PART ONE

ATOMIC STRUCTURE

Chapter 1

SUBATOMIC PARTICLES

INTRODUCTION

An atom *is the smallest individual particle of an element that can take part in the chemical reactions.* Whereas an **element** *is a substance which cannot, by any known chemical process, be split up into two or more simpler substances.*

- On another hand, **a molecule** *is the smallest particle of matter which can exist in free state*. Whereas **matter** *is anything is which occupies space and has mass.*

Atoms are built up from many smaller particles three of which are of direct interest to the chemists. These are the **proton,** the **electron** and the **neutron.**

The **Proton** *is positively charged subatomic particle which is found in the nucleus of an atom.*

- Its mass is about equal to that of hydrogen atom.

The **electron** *is negatively charged subatomic particle which is found around the nucleus of an atom.*

- The charge of an electron is equal but opposite to the charge of proton and its mass very small which is about $\frac{1}{1840}$ of the mass of the proton.

The **neutron** *is the subatomic particle with no charge (electrically neutral) which is found at the nucleus of an atom.*

- The mass of neutron is about equal to the mass of the proton.

PROPERTIES OF SUBATOMIC PARTICLES

Properties of subatomic particles are summarised in the table below.

Particle	**Symbols**	**Relative Electric Charge**	**Mass Number**	**Relative mass (in amu)**	**Actual Mass (kg)**
Electron	e^-, ${}_{-1}^{0}e$ or simply e	-1	0	0.0005486	9.109×10^{-31}
Proton	p^+ or ${}_{1}^{1}H$	$+1$	1	1.007276	1.673×10^{-27}
Neutron	n^0 or ${}_{0}^{1}n$	0	1	1.008665	1.675×10^{-27}

Where **1amu (atomic mass unit) = $\mathbf{1.660540 \times 10^{-27}}$kg**

Don't worry about memorizing mass of subatomic particles! You may use the following approximations:

$$\text{Mass of an electron} = 0\text{amu}$$

$$\text{Mass of a proton} = 1\text{amu}$$

$$\text{Mass of a neutron} = 1\text{amu}$$

ATOMIC NUMBER (Z)

Atomic number *is the number of protons present in the nucleus of an atom*.

- It is also known as **proton number.**

Each element has unique atomic number which is used to distinguish it from other elements-**no** two elements have the same atomic number!

What information can be derived from atomic number?

Various information can be derived from the atomic number including the following:

- It gives the number of protons present in the atom. (This can simply be deduced from its definition).
- It gives the number of electrons present in the **neutral atom.**
- For neutral atom:

$$\text{Number of protons} = \text{Number of electrons}$$

Here the reader should recognise the necessity of the word 'neutral' because for charged atom (ions) the fact **does not** hold as the formation of any ion whether is positive (cation) or negative (anion) must be accompanied with changing of number electrons while number of protons (atomic number) remain unchanged.

- It gives electronic configuration of the atom.
- This is done through knowing number of electrons present in the atom.
- It gives position of an element in periodic table.
- In the modern periodic table, elements are arranged according to increase in their atomic numbers. Also through electronic configuration of an atom of the element, **group, period** and **block** of the element in periodic table can be deduced.
- Since no two elements have the same atomic number, each element has unique position in the periodic table and hence atomic numbers act as **serial numbers** of elements in the periodic table.
- It can give a number of neutrons present in the atom.
- With given **mass number** (**A**), number of neutrons can easily be deduced by using the fact that:

$$\text{Mass number (A)} = \text{number of neutrons} + \text{number of protons (Z)}$$

$$\text{From which: } \mathbf{Number\ of\ neutrons} = \mathbf{A - Z}$$

MASS NUMBER (A)

Mass number *is the total number of protons and neutrons present in the nucleus of an atom.*

Thus; $\text{Mass number (A)} = \text{number of protons} + \text{number neutrons}$

But; $\text{Number of protons present in nucleus of an atom} = \text{Atomic number (Z)}$

Hence $\text{A} = \text{Z} + \text{Number of neutrons}$

Or $\text{Number of neutrons} = \text{A} - \text{Z}$

The reader should understand that since number of protons and neutrons can never contain fractions, the mass number must also be whole number.

Understand that:

Sub-atomic particles which are found in nucleus of an atom, i.e. proton and neutrons are collectively known as **nucleons**. Hence **mass number** is also known as **nucleons number**.

NUCLIDE

Nuclide *is a nucleus of a particular atom characterised by a defined atomic number and mass number.*

- For example sodium nuclide has atomic number of 11 and mass number of 23(it is denoted as $^{23}_{11}\text{Na}$)

Nuclides can be dived into three types namely;

- Isotopes
- Isobars
- Isotones

Isotopes *are atoms of the same element with the same atomic number but differ in their mass numbers.*

- According to modern periodic law; properties of elements are periodic function of their atomic numbers i.e. Properties of elements depend on their atomic numbers. Thus isotopes have the same chemical properties but they differ in their mass numbers.

The tendency of an element to show the property of possessing atoms of similar chemical properties but different mass numbers is known as **isotopy.**

- Elements show isotopy due to possibility of having atoms of the same element but differ in their number of neutrons.

That is from the formula: A = Z + number of neutrons. It is clearly understood that; if Z is the same while number neutrons is different, A must be also different.

Isotones *are atoms of different elements having different mass number and different atomic numbers but the same neutron number.*

- For example $^{39}_{19}\text{K}$ and $^{40}_{20}\text{Ca}$ are isotones with 20 neutrons in each.
- Another example of isotones are $^{14}_{6}\text{C}$ and $^{15}_{7}\text{N}$.

Isobars *are atoms of different elements with different atomic numbers but have the same mass number.*

- Example both argon and calcium with different atomic numbers of 18 and 20 respectively have the same mass number of 40.
- Another example of isobars are $^{14}_{6}\text{C}$ and $^{14}_{7}\text{N}$.

Notation of Isotopes

In order to distinguish between isotopes of the same element in writing symbols and formulae, a simple system is adopted. The isotope of any element X will have the symbol $^{\mathbf{A}}_{\mathbf{Z}}\mathbf{X}$**,** where A is the mass number of the isotope and Z is the atomic number of any atom of X.

- Since isotopes are differentiated by the mass numbers; the isotope $^{A}_{Z}\text{X}$ can be simply written as $\mathbf{X-A}$ isotope e.g. $\text{C}-13$ for $^{13}_{6}\text{C}$.

Thus for all the isotopes of any one element, Z is constant, and A varies because there are different numbers of neutrons in the different isotopes of the element.

MASS SPECTROMETRY

Mass spectrometry (also spelled **mass spectroscopy**) *is the analytical laboratory technique used to identify composition of a substance by their mass.*

- It involves determination of atomic mass and isotope abundance by using **mass spectrometer**.

Mass spectrometer on another hand *is an instrument which can measure the masses and relative concentrations of atoms and molecules.*

- It used to determine atomic mass and to detect presence of isotopes and their abundances.

Principle of mass spectrometer

1. The substance to be analysed is **vapourised** and is then introduced into **ionisation chamber** where a metal filament is heated strongly to produce enough energy to cause **ionisation** to occur, that is; positive ions are formed.
2. The positive ions produced are **accelerated** by negatively charged plates.
3. The positive ions produced are then **deflected** by the magnetic field according to their mass to charge ratio ($^{m}/_{z}$) such that the ions with greater value of the ratio are deflected less while ions with the smaller ratio are deflected more.
4. The movement of ions is **detected** to the photographic plate by producing a current. The current depends on the number (concentration) of ions produced.
5. The result is **recorded** in a graphical manner since the mass spectrometer has been calibrated to give both mass and intensity such that:

$$\text{Height of the peak in the graph (intensity)} = \text{Relative abundance,}$$

$$\text{Number of peaks} = \text{Number of isotopes}$$

Key words to memorize in the principle of mass spectrometer

The following six words may make the work of remembering principle of mass spectrometer easier.

1. Vapourisation and ionisation
2. Acceleration
3. Deflection
4. Detection
5. Recording

The words must be memorized in the same sequence.

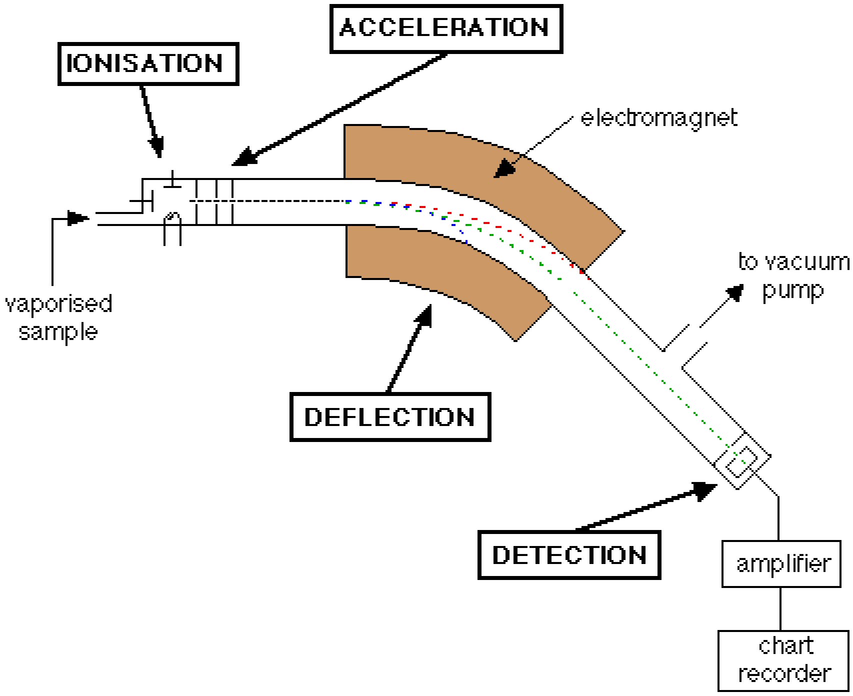


Figure: Mass spectrometer

More detailed explanation on working of mass spectrometer

Below is the detailed explanation on how things are going on in the mass spectrometer.

i) Ionisation

The **ionisation chamber** consist of **metal coil**, **iron repeller** and **electron trapper** as illustrated in the figure bellow (which is the part of mass spectrometer showing the ionisation process only).

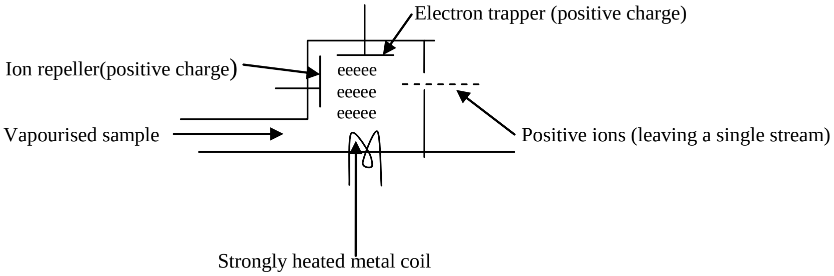


Figure: Ionisation chamber

What is going on in the ionisation chamber?

The electrically heated metal coil produces enough amount of heat to initiate the ionisation as per equation:

$$M(g) + Heat \rightarrow M^+(g) + e$$

The knocked off electrons collide with un-ionised atoms to cause more ionisation as per equation:

$$\mathrm{M(g) + e \rightarrow M^{+}(g) + 2e}$$

Therefore to summarise; the ionisation process in the ionisation chamber of the mass spectrometer is caused by:

- Heat energy from electrically heated metal coil
- Kinetic energy from fast moving electrons (leading to very energetic collision between the electrons and un-ionised gaseous atoms or molecules).

Note:

Electron bombardment is the alternative way of causing ionisation which is commonly brought about by a device known as **an electron gun**.

- So instead of using strong heated metal coil as the device of initiating ionisation in the ionisation chamber, the process may also be undertaken through **electron bombardment method** by using the **electron gun device** as per equation;

$$\mathrm{M(g) + \underset{\uparrow}{e} \longrightarrow M^{+}(g) + 2e}$$

An electron from the electron gun
to knock off more electron from M(g)

Two important dots!

- **Mass spectrometer always works with positive ions**. The statement is applicable even for non-metals (which normally ionises by gaining electrons) or noble gases (which normally do not form ions at all). It is also applicable for molecules of compound.
- **Most of the positive ions formed in the ionisation chamber will carry a charge of +1**, **why?** This is simply because it is more difficult (need greater amount of energy) to remove more electron from the positive ion (so as to form +2 and so on) than from neutral gaseous atom or molecule (so as to form +1).

To finish with the ionisation chamber…………!

The positive ions leave the ionisation chamber to the acceleration chamber by the influence of magnetic field exerted b y positively charged metal plates which act as ion repeller (Recall: like charge repels).

ii) Acceleration

The ionised sample passes through the **acceleration chamber** for acceleration so as to enable all particles to have the same speed (and of course the same kinetic energy).

- The acceleration chamber consist of number of plates the first one in contact with the ionisation chamber has very high positive potential while the last plate in contact with **deflection chamber** has zero potential. The intermediate plates have therefore some intermediate potential ranging between 0V and that of the first plate (about +10000V).

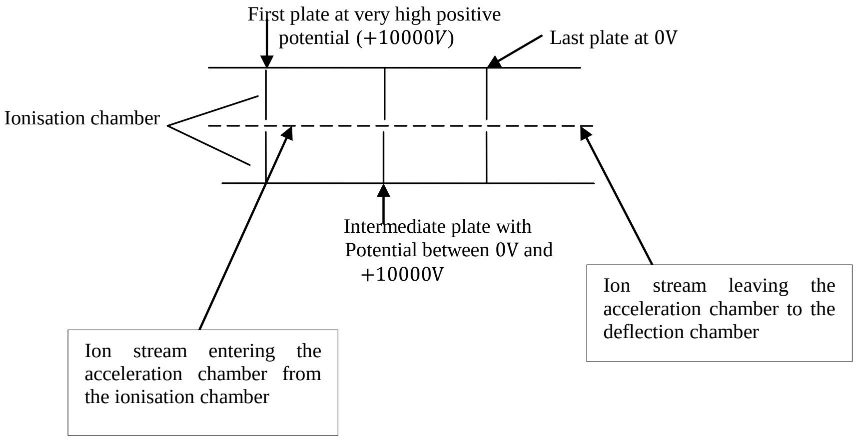


Figure: Acceleration chamber

So from the above figure it is clearly understood that positively charged ions are repelled away from very positive ionisation chamber through plates where the final one has 0V to the deflection chamber.

To conclude!

The acceleration of the ions is enabled by large potential difference between first plate and the last plate.

iii) Deflection

Different ions enter the **deflection chamber** as single stream where they are splitted into different stream through deflection by magnetic field exerted electromagnet present in the deflection chamber.

- The amount of deflection depends on:

1. **The mass of ion**
   Lighter ions (ions with smaller mass) are deflected more than heavier ones.
2. **The charge on the ions**
   Higher charged ions are more deflected than ions with lower charge.

Understand!

The two factors are always combined into mass–charge ratio, always symbolized as m/z (or sometimes m/e) where the greater m/z ratio means less deflection and vice-versa.

- If the ion has charge of +1(as we will expect in the most cases), the numerical value of m/z will be equal to that of atomic (or molecular) mass.

Ok, let us return to our chamber!

After entering the deflection chamber as single stream, ions will be deflected according to their m/z ratio and therefore forming different streams as illustrated in the next page.

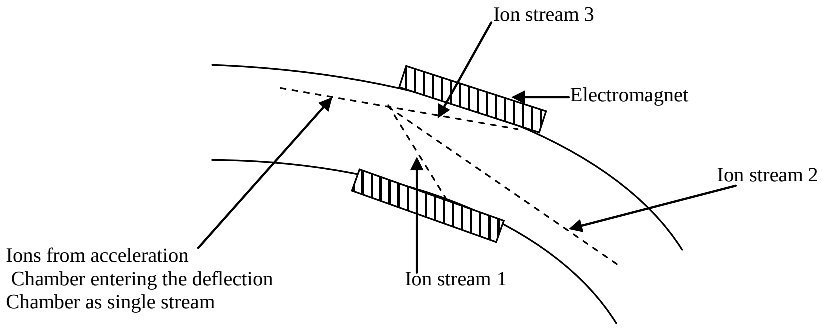


Figure: Deflection chamber

From the above figure it is clearly understood that:

Ion stream 1 is most deflected and therefore ions in this stream have smallest $\mathrm{m/z}$ ratio. If all ions have charge of +1, that means ions in stream 1 have smallest mass.

Ion stream 3 is least deflected and therefore ions in this stream have largest $\mathrm{m/z}$ ratio and of course largest mass if the charge of all ions (coming from the acceleration chamber) is +1.

Note:

Another factor which affects the extent of deflection of the ionised particle is the speed of the particle; greater speed means less deflection and vice-versa and **this explains why before entering the deflection chamber particles must be accelerated to the same speed** so that the only determining factor for the extent of deflection is $^{\mathrm{m}}/_{\mathrm{z}}$ ratio.

- If the speed would not be constant, the ambiguity would rise in the determination of $^{\mathrm{m}}/_{\mathrm{z}}$ ratio because if all other factors are kept constant: heavier particles have less speed suggesting that they are less deflected (if one considers the mass factor) or more deflected (if one considers the speed factor).

iv) Detection

From deflection chamber, only ion stream 2 pass through the machine to the ion detector, *What about ion stream 1 and 3?*

- The other ions collide with the walls where they take electrons and get neutralised. After that they get removed from the mass spectrometer by the **vacuum pump**.

The detector consists of metal box connected by a metal wire to an amplifier as shown in the next page.

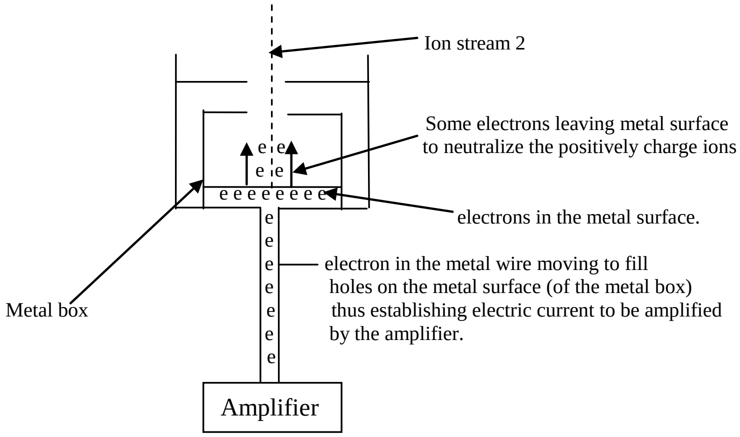


Figure: Ion detector

When an ion strikes the metal box its charge is neutralised by an electron jumping from the metal surface onto the ion.

- This leaves a hole amongst the electron in the metal surface and therefore the electrons in the metal wire will move towards the surface to fill it.
- A flow of electrons in the wire is detected as an electric current whose amount become large as amount of ions hitting the surface of the metal box is large. In other words **amount of electric current become large of if the relative abundance of ions of particular isotope is high.**
- This electric current be amplified and recorded.

That is all about ion stream 2 *what about other ions in stream 2 and 3? How are they detected?*

Stream 1 and 3 are detected by varying amount of magnetic field to enable them to be deflected onto the detector.

- Stream 1 (which was most deflected) is brought to the detector by reducing the amount of the magnetic field.
- Stream 3 (which was least deflected) is brought to the detector by increasing amount of the magnetic field.

v) Recording

The output from the amplifier is always recorded by **chart recorder** in the graphical manner which is known as the **mass spectrum**. (As illustrated in simplified diagram of mass spectrum shown in the next page);

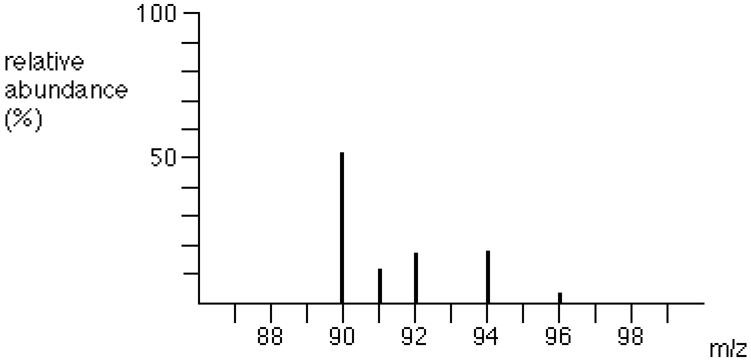


Figure: Mass spectrum

- The vertical axis of the mass spectrum represents **relative abundance** (or sometimes labelled **relative intensity**). The vertical scale corresponds to the current received by the chart recorder and hence number of ions of a particular isotope arriving at the detector such that the greater current, the more abundant ion.
- The horizontal axis of the mass spectrum represent $\mathrm{m/z}$ ratio (or relative atomic mass by assumption that $\mathrm{z} = 1$).

Definition of mass spectrum (plural: **mass spectra**)

Is a plot of relative abundances of ions forming a stream versus their mass to charge ratio (m/z) *values (commonly obtained from an instrument called mass spectrometer).*

Alternatively it can be defined as:

A plot of the relative abundances of ions forming a beam as function of their m/z *values.*

Mass spectrum is like fingerprint of an element!

Different elements, when analysed by mass spectrometry produce different mass spectra and hence the mass spectrum of an element acts like a fingerprint of element.

Interpretation of number of peaks in the mass spectrum

What is the number of peaks in the mass spectrum represents?

The exact answer of this question depends on whether the spectrum is for an element or a compound.

For an element:

In this case, the formation of different peaks is due to existence of isotopes.

- So if the mass spectrometry is done for simple atoms for an element: number of peaks becomes equal to the number of isotopes.

That is; for simple (uncombined) atoms of an element:

$$\text{Number of peaks} = \text{Number of isotopes}$$

For example: if a certain element, say x has three isotopes, then its mass a spectrum could appear as follows:

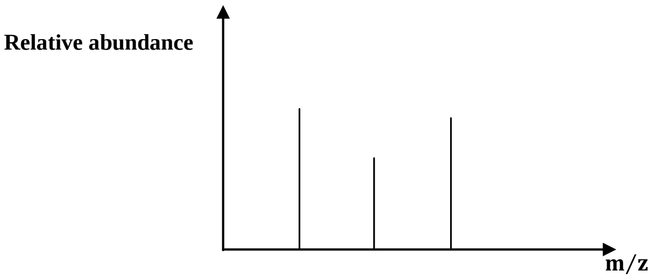


Figure: Mass spectrum of an element with three isotopes

Be careful!

The above fact remains true if and only if the atoms of element are in uncombined form.

- For an element which consist of more than one atom combined together to give a molecule:

$$\text{Number of peaks} \neq \text{Number of isotopes}$$

For example, if the element X has two isotopes, one with mass number of y and another with mass number of z with their respective notation of ^{y}X and ^{z}X: and the element exists as diatomic molecule of formula X_2, it is clearly understood that there are three ways of making this diatomic molecule.

- First way: one ^{y}X combine with another ^{z}X to give a molecules X_2 of molecular mass of $y + z$
- Second way: one ^{y}X combine with another ^{y}X to give a molecule, X_2 of molecular mass of $y + y = 2y$
- Third way: one ^{z}X combines with another ^{z}X to give a molecule, X_2 of molecular mass of $z + z = 2z$.

Hence in this case, the mass spectrum of element X will consist of three peaks with masses $y + z, 2y$ and $2z$ although there are only two isotopes of X.

For compound:

Like elements, mass spectrometry of compound (for example, organic compounds) gives different peaks too. *How these different peaks arise?*

- When an electron is knocked off from the organic molecule (for example heptane), the charge ion is formed as per equation.

$$C_7H_{16} + e \rightarrow C_7H_{16}^{+} + 2e$$

- The mass of positive charge formed in the above equation is known as **molecular** or **parent ion**. That is $C_7H_{16}^{+}$ is the molecular ion (or parent ion) in this example.
- This molecular ion is highly unstable, and therefore it undergoes fragmentation (fission) before reaching the detector and therefore giving different peaks.

Below are some possible fragmentations:

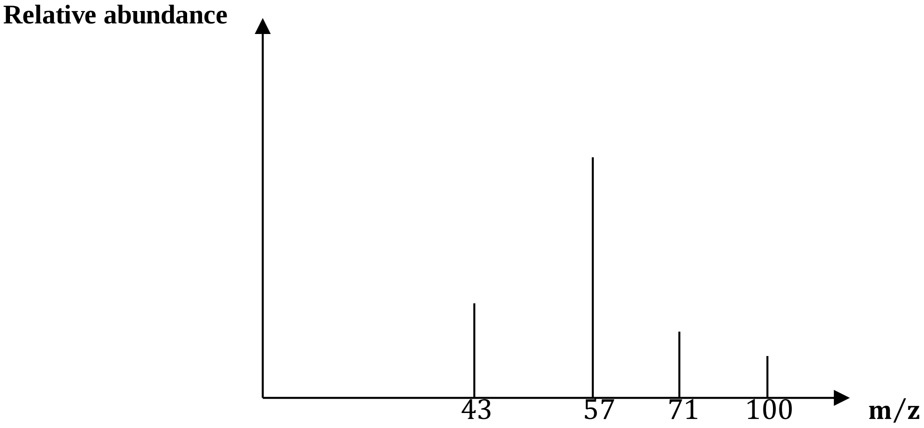
$$C_7H_{16}^{+} \rightarrow C_5H_{11}^{+} + C_2H_5^{\bullet}$$

$$C_7H_{16}^{+} \rightarrow C_4H_9^{+} + C_3H_7^{\bullet}$$

$$C_7H_{16} \rightarrow C_3H_7^{+} + C_4H_9^{\bullet} \qquad \text{etc.}$$

- Only charged radicals will reach the detector, uncharged radical will not be detected and will be driven off from the mass spectrometer through the vacuum pump. So in our example, the following ions will be detected:
  - $C_7H_{16}^{+}$ with a mass of 100
  - $C_5H_{11}^{+}$ with a mass of 71
  - $C_4H_9^{+}$ with a mass of 57
  - $C_3H_7^{+}$ with a mass of 43

And the mass spectrum could look like:



So the formation of different peaks in the mass spectrum of compounds is due to the formation of fragments (**daughter** or **product** ions) after disintegration of unstable molecular ion.

Here:

$$\text{Number of peaks} = \text{Number of daughter ions reached the detector}$$

WARNING!

Don't find the average mass of different fragments (peaks) to know the molecular mass of the compound. This is because in this case, the different peaks do not represent isotope like in the case of the element, they represent fragments ions which in actual sense are useless of far as molecular mass of the compound is concerned. *So how can we find molecular mass of the compound?*

- The more useful ion here is the molecular ion whose mass is equal to the molecular mass of the compound in the analysis. That is;

$$\text{Mass of molecular ion} = \text{molecular mass of the compound}$$

- Hence to know the molecular mass from mass spectrometry of the compound, just look for the peak with largest mass and the mass (largest mass) become the molecular mass of the compound-no need of touching calculator!

So returning to our example of mass spectrometry of C_7H_{16}, the parent ion is $C_7H_{16}^+$ whose mass is 100 and hence molecular mass of compound is 100g/mol.

Definitions of molecular and product ion:

Molecular (parent or **precursor) ion** *is the ion formed after removing electron(s) from a molecule of a compound which may undergo fragmentation to give product (or daughter) ion.*

Product (or **daughter) ion** *is the ion formed after fragmentation of a molecular ion.*

Important information from mass spectrum of an element

The mass spectrum of an element gives the following information:

i) Number of isotopes where:

$$\text{Number of peaks} = \text{Number of isotopes}$$

ii) Mass number of isotopes where:

$$\text{Mass number of isotopes} = {}^{\text{m}}/_{\text{z}} \text{ of peak}$$

(By assumption that each atom loose one electron only in the ionisation)

iii) Relative abundance of isotope where:

$$\text{Relative abundance} = \text{Height of peak}$$

Uses of mass spectrometry

Don't get tired to read about mass spectrometry, below are last four sentences which gives uses of mass spectrometer.

- A mass spectrometer (through mass spectrum) can be used to calculate the relative atomic mass of an element.
- Mass spectrometry can be used to identify elements from the mass number of isotopes.
- A mass spectrometer (through mass spectrum) can be used to find relative abundance of isotopes. *The specialized use of mass spectrometer to determine the relative abundance of isotopes in a given sample is known as* **isotope–ratio mass spectrometry(IRMS)**.
- Mass spectrometry can be used to determine the relative molecular mass of compound.

RELATIVE ATOMIC MASS (RAM OR A_r)

The relative atomic mass (RAM or **A_r)** *is the weighted average of the* ***relative isotopic mass*** *(**RIM** or I_r) of the isotopes of the element relative to the $\frac{1}{12}th$ mass of the $C-12$ isotope whose mass is taken as $12\ a.m.u$ exactly.*

Where the **relative isotopic mass (RIM or I_r)** may be defined as: *the mass of an atom of the isotope relative to the $\frac{1}{12}th$ mass of an atom of $C-12$ isotope whose mass is taken as $12\ a.m.u$ exactly.*

That is:

$$\mathrm{RAM} = \frac{\mathrm{RIM}}{\frac{1}{12}\text{th mass of C}-12\text{ isotope}}$$

Definition of atomic mass unit$(\mathbf{a.m.})$

Atom mass unit$(\mathbf{a.m.u})$ *is the one twelfth*$\left(\frac{1}{12}th\right)$ *of the mass of an isolated atom of carbon -12 isotope.*

(Sometimes a unit of Dalton (Da) is used instead of a.m.u such that **1a.m.u = 1Da**)

It is important for the reader to understand that:

The mass of an isotope with greatest abundance is known as **nominal mass.**

- The average atomic mass of various isotopes of an element is always close to the nominal mass. **If the isotope with greatest abundance has percentage abundance which is close to 100% then the average atomic mass become almost equal to the nominal mass**. For example the percentage abundance of O-16 isotope is 99% and the average atomic mass of oxygen is 15.9994 (which is approximately equal to 16).

Mass number versus atomic mass

Mass number is the summation of number of protons and number of neutrons present in the nucleus of an atom.

- Total mass of protons and neutrons results to the total mass of the atom. *However the summation is not exactly equal to the atomic mass why?*
- This is because some mass is lost as energy and thus enabling protons and neutrons to bind together in the nucleus (the energy is known as **nucleus binding energy**).

So in the reality, the atomic mass is slightly lower than the summation of mass of protons and mass of protons due to this binding energy.

That is; $\text{atomic mass} < \text{mass of protons} + \text{mass of neutrons}$

(However by approximation, the atomic mass is equal to that summation).

WARNING!

Don't talk about effect of neglecting mass of an electron as one of the reason of deviation of measured (experimental) atomic mass from expected (calculated) atomic mass.

- This is because the experimental atomic mass is lower than the expected atomic mass (summation of mass of protons and mass of neutrons). If the electrons would have an effect, the experimental atomic mass would be greater than expected one.

Numerically, mass number and atomic mass are almost equal!

The mass number (A) is obtained by correcting the atomic weight in $\mathrm{a.m.u}$ of an element to the nearest whole number.

- For example, atomic weight of aluminium is 26.9815 while its mass number is 27.

Understand alternative terms for atomic mass!

- Atomic mass of an element is always given as relative to the mass of $\mathrm{C}-12$ isotope and hence term **relative atomic mass** for the atomic mass.

- Due to presence of isotopes, atomic mass is always given as the average of mass of isotopes and hence the term **average atomic mass** or **average relative atomic mass** for the atomic mass.

Differences between mass number and atomic mass

	MASS NUMBER	ATOMIC MASS
01	It is an integer	It may take fraction (decimals)
02	It has no unit	Its unit is a. m. u
03	Its values are not included in the modern periodic table	Its values are included in the modern periodic table
04	It is applicable for particular isotope.	It is commonly the average of mass of various isotopes

Calculations of average atomic mass (A_r)

With given isotopic masses say m_1, m_2 and m_3 with respective intensities I_1, I_2 and I_3, the average atomic mass is given by the following formula:

$$\text{Average atomic mass } (A_r) = \frac{\sum(\text{ Isotopic mass} \times \text{intensity})}{\text{Total intensity}}$$

$$= \frac{M_1I_1+M_2I_2+M_3I_3}{I_1+I_2+I_3}$$

While for given percentage abundances, say $P_1\%, P_2\%$ and $P_3\%$ for isotopic masses $m_{1,}m_2$ and m_3 respectively, the above formula may be rewritten as follows;

$$A_r = \frac{\sum(\text{Isotopic mass} \times \text{percentage abundance})}{100}$$

$$= \frac{m_1P_1+m_2P_2+m_3P_3}{100}$$

Where $\sum$ means 'summation of'

Worked examples

Example 1

Magnesium has three stable isotopes of masses 23.985, 24.985, 25.982 a.m.u. The relative abundances of the three isotopes are 39.35, 5.065, and 5.585 respectively. Calculate the average atomic mass.

Solution

Using; $A_r = \frac{\sum(\text{ Isotopic mass} \times \text{intensity}}{\text{Total intensity}})$

$$= \frac{23.985 \times 39.35 + 24.985 \times 5.065 + 25.982 \times 5.585}{39.35 + 5.065 + 5.585} = 24.3 \text{ a.m.u}$$

The average atomic mass is 24.3 a.m.u

Example 2

A sample of pure unknown element **X** was analysed and the data is given in the table below. Calculate the relative atomic mass of **X** strictly to two decimal places.

Symbol	**Mass (a.m.u)**	**Natural abundance (%)**
${}^{20}_{10}X$	19.992	90.22
${}^{21}_{10}X$	20.994	0.257
${}^{22}_{10}X$	21.991	8.82

Solution

$$A_r = \frac{\sum(\text{Isotopic mass} \times \text{percentage adunbance})}{\text{Total percentage adunbances}}$$

$$= \frac{19.992 \times 90.22 + 20.994 \times 0.257 + 21.991 \times 8.82}{90.22 + 0.257 + 8.82} = 20.17$$

So the relative atomic mass of **X** is 20.17

Example 3

If ${}^{69}Ga$ and ${}^{71}Ga$ occur in proportions 60: 40, calculate the average atomic mass of Ga.

Solution

$A_r = \frac{\sum(\text{isotopic mass} \times \text{proportion})}{\text{Total proportions}} = \frac{69 \times 60 + 71 \times 40}{60 + 40} = 69.8$ (Under assumption that A=RIM)

The average atomic mass is 69.8

Example 4

The mass spectrum of an element enables the relative abundance of each isotope o f the element to be determined. Data relating to the mass spectrum of an element **X** whose atomic number is 35 appear as follows;

Mass number of isotopes	Relative Abundance
79	50.5%
81	49.5%

(i) Define the term **isotope**

(ii) Write down the conventional symbols for the two isotopes of **X**

(iii) Calculate the relative atomic of **X** to the three significant figures

Solution

(i) **Isotope** *is an atom of an element with the same atomic number as that of another atom of the same element but differ in mass number*. (The readers should recognise a little difference between definition of **isotopes** and **isotope**)

(ii) $^{79}_{35}\text{X}$ and $^{81}_{35}\text{X}$

(iii) $\text{A}_\text{r} = \frac{\sum(\text{isotopic mass} \times \text{percentage abundance})}{100} = \frac{79\times50.5+81\times49.5}{100} = 79.99$

So the relative atomic mass of **X** is 80.0 (To three significant figures)

Example 5

Silver consists of two isotopes $^{107}_{47}\text{Ag}$ and $^{109}_{47}\text{Ag}$ of atomic masses 106.91g/mol and 108.91g/mol respectively. The relative abundances of these isotopes are 51.88% for $^{107}_{47}\text{Ag}$ and 48.12% for $^{109}_{47}\text{Ag}$. Calculate the average atomic mass of Ag.

