# 2 ATOMIC STRUCTURE

## The atom

### COMPOSITION OF ATOMS

The smallest part of an element is an atom. It used to be thought that atoms are indivisible but they can be broken down into many different sub-atomic particles. All atoms, with the exception of hydrogen, are made up of three fundamental sub-atomic particles – protons, neutrons, and electrons.
The hydrogen atom, the simplest atom of all, contains just one proton and one electron. The actual mass of a proton is $1.672 \times 10^{-24}$ g but it is assigned a relative value of 1. The mass of a neutron is virtually identical and also has a relative mass of 1. Compared to a proton and a neutron an electron has negligible mass with a relative mass of only $\frac{1}{2000}$. Neutrons are neutral particles. An electron has a charge of $1.602 \times 10^{-19}$ coulombs which is assigned a relative value of –1. A proton carries the same charge as an electron but of an opposite sign so has a relative value of +1. All atoms are neutral so must contain equal numbers of protons and electrons.

### SUMMARY OF RELATIVE MASS AND CHARGE

| Particle | Relative mass | Relative charge |
|---|---|---|
| proton | 1 | +1 |
| neutron | 1 | 0 |
| electron | $5 \times 10^{-4}$ | –1 |

### SIZE AND STRUCTURE OF ATOMS

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

### MASS NUMBER *A*

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

### ATOMIC NUMBER *Z*

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

### SHORTHAND NOTATION FOR AN ATOM OR ION

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

### CHARGE

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

### EXAMPLES

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

### ISOTOPES

All atoms of the same element must contain the same number of protons, however they may contain a different number of neutrons. Such atoms are known as isotopes. Chemical properties are related to the number of electrons so isotopes of the same element have identical chemical properties. Since their mass is different their physical properties such as density and boiling point are different.
Examples of isotopes: $^{1}_{1}H$ $^{2}_{1}H$ $^{3}_{1}H$ $^{12}_{6}C$ $^{14}_{6}C$ $^{35}_{17}Cl$ $^{37}_{17}Cl$.

### RELATIVE ATOMIC MASS

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

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

and the relative atomic mass is 35.5. Accurate values to 2 d.p. for all the relative atomic masses of the elements are given in Table 5 of the IB data booklet. These are the values which must be used when performing calculations in the examinations.

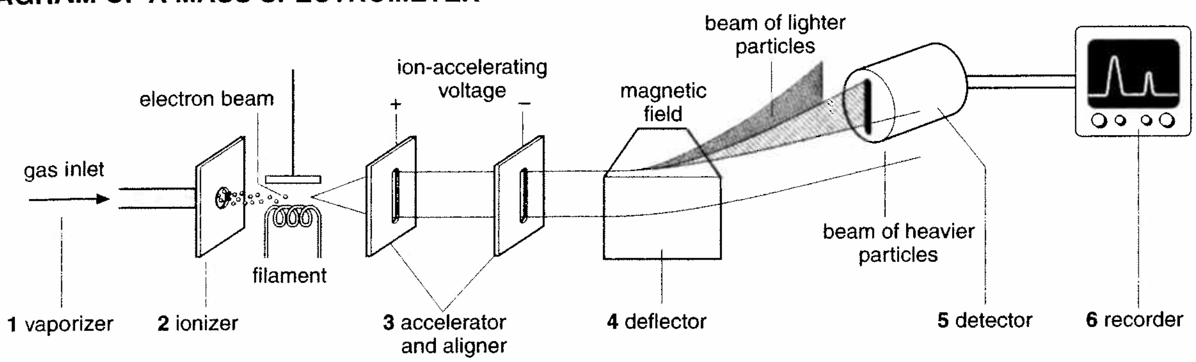
# Mass spectrometer and relative atomic mass

