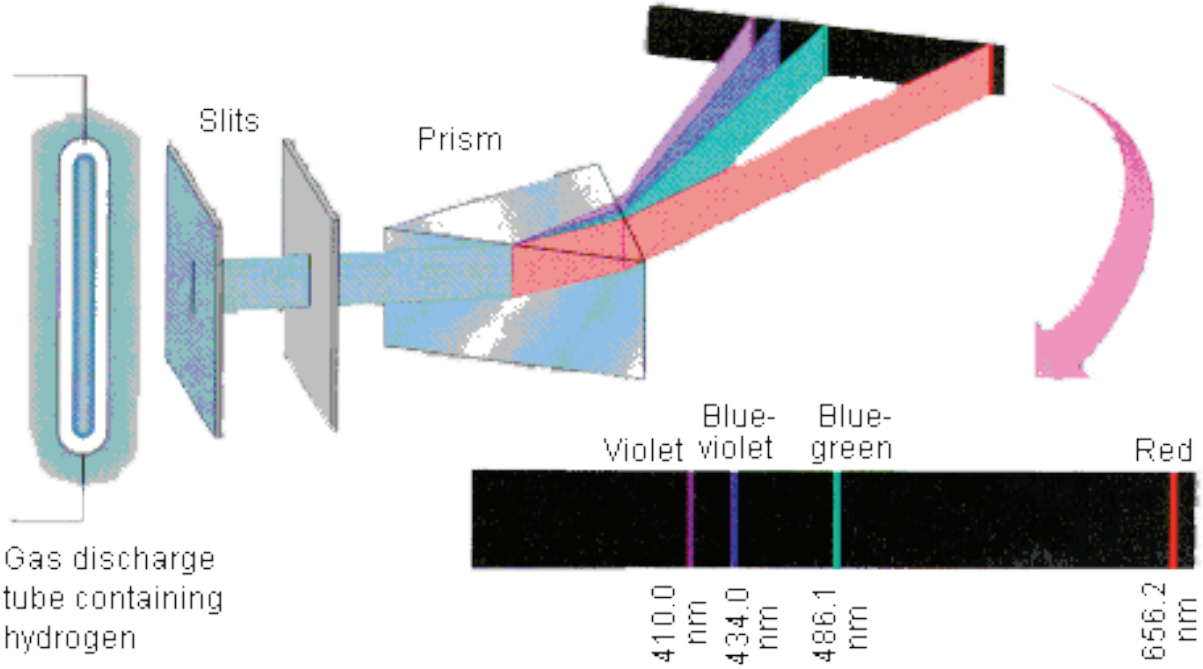
Unit 1
Inorganic Chemistry

Part 1

Electromagnetic Spectra
Electron Configuration
Spectroscopy



Learning Outcomes
Pupil Notes
Practice Questions
Answers to Practice Questions

Part 1. ELECTRONIC STRUCTURE

Electromagnetic Spectra & associated calculations

1.1 ***Electromagnetic radiation*** *may be described in terms of waves*

1.2 *Electromagnetic radiation can be specified by its wavelength (λ) and by its frequency(ν)*

1.3 *The* ***electromagnetic spectrum*** *is the range of frequencies or wavelengths of electromagnetic radiation*

1.4 *The unit of measurement of* ***wavelength*** *is the metre or an appropriate sub multiple.*

The unit of measurement of ***frequency*** *is the reciprocal of time in seconds (s^{-1}) and is called the Herz (Hz)*

1.5 *The* ***velocity*** *of electromagnetic radiation is constant and has a value of 3 x 10^8 ms^{-1}*

1.6 *Velocity, frequency and wavelength are related in the expression*

$$c = \lambda \nu$$

1.7 *Under certain circumstances electromagnetic radiation may be regarded as a stream of particles, rather than waves. These particles are known as* ***photons***

1.8 *The energy (E) of radiation, and the energy associated with photons, is related to frequency by planck's constant (h) in the expressions:*

$E = h\nu$ *for one photon*
$E = Lh\nu$ *for a mole of photons*

where L is Avogadro's Constant

Electronic Configuration & the Periodic Table

1.9 *The emission spectrum of hydrogen provides evidence of energy levels*

1.10 *Quantum theory states that matter can only emit or absorb energy in small fixed amounts (called quanta)*

1.11 *The energy of a bound electron in an atom is* ***quantised***

1.12 *An atom can be considered as emitting a photon of light energy when an electron moves from a higher energy level to a lower energy level*

1.13 *Each line of the* ***emission spectrum*** *represents radiation of a specific wavelength or frequency from which the difference in energy between the levels can be calculated*

1.14 *Emission spectra of elements with more than one electron provide evidence of **sublevels** within each principal energy above the first*

1.15 *The **principal energy levels** correspond to the principle shells. The second and subsequent shells contain subshells which correspond to energy sublevels*

1.16 *Subshells can be labelled s , p , d and f*

1.17 *The type of **subshells** within each principal shell is as follows*

First shell	*s subshell only*
Second shell	*s and p subshells*
Third shell	*s , p and d subshells*
Fourth shell	*s , p , d and f subshells*
other shells	*s , p , d and f subshells*

1.18 ***Heisenberg's uncertainty principle** states that it is impossible to define with absolute precision, simultaneously, both the position and the momentum of an electron*

1.19 *Electrons, like photons, display both wave and particle like properties. Treating bound electrons in atoms as waves leads to regions of **high probability** of finding the electrons. These regions are called atomic orbitals*

1.20 *There are four types of **orbitals**, namely s , p , d and f , each with a characteristic shape or set of shapes. Diagrams of the shapes of s and p orbitals can be drawn and recognised. Diagrams of d orbitals can be recognised*

1.21 *An orbital holds a maximum of two electrons as required by the **Pauli exclusion principle***

1.22 *The number of orbitals in each subshell is as follows:*

s subshell	*one s orbital*
p subshell	*three p orbitals*
d subshell	*five d orbitals*
f subshell	*seven f orbitals*

1.23 *In an isolated atom the orbitals within each shell are **degenerate***

1.24 *The **Aufbau principle** states that orbitals are filled in order of increasing energy*

1.25 *The relative energies corresponding to each orbital can be represented diagrammatically for the first four shells of a multi-electron atom*

1.26 ***Hund's Rule** states that when degenerate orbitals are available, electrons fill each singly keeping their spins parallel before spin pairing starts*

1.27 *Electron configurations using **spectroscopic notation** and **orbital box notation** can be written for elements of atomic numbers 1 to 36*

1.28 *The Periodic Table can be subdivided into four **blocks** (s, p, d and f) corresponding to the outer electron configurations of the elements in these blocks*

1.29 *The variation in first ionisation energy with increasing atomic number for the first 36 elements can be explained in terms of the relative **stability of different electron configuration**s and so provides evidence for these electron configurations*

1.30 *The relative values of first, second and subsequent ionisation energies can be explained in terms of the **stabilities of the electron configurations** from which the electrons are being removed*

Spectroscopy

1.31 *Atomic emission spectroscopy and atomic absorption spectroscopy involve transitions between electronic energy levels in atoms. Generally the energy differences correspond to the visible region in the electromagnetic spectrum, i.e. to the approximate wavelength range of 400 - 700 nm. Some applications use the ultra-violet region (approximately 200 - 400 nm)*

1.32 *In **emission spectroscopy** the sample is energised by heat or electricity causing electrons to be promoted to higher energy levels. The wavelength of the radiation emitted as electrons fall back to lower energy levels is measured*

1.33 *In **atomic absorption** spectroscopy, electromagnestic radiation is directed at the sample. Radiation is absorbed as electrons are promoted to higher energy levels. The wavelength of the absorbed radiation is measured.*

1.34 *Each **element** provides a **characteristic spectrum** which can be used to identify an element.*

1.35 *The amount of species can be **determined quantitatively** if the intensity of emitted or transmitted radiation is measured.*

PART 1

Electromagnetic spectrum and associated calculations

The work of Rutherford and others in the early part of the twentieth century resulted in the model of the atom in which negative electrons are arranged around a positive central nucleus.

It is the electrons, rather than the nucleus, which take part in chemical reactions and so it is necessary to understand the electronic structure of an atom to explain its chemical properties.

The key to understanding electronic structure and how electrons behave in an atom comes from the study of electromagnetic radiation.
In 1864 James Maxwell developed a theory describing all forms of radiation in terms of oscillating or wave-like electric and magnetic fields in space. Hence radiation such as light, microwaves, X-rays, television and radio signals is collectively called electromagnetic radiation.

Electromagnetic radiation may be described in terms of waves of varying length between 10^{-14} m and 10^{+4} m that travel in a vacuum at a constant velocity of approximately 3×10^8 m s^{-1}.

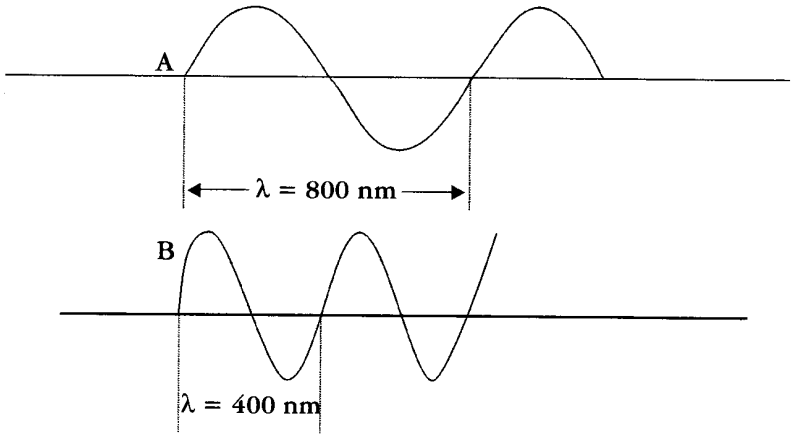
Two simple waveforms are shown in Figure 1.