Solution

$\text{A}_\text{r} = \frac{\sum(\text{isotopic mass} \times \text{percentage abundance})}{100} = \frac{51.88\times106.91+48.12\times108.91}{100} = 107.87\text{g/mol}$

The average atomic mass of Ag 107.87g/mol

Example 6

Copper has two naturally occurring isotopes. $\text{Cu}-63$ Have an atomic mass of 62.9296 amu and an abundance of 69.15%. What is the atomic mass of the second isotope? Given that average atomic mass of copper is 63.546 amu.

Solution

Percentage abundance of another isotope $= (100 - 69.15)\%$ or 30.85% (since summatioin of percentage abundance must be 100%)

Then using $\text{A}_\text{r} = \frac{\text{m}_1\text{P}_1+\text{m}_2\text{P}_2}{100}$

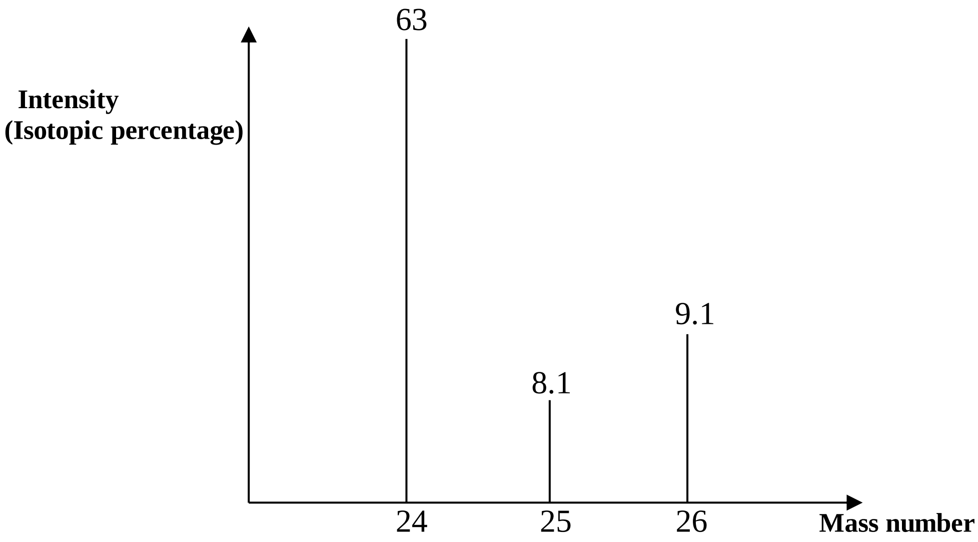
It follows that $63.546 = \frac{69.15\times62.9296+30.85\text{m}_2}{100}$

From which $\text{m}_2 = 64.9277$ amu

Hence the atomic mass of the second isotope is 64.9277 amu

Example 7

The diagram below shows the mass spectrum of magnesium. The heights of the three peaks and the mass number of isotopes are shown. Calculate the relative atomic mass of magnesium.



Solution

$$A_r = \frac{\sum(\text{Isotopic mass} \times \text{intensity})}{\text{Total intensity}} = \frac{24\times63+25\times8.1+26\times9.1}{63+8.1+9.1} = 24.3$$

Therefore, the relative atomic mass of magnesium is 24.3

Example 8

In a sample of 400 lithium atoms, it is found that 30 atoms are lithium-6 (6.015g/mol) and 370 atoms are lithium -7 (7.016g/mol).Calculate the average atomic mass of lithium.

Solution

$$\text{Using } A_r = \frac{\sum(\text{Relative abundance} \times \text{isotopic mass})}{\sum \text{Abundance}}$$

But abundance of isotopic is directly proportional to the number of atoms of the isotopes

It follows that: $A_r = \frac{\sum(\text{Number pf atoms of isotope x isotopic mass})}{\text{Total number of atoms in the sample}}$

$$= \left(\frac{370\times7.016+30\times6.015}{400}\right)\text{g/mol} = 6.941\text{g/mol}$$

Hence the average atomic mass of lithium is 6.941g/mol

Alternative solution:

Percentage abundance of Li $-$ 6 $= \frac{\text{Number of atoms of Li}-6\text{ in sample}}{\text{Total number of atoms in the sample}} \times 100\%$

$$= \frac{30}{400} \times 100\% = 7.5\%$$

And percentage abundance of Li $-$ 7 $= (100 - 7.5)\% = 92.5\%$

(Summation of percentage of abundance must be 100%)

- Then with those percentage abundances for $\mathrm{Li}-6$ and$\mathrm{Li}-7$, you may continue on your own to get the final answer.

Example 9

Natural rubidium has the average mass $85.4678\mathrm{amu}$ and is compared of isotope $\mathrm{Rb}-85(\mathrm{mass}=84.9117\mathrm{amu})$ and $\mathrm{Rb}-87$. The ratio of atoms $\frac{\mathrm{Rb}-85}{\mathrm{Rb}-87}$ in natural rubidium is 2.591. Calculate the mass of $\mathrm{Rb}-87$.

Solution

Using $\mathrm{A_r}=\frac{\sum(\text{Number of atoms of isotope}\times\text{isotopic mass})}{\text{Total number of atoms of isotopes}}$

Given that: $\frac{\text{Number of atoms of Rb}-85}{\text{Number of atoms of Rb}-87}=\frac{2.591}{1}$

That is for every 2.591 atoms of $\mathrm{Rb}-85$ there is 1 atom of $\mathrm{Rb}-87$.

So substituting $85.4678=\frac{2.591\times84.9117+1\times\mathrm{m}}{2.591+1}$

Where m stands for isotopic mass of $\mathrm{Rb}-87$

- When solving for m in the above equation, gives $\mathrm{m}=86.9087$ amu

Hence the mass of $\mathrm{Rb}-87$ is 86.9087 amu

Example 10

The mass spectrum of Cl_2 shows peaks at masses 70, 72 and 74 a.m.u. The heights of the peaks are in the ratio of 9:6:1 respectively. What is the relative abundance of ^{35}Cl ad ^{37}Cl? Hence calculate the average mass.

Solution

^{35}Cl – ^{35}Cl show peak at mass of 70

^{35}Cl – ^{37}Cl shows peak at mass of 72

^{37}Cl – ^{37}Cl shows peak at mass of 74

Thus % o f ^{35}Cl = $\left(\frac{9+\left(\frac{1}{2}\times6\right)}{9+6+1}\right)\times100\%=\frac{12}{16}\times100\%=75\%$

% of ^{37}Cl = $\left(\frac{1+\left(\frac{1}{2}\times6\right)}{9+6+1}\right)\times100\%=\frac{4}{16}\times100\%=25\%$

Thus the relative abundance of ^{35}Cl is 75%

The relative abundance of ^{37}Cl is 25%

Using;

$\mathrm{A_r}=\frac{\sum(\text{isotopic mass}\times\text{percentage abundance})}{100}=\frac{75\times35+25\times37}{100}=\frac{2625+925}{100}=35.5\ \mathrm{a.m.u}$

Therefore average mass of chlorine atom is 35.5 a.m.u

In this question it was instructed to find firstly relative abundances before finding average atomic mass, otherwise the following alternative solution **would** be applicable.

Using; $\frac{\sum(\text{isotopic mass}\times\text{intensity})}{\text{Total intensity}}$ = Average molecular mass

Then average molecular mass = $\frac{70\times9+72\times6+74\times1}{9+6+1}=71\ \mathrm{a.m.u}$

Since one molecule of chlorine consist of two atoms of chlorine (Chlorine is diatomic molecule), then average atomic mass = $\frac{1}{2} \times$ Average molecular mass

$$= \frac{1}{2} \times 71.\mathrm{m.u} = \ 35.5\ \mathrm{a.m.u}$$

Thus average atomic mass is 35.5 a.m.u

Let % abundance of ^{35}Cl be y that of ^{37}Cl be x.

Then x+y = 100 (Total % abundances must be 100)

From which, x = 100 - y

So using $\mathrm{A_r} = \frac{\sum(\text{isotopic mass} \times \text{percentage abundance})}{100}$

Then 35.5 = $\frac{35y+37(100-y)}{100}$

Or 3550 = 35y + 3700 – 37y

From which 2y = 150; y = 75 and x = 100-y = 100-75 = 25

Thus the relative abundance of ^{35}Cl is 75%

The relative abundance of ^{37}Cl is 25%

The above alternative solution is given for purpose of expanding your knowledge but it is **incorrect** according to the given instructions because of the word **'hence' ……..,** limit us to find relative abundances before calculating the average atomic mass and not vice-versa.

DIGGING DEEPER EXERCISE 1

Question 1

Nitrogen is made up of two isotopes, $\mathrm{N-14}$ and $\mathrm{N-15}$. Given nitrogen's atomic weight of 14.007, what is the percent abundance of each of isotopes?

Question 2

Oxygen is composed of three isotopes; one has a mass of 16.999 amu.This isotope make up 0.037% of oxygen. Of the other two, one has a mass of 15.995amu, and the other has a mass of 17.999amu. Calculate the abundance of the other two isotopes, using the average atomic mass of 15.9994amu.

Question 3

Beanium, a new 'element' has been discovered, Beanium is known to have three naturally occurring stable "isotopes". A sample of 77 'atoms' of Beanium was tested and the following results were obtained.

Isotope	Number in sample	mass
Black	55	10.26g
Brown	15	8.64g
White	7	8.67g

Calculate the 'atomic weight' of Beanium

Question 4

A sample of element X contains 100 atoms with a mass of 12.00 and 10 atoms with a mass of 14.00. Calculate the average atomic mass (in amu) of element X

Question 5

Sample of boron with relative atomic mass of 10.8 gives a mass spectrum with two peaks, one at $\mathrm{m}/\mathrm{z} = 10$ and another at $\mathrm{m}/\mathrm{z} = 11$. Calculate the ratio of the height of two peaks.

Question 6

A sample of argon (Ar) known to contain isotopes of mass numbers 36, 39 and 40 is introduced in a mass spectrometer. The sample is bombarded with electrons to form positively charge ions

a) Which ion ${}^{36}_{18}\mathrm{Ar}^{+}$ or ${}^{40}_{18}\mathrm{Ar}^{+}$, is likely to be deflected most in the magnetic field? Give a reason for your answer.
b) Some atoms lose two electrons in the ionisation chamber. Which ion ${}^{36}_{18}\mathrm{Ar}^{+}$ or ${}^{36}_{18}\mathrm{Ar}^{2+}$, is likely to be deflected most in the magnetic field? Give a reason for your answer.

Question 7

The following table gives isotopic composition data for argon and potassium.

Element	Atomic number	Relative isotopic mass	Relative abundance (%)
Argon	18	35.978	0.307
		37.974	0.060
		39.974	99.633
Potassium	19	38.975	93.3
		39.976	0.011
		40.974	6.69

a) Determine the relative atomic masses of argon and potassium

b) Explain why the relative atomic mass of argon is greater than that of potassium although potassium has larger atomic number

Question 8

The neutron was not discovered until more than 30 years after the discovery of the proton and the electron. Why was the neutron more difficult to detect?

Question 9

From the following nuclei select the isotopes and isobars

${}^{238}_{92}\mathrm{U}, {}^{234}_{90}\mathrm{Th}, {}^{234}_{92}\mathrm{U}\ {}^{238}_{93}\mathrm{Np}, {}^{234}_{91}\mathrm{Pa}$

Question 10

Clearly distinguish between atomic mass and mass number. In what ways do they differ?

Question 11

The average atomic mass of calcium is $40.08\mathrm{amu}$ .what is probably its most abundant isotope?

Question 12

What is meant by the expressions "Carbon-14" and "Silver-108"?

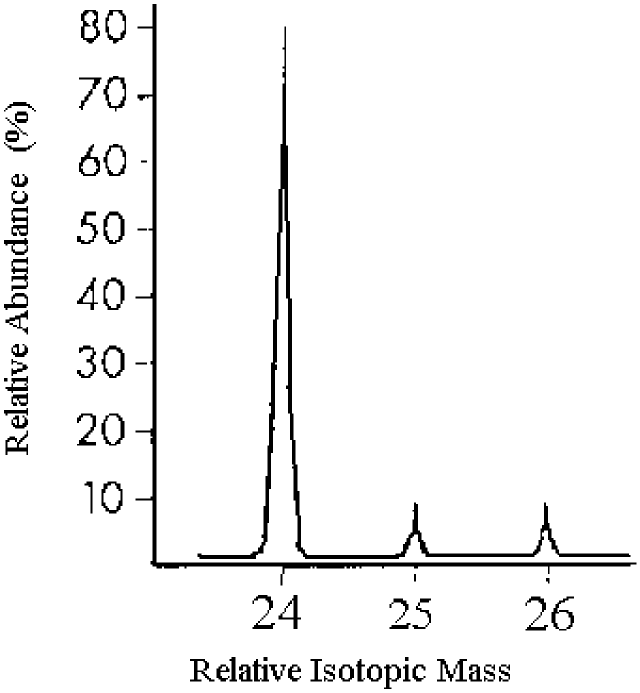
Question 13

Natural neon consists of a mixture of three isotopes: 90.92% $\mathrm{neon} - 20$, atomic mass $19.9924\mathrm{amu}$: $0.257\%\mathrm{neon} - 21$,atomic mass $20.9930\mathrm{amu}$ and 8.82% $\mathrm{neon} - 22$, atomic mass $21.9914\mathrm{amu}$.

a) Without doing any calculations, estimate the approximate average atomic mass of neon.

b) Calculate the average atomic mass of neon

Question 14



Using the mass spectrum of magnesium provided above, answer the following questions:

(a) How many isotopes are present?

(b) What is the RIM of each isotope?
(c) Show the nuclide symbols for each isotope.

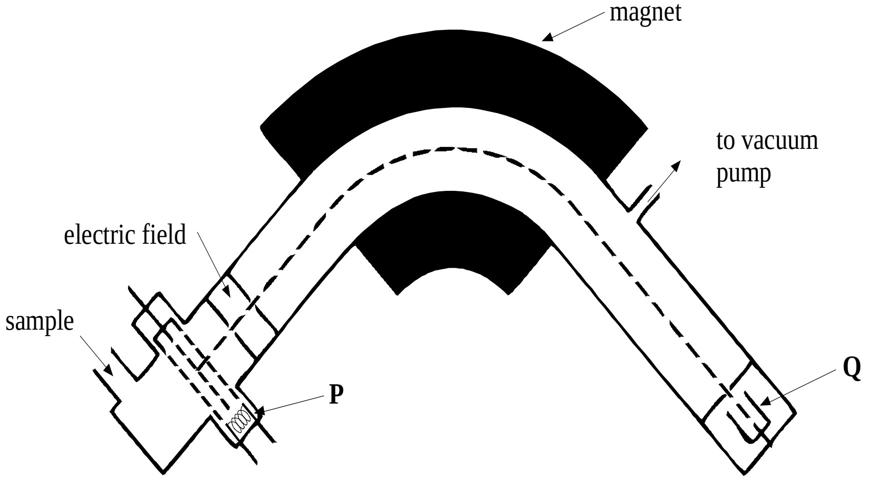
(d) Calculate the relative atomic mass (RAM) of magnesium.

Question 15

The RAM listed in the Periodic Table for Magnesium is 24.305. A form five student claims "there isn't a single magnesium atom in the universe with a mass of 24.305." Is this statement correct? Explain your answer.

Question 16

Figure below is a simplified diagram of a mass spectrometer.



Figure

(i) State and explain the purpose of the part of the mass spectrometer labelled **P**.

(ii) State the purpose of the *electric field* of the *magnet* and of the part labelled **Q.**

Question 17

For each of the following stage in a mass spectrometer, state which part of the spectrometer is responsible for it and how it works?

a. Ionisation
b. Acceleration
c. Deflection
d. Detection

Chapter 2

HYDROGEN SPECTRUM

INTRODUCTION

Definition of terms

Electromagnetic spectrum *is the arrangement of all types of radiation in order of increase of wavelength or decrease of frequency.*

Wavelength (λ) *is the distance between two successive points of the wave e.g. distance between two successive crests or successive troughs of a wave.* Its standard unit is metre (m). Other units are centimeters (m), nanometer (nm) and angstrom (A°) such that:

$$1\text{cm} = 10^{-2}\text{m}, 1\text{nm} = 10^{-9}\text{m and } 1\text{A}° = 10^{-10}\text{m}$$

Frequency (f) *is the number of complete oscillations (cycles) per second*. Its standard unit is Hertz (Hz) or s^{-1} such that 1Hz = s^{-1}.

Amplitude (a) *is the maximum displacement of the medium particles from their rest mean position.* Its standard unit is metre (m)

Wavenumber (also spelled **wave number),** $\mathcal{V}$**,** *is the number of wave per unit length*. The wave number is the reciprocal of wavelength.

That is: $\mathcal{V} = \frac{1}{\lambda}$

Relationship between wavelength, frequency and speed of radiation

Wavelength (λ), frequency (f) and speed (c) of radiation are related according to the following equation:

$$f = \frac{c}{\lambda} \text{ or } c = \lambda f$$

- Where speed of radiation (c) is 2.99792×10^{8}m/s (which is always approximated to 3×10^{8}m/s)
- Thus we can conclude from the relation; $f = \frac{c}{\lambda}$; c having constant value, $f \propto \frac{1}{\lambda}$; that is frequency of electromagnetic radiation varies inversely proportional to wavelength of the radiation

Also since $\mathcal{V}=\frac{1}{\lambda}$ where $\mathcal{V}$ is wavenumber

And from; $f = \frac{c}{\lambda}$; $\lambda = \frac{c}{f}$

From which; $\frac{1}{\lambda} = \frac{f}{c}$

Hence $\mathcal{V} = {}^{f}/_{c}$

Example 1

Most of the light from a sodium vapour lamp has wavelength of 589nm. What is

(i) Frequency and
(ii) Wave number of this radiation (c = 2.998×10^{8}m/s)

Solution

$$f = \frac{c}{\lambda}$$

Substituting the given data to the above equation:

$c = 2.998 \times 10^8/\text{m/s}$

And $\lambda = 589\text{nm} = 589 \times 10^{-9}\text{m}$ $(1\text{nm} = 10^{-9}\text{m})$

Then $f = \frac{2.998\times10^8\text{m/s}}{589\times10^9\text{m}} = 5.09 \times 10^{14}\text{s}^{-1}$

(i) The frequency of the radiation is $5.09 \times 10^{14}\text{s}^{-1}$.

Wavenumber of the radiation is given by the following equation:

$$\mathcal{V} = \frac{1}{\lambda}$$

But $\lambda = 589 \times 10^{-9}\text{m} = 5.89 \times 10^{-7}\text{m}$

Hence $\mathcal{V} = \frac{1}{5.89\times10^{-7}\text{m}}\text{m}^{-1} = 1.6978 \times 10^6\text{m}^{-1}$

(ii) The wave number of the radiation is $1.6978 \times 10^6\text{m}^{-1}$

Types of spectra

There are two main types of spectra, namely;

(i) Emission spectra
(ii) Absorption spectra

(i) Emission spectra

Emission spectra *are obtained from substances causing them to emit radiation through excitation of electrons.*

Emission spectra can be obtained from the following examples:

- Heating a substance to higher temperature, electrons acquire energy so that are promoted to higher energy and in the course of turning back to ground state emission of radiation occur. Here the **heat energy** causes the excitation of electrons.
- Electrical stimulation of a substance. Here the **electric energy** causes the excitation of electrons.

Types of emission spectra

There are three types of emission spectra. These are:

(a) Continuous spectra
(b) Band spectra
(c) Line spectra

(a) Continuous spectra

This is the arrangement of all possible radiation of all frequencies over a wide range of frequencies.

Continuous spectra can be obtained from the sun or any other glowing body. A common example of continuous spectra is a rainbow which is produced when sunrays are dispersed by rain drops or mist.

- Spectrum shows no clear cut way between one radiation and other. It shows the presence of radiation of all wavelengths.

Continuous spectrum of white light from the incandescent lightbulb can be represented as follows:

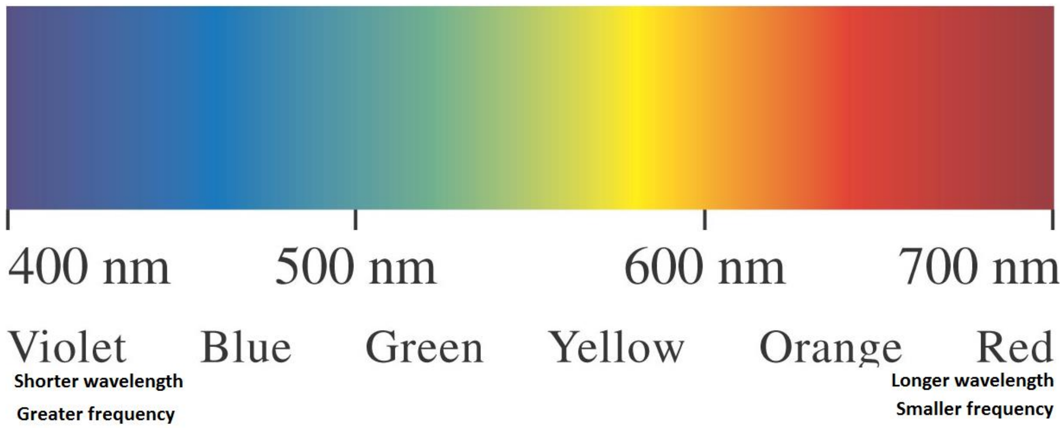


Figure: Continuous spectrum from incandescent lightbulb

(b) Band spectra

This consists of a well defined number of groups of closely packed lines.

Band spectra are usually emitted by molecules hence the term **molecular spectra** for band spectra. The spectrum shows clear cut way between radiations.

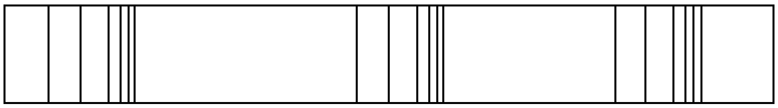


Figure: Emission band spectrum

(c) Line spectra

This consists of separate lines with very little or no grouping at all. The lines vary in intensity; some are sharp and others are diffuse.

- The line spectrum is emitted when an element in gaseous state is excited, for example in an electric discharge tube.

Each element has its characteristic line spectrum that can be used to indentify it hence line spectrum is commonly termed as ***atomic spectrum.***

- **So no two elements have the same atomic emission spectrum and hence like mass spectrum the atomic emission spectrum of an element also acts as a fingerprint of the element.**

In production of line spectra by application of heat, an electron from the atom rises from its ground state to some higher energy state (excited state) by absorption of the heat energy. When if fall back to its lower energy level (its ground state) it loses that energy in one or more steps and the surplus energy is emitted in the form of a line spectra.

It should be noted that:

- The wavelength of the lines emitted depends on the quantity of energy liberated and hence absorbed energy. The greater the energy absorbed by the atom the shorter the wavelength (and the higher the frequency of the emitted radiation)
- Line spectra give ideal of distribution and behaviour of electrons in different atoms.

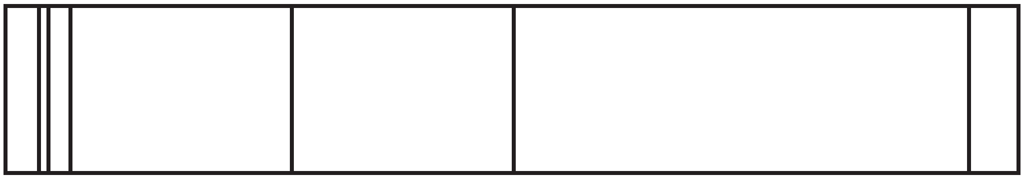


Figure: Emission line spectrum

(ii) Absorption spectra

Whatever colours an element gives off in emission spectrum it also absorbs in absorption spectrum.

- **Absorption spectra** *are formed when atoms of different element are made to absorb radiation.*

Absorption spectrum can be obtained from the following example:

> When light with a continuous spectrum passes through a low-density cold gas, specific colours of light are absorbed for exciting electrons in the gas, leaving dark lines in an absorption spectrum.

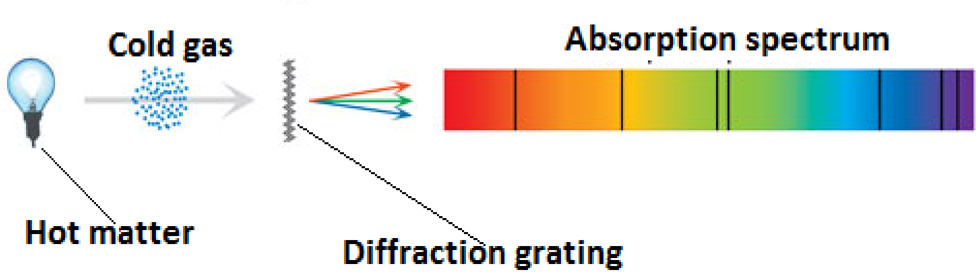


Figure: Absorption spectrum

The reader should understand that like in emission spectrum, absorption spectrum can also divided into three types which are line, band and continuous spectrum.

Emission versus absorption spectra

Emission spectra is formed when electrons pass from higher to lower energy level while absorption spectra consist of dark lines which are formed when the atom gain energy so that electrons pass from a lower to higher energy level.

- Emission spectrum can be obtained when excited electrons return to either ground state or lower energy excited state from higher energy excited state in **hot gas** while absorption spectrum can be obtained when electrons in **cold gas** are excited from ground state to excited state by absorbing energy.

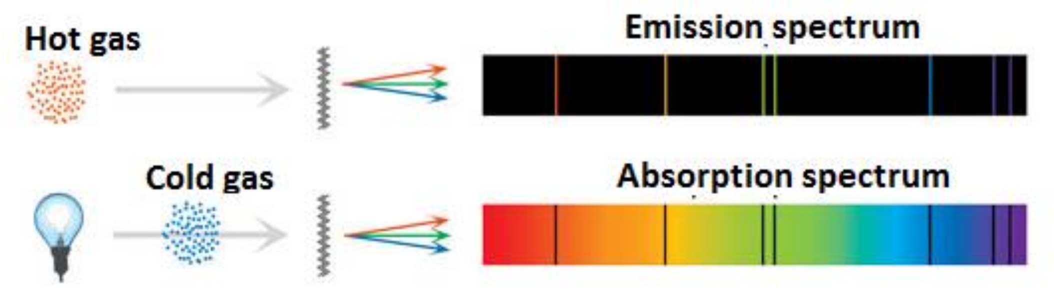


Figure: Emission and absorption spectrum

Differences between emission and absorption spectra

Emission spectrum		Absorption spectrum	
1	Is obtained due to emission of radiation from the substance	1	Is obtained when the substances absorbs radiation
2	White lines are formed on the black background	2	Black lines are formed on the white background
3	Formed when electrons in atoms or molecules are de-excited (returned) from higher energy level to lower energy level	3	Formed when electrons in atoms or molecules are excited from lower energy level to higher energy level

THE HYDROGEN SPECTRUM

As any other element, hydrogen has characteristic line spectrum.

- Hydrogen spectrum is obtained when high voltage is supplied to a discharge tube containing hydrogen gas at low pressure (Gases are good conductor of electricity at low pressure). This results to the formation of bright light.
- When the bright light (pinkish glow) from the discharge tube is analysed by passing through a grating (using simple spectroscope) a series of lines of the hydrogen spectrum are observed as follows:
  - **Balmer series:** if the energy supplied has wavelengths lying in **visible part of the spectrum**. This is seen as one orange, one blue, one purple and two violet lines.
  - **Lyman series:** if the energy supplied is in the **ultra violet (U.V) region**.
  - **Paschen series:** if the energy supplied is in the **infrared region**.
  - **Bracket series:** if the energy supplied is in the **infrared region**
  - **P-fund series:** if the energy supplied is in the **infrared region.**

The series are named in honour of their discovery.

Rydberg equation

All spectra lines can be proved to obey the following mathematical expression which is known as **Rydberg equation**:

$$\frac{1}{\lambda} = \mathcal{V} = \mathbf{R_H}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where:

λ is wavelength in meters (m),

$\mathcal{V}$ is wavenumber in $\mathrm{m^{-1}}$,

$\mathrm{R_H}$ ($\mathrm{R_h}$ or R are also used) is Rydberg constant $= 1.09678 \times 10^7\,\mathrm{m^{-1}}$,

$\mathrm{n_1}$ is an integer which represents the lower energy **excited state** or **ground state** of an electron,

$\mathrm{n_2}$ is an integer which represents higher energy level or **excited state** of the electron.

Thus from definitions of $\mathrm{n_1}$ and $\mathrm{n_2}$, it is clearly understood than $\mathrm{n_2}$ must be greater than $\mathrm{n_1}$, that is $\mathrm{n_1}$ and $\mathrm{n_2}$ are integers where $\mathrm{n_2} > \mathrm{n_1}$.

For your interest!

More general form Rydberg equation is;

$$\frac{1}{\lambda} = \mathbf{R_H\,Z^2}\left(\frac{1}{\mathbf{n_1^2}} - \frac{1}{\mathbf{n_2^2}}\right)$$

When **z** is atomic number

But for hydrogen (as far as hydrogen spectrum is concerned), $Z = 1$ and therefore the Rydberg equation for hydrogen spectrum become

$\frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{\mathrm{n_1^2}} - \frac{1}{\mathrm{n_2^2}}\right)$ as written earlier.

Definitions of ground and excited state

Ground state *is the minimum (lowest) potential energy a particular electron can acquire.* Ground state is also known as **vacuum state** or simply **vacuum**.

Excited state *is the higher energy which is below ionisation energy acquired by an electron after absorption of energy.*

It should be noted that once an electron is in excited state, the electron can return to its ground state or to the lower energy excited state by emitting energy in the form of radiation which is equal to the energy absorbed earlier in exciting the electron but once the electron is completely ionised the electron can never return to its ground state.

When an electron fall from higher energy level to n = 1, the spectral lines formed is known as Lyman series.

Thus from $\frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{\mathrm{n_1^2}} - \frac{1}{\mathrm{n_2^2}}\right)$; $\mathrm{n_1} = 1$ for Lyman series

That is for Lyman series;

$\frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{1} - \frac{1}{\mathrm{n_2^2}}\right)$ where $\mathrm{n_2}$ = 2, 3, 4 etc i.e. $\mathrm{n_2}$ is an integer greater than 1

For Balmer series; **(visible spectrum):** $\mathrm{n_1} = 2$

Then $\frac{1}{\lambda}$ $\mathrm{R_H}\left(\frac{1}{2^2} - \frac{1}{\mathrm{n_2^2}}\right)$ where $\mathrm{n_2}$ = 3, 4 etc

For Paschen series; $\mathrm{n_1} = 3$

Then $\frac{1}{\lambda} = R_H\left(\frac{1}{3^2}-\frac{1}{n_2^2}\right)$ where n_2 = 4, 5, 6 etc

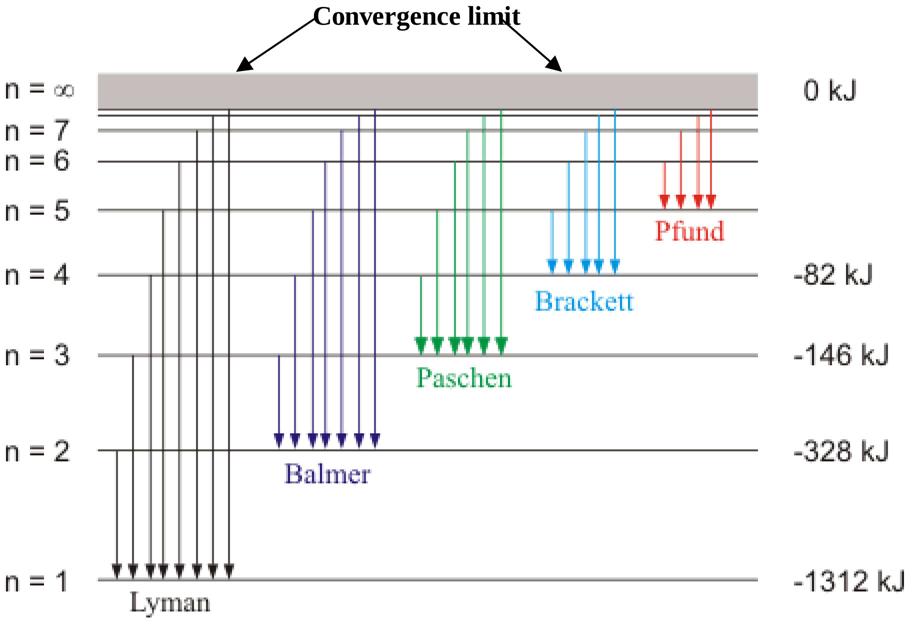
For Bracket series; $n_1 = 4$

Then $\frac{1}{\lambda} = R_H\left(\frac{1}{4^2}-\frac{1}{n_2^2}\right)$ where n_2 = 5, 6, 7 etc.

For P-fund series; $n_1 = 5$

Then $\frac{1}{\lambda} = R_H\left(\frac{1}{5^2}-\frac{1}{n_2^2}\right)$ where n_2 = 6, 7, 8 etc

The above facts can be summarised in the figure below:



Things to note from the above figure:

- As you go to higher energy level (as the value of **n** increases) the energy become less negative implying that they are less attracted to the nucleus.
  - Negative value of energy level implies that the electron in the energy level is attracted to the nucleus (by electrostatic force of attraction between positively charged nucleus and negatively charged electron). More negative energy means that the electron is more attracted to the nucleus and vice –versa.
  - So as the distance from the nucleus increases, the electrostatic force of attraction between nucleus and electron decreases and hence the energy becomes less negative.
  - When n = ∞, (n is too large) the energy is zero indicating that at this region the electron is no longer experiencing nuclear attractive force of the atom.
- Also as you go to higher energy level, the difference between energy levels become smaller and smaller that is: the lines become closer and closer.
  - Eventually the lines converge and the **convergence limit** is reached. Once the electrons reach the **convergence limit** the electron can never return to is ground state implying that the electron is full ionised. Here the distance from the nucleus is so large that attraction (nuclear attractive force of attraction) is negligible and hence the energy is zero.

- The first, second and third lines in Lyman series are n=2, n= 3 and n=4 respectively so:
- First line member of Lyman series implies n_2 = 2 and n_1 = 1
- Second line member of Lyman series implies n_2 = 3 and n_1 = 1
- Third line member of Lyman series implies n_2 = 4 and n_1 = 1
- Similarly for the first, second and third lines in Balmer series are n = 3, n = 4 and n=5 respectively. And the same concept applies for Paschen, Bracket and P-fund series.

Definition of convergence limit

This is the point at which an electron is completely removed from an atom such that the electron cannot return to its ground state.

Alternatively, **convergence limit** can simply defined as *the point at which an electron is completely ionised from an atom.*

Understand these facts!

- Since infrared and ultraviolet radiations cannot be seen by naked eyes; Lyman, Paschen, Brackett and P-fund series are said to form **invisible** part of hydrogen spectrum.
- Since $n = 1$ is closest to the nucleus, the electron on it experience strongest nuclear attractive force and it (the electron) need greatest energy (compared to other energy levels) to be excited.
- This high energy has too short wavelength to be seen by naked eyes and therefore Lyman series is found in the ultraviolet region which is **invisible**.
- Compared to the electron in $n = 1$, the energy required to excite electron from $n = 2$ is relatively small and has wavelength in the visible spectrum and hence Balmer series is found in the **visible** region of the atomic spectrum.
- Since $n = 3$,4 and 5 are farther from the nucleus, which means an electron in these energy levels are weakly held by nuclear attractive force such that only small amount of energy is enough to excite the electron.
- The wavelength of this small energy is too large to be observed by naked eyes and therefore Paschen, Bracket and P-fund series are found at infrared regions of the atomic spectrum and are **invisible spectra**.