## MASS SPECTROMETER

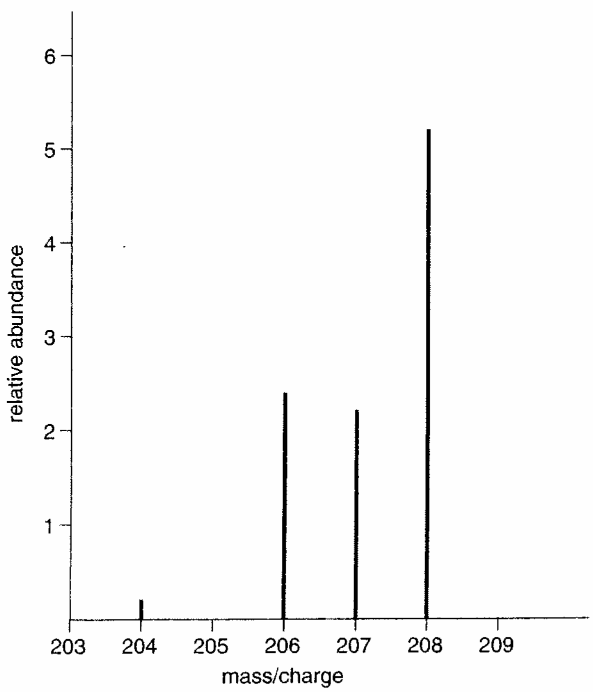
Relative atomic masses can be determined using a mass spectrometer. A *vaporized* sample is injected into the instrument. Atoms of the element are *ionized* by being bombarded with a stream of high energy electrons in the ionization chamber. In practice the instrument is set so that only ions with a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

