrared	ultraviolet

7. Which electronic transition in a hydrogen atom releases the most energy?

   A. $n = 1 \rightarrow n = 2$

   B. $n = 7 \rightarrow n = 6$

   C. $n = 6 \rightarrow n = 7$

   D. $n = 2 \rightarrow n = 1$

8. Which shows the sub-levels in order of **increasing** energy in the fourth energy level of an atom?

   A. $f < d < p < s$

   B. $p < d < f < s$

   C. $d < f < p < s$

   D. $s < p < d < f$

9. What is the electron configuration of copper?

   A. $[Ar]4s^2 3d^9$ C. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

   B. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ D. $[Ar]3d^9$

10. How many unpaired electrons are present in an atom of sulfur in its ground state?

   A. 1 C. 4

   B. 2 D. 6

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11. Which is the correct definition for the second ionization energy of carbon?

   A. $C(s) \rightarrow C(s) + 2e^-$ C. $C^+(s) \rightarrow C^{2+}(s) + 2e^-$

   B. $C(g) \rightarrow C(g) + 2e^-$ D. $C^+(g) \rightarrow C^{2+}(g) + 2e^-$

12. The first five ionization energies, in kJ mol^{-1}, for a certain element are 577, 1980, 2960, 6190 and 8700 respectively. Which group in the periodic table does this element belong to?

   A. 1 C. 3

   B. 2 D. 4

13. Which transition in the hydrogen emission spectrum corresponds to the first ionization energy of hydrogen?

   A. $n = \infty \rightarrow n = 1$ C. $n = \infty \rightarrow n = 2$

   B. $n = 2 \rightarrow n = 1$ D. $n = 4 \rightarrow n = 2$

14. Which ionization requires the most energy?

   A. $B(g) \rightarrow B^+(g) + e^-$ C. $N(g) \rightarrow N^+(g) + e^-$

   B. $C(g) \rightarrow C^+(g) + e^-$ D. $O(g) \rightarrow O^+(g) + e^-$

15. All of the following factors affect the value of the ionization energy of an atom **except** the:

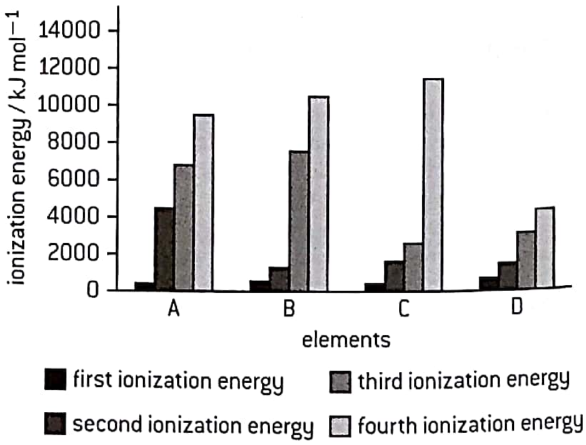
   A. mass of the atom

   B. charge on the nucleus

   C. size of the atom

   D. main energy level from which the electron is removed

16. The graph below shows the first four ionization energies of four elements A, B, C and D (the letters are not their chemical symbols). Which element is magnesium?



SHORT ANSWER QUESTIONS – ATOMIC STRUCTURE

1. a) Define the term relative atomic mass, A_r. [1]

   b) The relative atomic mass of naturally occurring chlorine is 35.45. Calculate the abundances of ^{35}Cl and ^{37}Cl in naturally occurring chlorine. [2]

   c) (i) State the electron configuration of chlorine. [1]

   (ii) State the electron configuration for a chloride ion, Cl^-. [1]

   d) Explain how ^{35}Cl and ^{37}Cl differ in their chemical properties. [2]

2. a) Explain why the relative atomic mass of cobalt is greater than the relative atomic mass of nickel, even though the atomic number of nickel is greater than the atomic number of cobalt. [1]

   b) Deduce the numbers of protons and electrons in the Co^{2+} ion. [1]

   c) (i) Deduce the electron configuration of the Co atom. [1]

