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|----------|--|----------|--|----------|--|----------|--|----------|--|----------|--|----------|--|----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|-----------|--|
| | | | | | | | | | | | | | | | | 1 H | | 2 He | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 Li | | | | | | | | | | | | 4 Be | | | | | | | | | | | | | | | | | | 5 B | | 6 C | | 7 N | | 8 O | | 9 F | | 10 Ne | | | |
| 11 Na | | | | | | | | | | | | 12 Mg | | | | | | | | | | | | | | | | | | 13 Al | | 14 Si | | 15 P | | 16 S | | 17 Cl | | 18 Ar | | | |
| 19 K | | 20 Ca | | 21 Sc | | 22 Ti | | 23 V | | 24 Cr | | 25 Mn | | 26 Fe | | 27 Co | | 28 Ni | | 29 Cu | | 30 Zn | | 31 Ga | | 32 Ge | | 33 As | | 34 Se | | 35 Br | | 36 Kr | | | | | | | | | |
| 37 Rb | | 38 Sr | | 39 Y | | 40 Zr | | 41 Nb | | 42 Mo | | 43 Tc | | 44 Ru | | 45 Rh | | 46 Pd | | 47 Ag | | 48 Cd | | 49 In | | 50 Sn | | 51 Sb | | 52 Te | | 53 I | | 54 Xe | | | | | | | | | |
| 55 Cs | | 56 Ba | | 57 La | | 58 Hf | | 59 Ta | | 60 W | | 61 Re | | 62 Os | | 63 Ir | | 64 Pt | | 65 Au | | 66 Hg | | 67 Tl | | 68 Pb | | 69 Bi | | 70 Po | | 71 At | | 72 Rn | | | | | | | | | |
| 87 Fr | | 88 Ra | | 89 Ac | | 90 Rf | | 91 Db | | 92 Sg | | 93 Bh | | 94 Hs | | 95 Mt | | 96 Uun | | 97 Uun | | 98 Uub | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | 99 Ce | | 100 Pr | | 101 Nd | | 102 Pm | | 103 Sm | | 104 Eu | | 105 Gd | | 106 Tb | | 107 Dy | | 108 Ho | | 109 Er | | 110 Tm | | 111 Yb | | 112 Lu | |
| | | | | | | | | | | | | | | | | 113 Th | | 114 Pa | | 115 U | | 116 Np | | 117 Pu | | 118 Am | | 119 Cm | | 120 Bk | | 121 Cf | | 122 Es | | 123 Fm | | 124 Md | | 125 No | | 126 Lr | |

2

Chemical Periodicity and the Periodic Table

2.1 Introduction

The concept of chemical periodicity is central to the study of inorganic chemistry. No other generalization rivals the periodic table of the elements in its ability to systematize and rationalize known chemical facts or to predict new ones and suggest fruitful areas for further study. Chemical periodicity and the periodic table now find their natural interpretation in the detailed electronic structure of the atom; indeed, they played a major role at the turn of the century in elucidating the mysterious phenomena of radioactivity and the quantum effects which led ultimately to Bohr's theory of the hydrogen atom. Because of this central position it is perhaps not surprising that innumerable articles and books have been written on the subject since the seminal papers by Mendeleev in 1869, and some 700 forms of the periodic table (classified into 146 different types or subtypes) have been proposed.⁽¹⁻³⁾ A brief historical survey of these developments is summarized in the Panel opposite.

There is no single *best* form of the periodic table since the choice depends on the purpose for which the table is used. Some forms emphasize chemical relations and valence, whereas others stress the electronic configuration of the elements or the dependence of the periods on the shells and subshells of the atomic structure. The most convenient form for our purpose is the so-called "long form" with separate panels for the lanthanide and actinide elements (see inside front cover). There has been a lively debate during the past decade as to the best numbering system to be used for the individual

¹ F. P. VENABLE, *The Development of the Periodic Law*, Chemical Publishing Co., Easton, Pa., 1896. This is the first general review of periodic tables and has an almost complete collection of those published to that time. J. W. VAN SPRONSEN, *The Periodic System of the Chemical Elements*, Elsevier, Amsterdam, 1969, 368 pp. An excellent modern account of the historical developments leading up to Mendeleev's table.