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

## DIAGRAM OF A MASS SPECTROMETER




## THE MASS SPECTRUM OF NATURALLY OCCURRING LEAD




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

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

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

## USES OF RADIOACTIVE ISOTOPES

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

# Emission spectra

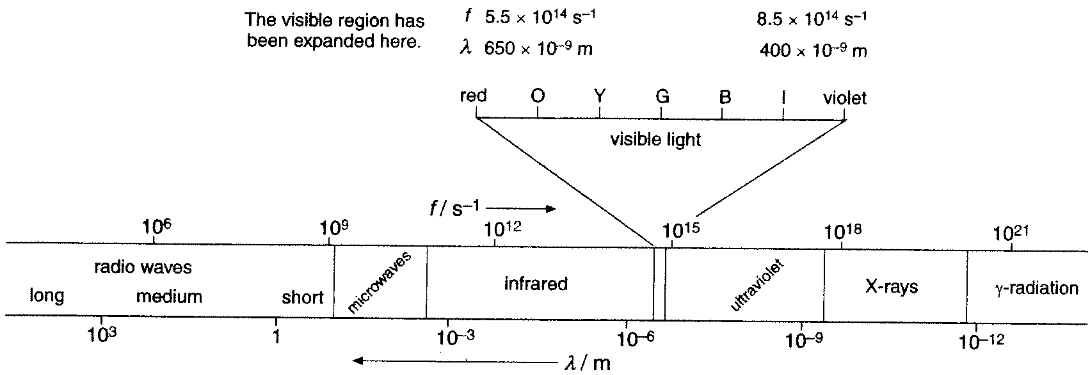
## THE ELECTROMAGNETIC SPECTRUM

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

$$c = \lambda \times f$$

$$(m\,s^{-1}) \quad (m) \quad (s^{-1})$$

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

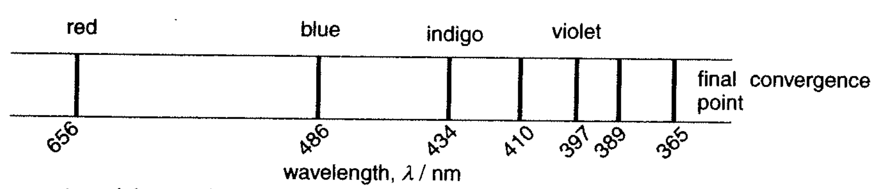



## ATOMIC EMISSION SPECTRA

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

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

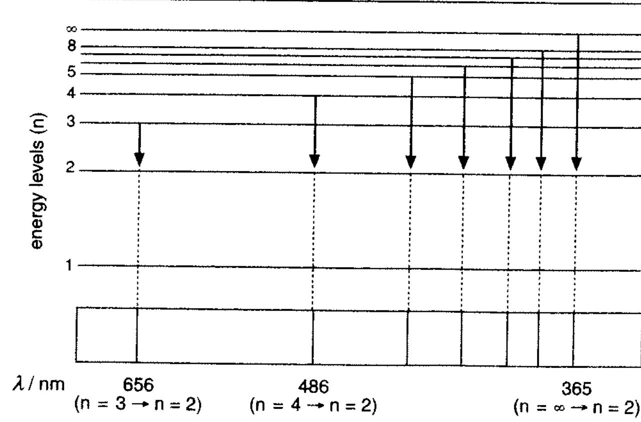
**The visible hydrogen spectrum**




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

## EXPLANATION OF EMISSION SPECTRA

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



# Electron arrangement

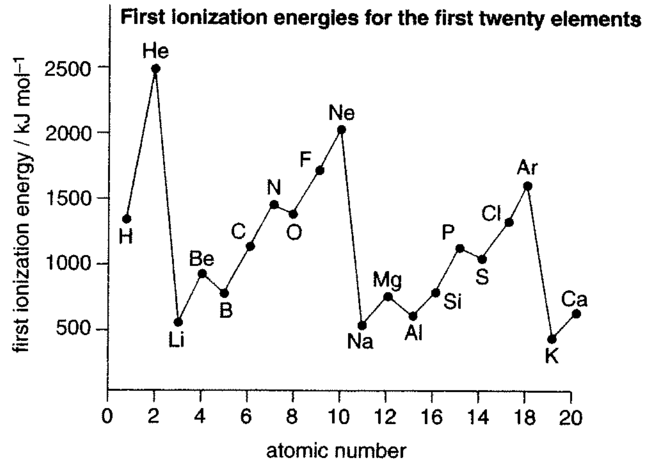
## EVIDENCE FROM IONIZATION ENERGIES

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

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

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

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




| Level | Maximum number of electrons |
|---|---|
| 1 (K shell) | 2 |
| 2 (L shell) | 8 |
| 3 (M shell) | 8 (or 18) |

## ELECTRON ARRANGEMENT

The arrangement of electrons in an atom is known as its electronic configuration. Each energy level or shell is separated by a dot (or a comma). The electrons in the highest main energy level (outermost level) are known as the **valence electrons**.

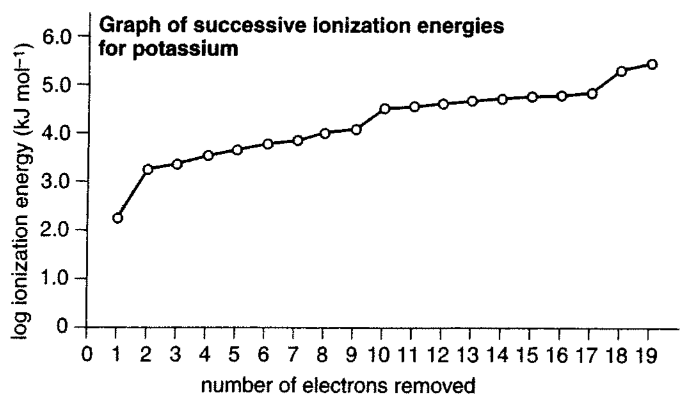
| Element | Electron configuration | Element | Electron configuration |
|---|---|---|---|
| H | 1 | Na | 2.8.1 |
| He | 2 (first level full) | Mg | 2.8.2 |
| Li | 2.1 | Al | 2.8.3 |
| Be | 2.2 | Si | 2.8.4 |
| B | 2.3 | P | 2.8.5 |
| C | 2.4 | S | 2.8.6 |
| N | 2.5 | Cl | 2.8.7 |
| O | 2.6 | Ar | 2.8.8 (third level full) |
| F | 2.7 | K | 2.8.8.1 |
| Ne | 2.8 (second level full) | Ca | 2.8.8.2 |