The **wavelength** of a wave is the distance between adjacent wavecrests or high points (or successive troughs or low points). This distance is measured in metres (m) or an appropriate sub-multiple such as nanometres (nm). A nanometre is 10^{-9} metres. The symbol for wavelength is the Greek letter λ (lambda).

Waves can also be specified by their **frequency**, symbol ν (Greek letter nu). For a wave travelling through some point in space the frequency is the rate of advance of any one wavecrest or the number of complete waves passing the point per unit time. The unit of measurement of frequency is the reciprocal of time in seconds (s^{-1}) and this unit is called the hertz (Hz).

Another unit of frequency often used by spectroscopists is the **wavenumber**, which is the reciprocal of the wavelength ($1/\lambda$). The wavenumber is the number of waves in one unit length of radiation, i.e. the number of waves per metre, and is measured in m^{-1}. The symbol for wavenumber is $\bar{\nu}$.

Figure 1



In Figure 1 the wavelength of wave A is twice that of wave B. Since both waves are travelling at the same speed, wave B completes two vibrations in the time wave A completes one. Thus the frequency of wave A is half that of wave B.

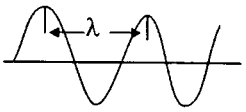
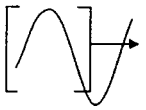
The relationship between wavelength, frequency and velocity is:

velocity = wavelength × frequency
(m s^{-1}) (m) (s^{-1})

$c = \lambda \times \nu$

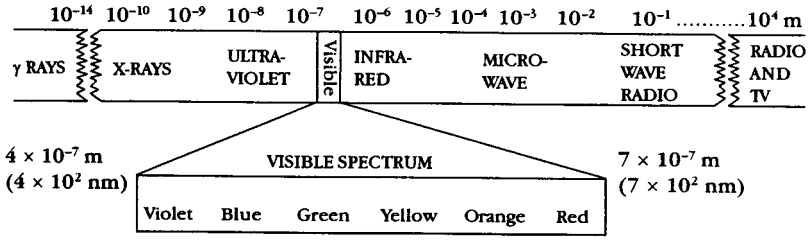
The above relationships are summarised in Table 1.

Table 1

Quantity	Symbol	Units	Description
Wavelength	λ (lambda)	Metres (m)	Distance between adjacent wave crests 
Velocity	*c*	m s^{-1}	Rate of advance of any one wave crest 
Frequency	ν (nu)	Hertz (Hz)	The number of wavelengths or cycles passing a point in 1 second 1 cycle per second = 1 Hz $\nu = c/\lambda$ or $\nu \propto 1/\lambda$ (for all electromagnetic radiation *c* is constant, 3×10^8 m s^{-1})
Wavenumber	$\bar{\nu}$	Waves per metre (m^{-1}) but many spectrometers are calibrated in waves per cm (cm^{-1}).	Number of waves in 1 metre or in 1 centimetre of radiation Often used in place of frequency $\bar{\nu} = \frac{1}{\lambda}$

The complete electromagnetic spectrum is shown in Figure 2.

Figure 2



From Figure 2 it can be seen that **visible light**, which is that part of the electromagnetic spectrum that excites the nerve cells of the human eye, constitutes only a very small part of the total spectrum. When electromagnetic radiation interacts with matter, there is a transfer of energy from the radiation to the receiving body. Sitting out in the sun to get a sun-tan or cooking with microwave ovens are good examples of this.

Energy can only be transferred in small bundles or packets, which are called **quanta**. These quanta of energy are of a definite size and therefore the transfer of energy can only occur in definite amounts. Because of this, it is necessary to consider that electromagnetic radiation is not only made up of waves, but can also be regarded as a stream of very small particles. These small particles are known as **photons**.

Electromagnetic radiation is said to exhibit wave-particle duality, i.e. it may be considered to be a stream of photons with wave properties, the energy of the radiation being related to the wavelength or frequency of the radiation by the equation:

for a photon,

$E = h\nu$ (where h is Planck's constant = 6.63×10^{-34} J s)

The relationship between the energy transferred by the emission or absorption of **one mole of photons** and the **frequency** of the radiation can be calculated as follows:

for one mole of photons,

$$E = Lh\nu \quad \text{or} \quad E = \frac{Lhc}{\lambda} \quad \text{or} \quad E = Lhc\,\bar{v}$$

where $\bar{v}$ is the wavenumber and L is the Avogadro constant.

Using these relationships, the energy of radiation is calculated in J mol^{-1}. Multiplying by 10^{-3} gives the energy in the more common unit kJ mol^{-1}.

Questions

1. Calculate the energy, in kJ mol^{-1}, corresponding to
   (a) a wavenumber of 1000 cm^{-1}
   (b) a wavelength of 620 nm.

2. The bond enthalpy of a Cl–Cl bond is 243 kJ mol^{-1}. Calculate the maximum wavelength of light that would break one mole of these bonds to form individual chlorine atoms.

Electronic configuration and the Periodic Table

If light from a tungsten filament lamp is passed through a glass prism, the light is split into the colours of the rainbow. This is known as a continuous spectrum as it consists of a continuous range of wavelengths. In contrast, if sufficient electrical energy is passed into a tube of gas at low pressure, the gas atoms or molecules are said to become excited and can emit electromagnetic radiation, e.g. light. When this is passed through a glass prism a line spectrum is obtained. A line spectrum shows up a characteristic number of discrete wavelengths. Glowing neon, for example, appears red to our eyes but when this red light is passed through a prism the light is shown to be composed of a few different colours and the spectrum consists of lines corresponding to the wavelengths of these different colours (see Figure 3).

Spectra like this are known as **emission spectra** since light **emitted** by the gases is analysed by passing it through a prism.

In modern spectrometers the light is separated into its different wavelengths using a diffraction grating instead of a prism. The light firstly passes through a series of narrow slits producing a fine beam or line of light before passing through the diffraction grating, and the emitted light is observed as a line spectrum, as shown in Figure 3.

Figure 3: *The emission spectrum of neon*

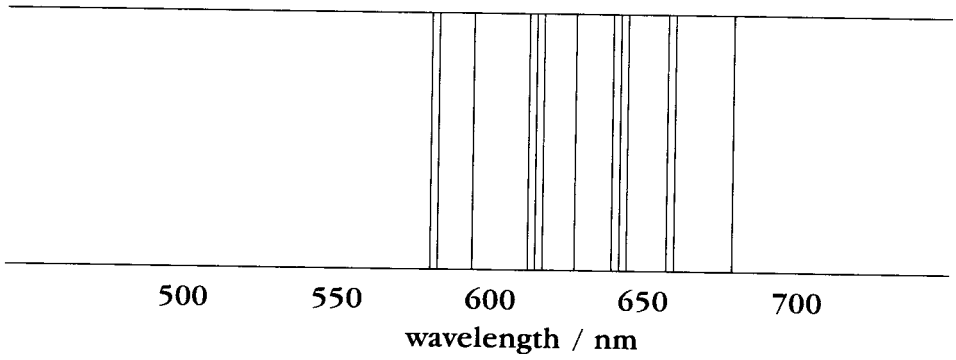
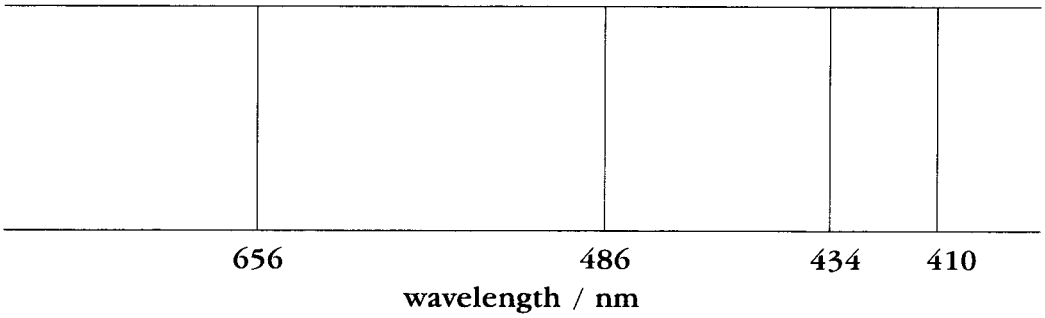


Figure 3 shows that the red light seen from glowing neon is actually made up of light of different wavelengths mainly from the red end of the visible spectrum. Examination of the emission spectrum of hydrogen shows that this consists of a number of lines of precise frequency, corresponding to precise emissions of energy (Figure 4).

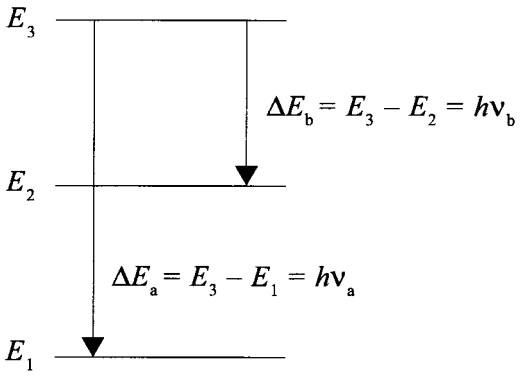
Figure 4: *The emission spectrum of hydrogen in the visible range (Balmer series)*



These lines correspond to well-defined energy changes and by using the relationship $E = Lh\nu$ the magnitude of these energy changes can be calculated.