² E. G. MAZURS, *Graphic Representation of the Periodic System during One Hundred Years*, University of Alabama Press, Alabama, 1974. An exhaustive topological classification of over 700 forms of the periodic table.

groups in the table; we will adopt the 1–18 numbering scheme recommended by IUPAC.⁽³⁾ The following sections of this chapter summarize:

- (a) the interpretation of the periodic law in terms of the electronic structure of atoms;
- (b) the use of the periodic table and graphs to systematize trends in physical and chemical properties and to detect possible errors, anomalies, and inconsistencies;
- (c) the use of the periodic table to predict new elements and compounds, and to suggest new areas of research.

2.2 The Electronic Structure of Atoms⁽⁴⁾

The ubiquitous electron was discovered by J. J. Thompson in 1897 some 25 y after the original work on chemical periodicity by D. I. Mendeleev and Lothar Meyer; however, a further 20 y were to pass before G. N. Lewis and then I. Langmuir connected the electron with valency and chemical bonding. Refinements continued via wave mechanics and molecular orbital theory, and the symbiotic relation between experiment and theory still continues

³ E. FLUCK, *Pure Appl. Chem.* **60**, 432–6 (1988); G. J. LEIGH (ed.), *Nomenclature of Inorganic Chemistry: IUPAC Recommendations 1990*, Blackwell, Oxford, 1990, 289 pp. The “Red Book”.

⁴ N. N. GREENWOOD, *Principles of Atomic Orbitals*, revised SI edition, Monograph for Teachers, No. 8, Chemical Society, London, 1980, 48 pp.

Mendeleev’s Periodic Table

Precursors and Successors

- 1772 L. B. G. de Morveau made the first table of “chemically simple” substances. A. L. Lavoisier used this in his *Traité Élémentaire de Chimie* published in 1789.
- 1817–29 J. W. Döbereiner discovered many triads of elements and compounds, the combining weight of the central component being the average of its partners (e.g. CaO, SrO, BaO, and NiO, CuO, ZnO).
- 1843 L. Gmelin included a V-shaped arrangement of 16 triads in the 4th edition of his *Handbuch der Chemie*.
- 1857 J. B. Dumas published a rudimentary table of 32 elements in 8 columns indicating their relationships.
- 1862 A. E. B. de Chancourtois first arranged the elements in order of increasing atomic weight; he located similar elements in this way and published a helical form in 1863.
- 1864 L. Meyer published a table of valences for 49 elements.
- 1864 W. Odling drew up an almost correct table with 17 vertical columns and including 57 elements.
- 1865 J. A. R. Newlands propounded his law of octaves after several partial classifications during the preceding 2 y; he also correctly predicted the atomic weight of the undiscovered element germanium.
- 1868–9 L. Meyer drew up an atomic volume curve and a periodic table, but this latter was not published until 1895.
- 1869 D. I. Mendeleev enunciated his periodic law that “the properties of the elements are a periodic function of their atomic weights”. He published several forms of periodic table, one containing 63 elements.
- 1871 D. I. Mendeleev modified and improved his tables and predicted the discovery of 10 elements (now known as Sc, Ga, Ge, Tc, Re, Po, Fr, Ra, Ac and Pa). He fully described with amazing prescience the properties of 4 of these (Sc, Ga, Ge, Po). Note, however, that it was not possible to predict the existence of the noble gases or the number of lanthanide elements.
- 1894–8 Lord Rayleigh, W. Ramsay and M. W. Travers detected and then isolated the noble gases (He), Ne, Ar, Kr, Xe.
- 1913 N. Bohr explained the form of the periodic table on the basis of his theory of atomic structure and showed that there could be only 14 lanthanide elements.
- 1913 H. G. J. Moseley observed regularities in the characteristic X-ray spectra of the elements; he thereby discovered atomic numbers *Z* and provided justification for the ordinal sequence of the elements.
- 1940 E. McMillan and P. Abelson synthesized the first transuranium element ${}_{93}\text{Np}$. Others were synthesized by G. T. Seaborg and his colleagues during the next 15 y.
- 1944 G. T. Seaborg proposed the actinide hypothesis and predicted 14 elements (up to *Z* = 103) in this group.