## *EVIDENCE FOR SUB-LEVELS*

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

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

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




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

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

# Sub-levels and orbitals

## TYPES OF ORBITAL

Electrons are found in orbitals. Each orbital can contain a maximum of two electrons each with opposite spins. The first level contains just one orbital, called an s orbital. The second level contains one s orbital and three p orbitals. The 2p orbitals are all of equal energy but the sub-level made up of these three 2p orbitals is slightly higher in energy than the 2s orbital. This explains why the first ionization energy of B is lower than Be as a higher energy 2p electron is being removed from the B compared with a lower energy 2s electron from Be.

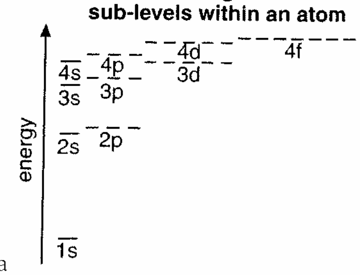
| Principal level (shell) | Number of each type of orbital s | p | d | f | Maximum number of electrons in level |
|---|---|---|---|---|---|
| 1 | 1 | – | – | – | 2 |
| 2 | 1 | 3 | – | – | 8 |
| 3 | 1 | 3 | 5 | – | 18 |
| 4 | 1 | 3 | 5 | 7 | 32 |

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

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

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

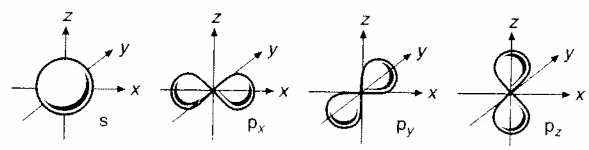
**Relative energies of sub-levels within an atom**




## SHAPES OF ORBITALS

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

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




## AUFBAU PRINCIPLE

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

e.g. F $1s^22s^22p^5$

V $1s^22s^22p^63s^23p^64s^23d^3$.

To save writing out all the lower levels the configuration may be shortened by building on the last noble gas configuration, e.g. V is more usually written:

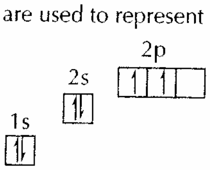
[Ar] $4s^23d^3$.

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

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

e.g.

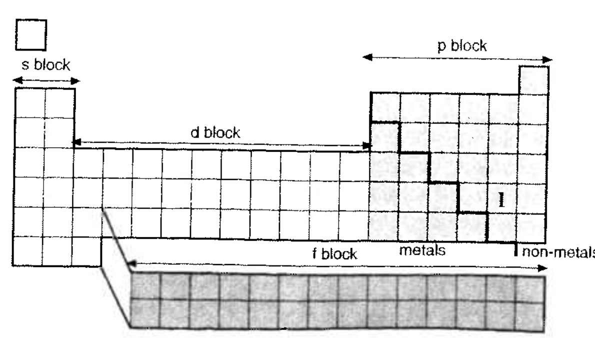
C $1s^22s^22p^2$




## ELECTRONIC CONFIGURATION AND THE PERIODIC TABLE

An element's position in the Periodic Table is related to its valence electrons so the electronic configuration of any element can be deduced from the Table, e.g. iodine ($Z$ = 53) is a p block element. It is in group 7 so its configuration will contain $ns^2np^5$. If one takes H and He as being the first period then iodine is in the fifth period so n = 5. The full configuration for iodine will therefore be:

$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^5$ or [Kr] $5s^24d^{10}5p^5$