Atoms are said to become **excited** when they absorb energy and emission spectra arise from the movement of electrons from a higher to a lower energy when the excited atom returns to its 'ground state'. The frequency of the line in the emission spectrum corresponds to the **difference in energy** between the two electronic energy levels. This is shown in Figure 5.

Figure 5



It follows that since the differences in energy between the levels are fixed, the energy levels themselves must be fixed. Thus, since the electrons must occupy these energy levels, the electrons themselves must have fixed energies. In other words the energies of electrons are **quantised** and an atom can be considered to be emitting a photon of light energy when an electron 'falls back' from a higher energy level to a lower energy level. Each line in the emission spectrum represents radiation of a specific wavelength or frequency from which these differences in energy can be calculated.

Although a hydrogen atom has only one electron, the emission spectrum of hydrogen has different series of lines in different parts of the electromagnetic spectrum. The differences in energy and hence the part of the electromagnetic spectrum in which the lines show up depend on the energy level to which the 'excited' electron falls back.

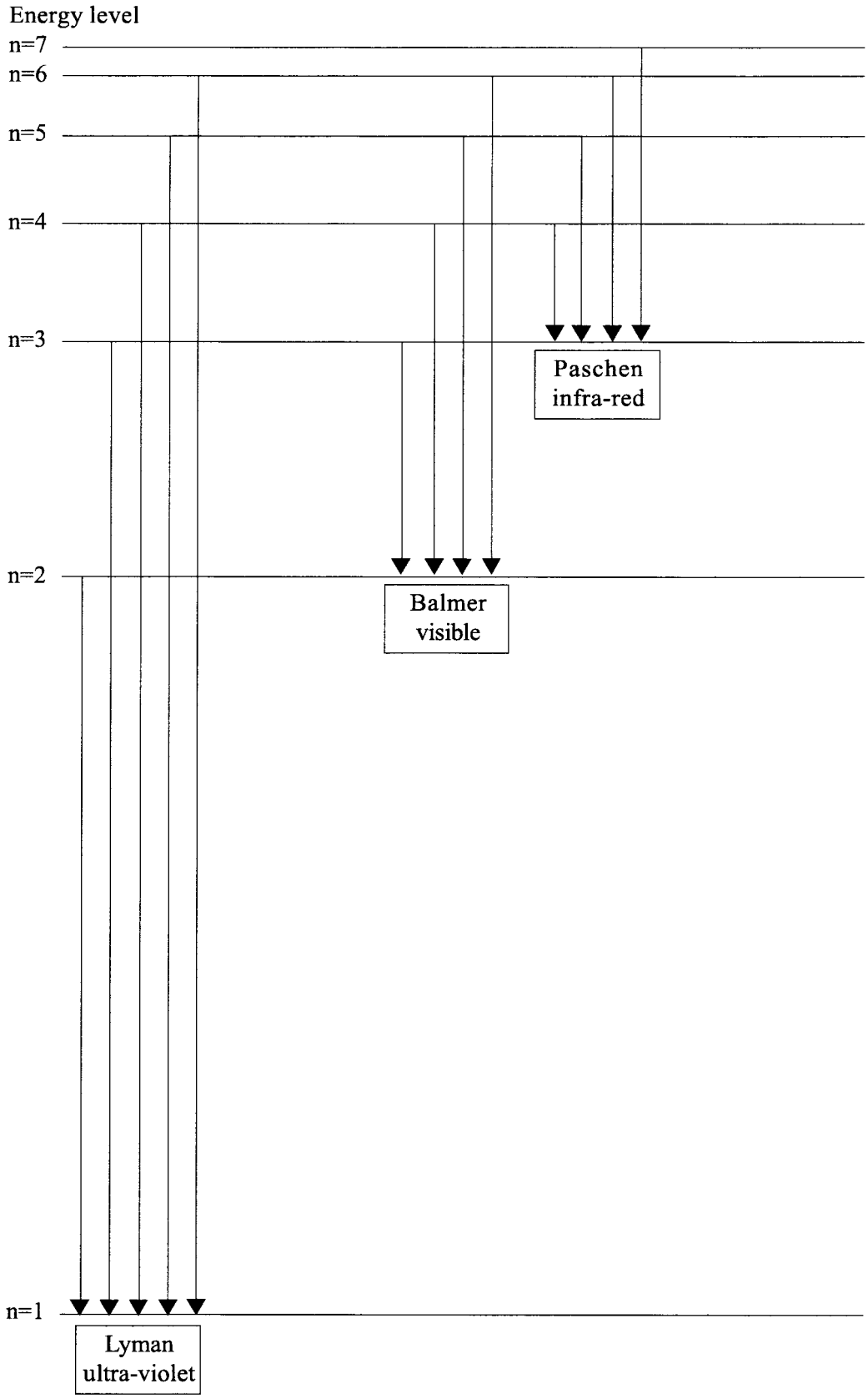
The full emission spectrum of hydrogen consists of one series of lines in the ultra-violet region, one series of lines in the visible region and several in the infra-red region. These series of lines are named after the scientists who discovered them (Table 2).

Table 2

Name of series	**Energy level to which excited electron falls**	**Part of the electromagnetic spectrum**
Lyman	$n = 1$	Ultra-violet
Balmer	$n = 2$	Visible
Paschen	$n = 3$	Infra-red
Brackett	$n = 4$	Infra-red
Pfund	$n = 5$	Infra-red

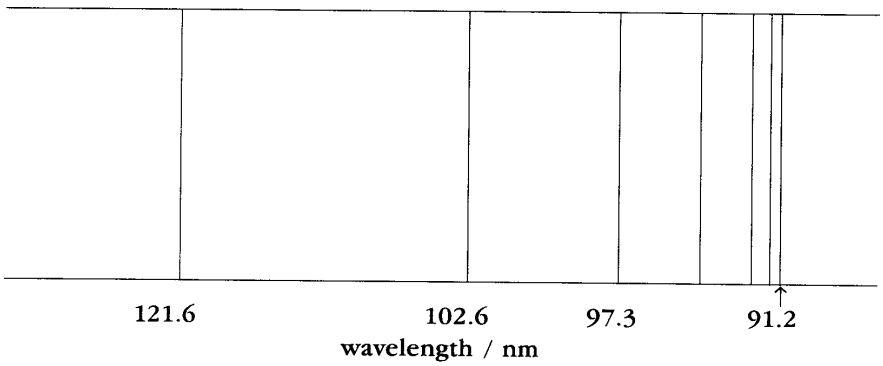
The electronic transitions that give rise to the Lyman, Balmer and Paschen series are shown in Figure 6.

Figure 6


Energy level
n=7
n=6
n=5
n=4
n=3
n=2
n=1
Paschen infra-red
Balmer visible
Lyman ultra-violet

The lines of the Lyman series correspond to changes in electronic energy levels from higher energy levels down to the $n = 1$ ground state.

Figure 7: *The Lyman series in the emission spectrum of hydrogen.*



It can be seen that as the energy increases, the energy levels become closer together until they converge. The difference in energy between the ground state and the convergence limit corresponds to the energy required for the electron to break away from the atom. This is its ionisation energy.

Question

3. Calculate the ionisation energy for hydrogen if the wavelength of the line at the convergence limit is 91.2 nm.

Much of the work required to interpret and explain emission spectra was done by the Danish scientist Niels Bohr, who developed a model for the electronic structure of atoms. The equations derived from Bohr's model were used successfully to calculate values for the radius of the hydrogen atom and its energy levels, including its ionisation energy.

The main points of Bohr's theory can be summarised as follows:
- the electron in a hydrogen atom exists only in certain definite energy levels
- a photon of light is emitted or absorbed when the electron changes from one energy level to another
- the energy of the photon is equal to the difference between the two energy levels (ΔE), which is related to the frequency by the equation $\Delta E = h\nu$.

These definite quantities of energy possessed by electrons are known as **quanta**.

Despite its success with hydrogen, Bohr's theory could not be used to explain the behaviour of atoms with more than one electron and a new science known as **quantum mechanics** was formulated.

Quantum mechanics considers electrons as waves as well as particles and, although it is highly mathematical, the results of the theory are fairly straightforward.

An electron can only possess certain fixed amounts of energy known as quanta. The energy of the electron can be defined in terms of **quantum numbers**.

Electrons in atoms are arranged in a series of **shells**. Each shell is described by a number, known as the **principal quantum number, *n***. The shells are numbered starting with the shell nearest the nucleus and working outwards. For the first shell $n = 1$, for the second shell $n = 2$ and so on. The higher the value of n, the higher the potential energy associated with the shell and the further from the nucleus the electron is likely to be found. The hydrogen atom has only one electron and its spectrum is fairly simple to interpret. Other elements are more complex and close examination of their spectra under high resolution shows that the lines are often not single lines but are split into doublets or triplets, etc. This suggests that the electron shells are further subdivided into **subshells.** These subshells are described by the letters s, p, d and f.

Calculations using quantum mechanics show that all shells have an s subshell and all the shells except the first have a p subshell. Likewise all the shells except the first and second have a d subshell and so on, as shown in Table 3. The subshells within a shell have different energies, increasing s → p → d → f.

Table 3

Shell	Subshells
1	1s
2	2s, 2p
3	3s, 3p, 3d
4	4s, 4p, 4d, 4f

Each type of subshell (s, p, d and f) contains one or more **energy levels** or **orbitals**. These are defined by another quantum number, the angular momentum quantum number *l*. This is related to the shape of the orbital and is given the values 0, 1, 2, …, (*n* – 1) as shown in Table 4.