Also you should understand that:

Among the infrareds (Paschen, Bracket and P-fund series), Paschen is nearest to the nucleus and hence Paschen series is said to found at ***near*** **infrared region**.

- On another hand P-fund is the farthest one and hence P-fund series is said found at ***far*** **infrared region**. Bracket series is said to be found just at infrared region.

Why there is a formation of different series?

Different series (Lyman, Balmer, Paschen, Bracket and P-fund) are **different spectral lines** whose formation can be explained as follows;

> In a discharge tube there are a large number of hydrogen atoms. When high power voltage is applied in the tube, these atoms are excited differently because they absorb different quantity of energy from the electrical discharge going on in the tube. When the electrons fall back to the ground state they many fall directly from excited state to the ground state or they may do so in steps. Since different excited electrons adopt different routes of energy changes, different lines are produced;

the Lyman series is formed when electrons fall to n = 1 energy level, Balmer series to n =2, Paschen series to n = 3, Bracket series to n = 4 and P-fund series to n = 5

Why Hydrogen spectra are line spectra and not continuous or band spectra?

This is simply because an electron absorbs and emits energy in discrete units of quanta and not continuously.

- This concept is well explained by **Quantum theory** which is going to be discussed in the next section.

Quantum theory

This is the theory advanced in 1900 after another theory termed as classical wave theory which will be discussed first for more convenience.

Classical wave theory

Classical wave theory of radiation state that: *Radiant energy is continuously generated*.

What does classical wave theory imply?

According to classical wave theory of radiation, the radiation energy can have any value from infinitely small to infinitely large.

Why the theory was not a hundred percent correct?

The classical wave theory could not provide a complete explanation of light emission by heated solids such as **blackbody radiation** and **photoelectric effect.**

Blackbody radiation

A blackbody *is a substance that absorbs all light that falls on but reflects none*.

- When a blackbody is heated it emits light. The colour of the light changes from red to yellow then to white as the temperature is increased; *what does this implies?*

The change in colour with temperature shows that the frequency of emitted radiations changes with temperature.

What is the contradiction of classical wave theory with respect to the blackbody radiation?

According to classical wave theory, when blackbody is heated the colour of radiation should stay the same and only the intensity is supposed to increase with temperature.

Photoelectric effect

This *is the effect observed when electrons are ejected from the surface of metals when beam of light of certain frequency strikes the surface*.

- The electrons which are ejected are known as *photoelectrons*.

Early studies of the photoelectric effect revealed the following facts:

- The number of electrons ejected from the surface of the metal depends upon intensity or brightness of incident radiation.
- The kinetic energy with which the electrons are ejected depends on the frequency of the incident light. It does not depend on intensity of radiation

- There is a minimum frequency below which no electrons are emitted regardless to how much the metal surface is illuminated. The frequency is called **threshold** or **critical frequency**

It should be understood that: the threshold frequency depends on the nature of metal. The alkali metals such as sodium, potassium, rubidium and cesium have a quite low threshold frequency.

(Alkali metals have very low threshold frequency because they have low ionisation energy such that their valence electrons are easily knocked off from the metals).

What are contradictions of classical wave theory with respect to photoelectric effect?

- According to the classical wave theory, the radiant energy is supposed to be distributed continuously and uniformly over the wave front. So the kinetic energy of electrons ejected was supposed to depend on the intensity of light and not on the frequency, that is high intensity of light would lead to high kinetic energy of electrons.
- Classical wave theory cannot explain why there is a threshold frequency. According to the theory if the metal is illuminated for sufficient time the electrons will gain sufficient energy and will be ejected.

Planck's quantum theory of radiation

Quantum theory is commonly termed as **Planck's quantum theory** or simply **Planck's theory** based on findings in the blackbody and photoelectric effects, Max Planck in 1901 postulated that radiant energy is quantized i.e. **it is radiated in the form of small packets of energy called photons.**

Postulates of Planck's theory

(i) Any radiation is associated with energy.
(ii) Radiant energy is emitted or absorbed in small packets as quanta **(radiant energy is quantized)**.
(iii) The energy associated with a quantum is proportional to the frequency.
That is: $E \propto f$
Introducing constant for proportionality, the equation of energy of the one quantum become:
$$E = hf$$
Where h is constant of proportionality which is known as **Planck constant** and its value is 6.626×10^{-34}Js.
(iv) The energy is absorbed or emitted in whole number of quanta
That is: $E = nhf$ where n= 1, 2,3,4,5 etc.

Definition of quantum (Plural, Quanta)

This *is a smallest countable, discrete packet of radiant energy that can be absorbed or emitted.*

WORKED EXAMPLES

Example 2

Calculate the wavelength of the first line in Balmer series. ($R_H = 1.097 \times 10^7 m^{-1}$)

Solution

Using $\frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{\mathrm{n}_1^2} - \frac{1}{\mathrm{n}_2^2}\right)$

For Balmer series $\mathrm{n}_1 = 2$

So the first line in Balmer series is n= 3, thus n_2= 3 substituting n_1, n_2 and given constant ($\mathrm{R_H}$) to the above equation gives;

$\frac{1}{\lambda} = 1.097 \times 10^7 m^{-1}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$

From which $\lambda = 6.56 \times 10^{-7}$m

Hence the wavelength of the first line in Balmer series is 6.56×10^{-7}m

Example 3

Calculate the energy of a photon of radiations whose wavelength is 5.89×10^{-5}cm emitted from sodium atoms when heated.

Given that c = 3×10^8m/s and h = 6.62×10^{-34}Js

Solution

Using Planck's equation: E = nhf

Where E is the radiation energy emitted
n is the number of photons
h is the Planck constant
f is the frequency of radiations

But f = $\frac{c}{\lambda}$ where λ is the wavelength in metres

Thus E = $\frac{\mathrm{nhc}}{\lambda}$ where n = 1 (a photon) and $\lambda = 589 \times 10^{-5}\mathrm{cm} = 5.89 \times 10^{-7}\mathrm{m}$

$$\mathrm{E} = \frac{1 \times 6.62 \times 10^{-34} \times 3 \times 10^8}{5.89 \times 10^{-7}}\mathrm{J/photon} = 3.372 \times 10^{-19}\mathrm{J/photon}$$

Hence energy of a photon of radiation is 3.372×10^{-19}J

Example 4

Using plank's equation, calculate the energy of photons of light for radiation of wavelength 242.4nm, the longest wavelength that will bring about the photo dissociation of O_2. What is the energy of (a) one photon (b) a mole of photons of this light?

($\mathrm{h} = 6.626 \times 10^{-34}$Js and c = 2.998×10^8m/s)

Solution

(a) For n = 1: E = hf = $\frac{\mathrm{hc}}{\lambda}$;

Where $\lambda = 242.4\mathrm{nm} = 242.4 \times 10^{-9}\mathrm{m}$
c = 2.998×10^8m/s and h = 6.626×10^{-34}Js

Then E = $\frac{6.626 \times 10^{-34} \times 2.998 \times 10^8}{242.4 \times 10^{-9}}$J/ photon = $8.195 \times 10^{-19}\mathrm{J/photon}$

Energy is $8.195 \times 10^{-19}\mathrm{J/photon}$

(b) One mole of photons has 6.02×10^{23}photons

Thus in the formula E = nhf = $\frac{\mathrm{nhc}}{\lambda}$; n = 6.02×10^{23} photons/mol

But $\frac{\mathrm{hc}}{\lambda}$ = 8.195×10^{-19} (from (a) above)

So E = $8.195 \times 10^{-19}\mathrm{J/photon} \times 6.02 \times 10^{23}$ photon/mol
= 4.9×10^5 J/mol or 4.9×10^2 kJ/mol

Hence energy of a mole of photon is 4.9×10^2 kJ/mol.

Example 5

If the wavelength of the first member of Balmer series in hydro gen spectra is 6563A°. Calculate the wavelength of the first member of the Lyman series.

Solution

Using $\frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{\mathrm{n}_1^2} - \frac{1}{\mathrm{n}_2^2}\right)$

For Balmer series $\mathrm{n}_1 = 2$

So the first line in Balmer series is n = 3, thus $\mathrm{n}_2 = 3$

Given that λ = 6563 A°

But 1 A° = 10^{-10}m

Therefore, 6563 A° $= 6563 \times 10^{-10}\mathrm{m} = 6.563 \times 10^{-7}\mathrm{m}$

Then substituting value of $\mathrm{n}_1, \mathrm{n}_2$ and λ in above equation so as to get the value of $\mathrm{R_H}$

$$\frac{1}{6.563\times10^{-7}\mathrm{m}} = \mathrm{R_H}\left(\frac{1}{2^2} - \frac{2}{3^2}\right) = \mathrm{R_H}\left(\frac{9-4}{36}\right)$$

From which $\mathrm{R_H} = 1.097 \times 10^7 m^{-1}$

But for Lyman series n_1 = 1 and n_2 = 2 for first member

Then $\frac{1}{\lambda} = 1.097 \times 10^7 m^{-1}\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 1.097 \times 10^7 m^{-1}\left(\frac{3}{4}\right)$

From which $\lambda = 1.215 \times 10^{-6}$m or 1215A°

Hence the wavelength of the member in Lyman series is 1215A°

Important tip! It is more appropriate to give the answer in the same form as that of question. Here the given wavelength was in A° so it is suggested that the answer must be also in A° as done in the solution.

DIGGING DEEPER EXERCISE 2

The following constants may be useful in answering questions:

Speed of light= $\mathbf{3.00 \times 10^{8} m/s}$

Planck's constant $\mathbf{= 6.63 \times 10^{-34} Js}$

Rydberg constant $\mathbf{= 1.1 \times 10^{7} m^{-1}}$

Question 1

A hydrogen electron makes a transition from $n = 2$ to $n = 3$

a) Is a photon emitted or absorbed during transition?
b) Calculate the energy, frequency and wavelength of the photon.
c) In what region of the electromagnetic spectrum would you look for the photons?

Question 2

a. Calculate the frequency and wavelength of the spectral line of hydrogen corresponding to a transition of electron from $n = 6$ to $n = 3$
b. In what region of the electromagnetic spectrum would this spectral line be?

Question 3

What is the wavelength (in nm) of the radiation required for a hydrogen electron transition from the 1s orbital to a 2p orbital?

Question 4

Give differences between line and band spectra**.**

Question 5

Calculate the ratio of the wavelength of the first spectral line of Lyman and Balmer series of hydrogen spectrum.

Question 6

A hydrogen atom with an electron in its ground state interacts with a photon of light with a wavelength of 1.22×10^{-6}m. Could the electron make a transition from the ground state to a higher energy level? If it does make a transition, indicate which one. If no transition can occur, explain.

Question 7

Explain where the different colours of light come from in the bright line spectrum of an element.

Chapter 3

ATOMIC THEORIES

Atomic theory *is that theory that attempt to describe the compete structure of an atom.* What is the atom made of? What is the structure of an atom? How do atoms behave? Various atomic theories which we are going to study in this chapter try to answer these and many more questions relating to atom.

DALTON'S ATOMIC THEORY

Assumptions of Dalton's atomic theory

Assumption 1: Matter is made up of very small indivisible particles called atoms

Assumption 2: Atoms can neither be created nor destroyed

Assumption 3: Atoms of the same element are all alike, that is, they have same mass, volume etc.

Assumption 4: Atoms of different elements are different that is; they have different mass and different properties

Assumption 5: Chemical combination takes place between small whole numbers of atoms.

Shortcomings of Dalton's atomic theory

Assumption 1: This assumption is not valid due to existence of three smaller particles in an atom. These particles are electrons, protons and neutrons.

Assumption 2: This assumption is not valid due to existence of both natural and artificial radioactivity. Radioactivity can either create or destroy atoms' nuclei.

Assumptions 3: This assumption is not valid due to existence of isotopes which are atoms of the same element with the same atomic number but differ in mass number due to difference in number of their neutrons. Example C - 12 and C – 14 are two atoms of the same carbon element with different mass number of 12 and 14 respectively.

Assumption 4: To large extent this assumption is valid. However presence of **isobars** makes assumption 4 invalid to some extent.

Assumption5: To large extent this assumption is valid and is supported by the law of chemical combination. Carbon however forms the very complex compounds of organic. For example;

- Molecular formula of chlorophyll is $C_{55}H_{7205}N_4Mg$
- Molecular formula of haemoglobin is $C_{2952}H_{4664}N_{812}O_{832}S_8F_4$

Also the element silicon occurs in some very complex silicates and thus reduces degree of correctness of the **assumption 5.**

THOMSON'S MODEL OF ATOM

Thomson passed a high voltage electric current through a **cathode ray tube**(**Gas discharge tube** or **Crookes tube** in the honour of its discoverer, William Crookes) and observed that the metal electrode gave off a green beam of "light".

- This beam could be attracted and deflected by a magnet, so it was not light but a stream of charged particles which he named **corpuscles** which are nowadays known as **electrons** and assigned a negative charge.

It did not matter what type of metal Thomson used for the electrodes, the beam of particles was always the same.

- Thomson interpreted this to mean that electrons were a fundamental part of all matter.

Thomson reasoned that if the electrodes were initially neutral, but gave off negative particles, then the atom must also contain positive charges.

- He believed that the electrons were embedded in a positive solid matrix, the way that raisins stick in raisin bun or plums stick in pudding.

As result of the above work, in 1898, Thomson suggested a model of an atom. He suggested *the atom to be full of some positive fluid in which electrons were embedded.* The total positive charge in that positive fluid is evenly systematically balanced by the negative charges of electrons. He further thought that the electrons were arranged in the form of ring shells.

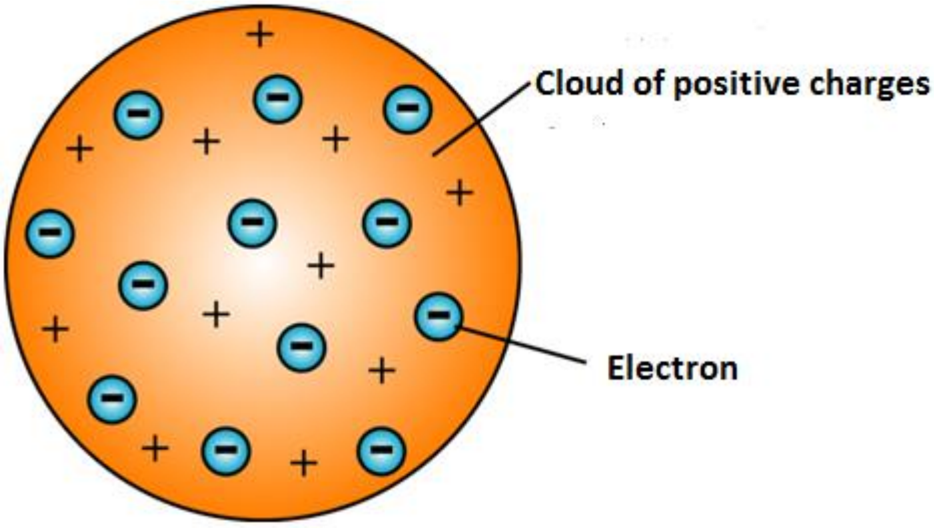


Figure: Thomson atomic model

So Thomson's model of atom can be summarised follows:

- The atom is full of some positive fluid
- Electrons are embedded in that positive fluid
- The total positive charge is equal to the total negative charge of electrons in the atom
- The electrons are arranged in the form of ring shells.

In one sentence, Thomson atomic model may be explained as *"An atom possesses a spherical shape in which the positive charge is uniformly distributed with electrons embedded over it"*

Advantage of Thomson's atomic model

The model explains satisfactorily how heating a substance starts radiating light.

Shortcomings of Thomson's atomic model

(i) Thomson's atomic model **does not explain the stability of an atom.**

According to the Thomson's model, the atom would look like the inside of a pumpkin.

i) It is not supported by Rutherford's $\propto -$ scattering experiment.

The experiment confirms the presence of very small positively charged nucleus in the atom which is completely against Thomson's atomic model.

ii) It cannot be used to explain atomic spectra.

Understand alternative terms for Thomson's atomic model!

- The Thomson's model is sometimes known as **plum-pudding atomic model (or raisin pudding model)**, because it suggests the atom to be full of some positive fluid like a **pudding** in which electrons were embedded like **plums** on that pudding.

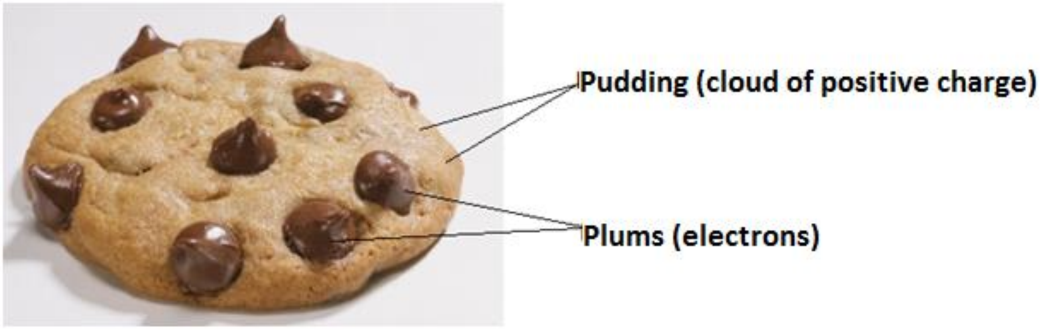


Figure: Thomson's model as plum-pudding model

- Also the Thomson's model suggests that the atom would look like inside the **watermelon** (where the red edible part resemble to the positive charge cloud and black seed resemble to negatively charged electrons in the atom) and hence the term **watermelon atomic model** for the model.

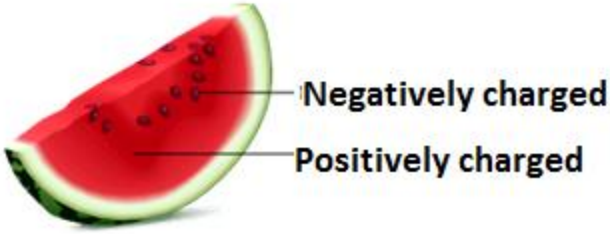


Figure: Thomson's model as watermelon model

- By similar reasoning, Thomson's atomic model is also known as **pumpkin atomic model**.

RUTHERFORD'S ATOMIC MODEL

Rutherford's atomic model came from findings of Rutherford's alpha (α) scattering experiment outlined below.

Rutherford's $\propto -$ray scattering experiment

In $\propto -\mathbf{ray}$ scattering experiment:

- A narrow beam of $\propto -$particles (positively charged particles) is passed through a thin gold foil.
- The gold foil is surrounded by screen made up of fluorescent zinc sulphide.
- Whenever an $\propto -$particle strike the zinc sulphide screen, a tiny flash of light will be produced at that point.

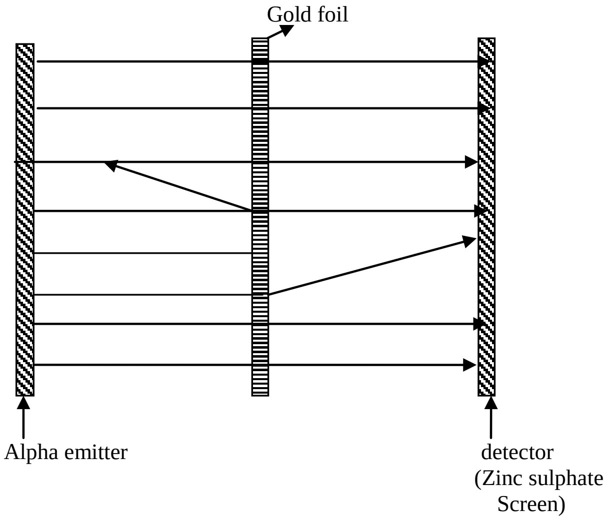


Figure: Rutherford's alpha scattering experiment

Observations from the experiment:

- Most the $\propto -$particles pass through the foil without either deflection or reflection.
- A small fraction of the $\propto -$particles were either deflected by small angle or reflected (bounced back).

Interpretations of observations:

- Most of the space in the atom is empty (that is why most of $\propto -$particles were neither reflected nor deflected).
- The positive charge in the atom is concentrated in very tiny central core called the nucleus (that is why very few $\propto -$particles were able to be either reflected or deflected).

WARNING!

- Most students (even some author) conclude that Rutherford through this famous Rutherford $\propto -$scattering experiment discovered protons. That is not correct, it just virtue truth! What is the real truth?
- The real truth is that, Rutherford discovered the nucleus (Not the proton!).

Assumptions of Rutherford's atomic model

Assumption 1: The whole of the positive charge and nearly the entire mass of an atom is concentrated in extremely small central core called nucleus.

Assumption 2: The electrons are distributed around the nucleus such that there is a lot of empty space in the atom.

Assumption 3: The amount of positive charge in the nucleus is equal to the amount of negative charge electrons so that the atom as whole is electrically neutral entity.

Assumption 4: Electrons revolve around the nucleus in a closed orbit at very high speed (as the planets do around the sun).

Assumption 5: The centrifugal force of revolving electrons is balanced by nuclear electrostatic force of attraction thus keeping the electrons in a constant path.

Assumption 6: No energy is emitted when electrons revolve around the nucleus.

Shortcomings (setbacks) of the Rutherford's model

The Rutherford's model is not acceptable because:

(i) It does not explain the stability of the atom.

- Any charged particle moving around another of oppositely charged continuously loses (emits) energy giving off electromagnetic radiation (according to the laws of electrodynamics). Thus when the electrons revolve around the nucleus in accordance to Rutherford's model, they will spiral to the nucleus and the atom collapse (see the figure below).
- This is simply because as the electrons emit radiation, the energy of electrons should gradually decrease leading to a constant decrease in the radius of the electrons orbit and hence electrons fall into the nucleus.

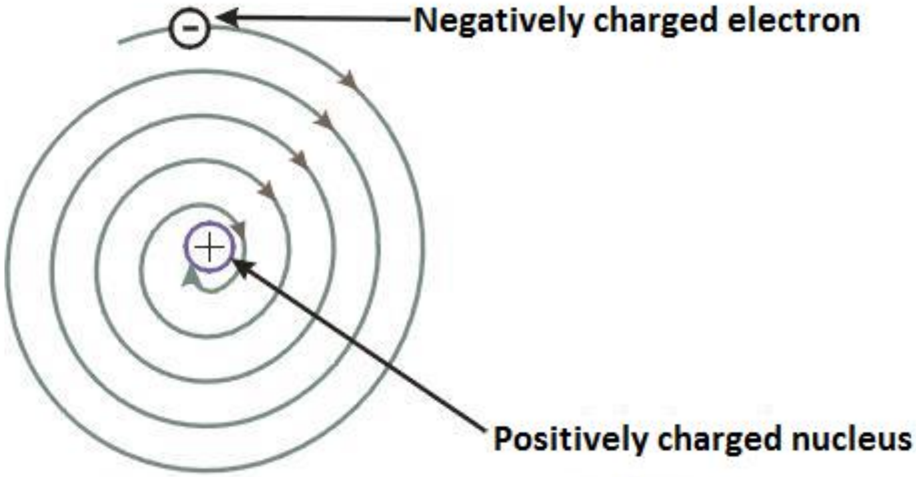


Figure: Collapse of the atom from the Rutherford's model

(ii) The model cannot be used to explain the hydrogen spectra (atomic spectra) which are the line spectra. The spectra provide the evidence of existence of energy levels contradicting with the model which suggests the atomic spectra to be continuous radiation spectrum as the model does not recognise presence of energy levels.

(iii) The model cannot explain the photoelectric effect.

Advantages of Rutherford's atomic model

Assumptions 1: This assumption is correct

Assumption 2: This assumption is correct

BOHR'S ATOMIC MODEL

Bohr passed an electric current through a glass tube containing hydrogen gas.

- He studied the light that the hydrogen gave off using a spectroscope.

If Rutherford's random electron model of the atom was correct, Bohr would have seen a continuous spectrum (a rainbow) that contained all of the colours of light.

- Instead, Bohr saw only four distinct bands of colour, separated by black (no light) regions.
- Bohr interpreted this to mean that the electrons could only be certain, discrete distances from the nucleus.

He proposed model of the atom, in which the electrons are orbiting the nucleus in fixed predictable orbits that are discrete distances form the nucleus.

Assumptions of Bohr's atomic model

Assumptions 1: An atom consists of very tiny positively charged nucleus. Nearly the entire mass of the atom is concentrated in the nucleus.

Assumption 2: The electrons in an atom revolve around the nucleus in a certain permitted circular orbits. The electrostatic force of attraction between the electron and the nucleus provides the necessary centripetal force.

Assumption 3: In an atom there are energy levels or energy states called **stationary states** in which electrons do not emit (radiate) energy, the energy of the orbits is quantized, that is they have fixed value of energy to enable electrons keeps on moving in the same orbit.

Assumption 4: The **angular momentum** of the electrons in stationary states (ground states) **quantized** and it is an integral multiple of $\frac{h}{2\pi}$

That is **angular momentum** = $\frac{\mathbf{nh}}{2\pi}$

Where $n = 1, 2,3,4,5$ etc, that is n stands for an integral multiple

But $\text{angular momentum} = \text{mvr}$

Hence $\text{mvr} = \frac{\text{nh}}{2\pi}$

Where m is the mass of the in kg

v is the velocity of the electron in m/s

r is the radius of the orbit in metres (m)

h is the plank's constant

Assumption 5: The electron can jump from one orbit to the other when it does so it emits or absorb energy

- Radiation is emitted when electrons move from higher to lower energy levels and the radiation emitted is equal to the energy difference between the two energy levels and is quantized; such that:

  $\Delta E = hf$; where f is the frequency of emitted radiation
- Quantum of energy is absorbed when electrons jump from lower energy level and the energy absorbed is equal to the energy difference between the two energy levels.

Definition of stationary state

Is any of several energy states an atom may occupy without emitting electromagnetic radiation.

- It may be **ground state** or **excited state**.

Advantages of Bohr's atomic model

1. Bohr's atomic model was successful in explaining spectra of hydrogen or ions consisting of one electron only e.g. Hydrogen and Li^{2+}
2. It is true that: the nearly entire mass of the atom is concentrated in the nucleus.

Shortcomings (drawbacks) of Bohr's atomic model

1. It does not explain the spectrum of multi-electron atoms.
2. It does not explain the relative intensity of spectral lines (that is why some spectral lines are brighter while others are dimmer).
3. The model does not explain how covalent bonding makes a molecule stable because the model does not recognise the existence of sub-energy levels.
4. The model viewed an electron as being placed at certain distance from the nucleus but it was proved by Werner Heisenberg in his **Heisenberg's uncertainty principle**, which states that, **"It is impossible at any moment to predict simultaneously the exact position and velocity of an electron in an atom"**
5. No clear justification was given for the quantization of angular momentum of electron and presence of stationary states.
6. Bohr's model suggests that the electron move in circular orbit in two dimensions while it has been proved that (in **quantum mechanical atomic model**) the motion is in three dimensions on the elliptical path.
7. It does not explain presence of **hyperfine spectral lines**.

By definition:

Hyperfine spectral lines *are extremely thin (fine) spectral lines which are formed after splitting one atomic spectral line into two or more components.*

- These spectral lines were not seen by Bohr and it needs more advanced instrument and very careful observation to see them.

8. It does not explain the **Zeeman** and **stark effect**.

By definition:

Zeeman effect (or **Zeeman splitting**) *is the splitting of a spectral line of atoms or molecules when subjected to static magnetic field.*

Stark effect (or **Stark splitting)** *is the splitting of a spectral line of atoms or molecules subjected to the electric field.*

Energy associated with an electron moving in a particular main energy level

Assume an electron (in the **hydrogen atom**) jump from one orbit of n energy level to new orbit of n_1 energy level with respective energy of E and E_1.

- From Rydberg equation:

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

Where λ is the wavelength of the energy absorbed,

R_H is Rydberg constant = $1.097 \times 10^7 m^{-1}$.

From Bohr's theory;

$$\Delta E = hf = \frac{hc}{\lambda} \qquad (f = \frac{c}{\lambda})$$

But $\Delta E = E_1 - E$

Thus $E_1 - E = \frac{hc}{\lambda}$

But from Rydberg equation

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

Then $E_1 - E = hc\,R_H\left(\frac{1}{n^2} - \frac{1}{n_1^2}\right)$

Where h is the plank's constant = 6.626×10^{-34}Js

c is the velocity of radiation = $2.998 \times 10^8 m/s$

So $E_1 - E = 6.626 \times 10^{-34} \times 2.998 \times 10^8 \times 1.097 \times 10^7\left(\frac{1}{n^2} - \frac{1}{n_1^2}\right)$

$E_1 - E = 2.179163 \times 10^{-18}\left(\frac{1}{n^2} - \frac{1}{n_1^2}\right)$

When n is too large, i.e. $n_1 = \infty$, $E_1 = 0$ and $\frac{1}{n_1^2} \approx 0$

Then $\Delta E = E_1 - E = 0 - E = -E$

Thus $-E = 2.179163 \times 10^{-18}\left(\frac{1}{n^2} - 0\right)$

From which; $-E = \frac{2.179163\times10^{-18}}{n^2}J$

But 1ev = $1.6 \times 10^{-19}J$

Then $\frac{-2.179163\times10^{-18}}{n^2}J = \frac{-2.179163\times10^{-18}}{n^2\times1.6\times10^{-19}}ev = \frac{-13.6ev}{n^2}$

Hence energy associated with an electron revolving in an energy level of **n** for **hydrogen atom** is given by:

$$\mathbf{E = \frac{-13.6ev}{n^2}\ ;\ where\ 1ev = 1.6 \times 10^{-19}J}$$

The negative sign in the above formula $\left(\frac{-13.6ev}{n^2}\right)$ implies that the electron in the shell (energy level) is attracted to the positively charge nucleus; that is it experience nuclear attractive force.

HEISENBERG'S UNCERTAINTY PRINCIPLE

It states that: *It is not possible at any moment to predict accurately both position and velocity (or momentum) of an electron in an atom simultaneously.*

This is because:

- The size of electron is very small such that radiations of high energy with very small wavelength are required to detect it thus disturbing position and speed (velocity) of the electron.
- In another hand if radiations of low energy with large wavelength are used position of electrons cannot be detected.

Hence if one (position or speed) is determined fairly accurately the other must correspond less accurate.

To find the approximate position of an electron

Use $\Delta x \times \Delta p = \frac{h}{4\pi}$

Where Δx is uncertainty in measuring in position which is given as an approximate distance from nucleus in metres.

Δp is uncertainty in measuring (determining) momentum in kgmsec^{-1}

h is Planck's constant.

The reader should understand that:

In actual sense the product $\Delta x\Delta p$ is always slightly greater than the value of $\frac{h}{4\pi}$ and hence sometimes Heisenberg equation is written as:

$$\Delta x\Delta p \approx \frac{h}{4\pi} \quad \text{(Or even } \Delta x\Delta p \geq \frac{h}{4\pi}\text{)}$$

Digging Heisenberg uncertainty equation!

From the equation:

$$\Delta x\Delta p \approx \frac{h}{4\pi};$$

$$\Delta p = m\Delta v$$

Where Δv is the uncertainty in the measurement of velocity (speed) of an electron. And m is the mass of the electron.

$$\text{It follows that: } \mathbf{\Delta x \times m\Delta v \approx \frac{h}{4\pi}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(i)}$$

Then from (i) above it is clearly understood that the right hand side of the equation, that is $\frac{h}{4\pi}$ is always a constant with a value of approximately 5.275×10^{-35} (taking $h = 6.626 \times 10^{-34}$ and $\pi = 3.14$). *What does this mean?*

The fact that $\frac{h}{4\pi}$ is very small constant implies that **if m could be a mass of large object like a car or stone, the product $\Delta x \times m\Delta v$ would be very large compared to the value of $\frac{h}{4\pi}$ and hence making the Heisenberg uncertainty equation insignificant.** This is the one of the two reasons of why Heisenberg uncertainty principle is not applicable in the daily life where macroscopic objects are commonly involved.

Also the equation may be rearranged to give the following equation:

$$\mathbf{\Delta x \approx \frac{h}{4\pi \times m\Delta v} \ldots\ldots\ldots\ldots\ldots\ldots\ldots. (ii)}$$

There are two information that can be extracted from (ii) above;

First information:

The uncertainty in determining position (Δx) of an object of mass, m, varies inversely proportional to the uncertainty in the determination of velocity (Δv) of the object.

- That means if the velocity of the object is determined with more accuracy then its position will determined with less accuracy as suggested in Heisenberg uncertainty principle.

Second information:

The uncertainty in determining position of an object (Δx) varies inversely proportional to the mass of the object (m).

- That means **for macroscopic object whose mass is large, Δx become very small and can be neglected. This is another reason, why Heisenberg uncertainty principle is always ignored in the daily life.**

So putting the two reasons together we may conclude that Heisenberg uncertainty principle is useless in the daily life where macroscopic objects are commonly involved because:

i) For large mass, m, the product $4\pi \times m\Delta v$ becomes very large compared to the value of $\frac{h}{4\pi}$ and therefore making the Heisenberg uncertainity equation inapplicable.
ii) For large mass, m, the uncertainty in the determination of the position of an object would be very small (negligible) even if the equation would be applicable.

Be careful!

Sometimes you may be given the constant $\hbar$(with value of about $1.055 \times 10^{-34} J_s$) instead of the most common Planck constant (with value of about $6.626 \times 10^{-34} J_s$).

- This constant relate to Planck constant as per equation :

$$\hbar = \frac{h}{2\pi}$$

- So from $\Delta x.\Delta P = \frac{h}{4\pi}$;
- The equation may be re-written as

$$\Delta x \Delta p = \frac{1}{2} \times \frac{h}{2\pi}$$

- But $\frac{h}{2\pi} = \hbar$
- Hence $\Delta x \Delta p = \frac{\hbar}{2}$; where $\hbar$ is the **reduced Planck constant**.

Therefore **with given value of $\hbar$ instead of h, use the equation$\Delta x \Delta p = \frac{\hbar}{2}$ instead of $\Delta x \Delta p = \frac{h}{4\pi}$.**

To conclude:

Because of the Heisenberg uncertainty principle, the position of an electron moving with a definite velocity cannot be determined exactly.

- It is only possible to predict the probability of an electron being at a given time and the probability is given by **Schrodinger wave equation** (the concept of Schrodinger wave equation is beyond the scope of this book).

The region in space around the nucleus where there is a maximum probability of finding an electron is called the **atomic orbital**.

WAVE – PARTICLE DUALITY

According to **De Broglie:**

"All material objects are dual in nature, that is; they exhibit both wave and particle characteristics"

Having things like mass is the particle characteristics while having things like wavelength and frequency is the wave characteristics

- So we may combine **Einstein's equation** and **Planck's equation** to get single equation follows:

Consider a photon of light; in **wave model** its energy is given by the following **Planck's equation**:

$$E = hf$$

Where h is Planck's constant

f is the frequency

In the **particle model** the energy is given by the following **Einstein's equation**:

$$E = mc^2$$

Where m is the mass of the photon

c is the velocity.

