

# **CHEMISTRY**

## **LEVEL 4C**

**(CHM415109)**

### **INTRODUCTORY**

### **QUANTUM**

### **THEORY**

**&**

### **PERIODIC TABLE**

### **THEORY SUMMARY**

**&**

### **REVISION QUESTIONS**

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## INTRODUCTION:

The historical development of our understanding of matter extends back to the times of Democritus at around 400 B.C. when he proposed that all matter was comprised of particles that were not infinitely subdivisible. He proposed that the process of cutting a substance such as a piece of copper in half, again and again and again, would ultimately reach a point where one would have a particle that was the fundamental building block of copper. The word *atom* comes from the Greek 'atomos' which means particle.

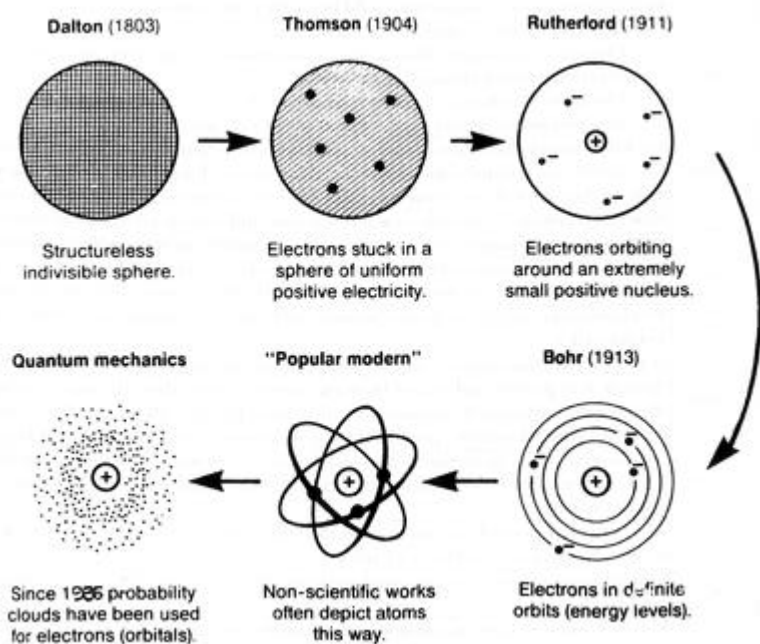
Other philosophers of the time such as Aristotle proposed that matter was infinitely subdivisible and no matter how many times you chopped the copper block in half, you would always have copper.

The historical development of our present day understanding of chemistry hardly changed for the next 1800 years until chemists such as Dalton and Avogadro moved from the alchemists' approach to a more scientific enquiry based study of matter.

To attempt to show the steps in our developing knowledge of chemistry is difficult but it is possible to see 6 or 7 distinct phases of development where each led to a better understanding of the nature of atoms and atomic structure.

i.e.

DATE	PERSON	CONCEPT
1803	John Dalton	Atoms as particles
1904	J.J. Thomson	Electrons and protons
1911	Ernest Rutherford	Orbiting electrons
1913	Neils Bohr	Electron energy levels
1932	James Chadwick	Neutron discovered
1926	Schrodinger	Quantum mechanical model
1932	Heisenberg	Refinement of quantum model



## HISTORICAL DEVELOPMENT OF ATOMIC STRUCTURE

# DEVELOPMENT OF THE ATOMIC THEORY:

(A TIME LINE FROM 400 B.C. TO PRESENT DAY)

Who	When	How
Democritus	-400	Theorised that if a substance sample divided in half and half again and so on then there will come to a point where could divide no further. Coined the term "atomos".
Boyle	1661	In the "Sceptical Scientist" abandoned the accepted Greek view that substances were made up of mystical elements (earth, wind, water and fire). He suggested that any substance that could not be broken down further was an element and two of these could be put together to form a compound. These were material substances that could be determined by experiment (he favoured experiment over theorising).
Boyle	1662	Concluded that since air was compressible then it must be comprised of discrete particles separated by a void.
Newton	1672	Thought that gases were made of particles
Dalton	1788	Supposing that gases have indivisible particles then he measured the masses of constituent elements of these gases. From this he found that the relative masses of the constituents for a particular gas are always in the same ratio. This is the law of "definite proportions".
Dalton	1803	Dalton extended his theory to say that some combinations of elements can have different proportions (he cited carbon monoxide and carbon dioxide, and methane and ethane). This is the law of "multiple proportions". Dalton referred to his assumed indivisible particles as "atoms"
Davey	1807	Separated metals such as sodium and potassium from molten metal salts. He went on to discover strontium, calcium and magnesium. He also proved that chlorine was an element by showing hydrochloric acid contained no oxygen (all acids were believed to contain oxygen until then)
Gay-Lussac	1809	He found when combining gases to react (eg hydrogen and oxygen) the ratio of their volumes for complete reaction was constant. This is the law of combining volumes.
Avogadro	1811	Used the law of combining volumes to inspire the hypothesis that identical volumes of gas contain the same number of particles. This true observation could have been used to calculate atomic weights but was ignored for decades.
Berzelius	1813	Thought that the existence of free radicals carried charge in electrolytes.
Fraunhofer	1814	Found that sunlight produced over 600 lines of darkness when the light was passed through a diffraction grating (he pioneered the use of this). He also applied his practice to starlight and found the line slightly shifted - but made no conclusion from this.
Prout	1815	Published an article that all elements were compositions of hydrogen and thus their weights have an integral value with relation to hydrogen's atomic weight.
Dulong and Petit	1820	Found atomic weight was inversely proportional to specific heat of an element. Rough relative atomic weights could then be determined
Berzelius	1828	Produced the first accurate table of atomic weights and suggested the chemical symbol system for elements we use today. Thus compounds could be easily represented.
Faraday	1832	Found two rules that bound electrochemistry 1. The mass of substance liberated at an electrode during electrolysis is proportional to the quantity of electricity driven through the solution 2. The mass liberated by a given quantity of electricity is proportional to the atomic weight of the element liberated and inversely proportional to it's valance
Kirchhoff	1859	Kirchhoff found that when heated to incandescence each element emitted a unique spectrum of light. He discovered caesium and rubidium using this process. Found that elements absorb the same coloured bands of light as they emit at incandescence (this showed sodium vapour must be in the sun's atmosphere).
Cannizzaro	1860	Brought Avogadro's thoughts back to the fore and convinced many chemists to take them seriously. Uniform atomic weights were on the way and with them being able to represent compounds uniformly.
Stas	1861	Initiated using oxygen with an atomic weight of 16 as standard for other atomic weights. Stas showed that atomic weights were far removed from integral values. Showed the atomic weight of carbon to be twelve
Newlands	1864	Newlands was laughed at for his periodic table based on patterns of 7 elements when arranged in atomic weight order.
Mendeleev	1869	Put the 63 known elements in a row and noticed the patterns of within the valences. From this he divided the row into periods and placed them one on top of the other. He noticed other similarities within properties of elements within each column - he called these groups. Although other scientists were sceptical of this periodic table, Mendeleev predicted three unknown elements that would be soon discovered
Crooks	1870	Produced a visible glow passing from a cathode to an anode. He found that this flow could turn a small vane - this he concluded was evidence that the flow was made up of small particles. He said that this was a fourth form of matter.
Helmholtz	1870	Thought that electrolysis was carried through solutions by "atoms of electricity" connected to the elemental atoms that appeared on the electrodes.
Meyer	1870	Plotted atomic volume against molecular weights then Mendeleev's periods were evident in the resultant graph.
Maxwell	1873	Maxwell showed that the phenomena of magnetism and electricity were inextricably linked. Through his work with creating electromagnetic radiation through an oscillating charge he found the speed of light was constant and its value. From this he surmised that light must be emitted by an oscillating charge.
Lecoq de Boisbaudran	1875	Using spectroscopy found an unknown element that he called gallium and isolated enough to be verified by other scientists. Mendeleev recognised this as one the elements he had predicted.