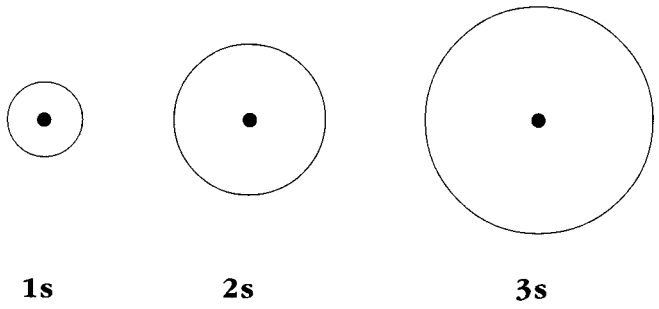
Table 4

Value of *n*	**Value of *l***	**Energy level**
1	0	1s
2	0 1	2s 2p
3	0 1 2	3s 3p 3d
4	0 1 2 3	4s 4p 4d 4f

Like photons, electrons can be considered to behave as particles and also as waves. Their behaviour is governed by **Heisenberg's uncertainty principle**, which states that 'it is impossible to define with absolute precision both the position and the momentum of an electron at the same instant'. This means that it is not possible to define a point in space where the electron is certain to be found and therefore it is necessary to define regions in space where the probability of finding an electron is high. These regions of high probability are called **atomic orbitals.**

An atomic orbital is generally considered to be the volume in space where the probability of finding an electron is greater than 90%. The overall size of each orbital is governed by the value of *n*, the principal quantum number, while the actual shape of the orbital is given by the value of *l*, the angular momentum quantum number. All s orbitals ($l = 0$) are spherical in shape, the diameter of the sphere increasing as *n* increases (Figure 8).

Figure 8



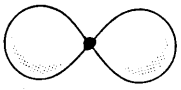
The probability of finding the s electron outwith the orbital is relatively low but not zero. For p, d and f orbitals, it is necessary to define a further quantum number, m_l, known as the magnetic quantum number, and this gives the multiplicity and spatial orientation of the orbital. Table 5 shows how m_l can have any integral value between $-l$ and $+l$.

Table 5

Value of *n*	**Value of *l***	**Value of m_l**	**Type of atomic orbital**
1	0	0	1s
2	0 1	0 –1, 0, +1	2s 2p
3	0 1 2	0 –1, 0, +1 –2, –1, 0, +1, +2	3s 3p 3d

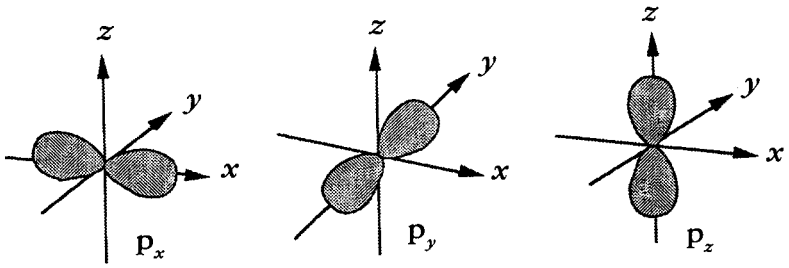
The p orbitals, unlike the s orbitals, are not spherical in shape but have two lobes and are usually described as being dumb-bell in shape, as shown in Figure 9.

Figure 9



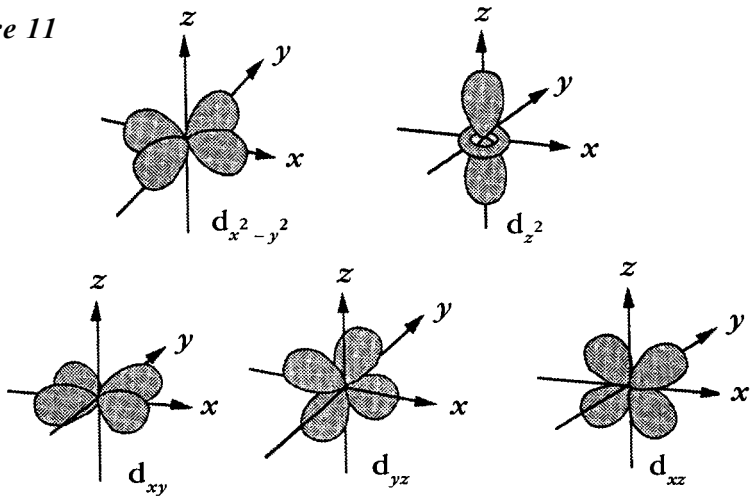
Since for the p orbitals $l = 1$ there are three possible values of m_l, namely –1, 0 and +1, there will be three p orbitals of equal energy (orbitals of equal energy are said to be **degenerate**). Because they have different values for m_l, they will have different orientations in space – in fact, they are arranged along the three mutually perpendicular principal axes x, y and z, as in Figure 10.

Figure 10



Likewise with the d orbitals ($l = 2$), there are five possible values of m_l (–2, –1, 0, +1, +2) and so when $n \geq 3$, there are five degenerate d orbitals. These have the individual names and shapes shown in Figure 11.

Figure 11



Each type of subshell contains one or more orbitals and the number of orbitals in a subshell is summarised in Table 6.

Table 6

Subshell	Number of orbitals
s	1
p	3
d	5
f	7

The three quantum numbers also allow us to define the orbital for an electron, as shown in Table 7.

Table 7

Type of quantum number	Symbol	Value	Main orbital property described
Principal	n	1, 2, 3, …	Orbital size/energy
Angular momentum	l	0, 1, 2, …(n – 1)	Orbital shape
Magnetic	m_l	$-l$, …0, …$+l$	Multiplicity and orbital orientation

In about 1920 it was realised that an electron behaves as if it has a spin, just as the planet earth has a spin. To describe an electron in a many-electron atom completely a fourth quantum number is therefore needed, namely the spin quantum number, m_S.

The spin quantum number can have one of only two values, +½ and –½. Thus, given values of the four quantum numbers, n, l, m_l and m_S, it is possible to define any single electron in an atom in terms of its energy and likely location.

In 1925, Wolfgang Pauli proposed what is now known as the **Pauli exclusion principle**: 'no two electrons in any one atom can have the same set of four quantum numbers'. This leads to two important conclusions:
- the maximum number of electrons in any atomic orbital is two
- if there are two electrons in an orbital, then they must have opposite spins (rather than parallel spins).

The number of orbitals and electrons in each subshell is given in Table 8.

Table 8

Type of subshell	Number of orbitals	Number of electrons
s	One s orbital	2
p	Three p orbitals	6
d	Five d orbitals	10
f	Seven f orbitals	14

In an **isolated** atom the orbitals within each subshell are degenerate. For example, the three different 2p orbitals ($2p_x$, $2p_y$ and $2p_z$) in an atom have equal energy.

Electronic configurations

There are two main ways in which the electronic configurations of atoms can be expressed.

Consider a hydrogen atom. It has one electron, which will occupy the orbital of lowest energy which is, of course, the 1s orbital. This can be expressed as $1s^1$, i.e. one electron in the 1s orbital.

Helium will have both its electrons in the 1s orbital and this can be written as $1s^2$.

The other way in which the electronic configuration can be expressed is by using a notation in which an orbital is represented by a box and each electron by an arrow. Using this notation the electronic configuration of hydrogen can be represented as

H $\underset{1s}{\boxed{\uparrow}}$ and helium can be represented as He $\underset{1s}{\boxed{\uparrow\downarrow}}$

One arrow pointing upwards and the other pointing downwards shows that the two electrons in the orbital have opposing spins, in keeping with the Pauli exclusion principle (Table 9).

Table 9

1st electron	**2nd electron**
n = 1 (first shell)	n = 1 (first shell)
l = 0 (s orbital)	l = 0 (s orbital)
$m_l = 0$	$m_l = 0$
$m_S = +½$	$m_S = -½$

If the electronic configuration of helium were to be represented with both arrows pointing in the same direction, i.e. parallel spins, this would be incorrect since it would not conform to the Pauli exclusion principle because

the two electrons would have the same values for all four quantum numbers (Table 10).

Table 10

1st electron	2nd electron
n = 1 (first shell)	n = 1 (first shell)
l = 0 (s orbital)	l = 0 (s orbital)
$m_l = 0$	$m_l = 0$
$m_s = +½$	$m_s = +½$

Before we can write the electronic configuration for multi-electron atoms, it is necessary to know the order in which the various orbitals are filled. The **aufbau principle** states that the orbitals of the lowest energy levels are always filled first. Thus, provided the relative energies of the orbitals are known, the electronic configuration can be deduced.

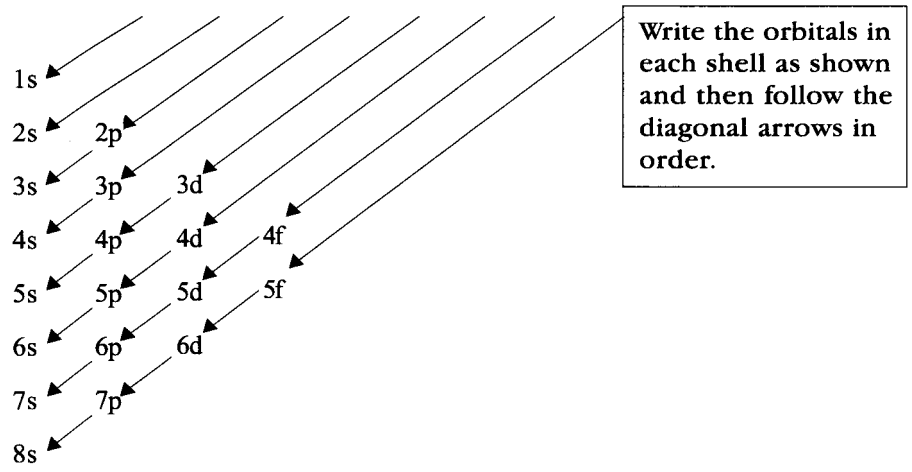
Spectroscopic data give the following arrangement of the energies of the orbitals:

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

increasing energy

This may seem very complicated and another method of working out the increasing relative energies is given in Figure 12. Another useful method is to remember that electrons are assigned to orbitals in order of increasing (n + l). For two subshells with equal values of (n + l), electrons are assigned first to the orbital with lower n.