Equating Plank's and Einstein's equation (Law of conservation of energy)

$$hf = mc^2$$

But $f = \frac{c}{\lambda}$

Then $\frac{hc}{\lambda} = mc^2$

$\frac{h}{\lambda} = mc$ or $\lambda = \frac{h}{mc}$

Hence $\boldsymbol{\lambda = \frac{h}{mc}}$

The last equation is known as **De Broglie equation** and λ obtained according to the above formula is known as **De Broglie wavelength**.

Important thing to notice from the De-Broglie equation:

De-Broglie wavelength varies inversely proportional to the mass of the object which means when mass is large, the De-Broglie wavelength become very small and therefore immeasurable.

- In other words; De-Broglie concept is useless for macroscopic objects like stone because with large mass the De-Broglie wavelength is too small to be measured.
- De-Broglie concept is significant for microscopic objects like electrons whose mass is very small.

Wave-particle duality of an electron

An electron exhibit wave – particle duality also. Thus when an electron is in motion its wavelength is inversely proportional to its **momentum (mc)** whereby Planck's constant (h) is the constant for proportionality.

Particle characteristics of an electron

As a particle an electron has mass, charge and momentum.

Wave characteristics of an electron

As a wave an electron has frequency, wavelength and energy. Electron can also undergo diffraction and can produce interference to justify its wave nature.

Photoelectric effect as evidence of a light behaving as a particle

Light (electromagnetic radiation) is also dual in nature. It may behave as wave as well as particle.

- Light has **wavelength**, **frequency**, and **amplitude** to justify its wave nature. It shows the following properties as a wave;
  i) It undergoes reflection
  ii) It undergoes refraction
  iii) It undergoes diffraction
  iv) It undergoes interference
  v) It undergoes polarisation

Despite of many common evidences of light behaving as a wave there are also some evidences which show that the light is behaving like a particle.

- The fact that light can be emitted or absorbed in very tiny packets (particles) of energy called photon is the main justification of light behaving as a particle.

Presence of light particles (photons) can be verified by **photoelectric effect**.

Recall: **photoelectric effect** *is the ejection of electrons from an atom on the metal surface when the electromagnetic radiation (light) is made to strike the atom.*

Photoelectric effect is very useful phenomenon on understanding wave- particle duality of electromagnetic radiation. Now the question become, ***what observation from the photoelectric effect suggests that the light (electromagnetic radiation) behaves as a particle?*** Don't worry, look for the answer below.

Wrong expectation!

It was thought that electrons were excited from the atom by absorbing the energy in the light wave (not light particle!). And then using that energy to jump out of the metal and therefore exhibiting photoelectric effect.

- So with that point of view (of looking a light as merely a wave) it was expected that the more energy the electrons could absorb, the more energy they could use to jump out. But this is just a shadow of real truth, how?
- By that point of view it was expected that when the light intensity is increased the electrons would gain more energy and hence making them to jump from the metal surface to higher energy level but that did not happen at all!

What a surprise!

Surprisingly even after increasing light intensity the electrons were emitted at the same energy as before. The only change which was noticed is that after increasing intensity of incident light the number of electrons emitted was increased. This observation made the original assumption invalid, it is virtual truth! What is the real truth?

The real truth!

The real truth lies on the presence of photon.

- A photon is almost massless particle carrying a small amount of energy.
- Each photon can excite only one electron at a time
- When light increased, intensity is increased, number of photons (light particles) is also increased and hence greater number of electrons (sub-atomic particles) are knocked off (replaced by photons) from the metal surface (the energy of the electron does not change because the energy of each photon is still the same). This justify that light comprises of particles (photons) and behave as a particles too.

Other particle properties of light (which are also of course wave properties) include:

i) Light can be bounced through reflection
ii) Light can be bounced bent through refraction
iii) Light can be dispersed (scattered) through diffraction.

WORKED EXAMPLES

Example 1

A diode laser emits at wavelength of $987\mathrm{nm}$. All of the radiation it emits is absorbed in a detector which measures a total energy of $0.52\mathrm{J}$ over a period of 32 sec. How many photons per second are being emitted by the laser?

Solution

Energy of one photon is given by the following Planck's equation $\mathrm{E} = \mathrm{hf} = \frac{\mathrm{hc}}{\lambda}$

Substituting $\mathrm{E} = \frac{6.63\times10^{-34}\mathrm{J}\times3\times10^{8}\mathrm{m/s}}{987\times10^{-9}\mathrm{m}} = 2.0152 \times 10^{-19}\mathrm{J/photon}$

But total energy emitted in $32\mathrm{sec} = 0.52\mathrm{J}$

And the total energy=Energy per photon×Number of photons

Thus Number of photons emitted (in 32s)

$$= \frac{\text{Total energy}}{\text{Energy per photon}} = \frac{0.52\text{J}}{2.0152\times10^{-19}\text{J/photon}} = 2.58 \times 10^{18} \text{ photons}$$

And number of photons emitted per second

$$= \frac{\text{Total number of photons emitted}}{\text{Time taken}} = \frac{2.58\times10^{18}\text{ photons}}{32\text{sec}}$$

$$= 8.0625 \times 10^{16}\text{photon/sec}$$

Hence 8.0625×10^{16} photons were emitted in one second.

Example 2

Calculate the wavelength of the line in Balmer series associated with energy transitions: $E_4 \rightarrow E_2$, where:

$$E_4 = -1.362 \times 10^{-19}\text{J}$$

$$E_2 = -5.498 \times 10^{-19}\text{J}$$

$$h = 6.63 \times 10^{-34}\text{Js}$$

$$c = 3 \times 10^{8}\text{m/s}$$

Solution

$\Delta E = hf = \frac{hc}{\lambda}$; But $\Delta E = E_4 - E_2$

Thus $E_4 - E_2 = \frac{hc}{\lambda}$

$$(-1.362 - -5.498) \times 10^{-19} = \frac{6.63\times10^{-34}\times3\times10^{8}}{\lambda}$$

From which; $\lambda = 4.8 \times 10^{-7}$m or 4800A°

Hence the wavelength is 4.8×10^{-7}m or 4800A°

Example 3

An electromagnetic radiation was emitted in the Balmer series as result of electron transition between n = 2 and n = 5. Calculate:

(a) The energy of radiation in kJ/mol
(b) The frequency of radiation
(c) The wavelength of radiation in metres

Where;

$h = 6.63 \times 10^{-34}$Js R= 1.097×10^{7}/m and c = 3×10^{8}m/s

Solution

From $\Delta E = hf$ where $f = \frac{c}{\lambda}$ (for n = 1)

$$\Delta E = \frac{hc}{\lambda}$$

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

Then $\Delta E = hcR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) {}^{\text{J}}/_{\text{Photon}}$

$$\Delta E = 6.63 \times 10^{-34} \times 3 \times 10^{8} \times 1.097 \times 10^{7} \left(\frac{1}{2^2} - \frac{1}{5^2}\right) {}^{J}/_{Photon}$$

$$\Delta E = 2.18 \times 21 \times 10^{-20} \, {}^{J}/_{Photon}$$

But 1 mole of photo contains 6.02×10^{23} photons

Thus energy radiated in J/mol is;

$$2.18 \times 21 \times 10^{-20} \, {}^{J}/_{photon} \times \; 6.02 \; \times 10^{23} \, {}^{photon}/_{mol}$$

In kJ/mol = $\frac{2.18 \times 21 \times 10^{-20} \times 6.02 \times 10^{23}}{1000}$ kJ/mol = 275.6 kJ/mol

Hence energy radiation in kJ/mol is 275.6kJ/mol

(b) From $\Delta E = hf$

$$f = \frac{\Delta E}{h} = \frac{2.18 \times 21 \times 10^{-20} J}{6.63 \times 10^{-34} Js} = 6.9 \times \; 10^{14} Hz$$

Hence the frequency of is 6.9×10^{14}Hz

(c) Using $\lambda = \frac{c}{f} = \frac{3 \times 10^{8}}{6.9 \times 10^{14}} m = 4.35 \times 10^{-7} m$

Hence the wavelength of the radiation is 4.35×10^{-7}m

Alternative solution:

Using $\Delta E = \frac{hc}{\lambda}$

From which $\lambda = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{2.18 \times 21 \times 10^{-20}} m$

$= 4.34 \times 10^{-7}$m

Hence the wavelength o f the radiation is $4.34 \times \; 10^{-7}$m.

Example 4

Calculate the ionisation energy of hydrogen.

Given that $R_H = 1.097 \times 10^{7} m^{-1}$, $h = 6.63 \times 10^{-34}$Js and $c = 3 \times 10^{8} m/s$

Solution

Using $\Delta E = hf = \frac{hc}{\lambda}$

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

So $\Delta E = hc \, R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

In ionisation; the most loosely held electrons is removed i.e. an electron which is found in outmost energy level. For hydrogen this electron is found at energy level of n = 1

So in ionizing hydrogen an electron is removed from energy level of n= 1 to infinity. Thus $n_1 = 1$ and $n_2 = \infty$

Substituting given value of h, c and R_H including values of n_1 and n_2 in above equation of ΔE gives:

$\Delta E = 6.63 \times 10^{-34} \times 3 \times 10^{8} \times 1.097 \times 10^{7}(1-0)\ ^{J}/_{electron}$

$= 2.18 \times 10^{-18}\ ^{J}/_{electron}$

Thus ΔE is 2.18×10^{-18}J for one electron

But from definition of ionisation energy: **ionisation energy must be for one mole of electrons**, that is it must be given in: Units of energy/mol

And one mole of electrons contain Avogadro's number (6.02×10^{23}) of electrons

Therefore ionisation energy of hydrogen:

$= 2.18 \times 10^{-18}\ ^{J}/_{electron} \times 6.02 \times 10^{23}\ ^{electron}/_{mol}$

= 1312360J/mol or 1312.36kJ/mol

Hence ionisation energy of hydrogen is 1312.36kJ/mol

The reader should note that:

Whenever the formula $\Delta E = hf$ is used instead of more general formula of $\Delta E = nhf$ the assumption is that n = 1, so the energy obtained according to the formula $\Delta E = hf$ is for one particle (one electron, one photon etc). So for one mole of particles, $n = 6.02 \times 10^{23}$ which must be multiplied to the result as the formula $\Delta E = nhf$ suggests.

Alternative solution:

Energy associated with an electron of any energy level of hydrogen is given by:

$E = \frac{-13.6ev}{n^2}$ where n is the energy level

In ionizing hydrogen an electron jump from n = 1 to infinity,

So the ionisation energy for one electron = $E_\infty - E_1 = \Delta E$

But $E_\infty = \frac{-13.6ev}{\infty^2} = 0ev\ (n = \infty)$

And $E_1 = \frac{-13.6ev}{1^2} = -13.6ev\ (n = 1)$

So in ionizing one electron the energy which is required is:

$0 - -13.6ev = 13.6ev$ per one electron

For one mole of electrons the energy become;

$13.6 \times 6.02 \times 10^{23}$ev per one mole

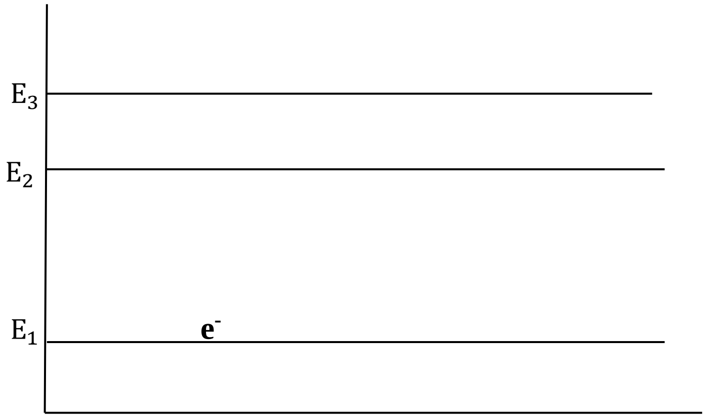
But 1ev = 1.6×10^{-19}J

Hence the ionisation energy is $13.6 \times 6.02 \times 1.6 \times 10^{4}$J/mol = 1309952J/mol or 1309.952kJ/mol

The reader should note that the second method does not need values for h, c and R_H so whenever at least one of the three values is not given it is recommended to use the second method (Remembering constant values does not justify the use of the first method, the constant values should be used if and only if you are given them in the examination regardless to whether you remember them or not).

Example 5

Consider an atom with energy level diagram shown below. An electron is located at E_1.



State what will happen if the atom is exposed to incident radiation of the following energies:

(i) Less than $E_2 - E_1$
(ii) Equal to $E_2 - E_1$
(iii) Less than $E_3 - E_1$ but greater than $E_2 - E_1$
(iv) Equal to $E_3 - E_1$
(v) Greater than $E_3 - E_1$

Solution

(i) Nothing will happen
(ii) Transition will occur between E_2 and E_1
(iii) Nothing will happen
(iv) Transition will occur between E_3 and E_1
(v) Nothing will happen

Example 6

An electron in potassium metal was excited from its ground energy level to a higher energy level after being heated. On returning to its ground state, a violet light of wavelength 4.34×10^{-7}m was emitted. Calculate the energy difference between the ground level and the higher energy level reached by the electron (h = 6.626×10^{-34}Js and $c = 3 \times 10^8 \mathrm{m/s}$)

Solution

Generally: $\Delta E = nhf$

But for n = 1 (An electron), the formula becomes; $\Delta E = hf$

But f = $\frac{c}{\lambda}$

Thus $\Delta E = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3\times10^{8}}{4.34\times10^{-7}}\mathrm{J} = 4.58 \times 10^{-19}J = \frac{4.58 \times 10^{-19}}{41.6 \times 10^{-19}}\mathrm{ev} = 2.8625\mathrm{ev}$

Hence the energy difference is 4.58×10^{-19}J or 2.8625ev

Example 7

The uncertainty in the momentum of a particle is $2.5 \times 10^{-14}\mathrm{gcmsec}^{-1}$

Find its approximate position (h $= 6.626 \times 10^{-34}$ and π 3.14)

Solution

Using $\Delta x \Delta p = \frac{h}{4\pi}$ $\Delta p = 2.5 \times 10^{-14}\text{gcmsec}^{-1}$

Converting given Δp into kgmsec^{-1}

$1\text{g} = 10^{-3}\text{kg}$ $1\text{cm} = 10^{-2}\text{m}$

Thus $2.5\times 10^{-14}\text{gcmsec}^{-1} = 2.5\times 10^{-14} \times 10^{-3} \times 10^{-2}\text{kgmsec}^{-1}$

$= 2.5 \times 10^{-19}\text{kgmsec}^{-1}$

Then from $\Delta x \Delta p = \frac{h}{4\pi}$

$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{6.626\times10^{-34}}{4\times3.14\times2.5\times10^{=19}}\text{m} = 2.11\times 10^{-16}\text{m}$$

Hence the approximate position is 2.11×10^{-16}m from the nucleus.

Example 8

What is the de Broglie's wavelength for a neutron travelling with a velocity 5% of the speed of light (speed of light = 3×10^{8}m/s, h = 6.626×10^{-34} and mass of neutron = 1.61×10^{-27}kg)

Solution

According to De Broglie's equation

$$\lambda = \frac{h}{mv}$$

Where λ is De Broglie's wavelength

V is the speed o f neutron

m is the mass of neutron

But v = $\frac{5}{100} \times 3 \times 10^{8}$m/s = 1.5×10^{7}m/s

$$\lambda = \frac{6.626\times10^{-34}}{1.61\times10^{-27}\times1.5\times10^{7}}$$

$= 2.74\times 10^{-14}$m

Hence de – Broglie wavelength is 2.74×10^{-14}m

Example 9

What is the minimum uncertainty in position as imposed by the uncertainty principle on 100g ball thrown at $42 \pm 1\text{m/s}$? (Hint: $\pm\text{m/s}$ means maximum error in the measurement of speed of the ball is 1m/s)

Solution

From the uncertainty principle, the minimum uncertainty in the position may be found from the following equation. $\Delta x \Delta p = \frac{h}{4\pi}$

From which: $\Delta x = \frac{h}{4\pi(\Delta p)} = \frac{h}{4\pi(m\Delta c)}$

Where $m = 100\text{g} = 0.1\text{kg}$ and $\Delta c = 1\text{m/s}$

Then $\Delta x = \frac{6.63\times10^{-34}}{4\times3.14\times0.1\times1} = 5.28\times10^{-34}\text{m}$

Hence the minimum uncertainty in the position is $5.28\times10^{-34}\text{m}$

Example 10

A car weighing $3\times10^{3}\text{kg}$ is moving on a highway. Its speed can be measured with an accuracy of $\pm0.0025\ \text{mile/hour}$ and its position with an accuracy of $\pm0.01\text{mile}$. Is the Heisenberg uncertainty principle valid? (1mile = $1.6\times10^{3}\text{m}$)

Solution

$$\Delta v = \frac{0.0025\text{mile}}{\text{hour}} = \frac{0.0025\times1.6\times10^{3}\text{m}}{3600\text{s}} = 1.11\times10^{-3}\text{m/s}$$

Then $\Delta p = m\Delta v = 3\times10^{3}\times1.11\times10^{-3}\text{m/s} = 3.33\text{kgm/s}$

And $\Delta x = 0.01\text{mile} = 0.01\times1.6\times10^{3}\text{m} = 16\text{m}$

It follows that; $\Delta x\Delta p = 16\times3.33 = 53.28$

But; $\frac{h}{4\pi} = \frac{6.626\times10^{-34}}{4\times3.14} = 5.275\times10^{-35}$

Since $\Delta x\Delta p$ is very large compared to $\frac{h}{4\pi}$, the uncertainty principle is not valid here.

DIGGING DEEPER EXERCISE 3

The following constants may be useful in answering questions:

Speed of light$= \mathbf{3.00 \times 10^{8} m/s}$

Planck's constant $= \mathbf{6.63 \times 10^{-34} Js}$

Rydberg constant $= \mathbf{1.1 \times 10^{7} m^{-1}}$

Question 1

In what way does the photoelectric effect support the particles theory of light?

Question 2

Under what circumstances can an atom emit a photon? Give two possibilities.

Question 3

Why Bohr's orbits called stationary states?

Quest ion 4

Compare and contrast the models of the atom that were proposed by Rutherford and Thomson.

Question 5

Compare and contrast the models of the atom that were proposed by Rutherford's and Bohr.

Question 6

A beam of electrons and beam of protons are moving with the same speed. Which has longer De Broglie wavelength?

Question 7

What does the 'photoelectric effect' say about nature of light?

Question 8

If matter has wave nature why is this wave- like character not observed in our daily experiences?

Question 9

An electron and proton have the same kinetic energy and are moving at non-relativistic speeds. Determine the ratio of the De-Broglie wavelength of the electron to that of the proton.

Give that:

Mass of an electron$= 9.11 \times 10^{-31}$kg

Mass of proton $= 1.67 \times 10^{-27}$kg

Question 10

Calculate:

a. The de Broglie wavelength of an electron moving with a velocity of $5 \times 10^{5} \mathrm{m/s}$ and
b. Relative de Broglie wavelength of an atom of hydrogen and atom of oxygen moving with the same velocity.

Given that:

Mass of an electron$= 9.11 \times 10^{-31}$kg

Atomic mass of $\mathrm{O} = 16$

Atomic mass of $\mathrm{H} = 1$

Question 11

In 1905, Ernest Rutherford carried out an experiment to determine the nature of atoms. He fired alpha particles at a thin gold foil. After carrying out the experiment he concluded that the atoms were mainly empty space, and that most of the matter was contained in a small, very dense, positively charged object that was more massive than the alpha particle. The object later became called the nucleus.

a. If there was air between the alpha source and the gold foil, the air would become ionised. Explain what is meant by the term "ionised".
b. Describe the results of the experiment and explain clearly how he linked his result to his conclusion.

Chapter 4

QUANTUM NUMBERS

INTRODUCTION

The most important conclusion from the wave mechanical model of the atom is that: *Electrons occupy certain regions in space, called* ***orbital****.*

What is an atomic orbital?

Atomic orbital *is the region around the nucleus of an atom where there is a high probability of finding electrons.* They accommodate a maximum of two electrons.

- Atomic orbitals are also known as **electron clouds**.

An electron can be described better by the study of **quantum numbers** which can be defined as *levels used to describe electrons at their stationary states.*

- Quantum number determine all what is to be known about an electron, that is; allowed energy, shape of the orbital and direction of the spin. There are four types of quantum number which are
    - Principle quantum number
    - Subsidiary quantum number
    - Magnetic quantum number
    - Spin quantum number

PRINCIPLE QUANTUM NUMBER (n)

Principal quantum number *is the main energy level in which the electron is placed.*

- Principal quantum number was **proposed by Bohr to explain the hydrogen atomic spectrum.**

Principal quantum number is also known as **primary quantum number**.

- It is denoted by whole numbers and letters where:

K stands for n =1
L stands for n=2
M stands for n=3
N stands for n=4

Thus letters: K, L, M, N and numbers 1, 2, 3, 4 are used interchangeably to denote principle quantum number.

- Theoretically principal quantum number takes any positive integer number from 1 to infinity

What information can be deduced from principal quantum number?

Principle quantum number:

- **Specify probable distance of an electron (orbital) from the nucleus.**

The larger **n** is, the greater the average distance of an electron in the orbital from the nucleus.

- **Specify the energy of an electron**

Greater value of **n** means greater energy of an electron with that principal quantum number (of n). This is because:

- As the value of n increases, the distance of the electron from the nucleus increases thus decreasing the electron-nucleus electrostatic force of attraction and hence higher energy to the electron.
- Also electron in shells closer to nucleus shield electrons in other orbitals (which are further from nucleus) from the nuclear attractive force. This makes nuclear attractive force to fail to reach the electron in orbitals or shells which are farther from the nucleus.

The effect whereby nuclear attractive force fails to reach to some shells or orbitals properly is known as **screening effect** and is another reason why the energy of the electron increases as the principal quantum number increases.

- In two 'dots', the energy of electron become high as the principal quantum number become larger due to:
  - Increase in distance of an electron from the nucleus
  - Increase in screening effect.

The two reasons make the electron with greater principal quantum number to be weakly held by nuclear attractive force and therefore higher energy to the electron.

- **Specify stability of an electron**
- An electron in an orbital with greater value of n is weakly held by nuclear attractive force making easier for it removed from an atom and hence that electron has higher energy and is unstable.

AZIMUTHAL QUANTUM NUMBER (l)

Azimuthal quantum number has the following alternative terms:

(i) Subsidiary quantum number
(ii) Angular momentum quantum number
(iii) Secondary quantum number
(iv) Orbital quantum number

The student should be able to memorize the four terms because they are commonly used interchangeably.

Azimuthal quantum number *is the energy sublevel in which electron is placed and specifies the shape of an orbital of an electron.*

Azimuthal quantum number is the result of **Sommerfeld theory** (which suggested that the *stationary orbits in which electrons are revolving around the nucleus in the atom are not circular but elliptical shape*) hence the term **Sommerfeld azimuthal quantum number**.

- **Sommerfeld proposed the presence of the azimuthal quantum number to explain the presence hyperfine spectral lines in the hydrogen spectrum**.

Azimuthal quantum numbers take the values from 0 to (n-1) that is; 0, 1, 2, 3….. (n-1)

Example if:

$$n = 1 \text{ then } l = 0 \qquad (\text{where } n - 1 = 1 - 1 = 0)$$

$n = 2$ then $l = 0, 1$ (where $n - 1 = 2 - 1 = 1$)
$n = 3$ then $l = 0, 1, 2$ (where $n - 1 = 3 - 1 = 2$)
$n = 4$ then $l = 0, 1, 2, 3$ (where $n - 1 = 4 - 1 = 3$)

Each number refers to specific type of orbital

$l = 0$ stands for s – orbital	('s' from 'sharp')
$l = 1$ stands for p-orbital	('p' from 'principle')
$l = 3$ stands for d-orbital	('d' from 'diffuse')
$l = 3$ stands for f-orbital	('f' from 'fundamental')

Have you noticed this?

Number of sub-energy levels in a certain main energy level with principal quantum number is equal to n.

For example:

- $n = 1$ has only one sub-energy level (s-sub-energy level) with $l = 0$
- $n = 2$ has two sub-energy levels (s and p sub-energy levels) with $l = 0, 1$
- $n = 3$ has three sub energy levels(s, p and d sub energy levels) with $l = 0, 1, 2$

Shapes of atomic orbitals

s –orbital are spherical and the size of the orbital increase with an increase in principle quantum number.

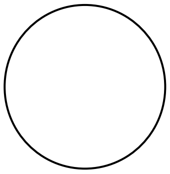


Figure: Spherical shape of s-orbital

p-orbital is dumb-bell shaped and their sizes increase with an increase in principle quantum number.

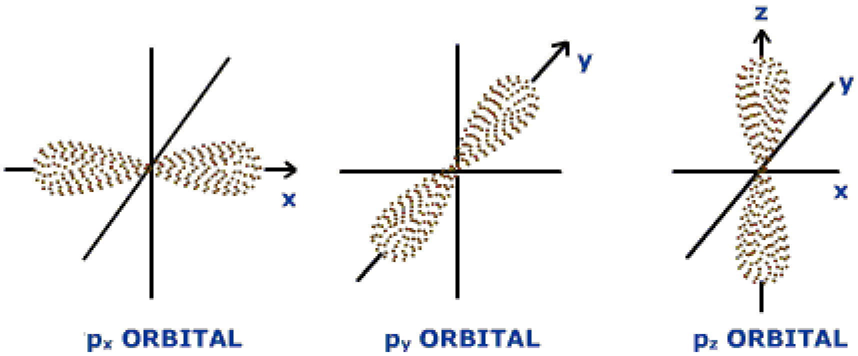


Figure: Dumb-bell shape of p-orbital

d-orbitals are double dumb bell shaped and their sizes increase with an increase in principal quantum number.

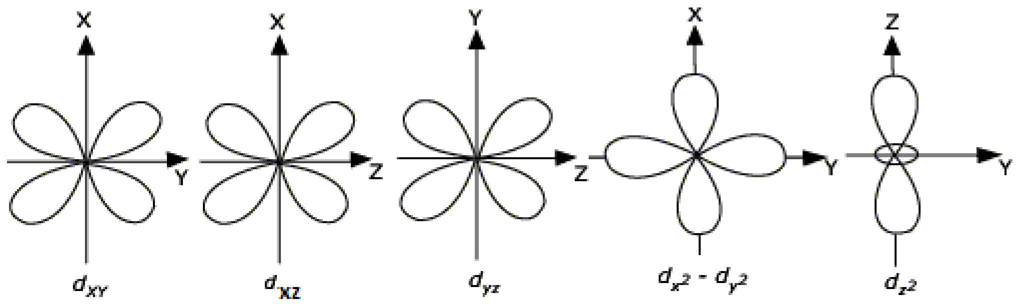


Figure: Dumb-bell shape of d-orbitals

Size of an orbital of specific type increase with an increase in the value of principal quantum number; greater value of n (principal quantum number) means the orbital has larger size. For example size of s-orbital in the first four shells is according to the following order:

$$\mathrm{1s - orbital < 2s - orbital < 3s - orbital < 4s - orbital}$$

↓ Has smallest size

↓ Has largest size

Important information which can be deduced from azimuthal quantum number includes:

i) Probable distance of an electron from the nucleus

- With given principal quantum number, two electrons of the same atom in different sub energy levels have slight difference in their distance from the nucleus of the atom.
- The distance increase as the azimuthal quantum number become bigger
- So the distance of electrons **with same principal quantum number** but differ in azimuthal quantum number is of the following order:

s- electron (electron in s-orbital)<p- electron$< \mathrm{d - electron < f - electron}$

↓ Is closest to nucleus

↓ Is farthest from nucleus

- This implies that with given principal quantum number, s-orbital is closest to the nucleus while f-orbital are farthest.
- You may wonder, how two electrons with the same principal quantum number (in the same shell!) have difference distance from the nucleus? Don't worry here is the reason!

This is because there is repulsion between electrons thus making the electrons to be as far as possible to minimise the repulsion (keep in mind at the same time electrons are attracted to the nucleus). So due to repulsion between electron themselves, electron will arrange themselves in the atom such that the repulsion is balanced by nuclear attractive force.

In just one sentence!

Is the repulsion between electrons which make different orbitals with same principal quantum number to have different distance from the nucleus.

You are certainly going to like to hear that: the same reasons of repulsion between electrons explain why electrons are arranged into different energy levels.

ii) Energy of an electron

With given principal quantum number, different electrons in different sub-energy levels(with different azimuthal quantum number)have slightly different energy due to the following reasons:

- Slightly different in the distance from the nucleus
- Screening effect exerted by electrons in orbitals which are closer to the nucleus.
- Generally the energy of different electrons with the same principal quantum number but differ in their azimuthal quantum number become high as the azimuthal quantum number become bigger and is of the following order:

$$\underset{\substack{\downarrow \\ \text{Has lowest energy}}}{\mathrm{s} - \text{electron}} < \mathrm{p} - \text{electron} < \mathrm{d} - \text{electron} < \underset{\substack{\downarrow \\ \text{Has highest energy}}}{\mathrm{f} - \text{electron}}$$

That is the same as saying that: s-orbital has lowest energy and f-orbital has highest energy provided that the principal quantum number is the same.

Digging deeper!

Among the four quantum numbers, only two first quantum numbers specify the energy of the orbital (or electron).

- Thus sum of n (main energy level) and l (energy sublevel), that is (n+l), is used to determine which orbital has lower energy level than the other; the lower value of (n+l), the lower the energy. Therefore the electron in the orbital with lower value of (n+l) has lower energy.
- For example: comparing 4s and 3d

From 4s, $n= 4$ and $l = 0$ ($s = 0$)

Then $n+l= 4 +0 = 4$

And form 3d, $n= 3$ and $l = 2$ ($d = 2$)

Then $n+l = 3+2 = 5$

Thus 4s has lower sum of (n+l) than 3d and hence 4s-electron has lower energy than 3d-electron.

What happen if two orbitals have the same value of (n+l)?

If two orbitals have the same values of (n+l) then the one with the lower value of n (main energy level) has lower energy.

For example: Comparing 3p and 4s

From 3p, $n= 3$ and $l = 1$ ($p=1$)

Then n+l = 3+1 = 4

From 4s, n=4 and l = 0 (s= 0)

Then n+l = 4+0 = 4

Thus 3p and 4s have the same value of (n+l) which is 4. But because 3p has n=3 which is lower than that of 4p which is 4, 3p-orbital has lower energy than 4s-orbital and whence 3p-electron has lower energy than 4s-electron.

- From the above discussion, the following order of energy of orbitals with different principal quantum numbers can be deduced.

$$1s < 2s < 2\text{p} < 3\text{s} < 3\text{p} < 4s < 3\text{d} < 4\text{p} < 5s < 4d \text{ etc.}$$

Don't overlook!

The concept is valid if and only if there is more than one electron. In other words it is applicable for multi-electron atoms only, why?

- This is because in an atom with single electron there is no repulsion between electrons thus making all orbitals with the same principal quantum number to have the same distance from nucleus. Also this automatically eliminates the possibility of having screening effect and hence the energy of different orbitals with the same principal quantum number remains the same.
- The only factor which determines the energy of orbital in an atom with single electron like hydrogen is the principal quantum number. Thus the energy of different orbital in an atom with sing electron like hydrogen is of the following order;

$$1\text{s} < 2s = 2\text{p} < 3s = 3\text{p} = 3\text{d} < 4s = 4\text{p} = 4\text{d} = 4\text{f etc.}$$

MAGNETIC QUANTUM NUMBER (m or m_l)

Magnetic quantum number *is the quantum number which determines the orientation of the designated orbital.* It differentiates orbital that have the same shape and energy but have different direction when they are subjected to the **magnetic** field (Zeeman effect) and hence the term magnetic quantum number. It is also known as **sub-orbital number**

Magnetic quantum number was discovered by Landé and hence the term **Landé magnetic quantum number.** (Other literature mentions that the number was discovered by Sommerfeld. Landé was a student of Sommerfeld).

Landé proposed presence of magnetic quantum number to explain Zeeman and Stark effect. Zeeman effect and Stark effect is therefore said to support presence of magnetic quantum number and hence support the presence of atomic orbitals.

- The total magnetic quantum numbers is equal to the total number of orbital of that type and is given by 2l+1 (for given value of l; number of orbitals = 2l+1).

Thus if:

l = 0 then 2l+1 = 1 implying that there is one s-orbital

l = 1, then 2l+1 = 3 implying that there are three p-orbital

l = 2, then 2l +1 = 5 implying that there are five d-orbital

l = 3, then 2l + 1= 7 implying that there are seven d-orbital

Hence: Number of orbital in s sub-energy level is 1

Number of orbital in p sub-energy level is 3

Number of orbital in d sub-energy level is 5

Number of orbital in f sub-energy level is 7

Magnetic quantum number is restricted by subsidiary quantum numbers (l) and it is represented by zero (0), positive and negative integers, that is; from –l to +l including zero.

So if:

n=1, l = 0 and m_l= 0 (1 s-orbital) → Total of 1 orbital in n = 1

$$\left.\begin{array}{l} n = 2,\ l = 0,\ \text{where } m_l = 0 \text{ (1 s-orbital)} \\ l = 1 \text{ where } m_l = -1, 0, +1 \text{ (3 p-orbitals)} \end{array}\right\} \text{Total of 4 orbital in } n = 2$$

$$\left.\begin{array}{l} n = 3,\ l = 0,\ \text{where } m_l = 0 \text{ (1 s - orbital)} \\ l = 1,\ \text{where } m_l = -1, 0, +1 \text{(3 p-orbitals)} \\ l = 2 \text{ where } m_l = 2, -1, 0, +1, +2 \text{ (5 d-orbitals)} \end{array}\right\} \text{Total of 9 orbitals in } n = 3$$

$$\left.\begin{array}{l} n = 4,\ l = 0,\ \text{where } m_l = 0 \text{ (1 s-orbital)} \\ l = 1,\ \text{where } m_l = -1, 0, +1 \text{ (3 p-orbital)} \\ l = 2,\ \text{where } m_l = -2,-1, 0, +1,+2 \text{ (5 d-orbitals)} \\ l = 3,\ \text{where } m_l = -3,-2,-1, 0, +1, +2,+3 \text{ (7 f-orbital)} \end{array}\right\} \text{Total of 16 orbitals in } n = 4$$

To insist!

- When $l = 0$, m can only be 0 meaning that there is only one s-orbital.
- When l=1, m = -1, 0, +1 implying that there are three p-orbitals. Whereas:

⇒ $\mathbf{-1}$ corresponds to the $\mathbf{p_x}$ orbital indicating specific p-type orbital on the $x -$ axis

⇒ **0** stands for $\mathbf{p_y}$ orbital lying on the y-axis

⇒ **+1** stands for $\mathbf{p_z}$ orbital on the z-axis.

- When $l = 2, m = -2, -1, 0, +1, +2$ implying that there are five d-orbitals. Whereas:

⇒ $\mathbf{-2}$ stands for $\mathbf{d_{xy}}$ **orbital**

⇒ $\mathbf{-1}$ stands for $\mathbf{d_{xz}}$ **orbital**

⇒ **0** stands for $\mathbf{d_{yz}}$ **orbital**

⇒ $\mathbf{+1}$ stands for $\mathbf{d_{x^2-y^2}}$ **orbital**

$\Rightarrow +\mathbf{2}$ stands for $\mathbf{d_{z^2}}$ **orbital**

Note:

Maximum practical value of l is 3 because greatest atomic number of known element is 118 which has maximum value of l=3 in its electronic structure.