Who	When	How
Cleve	1879	Cleve recognised the element scandium discovered by Nilson was one of Mendeleev's missing elements
Hertz	1883	Provided evidence that backed up Maxwell's equations.
Raoult	1883	Showed that the amount a freezing point is decreased and boiling point increased is proportional to the number of particles of solute present.
Arrhenius	1884	Hypothesised the theory of ionic dissociation after studying ionic and organic substances physical behaviour (effect on freezing point of water) and their conductivities. This was initially rejected as it implied that atoms had some internal structure.
Balmer	1885	Noticed patterns within the dark lines within the emission spectrum of hydrogen and devised a simple formula that gave all the wavelengths in this series - this was only an empirical formula.
Raoult	1886	Proposed that the number molecules in vapour is proportional to the molecules in solution. This allowed molecular weights in solution to be calculated.
Winkler	1886	Winkler discovered the third element when finding that there was a missing constituent of some silver ore he was studying. He called this germanium.
Lorentz	1890	Lorentz theorised that atoms consist of charged particles and that these oscillating produced light observed as an emission from elements. He deduced that particles mass varied with their velocity and light must have an infinite velocity (as it had no mass).
Nernst	1891	Nernst pointed out that positive and negative ions could be insulated by water so they would not be attracted to each other. This left them free to conduct an electric current.
Stoney	1891	Stoney suggested the minimum electrical charge he called an electron.
Goldstein	1895	Showed that the rays going in the opposite direction the cathode rays were positive. These were used as evidence of protons.
Thompson	1897	Followed Crooks work to show the flow of electricity in a vacuum tube could be deflected by a magnetic field. This showed that the "particles" were negatively charged. He calculated the mass of these particles (as $1/1837$ the mass of a hydrogen atom). The charge on the this was accepted as a unit of electrical current called the electron. He proposed the "pudding" model of the atom where a positive sphere had electrons embedded within it.
Becquerel	1899	Found that the particles emitted from uranium were charged and could be electrons and theorised that they must come from the atoms themselves. Thus atoms had some form of internal structure.
Planck	1900	Planck directly related frequencies of electromagnetic radiation to energy by a simple constant. This was the start of quantum (coined by Planck) approach to unobservable phenomena, with this he assumed that energy is not infinitely divisible it occurred in quanta.
Rutherford	1900	Completed identifying Alpha, Beta and Gamma radiations in terms of rank properties not composition.
Einstein	1905	Einstein confirms that the speed of light is the fastest anything can go with his special theory of relativity.
Rutherford	1907	He demonstrated alpha particles were helium atoms without electrons and that thought that there must be a fundamental positive particle that could be derived from hydrogen - he called it a proton.
Rutherford	1908	Noticed scattering patterns of Alpha particles were consistent with a substance that had massive positive points with mostly space around them
Rutherford	1911	Proposed his model of an atom with a dense and tiny positive nucleus with the outer regions containing electrons.
Perrin	1913	Using Einstein's work on Brownian motion found first accurate size for an atom.
Richards	1913	Confirmed isotopic nature of elements and calculated many atomic weights with far greater accuracy. This was the last of the era of determining atomic weights as opposed to actual masses using electromagnetic methods.
Soddy	1913	Soddy demonstrated that the numerous products of radioactive decay were isotopes (a term he coined) of known atoms - allowing the periodic table to remain intact.
Aston	1919	Showed that a sample containing charged neon particles produced two fine lines, when accelerated towards photographic paper and their paths changed through a magnetic field, which related to the atomic weights of the two isotopes of neon. When the relative darkness of these lines was used to calculate the average atomic weight of neon it was spot on. This was the first accurate mass spectrograph that went on to be so useful in studying other elements and compound composition and confirmed Soddy's isotope theory.
Bohr	1921	Bohr puts forward a modified version of Rutherford's model of the atom. Using hydrogen as an example he successfully modeled discrete energy levels within the electron orbits (a term he substantiated within the mathematics of his theory). Unfortunately his model did not extend to more complex atoms.
Aston	1925	A more accurate mass spectrometer than developed by Aston resulted in the measurement of binding energies within atoms, predicted by Harkins.
Schrödinger	1926	Giving a new perspective to the Bohr model, he showed that electrons could inhabit orbits as waves without releasing energy - meaning that electrons can inhabit stable and varied orbits. These orbits were associated with discrete numbers of wavelengths - thus discrete orbits were described in terms of wave mechanics. These caused the spectral lines observed earlier
Chadwick	1932	Chadwick discovered the neutron by observing interactions with paraffin - knocking out protons
Heisenberg	1932	Heisenberg pointed out that neutrons, with about the same mass as a proton, could be part of the nucleus of atoms providing a far better theoretical explanation of electrons pairing with extra protons in the nucleus (as had been held for the last decade or so). This explained isotopes perfectly. He maintained that the protons and neutrons in the nucleus could be held together by exchange forces

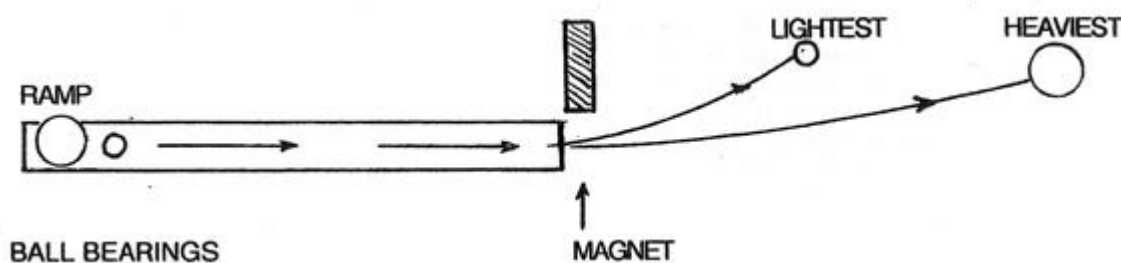
## MASS SPECTROSCOPY:

The first mass spectrometer was built by Francis Aston in 1919 and was used to confirm the existence of isotopes although the discovery of the neutron didn't occur until Chadwick's research in 1932.

The basic principle involves combining electric and magnetic fields so that positive ions can be accelerated and then deflected by varying amounts in accordance with their mass.

This is best understood if we use a more familiar model.

- (i) Steel ball bearings of different masses are rolled down a ramp with gravity being the accelerating field.
- (ii) At the bottom of the ramp, on one side, we place a magnet which attracts the steel ball bearings as they pass.
- (iii) The attracting effect of the magnet results in the ball bearings moving in circular paths where the radius is dependent upon the masses.
- (iv) The lightest ball bearing will be deflected most and the heaviest ball bearing is deflected least. (see diagram)



This process of combining gravitational and magnetic fields to separate the ball bearings is essentially the basis of the mass spectrometer except that we are using an electric field to accelerate ions rather than a gravitational field to accelerate ball bearings!

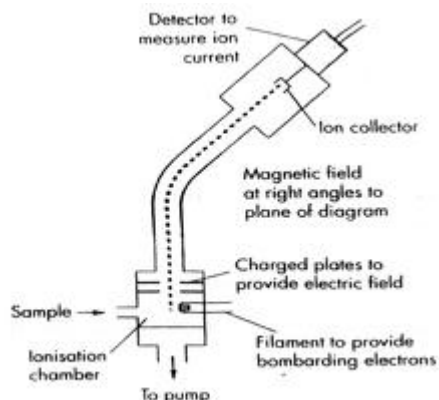
## HOW DOES A MASS SPECTROMETER WORK?

- (i) The sample for analysis is firstly vaporised (if it is not already a gas).
- (ii) The gas then enters a low pressure ionisation chamber where it is bombarded with electrons resulting in the formation of mostly  $1^+$  ions, i.e.



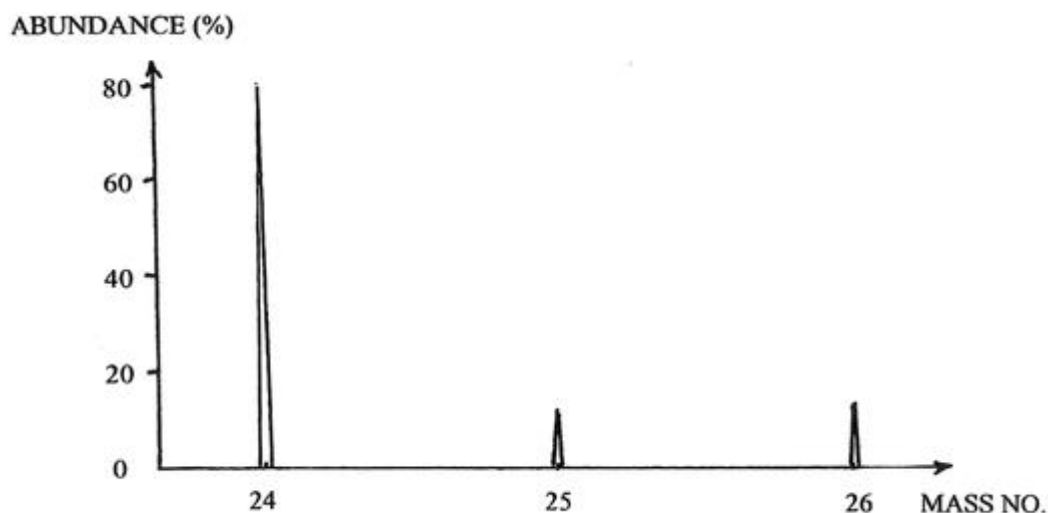
- (iii) These ions are now accelerated to high speeds using an electric field. They move towards a negatively charged plate with a hole in its centre.
- (iv) A stream of positive ions passes through the hole and is then acted on by a magnetic field at right angles to the electric field.
- (v) This magnetic field causes the  $1^+$  ions to move in curved paths with radius proportional to their masses.
- (vi) By changing the strengths of the electric and magnetic fields, different mass ions will arrive at the detector at different field strengths.
- (vii) A detector identifies the ions and their abundance. The detection is based upon either:
  - the current produced by the ions, or
  - the intensity of the 'spot' formed on a photographic plate.
- (viii) The picture/graph obtained is called a "mass spectrogram".