Figure 12



When the situation is reached where more than one degenerate orbital is available for the electrons, it is necessary to use **Hund's rule of maximum multiplicity**, which states that 'when electrons occupy degenerate orbitals, the electrons fill each orbital singly, keeping their spins parallel before spin pairing occurs'. For example, the electronic configuration of a nitrogen atom using spectroscopic notation is written as follows:

$1s^2\ 2s^2\ 2p^3$

and using orbital box notation to show electron spins:

(Compare these electronic configurations with the electron arrangement 2, 5 given in the Data Booklet).

Question

4. Using both spectroscopic and orbital box notations write down the electronic configurations for:

(a) lithium
(b) oxygen
(c) sodium
(d) aluminium
(e) phosphorus
(f) argon
(g) calcium
(h) Li^+
(i) F^-
(j) Mg^{2+}
(k) S^{2-}
(l) K^+

Remember that the electronic configuration should have the same number of electrons in each shell as the corresponding electron arrangement in the Data Booklet.

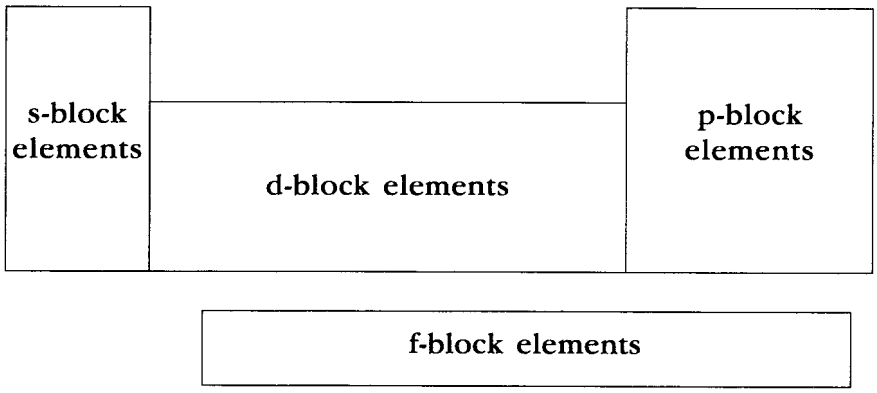
The electronic configuration for neon, Ne, is $1s^2\ 2s^2\ 2p^6$ and that of argon, Ar, is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

It is often acceptable to write the electronic configurations of other species in a shortened version, taking account of the electronic configuration of the preceding noble gas. For example, the electronic configuration for sodium can be written as [Ne] $3s^1$, where [Ne] represents $1s^2\ 2s^2\ 2p^6$, and that of calcium can be written as [Ar] $4s^2$ where [Ar] represents $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

The Periodic Table can be subdivided into four blocks (s, p, d and f) corresponding to the outer electronic configurations of the elements within these blocks.

All the Group 1 elements (the alkali metals) have electronic configurations that end in s^1 and all the Group 2 elements (the alkaline-earth metals) have electronic configurations that end in s^2. Because the elements in Groups 1 and 2 have their outermost electrons in s orbitals, these elements are known as s-block elements. The elements in Groups 3, 4, 5, 6, 7 and 0 are known as the p-block elements as their outermost electrons are in p subshells. The elements where d orbitals are being filled are known as the d-block elements and those in which f orbitals are being filled are the f-block elements. This is shown in Figure 13.

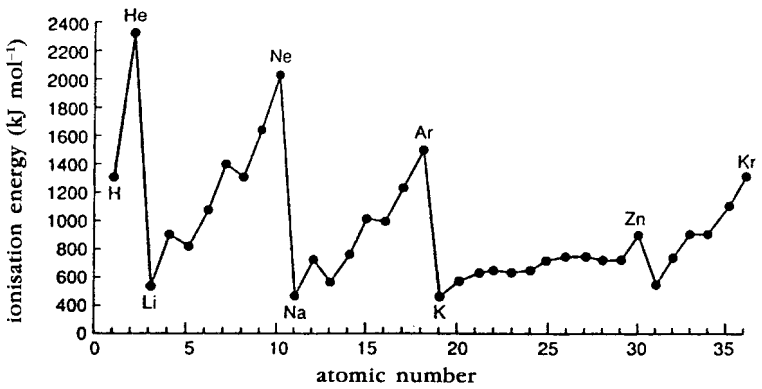
Figure 13



Ionisation energy

Figure 14 shows how the first ionisation energy varies with atomic number for elements 1 to 36.

Figure 14



The highest points are the noble gases (Group 0) and the lowest points are those of the alkali metals (Group 1).

The first ionisation energy for an element E is the energy required to remove one mole of electrons from one mole of atoms in the gas state, as depicted in the equation

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

There are three main factors that affect the ionisation energies of an element:
- the atomic size – the greater the atomic radius, the further the outermost electron is from the attraction of the positive nucleus and therefore the lower will be the ionisation energy
- the nuclear charge – the more protons in the nucleus, the harder it will be to remove an electron and consequently the greater will be the ionisation energy
- the screening effect – the inner electrons shield the outermost electrons from the attraction of the positively charged nucleus and so the more electron shells between the outer electron and the nucleus, the lower will be the ionisation energy.

Looking at Figure 14 there are two obvious patterns. In general,
- the ionisation energy increases across a period
- the ionisation energy decreases down a group.

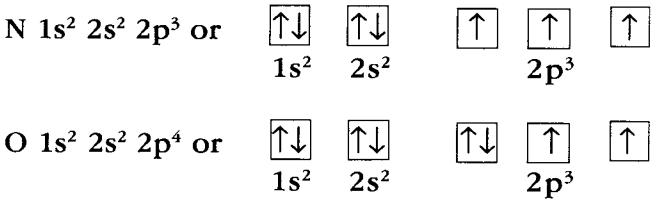
However, looking more closely, it can be seen that the first ionisation energies do not increase smoothly across a period. This irregularity is evidence for the existence of subshells within each shell. For example, the reason that the first ionisation energy of boron is lower than that of beryllium can be explained by considering their electronic configurations:

Be $1s^2\ 2s^2$
B $1s^2\ 2s^2\ 2p^1$

Accordingly, removal of the outer electron from a boron atom involves taking one electron from the 2p subshell, but with a beryllium atom this electron comes from the full 2s subshell. Since full subshells are relatively stable, it follows that the first ionisation energy of beryllium is greater than that of boron.

A similar argument can be used to explain the higher first ionisation energy of magnesium ($1s^2\ 2s^2\ 2p^6\ 3s^2$) compared to aluminium ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$).

The higher first ionisation energy of nitrogen compared to oxygen can also be explained by considering their electronic configurations:



Since half-full subshells are relatively stable and because nitrogen has a half-full subshell it has a higher ionisation energy than oxygen. A similar argument can be used to explain the higher first ionisation energy of phosphorus compared to sulphur. There will also be electron–electron repulsions between two electrons in the same orbital.

Likewise the relative values of first, second and subsequent ionisation energies can be explained in terms of the stabilities of the electronic configurations from which the electrons are removed.

For example, the sodium atom, Na, has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^1$ and the first ionisation energy of sodium is small (502 kJ mol^{-1}). The sodium ion, Na^+, has the electronic configuration of the noble gas neon, $1s^2\ 2s^2\ 2p^6$, and because this is a more stable electronic configuration, the second ionisation energy of sodium is significantly greater (4560 kJ mol^{-1}). This second electron to be removed from the sodium is in a shell much closer to the attraction of the nucleus and therefore much more energy is required to overcome this attraction.

Spectroscopy

Just as specific lines in the emission spectra of elements give information about the electronic structure of these elements, the technique of **atomic emission spectroscopy** (AES) can be used to detect the presence of these elements. Each individual element provides a characteristic spectrum that can be used to identify that particular element. Both AES and **atomic absorption spectroscopy** (AAS) involve transitions between electronic energy levels in atoms. Individual spectral lines correspond to definite electronic transitions. In general the energy difference corresponds to the

visible region of the electromagnetic spectrum (approximate wavelength 400–700 nm) but in some applications the ultra-violet region (approximate wavelength 200–400 nm) is used.

In AES a gaseous sample is excited with thermal or electrical energy, causing electrons to be promoted to higher energy levels. The wavelength of the radiation emitted as the electrons fall back to lower energy levels is recorded.

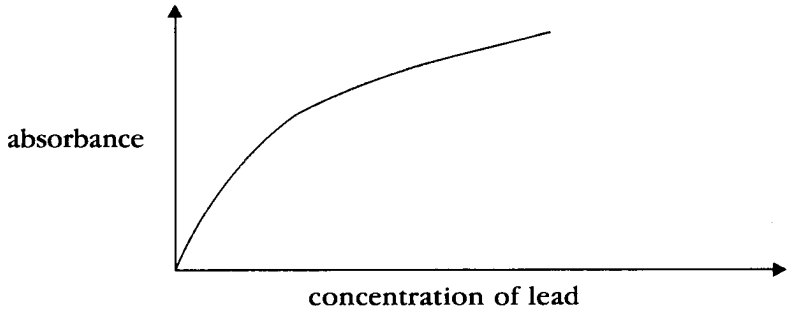
This technique can be used to detect metal elements in, for example, foodstuffs or effluent water since each element has a known characteristic spectrum. The element present can also be determined quantitatively by measuring the intensity of the emitted radiation. The greater the amount of that element present in the sample, the greater will be the intensity of its characteristic radiation.