today. It should always be remembered, however, that it is incorrect to “deduce” known chemical phenomena from theoretical models; the proper relationship is that the currently accepted theoretical models interpret the facts and suggest new experiments — they will be modified (or discarded and replaced) when new results demand it. Theories can never be proved by experiment — only refuted, the best that can be said of a theory is that it is consistent with a wide range of information which it interprets logically and that it is a fruitful source of predictions and new experiments.

Our present views on the electronic structure of atoms are based on a variety of experimental results and theoretical models which are fully discussed in many elementary texts. In summary, an atom comprises a central, massive, positively charged nucleus surrounded by a more tenuous envelope of negative electrons. The nucleus is composed of neutrons (${}^1_0\text{n}$) and protons (${}^1_1\text{p}$, i.e. ${}^1_1\text{H}^+$) of approximately equal mass tightly bound by the force field of mesons. The number of protons (Z) is called the atomic number and this, together with the number of neutrons (N), gives the atomic mass number of the nuclide ($A = N + Z$). An element consists of atoms all of which have the same number of protons (Z) and this number determines the position of the element in the periodic table (H. G. J. Moseley, 1913). Isotopes of an element all have the same value of Z but differ in the number of neutrons in their nuclei. The charge on the electron (e^-) is equal in size but opposite in sign to that of the proton and the ratio of their masses is 1/1836.1527.

The arrangement of electrons in an atom is described by means of four quantum numbers which determine the spatial distribution, energy, and other properties, see Appendix 1 (p. 1285). The principal quantum number n defines the general energy level or “shell” to which the electron belongs. Electrons with $n = 1, 2, 3, 4, \dots$, are sometimes referred to as K, L, M, N, \dots , electrons. The orbital quantum number l defines both the shape of the electron charge distribution and its orbital angular

momentum. The number of possible values for l for a given electron depends on its principal quantum number n ; it can have n values running from 0 to $n - 1$, and electrons with $l = 0, 1, 2, 3, \dots$, are designated s, p, d, f, \dots , electrons. Whereas n is the prime determinant of an electron's energy this also depends to some extent on l (for atoms or ions containing more than one electron). It is found that the sequence of increasing electron energy levels in an atom follows the sequence of values $n + l$; if 2 electrons have the same value of $n + l$ then the one with smaller n is the more tightly bound.

The third quantum number m is called the magnetic quantum number for it is only in an applied magnetic field that it is possible to define a direction within the atom with respect to which the orbital can be directed. In general, the magnetic quantum number can take up $2l + 1$ values (i.e. $0, \pm 1, \dots, \pm l$); thus an s electron (which is spherically symmetrical and has zero orbital angular momentum) can have only one orientation, but a p electron can have three (frequently chosen to be the x, y , and z directions in Cartesian coordinates). Likewise there are five possibilities for d orbitals and seven for f orbitals.

The fourth quantum number m_s is called the spin angular momentum quantum number for historical reasons. In relativistic (four-dimensional) quantum mechanics this quantum number is associated with the property of symmetry of the wave function and it can take on one of two values designated as $+\frac{1}{2}$ and $-\frac{1}{2}$, or simply α and β . All electrons in atoms can be described by means of these four quantum numbers and, as first enumerated by W. Pauli in his *Exclusion Principle* (1926), each electron in an atom must have a unique set of the four quantum numbers.