## SIMPLIFIED DIAGRAM OF A MASS SPECTROMETER:



Q1. Magnesium exists as three naturally occurring stable isotopes; i.e.  
 magnesium-24 ( $^{24}\text{Mg}$ ) natural abundance = 79%  
 magnesium-25 ( $^{25}\text{Mg}$ ) natural abundance = 10%  
 magnesium-26 ( $^{26}\text{Mg}$ ) natural abundance = 11%

Draw the mass spectrum for Mg.



Q2. Chlorine exists as two naturally occurring stable isotopes; i.e.  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ .

When analysed in a mass spectrometer, the molecular ions formed are  $\text{Cl}_2^+(\text{g})$ .

How many peaks will appear in the mass spectrum and at what mass numbers will they appear?

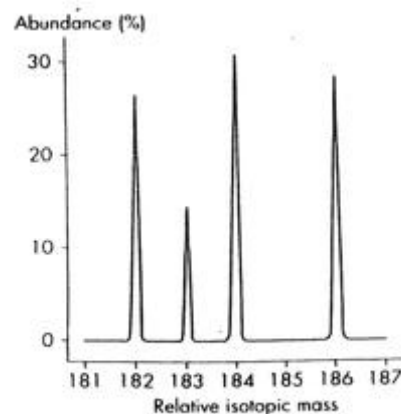
ANS. Three peaks will occur, one at each of mass numbers 70, 72 and 74.

Q3. On the right is shown the mass spectrum for tungsten (W).

(i) Use this mass spectrum to identify the isotopes of tungsten that occur naturally.

(ii) Use the answer for part (i) and the relative abundances to determine the  $A_r(\text{W})$ . (183.7)

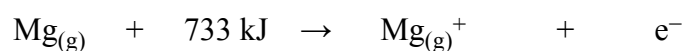
(iii) Find the number of neutrons in 1 million tungsten atoms. (109.7 million)



## IONIZATION ENERGY:

### (i) DEFINITION:

The ionization energy of an atom is the least amount of energy required to remove the most loosely bound electron from a gaseous atom. e.g. for magnesium the energy required is 733 kJ per mole of Mg atoms:



The removal of electrons can be achieved by two different means of energy **input** using:

- (i) light energy ('photo-ionization')
- (ii) electrons ('electron bombardment')

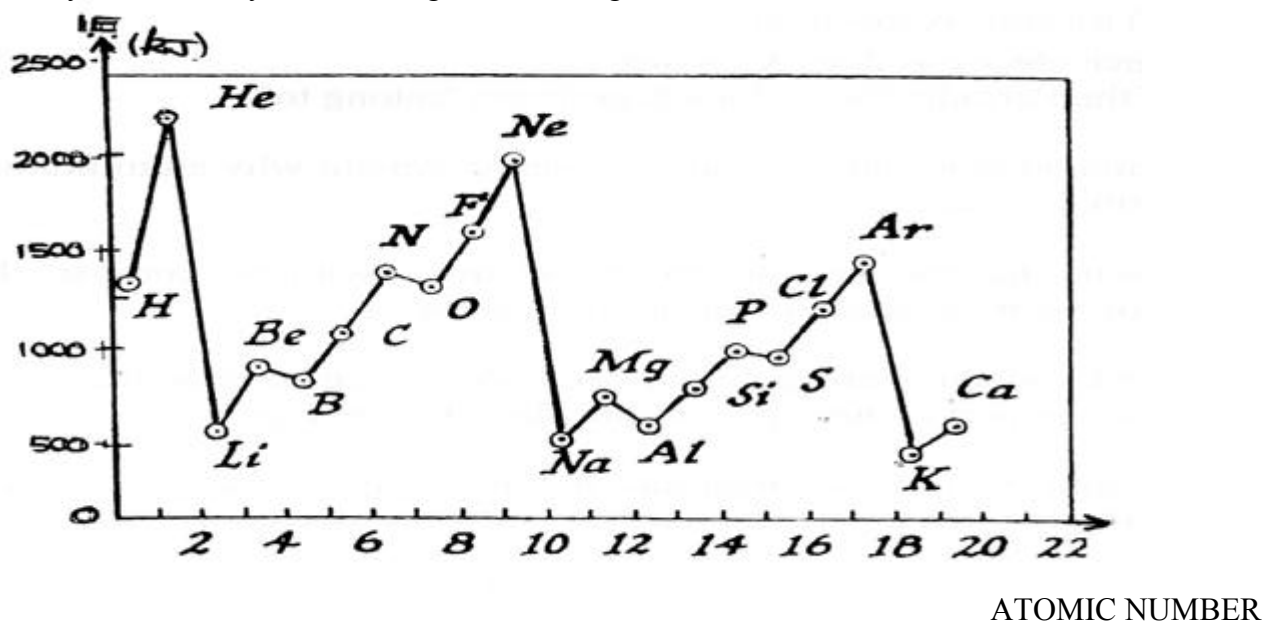
### (ii) TRENDS IN THE FIRST IONIZATION ENERGY:

The ionization energies ( $E_1$ ) for the first 20 elements are shown below.

ATOMIC NO.	ELEMENT	E1 (kJ/mol)
1	H	1312
2	He	2371
3	Li	520
4	Be	899
5	B	800
6	C	1086
7	N	1403
8	O	1313
9	F	1680
10	Ne	2080
11	Na	495
12	Mg	733
13	Al	577
14	Si	786
15	P	1063
16	S	999
17	Cl	1256
18	Ar	1520
19	K	418
20	Ca	590

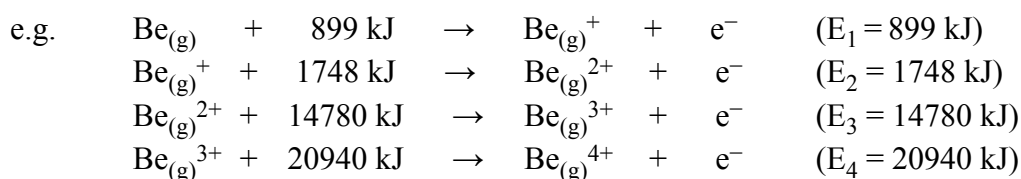


- When the ionization energy data from the previous page are plotted as shown below, we notice:
- relative minima occur for Li, Na and K suggesting that these elements can lose an electron easily.
  - relative maxima occur for He, Ne and Ar suggesting that these elements cannot lose an electron easily.
  - First ionization energies show a general increase across each period due to the outer electrons being in the same valence orbitals (thus approx. the same distance from the nucleus) and yet attracted by an increasing nuclear charge.



### (iii) SUCCESSIVE IONIZATION ENERGIES:

Although we are often considering just the removal of the first electron (i.e. the first ionization energy " $E_1$ ") chemists have learnt a good deal of information about electron energy levels by measuring successive ionization energies. The removal of a second electron requires the second ionization energy given by  $E_2$ , the removal of a third electron requires the third ionization energy given by  $E_3$  .....etc



There is no fifth ionization energy for beryllium ( $E_5$ ) because there are only 4 electrons per Be atom to be removed!

By looking at the data above we can see that the first and second ionization energies for beryllium are both fairly low (both under 2000 kJ) whereas the third I.E. shows a huge increase to nearly 15000 kJ. This suggests that Be atoms have two outer or **valence electrons** that are easily removed.

#### (iv) QUESTIONS ON IONIZATION ENERGY:

Q1. Why do the first ionization energies of elements show a general:

- (i) increase across any given period of the Periodic Table.
- (ii) decrease down any given group of the Periodic Table.

Q2. Why does boron have a lower ionization energy than beryllium even though boron has a higher nuclear charge?

Q3. An element X has successive ionization energies of  $E_1 = 733$  kJ/mole,  $E_2 = 1440$  kJ/mole and  $E_3 = 15780$  kJ/mole respectively.

- (a) How many valence electrons does X possess?
- (b) Which group of the Periodic Table does X probably belong to?

Q4. In terms of ionization energies and orbital occupancy explain why aluminium forms 3+ ions but does not form 4+ ions.

Q5. As  $\text{Na}^+$  is isoelectronic (has the same number of electrons) with Ne, compare the first ionization energy of neon with the second ionization of sodium.

Q6. (i) Why is the second ionization energy of an atom *always* greater than the first I.E.?  
(ii) Why does this rule in part (i) **not** apply to the element hydrogen?

Q7. The ionization of both atomic hydrogen and helium involves the removal of a 1s electron and yet  $E_1$  for He is much greater than  $E_1$  for hydrogen. Explain.