AES detects both metallic and non-metallic elements. In fact, the element helium was discovered by the English scientist Sir Norman Lockyer, who pointed his telescope at the sun during the eclipse of 1868 and examined the light using a spectroscope. He observed bright emission lines but found it impossible to identify the source of the strong yellow light on earth. In 1870 Lockyer suggested that the spectrum was due to an unknown element which he thought was a metal and named helium after the Greek sun god, Helios. Lockyer was eventually knighted for his discovery but initially he was ridiculed. His critics were silenced when the Scottish chemist Sir William Ramsay managed to isolate helium from the uranium-containing mineral cleveite. Ramsay went on to discover the entire group of noble gases and was awarded the Nobel Prize for chemistry in 1904.

In AAS electromagnetic radiation is directed through a gaseous sample of the substance. Radiation corresponding to certain wavelengths is absorbed as electrons are promoted to higher energy levels. The wavelength of the absorbed radiation is measured and used to identify each element, as each element has a characteristic absorption spectrum. The amount of the species present in the sample can also be determined by quantitative measurement of the amount of light absorbed by the atomised element. The measured absorbance is proportional to the concentration of the element in the sample.

For example, AAS can be used to measure the concentration of lead in water, down to levels of 0.2 mg l^{-1}, or in other words 0.2 parts per million (ppm). The sample is firstly atomised using a flame or by electrical heating. Some of the radiation emitted from a special lamp is absorbed by the lead in the sample. The more radiation that is absorbed, the greater is the amount of lead present in the sample. In order to determine the exact quantity of lead present, a calibration curve needs to be plotted by measuring quantitatively the absorbances of aqueous solutions containing lead of known concentrations (Figure 15). Using the absorbance reading of the sample being analysed the concentration of the lead can be determined from the calibration curve.

Figure 15



A more sensitive form of AAS uses electricity to heat a graphite furnace to approximately 2600°C instead of using a flame to vaporise the sample.

As before, identification of the element is possible because each element has its own well-defined characteristic absorption spectrum at known wavelengths. In addition, the amount of absorbance is proportional to the concentration of the element in the sample.

ANSWERS TO QUESTIONS IN NOTES

Question 1

Calculate the energy, in kJ mol^{-1}, corresponding to
(a) a wavenumber of 1000 cm^{-1}
(b) a wavelength of 620 nm.

Answer

(a) $\bar{\nu} = 1000\ cm^{-1} = 1 \times 10^{3}\ cm^{-1} = 1 \times 10^{5}\ m^{-1}$

$E = Lhc\,\bar{\nu} = 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3.00 \times 10^{8} \times 1 \times 10^{5}$

$= 11974\ J\ mol^{-1} = \underline{11.974\ kJ\ mol^{-1}}$

(b) $\lambda = 620\ nm = 620 \times 10^{-9}\ m$

$$E = \frac{Lhc}{\lambda} = \frac{6.02\times10^{23}\times6.63\times10^{-34}\times3.00\times10^{8}}{620\times10^{-9}}$$

$= 193125\ J\ mol^{-1} = \underline{193.1\ kJ\ mol^{-1}}$

Question 2

The bond enthalpy of a Cl—Cl bond is 243 kJ mol^{-1}. Calculate the maximum wavelength of light that would break one mole of these bonds to form individual chlorine atoms.

Answer

$$E = \frac{Lhc}{\lambda} \text{ and so, } \lambda = \frac{Lhc}{E}$$

$$\lambda = \frac{6.02\times10^{23}\times6.63\times10^{-34}\times3.00\times10^{8}}{243\times10^{3}}$$

$= 4.93 \times 10^{-7}\ m$

$= 493\ nm$

Question 3

Calculate the ionisation energy for hydrogen if the wavelength of the line at the convergence limit is 91.2 nm.

Answer

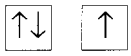
$$E = \frac{Lhc}{\lambda} = \frac{6.02\times10^{23}\times6.63\times10^{-34}\times3.00\times10^{8}\times10^{-3}}{91.2\times10^{-9}}$$

$= 1312.9 \text{ kJ mol}^{-1}$

Question 4 (with answer alongside)

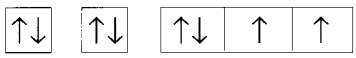
Using both spectroscopic and orbital box notations write down the electronic configurations for:

(a) lithium



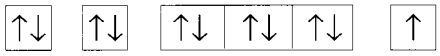
$1s^2\ 2s^1$

(b) oxygen



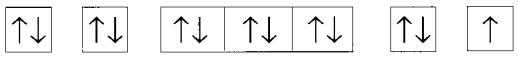
$1s^2\ 2s^2\ 2p^4$

(c) sodium



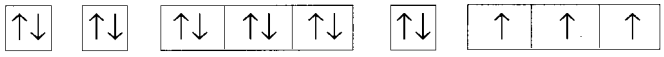
$1s^2\ 2s^2\ 2p^6\ 3s^1$

(d) aluminium



$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

(e) phosphorus

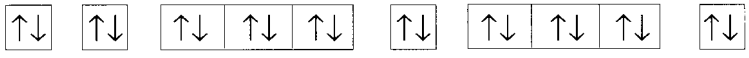


$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

(f) argon

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

(g) calcium



$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

(h) Li^+

$1s^2$

(i) F^-

$1s^2$ $2s^2$ $2p^6$

(j) Mg^{2+}

$1s^2$ $2s^2$ $2p^6$

(k) S^{2-}

$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$

(l) K^+

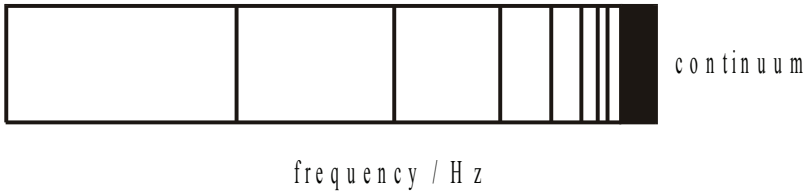
$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$

Questions

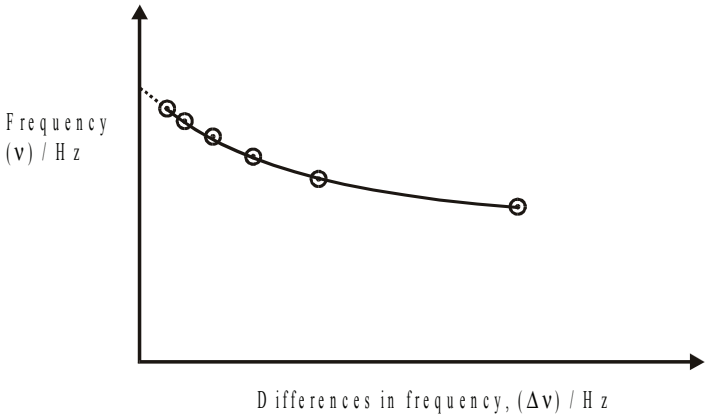
1. Photochemical reactions can be initiated by visible or ultra-violet light. Calculate the frequency of radiation that would, in theory, start a reaction involving bromine (see page 9 of the Data Booklet).

SY/88 **(4)**

2. The emission spectrum of an element is seen as a series of bright coloured lines on a dark background.



Within a series the intervals between the frequencies of each line decrease until the lines are so close together that they converge to form a continuous spectrum or continuum as shown in the diagram. A graphical method can be used to find the start of the continuum. A plot of v against Δv can be extrapolated back to find where Δv is 0. This is the start of the continuum.



a) What causes a line in an emission spectrum? **1**

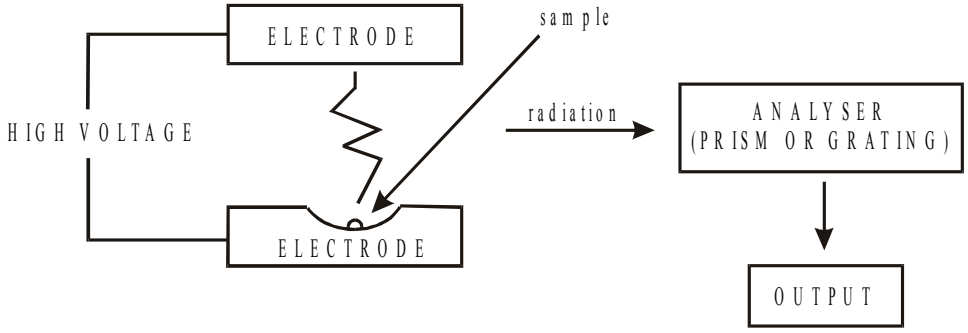
b) Why do the lines converge as they reach the continuum? **1**

c) ***i)*** Calculate the energy, in kJ mol^{-1}, of the emission line at the start of the continuum if the curve Δv intersects the y-axis (v) at 1.26×10^{15} Hz. **2**

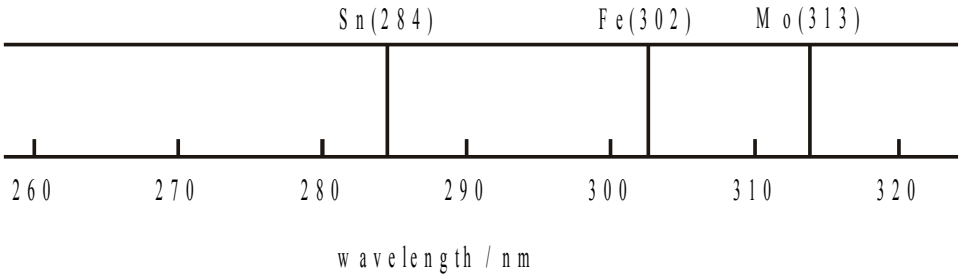
ii) What does this energy represent? **1**

SY/99 **(5)**

3. The following technique is used to detect trace elements in steels and other alloys. The metal sample is sparked as shown in the diagram.