Keep in memory that:

- l takes integer values from 1 to $n-1$

  m_l Takes value from –l to +l including zero
- Number of integers (including zero) in m_l is equal to number of orbitals e.g if m_l = -1, 0 +1 there are three different integers so there are three orbitals.
- If: n = 1 total number of orbitals is 1 = 1^2
  n = 2 total number of orbitals is 4 = 2^2
  n = 3 total number of orbitals is 9 = 3^2
  n = 4 total number of orbital is 16 = 4^2

Hence total number of orbitals in nth energy level = n^2

Where n is the main energy level (principle quantum number)

- Since an orbital can take a maximum of two electrons, maximum number of electron in the energy level is given by $2n^2$
- Any two electrons having the same value of n and l but with different values of m_l are **degenerate** (have the same energy).

SPIN QUANTUM NUMBER (m_s or s)

This *is the quantum number which gives the direction in which electrons are spinning.* It takes values of $+{}^1/_2$ and $-{}^1/_2$.

- $+{}^1/_2$ Indicates that the electron is spinning in the clockwise direction and is shown by using an arrow pointing upward (↿ or ↑).
- $-{}^1/_2$ indicates that the electron is spinning in the anti-clockwise direction and is shown by using an arrow pointing downward(⇂ or ↓)

Since electrons exists in pairs m_s is always denoted by $\pm\frac{1}{2}$ and not net magnetic field. The value of spin quantum number (m_s) does not depend on any of the three quantum numbers.

Spin quantum number was proposed by Goudsmit and Unlenbeck to explain the double line structure of alkali metal spectra.

APPLICATION OF QUANTUM NUMBERS

1. **Quantum numbers are used in determination of the maximum number of electrons a shell have whereby;**
   Total number of spins = Total number of electrons

Example 1

By using quantum numbers deduce total number of electrons in the first shell

Solution

Principle quantum number, n	1
Azimuthal quantum number, l	0
Magnetic quantum number, m_l	0
Spin quantum number, m_s	$\pm {}^{1}/_{2}$

There are total of two electrons

Example 2

What is the total number of electrons in the second shell?

Solution

Principle quantum number, n	2			
Azimuthal quantum number, l	0	1		
Magnetic quantum number, m_l	0	-1	0	+1
Spin quantum number, m_s	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$

Thus total number of electrons is 8

Example 3

Deduce maximum number of electrons which can be contained in third shell

Solution

N	3								
L	0	1			2				
m_l	0	-1	0	+1	-2	-1	0	+1	2
m_s	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$	$\pm {}^{1}/_{2}$

Thus maximum number of electrons is 18

Example 4

Find maximum number of electrons which can be contained in a shell with principle quantum of 4

Solution

n	4															
l	0	1			2					3						
m_l	0	-1	0	+1	-2	-1	0	+1	+2	-3	-2	-1	0	+1	+2	+3
m_s	$\pm{}^1/_2$	$\pm 1/2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$	$\pm{}^1/_2$

Thus a maximum of 32 electrons can be contained in a shell with principle quantum number of 4.

2: Quantum numbers are 'address' of an electron

The four quantum numbers gives about all information we want to know about an electron and therefore acting as the **address** of an electron.

The reader should understand that:

The first three quantum number(n, l and ml)specify a particular orbital. They are ′address′of the orbital.

For example; $n = 2, l = 1, m_l = 0$ represents specific $2p_y$ − orbital.

2: Quantum numbers are used determining electronic distribution (configuration) in an atom

This can be done with combination of application of rules for electron distribution in an atom. It is going to be discussed in detail in the next section.

WORKED EXAMPLES

Example 5

What type of orbital may be specified by the following quantum numbers?

i. $n = 1, l = 0$

ii. $n = 2, l = 1, m_l = 0$

iii. $n = 2, l = 1$

iv. $n = 3, l = 1, m_l = +2$

Solution

i. 3s − orbital iii. 2p − orbitals(which may be $2p_x$,$2p_y$, or $2p_z$ orbital)

ii. $2p_y$ − orbital iv. $3d_{z^2}$ − orbital

Example 6

Assign quantum numbers for the following orbitals:

- i. $3s - \text{orbital}$
- ii. $3P_z - \text{orbital}$
- iii. $2P_x - \text{orbital}$
- iv. $3d_{x^2-y^2} - \text{orbital}$

Solution

- i. $n = 3, l = 0\ m_l = 0$
- ii. $n = 3, l = 1\ \ m_l = +1$
- iii. $n = 2, l = 1\ m_l = -1$
- iv. $n = 3, l = 2\ m_l = +1$

DIGGING DEEPER EXERCISE 4

Question 1

Using s, p, d, f notations to describe the following quantum numbers:

a) $n = 1, l = 0$
b) $n = 3, l = 2$
c) $n = 4, l = 3$
d) $n = 5, l = 4$
e) $n = 4, l = 2$
f) $n = 6, l = 4$

Question 2

Give the differences between orbit and orbital

Question 3

Write down the quantum numbers 'n' 'l', and 'm' for the following orbitals:

i) $3d_{x^2-y^2}$
ii) $4d_{z^2}$
iii) $3d_{xy}$
iv) $4d_{xz}$
v) $2P_z$
vi) $3P_x$
vii) $5f$
viii) $2P_y$
ix) $4s$
x) $3d$

Question 4

Which of the following orbitals are not possible?

$1p, 2s, 2p, 3f, 3d, 4f, 4d, 2f$

Give reason for your choices

Question 5

Which of the following sets of quantum numbers are allowed and which are not? For those which are not allowed state why?

a) $n = 2, l = 1, m_l = 0$
b) $n = 2, l = 2, m_l = 2$
c) $n = 2, l = 1, m_l = -1$
d) $n = 2, l = 1, m_l = -2$

Question 6

Give the values for the quantum numbers n, l, m_l for each orbital in the $4d$ subshell

Question 7

a. What is the maximum number of electrons in the 2p sub shell of an atom?
b. Give the complete set of quantum numbers for each of those electrons.

Question 8

List down four information that can be obtained from principal quantum number.

Question 9

What is the notation of the sub shell in which $n = 4$ and $l = 3$? how many orbitals are in this sub shell?

Chapter 5

ELECTRONIC CONFIGURATION

RULES OF WRITING ELECTRONIC CONFIGURATION

Electronic configuration *is a particular arrangement of electrons in different orbitals of an atom*. There are three main rules governing the filling of electrons in orbital and these are:

- Aufbau principle
- Hund's rule
- Paul's exclusion principle

There is also another rule which the reader may find useful in writing electronic configuration of some few elements. The rule is known as full and half full rule (half full filled rule).

Aufbau principle

Aufbau is the German word meaning **building up** (or **construction**) hence Aufbau principle is also known as **building principle**.

It states that: *In the ground state, electrons tend to occupy the orbital with minimum energy.* Aufbau principle suggests that, *"Electrons are lazy!"*

- Thus when the electrons are added to an atom they will go to any available lowest energy and they follow the following order:

1s, 2s, 2p, 3s,3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p where Arabic numbers (1,2,3…) represent principle quantum numbers (main energy level) and the small letter stands for energy sublevel (azimuthal quantum numbers).

The order can easily memorized by using **Aufbau diagram** shown in the figure below:

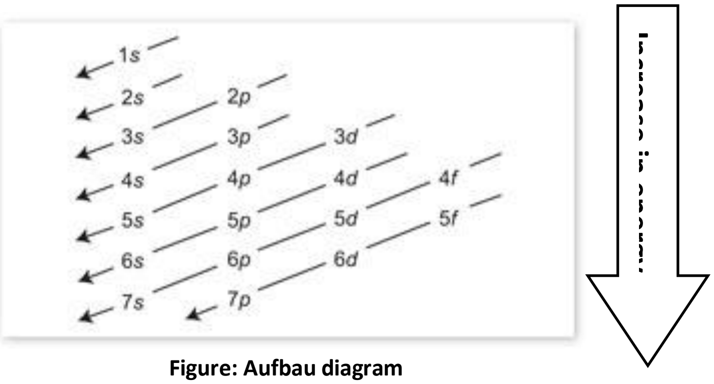


Figure: Aufbau diagram

The electronic configuration based on Aufbau principle has lower energy and hence it is more stable electronic structure.

Things to note from above Aufbau diagram

- Filling maximum number of electrons in each of orbitals in the above diagram give 118 as a total number of electrons. This is equal to the total number of all discovered and undiscovered elements.
- First row has only ***1s*** because $n = 1$ and therefore l can only be 0(n-1 or 1-1).

- Second row has ***2s*** and ***2p*** because for $n = 2$, ***l*** may be 0(s) or 1(p) that is 1 may take any value from 0 to $n - 1$. Similarly for third row where there is 3s, 3p and 3d and also for fourth row where it ended with 4f ($n = 4, l = 3 = n - 1 = 4 - 1$).
- There is no 5g in fifth row because practical maximum value of l for all known and potential elements is 4(f).
- The sixth row has no 6f because for all discovered and undiscovered elements, there is no element with 6f occupied with electrons. Similar reason explains why there is no 7d and 7f in the last row.

How the order was formed?

The order is formed by applying (n+l) rule studied in the **chapter 4** to determine the energy of orbital. To make things clearer, understand the following sub-rules:

- *In an atom, the electron will occupy the orbital with lowest possible value of (n+l).* This is also known as **Madelung rule**.
- In an atom, the electron will occupy the orbital with lower value of n provided that the available orbitals have the same sum of (n+l).

Hund's rule

Hund's rule (Also termed as **Hund's rule of maximum multiplicity**) state that: *Electrons are not allowed to pair up unless the empty orbitals of the same type with the same energy are singly occupied with parallel spins electrons.* It suggests that, *"Electron are unfriendly!"*

Orbitals of the same type which have the same energy are known as **degenerate orbitals.** Therefore the Hund's rule can also be stated as: *Electrons are not allowed to pair up unless the empty degenerate orbitals are singly occupied with parallel spins electrons.*

Why pairing is not allowed until all degenerate orbitals are singly occupied with of parallel spins of electrons?

The electrons carry the same electric charge. To overcome repulsion between like charges, the electrons try to get as far apart as possible. They do so by seeking out empty orbitals of similar energy in preference to pairing up with electrons so as to get stability. In one sentence summary this can be summarised in the 'dash' below.

- Hund's rule is justified by the fact the *there is repulsion between electrons and therefore these electrons will stay in particular sub-energy level as far as possible so as to overcome repulsion.*

Another reason is to justify Hund's rule *is the increased stability due to decrease in the screening of electron-nuclear attraction.*

- Putting all two reasons in two 'dots' we may conclude that: When electrons are arranged according to Hund's rule, there is increased stability due to:
  - Reduced electron-electron repulsion due to increase in distance between electrons.
  - Decrease in the screening (shielding) of electron-nuclear attraction.

Hund's rule is more important in feeling electrons in p, d and f –orbitals which have more than one orbital. It has no application in s sub-energy level where there is only one s-orbital.

Paul's exclusion principle

It states that: *No two electrons in the same atom can have the same all four quantum numbers.*

- Thus according this form of Paul Exclusion principle, **the four quantum numbers act as *fingerprint* or *signature* of an electron.**

It can also be stated as: *If two electrons occupy the same orbital, the electrons must have parallel spin.*

- This form of Paul exclusion principle suggest that, *"Only electrons with opposite 'sex' may kept together in an orbital (room of electron)"*

So according to the principle, two electrons may have the same three quantum number but must have the different spin quantum numbers and maximum number of electrons in an orbital can have is two which must be spinning in an opposite direction.

- Paul exclusion principle is justified by the fact that: Due to repulsion between electrons; the two electrons in an orbital must spin in opposite direction so as to establish magnetic field with opposite poles (north and south pole) so as to overcome the repulsion and therefore enabling the repelling electrons to stay in the same orbital. (Remember if one electron spin in clockwise direction the north pole appear on the top and south pole appear at the bottom while another electron in the orbital spinning in anti-clockwise direction has north pole at the bottom and south pole on the top and hence the attraction between the two electrons in the orbital).

Rules of writing electronic configuration are like rules of arranging tenants in your new apartment!

Below is the interesting imaginative story which will certainly make rules of writing electronic configuration to stick in your brain for your life-time!

*Imagine you are the landlord of new **apartment (atom!)** with number of **floors** (**energy levels!)** and rooms (**orbitals!**) in each floor. Each room has capacity of accommodating two people (tenants). Your task is to fill **tenants** (**electrons**!) in the rooms of your apartment according to certain specific rules.*

The first rule** of arranging tenants (residents) in your apartment is **"from the bottom up"**. That is rooms must be filled from the ground floor up. Fill the one room on the first floor before starting to put new tenants on the second floor and so on! This rule resemble to **Aufbau principle!

The second filling rule** for your apartment is **"singles first."** That is you want to have the tenants more comfortable by spreading them out as much as possible. For that reason singles are placed in rooms before couples (if couples must be placed into room then all of the other rooms on that floor must already have a single in them).This resembles to **Hund's rule of maximum multiplicity.

The last rule** of your apartment is "**opposite gender only."** That is when two tenants (electrons) are placed in a room they must of opposite genders (**opposite spin!**). Neither men may not room together nor women may room together. This resembles to **Paul exclusion principle.

Relax, enjoy chemistry! Let us finish with the 'full and half full rule'!

Full and half full rule

It may be stated as: *For d and f orbitals the full or half full configurations in the sub – shells are very stable configuration with minimum energy content.*

Thus according to this rule:

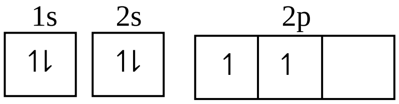
The stable electronic configuration is obtained when d-orbitals contain 10 or 5 electrons and when f –orbitals contain 14 or 7 electrons.

DRAWING ELECTRONIC CONFIGURATION

There are two ways by which are used to write the electronic configuration of an atom. These are:

Orbital method which is done by showing main energy level and energy sublevel followed by superscript on the energy sub-level representing a number of electrons present in the sub-level; For example $1s^2 2s^2 2p^2$ is an electronic configuration by orbital method of an element with atomic number of 6.

Box method which is done by using boxes and arrows; boxes represent orbitals in each energy sub-level while arrows represent electrons present in the orbitals. Example: An element with atomic number of 6 has the following electronic configuration by box methods.



Be aware of this!

Box method gives the distribution of electrons in the atom and hence the term; **electronic distribution** is used to mean electronic configuration of the atom by the box method.

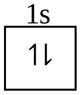
Example 1

Write electronic configuration of (i) Helium (ii) Neon (iii) Argon by:

(a) Box method
(b) Orbital method

Solution

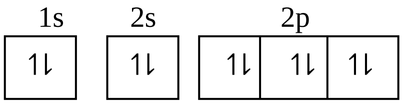
(i) Atomic number of Helium (He) is 2
  (a) Thus by box method the configuration become:



  (b) By orbital method: [He] = $1s^2$

(ii) Atomic number of Neon (Ne) is 10
  (a) By box method:

[Ne] =



(b)By orbital method:

[Ne]= $1s^2 2s^2 2p^6$

(iii) Atomic number of Argon (Ar) is 18

(a) By box method [Ar] is;

1s	2s	2p			3s	3p		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

(b) By orbital method

[Ar] = $1s^2 2s^2 2p^6 3s^2 3p^6$

Whereby [ ] means 'electronic configuration of' e.g. [Ar] means: electronic configuration of Argon.

Electronic configurations of noble gases like He, Ne and Ar are always used to shorten electronic configurations of other elements as outlined below:

- [He] is used to shorten an electronic configuration of first **two** electrons for an atom with atomic number of greater than 2 but less than 10. [He] ends with $1s^2$ and therefore the next element after He ends with $2s^1$.
- [Ne] is used to shorten an electronic configuration of first **ten** electrons for an atom with atomic number of greater than 10 but less than 18. [Ne] ends with $2p^6$ and therefore the next element after Ne ends with $3s^1$.
- [Ar] is used to shorten electronic configuration of first **18** electrons for an atom with atomic number of greater than 18 but less than 36. [Ar] ends with $3p^6$ and therefore the next element after Ar ends with $4s^1$.
- [Kr] is used to shorten an electronic configuration of first **36** electrons for an atom with atomic number of greater than 36 but less than 54. [Kr] ends with $4p^6$ and therefore the next element after Kr ends with $5s^1$.
- [Xe] is used to shorten an electronic configuration of first **54** electrons for an atom with atomic number of greater than 54 but less than 86. [Xe] ends with $5p^6$ and therefore the next element after Xe ends with $6s^1$.
- And finally [Rn] is used to shorten an electronic configuration of first **86** electrons for an atom with atomic number of greater than 86. [Rn] ends with $6p^6$ and thereore the next element after Rn ends with $7s^1$.

Warning!

It is not allowed to use shorthand notation of noble gas to represent electronic configuration of the noble gas itself. For example it is wrong to write [Ar] for electronic configuration of Ar. Instead the full electronic configuration, that is $1s^2 2s^2 2p^6\ 3s^2 3p^6$ should be used.

Valence and core electrons

Inner electrons (electrons in inner shells) are known as **core electrons.**

- For example, with the electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ \ 3p^5$, chlorine has a total of **ten (10) core electrons** in $1s^2\ 2s^2\ 2p^6$ where $2 + 2 + 6 = 10$.

An inner shell electronic configuration corresponding to one of the noble gases is known as **noble –gas core.**

- Returning to our example of chlorine, $\mathbf{1s^2\ 2s^2\ 2p^6}$ is the electronic configuration gas of Ne which is noble gas and hence in the electronic configuration of Cl, $\mathbf{1s^2\ 2s^2\ 2p^6}$ is the **noble gas core**.

The noble-gas core together with $(n-1)d^{10}$ *(where n is the outermost shell) is known as* **pseudo-noble core** because the electrons are usually not involved in chemical reaction.

- For example, with the electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$, $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}}$ is the pseudo-noble gas core in the electronic configuration of zinc which comprises of electronic configuration of argon noble gas $(\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6})$ and $\mathbf{3d^{10}}$ $((n-1)d^{10}$ where $n = 4)$
- Where *an electron outside pseudo-noble gas core is known as* **valence electron**. For example the two 4s-electrons are valence electrons in zinc atom.

The shell in which valence electron is found is known as **valence shell** (also termed as the **outermost shell**).

- Whereas *the shell just inner to the outermost shell is known as* **penultimate shell**. In other words if **n** is the principal quantum number of the outermost shell then **n-1** become the principal quantum number of the penultimate shell or (n-1)th shell is the penultimate shell. For example, valence shell for sodium is 3 and therefore $n = 2\ (3 - 1)$ is the penultimate shell in the sodium.

Example 2

Write electronic configuration of elements with the following atomic numbers: (i) 13 (ii) 9 (iii) 27 (iv) 21

Solution

(i) $[Ne]3s^2 3p^1$
(ii) $[He]\ 2s^2 2p^5$
(iii) $[Ar]4s^2 3d^7$
(iv) $[Ar]4s^2 3d^1$

Example 3

By using boxes and arrows draw electronic configuration of the following elements:

(i) Chromium (Cr)
(ii) Copper (Cu)

Solution

(i) Chromium has atomic number of 24. Its electronic configuration is:

1s	2s	2p			3s	3p			4s	3d				
↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿	↿	↿	↿	↿	↿

Here all 3d orbitals are singly occupied with electrons before pairing in 4s-orbital due to stability of half filled electronic structure (full and half filled rule)

(ii) Copper has atomic number of 29. Its electronic configuration is;

1s	2s	2p			3s	3p			4s	3d				
↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂

Here all 3d orbitals are paired up with electrons before pairing in 4s-orbital due to stability of fully filled electronic structure (full and half filled rule).

Example 4

Assign quantum numbers for the following:

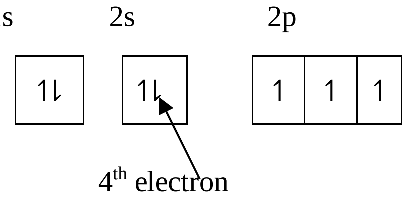
i. 4th electron in nitrogen

ii. Last electron in oxygen

iii. Valence electron in sodium

Solution

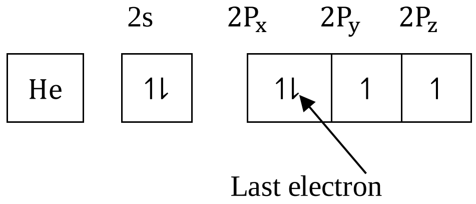
i. Electronic configuration of nitrogen is



Thus quantum numbers for the fourth electron in the nitrogen are as follows:

$$n = 2, l = 0, m_l = 0, m_s = {}^{-1}/_{2}$$

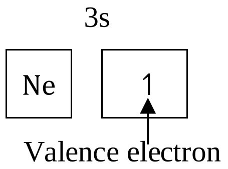
ii. Electronic configuration of oxygen is



Thus quantum numbers for the last electron in the oxygen are as follows:

$$n = 2, l = 1, m_l = -1, m_s = {}^{-1}/_{2}$$

iii. Electronic configuration of sodium is



Thus quantum numbers for the valence electron in the sodium are as follows:

$$n = 3, l = 0, m_l = 0\ , m_s = {}^{+1}/_{2}$$

Electronic configuration of first 30 elements

ELEMENT	SYMBOL	ATOMIC NUMBER	ELECTRONIC CONFIGURATION
Hydrogen	H	1	$1s^1$
Helium	He	2	$1s^2$
Lithium	Li	3	$[He]2s^1$
Beryllium	Be	4	$[He]2s^2$
Boron	B	5	$[He]2s^2 2p^1$
Carbon	C	6	$[He]2s^2 2p^2$
Nitrogen	N	7	$[He]2s^2 2p^3$
Oxygen	O	8	$[He]2s^2 2p^4$
Fluorine	F	9	$[He]2s^2 2p^5$
Neon	Ne	10	$[He]2s^2 2p^6$
Sodium	Na	11	$[Ne]3s^1$
Magnesium	Mg	12	$[Ne]3s^2$
Aluminium	Al	13	$[Ne]3s^2 3p^1$
Silicon	Si	14	$[Ne]3s^2 3p^2$
Phosphorous	P	15	$[Ne]3s^2 3p^3$
Sulphur	S	16	$[Ne]3s^2 3p^4$
Chlorine	Cl	17	$[Ne]3s^2 3p^5$
Argon	Ar	18	$[Ne]3s^2 3p^6$
Potassium	K	19	$[Ar]4s^1$
Calcium	Ca	20	$[Ar]4s^2$
Scandium	Sc	21	$[Ar]3d^1 4s^2$
Titanium	Ti	22	$[Ar]3d^2 4s^2$
Vanadium	V	23	$[Ar]3d^3 4s^2$
Chromium	Cr	24	$[Ar]3d^5 4s^1$
Manganese	Mn	25	$[Ar]3d^5 4s^2$
Iron	Fe	26	$[Ar]3d^6 4s^2$
Cobalt	Co	27	$[Ar]3d^7 4s^2$
Nickel	Ni	28	$[Ar]3d^8 4s^2$
Copper	Cu	29	$[Ar]3d^{10} 4s^1$
Zinc	Zn	30	$[Ar]3d^{10} 4s^2$

The student should note that: for first 30 elements, the unusual distribution of element by application of full and half filled rule applies for elements with atomic number of 24 and 29 only.

Be aware of this fact!

Although conventional wisdom may suggest that the final electron to enter the atom of transition elements (atomic number of 21 up to 30) is 3d electron, experimentally it has been proved that **the final electron is 4s electron.** The detailed explanation of this is beyond the scope of this book.

Electronic configuration of atoms in excited state

In exciting electrons; the electrons move from the lower to the higher energy level so as to form more unpaired orbitals (to increase number of orbitals with unpaired electrons) thus increasing the ability of the element to form covalent compound through covalent bond formation. This process does not involve changing of number of electrons.

Thus:

$$\text{Number of electrons in atom at ground state} = \text{number of electrons at the excited state}$$

Total number of unpaired electrons in the atom is known as **covalency.**

- So since exciting electrons increase the number of unpaired electrons, the process in said to increase the covalency of the atom.

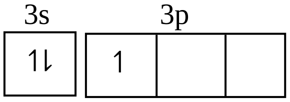
Example 5

Write electronic configuration to show excited state of:

(i) Aluminium (ii) Silicon (iii) Phosphorous

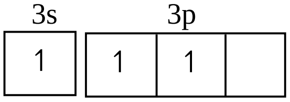
Solution

(i) Aluminium has atomic number of 13

$[Al] = [Ne]$ 

…………………..At ground state

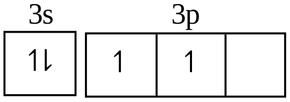
To increase number of unpaired electrons, one s-electron must be promoted to higher energy p-orbital at excited state as follows:

$[Al] = [Ne]$ 

…………………..At excited state

(Since at excited state Al has 3 unpaired electrons, the element is said to has **covalency of 3 at excited state** compared to **covalency of 1 at ground state**)

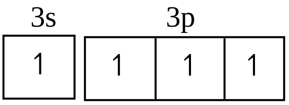
(ii) Silicon has atomic number of 14

$[Si] = [Ne]$ 

…………………..At ground state

To increase number of unpaired electrons, one s-electron must be promoted to higher energy p-orbital at excited state as follows:

$[\mathrm{Si}] = [\mathrm{Ne}]$

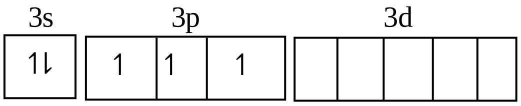


……………………..At excited state

(Since at excited state Si has 4 unpaired electrons, the element is said to has **covalency of 4 at excited state** compared to **covalency of 2 at ground state**)

(iii) Phosphorous has atomic number of 15

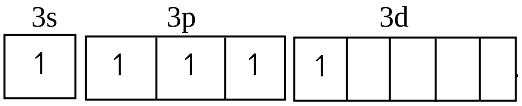
$[\mathrm{P}] = [\mathrm{Ne}]$



....At ground state

To increase number of unpaired electrons, one s-electron must be promoted to higher energy d-orbital at excited state as follows:

$[\mathrm{P}] = [\mathrm{Ne}]$



…At excited state

(Since at excited state P has 5 unpaired electrons, the element is said to has **covalency of 5 at excited state** compared to **covalency of 3 at ground state**)

Example 6

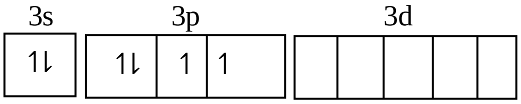
Write electronic configuration of sulphur at excited state to show:

(i) Its covalency of 4
(ii) Its covalency of 6

Solution

Sulphur has atomic number of 16

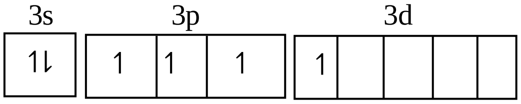
$[\mathrm{S}] = [\mathrm{Ne}]$



....At ground state

(c) To increase number of unpaired electrons to four so as to have covalency of four in S, one p-electron must be promoted to higher energy d-orbital at excited state as follows:

$[\mathrm{S}] = [\mathrm{Ne}]$



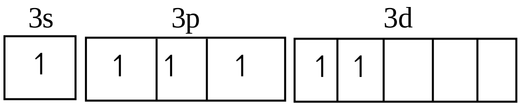
....At excited state

Important fact to understand!

In (i) above the excited electron comes from 3p-orbital and not 3s-electron. This is because it easier to promote an electron from p-orbital to d-orbital than promoting an electron from s-orbital to d-orbital due to the smaller energy difference between p and d sub-energy levels compared to the difference between s and d sub-energy levels. Thus if only one electron is required for promotion, the electron must be from the p-orbital.

(ii) To have six unpaired electrons (covalency of 6), one s-electron and one p-electron (from the paired orbital) must be promoted to higher energy d-orbital as follows:

[S] = [Ne]



....At excited state

Example 7

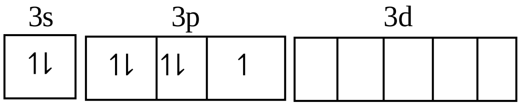
Write electronic configuration of chlorine at excited state to show

(i) Its covalency of 3
(ii) Its covalency of 5
(iii) Its covalency of 7

Solution

Atomic number of chlorine is 17

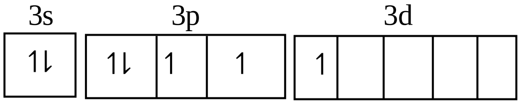
[Cl] = [Ne]



....At ground state

(i) To increase number of unpaired electrons to three so as to have covalency of three in Cl, one p-electron must be promoted to higher energy d-orbital at excited state as follows:

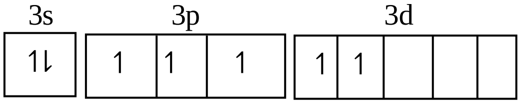
[Cl] = [Ne]



....At excited state

(ii) To have five unpaired electrons (covalency of 5), two p-electrons (from paired p-orbitals) must be promoted to higher energy d-orbital as follows:

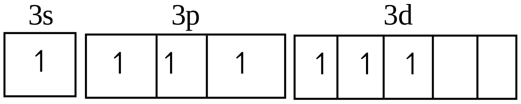
[Cl] = [Ne]



....At excited state

(ii) To have seven unpaired electrons (covalency of 7), one s-electron and two p-electrons (from paired p-orbitals) must be promoted to higher energy d-orbital as follows:

[Cl] = [Ne]



....At excited state

Electronic configuration of ions (charged atoms)

Formation of charged atoms (ions) must be accompanied with either removal or addition of electrons to an atom so as to form either positively charged ion (cation) or negatively charged (anion) respectively. So this change in number of electrons must be considered in writing electronic configuration of the ions.

Very important to note that:

In removing electrons(s) from the atom so as to form the cation, the electron is removed from outermost energy level; that is from the orbital with greatest principal quantum number regardless to the order of filling electrons to the orbital. To insist this study carefully **example 7** below.

Example 8

Draw electronic configuration of the following ions

(i) Fe^{2+}
(ii) zn^{2+}
(iii) Fe^{3+}

Solution

(i) Iron has atomic number of 26

So, $[Fe] = [Ar]$

3d					4s
↿⇂	↿	↿	↿	↿	↿⇂

Here outermost shell is n = 4, so two electrons which are to be removed so as to form Fe^{2+} must be from 4s-orbital.

Hence $[Fe^{2+}] = [Ar]$

3d					4s
↿⇂	↿	↿	↿	↿	

(ii) Zinc has atomic number of 30

So, $[Zn] = [Ar]$

3d					4s
↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂

Again the outermost shell is n = 4, so two electrons which are to be removed so as to form Zn^{2+} must be from 4s-orbital.

Hence $[Zn^{2+}] = [Ar]$

3d					4s
↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	

(iii) From [Fe] in (i) above, $[Fe^{3+}]$ can be deduced as follows; (After removing 3 electrons from Fe).

Hence $[Fe^{3+}] = [Ar]$

3d					4s
↿	↿	↿	↿	↿	

Example 9

Show electronic distribution of the following ions (i)Cl^- (ii) Mg^{2+}

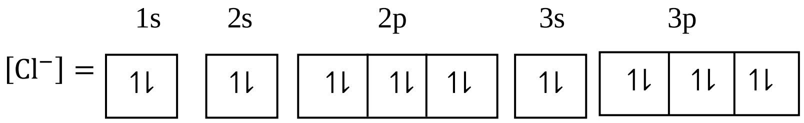
Solution

(i)

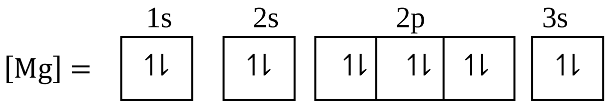
$[Cl] =$

1s	2s	2p			3s	3p		
↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿

Cl^- is formed after addition of one electron to the unpaired p_z −orbital in the above distribution.

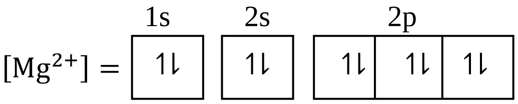


(ii)



Mg^{2+} is obtained after removing two s-electrons from above distribution.

Thus



Don't forget that: If it asked to show electronic distribution boxes and arrows must be used to show the electronic configuration.

DIGGING DEEPER EXERCISE 5

Question 1

By referring to the rules of writing electronic configuration justify the following statements;

i. Electron are lazy
ii. Electron are unfriendly
iii. Quantum numbers are fingerprints for electrons

Question 2

Arrange the following orbitals in order of increasing their energies for:

i. Hydrogen atom
ii. Copper atom

$$1s, 2s, 2p, 3d, 4s, 4p, 3p, 3s$$

Question 3

For each of the following electronic configuration state whether it is valid. Give reason for invalid ones

i. $1s^2\ 2s^2 2p^6 3s^2 3p^6 4s^2 4d^{10} 4p^5$
ii. $1s^2\ 2s^2\ 2p^6\ 3s^3\ 3p^5$
iii. $[Ra]7s^2\ 5f^5$
iv. $[Kr]5s^2 4s^{10} 5p^5$
v. $[Xe]$

Question 4

How electronic configuration of chromium is said to violate Aufbau principle

Question 5

a) Write configuration of the following ions:
   i. Fe^{2+} ii. Fe^{3+} iii. Mn^{2+} iv. Mn^{3+}
b) From the configuration in a) above, compare stability of :
   i. Fe^{2+} versus Mn^{2+}
   ii. Fe^{3+} versus Mn^{3+}

Question 6

Although both He and Be have the same outermost electronic configuration of ns^2(where n is the outermost energy level), He is more stable. Explain

Question 7

With reference to xenon at ground state, how many electrons have the following set of quantum number?

i. $n = 4$
ii. $n = 4, l = 2$
iii. $l = 0$
iv. $n = 2, l = 2, m_l = -1, s = {}^1\!/_2$
v. $n = 4, l = 3$

Question 8

Write atomic number of an atom whose dispositive ion has electronic configuration of $1s^2 2s^2 2p^6$.

Question 9

An atom X may gain electrons to form anion; X^{3-} with the electronic configuration of $1s^2\ 2s^2\ 2p^6$.what is the atomic number of X.

Question 10

Paul Exclusion principle may be stated as; *"No two electrons in an atom may have all four quantum numbers the same."* Explain two pieces of information which may be extracted from the principle.

Question 11

Write the electronic configuration of the following using the shorthand arrow and box method.
i. Mg^+ ii) Mn^{2+} iii) Fe^{3+} iv) V^{3+}

Question 12

Write the electronic configuration of the following by the orbital method

i) N^{3-} ii) Ar iii) Sc^{3+}.

Question 13

With reference to calcium at ground state, how many electrons have the following quantum numbers?

i. $m_l = 0$
ii. $l = 1$

EXAMINATION QUESTIONS FOR PART ONE

Question 1

A sample of naturally occurring silicon consists $Si-28(27.9769\ amu), Si-29(28.9765\ amu)$ and $Si-30(29.9738\ amu)$. If the atomic mass of silicon is 28.0855 and the natural abundance of $Si-29$ is 4.67%, what are the natural abundances of $Si-28$ and $Si-30$?

Question 2

Pb has an average atomic mass of $207.19amu$.The three major isotopes of Pb are $Pb-206\ (205.98amu); Pb-207(206.98amu)$; and $Pb-208(207.98amu)$. If the isotopes of $Pb-207$ and $Pb-208$ are present in equal amounts, calculate the percentage abundance of $Pb-206, Pb-207, Pb-208$.

Question 3

The atomic weight of naturally occurring neon is 20.18 amu.