Q8. Qualitatively sketch a graph of the first 5 successive I.E.s for:

- (i) sodium            (ii) silicon            (iii) aluminium            (iv) calcium.

Q9. Given that the first ionization energy for magnesium is 733 kJ/mol, would the value of  $E_1$  for an *excited* Mg atom be greater or less than 733 kJ/mol? Explain.

Q10. Element X is investigated and found to have:

First ionization energy ( $E_1$ ) = 1,290 kJ mol<sup>-1</sup>.

Second ionization energy ( $E_2$ ) = 13,680 kJ mol<sup>-1</sup>.

Third ionization energy ( $E_3$ ) = 15,070 kJ mol<sup>-1</sup>.

(i) To which group of the Periodic Table does X most likely belong? Explain your reasoning.

(ii) What is the likely formula for:

- the oxide of element X?
- the chloride of element X?

(iii) Why is the third ionization energy ( $E_3$ ) greater than the second ionization energy ( $E_2$ )?

Q11. Explain why the decreasing ionization energies as we progress down Group I of the periodic table mean that the elements become increasingly strong reducing agents whereas the decreasing ionization energies as we progress down Group VII means that the elements become increasingly weak oxidisers.

# ATOMIC STRUCTURE

## A QUANTUM MECHANICAL VIEW

### 1. EMISSION SPECTRA

(a) Emission of light from a heated or bombarded atom results from a sequence of steps that make up an "ELECTRONIC TRANSITION".

In summary:

- all atoms are normally in the lowest energy or "GROUND" state.
- absorption of energy occurs by heating or  $e^-$  bombardment
- electron(s) are "PROMOTED" to higher energy levels
- the atom is now said to be in an "EXCITED" state: this occurs only momentarily
- electron(s) now drop back through an energy gap  $\Delta E$  to the lower energy levels
- energy is now "EMITTED" in the form of a photon (quantum) of light
- the photon's energy (colour/type) is determined by the energy gap  $\Delta E$
- frequency of the emitted light ( $f$ ) is given by the Planck Equation  $\Delta E = hf$  where  $h = \text{Planck's Constant} = 3.99 \times 10^{-13} \text{ kJ s mol}^{-1}$
- the atom is now back in its "ground" state.

(b) The emission spectra for the various elements are like 'fingerprints', uniquely identifying each element.

(c) Because only a limited number of energy lines are found in each emission spectrum, we conclude that there must be a limited number of possible energy states for an atom; ie atoms are "QUANTIZED"

(d) The "bookshelf" analogy is a useful way of explaining this concept; i.e. books can only be on shelves 1,2,3, ..... but not in-between!

### WAVE MODEL FOR LIGHT & ELECTRONS:

(a) In 1923 de Broglie postulated the duality of light - suggesting that light behaved as both particles (photons/quanta) and waves.

(b) By 1926 Schrödinger had extended the particle~wave model to explain the properties of electrons.

(c) This new approach was quite different from the classical Newtonian physics and was named QUANTUM MECHANICS.

(d) A key feature of the quantum mechanical view of the atom is that electrons are located in regions of the atom called ORBITALS which are cloud-like regions surrounding the nucleus. The energy of each orbital is found by solving complex quantum mechanical equations.

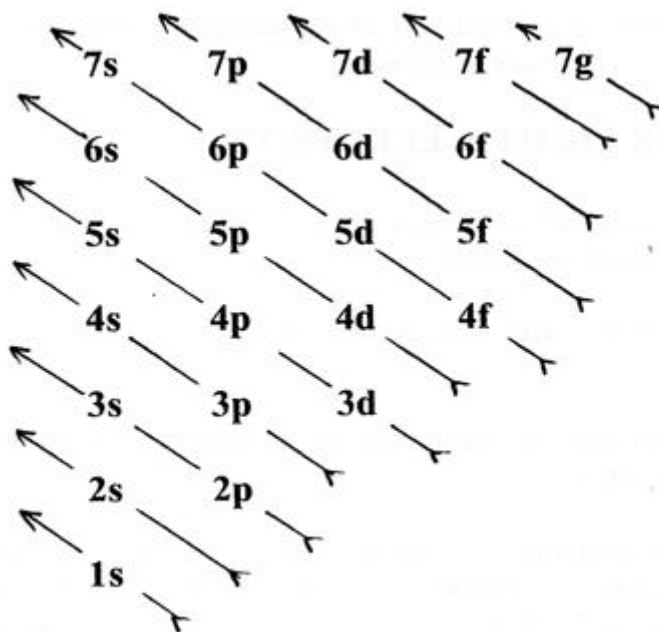
(e) An orbital can be thought of as a region in which the probability of locating the electron is greater than a certain value e.g. 95% (c.f. bees around a hive).

## SHELLS, SUBSHELLS & ORBITALS:

- (i) Shells are the major energy levels (historically called K, L, M, N,... )
- (ii) Within each shell there are subshells of similar but not identical energy
- (iii) These subshells are labelled s, p, d, f,.....
- (iv) 's' subshells are spherical regions (clouds) and 'p' are dumbbell shaped etc.
- (v) subshells within a shell are made up of orbitals all of which have identical energy
  - 's' subshells have only 1 orbital
  - 'p' subshells have 3 orbitals
  - 'd' subshells have 5 orbitals
  - 'f' subshells have 7 orbitals
  - 'g' subshells have 9 orbitals etc.....

## ELECTRON ACCOMMODATION IN ORBITALS:

- (i) Pauli Exclusion Principle:
  - "An atomic orbital can hold a maximum of 2 electrons, i.e. it may hold 0, 1 or 2 e<sup>-</sup>"
- (ii) The two electrons that occupy the same orbital have the same energy but have opposite angular momentum i.e. opposite "spin".
- (iii) Hund's Rule:
  - "All orbitals of equal energy acquire 1 electron before any accepts 2"
- (iv) Electrons occupy the lowest possible energy levels except when excitation occurs.
  - ie. atoms are normally in the "ground state".
- (v) The order of filling of the orbitals in increasing energy level in a many electron atom is:



i.e. the filling sequence is:

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < \dots$

## EXAMPLES OF ELECTRON CONFIGURATIONS:

Using the filling sequence for the orbitals as discussed above, we see that the ground state electronic configuration for any atom or ion is simply found by allocating the number of electrons to the lowest possible vacant orbitals.

For example:

- (a) Hydrogen:  $H = 1s^1$   
(b) Sodium:  $Na = 1s^2 2s^2 2p^6 3s^1$  or  $(Ne) 3s^1$   
(c) Oxygen:  $O = 1s^2 2s^2 2p^4$  or  $(He) 2s^2 2p^4$   
(d) Zinc:  $Zn = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$  or  $(Ar)4s^2 3d^{10}$  etc.....

Q12. Give the ground state configuration for:

- (i) a potassium atom (ii) a sulfur atom  
(iii) a calcium atom (iv) an aluminium atom  
(v) a chlorine atom (vi) an aluminium ion  
(vii) a fluoride ion (viii) a rubidium ion

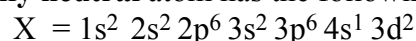
Q13. The ground state electronic configuration for a sulfide ion ( $S^{2-}$ ) is the same as the ground state electronic configuration for an argon atom.

Based on this fact:

- (i) what are the similarities between  $S^{2-}$  and Ar?  
(ii) what are some of the differences between  $S^{2-}$  and Ar?  
(iii) compare the size (radii) of  $S^{2-}$  and Ar.

Q14. Give the ground state electronic configuration for each of the **EIGHT** elements that comprise **PERIOD 3**.

Q15. An **electrically neutral** atom has the following electronic configuration:



- (i) identify the element X  
(ii) what is special about this atom of element X?

Q16. Give the general form for the electronic configuration for:

- (i) the "alkali metals" i.e. Group IA  
(ii) the "alkali earths" i.e. Group IIA

Q17. An element has as part of its valence orbital electron configuration the following arrangement:



- (i) what group of the Periodic Table does X belong to?  
(ii) how many valence electrons does X have.  
(iii) what is the formula of the compound formed between X and calcium?  
(iv) draw the electron-dot representation for the compound formed by X and sulfur.