The output from one sample was as shown below.



a) In which region of the spectrum do these lines lie? **1**

b) Calculate the energy, in kJ mol^{-1}, of the line due to tin. **3**

c) Explain how this sparking procedure relates to the formation of the lines in the spectrum. **2**

d) Give one reason why elements are added in trace amounts to steels. **1**

SY/85 ***(7)***

4. When sodium vapour street lights are first switched on, they glow red before turning orange-yellow. This is because they contain some neon, which produces the red colour as the lamps warm up.

a) Explain how the orange-yellow colour is produced by the sodium. **3**

b) How would the light coming from one of these street lights be analysed to prove the presence of both sodium and neon? **2**

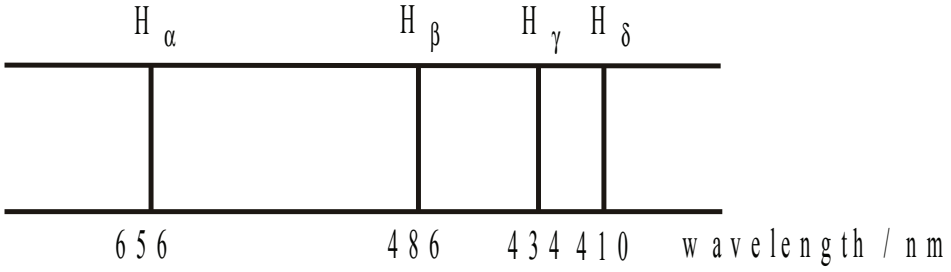
SY/92 **(5)**

5. In the emission spectrum for hydrogen, there are several different series of 'spectral lines'. These lines result from electrons emitting energy as they fall back from higher to lower energy levels. Each spectral line may be represented by the equation:

$$\frac{1}{\lambda} = R_h \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where λ = wavelength of the spectral line
R_h = a constant, $1.097 \times 10^7 m^{-1}$
n_1 = energy level to which the electron falls
n_2 = energy level from which the electron falls.

The Balmer series occurs in the visible part of the electromagnetic spectrum, n_1 having a value of 2 for each line in the series. The first four spectral lines for this series are shown in the diagram.

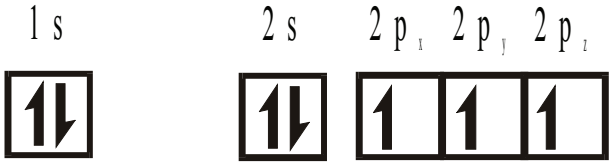


a) Use the equation to calculate the wavelength of the spectral line in the Balmer series that corresponds to the value $n_2 = 4$. State the colour of this spectral line. **3**

b) Lyman discovered a series of spectral lines for hydrogen in the ultra-violet region of the electromagnetic spectrum. What value must n_1 have for this series?
Give a reason for your answer. **2**

SY/96 **(5)**

6. The electron configuration for nitrogen is:



a) What do the symbols ↑ and ↓ represent? **1**

b) What is the significance of x, y and z in the 2p sublevel? **1**

c) ***i)*** Describe the shape of the s and p orbitals. **2**

ii) Describe the position of the p orbitals relative to each other. **1**

d) Why is the $2p_z$ electron for nitrogen not placed in the $2p_x$ or $2p_y$ orbital? **1**

e) Phosphorus is in the same group as nitrogen but has 15 electrons.
A student wrote the following configuration for phosphorus:

Explain the two mistakes in the student's answer. **2**

(8)

7. The number of orbitals and the number of electrons in an energy level or sublevel is limited.

a) Give the number of orbitals that make up:

i) the s sublevel **1**
ii) the d sublevel. **1**

b) Give the number of electrons that are needed to completely fill:

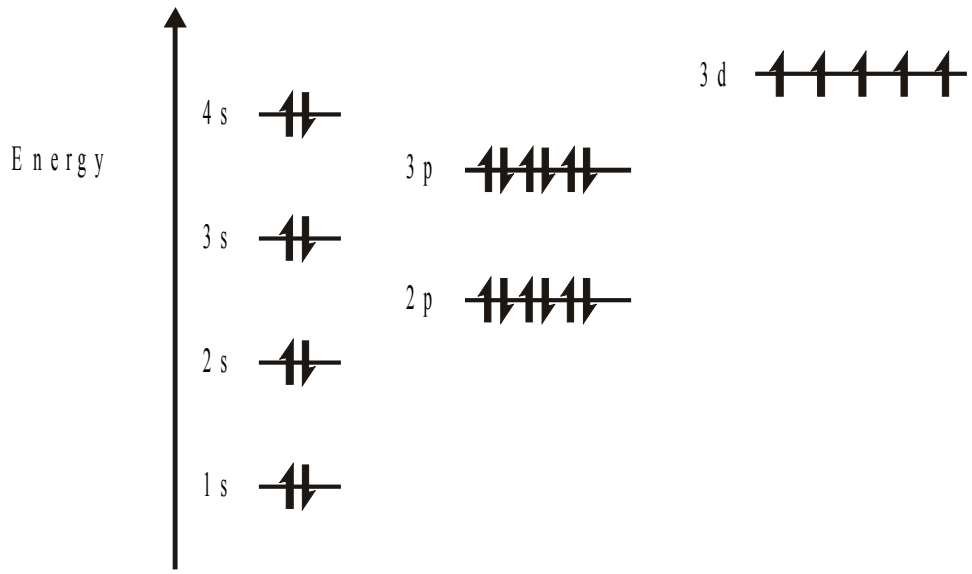
i) the p sublevel **1**
ii) the first energy level **1**
iii) the third energy level. **1**

c) Give the sublevels in:

i) the first energy level **1**
ii) the fourth energy level. **1**

(7)

8. The electron configuration of an atom of element Y in the ground state can be represented as:



a) Identify element Y. **1**

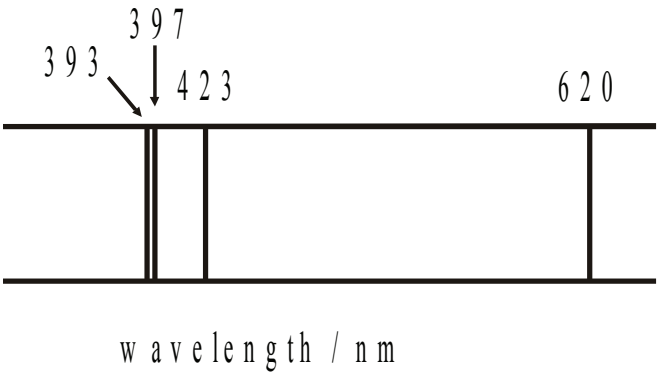
b) The electron configuration of an atom or ion may also be expressed in another form, e.g. $1s^2\ 2s^2\ 2p^1$ for boron.

Give the electron configuration for Y in this form. **1**

c) Give the electron configuration of the ion Y^{3+}. **1**

SY/84 **(3)**

9. The diagram below represents part of the emission spectrum of a metal.



a) Which line corresponds to the highest energy electron transition?
Give a reason for your answer. **2**

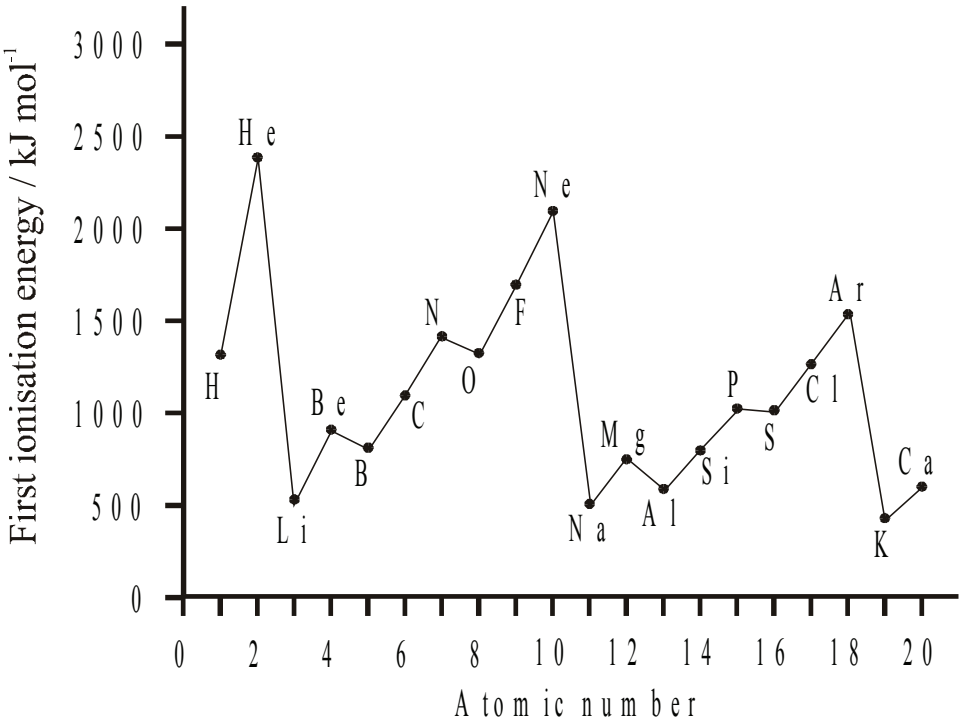
b) In what way would an absorption spectrum of the metal differ in appearance from the above? **1**

c) Calculate the wavenumber, in cm^{-1}, of the 620 nm line. **2**

d) What colour would be observed if a salt of this metal were placed in a bunsen flame? **1**