Naturally occurring neon is composed of two isotopes:

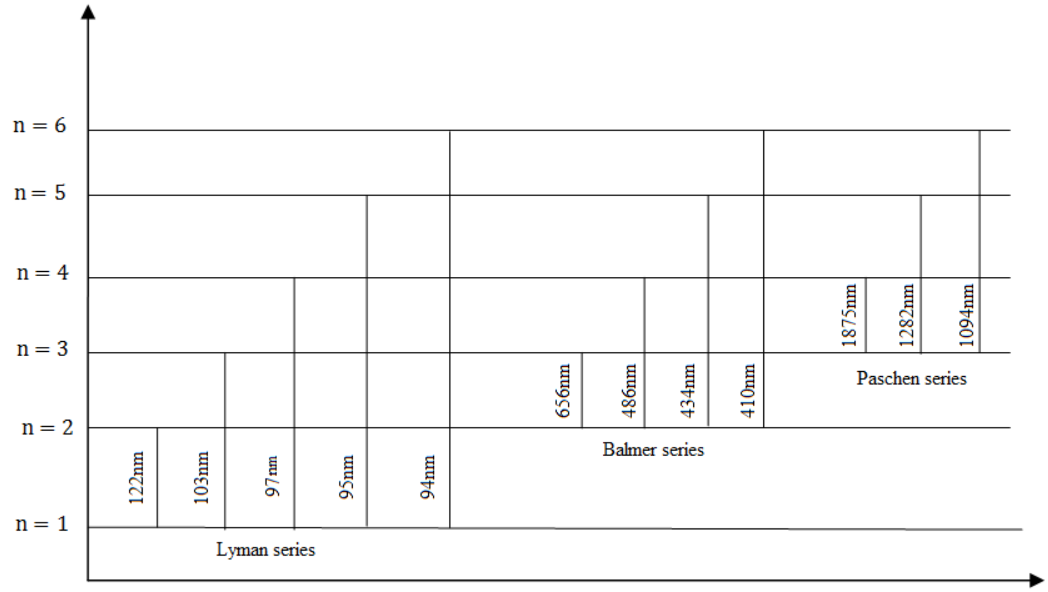
$Ne-20$: $19.99amu$

$Ne-22$: $21.99amu$

Calculate the number of $Ne-22$ atoms in $12.55g$ sample of naturally occurring neon.

Question 4

Consider the following diagram:



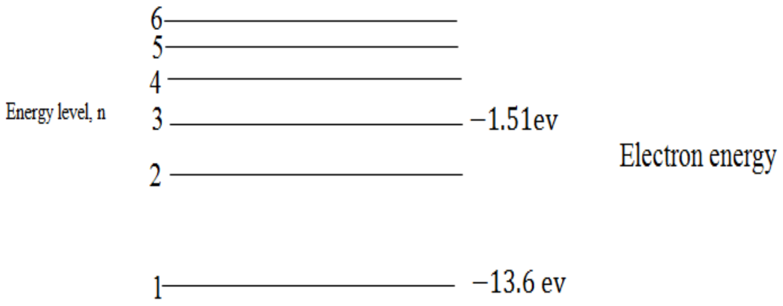
a) The above diagram illustrates the Bohr model of the hydrogen atom
   i) Explain what horizontal and vertical lines represent.
   ii) Explain how this model explains emission line spectral and absorption line spectra.

b) The line between $n = 5$ and $n = 2$ is labeled 434nm. Show that this is correct for a hydrogen atom
   a) Calculate the energy of a hydrogen atom in its ground state. Express your answer in ev.

Question 5

The electron in the hydrogen atom emits or absorbs electromagnetic radiation when it moves between energy levels.

The visible part of the spectrum emitted by hydrogen can be seen in the laboratory by applying a high voltage to a hydrogen discharge tube. The diagram below represents some of the electron energy levels in the hydrogen atom.



a) To which energy level does the electron drop when it emits visible light?
b) Absorption spectrum for hydrogen gas consists of a series of dark lines within the full spectrum of colours. Explain clearly how the dark line in the red part of the spectrum is produced.
c) Calculate the frequency of the photon produced when an electron drops from the second excited state to the ground state.

An electron in energy level 4 jumps to a higher energy level, and then drops down to the ground state, releasing a photon of frequency 3.2×10^5Hz.

d) Calculate the frequency of photon required for the first jump.

Question 6

Nuclear reactions in the sun produced light. The main element in the sun is hydrogen. The spectrum of hydrogen can be observed in the laboratory with a hydrogen discharged tube. The visible lines in the hydrogen spectrum are called the Balmer series and are described by the formula: $\frac{1}{\lambda} = \mathrm{R}\left(\frac{1}{\mathrm{S}^2} - \frac{1}{\mathrm{L}^2}\right)$

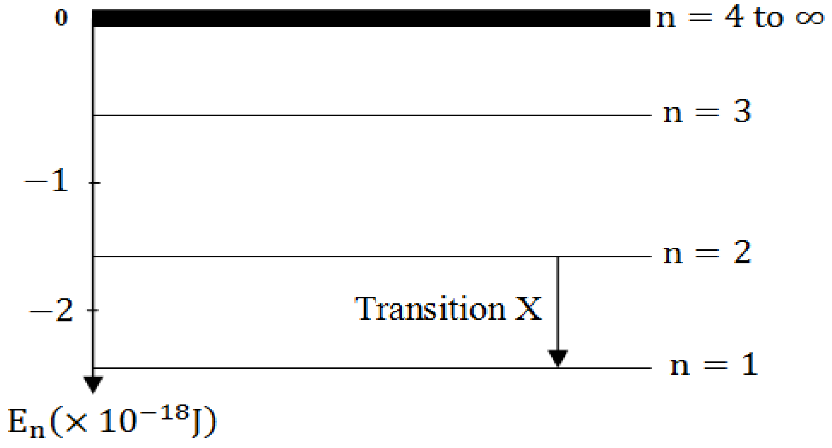
Where $\mathrm{s} = 2$

a) Calculate the wavelength of the lowest frequency line in the Balmer series.
b) Explain how light of this particular frequency is produced in the hydrogen atom
c) An electron in the 6th excited state (L=7) returns to the ground state in two jumps. It releases one photon with a wavelength of 2.165×10^{-6}m. what is the wavelength of the second photon?

Question 7

Light from stars is photons of electromagnetic radiation created by electron transitions between energy states. These photons produce spectra that identify the atoms that are producing light. A common element that produces light from star is hydrogen.

The possible energy states (levels) of the hydrogen atom electrons are shown in the next page.



a) In which part of this electromagnetic spectrum is the radiation emitted by transition X?
b) Calculate the wavelength of the photons emitted by the transition.
c) Explain which transition produces the red line in the visible part of the hydrogen atom.
d) In order for an electron in a hydrogen atom to move from the third energy level to the fifth energy level, a photon of electromagnetic radiation must be absorbed. Calculate the energy of this photon.

Question 8

Three experiments or pieces of scientific equipment were key to our present understanding of atomic structure. For each of the following, outline major discovery that it contributed to:

a. Crookes tube
b. Rutherford's gold foil experiment
c. The bright line spectrum for hydrogen atom

Question 9

The human eye can detect 3.15×10^{-17}J of 510nm radiation. How many photons does this correspond?

Question 10

What is the maximum number of electrons in an atom that can have the following quantum numbers?

i) $n = 4, l = 3, m_l = -3$
ii) $n = 5, l = 3$
iii) $n = 2, m_s = -{}^{1}/_{2}$

Question 11

Most of cell phones use electromagnetic radiation in the radio-frequency range, i.e.100KHz to 1GHz; calculate the maximum energy that a photon in this range can have. Convert it to a per mole basic and compare to the energy of covalent bond ($> 100kJ/mol$). Based on this comparison, how likely is cell phone radiation to cause breaking of chemical bonds in the body?

Question 12

A sample of chlorine containing 75% of the isotope chlorine-35 and 25% of the isotope chlorine-37 was analysed by mass spectrometry. Three corresponding to Cl_2^+ were recorded.

a. Why were three peaks recorded?
b. What are the relative masses of the three peaks
c. What are the relative amounts in the three peaks?

Question 13

What maximum number of electrons may have the following quantum numbers?

i. $n = 2, m_l = 0$
ii. $n = 3, l = 1$
iii. $n = 2, l = 1$
iv. $n = 3, l = 1, m_l = -1$
v. $n = 3, l = 1, m_l = 0\ s = {}^{+1}/_{2}$

Question 14

Why the following set of quantum numbers is invalid?

i. $n = 3, \quad l = 2\ , m_l = +1, m_s = +1$
ii. $n = 4, \quad l = 3, \ m_l = -4, m_s = + {}^{1}/_{2}$

Question 15

An electron and proton both moving at non-relativistic speeds have the same De-Broglie wavelength. Which one of the two particles has greater of the following?

i. Momentum
ii. Speed
iii. Kinetic energy
iv. Frequency

Question 16

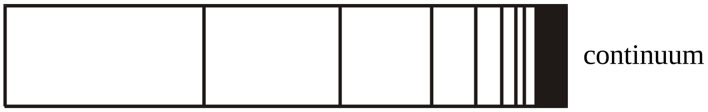
An electron moves in a straight line with a constant speed $V = 1 \times 10^{6} \mathrm{m/s}$ which has been measured to a precision of 0.2%.What is the maximum precision with which its position could be simultaneously measured? Mass of an electron= 9.11×10^{-31}kg

Question 17

A measurement established the position of a proton with an uncertainty of 1.5×10^{-11}m; find the minimum uncertainty in the proton's position in 2 seconds later (Mass of a proton= 1.67×10^{-27}kg)

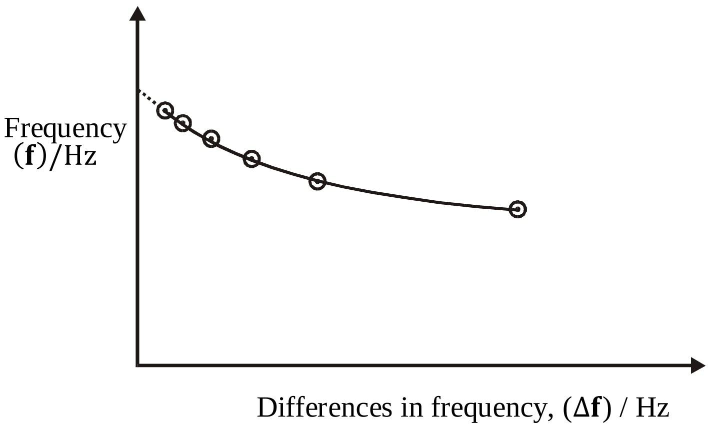
Question 18

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



frequency / Hz

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 **f** against **Δf** can be extrapolated back to find where **Δf** is 0. This is the start of the continuum.



(a) What causes a line in an emission spectrum?

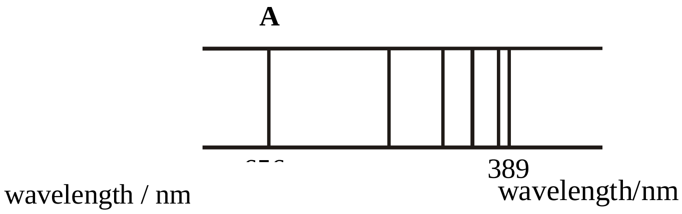
(b) Why do the lines converge as they reach the continuum?

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

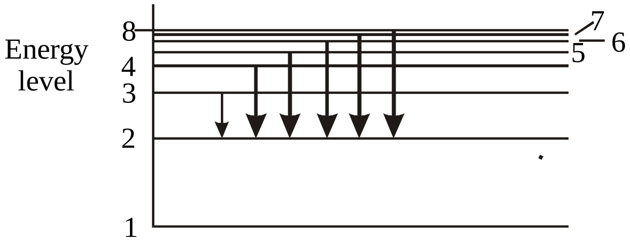
(ii) What does this energy represent?

Question 19

Below is a simplified diagram of the Balmer series in the emission spectrum of atomic hydrogen.



Spectral lines arise as a result of electronic transitions in atoms. The Balmer series is produced by the transitions shown in the following diagram.

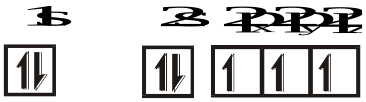


(a) What transition corresponds to a line A in the spectrum? Explain your answer.

(b) Calculate the energy difference, in kJmol^{-1}, that gives rise to line A, with wavelength 656 nm.

Question 20

The electron configuration for nitrogen is:



(a) What do the symbols ↑ and ↓ represent?

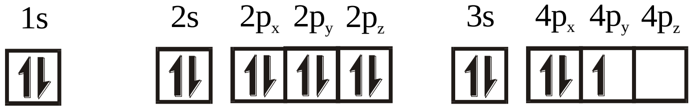
(b) What is the significance of *x*, *y* and *z* in the 2p sublevel?

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

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

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

(e) Phosphorus is in the same group as nitrogen but has 15 electrons. **Virtue**, a form five student wrote the following configuration for phosphorus:



Explain the two mistakes in the **Virtue's** answer.

Question 21

There are four statements that you have come across in your study of electrons and atomic orbitals. These statements are:

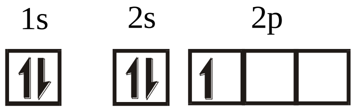
(1) The Aufbau principle

(2) Heisenberg's uncertainty principle

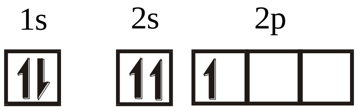
(3) The Pauli exclusion principle

(4) Hund's rule of maximum multiplicity

(a) The electronic configuration for boron is given by (i) and not (ii).



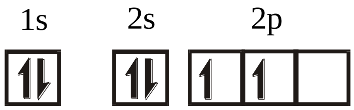
(i)



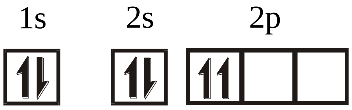
(ii)

Explain why (ii) is wrong and identify which of the above statements justifies your choice.

(b) The electronic configuration for carbon is given by (iii) and not (iv).



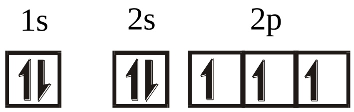
(iii)



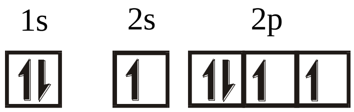
(iv)

Explain why (iv) is wrong and identify which of the above statements justifies your choice.

(c) The electronic configuration for nitrogen is given by (v) and not (vi).



(v)



(vi)

Explain why (vi) is wrong and identify which of the above statements justifies your choice.

Question 22

(a) Draw diagrams, including axes, to represent a 2s orbital and the three 2p orbitals.

(b) What does an orbital diagram represent?

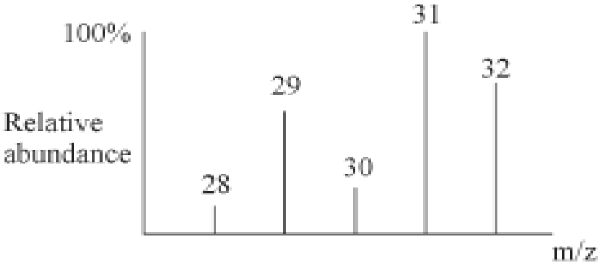
(c) What is the significance of the number 2 in the terms 2s and 2p?

(d) The three 2p orbitals are often degenerate. What does the term 'degenerate' mean in this context?

(e) Draw an energy level box diagram to represent the relative energies of the 1s, 2s and 2p orbitals in an isolated atom.

Question 23

The mass spectrum of a molecule of empirical formula CH_4O is shown below.



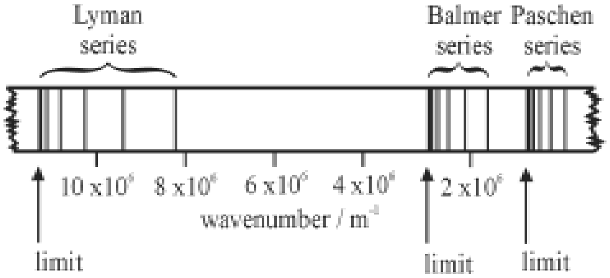
(a) Suggest a formula for an ion for each peak in the above spectrum. Identify the parent ion.

(b) What is measured by the peak height in the above spectrum?

(c) Occasionally two electrons can be removed from each fragment produced. Where will these peaks appear in the mass spectrum?

Question 24

The diagram below represents a section of the line emission spectrum for hydrogen.



(a) If the spectrum of hydrogen is viewed through a spectroscope only one set of lines is seen.

(i) Why is this?

(ii) Which series is seen?

(b) Explain how any particular line in this spectrum is produced.

(c) The last line or convergence limit of the Lyman series has a wavenumber of approximately 11×10^6 m^{-1}. Calculate the energy equivalent of this in $kJmol^{-1}$.

(d) What does the energy referred to in (c) correspond to?

Question 25

Imagine a universe in which the value of the magnetic spin quantum number, m_s, can be + ½, 0, or – ½. Assuming that all of the other quantum numbers can take only the values possible in our world and the Pauli Exclusion Principle applies, give the following:

a. The new electronic configuration of phosphorus.

b. The atomic number of the element with a complete n=3 shell.

c. The number of unpaired electrons in aluminum.

Question 26

a) State:
i. Aufbau principle
ii. Hund's rule of maximum multiplicity
iii. The uncertainty principle
b) i. What is atomic spectrum?
 ii. How does atomic spectrum differ from a continuous?
c) The wavelength of lines in the balmier series of hydrogen spectrum is given by the expression:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

Where n is an integer greater than 2.

i. Draw an energy level diagram to show the origin of second and fourth lines in the Balmer series.
ii. Calculate the frequency of the first line in the Balmier series.
$(R_H = 1.09678 \times 10^7\ m^{-1})$

Question 27

a) Explain why ground state electronic configuration of Cr and Cu are different from what might be expected.
b) What is the total number of electrons that can be held in all orbitals having the same principle quantum number n?

Question 28

The following value is the only allowed energy levels of hypothetical one-electron atom.

$$E_6 = -2 \times 10^{-19}J \quad E_5 = -7 \times 10^{-19}J$$
$$E_4 = -11 \times 10^{-19}J \quad E_3 = -15 \times 10^{-19}J$$
$$E_2 = -17 \times 10^{-19}J \quad E_1 = -20 \times 10^{-19}J$$

a) If the electron was in the n = 3 level, what would be the highest frequency and minimum wavelength of radiation that could be emitted?
b) What is the ionisation energy (in kJ/mol) of the electron in its ground state?
c) If the electron was in the n = 4 level what would be the shortest wavelength of radiation that could be absorbed without causing ionisation.

Question 29

The energy of the electron in hydrogen atom in the ground state is given by;

$$E_1 = \frac{-2.178\times10^{-18}}{n_1^2}\text{Joules}$$

The energy of the same electron if it occupies a higher level n_2 is given by:

$$E_2 = \frac{-2.178\times10^{-18}}{n_2^2}\text{Joules}$$

i. Why is the energy negative?

ii. Calculate the energy in joules and the wavelength in metres of the light which must be absorbed by atom to excite its electron from $n = 1$ to $n = 2$.

Question 30

Soap bubbles pick up colour because they reflect light with wavelength equal to the thickness of the walls of the bubble .What frequency of light will be reflected by a soap bubble of 6 nanometers thick?

Question 31

a) Give four ideas of Daltons atomic theory

b) Write the electronic configuration of

  i. Cu
  ii. Mg^{2+}
  iii. Cr
  iv. Li^{+}

c) State the postulates of Bohr's atomic theory, briefly state the shortcomings of the theory

Question 32

Define the following terms

i. Quantization of angular momentum
ii. Azimuthal quantum number
iii. Wave particle duality of matter

b) Briefly explain the physical significance of the state $n = \infty$ and $E = 0$ for hydrogen atom.

Question 33

An electromagnetic radiation of wavelength $2420A°$ is sufficient to ionize the sodium atom. Calculate the ionisation energy of sodium atom in kJ/mol.

Question 34

Calculate the wavenumber for the longest wavelength transition in Balmier series of atomic hydrogen.

Question 35

When an electron jumps from certain higher energy level, E_2, to its ground state E_1, green light in the Ballmer series is emitted. If the energy released during this transition is 4.071×10^{-19}J, Determine the:-

i. Wavelength of the green light

ii. Higher energy level E_2, from which the electron jumps to the ground energy level, E_1.

Question 36

The atomic spectrum of hydrogen in the visible region is given by the following relationship;

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

a) What do symbol λ, R_H, n_1 and n_2 represent

b) Calculate the frequency of the third line of visible spectrum.

Question 37

A hydrogen emission spectral line in a infra-red region at 1875nm corresponds to a transition from a higher level to n=3 level. Calculate the value of n for the higher energy level.

Question 38

The first ionisation energy of sodium atom is 145.684kJ/mol. Calculate the wavelength of electromagnetic radiation in angstrom which is sufficient to ionize the atom.

Question 39

Alpha particles emitted from Barium have energy of 4.8Mev. Given that a mass of alpha particles is 6.6×10^{-27}kg and $1\text{Mev} = 10^{6}\text{eV}$; calculate De-Broglie's wavelength.

Question 40

a. State the following:
   - i. Hund's rule
   - ii. Pauli's exclusion principle
   - iii. Hybridisation
   - iv. Quantization of energy
   - v. Wave particle duality of matter

b. Calculate the energy emitted when electrons of 1g atoms of hydrogen undergo transition giving line of lowest energy in the visible region of its atomic spectrum.

Question 41

State whether each of the following sets of quantum number is permissible for an electron in an atom. If a set is not permissible, explain why?

a. $\text{n} = 1,\ \text{l} = 1,\ \text{m}_\text{l} = 0,\ \text{m}_\text{s} = +{}^{1}/_{2}$
b. $\text{n} = 3,\ \text{l} = 1,\ \text{m}_\text{l} = -2,\ \text{m}_\text{s} = -{}^{1}/_{2}$
c. $\text{n} = 2\ \ \text{l} = 1,\ \text{m}_\text{l} = 0,\ \text{m}_\text{s} = +{}^{1}/_{2}$
d. $\text{n} = 2,\ \text{l} = 0\ \ \text{m}_\text{l} = 0\ \ \text{m}_\text{s} = -1$

Question 42

In order to obtain a mass spectrum of an element, a gaseous sample of the element is first ionised. Describe how ionisation is achieved in mass spectrometer. Give three reasons why ionisation is necessary.

Question 43

Some data obtained from the mass spectrum of a sample of carbon are given below.

Ion	$^{12}\text{C}^{+}$	$^{13}\text{C}^{+}$
absolute mass of one ion/g	1.993×10^{-23}	2.158×10^{-23}
Relative abundance %	98.9	1.1

Use these data to calculate a value for:

(i) the mass of one neutron,
(ii) the relative atomic mass of ^{13}C and
(iii) the relative atomic mass of carbon in the sample.

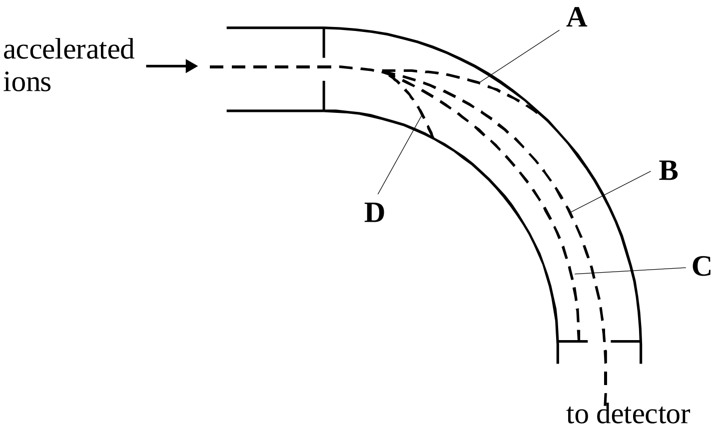
You may neglect the mass of an electron.

Question 44

The diagram below shows a section of mass spectrometer between the acceleration stage and the detection stage. The accelerated ions are from a sample of krypton which has been ionised as follows:

$$\mathrm{Kr(g)} \longrightarrow \mathrm{Kr^{+}(g)} + \mathrm{e}$$

The ions are deflected in four distinct paths, **A, B, C** and **D.** Ions are detected and a mass spectrum is then produced.



i) What accelerates the $\mathrm{Kr^{+}}$ ions before being deflected?
ii) What deflects the moving ions around a curved path?
iii) Why do the $\mathrm{Kr^{+}}$ ions from this sample of krypton separate into four paths?
iv) What adjustment could be made to the operating conditions of the mass spectrometer in order to direct the ions following path C onto the detector?
v) For each type of ion what two measurements can be made from the mass spectrum?
vi) What factors, other than the mass to charge ratio of an ionised particle, determines how much that particle is deflected in a magnetic field of a given strength.

Question 45

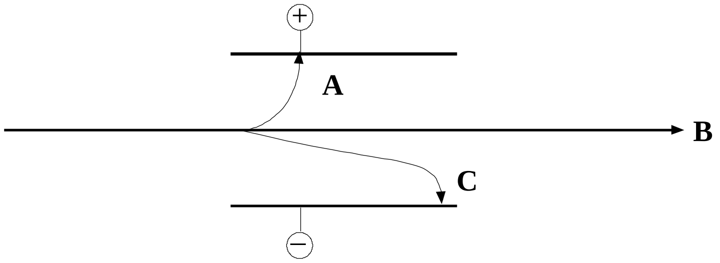
The table below shows some data about fundamental particles.

Particle	**Proton**	**Neutron**	**Electrons**
Mass /g	1.6725×10^{-24}	1.6748×10^{-24}	0.0009×10^{-24}
Relative charge			

a. Complete the table by giving a value for the relative charge of each particle.
b. Calculate the mass of an atom of hydrogen which is made from a proton and an electron.
c. Calculate the mass of one mole of such hydrogen atoms giving your answer to four decimal places (the Avogadro's constant = $\mathrm{L} = 6.0225 \times 10^{23}\,\mathrm{mol^{-1}}$).
d. An accurate value for the mass of one mole of hydrogen atoms is $1.0080\mathrm{g}$. Give one reason why this value is different from your answer to part (c).

Question 46

a. The diagram in the figure below shows the behaviour of the three fundamental particles when passes through an electric field.



i) Identify the particles represented by **A**, **B** and **C**.
ii) Explain the shapes and directions of the path traced by the fundamental particles as they pass through the electric field.

Question 47

The following questions refer to the operation of a mass spectrometer.

a. Name the device used to ionize atoms in a mass spectrometer.
b. Why is it necessary to ionize atoms before acceleration?
c. What deflects the ions?
d. What is adjusted in order to direct ions of different mass to charge ratio onto the detector?

Question 48

A sample of copper contain the two isotope $^{63}\mathrm{Cu}$ and $^{65}\mathrm{Cu}$ only. It has a relative atomic mass,A_r, less than 64.The mass spectrum of this sample shows major peaks with m/z value of 63 and 65, respectively.

i) Explain why the A_r of this sample is less than 64.
ii) Explain how Cu atoms are converted into Cu^+ ions in a mass spectrometer.
iii) In addition to the major peaks at $m/z = 63$ and 65, much smaller peaks at $m/z = 31.5$ and 32.5 are also present in the mass spectrum. Identify the ion responsible for the peak at $m/z = 31.5$ in the mass spectrum.
iv) Explain why your chosen ion has this m/z value and suggest one reason why this peak is very small.

Question 49

a. Ozone in the upper atmosphere absorbs light with wavelength of 220 to 290nm.What are the frequency (in Hz) and energy (in J) of the most energetic of these photons?
b. Carbon-carbon bonds form the backbone of nearly every organic and biological molecule. The average bond energy of $\mathrm{C-C}$ bond is $347\mathrm{kJmol^{-1}}$. Calculate the wavelength (in nm) of the least energetic photon that can break this bond.

   Compare this value to that absorbed by ozone and comment on the ability of the ozone layer to prevent $\mathrm{C-C}$ bond disruption.

Question 50

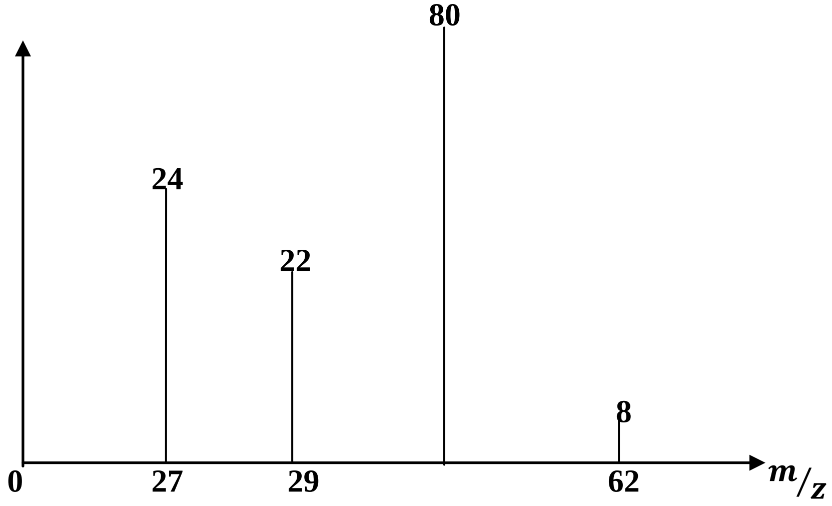
a. Define the following terms;
   i. Atomic mass unit
   ii. Isotopy

b. Boron has an atomic mass of 10.81amu according to the periodic table. However, no single atom of boron has a mass of 10.81amu.Suggest a reason of this.

c.

i. Define mass spectrum

ii. The following mass spectrum is for a compound determined to have empirical formula of C_3H_7X



Work out the molecular mass of this compound and hence identify the halogen.

d. Naturally occurring iodine has an atomic mass of 126.9045.
A 12.3849g sample of iodine is accidentally contaminated with 1.00007g of I-129, a synthetic radioisotope of iodine used in the treatment of certain diseases of thyroid gland. The mass of I-129 is 128.9050amu. Find the apparent "atomic mass" of the contaminated iodine.

Question 51

Two important concepts that relate to the behaviour of electrons in atomic system are the **Heisenberg uncertainty principle** and the **wave-particle duality** of matter.

a. State the Heisenberg uncertainty principle as it relates to determining the position and momentum of an object.

b. What is the meaning of "Wave-particle duality" and derive the equations which justify the concept.

c. What aspect of the Bohr Theory of the atom is considered unsatisfactory as result of Heisenberg uncertainty?

d. Explain why the wave nature of particles is not significant when describing the behaviour of macroscopic objects, but is very significant when describing the behaviour of electrons.

Question 52

The emission spectrum of hydrogen consists of several series of sharp emission lines in the ultraviolet, visible and infrared regions of the spectrum.

a. Mention series which are found in the infrared regions
b. What feature of the electronic energies of the hydrogen atom explains why the emission spectrum consists of discrete wavelengths rather than a continuum of wavelengths?
c. Account for existence of several series of lines in the spectrum. What quantity distinguishes one series of lines from another?
d. Draw an electronic energy level diagram for the hydrogen atom and indicate on it the transition corresponding to the line of lowest frequency in the Balmer series
e. What is the difference between an **emission spectrum** and an **absorption spectrum**? Explain why the absorption spectrum of atomic hydrogen at room temperature has only the lines of the Lyman series.

Question 53

The Rydberg equation enables you to calculate the frequency of a line in the hydrogen spectrum. The version of the Rydberg equation in terms of frequency is:-

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

a. Calculate the frequency of the line produced when and electron falls back from the infinity level to the $n = 1$
b. Write the equation which relates the energy gap between two levels and the frequency of the light emitted
c. Use the equation you have written in (b) to calculate the energy in eV needed to move an electron form the 1- level to the infinity level. State clearly any assumption you have made in your calculations.
d. Use the result obtained in (c) to calculate the ionisation energy of hydrogen.

Question 54

a. Define the following terms:
    i. Angular momentum quantum number
    ii. Primary quantum number
    iii. m_l
b. What is the maximum number of electrons that an orbital with a magnetic quantum number of 2 could hold?

c.

i. How many electrons on an atom of argon have m=+1?

ii. Explain why are up to ten electrons on a set of d-orbitals?

iii. What is the maximum number of electrons that are allowed to have the following set of quantum numbers in one atom? $n = 4$ and $m_l = +2$

iv. Which element has the last electron in its atom with the following quantum numbers?

$$n = 3, \quad l = 1, \quad m_l = -1, \quad m_s = -\frac{1}{2}$$

Question 55

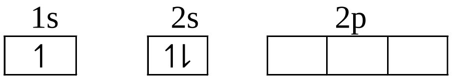
a. With respect to the electronic configuration justify the following statement:

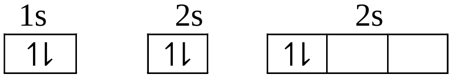
i. *Electrons are lazy*

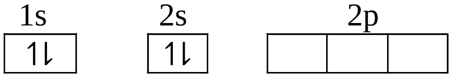
ii. *Electrons are unfriendly*

iii. *Quantum numbers are signature for electrons in the atom*

b. State the rule violated in each of the following electronic configuration







c.

Give set of quantum numbers of

i. Last electron in copper

ii. 26th electron in cobalt

ANSWERS TO DIGGING DEEPER EXERCISES

Exercise 1

Question 1

$\mathrm{N}-14(99.3\%)$, $(\mathrm{N}-15(0.7\%)$.

Question 2

$99.76(0-16), 0.203\%(0-18)$

Question 3

0.358g per beanium atom.

Question 4

12.18 amu.

Question 5

$\mathrm{B}-11:\mathrm{B}-10=4:1$

Question 6

a) $^{36}_{18}\mathrm{Ar}^{+}$ having lighter mass, has smaller mass-charge ratio and hence will be more deflected.
b) $^{36}_{18}\mathrm{Ar}^{2+}$ having greater positive charge has smaller mass-charge ratio and hence will be more deflected.

Question 7

a) $\mathrm{Ar(Argon)} = 39.96$ (b)$\mathrm{Ar\ (potassium)} = 39.11$
b) Although potassium atoms have one more proton than argon atoms, the most abundant isotope of argon has 22 neutrons which are 2 more neutrons than potassium which has only 20 neutrons.

- Thus the increase in number of neutrons of Ar outweighs the increase in number of protons (atomic number) of K, making average atomic weight of Ar close to 40 while that of k is close to 39.

(Notice that: the question asks to explain why? And not just 'why' so understanding that little difference between the two in approaching the question).

Question 8

Most of the instruments used for investigating the structure of the atom are based on the use of measurement of electric charge. As the **neutron is uncharged** particle, it was not detected by these instruments.

Question 9

Isotopes are $^{238}_{92}\mathrm{U}$, $^{234}_{92}\mathrm{U}$

Isobars are i. $^{238}_{92}\mathrm{U}$ and $^{238}_{93}\mathrm{Np}$,
ii. $^{234}_{90}\mathrm{Th}$, $^{234}_{92}\mathrm{U}$, $^{234}_{91}\mathrm{Pa}$

Question 10

	Atomic mass		Mass number
	Definition: Is the weighed average mass of all isotopes of an element		Definition: Is the number of protons plus the number of neutrons in the nucleus of an atom
	Units are amu		Has no unit
	It is reported on the periodic table		It is not reported on the periodic table
	It is actually an average mass		It is a counted value, not a mass
	It can have a decimal value		It is always a whole number

Question 11

$\mathrm{Ca}-40$ is probably the most abundant isotope (because the average atomic mass is usually close to the mass number of the most common isotope).

Question 12

- Carbon-14 refers to the isotope of carbon with mass number of 14.
- Silver-108 refers to the isotope of silver with mass number of 108.