Q18. Give the name, symbol and ground state electronic configuration for the element that is in:

- (i) period 2 , group V which is also called period 2 , group 15  
(ii) period 3 , group IV which is also called period 3 , group 14  
(iii) period 4 group III which is also called period 4, group 13  
(iv) period 3 group IV which is also called period 3 , group 14

## ORBITALS & THEIR SHAPES:

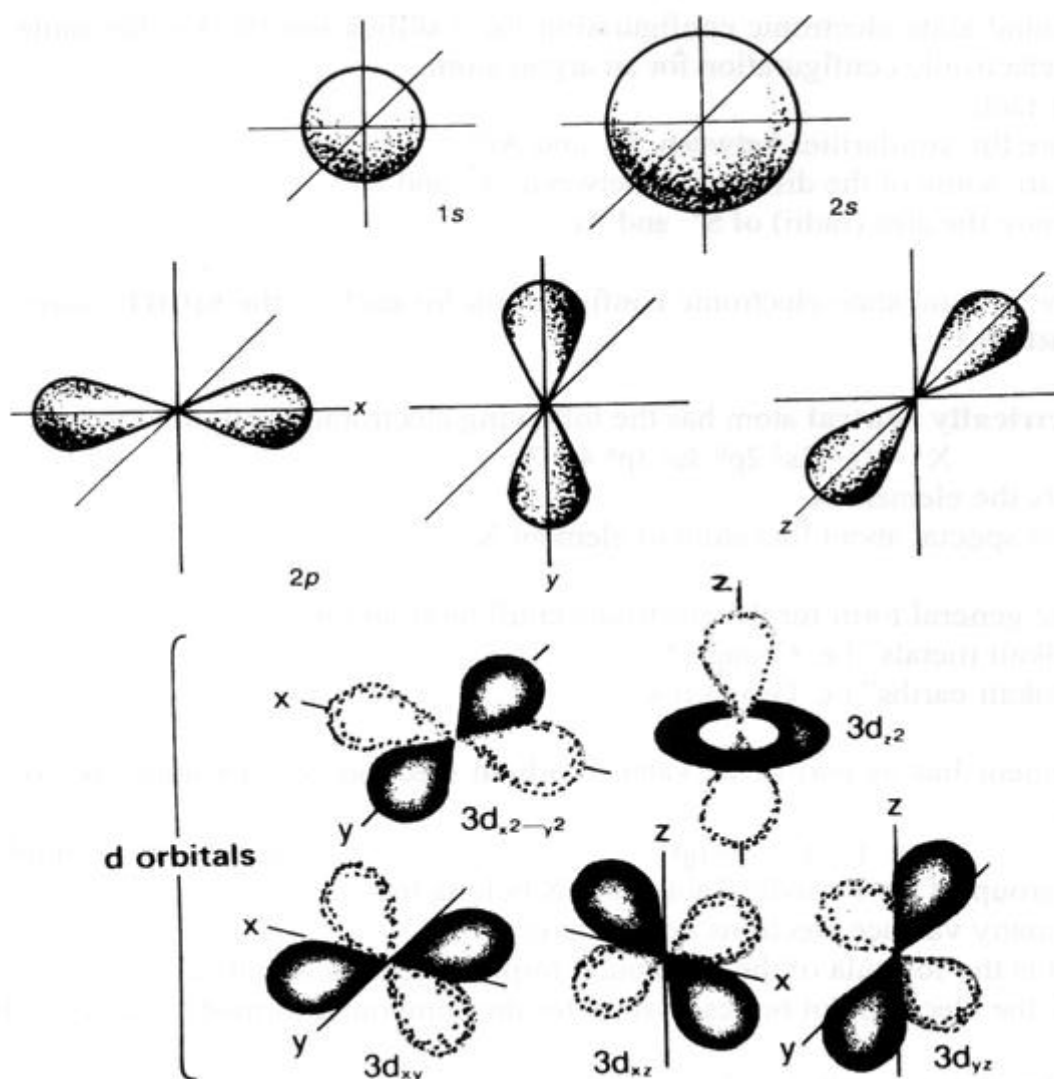
Remember that the words *orbital* and *orbit* are very different in their meanings. An orbit involves a very predictable path being followed such as occurs with the Moon's movement around the Earth.

The term 'orbital' refers to a region of space surrounding an atom where an electron is likely to be located within a given probability. Just as we can specify the likelihood of locating bees around a hive to a given probability, so too can we specify the probability of locating electrons. Rather than being distinct pathways as occur with *orbits*, orbitals are thus probability distributions that appear as three dimensional 'cloud' like regions with cloud-like shapes depending upon the orbitals concerned.

's' orbitals are spherical in shape.

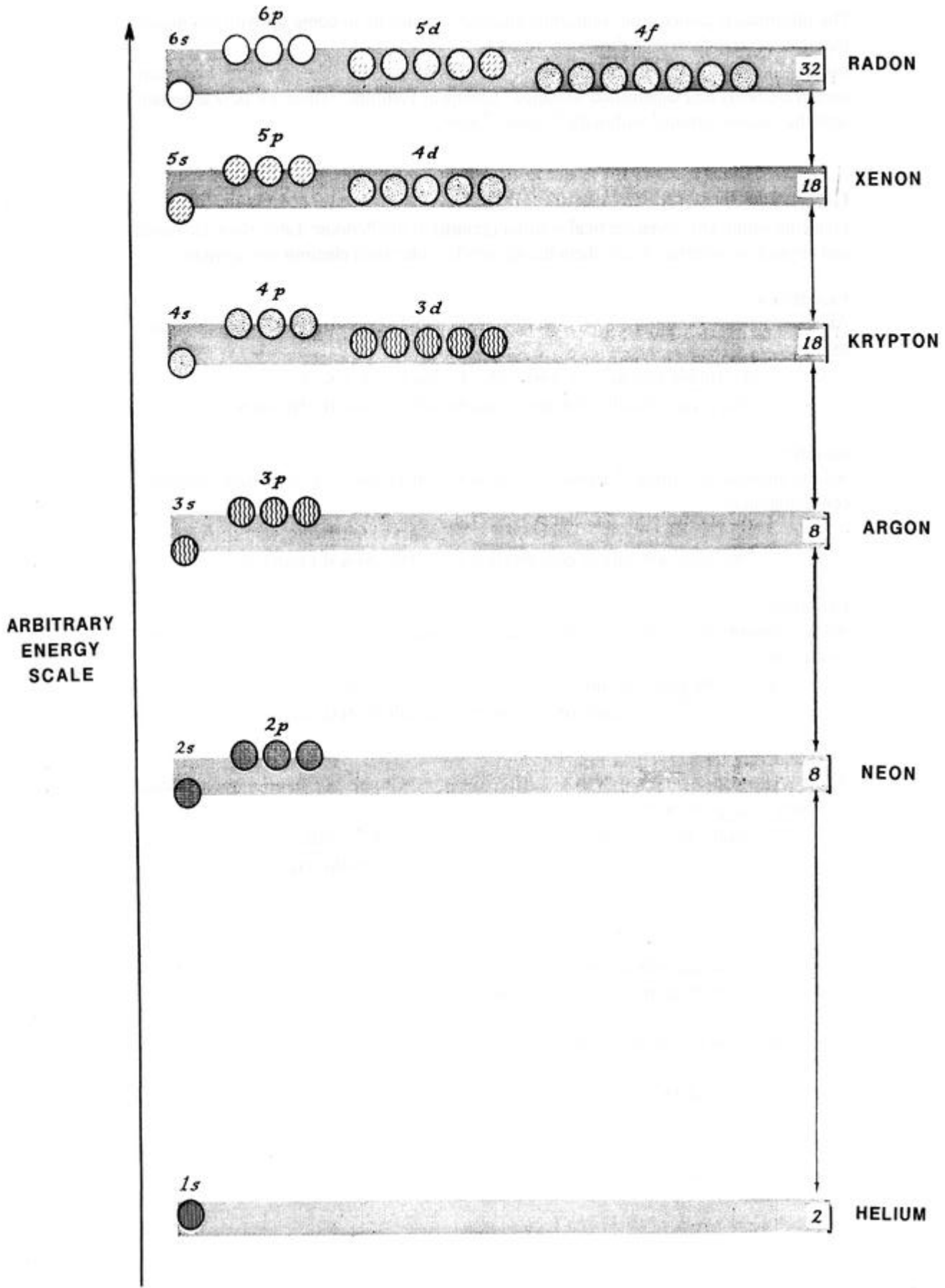
'p' orbitals are dumbbell in shape (somewhat 'propeller' shaped).

'd' orbitals are double dumbbell in shape or even more complex.



### SHAPES OF ORBITALS

# A SCHEMATIC ENERGY LEVEL DIAGRAM OF THE ORBITALS FOR A MANY ELECTRON ATOM:



# THE PERIODIC TABLE

The information gained from ionization energies enables us to come up with the model for electron arrangement as shown on page 15.

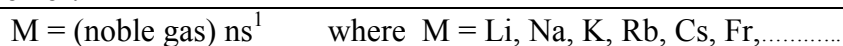
Long before such a model had been developed, chemists recognised similarities between certain elements and established so-called “Chemical Families” which we now associate with the various ‘groups’ within the Periodic Table.

## GROUPS OF THE PERIODIC TABLE

Elements within any given **vertical column (group)** of the Periodic Table show chemical and physical similarities due to them having similar outer shell electron arrangements.

### EXAMPLE 1.

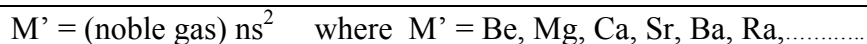
All the elements in Group IA (also written as Group 1) have a ground-state electronic configuration of:



This gives a family of elements that we call the **ALKALI METALS**.