   (ii) Deduce the electron configuration of the Co^{2+} ion. [1]

3. $^{99}_{43}Tc$ is a radioactive isotope of technetium.

   a) (i) Define the term isotope. [1]

   (ii) Determine the number of neutrons in one atom of technetium-99. [1]

   (iii) Technetium-99 is used as a tracer in medicine. Suggest a reason why it is potentially dangerous. [2]

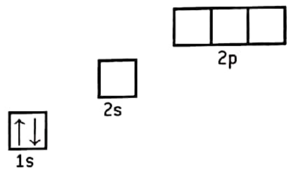
   b) Carbon in living organisms consists of two isotopes, ^{12}C and ^{14}C, in a fixed ratio. This ratio remains constant in a living organism as the carbon is constantly being replaced through photosynthesis. Once an organism dies the ^{14}C slowly decays to ^{14}N with a half-life of 5300 years.

   (i) Identify the number of protons, neutrons and electrons in carbon-12 and in carbon-14. [2]

   (ii) Suggest the identity of the particle that is emitted when an atom of ^{14}C is converted into an atom of ^{14}N. [1]

   (iii) Discuss how the decay of carbon-14 can be used in carbon dating. [2]

4. Annotate the 2s and 2p boxes, using ↑ or ↓ to represent a spinning electron, to complete the electron configuration for an oxygen atom. [1]



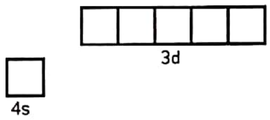
5. Draw and label an energy level diagram for the hydrogen atom. In your diagram show how the series of lines in the ultraviolet and visible regions of its emission spectrum are produced, clearly labelling each series. [4]

6. The electron configuration of chromium can be expressed as $[Ar]4s^x3d^y$.

   (i) Explain what the square brackets around argon, [Ar], represent. [1]

   (ii) State the values of x and y. [1]

   (iii) Annotate the diagram below showing the 4s and 3d orbitals for a chromium atom using an arrow, ↑ or ↓, to represent a spinning electron. [1]



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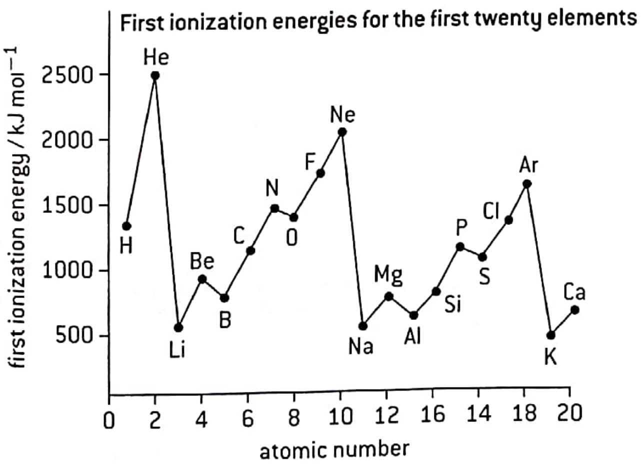
7. The graph below shows the first ionization energy plotted against atomic number for the first 20 elements.



   a) Define the term *first ionization energy*. [2]

   b) Explain the following:

   (i) why there is a general increase in the value for the first ionization energy across period 2 from Li to Ne [2]

   (ii) why the first ionization energy of neon is higher than that of sodium [2]

   (iii) why the first ionization energy of beryllium is higher than that of boron [2]

   (iv) why the first ionization energy of sulfur is lower than that of phosphorus. [2]

   c) Predict how the graph for the second ionization energy plotted against atomic number for the first 20 elements differs from the graph shown above. [3]

8. Electrons are much too small to ever be 'seen'. Discuss the evidence that electrons exist in fixed energy levels and that these levels can be split into sub-levels. [5]

9. The first ionization energy of hydrogen is 1312 kJ mol^{-1}. Determine the frequency and wavelength of the convergence line in the ultraviolet emission spectrum of hydrogen. (Use information given in Sections 1 and 2 of the IB data booklet.) [3]