Question 13

a) About 20 (which is the mass number of most abundant isotope)
b) 20.17amu

Question 14

(a) Three (b) 24, 25, 26 (c) ${}^{24}_{12}\mathrm{Mg}$, ${}^{25}_{12}\mathrm{Mg}$, ${}^{26}_{12}\mathrm{Mg}$. (d) 24.3

Question 15

The statement is **correct.**

Explanation:

Due to presence of isotopes, RAM listed in the periodic table is just an average of relative isotopic mass of isotopes of magnesium.

Question 16

i. Hint: state the purpose (which is to do the ionisation of the sample) and then explain how the ionisation of the sample occurs.
ii. Purpose of the electric field: to deflect ions
Purpose of Q: to detect ions

Question 17

Refer to the text

Exercise 2

Question 1

a) Absorbed (Because energy level increase from $n = 2$ to $n = 3$)
b) 3.037×10^{-19}J, 4.58×10^{14}Hz, 655nm
c) Visible

Question 2

a. 2.75×10^{14}Hz, 1091nm (b) Near infrared region (or simply infrared region)

Question 3

121.1nm (Hint: $n_1 = 1$ for 1s and $n_2 = 2$ for 2p)

Question 4

Differences between line and band spectra

Line spectrum		Band spectrum	
1	It consists of sharp and well defined lines	1	It consists of closely spaced packed lines called bands
2	It is characteristics of atoms	2	It is characteristic of molecules
3	It is formed due to the excitation and de-excitation of electrons in the atoms	3	It is formed due to the vibrations and rotations of atoms in molecules
4	It is also known as atomic spectra	4	It is also known as molecular spectra

Question 5

$\frac{5}{27}$

Question 6

Minimum energy to cause excitation of electron in the hydrogen atom at ground state is obtained when the electron transit from n=1 (ground state) to n=2.

- This energy has maximum wavelength possible for causing the excitation.
- Then by using Rydberg equation:

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

- Substituting $\frac{1}{\lambda} = 1.1 \times 10^{-7}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$

From which $\frac{1}{\lambda} = 1.21 \times 10^{-7}$m

Thus the maximum possible wavelength to cause the excitation of electrons in the hydrogen atom is 1.21×10^{-7}m .

But the given wavelength (1.22×10^{-6}m) is greater than the maximum possible wavelength for the excitation to occur; hence **no excitation will occur** because wavelength has too small energy to cause the excitation.

Question 7

- When electrons are excited by the addition of energy, they absorb this energy and move out further from the nucleus.
- When the electrons drop back closer to the nucleus, they give the off added energy as light.
- Depending on how far electrons were from the nucleus, they will give off light of different wavelengths in different colours when they drop back.

Exercise 3

Question 1

In order for an electron to be ejected from a metal surface the electron must be struck by a single proton with at least the minimum energy to knock the electron loose and hence the proton act as the light particle.

Question 2

A photon can be emitted when an electron moves either from:

- An excited state to its ground state or
- A higher energy excited state to a lower energy excited state.

Question 3

Because the energies of the orbits in which electron revolve are fixed making the orbits stable.

Question 4

They are similar in the following manner:

- They both include electron as the sub-atomic particle.
- They both include proton as another sub-atomic particle
- Neither of their models included neutrons as the sub-atomic particles
- They both include the fact that an atom is electrically neutral

They are different in the following manner:

- Rutherford's model recognised the presence of nucleus **while** Thomson's model did not
- In Rutherford's model, the atom is mostly empty space and this is where the electrons are found **while** Thomson's model suggested that the atom was a solid sphere, with the electron embedded in among the positive protons.
- Rutherford's model suggested that protons are contained in very small core of an atom **while** Thomson's model suggested that protons occupy the whole space of the atom as positive fluid.

Question 5

Refer to the text and then answer the question in similar approach as the **Question 4**.

Question 6

From $\lambda = \frac{h}{mv}$

The De Broglie wavelength varies inversely proportional to the mass and hence electrons having smaller mass (than protons) have longer the De Broglie wavelength.

Question 7

Light carries **quanta** (fixed amount) of energy and travels in packets called photons. Atoms can **absorb** or emit **photons** of specific energies.

Question 8

In the daily life, macroscopic objects are more common. Those macroscopic objects have too small de Broglie wavelength to be detected and hence they do not exhibit wave characteristic.

Question 9

From De-Broglie equation: $\lambda = \frac{h}{mc}$

But from: $K:E \quad = {}^{1}/_{2}\,mc^2$ or $c = \sqrt{\frac{2\ K:E}{m}}$

Then substituting the above expression for c in the De-Broglie equation gives:

$$\lambda = \frac{h}{m\sqrt{\frac{2\ K:E}{m}}} = \frac{h}{\sqrt{2mK:E}}$$

For electron: $\lambda_e = \frac{h}{\sqrt{2m_eK:E}}$

For proton: $\lambda_p = \frac{h}{\sqrt{2m_pK:E}}$

Then $\frac{\lambda e}{\lambda_p} = \frac{h}{\sqrt{2meK:E}} \div \frac{h}{\sqrt{2m_pK:E}} = \sqrt{\frac{2m_pK:E}{2m_eK:E}}$

$\frac{\lambda_e}{\lambda_p} = \sqrt{\frac{m_p}{m_e}} = \sqrt{\frac{1.67\times10^{-27}\text{kg}}{9.11\times10^{-31}\text{kg}}} = 42.8$

Hence the ratio of De- Broglie wavelength of electron to that of proton is 42.8

Question 10

(a)1.46×10^{-9}m (b) $\frac{\lambda_H}{\lambda_O} = 16$

Question 11

a) Ionize describes the process where radiation knocks electrons out of atoms turning the atoms into ions (positively charged)

b)

i. Result: most of the alpha particles went straight through.
Conclusion: atoms were mainly empty space.

ii. Result: some of the alpha particles were deflected because the nucleus was positively charged and repelled the positively charged alpha particles.
Conclusion: most of the matter was contained in a small, very dense, positively charged nucleus.

iii. Result: a few of the alpha particles were repelled straight back because the mass of the atom was concentrated in the nucleus.
Conclusion: most of the matter was contained in a very small, very dense, positively charged nucleus.

Exercise 4

Question 1

a) 1s b) 3d c) 4f d) 5g (it is just hypothetical)
e) 4d f) 6g (it is also just hypothetical)

Question 2

	ORBIT		ORBITAL
01	It is a defined circular (more specific, elliptical path followed by electron around the nucleus	01	Is the region around the nucleus of an atom where there is a maximum probability of finding an electron
02	It represents two dimension motion of electron around the nucleus	02	It represents three dimensional motion of electron around the nucleus
03	Orbit is elliptical in shape	03	Orbital have different shape
04	The maximum number of electrons in an orbit is $2n^2$ where n is the orbit number	04	The maximum number of electrons in an orbital is 2

Question 3

i. $n = 3, l = 2, m = +1$ vi. $n = 3, l = 1, m = -1$
ii. $n = 4, l = 2, m = +2$ vii. $n = 5, l = 3, m = -3, -2, -1, 0, +1, +2$ or $+3$
iii. $n = 3, l = 2, m = -2$ viii. $n = 2, l = 1, m = 0$
iv. $n = 4, l = 2, m = -1$ ix. $n = 4, l = 0, m = 0$
v. $n = 2, l = 1, m = +1$ x. $n = 3, l = 2, m = -2, -1, 0, +1$ or $+2$

Question 4

i. 1p because 1p means $n = 1, l = 1$ and l never be equal to l
ii. 3f because 3f means $n = 3, l = 3$ and l can never be equal to l
iii. 2f because 2f means $n = 2, l = 3$ and I can never be greater than n

Question 5

a) Allowed
b) Not allowed because l must be less than n(1 cannot be equal to n)
c) Allowed
d) Not allowed because magnitude of ml cannot be greater than that of l(ml must take values from $-l$ to $+l$)

Question 6

$n = 4, l = 2, m_l = -2, -1, 0, +1$ or $+2$

Question 7

a. Six
b.

n	2					
l	1					
m_l	-1		0		$+1$	
m_s	$+1/2$	$-1/2$	$+1/2$	$-1/2$	$+1/2$	$-1/2$

Question 8

i. **Probable distance of an electron from the nucleus**
  - Greater value of principal quantum number means greater distance from the nucleus.

ii. **Energy of an electron**
  - Greater value of principal quantum number means greater energy of an electron with that principal quantum number.

iii. **Stability of an electron**
  - Greater value of principal quantum number means less stability of an electron with that principal quantum number.

iv. **Size of an orbital**
  - Greater value of principal quantum number means greater size of an orbital with that principal quantum number.

Question 9

Notation: 4f

Number of orbitals: 7 $(2l + 1 = (2 \times 3) + 1 = 7)$

Exercise 5

Question 1

i. This is accordance to Aufbau principle which states that: Electrons tend to occupy the orbitals of lower energy before those of higher energy.
ii. This is accordance to Hund's rule which states that :pairing of electrons in orbitals of the same type with the same energy is not allowed until each orbital is singly occupied with electron
iii. This is accordance to Pauli's Exclusion Principle principle which may be stated as: No two electrons in the same atom may have the same all four quantum numbers.

Question 2

i. $1s < 2s = 2p < 3s = 3p = 3d < 4s$
ii. $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$

Question 3

i. Not valid: violate Aufbau principle
ii. Not valid: Violate Paul Exclusion principle and Aufbau principle
iii. Not valid: Ra is not a noble gas and therefore it cannot be used in shorting configuration of other atoms.
iv. Valid
v. Not valid: Configuration of noble gas cannot used to shorten the configuration of the noble gas itself

Question 4

With the configuration $[Ar]3d^5 4s^1$, the configuration is said to violate Aufbau principle because electrons are filled in 3d orbitals before totally occupying the $4s -$ orbital

Question 5

a.

i. $[\,Fe^{2+}] = [Ar]$

3d

1⇂	1	1	1	1

ii. $[Fe^{3+}] = [Ar]$

3d

1	1	1	1	1

iii. $[Mn^{2+}] = [Ar]$

3d

1	1	1	1	1

iv. $[Mn^{3+}] = [Ar]$

3d

1	1	1	1	

b.

i. Mn^{2+} is more stable than Fe^{2+} because has extra stability of completely a half filled electronic configuration.
ii. Fe^{3+} is more stable than Mn^{3+} because has extra stability of completely a half filled electronic configuration.

Question 6

- Be has outermost energy level with principle quantum number of n = 2 which has p-sub energy level. This means that there are empty p-orbitals in Be unlike in He which has extra stability of completely full filled electronic structure as there is no p-sub energy level in principal quantum of n = 1 which is the outermost energy level of He.
- Valence electron in n = 2 of Be are further from the nucleus than valence electron in n = 1 of He.This means electrons in Be are more loosely bound by nucleus than closer firmly bound valence electron of He thus making He more stable.

Question 7

Electronic configuration of Xe is

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6$

i. Total number of electrons in $n = 4(4s^2 4p^6 4d^{10})$ is

$$2 + 6 + 10 = 18$$

Hence 18 electrons have $n = 4$ in the xenon

ii. $n = 4, l = 2$ is for 4d orbitals which have 10 electrons $(4d^{10})$

Hence 10 electrons have$n = 4, l = 2$.

iii. $ml = 0$ stand for s-orbital which are $1s^2\ 2s^2 3s^2 4s^2\ 5s^2$ for Xe with total number of $2 + 2 + 2 + 2 + 2$ or 10 electrons

Hence 10 electrons have $ml = 0$ in the xenon

iv. Four quantum numbers specify only one electron in the Xe

Hence only 1 electron has $n = 2\quad l = 2,\ ml = -1,\ s = {}^1\!/_2$ in the xenon

v. $n = 4, l = 3$ stands for 4f orbital which has no electron in xe

Hence 0 electrons has $n = 4,\ l = 3$ in the xenon

Question 8

Dipositive ion (ion with a charge of +2) is formed after removing two electrons from an atom.

- So the given electronic configuration with 10 electrons was obtained after removing 2 electrons from the atom.
- Thus the actual total number of electrons in the neutral atom is $10 + 2 = 12$ electrons.
- And for neutral atom.

Number of electrons =Atomic number

Hence atomic number of the atom is 12.

Question 9

- The anion x^{3-} with electronic configuration of 10 electrons is formed after x gaining three electrons
- So number of electron in the neutral atom of x is $10 - 3$ or 7 electrons.

But for neutral atom

$$\text{Atomic number} = \text{Number of electrons}$$

Hence the atomic number of x is 7.

Question 10

i. **In an orbital, a pair of electrons must contain opposite spin.**
   - This is because, the particular orbital in an atom have unique values of the first three quantum numbers (n, l and m_l). So the two electrons must be spinning in opposite direction so as to have different value of m_s (spinning quantum numbers).

ii. **Maximum number of electrons in orbital is two.**
   - This is because; there are only two possible directions for spinning of electrons which are clockwise and anticlockwise. Having more than two electrons will make more than one electron to spin either in clockwise or anticlockwise direction and therefore the two electrons in the orbital would have the same value of m_s and as they belong to the same orbital ,all four quantum numbers would be the same.

Question 11

i.

	3s
[Ne]	1

ii.

	3d				
[Ar]	1	1	1	1	1

iii.

	3d				
[Ar]	1	1	1	1	1

iv.

	3d				
[Ar]	1	1			

Question 12

i. $1s^2 2s^2 2p^6$
ii. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
iii. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Question 13

Electronic configuration of calcium is

$1s^2\ 2s^2 2p_x^2 2p_y^2\ 2p_z^2\ 3s^2 3p_x^2 3p_y^2 3p_z^2 4s^2$

i. For calcium atom, $m_l = 0$ represents s and p_y orbitals in the following:
$1s^2 2s^2 2p_y^2\ 3s^2 3p_y^2 4s^2$
Thus the total number of electrons is $2 + 2 + 2 + 2 + 2 + 2 = 12$

Hence the number of electrons in calcium with quantum number $m_l = 0$ is 12.

ii. $l = 1$ stands for the p orbitals which for calcium are:
$2p_x^2 2p_y^2\ 2p_z^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$
Thus the total number of electrons is $2 + 2 + 2 + 2 + 2 + 2 = 12$

Hence the total number of electrons in calcium with quantum number $l = 1$ is 12.

SOLUTIONS TO EXAMINATION QUESTIONS

Question 1

Using $\mathrm{Ar} = \frac{\mathrm{m_1P_1+m_2P_2+m_3P_3}}{100}$

Substituting $28.0855 = \frac{27.9769\mathrm{P_1}+28.9765\times4.67+29.9738\mathrm{P_3}}{100}$

From which:$27.9769\mathrm{P_1} + 29.9738\mathrm{P_3} = 2673.2297 \ldots \ldots \ldots \ldots \ldots$ (i)

But: $\mathrm{p_1 + p_2 + p_3} = 100$ Or

$\mathrm{P_1} + 4.67 + \mathrm{P_3} = 100$ or $\mathrm{P_1 + P_3} = 95.33 \ldots \ldots \ldots \ldots \ldots \ldots . . \ldots \ldots$ (ii)

Solving (i) and (ii) simultaneously gives:

$\mathrm{P_1} = 92.23\%$ and $\mathrm{P_3} = 3.1\%$

Hence natural abundance of $\mathrm{Si} - 28$ and $\mathrm{Si} - 30$ are 92.23% and 3.1% respectively

Question 2

Using $\mathrm{Ar} = \frac{\mathrm{M_1P_1+M_3P_3}}{100}$

Substituting $207.19\mathrm{g} = \frac{205.98\mathrm{P_1}+206.98\mathrm{P_2}+207.98\mathrm{P_3}}{100}$

From which: $205.98\mathrm{P_1} + 206.98\mathrm{P_2} + 207.98\mathrm{P_3} = 20719 \ldots \ldots \ldots$ (i)

Also: $\mathrm{P_1 + P_2 + P_3} = 100$

But: $\mathrm{P_2 = P_3 = P(Pb - 207\ and\ Pb - 208\ present\ in\ equal\ amount)}$

Then equation (i) becomes:

$205.98\mathrm{P_1} + 206.98\mathrm{P} + 207.98\mathrm{P} = 20719$

Or $205.98\mathrm{P_1} + 414.96\mathrm{P} = 20719 \ldots \ldots \ldots \ldots \ldots$ (iii)

And equation (ii) becomes:

$\mathrm{P_1 + P + P} = 100$ or $\mathrm{P_1} + 2\mathrm{P} = 100 \ldots \ldots \ldots \ldots .$ (iv)

Solving (i) and (ii) simultaneously gives:

$\mathrm{P_1} = 19.3\%, \mathrm{P} = 40.3\%$

Hence percentage abundance of each isotope is as follows:

$\mathrm{Pb} - 206{:}\ 19.3\%, \mathrm{Pb} - 207{:}\ 40.3\%, \mathrm{Pb} - 208{:}\ 40.3\%$

Question 3

Using $\mathrm{n} = \frac{\mathrm{m}}{\mathrm{mr}}$;

Number of moles of $\mathrm{Ne(both\ Ne - 20\ and\ Ne - 22)}$

$= \frac{12.55}{20.18}\mathrm{mol} = 0.6219\mathrm{mol(Notice\ the\ use\ of\ average\ atomic\ mass\ 20.18)}$

Using $\mathrm{N = nNA}$

Total number of Ne atoms (Again both $\mathrm{Ne} - 20$ and $\mathrm{Ne} - 22$ atoms)

$= 0.6219 \times 6.02 \times 10^{23}\ \mathrm{atoms} = 3.743838 \times 10^{23}\ \mathrm{atoms}$

Now, let number of $\mathrm{Ne} - 22$ be X

Then number of atom of $\mathrm{Ne} - 20$ will be $3.743838 \times 10^{23} - \mathrm{X}$

And by using,

$$\mathrm{Ar} = \frac{\sum(\text{Number of atoms of isotope} \times \text{isotopic mass})}{\text{Total number of atoms}}$$

$$20.18 = \frac{21.99\mathrm{X} + (3.743838 \times 10^{23} - \mathrm{X})19.99}{3.743838 \times 10^{23}}$$

Solving the above equation, gives $\mathrm{X} = 3.5567 \times 10^{22}$

Hence there were 3.5567×10^{22} atoms of $\mathrm{Ne} - 22$ in the given sample.

Question 4

a)

i)

- Horizontal lines represent quantized energy levels.
- Vertical lines represent transition of electrons between different quantized energy levels.

ii)

- Through excitation of electron, quanta of radiation energy are absorbed and therefore giving absorption line spectra.
- When the **excited electron**s return **to ground state or to lower energy excited state** quanta of radiation energy is emitted and therefore giving emission spectrum.

b)

Wavelength of a line in the hydrogen emission spectrum of is given by the following Rydberg equation:

$$\frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{\mathrm{n}_1^2} - \frac{1}{\mathrm{n}_2^2}\right)$$

Substituting given values to the above equation gives

$$\frac{1}{\lambda} = 1.1 \times 10^7\left(\frac{1}{2^2} - \frac{1}{5^2}\right),$$

From which $\lambda = 4.329 \times 10^{-7}\mathrm{m}$ or $432.9\mathrm{nm}$

From the wavelength corresponding to the given transition is approximately 433nm which is almost the same with the given value of 434nm. So as the transition of electron obey Rydberg equation for the hydrogen, the given wavelength is correct for hydrogen atom.

c)

Assume an electron in hydrogen atom jump from its ground state of n= 1to higher energy of n_1 with respective energy of E and E_1.

- From Rydberg equation:

$$\frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{1^2} - \frac{1}{\mathrm{n}_1^2}\right)$$

Where λ is the wavelength of the energy absorbed,

$\mathrm{R_H}$ is Rydberg constant = $1.097 \times 10^7\mathrm{m}^{-1}$.

From Bohr's theory;

$$\Delta\mathrm{E} = \mathrm{hf} = \frac{\mathrm{hc}}{\lambda} \qquad (\mathrm{f} = \frac{\mathrm{c}}{\lambda})$$

But $\Delta\mathrm{E} = \mathrm{E}_1 - \mathrm{E}$

Thus $\mathrm{E}_1 - \mathrm{E} = \frac{\mathrm{hc}}{\lambda}$

But from Rydberg equation

$$\frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{1^2} - \frac{1}{\mathrm{n}_1^2}\right)$$

Then $\mathrm{E}_1 - \mathrm{E} = \mathrm{hc}\,\mathrm{R_H}\left(\frac{1}{\mathrm{n}^2} - \frac{1}{\mathrm{n}_1^2}\right)$

Where h is the plank's constant = $6.626 \times 10^{-34}\mathrm{Js}$

c is the velocity of radiation $= 2.998 \times 10^8\mathrm{m/s}$

So $\mathrm{E}_1 - \mathrm{E} = 6.626 \times 10^{-34} \times 2.998 \times 10^8 \times 1.097 \times 10^7\left(\frac{1}{1^2} - \frac{1}{\mathrm{n}_1^2}\right)$

$\mathrm{E}_1 - \mathrm{E} = 2.179163 \times 10^{-18}\left(\frac{1}{1^2} - \frac{1}{\mathrm{n}_1^2}\right)$

When n is too large, i.e. $\mathrm{n}_1 = \infty$, $E_1 = 0$ and $\frac{1}{\mathrm{n}_1^2} \approx 0$

Then $\Delta\mathrm{E} = \mathrm{E}_1 - \mathrm{E} = 0 - \mathrm{E} = -\mathrm{E}$

Thus $-\mathrm{E} = 2.179163 \times 10^{-18}\left(\frac{1}{1^2} - 0\right)$

From which; –E = $\frac{2.179163\times10^{-18}}{1}$J

But 1ev = 1.6×10^{-19}J

Then $\frac{-2.179163\times10^{-18}}{1}\text{J} = \frac{-2.179163\times10^{-18}}{1\times1.6\times10^{-19}}\text{ev} = -13.6\text{ev}$

Hence the energy is -13.6ev

Question 5

a) $n = 2$(where Balmer series if formed)

b) Dark lines are formed when electrons in $n = 2$ (lower energy excited state) hydrogen atoms are further excited to higher energy level by absorbing radiation energy of wavelength in the visible spectrum.

- This is because when excited electron from higher energy level to $n = 2$ (Balmer series), it forms emission visible spectrum which inturn implies that only an electron in $n = 2$ will be excited by absorption of the same amount of energy in the visible spectrum, turning the red line into dark line.

c) Ground state in hydrogen has $n = 1 = n_1$

Therefore second excited state has $n = 3 = n_2$

Using $f = \frac{C}{\lambda}$

But from Rydberg equation:

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

It follows that; $f = CR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Substituting $f = 3\text{x}10^8 \times 1.1 \times 10^7\left(\frac{1}{1^2} - \frac{1}{3^2}\right)$Hz

$= 2.93 \times 10^{15}$Hz

Hence the frequency is 2.93×10^{15}Hz

d) Using $f = CR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Where $n_1 = 1$(an electron dropped to the ground state after the first jump)

$n_2 =$ Is the higher energy level attained after the first jump which is unknown?

Substituting $3.2 \times 10^{15} = 3 \times 10^8 \times 1.1 \times 10^7 = \left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$

From which $n_2 = 5.7 \approx 6$

So for first jump: $n_1 = 4, n_2 = 6$(as the same energy absorbed in jumping from n=4 to n=6 will be emitted).

Then using again

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

$= 3 \times 10^8 \times 1.1 \times 10^7\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$Hz

$= 3 \times 10^8 \times 1.1 \times 10^7\left(\frac{1}{4^2} - \frac{1}{6^2}\right)$Hz

$= 1.146 \times 10^{14}$Hz

Hence the frequency of photon required for first jump is 1.146×10^{14}Hz

Question 6

a) The lowest frequency in the Balmer series is obtained when an electron fall from $L = 3$. (since the frequency is direct proportional to the energy, the lowest frequency is obtained when the energy difference between the two energy level is minimum which is $E_3 - E_2$ for Balmer series).

Then using:

$$\frac{1}{\lambda} = R\left(\frac{1}{S^2} - \frac{1}{L^2}\right)$$

$$\frac{1}{\lambda} = 1.1 \times 10^7\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

From Which $\lambda = 6.55 \times 10^{-7}$m

Hence the wavelength is 6.55×10^{-7}m

b) The light is formed when the excited electron in the hydrogen atom fall from L=3 to $S = 2$ and therefore emitting energy in terms of radiation (light).

c) For first jump:

L=7: S is unknown

Substituting $\frac{1}{2.165\times10^{-6}} = 1.1\times10^{7}\left(\frac{1}{S^2}-\frac{1}{7^2}\right)$

From which: $S = 4$

For second jump;

$S = 1$(Ground state)

$L = 4$ (S of the first jump is the L or excited state of the second jump)

Then substituting that value in:

$$\frac{1}{\lambda} = R\left(\frac{1}{S^2}-\frac{1}{L^2}\right)$$

$$\frac{1}{\lambda} = 1.1\times10^{7}\left(\frac{1}{1^2}-\frac{1}{4^2}\right)$$

From which $\lambda = 9.697\times10^{-8}$m

Hence the wavelength of the second photon is 9.697×10^{-8}m

Question 7

a) Ultraviolet region

b) Using Rydberg equation $\frac{1}{\lambda} = 1.1\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$

Substituting $\frac{1}{\lambda} = 1.1\times10^{7}\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$

From which $\lambda = 1.212\times10^{-7}$m

The wavelength of photon emitted is 1.212×10^{-7}m

c) Electron transition from higher energy excited state to $n = 2$

d) The amount of radiation energy absorbed in the excitation of the electron is equal to the amount of radiation energy emitted when the electron return to the ground state and is given by the following equation.

$$\Delta E = hf = \frac{hc}{\lambda}$$

But from Rydberg equation:

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

Then $\Delta E = hcR_H\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) = 6.63\times10^{-34}\times3\times10^{8}\times1.1\times10^{7}\left(\frac{1}{3^2}-\frac{1}{5^2}\right)$J

$= 1.556\times10^{-19}$J

Hence the energy of the photon is $= 1.556\times10^{-19}$J

Question 8

a. Thomson used it to discover the electron and that the electron is negatively charged.

b. Rutherford shot alpha particles through gold foil and discovered the atomic nucleus.

- He learned that all atoms have a dense, positively charged tiny core and that electrons are found in space around the nucleus.

c. Bohr discovered that electrons can only be certain, discrete distance from the nucleus.

- The electrons orbit the nucleus in fixed predictable orbital whose energy is quantized rather than circling it randomly in an electron cloud.

Question 9

Energy of one photon is given by the following Planck's equation: $E = hf = \frac{hc}{\lambda}$

Substituting $E = \frac{6.63\times10^{-34}\text{Js}\times3\times10^{8}\text{ m/s}}{510\times10^{-9}\text{m}}$

$= 3.9 \times 10^{-19}\mathrm{J/photon}$

Using number of photons $= \frac{\text{Total energy}}{\text{Energy per photon}}$

$= \frac{3.15\times10^{-17}\mathrm{J}}{3.9\times10^{-19}\mathrm{J/photons}} = 81$ photons

Hence the given energy corresponds to 81 photons

(Don't forget to approximate the answer to the nearest whole number because photons is discrete data, it can never be a fraction)

Question 10

1. Two (2) electrons the three set of quantum numbers specify specific type of an orbital and maximum number of electrons in the orbital (2)
2. Fourteen(14) electrons(This is 5f orbitals and maximum number of electrons in f orbitals is 14)
3. Four (4) electrons (Maximum number of electrons in $\mathrm{n} = 2$ 1s $2\mathrm{n}^2 = 2 \times 2^2 = 8$, a half of them which is $^1/_2 \times 8 = 4$ spinning in anti-clockwise direction with $\mathrm{m_s} = -{}^1/_2$).

Question 11

Since radiation energy varies directly proportional to its frequency maximum energy corresponds to the maximum frequency which is$1\mathrm{GHz} = 10^9\mathrm{Hz}$.

Using $\mathrm{E} = \mathrm{hf}$: (Planck's equation)

$\mathrm{E} = 6.63 \times 10^{-34}\mathrm{Js} \times 10^9\mathrm{Hz} = 6.63 \times 10^{-25}\mathrm{J/photon}$

Hence maximum energy, a photon can have $6.63 \times 10^{-25}\mathrm{J}$

Converting the energy to $\mathrm{J/mol}$

Using total energy=Energy per photon × Number of photons

But for one mole of photons:

Number of photons=Avogadro's number=$6.02 \times 10^{23}\mathrm{photons/mol}$

Thus energy in $\frac{\mathrm{J}}{\mathrm{mol}} = 6.63 \times \frac{10^{-25}\mathrm{J}}{\mathrm{photons}} \times 6.02 \times 10^{23}\mathrm{photon/mol}$

$= 0.399\mathrm{J/mol}$

Hence the maximum energy per mole basis is approximately$0.4\mathrm{J/mol}$.Comparison

$0.4\mathrm{J/mol}$(Maximum radiation energy from all phones) is very small compared to the energy required to break the covalent bond and therefore cell phone radiation is highly unlikely to cause chemical changes in the body.

Question 12

a) This is because there are three possibilities of forming diatomic molecule from the two isotopes which are:
- Two $\mathrm{Cl} - 35$ atoms combine to form $\mathrm{Cl_2}\left({}^{35}\mathrm{Cl} - {}^{35}\mathrm{Cl}\right)$
- One $\mathrm{Cl} - 35$ atom combine with another atom of $\mathrm{Cl} - 37$ to form $\mathrm{Cl_2}$ $\left({}^{35}\mathrm{Cl} - {}^{37}\mathrm{Cl}\right)$
- Two $\mathrm{Cl} - 37$atoms combine to form$\mathrm{Cl_2}\left({}^{37}\mathrm{Cl} - {}^{37}\mathrm{Cl}\right)$.

b)
- ${}^{35}\mathrm{Cl} - {}^{35}\mathrm{Cl}$ has $(35 + 35)\mathrm{amu} = 70\mathrm{amu}$
- ${}^{35}\mathrm{Cl} - {}^{37}\mathrm{Cl}$ has $(35 + 37)\mathrm{amu} = 72\mathrm{amu}$
- ${}^{37}\mathrm{Cl} - {}^{37}\mathrm{Cl}$ has $(37 + 37)\mathrm{amu} = 74\mathrm{amu}$

c)
- Intensity of corresponding ${}^{35}\mathrm{Cl} - {}^{35}\mathrm{Cl}$ is proportional to probability of getting first ${}^{35}\mathrm{Cl}$ and second ${}^{35}\mathrm{Cl} = \frac{75}{100} \times \frac{75}{100}$
- Intensity corresponding to ${}^{35}\mathrm{Cl} - {}^{37}\mathrm{Cl}$ is proportional to the probability of getting first ${}^{35}\mathrm{Cl}$ and second ${}^{37}\mathrm{Cl}$ or first ${}^{37}\mathrm{Cl}$ and second ${}^{37}\mathrm{Cl} = \left(\frac{75\times25}{100}\right)$
- Intensity corresponding to ${}^{37}\mathrm{Cl} - {}^{37}\mathrm{Cl}$ is proportional to the probability of getting first ${}^{37}\mathrm{Cl}$ and second ${}^{37}\mathrm{Cl} = \frac{25}{100} \times \frac{25}{100}$

Thus the relative amount of the three isotopes is:

$\frac{75\times25}{100}$ $: 2\left(\frac{75\times25}{100}\right) : \frac{25}{100}\times\frac{25}{100}$

Or $75\times75 : 2\times75\times25 : 25\times25$ or $\frac{75\times75}{25\times25} : \frac{2\times75\times25}{25\times25} : \frac{25\times25}{25\times25}$

$= 9:6:1$

Hence the relative amount of three isotopes is $9:6:1$ for $70,72$ and 74amu respectively

Question 13

i. If $n = 2$ and $m_l = 0$, l may be either 0 or 1 in the following two set of quantum numbers.

$1:\ n = 2, l = 0, m_l = 0 \Longrightarrow 2s - \text{orbital}$

$2 : n = 2, l = 1,\ m_l = 0 \Longrightarrow 2P_y - \text{orbital}$

Each set of the first three quantum numbers specify a particular orbital which may contain maximum of two electrons making a total of $4(2\times2)$electrons in the two sets.

- Hence maximum number of electrons with given quantum number is 4

ii. If $n = 3$ and $L = 1$, ml may be $-1, 0$ or $+1$ in the following three sets of quantum numbers:

$1: n = 3, l = 1,\ m_l = -1 \Longrightarrow 3P_x - \text{orbital}$

$2:\ n = 3, l = 1, m_l = 0 \Longrightarrow 3P_y - \text{orbital}$

$3:\ n = 3, l = 1, m_l = +1 \Longrightarrow 3P_z - \text{orbital}$

Each set of the first three quantum number specify a particular orbital with maximum of two electron in the orbital thus making a total of 2×3 or 6 electrons in the three sets.

- Hence the maximum number of electrons with the given quantum numbers is 6.

iii. If $n = 2$, and $l = 1$, ml may be either $-1, 0$ or $+1$ in the following three sets of quantum numbers:

$1: n = 2, l = 1, m_l = -1 \Longrightarrow 2P_x - \text{orbital}$

$2: n = 2, l = 1, m_l = 0 \Longrightarrow 2P_y - \text{orbital}$

$3: n = 2, l = 1, m_l = +1 \Longrightarrow 2P_z - \text{orbital}$

Each set of the first three quantum numbers specify a particular orbital with maximum of two electrons in the orbital. This makes a total of 2× 3 or electrons in the three sets

- Hence maximum number of electrons with the given quantum numbers is 6

iv. The given first three quantum numbers specify a particular orbital which is $2P_x - \text{orbital}$ which may contain a maximum of two electrons.

- Hence maximum number of electrons with given quantum numbers is 2

v. The given four quantum numbers specify a particular electron.

- Hence maximum number of electrons with given quantum number is 1

Question 14

i. m_s cannot be whole number,can be $+{}^1\!/_2$ or $-{}^1\!/_2$

ii. m_l must lie between $-l$ and $+l$, its magnitude cannot be greater than that of l.

Question 15

From de Broglie equation

a. For electron: $\lambda_e = \frac{h}{pe}$

For proton: $\lambda p = \frac{h}{p_p}$

But $\lambda_e = \lambda p$ (The two particles have the same de-Broglie wavelength)

It follows that:

$\frac{h}{pe} = \frac{h}{p_p}$

From which $P_e = P_p$

Hence both particles will have the **same momentum**

b. From $P = mc$ or $c = \frac{P}{m}$.

Thus for a given momentum, speed varies inversely to the mass.

- Since mass of electron is smaller than that of proton and the two have the same momentum (momentum is constant), speed of electron must be greater than that of proton.

c. Using $K.E = \frac{1}{2}mc^2$

Then by multiplying m to both denominator and numerator of the above equation gives:

$$\mathrm{K.E} = \frac{(\mathrm{mc}^2)\times \mathrm{m}}{2\times \mathrm{m}} = \frac{\mathrm{m}^2\mathrm{C}^2}{2\mathrm{m}} = \frac{(\mathrm{mc})^2}{2\mathrm{m}} = \frac{\mathrm{P}^2}{2\mathrm{m}}$$

Then equation suggest that, for given momentum, kinetic energy varies inversely proportional to the mass.

- Since mass of the electron is smaller than that of the proton and the two particles have the same momentum ,kinetic energy of the electron must be greater than that of the proton
- Hence the particles with greater kinetic energy is electron

d. From Planck's theory:

$E \propto f$ (Energy varies directly proportional to frequency) thus the particle with greater energy will have greater frequency too.

Hence the particle with greater frequency is the electrons.