It can now be seen that there is a direct and simple correspondence between this description of electronic structure and the form of the periodic table. Hydrogen, with 1 proton and 1 electron, is the first element, and, in the ground state (i.e. the state of lowest energy) it has the electronic configuration $1s^1$ with zero orbital angular momentum. Helium, $Z = 2$, has the configuration $1s^2$, and this completes the first period since no

other unique combination of $n = 1$, $l = m = 0$, $m_s = \pm \frac{1}{2}$ exists. The second period begins with lithium ($Z = 3$), the least tightly bound electron having the configuration $2s^1$. The same situation obtains for each of the other periods in the table, the number of the period being the principal quantum number of the least tightly bound electron of the first element in the period. It will also be seen that there is a direct relation between the various blocks of elements in the periodic table and the electronic configuration of the atoms it contains; the s block is 2 elements wide, the p block 6 elements wide, the d block 10, and the f block 14, i.e. $2(2l + 1)$, the factor 2 appearing because of the spins.

In so far as the chemical (and physical) properties of an element derive from its electronic configuration, and especially the configuration of its least tightly bound electrons, it follows that chemical periodicity and the form of the periodic table can be elegantly interpreted in terms of electronic structure.

2.3 Periodic Trends in Properties^(5,6)

General similarities and trends in the *chemical* properties of the elements had been noticed increasingly since the end of the eighteenth century and predated the observation of periodic variations in *physical* properties which were not noted until about 1868. However, it is more convenient to invert this order and to look at trends in atomic and physical properties first.

2.3.1 Trends in atomic and physical properties

Figure 2.1 shows a modern version of Lothar Meyer's atomic volume curve: the alkali metals

⁵ R. RICH, *Periodic Correlations*, W. A. Benjamin, New York, 1965, 159 pp.

⁶ R. T. SANDERSON, *Inorganic Chemistry*, Reinhold Publishing Corp., New York, 1967, 430 pp.

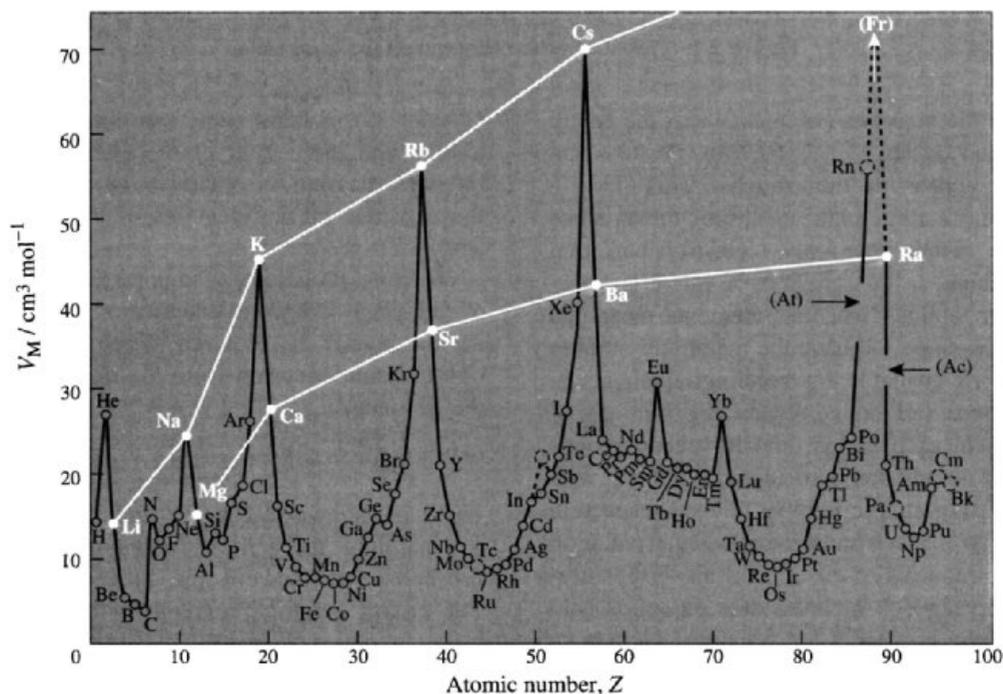


Figure 2.1 Atomic volumes (molar volumes) of the elements in the solid state.

