SECTION 3

THE ELECTRONIC STRUCTURE OF ATOMS OF THE ELEMENTS

To understand why pure substances have particular compositions and properties we need to know about the "electronic structure" of the atoms (i.e. the way the electrons are arranged about the nucleus of the atoms of different elements). Then we can rationalise the ratio in which atoms combine and whether they are molecular, polymeric or ionic, [e.g. why gaseous nitrogen consists of discrete N_2 molecules; methane, ammonia, water and hydrogen fluoride consist of discrete molecules of CH_4, NH_3, H_2O, HF respectively; why sodium chloride consists of Na^+ and Cl^- ions; why metals exist in nature mainly as cations, M^{x+}; why free-radicals are reactive.

Early last century a model of the atom (Bohr model) in which electrons circulated around the nucleus in orbits, just as planets do around the sun, was developed. This model proved inadequate to explain many phenomena and was replaced in the 1920's, when it was postulated that the behaviour of electrons in atoms could be described by mathematical equations similar to those used to describe the motion of standing waves in a string. From this model the electrons can be visualised as electron clouds of various shapes with the nucleus of the atom at their centre.

Electronic structure of atoms: The arrangement of electrons around the nucleus of the atom.

The properties of atoms can be understood in terms of **Quantum Theory**, which involves the **Heisenberg Uncertainty Principle** and the **Schrödinger Wave Equation**.

Quantum Theory: A theory that states that the energy of an object can only change by discrete steps. A change involves a packet of energy called a **quantum**.

Heisenberg Uncertainty Principle: The position and momentum of a particle cannot both be known simultaneously. This implies that in an atom the position and momentum of an electron cannot both be known simultaneously. (Thus a model of an atom containing electrons in fixed orbits around the nucleus is untenable.)

Schrödinger Wave Equation: A mathematical expression ascribing wave-like properties to matter. When applied to atoms it describes the properties of electrons in atoms. This equation gives rise to the concepts of **energy levels**, **atomic orbitals** and **quantum numbers**.

Electronic energy levels: Allowed energies of electrons in atoms.

Atomic orbital: A mathematical expression from the **Schrödinger Wave Equation** from which, for each energy level, the probability of finding the electron at different positions from the nucleus can be calculated. The atomic orbital can be depicted as an "electron-cloud" with the nucleus at the centre, the denser the cloud the greater the probability of the electron being there. Only two electrons can occupy the same orbital.

Quantum numbers: Numbers which label the orbital and spin of an electron.

Electron pair: Two electrons in the same orbital. They must have opposite spins.

Spin of an electron: The intrinsic angular momentum of an electron. Occurs in only two senses denoted $\uparrow$ and $\downarrow$.

Electron shells: The electrons in an atom exist in shells, each shell being made up of atomic orbitals or subshells.

Principal quantum number: Symbol n, an integer, 1,2 3... which defines the shell. The smaller n is, the lower the energy of the electron (more energy required to remove the electron from the atom), and the closer on average it is to the nucleus. First character in designation of an orbital.

Azimuthal quantum number: Symbol l, defines the subshell or kind of orbital, and can have the values 0,1,...,n-1. An orbital with $l = 0$ is called an *s* orbital; with $l = 1$ is called a *p* orbital; with $l = 2$ is called a *d* orbital; with $l = 3$ is called an *f* orbital. Second character in designation of an orbital.

Magnetic quantum number: Symbol m_1, specifies the particular orbital of a subshell and can have values $-l$, $-l$+1,...0,...,l-1,l.

Spin quantum number: Symbol m_s, specifies the spin of an electron and can have values of +½ ($\uparrow$) or -½ ($\downarrow$).

Occupancy of shells: The first shell, $n = 1$, can hold 2 electrons in one orbital, labelled 1*s*. ($l = 0$ for an *s* orbital)
The second shell, $n = 2$, can hold 8 electrons in four orbitals, one labelled 2*s* and three labelled 2*p*. ($l = 1$ for a *p* orbital).
The third shell can hold 18 electrons in nine orbitals, one 3*s*, three 3*p* and five 3*d*. ($l = 2$ for a *d* orbital)
The fourth shell, $n = 4$, can hold 32 electrons in 16 orbitals, one 4*s*, three 4*p*, five 4*d* and seven 4*f*. ($l = 3$ for an *f* orbital)

Within a shell the energy levels of the orbitals (subshells) is $s < p < d < f$.

The bottom line in each entry of the preceding periodic table gives the number of electrons in the shells in the **ground state** of that element [e.g. potassium, K, 2.8.8.1, has 2 in the first shell, 8 in the second, 8 in the third and one in the fourth.].

Ground state: The state of an atom when all the electrons are in the lowest allowed energy levels.