### EXAMPLE 2.

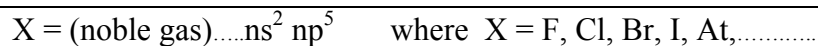
All the elements in Group IIA (also written as Group 2) have a ground-state electronic configuration of:



This gives a family of elements that we call the **ALKALI EARTHS**.

### EXAMPLE 3.

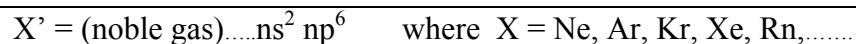
All the elements in Group VIIA (also written as Group 17) have a ground-state electronic configuration of:



This gives a family of elements that we call the **HALOGENS**.

### EXAMPLE 4.

All the elements in Group VIIIA (also written as Group 18) have a ground-state electronic configuration of:



This gives a family of elements that we call the **NOBLE GASES**.



Q19. Give the ground state electronic configuration for each of the Alkali Metals and explain why these elements all have the tendency to form 1+ ions but never 2+ ions.

Q20. What would be the general format for the ground state electronic configuration for the elements that comprise Group VIA (Group 16) which are sometimes referred to as the **CHALCOGENS**?  
(noble gas).....ns<sup>2</sup> np<sup>4</sup>

Q21. In example 4 above, why was the element helium (He) a special case and not represented by the standard format X' = ( ).....ns<sup>2</sup> np<sup>6</sup> even though it is a noble gas?



## PERIODS OF THE PERIODIC TABLE

Elements across any given **horizontal row** of the Periodic Table make up a **PERIOD** of the Periodic Table. Each period corresponds to the filling of a particular main quantum level and because these levels can accommodate differing numbers of electrons, the periods differ in length.

For example:

PERIOD	ELEMENTS	NUMBER OF ELEMENTS
1	H ↔ He	2
2	Li ↔ Ne	8
3	Na ↔ Ar	8
4	K ↔ Kr	18
5	Rb ↔ Xe	18
6	Cs ↔ Rn	32

Elements within the same period do **not** show chemical and physical similarities but show a trend of changing properties as electrons are progressively added to the same quantum level.

e.g. **PERIOD 2**

starts with Li = (He)  $2s^1$  and the **second** level fills up and ends with Ne = (He)  $2s^2 2p^6$

e.g. **PERIOD 3**

starts with Na = (Ne)  $3s^1$  and the **third** level fills until we end with Ar = (Ne)  $3s^2 3p^6$

Across any given period of the Periodic Table, the general trends in properties are typically:

**LEFT SIDE OF PERIODIC TABLE** ↔ **RIGHT SIDE OF PERIODIC TABLE**

Group IA metallic elements ↔ Group VIIIA non-metallic elements

Group IA basic oxides ↔ Group VIIA acidic oxides









Group IA electropositive elements ↔ Group VIIA electronegative elements

Group IA powerful reducing agents ↔ Group VIIA powerful oxidisers

Group IA low ionization energy ↔ Group VIIIA high ionization energy

A more detailed view of the changing properties across the Periodic Table is shown on the next page (18) where the variations across period 3 are shown.

### PERIOD 3 ELEMENTS: SOME TRENDS ACROSS THE PERIOD

ELEMENT	SODIUM	MAGNESIUM	ALUMINIUM	SILICON	PHOSPHORUS	SULFUR	CHLORINE	ARGON	
SYMBOL	Na	Mg	Al	Si	P	S	Cl	Ar	
ATOMIC NUMBER	11	12	13	14	15	16	17	18	
ELECTRON CONFIGURATION	(Ne) 3s <sup>1</sup>	(Ne) 3s <sup>2</sup>	(Ne) 3s <sup>2</sup> 3p <sup>1</sup>	(Ne) 3s <sup>2</sup> 3p <sup>2</sup>	(Ne) 3s <sup>2</sup> 3p <sup>3</sup>	(Ne) 3s <sup>2</sup> 3p <sup>4</sup>	(Ne) 3s <sup>2</sup> 3p <sup>5</sup>	(Ne) 3s <sup>2</sup> 3p <sup>6</sup>	
METAL OR NON-METAL	METAL	METAL	METAL	NON-METAL	NON-METAL	NON-METAL	NON-METAL	NON-METAL	
CHLORIDE FORMULA	NaCl	MgCl <sub>2</sub>	AlCl <sub>3</sub>	SiCl <sub>4</sub>	PCl <sub>3</sub> PCl <sub>5</sub>	SCl <sub>2</sub>	Cl <sub>2</sub>	none	
BONDING IN CHLORIDE	IONIC	IONIC	IONIC	COVALENT	COVALENT	COVALENT	COVALENT	-	
FORMULA FOR OXIDE	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>6</sub> P <sub>4</sub> O <sub>10</sub>	SO <sub>2</sub> SO <sub>3</sub>	Cl <sub>2</sub> O	none	
ACID-BASE NATURE OF OXIDE	BASIC	BASIC	AMPHOTERIC	NEUTRAL	ACIDIC	ACIDIC	ACIDIC	-	
ELECTRO ± NATURE	ELECTRO POSITIVE	INCREASINGLY ELECTROPOSITIVE	←	←	INCREASINGLY ELECTRONEGATIVE	←	ELECTRO NEGATIVE	NO REACTIONS	
REDOX NATURE	POWERFUL REDUCER	INCREASINGLY POWERFUL REDUCERS	←	←	INCREASINGLY POWERFUL OXIDISERS	←	POWERFUL OXIDISER	-	
FIRST IONIZATION (kJ mol <sup>-1</sup> )	494	733	577	786	1063	999	1256	1520	
RELATIVE ATOMIC RADIUS									exception

## REVIEW QUESTIONS ON PERIOD 3 ELEMENTS

Q22. Why do the first ionization energies ( $E_1$ ) of the individual elements increase across a given period such as period 3 of the Periodic Table?

Q23. Consider the 8 elements that comprise period 3; i.e.

Na	Mg	Al	Si	P	S	Cl	Ar
----	----	----	----	---	---	----	----

- ANS.
- (i) Which element has the lowest first ionization energy ( $E_1$ )? (Na)
- (ii) Which element has the highest first ionization energy ( $E_1$ )? (Ar)
- (iii) Which element has the highest second ionization energy ( $E_2$ )? (Na)
- (iv) Which element does not react to form any compounds? (Ar)
- (v) Which element is the most reactive non-metal? (Cl)
- (vi) Which element is the most reactive metal? (Na)
- (vii) Which elements form basic oxides? (Na, Mg)
- (viii) Which of these elements form acidic oxides? (P, S, Cl)
- (ix) Which element is a semi-conductor of electricity? (Si)
- (x) Which element exists as a covalent network solid? (Si)
- (xi) Which element forms an ionic chloride with formula  $XCl_2$ ? (Mg)
- (xii) Which element forms a covalent chloride with formula  $XCl_2$ ? (S)
- (xiii) Which element has the lowest boiling point? (Ar)
- (xiv) Which element forms acidic oxides with the formulae  $XO_2$  and  $XO_3$ ? (S)
- (xv) Which element forms an amphoteric oxide? (Al)
- (xvi) Which element exists as tetra-atomic molecules  $X_4$ ? (P)
- (xvii) Which elements exist in two or more allotropic forms? (P, S)
- (xviii) Which element forms a covalent chloride  $XCl_3$ ? (P)
- (xix) Which element exists as diatomic molecules  $X_2$ ? (Cl)
- (xx) Which element has the greatest difference between the third and fourth ionization energies; i.e.  $E_3$  and  $E_4$ ? (Al)

## GROUP IA (ALKALI METALS)

### PROPERTIES:

ELEMENT	ELECTRON CONFIGUR <sup>N</sup>	E <sub>1</sub> (kJ mol <sup>-1</sup> )	ATOMIC RADIUS (pm)	M.P. (°C)	DENSITY (g mL <sup>-1</sup> )
<b>Li</b>	(He) 2s <sup>1</sup>	526	67	180	0.53
<b>Na</b>	(Ne) 3s <sup>1</sup>	504	98	98	0.97
<b>K</b>	(Ar) 4s <sup>1</sup>	425	135	64	0.86
<b>Rb</b>	(Kr) 5s <sup>1</sup>	410	148	39	1.53
<b>Cs</b>	(Xe) 6s <sup>1</sup>	380	167	29	1.87

(E<sub>1</sub> = first ionization energy, pm = picometres = 10<sup>-12</sup>m and M.P = melting point)

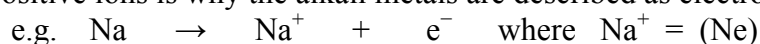
(i) This chemical family comprises the highly reactive metallic elements lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr).

Francium is a synthetic and radioactive element that will not be of great concern to us in this discussion.