## IB QUESTIONS – ATOMIC STRUCTURE

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

I. $^{1}_{1}H$  II. $^{35}_{17}Cl^-$  III. $^{39}_{19}K^+$

**A.** I only  **C.** I and II only

**B.** II only  **D.** II and III only

**2.** The atom with the same number of neutrons as $^{54}Cr$ is

**A.** $^{50}Ti$  **B.** $^{51}V$  **C.** $^{53}Fe$  **D.** $^{55}Mn$

**3.** All isotopes of tin (Sn) have the same

I. number of protons

II. number of neutrons

III. mass number

**A.** I only  **C.** III only

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

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

**A.** $^{14}_{6}C$ and $^{14}_{7}N$  **C.** $^{32}_{16}S$ and $^{32}_{16}S^{2-}$

**B.** $O_2$ and $O_3$  **D.** $^{206}_{82}Pb$ and $^{208}_{82}Pb$

**5.** The atomic and mass numbers for four different nuclei are given in the table below. Which two are isotopes?

| | atomic number | mass number |
|---|---|---|
| I. | 101 | 258 |
| II. | 102 | 258 |
| III. | 102 | 260 |
| IV. | 103 | 259 |

**A.** I and II  **C.** II and IV

**B.** II and III  **D.** III and IV

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

**A.** $^{32}S^-$  **B.** $^{33}S^{2-}$  **C.** $^{34}S^-$  **D.** $^{35}S^{2-}$

**7.** Spectra have been used to study the arrangements of electrons in atoms. An emission spectrum consists of a series of bright lines that converge at high frequencies. Such emission spectra provide evidence that electrons are moving from

**A.** lower to higher energy levels with the higher energy levels being closer together.

**B.** lower to higher energy levels with the lower energy levels being closer together.

**C.** higher to lower energy levels with the lower energy levels being closer together.

**D.** higher to lower energy levels with the higher energy levels being closer together.

**8.** Which electron transition in a hydrogen atom releases the most energy?

**A.** $n = 2 \rightarrow n = 1$  **C.** $n = 6 \rightarrow n = 3$

**B.** $n = 4 \rightarrow n = 2$  **D.** $n = 7 \rightarrow n = 6$

**9.** An element has the electronic configuration 2.7. What would be the electronic configuration of an element with similar chemical properties?

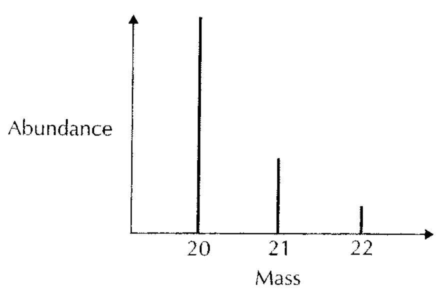
**A.** 2.6  **B.** 2.8  **C.** 2.7.1  **D.** 2.8.7

**10.** An element with the symbol *Z* has the electron configuration 2.8.6. Which species is this element most likely to form?

**A.** The ion $Z^{2+}$  **C.** The compound $H_2Z$

**B.** The ion $Z^{6+}$  **D.** The compound $Z_6F$

*The following diagram should be used to answer question 11.*




**11.** According to the mass spectrum above, the relative atomic mass of the element shown is best expressed as

**A.** 20.0.  **C.** 21.0.

**B.** between 20.0 and 21.0.  **D.** between 21.0 and 22.0.

**12.** The first four ionization energies (kJ mol$^{-1}$) for a particular element are 550, 1064, 4210 and 5500 respectively. This element should be placed in the same Group as

**A.** Li  **B.** Be  **C.** B  **D.** C

**13.** Which ionization requires the most energy?

**A.** $Na(g) \rightarrow Na^+(g) + e^-$

**B.** $Na^+(g) \rightarrow Na^{2+}(g) + e^-$

**C.** $Mg(g) \rightarrow Mg^+(g) + e^-$

**D.** $Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$

**14.** Which one of the following atoms in its ground state has the greatest number of unpaired electrons?

**A.** Al  **B.** Si  **C.** P  **D.** S

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

**A.** mass of the atom.

**B.** charge on the nucleus.

**C.** size of the atom.

**D.** main energy level from which the electron is removed.