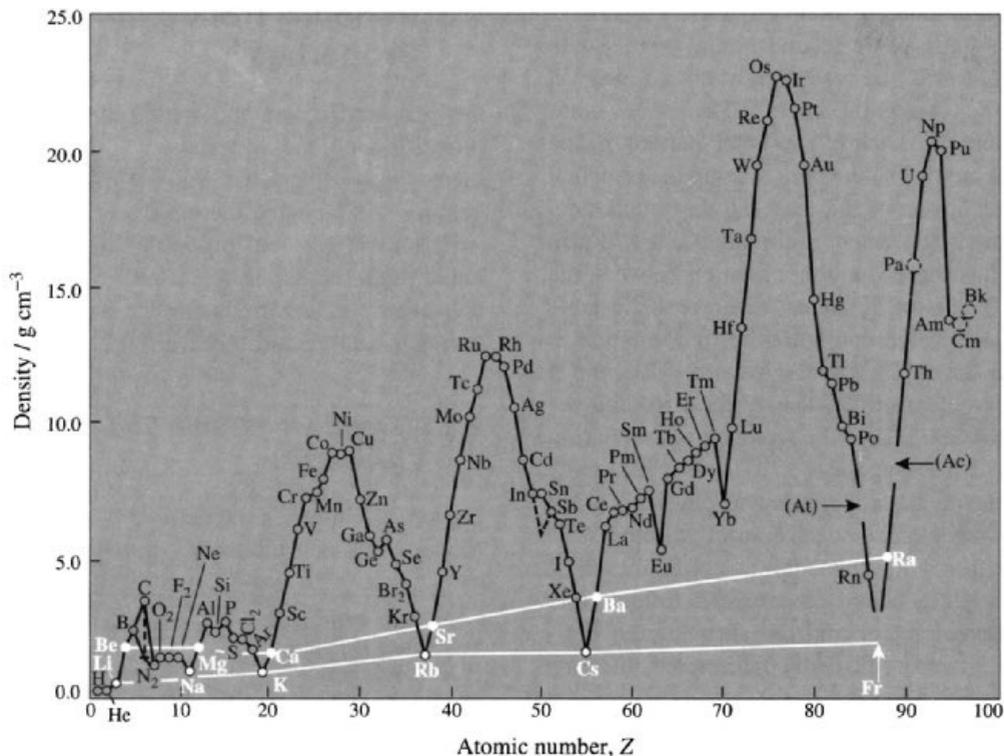
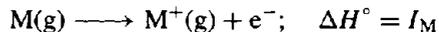


Figure 2.2 Densities of the elements in the solid state.

appear at the peaks and elements near the centre of each period (B, C; Al, Si; Mn, Fe, Co; Ru; and Os) appear in the troughs. This finds a ready interpretation on the electronic theory since the alkali metals have only 1 electron per atom to contribute to the binding of the 8 nearest-neighbour atoms, whereas elements near the centre of each period have the maximum number of electrons available for bonding. Elements in other groups fall on corresponding sections of the curve in each period, and in several groups there is a steady trend to higher volumes with the increasing atomic number. Closer inspection reveals that a much more detailed interpretation would be required to encompass all the features of the curve which includes data on solids held by very diverse types of bonding. Note also that the position of helium is anomalous (why?), and that there are local anomalies at europium and ytterbium in the lanthanide elements (see

Chapter 30). Similar plots are obtained for the atomic and ionic radii of the elements and an inverted diagram is obtained, as expected, for the densities of the elements in the solid state (Fig. 2.2).