(ii) All these metallic elements have just one valence electron; i.e. one more electron than the nearest noble gas.

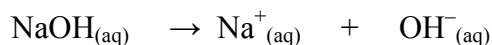
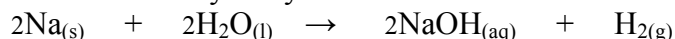
(iii) They all have very low first ionization energy (E<sub>1</sub>) values and very high second ionization energy (E<sub>2</sub>) values. The values of E<sub>1</sub> decrease down the group.

(iv) These metals react readily by the loss of one electron thus forming 1+ ions where the 1+ ion achieves stability by having a noble gas electron configuration. This high tendency to form positive ions is why the alkali metals are described as electropositive.

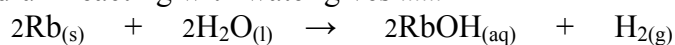


(v) As highly reactive metals that are electron donors, these elements are powerful reducing agents. The alkali metal reactivity increases **down** the group because the outer single valence electron is progressively further and further from the nucleus and thus not as strongly held and therefore more easily lost.

(vi) Each of the alkali metals reacts explosively with water to form the metal hydroxide and hydrogen gas. The formation of hydroxyl ions makes the solution alkaline or basic. e.g.



(Note that by knowing any chemical equations for the reaction of sodium; eg with water as shown, one can immediately predict what the equations will be for any member of this family. One only has to replace sodium's symbol in the equation with the other alkali metal's symbol e.g., rubidium reacting with water gives .....

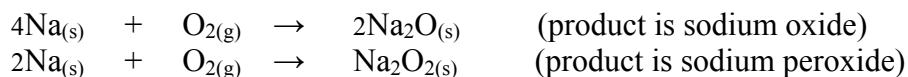


## GROUP IA (ALKALI METALS)

### CONTINUED:

(vii) The reactivity of these metals increases with atomic number (i.e. down the group) due to the outer valence electron being further from the nucleus and thus, less strongly attracted; (see diagram below)

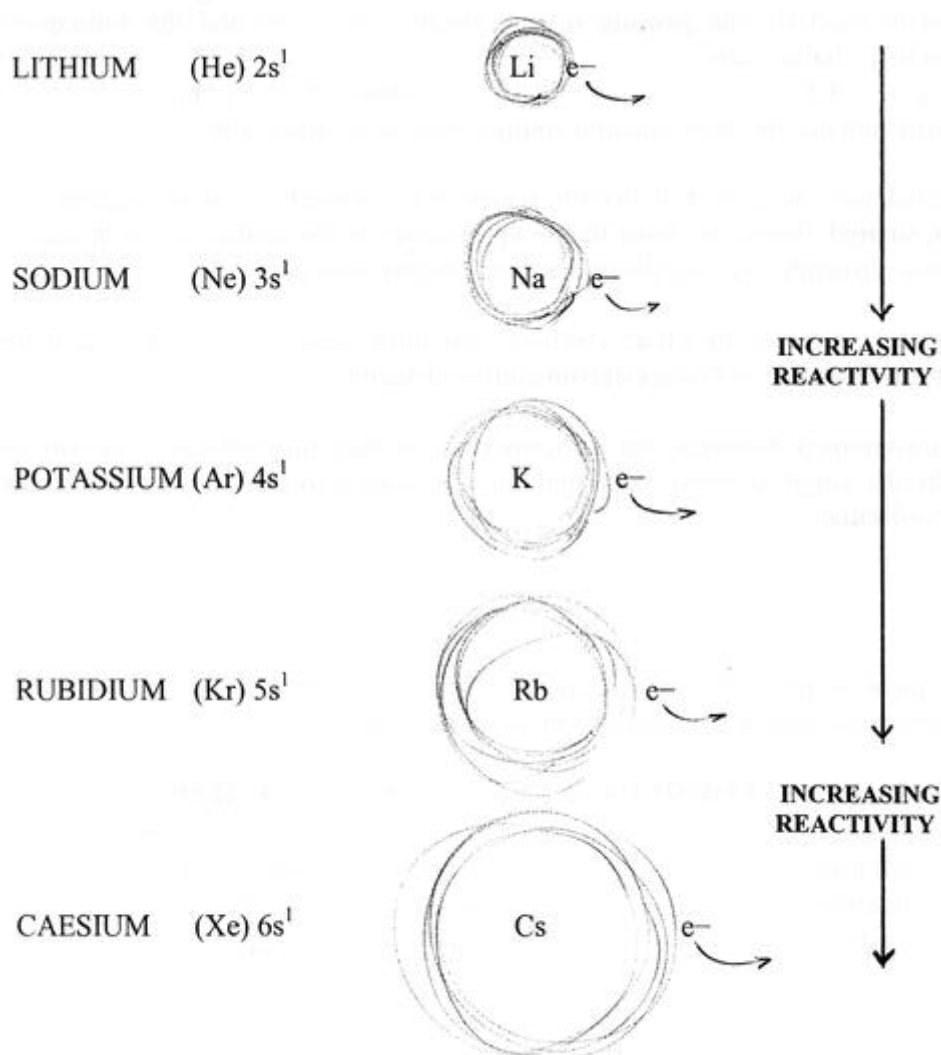
(viii) The alkali metals react rapidly with oxygen at room temperature to form metal oxides and even metal peroxides e.g.



To prevent these reactions with O<sub>2</sub> gas, the very reactive alkali metals are normally stored under paraffin oil or kerosene.

(ix) All the commonly encountered compounds formed by the alkali metals are ionic with the alkali metal present in the M<sup>+</sup> ionic state.

Practically all of these ionic solids are white crystalline, water soluble compounds with high melting points.



## GROUP VII or 17 (THE HALOGENS)

### PROPERTIES:

ELEMENT	ATOMIC NUMBER	ELECTRON CONFIGUR <sup>N</sup>	ATOMIC RADIUS (pm)	M.P. (°C)	B.P. (°C)
<b>F</b>	9	(He) 2s <sup>2</sup> 2p <sup>5</sup>	68	-220	-188
<b>Cl</b>	17	(Ne) 3s <sup>2</sup> 3p <sup>5</sup>	99	-101	-35
<b>Br</b>	35	(Ar)....4s <sup>2</sup> 4p <sup>5</sup>	114	-7	58
<b>I</b>	53	(Kr)....5s <sup>2</sup> 5p <sup>5</sup>	133	114	183
<b>At</b>	85	(Xe)....6s <sup>2</sup> 6p <sup>5</sup>	-	-	-

(pm = picometres = 10<sup>-12</sup>m      M.P = melting point      B.P = boiling point)

(i) These elements form a family with many similarities in terms of their properties although astatine is of limited concern to us here as it is highly radioactive and thus unstable.

(ii) Each of the halogens is one electron less than a noble gas configuration and thus they tend to react by the **gaining** of one electron per atom and the subsequent formation of 1- halide ions.

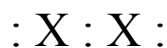


The chloride ion has the same electron configuration as an argon atom.

(iii) The halogens are powerful electron acceptors i.e. powerful oxidising agents. The oxidising strength decreases down the group because, as the atomic radius increases, the electron attracting capacity decreases; (see diagram next page)

(iv) The high tendency to attract electrons and form negative ions means that the halogens are described as being **electronegative** elements.

(v) As uncombined elements, the halogens exist as diatomic molecules X<sub>2</sub> with an intramolecular single covalent bond and van der Waal's forces between molecules; i.e. intermolecular.



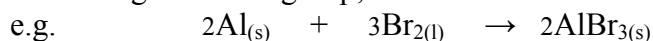
(vi) The physical properties of the halogen elements are determined by the van der Waal's forces increasing with size and mass of the molecules. e.g.