Electron configuration: A statement of the arrangement of electrons in the orbitals [e.g. Cl, $1s^2 2s^2 p^6 3s^2 p^5$]. Each principal quantum number is shown only once and the number of electrons in each subshell is shown as a superscript following the symbol for the orbital.

The ground state electron configuration of any element can be written down by filling the orbitals in order using the energy levels:

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

[e.g. cobalt, Co, Z = 27, thus 27 electrons. $1s^2 2s^2 p^6 3s^2 p^6 4s^2 3d^7$. This may be written as $1s^2 2s^2 p^6 3s^2 p^6 d^7 4s^2$.]

Valence electrons: Those electrons in the outermost shell and in unfilled subshells [e.g. Cl has 7 valence electrons ($3s^2p^5$) and Co has 9 valence electrons ($3d^74s^2$)]. Valence electrons are involved in chemical bonds - *section 4*.

The Periodic Table: A table showing the elements in rows and columns in a manner which shows up relationships between the properties of the elements.

Periods: Rows of the periodic table. Elements in the same row are in the same period [e.g. calcium, Ca, and copper, Cu, are both in the 4th period]. The number of the period (row) is equal to the principal quantum number of the outermost valence shell of the atoms.

Groups: Columns of the periodic table. Elements in the same column are in the same group and have the same number of valence electrons (which accounts for their similarities) [e.g. carbon, C, and tin, Sn, are both in group 14 and both have four valence electrons]. This numbering replaces a previous system, shown as Roman numbers on the table, still used by some older chemists.

Blocks: Groups having the same valence orbitals. Groups 1-2 are *s*-block because their elements have only *s* valence electrons; groups 3-12 are *d*-block because their elements have only *s* and *d* valence electrons; groups 13-18 are *p*-block because their elements have *s* and *p* valence electrons.

Alkali metals: The metals (elements) of group 1.

Alkaline earth metals: The metals (elements) of group 2.

Halogens: Elements of group 17 [e.g. chlorine].

Halide: A binary compound of a halogen and another element [e.g. HCl, $CaCl_2$, PCl_3], or with a group [e.g. CH_3Cl, chloromethane but also called methyl chloride; see *section 6-2*].

Halide ion: Monoatomic anion of a halogen [e.g. chloride ion, Cl^-].

Transition metals: The metals (elements) of the *d*-block.

Ionisation energy: The first ionisation energy is the minimum energy required to remove an electron from a neutral atom in the gas phase:

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

The second ionisation energy is the minimum energy to remove an electron from this gaseous ion:

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

Similarly for successive ionisation energies (I.E.). The variation of I.E with position in the periodic table is important in understanding the chemical properties of the elements. In general the ionisation energy increases from left to right in a period as the number of protons in the nucleus is increasing and therefore the attractive force between it and the electron is increasing. The first I.E. of the first element of a period is much lower than that of the last element in the previous period as the electron lost is from a shell of higher principal quantum number and hence energy.

Excited state: The state of an atom when an electron is in an orbital of energy greater than that in the ground state. When an electron changes energy level (orbital) a quantum of energy is emitted or absorbed as a **photon**.

Photon: A particle-like package of electromagnetic radiation. The energy, E, of the photon is related to the frequency, v, of the radiation by the expression $E = hv$ where h is the Planck constant.

EXERCISES

Write the electron configuration of the ground states of the following elements:

1. *Example*: selenium, Se
   Answer: From the periodic table Z = 34; there are 34 electrons to be placed in the orbital energy series.

   $1s^2 2s^2 p^6 3s^2 p^6 4s^2 3d^{10} 4p^4$
   2, 10, 18, 20, 30, 34 accumulative number of electrons
   or $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^4$

2. carbon 3. fluorine 4. iron 5. arsenic 6. silver

7-12. Give a possible value for the principal quantum number and for the azimuthal quantum number for a valence electron of the elements in questions 1-6 above.

7. *Example*: selenium, Se
   Answer: For Se the valence electrons are 4*s* and 4*p*.
   For 4*s* $n = 4$, $l = 0$
   For 4*p* $n = 4$, $l = 1$

Give the orbital of an electron with each of the following quantum numbers:

13. *Example*: $n = 3$, $l = 2$
    Answer: 3*d*

14. $n = 2$, $l = 1$ 15. $n = 5$, $l = 0$ 16. $n = 6$, $l = 3$

In which period, group and block of the periodic table are the following elements?

17. *Example*: Strontium
    Answer: group 2, 5th period, *s*-block

18. xenon 19. gold 20. silicon 21. lithium

22. The second ionisation energy of sodium is much greater than that of magnesium. Explain in terms of their electron configurations. (Hint: write down the electron configurations and see which electrons are being lost.)