Of more fundamental importance is the plot of first-stage ionization energies of the elements, i.e. the energy I_M required to remove the least tightly bound electron from the neutral atom in the gas phase:



These are shown in Fig. 2.3 and illustrate most convincingly the various quantum shells and subshells described in the preceding section. The energy required to remove the 1 electron from an atom of hydrogen is 13.606 eV (i.e. 1312 kJ per mole of H atoms). This rises to 2372 kJ mol⁻¹ for He (1s²) since the positive charge on the helium nucleus is twice that of the

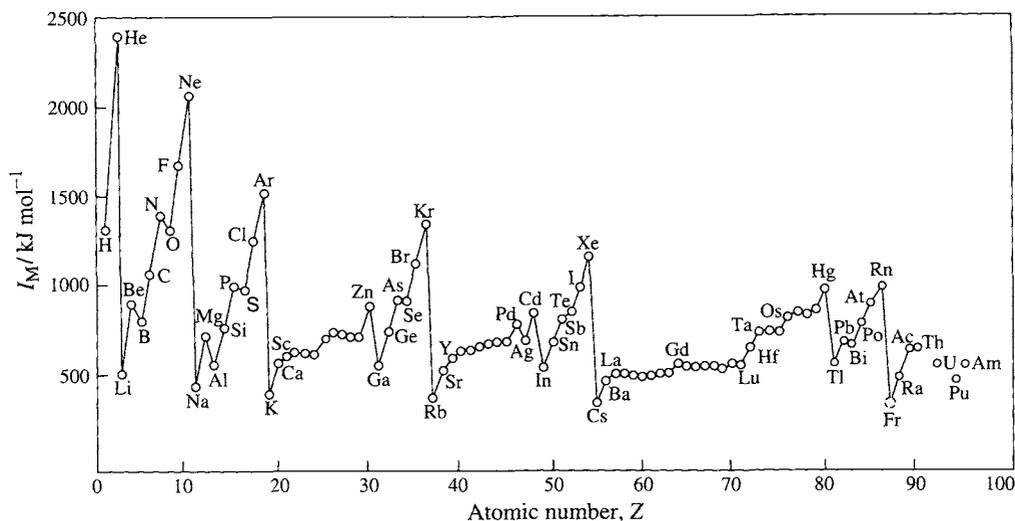


Figure 2.3 First-stage ionization energies of the elements.

proton and the additional charge is not completely shielded by the second electron. There is a large drop in ionization energy between helium and lithium ($1s^22s^1$) because the principal quantum number n increases from 1 to 2, after which the ionization energy rises somewhat for beryllium ($1s^22s^2$), though not to a value which is so high that beryllium would be expected to be an inert gas. The interpretation that is placed on the other values in Fig. 2.3 is as follows. The slight decrease at boron ($1s^22s^22p^1$) is due to the increase in orbital quantum number l from 0 to 1 and the similar decrease between nitrogen and oxygen is due to increased interelectronic coulomb repulsion as the fourth p electron is added to the 3 already occupying $2p_x$, $2p_y$, and $2p_z$. The ionization energy then continues to increase with increasing Z until the second quantum shell is filled at neon ($2s^22p^6$). The process is precisely repeated from sodium ($3s^1$) to argon ($3s^23p^6$) which again occurs at a peak in the curve, although at this point the third quantum shell is not yet completed (3d). This is because the next added electron for the next element potassium ($Z = 19$) enters the 4s shell ($n + l = 4$) rather than the 3d ($n + l = 5$). After calcium ($Z = 20$) the 3d shell fills and then the 4p ($n + l = 5$, but n higher than for 3d). The

implications of this and of the subsequent filling of later s, p, d, and f levels will be elaborated in considerable detail in later chapters. Suffice it to note for the moment that the chemical inertness of the lighter noble gases correlates with their high ionization energies whereas the extreme reactivity of the alkali metals (and their prominent flame tests) finds a ready interpretation in their much lower ionization energies.