SY/84 **(6)**

10. The first 20 elements show many periodic properties, e.g. the variation in first ionisation energy (IE).



a) Predict, from the graph, the first IE of rubidium. **1**

b) Explain why the noble gases have the highest values of IE in each period. **1**

c) ***i)*** Explain why the Group 1 metals have the lowest value of IE. **1**

ii) Explain why the values of IE decrease Li to Na to K. **1**

d) Explain the general increase in value of IE from Li to Ne. **1**

e) ***i)*** Explain the drop in value of IE from Be to B. **1**

ii) Explain the drop in value of IE from N to O. **1**

(7)

11. The concentration of calcium ions in a sample of tap water can be measured by atomic emission spectroscopy (flame photometry).

a) How might the sample be energised? **1**

b) State the effect this has on the electrons of the calcium ions. **1**

c) ***i)*** How then is energy emitted?
(Answer in terms of the electrons.) **1**

ii) What is detected by the spectrometer? **1**

d) How can the chemist operating the spectrometer be certain that the emission that is measured is caused only by the calcium ions? **1**

e) What property of this emission will be measured (and used to estimate the calcium ion concentration)? **1**

f) Describe briefly the laboratory procedures necessary to construct a calibration curve. **2**

g) State how the calibration curve would be used to find the calcium ion concentration in the water sample. **2**

h) The same analysis could be performed by atomic absorption spectroscopy.

i) Why would it be important to use a lamp that gives light of a certain wavelength? **1**

ii) What would be measured by the spectrometer using this technique? **1**

(12)

Answers

1. Br–Br bond enthalpy = 194 kJ mol^{-1} (1)

E = Lhν for one mole of bonds (See units above.) (1)

ν = E/Lh = 194000/6.63 × 10–34 × 6.02 × 1023 J/Js
(Showing these units helps to get the units right for the next line.) (1)
= 4.86×10^{14} s^{-1} (or Hz) (1)

(4)

2. ***a)*** An excited electron returns to ground state, emitting energy difference as visible light of a specific wavelength. 1

b) The energy gaps between energy levels decrease with increasing energy, i.e. the higher energy levels get closer and closer together. 1

c) ***i)*** $\Delta E = h\nu$
$= 6.63 \times 10^{-34} \times 1.26 \times 10^{15}$ J
$= 8.35 \times 10^{-19}$ J (1)

But IE = $L \times \Delta E$
$= 6.02 \times 10^{23} \times 8.35 \times 10^{-19}$ J mol^{-1}
$= 50.27 \times 104$ J mol^{-1}
$= 502.7$ kJ mol^{-1} (1)

2

(ii) The first ionisation energy of the element.
(Check page 10 of the Data Booklet to confirm that this is a likely answer.) 1

(5)

3. ***a)*** The ultra-violet region 1
(See page 14 of the Data Booklet: ultra-violet includes
λ= 310 nm; visible runs from ~700 nm to ~400 nm.)

b) $E = Lhc/\lambda$ (1)
$= 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3 \times 10^{8}/284 \times 10^{-9}$ (1)
$= 0.422 \times 10^{(23 - 34 + 8 + 9)}$ J mol^{-1}
$= 422$ kJ mol^{-1} (1)

3

c) Energy from the spark excites some electrons to a higher energy level. (1)
When these electrons return to ground state a specific amount of energy is released and this shows up as a line of measurable wavelength (or frequency) in the spectrum. (1) 2

(d) To gain a wider range of properties, e.g. harder, resistant to corrosion, etc. 1

(7)

4. ***a)*** Electrons are excited by electric discharge to a higher level. (1)
These electrons emit energy as they return to a lower energy level. (1)
The quantity of energy emitted depends on the energyvalues of the two energy levels involved. (Many lines may be produced and each will represent a specific electronic jump.) (1) 3

b) Pass the light through a prism and examine the spectrum produced on a screen. (1)
Spectral lines characteristic of sodium and of neon would be seen. (1) 2
(5)

5. ***a)*** The Balmer series is, for $n_1 = 2$:

$1/\lambda = R_h (1/2^2 - 1/4^2)$
$= 1.097 \times 10^7 \times (1/4 - 1/16)$
$= 1.097 \times 10^7 \times 3/16$
$= 2.06 \times 10^6$ (1)

$\lambda = 1/(2.06 \times 10^6) = 0.485 \times 10^{-6}$
$= 485$ nm (1)

This line will be blue-green (see page 14 of the Data Booklet). (1) 3

b) $n_1 = 1$ (1)

All the jumps must be of shorter wavelength,
i.e. of higher energy than those for $n_1 = 2$. (1) 2 **(5)**

6. ***a)*** An electron 1

b) Each letter represents an orbital orientated along the x-, y- or z-axis. 1

c) ***i)*** s orbitals are spherical and symmetrical aroundthe nucleus. (1)

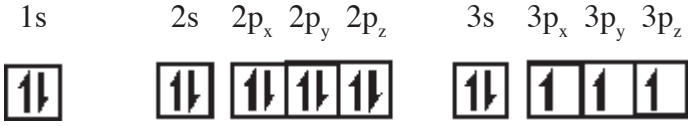
p orbitals are dumb-bell shaped and are symmetrical around each axis. (1) 2

ii) The p orbitals are arranged mutually at right angles. 1

d) Electrons are placed singly in degenerate orbitals before pairing occurs in one orbital. 1

e) Error 1: The '4p' orbitals should be labelled '3p'. (1)
Error 2: Hund's rule states that electrons will occupy degenerate orbitals singly before any one is doubly filled. (1)

The correct configuration is:



2 ***(8)***

7. ***a)*** ***i)*** 1 1
ii) 5 1

b) ***i)*** 6 1
ii) 2 1
iii) 18 1

c) ***i)*** 1s 1
ii) 4s 4p 4d 4f 1 ***(7)***

8. ***a)*** Manganese 1

b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$ or $[Ar]\ 4s^2\ 3d^5$ 1

c) $[Ar]\ 4s^0\ 3d^4$ (the 4s term may be omitted) 1 **(3)**

9. ***a)*** Since $E = hc/\lambda$ or $E \propto 1/\lambda$, shorter wavelengths correspond to higher energy. (1)

It can be assumed that these lines represent a part of a series of lines which converge (at a continuum, not shown) at the higher energy end, i.e. to the left on the diagram shown in the question. Both arguments lead tothe conclusion than 393 nm represents the highest energy value shown. (1) 2

b) Instead of coloured lines on a black background, there would be black lines on a λ coloured background (of the visible spectrum). 1

c) $\nu = 1/\lambda = 1/620 \times 10^{-7}$ (1)
$= 16129\ cm^{-1}$ (Remember the units.) (1) 2

(d) The orange-red of the 620 lines would probably swamp the less intense blue-green lines. 1 **(6)**

10. ***a)*** 380 kJ mol^{-1} (±20 kJ mol^{-1}) 1

b) There is a huge energy requirement to break the noble gases into a stable octet. or It is very difficult to remove an electron from a full energy level. 1

c) ***i)*** The Group 1 metal has the largest radius in that period and has the smallest nuclear charge in that period.
Both facts lead to a lesser attraction for the outermost electron. 1

ii) Each new energy level means a larger radius (less attraction for the outermost electron) and provides a greater shielding effect (again reduced attraction by the nucleus). 1

d) Two factors apply: the steady increase in nuclear charge and the slight decrease in atomic radius from Li to Ne makes the attraction of the nucleus for outer electrons greater. 1

e) ***i)*** Be $1s^2\ 2s^2$
B $1s^2\ 2s^2\ 2p^1$, i.e. B has started a new subshell so its outermost electron is relatively easier to remove than that of Be, where a complete subshell has to be broken into. 1

ii) Half-full shells are relatively stable so N (with a half-filled p subshell) has a higher IE than O, which hasone electron more. 1 **(7)**

11. ***a)*** By spraying as a solution into a Bunsen flame or by electric discharge through a gaseous sample or by electric sparking between graphite electrodes 1

b) Valence electrons are excited and promoted to higher energy levels. 1

c) ***i)*** Electrons return to a lower energy level, includingthe ground state, emitting energy equal to the energy difference between the two levels involved as light. 1

ii) A spectral line on the spectrum for each 'jump' or a series of characteristic spectral lines or the intensity of light of one spectral line. 1

d) By using an appropriate filter. 1

e) The intensity of the light emitted. 1

f) Make up standard solutions of $Ca^{2+}_{(aq)}$. (1)
Use the solutions to make a graph of intensity of radiation vs concentration of solution. (1) 2

g) Measure the intensity of radiation of the water sample (being tested). (1)
The concentration is read from the graph. (1) 2

h) ***i)*** Each lamp gives out radiation characteristic of a specific metal. Particles of the metal in the sample absorb a measurable amount of this light in proportion to their concentration as electrons are promoted. 1

ii) The quantity of energy absorbed, i.e. the difference in intensity, between the incident light and the transmitted light. 1

(12)