Question 16

From Heisenberg equation: $\Delta x \times \Delta p = \frac{h}{4\pi}$

Where $\Delta p = m\Delta c$:

And $\Delta c = \frac{0.2}{100} \times 1 \times \frac{10^6 m}{s} = 2000 m/s$

If follows that: $\Delta x = \frac{h}{(4\pi)p} = \frac{h}{(4\pi)m\Delta c}$

Substituting $\Delta x = \frac{6.63\times10^{-34}}{4\times3.14\times9.11\times10^{-31}\times2000} = 2.9\times10^{-8} m$

Hence maximum precision in the position measurement is $2.9\times10^{-8} m$

Question 17

From Heisenberg equation: $\Delta x\Delta p = \frac{h}{4\pi}$

But $\Delta p = m\Delta c$

Then $\Delta x(m\Delta c) = \frac{h}{4\pi}$

From which: $\Delta c = \frac{h}{4\pi\times m\times\Delta x}$

Substituting $\Delta c = \frac{6.63\times10^{-34}}{4\times3.14\times1.67\times10^{-27}\times1.5\times10^{-11}} = 2107 m/s$

Thus the uncertainty in the position after 2 seconds is $2107 m/s \times 2s = 4214 m$

Question 18

a) An excited electron returns to ground state or to lower energy excited state, emitting quanta of radiation energy as visible light of a specific wavelength.

b) The energy difference between successive energy levels decreases with increasing energy which means the higher energy levels get closer and closer together.

c)

i. From Bohr theory: energy of quanta ('n' photons) is given by;

$\Delta E = nhf$

But for 1 mol, $n = 6.02\times10^{23}$ photons

Thus energy in $J/mol = 6.02\times10^{23}\times6.63\times10^{-34}\times1.26\times10^{15} J/mol$

$= 502899 J/mol$ Or $502.899 kJ/mol$

Hence the energy is $502.899 kJ/mol$

ii. The energy represents first **ionisation energy** of the element.

Question 19

a) $n = 3$ to $n = 2$

Explanation

Line A represents the transition of smallest energy gap because has longer wavelength than all the others shown. And as for Balmer series the lower energy level is $n = 2$, the smallest energy gap will be obtained when the higher energy level is $n = 3$.

b) From Bohr theory: energy of quanta is given by:

$$\Delta E = nhf = \frac{nhc}{\lambda}$$

Where $n = 6.02 \times 10^{23}$ protons for one mole

Then substituting $\Delta E = \frac{6.02\times10^{23}\times6.63\times10^{-34}\times3\times10^{8}}{656\times10^{-9}} J/mol$

$= 182527 J/mol$ Or $182.527 kJ/mol$

Hence the energy difference is $182.527 kJ/mol$.

Question 20

(a) An electron where the upward arrow represents an electron spinning in clockwise direction while the downward arrow represents an electron spinning in anti-clockwise direction.

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

(c) (i) s orbitals are spherical and symmetrical around the nucleus.
p orbitals are dumb-bell shaped and are symmetrical around each axis.
(ii) The p orbitals are arranged mutually at right angles.

(d) According to Hund's rule; electrons are placed singly in degenerate orbitals before pairing occurs in one orbital.

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

Question 21

(a) (ii) is wrong because the 2s electrons have all four quantum numbers the same as they have parallel spin in the same orbital. This violates Pauli's exclusion principle.

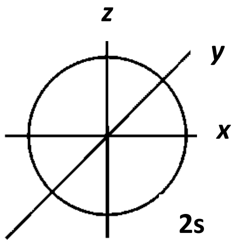
(b) (iv) is wrong because:

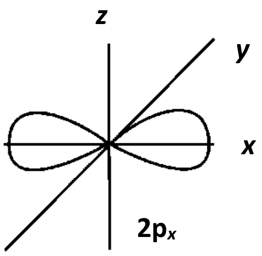
- Pairing in the $2p_x$ has been done before the two 2p electrons occupying two degenerate 2p orbitals (with parallel spin). This violate Hund's rule.
- Also the two 2p electrons have parallel spin in the same orbital. This violates Pauli's exclusion principle.

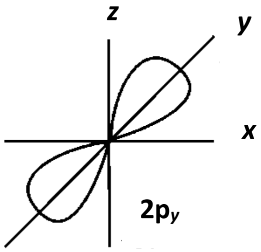
(b) (vi) is wrong because the 2p sublevel which has higher energy than 2s sublevel is filled with electrons before1s is completely filled with electrons. This violates the Aufbau principle.

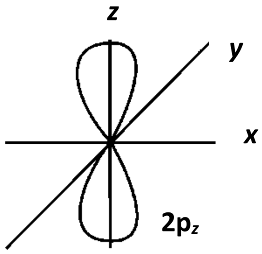
Question 22

(a)







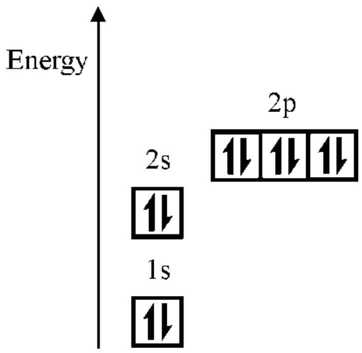


(b) A region where one or (at most) two electrons are likely to be found.

(c) It signifies the second energy level.

(d) Of equal energy.

(e)



Question 23

(a)

ION	m/z
CH_4O^+	32
CH_3O^+	31
CH_2O^+	30
CHO^+	29
CO^+	28

The parent ion is CH_4O^+.

(b) The relative abundance of each ion formed.

(c)

ION	m/z where z=2
CH_4O^+	16
CH_3O^+	15.5
CH_2O^+	15
CHO^+	14.5
CO^+	14

Question 24

a)

i. Only a small part of the diagram in the question represents the visible spectrum. Other parts represents invisible spectrum.

ii. Balmer series.

b) An electron is excited from its ground state to a higher energy level. On returning to the ground state, it emits energy in forms of radiation with amount equal to the energy difference of the two energy levels involved.

i.

c) From Bohr theory:

$$\Delta E = nhf = \frac{nhc}{\lambda}$$

Where $\frac{1}{\lambda}$ = Wave number

Substituting $\Delta E = 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3 \times 10^{8} \times 11 \times 10^{6} J/mol$

$= 1317116 J/mol$ Or $1317.116 kJ/mol$

Hence the energy is $1317.116 kJ/mol$

d) The ionisation energy of hydrogen.

Question 25

a. $1s^3 2s^3 2p^9$

b. The electronic configuration of the element with a complete n=3 shell $1s^3 2s^3 2p^9 3s^3 3p^9 4s^3 3d^{15}$ (Notice that n=3 has 3s, 3p and 3d sublevels which must be completely filled with electrons for n=3 to be completely filled with electrons).

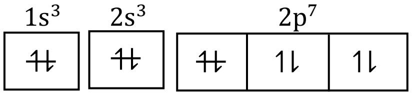
- Thus total number of electrons in the atom $= 3 + 3 + 9 + 3 + 9 + 3 + 15 = 45$

But for neutral atom:

$$\textbf{Total number of electrons} = \textbf{Atomic number}$$

Hence the atomic number of the element is 45

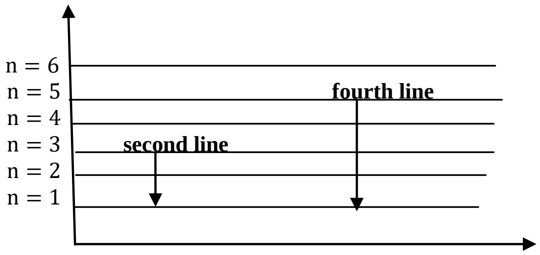
c. The electronic configuration of aluminium would be:



Hence there are **0** unpaired electrons.

Question 26(c)

i. Diagram to show the origin of second and fourth line in balmier series.



ii. It is given that: $\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$

Frequency, $f = \frac{c}{\lambda}$

Then: $f = cR_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$

For the first line in the balmier series, $n = 3$

$$f = 3 \times 10^8 \times 1.09678 \times 10^7\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 4.57 \times 10^{14}\ \text{Hz}$$

The frequency for the first line in the Balmer series is 4.57×10^{14} Hz

Question 27

a) Due to stability for completely a half filled and full filled electronic structure in d-orbitals for Cr and Cu respectively which in turn is caused by the intersection of d and s subenergy level. This make the electronic configuration of Cr to be $[Ar]3d^5 4s^1$ and not $[Ar]3d^4 4s^2$ while that of Cu is $[Ar]3d^{10} 4s^1$ and not $[Ar]3d^9 4s^2$.

b) Number of orbitals presents in given principal quantum number, n, is n^2 And maximum number of electrons in an orbital is 2

Hence total number of electrons that can be held in all orbitals having the same principal quantum number is n^2.

Question 28

a) Maximum frequency and minimum wavelength is obtained when maximum energy is emitted and (in this case) this occur when an electrons falls from $n = 3$ to $n = 1$

Energy remitted $= E_1 - E_3 = \Delta E$

$= -20 \times 10^{-19} - (-15 \times 10^{-19})$

$= -5 \times 10^{-19}$(energy sign means energy is emitted)

But $\Delta E = hf$

From which $f = \frac{\Delta E}{h} = \frac{5\times10^{-19}}{6.63\times10^{-34}}\text{Hz} = 7.54 \times 10^{14}\text{Hz}$

Highest frequency of radiation is $7.54 \times 10^{14}\text{Hz}$

Using $\lambda = \frac{c}{f} = \frac{3\times10^{8}}{7.54\times10^{14}} = 3.98 \times 10^{-7}\text{m}$

Minimum wavelength of the radiation is $3.98 \times 10^{-7}\text{m}$

b) An electrons is said to be complete ionised if it jumps from n=1 to infinity;(for and atom with only one electron, valency shell is n=1)

But $E_\infty = 0\text{J}$

Thus the energy absorbed in ionizing one electron $= 0 - E_1 = 20 \times 10^{-19}\text{J/electron}$

Energy absorbed per one mole of electrons $= 20 \times 10^{-19}\text{J/electron} \times 6.02 \times 10^{23}\text{J/mol}$

$= 1204000\text{J/mol} = 1204\text{kJ/mol}$

Hence the ionisation energy of the element is 1204kJ/mol

c) Shortest the wavelength is obtained when the absorbed energy is maximum. If the electron is in $n = 4$ the maximum energy absorbed without causing ionisation is obtained when the electron absorb the energy so as to jump up to just before reaching the convergent limit where the energy is almost 0J.

Thus maximum energy absorbed $= 0 - 11 \times 10^{-19} = 11 \times 10^{-19}\text{J} = \Delta E$

But $\Delta E = hf = \frac{hc}{\lambda}$ or$\lambda = \frac{hc}{\Delta E} = \frac{6.63\times10^{-34}\times3\times10^{8}}{11\times10^{-19}} = 1.8 \times 10^{-7}\text{m}$ (From Bohr Theory)

Hence the shortest wavelength is $1.8 \times 10^{-7}\text{m}$.

Question 29

(i) The energy is negative to indicate that the electron (has negative charge) in the hydrogen atom is **attracted** to the nucleus (has positive) in electron-nucleus electrostatic force of attraction.

$\Delta E = E_2 - E_1$

$= \frac{-2.178\text{x}10^{-18}}{2^2} - \frac{-2.178\text{x}10^{-18}\text{J}}{1^2} = 1.6335 \times 10^{-18}\text{J}$

Hence $1.6335 \times 10^{-18}\text{J}$ must be absorbed

Using $\Delta E = \frac{hc}{\lambda}$; $\lambda = \frac{hc}{\Delta E} = \frac{6.63\times10^{-34}\times3\times10^{8}\text{m}}{1.6335\times10^{-18}} = 1.22 \times 10^{-7}\text{m}$

Hence the wavelength is $1.22 \times 10^{-7}\text{m}$

Question 30

Thickness of soap bubble = wavelength $= 6\text{nm} = 6 \times 10^{-9}\text{m}$

Using $f = \frac{c}{\lambda} = \frac{3\times10^{8}}{6\times10^{-9}} = 5 \times 10^{16}\text{Hz}$

Question 31 (b)

i. $[\text{Ar}]3d^{10}4s^{1}$
ii. $1s^{2}2s^{2}2p^{6}$
iii. $[\text{Ar}]3d^{5}4s^{1}$
iv. $1s^{2}$

Question 32

(b) When the electron is in $n = \infty$ where $E = 0$ implies that it experiences zero nuclear attraction and therefore the electron is completely ionised from the atom. So $n = \infty$ and $E = 0$ is very useful in the determining the ionisation energy of hydrogen.

Question 33

$$E = hf = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{2420 \times 10^{-10}} = 8.219 \times 10^{-19}\text{J/electron}$$

For one mole of electron

$E = 8.219 \times 10^{-19}\text{J/electron} \times 6.02 \times 10^{23}\text{electron/mole}$

$= 494783.8\text{J} = 494.7838\text{kJ/mol}$

Question 34

For Balmier series, the ground state is n=2; the longest wavelength is obtained when there is minimum energy emitted and this occur when an electron falls from n=3 to n=2(for Balmer series)

Using $\frac{1}{\lambda} = R_H(\frac{1}{n_1^2} - \frac{1}{n_2^2})$

But $\frac{1}{\lambda} = \text{wave number}$

Wave number= $R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Where $R_H = 1.1 \times 10^{7}\text{m}^{-1}$; $n_1 = 2$ and $n_2 = 3$

Then wave number= $1.1 \times 10^{7}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 1527778\text{m}^{-1}$

Thus the wave number of longest wavelength is 1527778m^{-1}

Question 35

i. $\Delta E = hf$; but $f = \frac{c}{\lambda}$

It follows that: $\Delta E = \frac{hc}{\lambda}$

From which $\lambda = \frac{hc}{\Delta E} = \frac{6.63\times10^{-34}\times3\times10^{8}}{4.071\times10^{-19}} = 4.886 \times 10^{-7}\text{m}$

Wavelength of green light is $4.886 \times 10^{-7}\text{m}$

ii. $\Delta E = E_1 - E_2$

Where $\Delta E = -4.071 \times 10^{-19}$J(negative sign is included because the energy is released)

$E_1 = \frac{-13.6\text{eV}}{2^2}$ (Using $E = \frac{-13.6\text{eV}}{n^2}$ (And the light was in Balmer series for which n=2)

$1\text{eV} = 1.6 \times 10^{-19}\text{J}$

$$E_1 = \frac{-13.6 \times 1.6 \times 10^{-19}}{2^2}\text{J} = -5.44 \times 10^{-19} = \Delta E + E_2 = -4.071 \times 10^{-19}\text{J} + E_2$$

From which $E_2 = -1.369 \times 10^{-19}\text{J}$

Thus the higher energy level is $-1.369 \times 10^{-19}\text{J}$

Question 36

a) λ represents the wavelength in metres

R_H represents Rydberg constant

n_1 represents lower energy level which is n_1=2 for visible region

n_2 represent the higher energy level, that is $n_2 > 2$

b) For visible spectrum , n_1=2

Thus the third line in visible spectrum is $n_2 = 5$

Thus the given equation becomes:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{5^2}\right)$$

But $f = \frac{c}{\lambda}$

It follows that: $f = cR_H\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 3 \times 10^8 \times 1.1 \times 10^7 \times \left(\frac{1}{4} - \frac{1}{25}\right) = 6.93 \times 10^{14}$Hz.

The frequency of the third line of the visible spectrum is 6.93×10^{14}Hz

Question 37

$\Delta E = hf = \frac{hc}{\lambda} = \frac{6.63\times10^{-34}\times3\times10^8}{1875\times10^{-9}} J = 1.0608 \times 10^{-19} J$

(Negative sign will be included in calculations because the ΔE is the energy emitted)

Using $E = \frac{-13.6eV}{n^2}$

For n =3

$E = \frac{-13.6\times1.6\times10^{-19}J}{3^2} = -2.42 \times 10^{-19} J$

Let the higher energy level be E_n

Then $\Delta E = E_3 - E_n = -2.42 \times 10^{-19} J - E_n = -1.0608 \times 10^{-19} J$

From which; $E_n = -1.3592 \times 10^{-19} J$

But $E_n = \frac{-13.6eV}{n^2}$

Then $= -1.3592 \times 10^{-19} = \frac{-13.6\times1.6\times10^{-19}J}{n^2}$

From which n=4 (To nearest integer)

Thus for the higher energy level, n=4.

Question 38

From Bohr Theory;

$\Delta E = nhf = \frac{nhc}{\lambda}$ where $n = 6.02 \times 10^{23}$ photons (or electrons) if the energy is in J/mol.

Substituting $145.684 \times 10^3 J/mol = \frac{6.02\times10^{23}\times6.63\times10^{-34}\times3\times10^8}{\lambda}$

From which; $\lambda = 8.219 \times 10^{-7}$m

But $1A° = 10^{-10}$m

So $8.219 \times 10^{-7}m = \frac{8.219\times10^{-7}m}{10^{-10}} A° = 8219A°$

The wavelength of radiation is 8219A°

Question 39

De-Broglie wavelength is given by;

$\lambda = \frac{h}{mv}$

But $K.E = \frac{1}{2}mv^2$

From which $v = \sqrt{\frac{2K.E}{m}}$

Thus $\lambda = \frac{h}{m\sqrt{\frac{2K.E}{m}}} = \frac{h}{\sqrt{2mK.E}}$

Where $m = 6.6 \times 10^{-27}$kg

$K.E = 4.8MeV = 4.8 \times 10^6 \times 1.6 \times 10^{-19} J$

$h = 6.63 \times 10^{-34} Js$

$\lambda = \frac{6.63\times10^{-34}Js}{\sqrt{2\times6.6\times10^{-27}\times4.8\times10^6\times1.6\times10^{-19}}} = 6.58 \times 10^{-15}$m

The De-Broglie wavelength is $6.58 \times 10^{-15}\text{m}$

Question 40

(b) Visible hydrogen spectrum is formed when an electron fall from higher energy level to $n = 2$.

Thus from Rydberg equation;

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

n_1=2 for visible spectrum.

The lowest energy will be emitted when the electron falls from $n = 3$, that is $n_2 = 3$

From Bohr Theory, energy of one quantum is given by;

$$\Delta E = hf = \frac{hc}{\lambda}$$

It follows that:

$$\Delta E = hf = hcR_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right);$$

Substituting $\Delta E = 6.63 \times 10^{-34} \times 3 \times 10^8 \times 1.1 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{J/electron} = 3.0388 \times 10^{-19}\text{J/electron}$

Using $n = \frac{m}{M_r}$;

Number of moles of H atoms $= \frac{1\text{g}}{1\text{g/mol}} = 1\text{mol} = 6.02 \times 10^{23}\text{atoms}$

But each atom of hydrogen contains one electron;

Thus total number of electrons in 1g of H is 6.02×10^{23}electrons

Hence the total energy emitted is $3.0388 \times 10^{-19} \times 6.02 \times 10^{23}\ \text{J} = 182935.76\text{J}$ or 182.93576kJ

Question 41

a) Not permissible because l cannot be equal to n.

b) Not permissible because magnitude of m_l cannot be greater than that of l; m_l must range between –l and +l.

c) Permissible

d) Not permissible because m_s can only be either $+{}^{1}/_{2}$ or $-{}^{1}/_{2}$. It cannot take whole number.

Question 42

How the sample gets ionised? It is more than easier for you! Do it on your own.

Reasons for the ionisation:

Ionisation of the sample is necessary because it enable particles (gaseous ions) to be:

i. **Accelerated** by electric field in the acceleration chamber
ii. **Deflected** by magnetic field in the deflection chamber
iii. **Detected** in the detector

Question 43

i. Carbon has an atomic number of 6
Thus in $^{12}C^+ : A = 12, z = 6 = \text{Number of protons}$
And number of neutrons $= A - z = 12 - 6 = 6$
Using mass of an atom = mass of protons + mass of neutrons
And if we let:
Mass of one proton $= p$
Mass of one neutrons $= n$

It follows that:

$$6p + 6n = 1.993 \times 10^{-23} \ldots\ldots\ldots\ldots\ldots (i)$$

And for $^{13}C^{+}: A = 13, z = 6$

Then number of neutrons $= A - z = 13 - 6 = 7$

And therefore $6p + 7n = 2.158 \times 10^{-23} \ldots\ldots\ldots\ldots\ldots (iii)$

Taking $(iii) - (i)$ gives:

$$n = 1.65 \times 10^{-24}g$$

Hence the mass of one neutron is $1.65 \times 10^{-24}g$

Alternative solution for (i)

^{12}C and ^{13}C are isotopes with the same number of protons but different number of neutrons.

Thus ^{13}C has one more neutron compared to ^{12}C.

So the difference in mass between $^{13}C^{+}$ and $^{12}C^{+}$ is mass of one extra neutron present in the $^{12}C^{+}$.

Hence mass of one neutron $= (2.158 \times 10^{-23} - 1.993 \times 10^{-23})g = 1.65 \times 10^{-24}g$

ii. Numerically, the relative atomic mass of ^{13}C is equal to the mass of one mole of ^{13}C atoms.

Thus relative atomic mass of ^{13}C

= Mass of one atom of ^{13}C × Avogadro's constant

$$= 2.158 \times 10^{-23} \times 6.02 \times 10^{23} = 12.9912$$

Hence the relative atomic mass of ^{13}C is 12.9912

iii. Using $A_r = \frac{m_1P_1 + m_2P_2}{P_1 + P_2}$

Where $m_2 = 12.9912, P_2 = 1.1\%, P_1 = 98.9\%$

And $m_1 = 1.993 \times 10^{-23} \times 6.02 \times 10^{-23} = 11.9979$

Then $A_r = \frac{(11.9979 \times 98.9) + (12.9912 \times 1.1)}{(98.9 + 1.1)} = 12.0088amu$

Hence the relative atomic mass of carbon in sample is 12.0088amu

Question 44

i. Electric field from charged plates.

ii. Electromagnet (or simply magnet).

iii. Presence of different isotopes of K_r with different $\frac{m}{z}$ ratio.

iv. Reducing strength of the magnetic field.

v. 1: **Mass to charge ratio** ($^{m}/_{z}$ ratio) of isotope (or simply isotopic mass).
2: **Abundance** of each isotope

vi. **Speed** of the ionised particle.

Question 45

(a)

Particle	**Proton**	**Neutron**	**Electrons**
Mass /g	1.6725×10^{-24}	1.6748×10^{-24}	0.0009×10^{-24}
Relative charge	$+1$	0	-1

b) Mass of the H atom $=$ mass of a proton $+$ mass of an electron

$$= (1.6725 \times 10^{-24} + 0.0009 \times 10^{-24})g$$
$$= 1.6734 \times 10^{-24}g$$

Hence the mass of an atom of hydrogen is $1.6734 \times 10^{-24}g$

c) Mass of one mole of H atoms $=$ mass of one atom $\times$ Avogadro's constant

$$= 1.6734 \times 10^{-24} \times 6.0225 \times 10^{23} = 1.0078g$$

Hence mass of one mole of H atoms is 1.0078g

d) Due to presence of other heavier **isotopes** of hydrogen.

Warning!

Don't talk about the effect of nuclear binding energy here! The energy explains why the observed atomic mass is less than the expected one. In this case, the observed (accurate) atomic mass is greater than the expected one. So the only possible reason for this observation will be the presence of heavier isotopes of hydrogen.

Question 46

i. **A** is electron
B is neutron
C is proton

ii. **Explanation for the directions:**

- An electron (**A**) being **negatively charged** is attracted (deflected) towards positive plate.
- A proton (**C**) being **positively charged** is attracted (deflected) towards negative plate.
- A neutron (**B**) having **no charge** is undeflected.

Explanation for the shape:

The shapes of path traced by A and C suggest that A is more deflected. This is because **A** (electron) has less mass than **C** (proton).

Question 47

a) Metal coil (or electron gun).
b) Only charged particles (ions) can be attracted or accelerated by electric (or magnetic) field.
c) Magnetic field (or simply magnet).
d) Magnetic field

Question 48

i. $^{63}\mathrm{Cu}$ is **more abundant** than $^{65}\mathrm{Cu}$ and therefore $\mathrm{A_r}$ become close to 63.

ii. There are two ways of converting Cu atoms to $\mathrm{Cu^+}$ ions:

First way: Heat energy from strongly heated metal coil as per equation;

$$\mathrm{Cu(g) + heat \longrightarrow Cu^+(g) + e}$$

Second way: Strong energetic collision between high speed electron (which has high kinetic energy) and un-ionised Cu atoms leading to the loss of electron in the Cu atoms as per equation:

$$\mathrm{Cu(g) + e \longrightarrow Cu^+(g) + 2e}$$

iii. **Dipositive ion** of $^{63}\mathrm{Cu}$ which is $^{63}\mathrm{Cu^{2+}}$

iv. $\frac{m}{z}$ for $^{63}\mathrm{Cu^{2+}}$: $m = 63, z = 2$; Therefore $\frac{m}{z} = \frac{63}{2} = 31.5$

Reason:

More energy is needed to remove second electron and therefore making the process of removing two electrons in Cu atoms more difficulty than removing one electron only.

Question 49

a) Since wavelength varies inversely proportional to energy, most energetic photon has shortest wavelength which is given as 220nm (or 220×10^{-9}m)

- Then using $f = \frac{c}{\lambda} = \frac{3\times10^8\mathrm{m/s}}{220\times10^{-9}\mathrm{m}} = 1.3636 \times 10^{15}\mathrm{Hz}$

Hence the frequency of the most energetic photon is $1.3636 \times 10^{15}\mathrm{Hz}$

Using energy, $E = hf = 6.63 \times 10^{-34} \times 1.3636 \times 10^{15}\mathrm{J} = 9.0407 \times 10^{-19}\mathrm{J}$

Hence the energy of most energetic photon is $9.0407 \times 10^{-19}\mathrm{J}$

b) Using $E = nhf = \frac{nhc}{\lambda}$

Where E= $347\mathrm{kJ/mol} = 347 \times 10^3\mathrm{J/mol}$, $c = 3 \times 10^8\mathrm{m/s}$

$n = 6.02 \times 10^{23}$ photon/mol, $h = 6.63 \times 10^{-34}\mathrm{Js}$

Substituting $347 \times 10^3 = \frac{6.02\times10^{23}\times6.63\times10^{-34}\times3\times10^8}{\lambda}$

From which $\lambda = 3.45 \times 10^{-7}\mathrm{m} = 345\mathrm{nm}$

Hence the wavelength of the least energetic photon that can break the $\mathrm{C-C}$ bond is 345nm

Comparison:

The photon with 345nm is not blocked by ozone, (it is not energetic enough to be absorbed by ozone which absorb a light with wavelength in ranged from 220 to 290nm) so $C - C$ bond disruption is still possible even with presence of the ozone layer.

Question 50

a) Refer to the text

b) Due to existence for of isotopes, the value recorded in the periodic table is just an average of isotopic masses.

c) For mass spectrum of molecules, the peak with the greatest $^{m}/_{z}$ ratio is the peak of the molecular ion.

- Thus the molecular ion for the given mass spectrum has $^{m}/_{z}$ of 62
- Assuming a molecule ionises by losing one electron only, $z = 1$ and therefore the molecular mass of the compound is 62g/mol.
- If follows that:

$$(3 \times 12) + (7 \times 1) + x = 62 \text{ Where x is the atomic mass of the halogen X}$$

- Then $x = 62 - 43 = 19$
- The halogen with atomic mass of 19 is Fluorine

Hence:

- The molecular mass of the compound is 62g/mol
- The halogen is Fluorine

d) Using $n = \frac{m}{mr}$:

Number of moles of iodine with atomic mass of 126.9045

$$= \frac{12.3849\text{g}}{126.9045\text{ g/mol}} = 0.09759 \text{ mol}$$

Number of moles of iodine with atomic mass of 128.9050 (I − 129)

$$= \frac{1.00007\text{g}}{128.9050\text{ g/mol}} = 0.007758 \text{ mol}$$

Then the average atomic mass can be found by using the following formula:

$$A_r = \frac{\sum(\text{Number of moles of isotope} \times \text{isotopic mass})}{\text{Total number of moles}}$$

$$\text{Substituting } A_r = \frac{(0.09759 \times 126.9045) + (0.007758 \times 128.9050)}{(0.09759 + 0.007758)}$$

$$= 127.0518 \text{ amu}$$

Hence the apparent atomic mass of the contaminated iodine is 127.0518 amu

Alternatively:

Finding percentage of number of moles (of atoms) each kind of iodine in the mixture

$$\% \text{ iodine with mass of } 126.9045 = \left(\frac{0.09759}{0.09759 + 0.007758}\right) \times 100\% = 92.6358\%$$

$$\% \text{ iodine with atomic mass of } 128.9050(\text{I} - 129) = (100 - 92.6358)\% = 7.3642\%$$

$$\text{Using } A_r = \frac{M_1P_1 + M_2P_2}{P_1 + P_2} = \frac{(92.6358 \times 126.9045) + (7.3642 \times 128.9050)}{100} = 127.0518 \text{ amu}$$

Hence the apparent of the atomic mass of the contaminated iodine is 127.0518 amu

Question 51

a) Hint: state as in the text but replace velocity with momentum in the statement.

b) Refer to the text

c) Bohr considered an electron being orbiting the nucleus in the fixed path with fixed distance from the nucleus while according to the Heisenberg's uncertainty principle, "It is impossible at any moment to predict simultaneously the exact position and velocity of an electron in an atom."

d) From the De-Broglie equation;

$$\lambda = \frac{h}{me}$$

Where De-Broglie wavelength varies inversely proportional to the mass of particle; so for macroscopic object whose mass is large, the wavelength becomes too small to be measured unlike in electrons whose mass is very small.

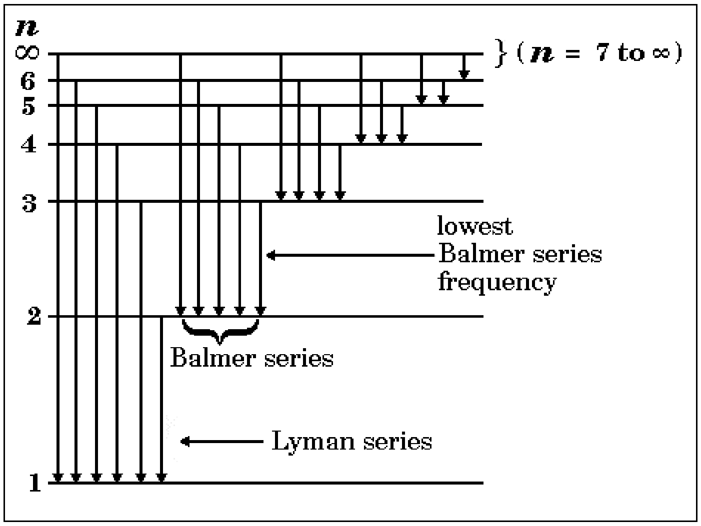
Question 52

a) Paschen series, Bracket series and P-fund series.

b) Electronic energies are quantized.

c)
- Excited electron may fall to the ground state either directly or in steps.
- Different energy of energy levels

d)



e)
- Refer to the text for the difference between emission spectrum and absorption spectrum.
- The room temperature is not sufficient to excite an electron in the hydrogen atom and therefore the electron is at ground state where $n = 1$.

Question 53

a) $n_1 = 1, n_2 = \infty$

Substituting $f = 3 \times 10^8 \times 1.1 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$

$= 3.3 \times 10^{15}(1 - 0) = 3.3 \times 10^{15}\text{Hz}$

Hence the frequency of the line produced is $3.3 \times 10^{15}\text{Hz}$

b) From Bohr theory

$\Delta E = hf$

But $f = cR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ (Given)

Hence $\Delta E = hcR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

c) Substituting $\Delta E = 6.63 \times 10^{-34} \times 3 \times 10^8 \times 1.1 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$

$= 2.1879 \times 10^{-18}\text{J}$

But $1\text{ev} = 1.6 \times 10^{-19}\text{J}$

Then $2.1879 \times 10^{-18}\text{J} = \frac{2.1879\times10^{-18}}{1.6\times10^{-19}}\ \text{ev} = 13.67\text{ev}$

Hence the energy needed is 13.67ev

Assumption made:

The energy absorbed in moving the electron from 1-level to infinity is the same as the energy emitted in moving the electron from the infinity to the 1-level.

d) From (c), the energy required to remove the electron from 1-level to infinity is $2.1879 \times 10^{-18}\text{J}$.This corresponds to the ionisation if it is converted to J/mol.
- But one mole $=6.02 \times 10^{23}$ photons
- So the energy is $\text{J/mol} = 2.1879 \times 10^{-18} \times 6.02 \times 10^{23}\text{J/mol}$

$= 1317116\text{J/mol}$ or 1317.116kJmol

Hence the ionisation energy of hydrogen is 1317.116kJ/mol

Question 54

a) Refer to the text for (i) and (ii)

(iii) Is the symbol of magnetic quantum number.

b) Two electrons (magnetic quantum numbers specify a particular orbital and maximum number of electrons in an orbital is always two).

c)

i. Electronic configuration of argon is:

$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_y^2\ 3p_z^2$

In this case, $m = +1$ stands for P_z-orbital in $2P_z^2$ and $3P_z^2$ with total of 2+2=4 electrons.

Hence there are **4 electrons** with m=+1 in the argon

ii. For d orbitals l=2

Thus total number of d-orbitals is $2l + 1 = (2 \times 2) + 1 = 5$

But each orbital may contains maximum of two electrons:

Thus total number of electron in d-orbitals $= (2 \times 5)$ or 10 electrons

iii.

$n = 4$ and $m_l = +2$ may occur when $l = 3$ or 2 in following two sets of quantum numbers:

1. $n = 4, l = 3, m_l = +2 \Rightarrow$ for first orbital
2. $n = 4, l = 2, m_l = +2 \Rightarrow$ for second orbital

With maximum of two electrons in each orbital, maximum number of electrons with the given quantum numbers in the single atom is 4.

iv. The given quantum numbers represent the last electron in $3p_x^2$.

- The element which end with $3p_x^2$ in its electronic configuration have the following full electronic configuration: $1s^2 2s^2 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2 3p_x^2\ 3p_y^1\ 3p_z^1$
- The configuration gives a total of $2 + 2 + 2 + 2 + +2 + 2 + 2 + 1 + 1$ or 16 electrons.
- With a total of 16 electrons, the element has atomic number of 16
- The element with atomic number of 16 is sulphur.

Hence the element is **sulphur**.

Question 55

a) Refer to the text

b)

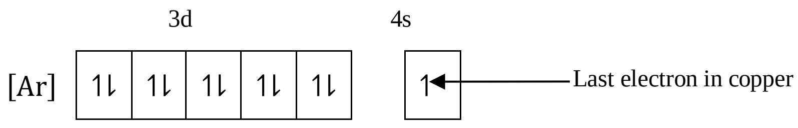
i) The rule violated is **Aufbau principle** which state that……………… (You may complete on your own).

ii) The rule violated is **Hund's rule** which state that ………………… (It is very easy for you; complete it!)

iii) It is correct. No rule is violated

c)

i. Electronic configuration of copper is

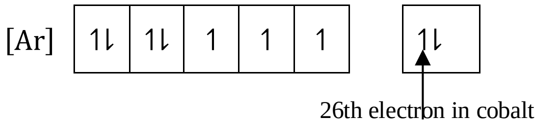


Hence the quantum numbers for the last electron in copper are:

$n = 4,\ l = 0,\ m_l = 0,\ m_s = +{}^{1}/_{2}$

ii. Electronic configuration of cobalt is

3d 4s



26th electron in cobalt

Hence the quantum numbers for the 26th electron in cobalt are:

$$n = 4, l = 0, m_l = 0, m_s = +{}^{1}/_{2}$$