HALOGEN	FORMULA	STATE AT S.L.C.	COLOUR
fluorine	F <sub>2</sub>	gas	pale yellow
chlorine	Cl <sub>2</sub>	gas	pale green/yellow
bromine	Br <sub>2</sub>	liquid	reddish brown
iodine	I <sub>2</sub>	solid	deep purple

## GROUP VII or 17 (THE HALOGENS)

### CONTINUED:

(vii) The halogens react with most metals to form ionic metal halides with the reactivity decreasing down the group;



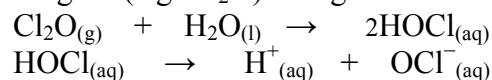
(viii) The halogens react with many non-metals to form covalent halides, once again with the reactivity decreasing down the group;

Examples:  $\text{CBr}_4$   $\text{PCl}_5$   $\text{HF}$   $\text{HBrO}_3$   $\text{SF}_6$   $\text{Cl}_4$

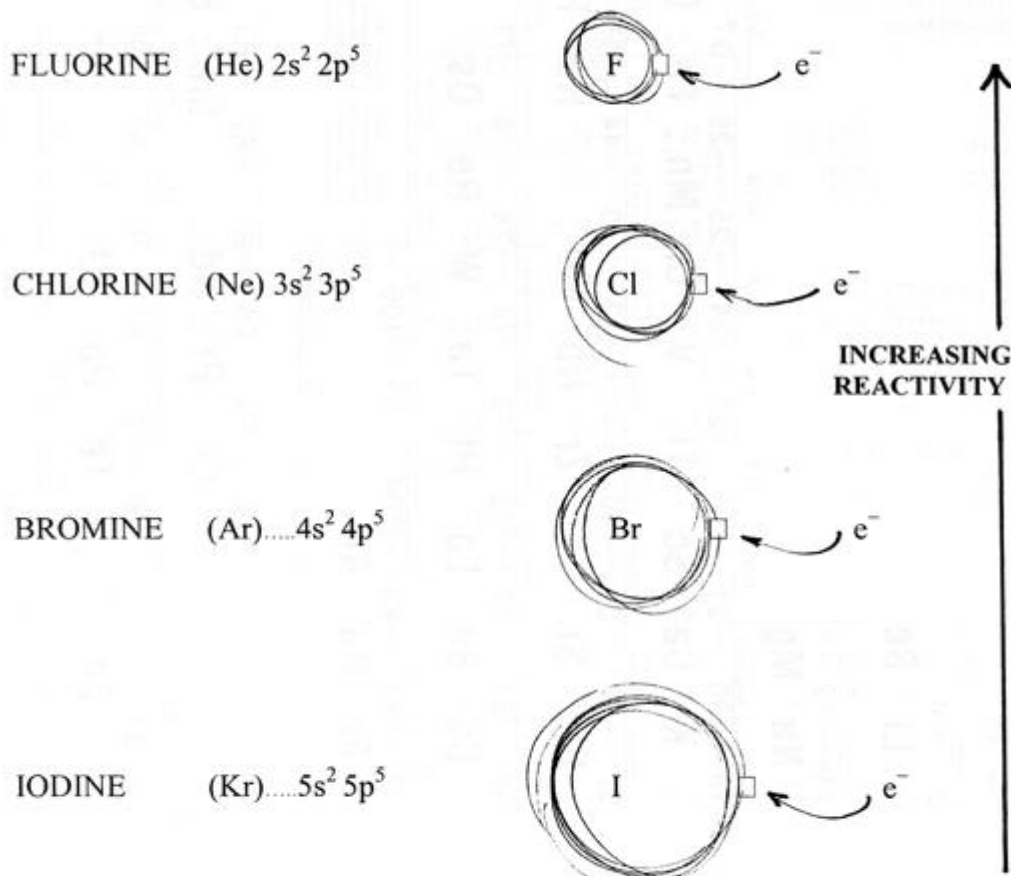
(ix) The hydrogen halides (HX) are water soluble covalent gases which, in aqueous solution ionise to give acidic solutions; i.e.



(x) The oxides of the halogens (e.g.  $\text{Cl}_2\text{O}$ ) also give acidic aqueous solutions.



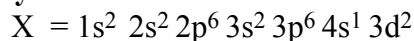
(xi) In the diagrams below,  $\square$  is used to represent the *electron vacancy* in the outer (valence) 'p' orbital of the halogen atom. The smaller the atomic radius, the greater the electron attracting capacity of the halogen; i.e. fluorine with the smallest radius is the most reactive element in this chemical family and the reactivity decreases down the group!



# PERIODIC TABLE REVIEW QUESTIONS

Q24. Give the ground state electronic configuration for each of the **EIGHT** elements that comprise **PERIOD 3**.

Q25. An **electrically neutral** atom has the following electronic configuration:

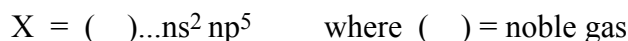


- Identify the element X
- What is special about this atom of element X?

Q26. Give the general form for the electronic configuration for:

- the "alkali metals" i.e. Group I
- the "alkali earths" i.e. Group II

Q27. An element has as part of its valence orbital electron configuration the following arrangement:

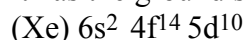


- what group of the Periodic Table does X belong to?
- how many valence electrons does X have.
- what is the formula of the compound formed between X and calcium?
- draw the electron-dot representation for the compound formed by X and sulfur.

Q28. Give the name, symbol and ground state electronic configuration for the element that is in:

- period 2 , group V
- period 3 , group IV
- period 4 group III

Q29. Which element has the ground state electronic configuration of:



Q30. Give the ground state electronic configuration for:

- (a) Kr                      (b) Br<sup>-</sup>                      (c) Rb<sup>+</sup>

- what do all three have in common?
- what are three differences?
- what is the order for the particle's atomic/ionic radii (smallest first) ? Explain.

Q31. Why do the atomic radii of elements tend to **DECREASE** across any given period of the Periodic Table?

Q32. Describe the trend in change of chemical properties as one progresses across any given row (period) of the Periodic Table.

Q33. Why do the Alkali Metals become increasingly reactive down the group whereas the opposite is true for the Halogens?



Q34. Consider the following elements with ground states shown:



What is the most likely chemical formula for the compound formed (if any) between:

- |               |                |
|---------------|----------------|
| (i) A and C   | (ii) D and C   |
| (iii) B and F | (iv) C and E   |
| (v) D and B   | (vi) C and F ? |

Q35. Give a graphical sketch of the successive ionization energies ( $E_1$  to  $E_5$ ) for the element magnesium.

Q36. Use your graph from Q35 to explain why Mg forms  $2+$  ions but not  $3+$  ions in normal chemical reactions.

Q37. Describe the steps involved in the process in which (e.g.) copper compounds when heated by a bunsen burner produce a bright green light.

Q38. What are some of the predicted properties of the following *unknown* elements?

- |                 |                  |                   |
|-----------------|------------------|-------------------|
| (i) element 117 | (ii) element 118 | (iii) element 119 |
|-----------------|------------------|-------------------|

Q39. Before the year 1604, only 12 elements had been discovered. What scientific reasons account for the fact that about 100 more elements were later discovered?

Q40. Why were the “Noble Gases” (Group VIII) amongst the last of the elements to be discovered?

Q41. What is meant by the term “periodicity”? What are some examples of the properties of elements that vary periodically?

Q42. Why did Mendeleev’s Periodic table have:

- (i) Zn in the same group as Ca?
- (ii) Ag in the same group as Na?

Q43. Mendeleev based his Periodic Table on his calculated relative atomic masses ( $A_r$ ). This would have meant that he initially placed iodine (mass = 126.9) in Group VI and the element tellurium (mass = 127.9) in Group VII. He realised this order was wrong but couldn’t explain the reason. What is the modern day explanation for having their order reversed?

Q44. What was Ernest Rutherford’s nuclear model of the atom and what dramatic experiment led him to this nuclear model?

Q45. Henry Moseley made a major discovery using X-rays which led to a new ordering concept for the elements. What was this development?

Q46. The development of the Mass Spectrometer enabled chemists to identify different types of the same element. How was this achieved and what ‘new’ particle was postulated to explain this occurrence?

Q47. Why was the neutron difficult to detect?

Q48. What is the difference between an emission spectrum and an absorption spectrum? Give examples.

Q49. The successive ionisation energies for any given element give a very important and direct indication of the energy levels for the electrons of that element.

Sketch a graph of the likely successive ionisation energies for the element aluminium from  $E_1$  to  $E_{13}$ .

Q50. Describe at a basic level the quantum mechanical model of electron structure including the distinction between shells, subshells and orbitals.

Q51. Selenium (Se) is immediately below sulfur (S) in group VI of the periodic table. What is the likely chemical formula for:

- (i) calcium selenide?
- (ii) sodium selenide

Q52. An element has an atomic number of 27. Give the ground state electronic configuration for a neutral atom of this element.

Q53. Which of the following electronic configurations does **NOT** represent an atom in its lowest energy (ground) state?

- A.  $1s^2 2s^2 2p^5$
- B.  $1s^2 2s^2 2p^6 3s^2 3p^1$
- C.  $1s^2 2s^2 2p^6 3s^2 3p^5 4s^1$
- D.  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

The next 2 questions refer to the elements with outer-shell configurations shown:

"A" = (noble gas)  $ns^2$

"C" = (noble gas)  $ns^2 np^5$

"B" = (noble gas)  $ns^2 np^4$

"D" = (noble gas)  $ns^1$

Q54. Give the chemical formula and describe the likely bonding for the compound formed by

- (i) A and B.
- (ii) A and C.
- (iii) B and C.

Q55. Which elements from period 3 would correspond to A, B, C and D?

Q56. The term 'isoelectronic' means 'possessing the same number of electrons'.

Give the symbols and charges of:

- (i) three **non-metallic** ions that are isoelectronic with an argon atom.
- (ii) three **metallic** ions that are isoelectronic with an argon atom.
- (iii) Arrange the 6 ions listed above in order of **increasing** ionic radius. Explain your reasoning.