Electronegativities also show well-developed periodic trends though the concept of electronegativity itself, as introduced by L. Pauling,⁽⁷⁾ is rather qualitative: "Electronegativity is the power of an atom *in a molecule* to attract electrons to itself." It is to be expected that the electronegativity of an element will depend to some extent not only on the other atoms to which it is bonded but also on its coordination number and oxidation state; for example, the electronegativity of a given atom increases with increase in its oxidation state. Fortunately, however, these effects do not obscure the main trends. Various measures of electronegativity have been proposed by L. Pauling, by R. S. Mulliken, by A. L. Allred

⁷ L. PAULING, *J. Am. Chem. Soc.* **54**, 3570 (1932); *The Nature of the Chemical Bond*, 3rd edn., pp. 88–107. Cornell University Press, Ithaca, NY, 1960.

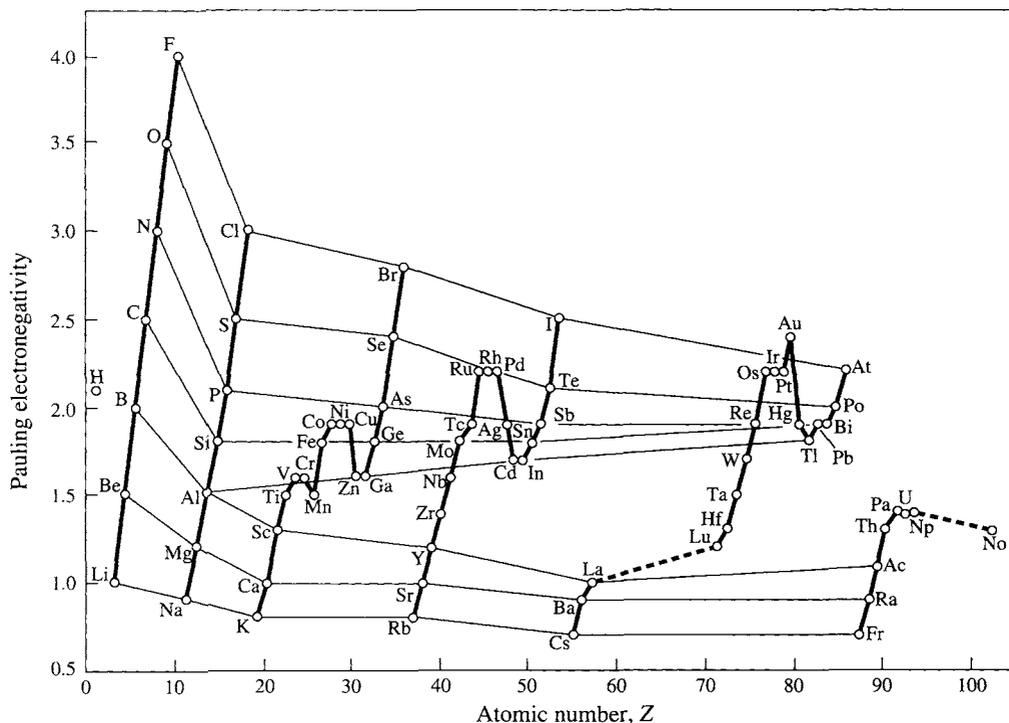


Figure 2.4 Values of electronegativity of the elements.

and E. Rochow, and by R. T. Sanderson, and all give roughly parallel scales. Figure 2.4, which incorporates Pauling's values, illustrates the trends observed; electronegativities tend to increase with increasing atomic number within a given period (e.g. Li to F, or K to Br) and to decrease with increasing atomic number within a given group (e.g. F to At, or O to Po). Numerous reviews are available.⁽⁸⁾

Many other properties have been found to show periodic variations and these can be displayed graphically or by circles of varying size on a periodic table, e.g. melting points of the elements, boiling points, heats of fusion, heats of vaporization, energies of atomization, etc.⁽⁶⁾ Similarly, the properties of simple binary

compounds of the elements can be plotted, e.g. heats of formation, melting points and boiling points of hydrides, fluorides, chlorides, bromides, iodides, oxides, sulfides, etc.⁽⁶⁾ Trends immediately become apparent, and the selection of compounds with specific values for particular properties is facilitated. Such trends also permit interpolation to give estimates of undetermined values of properties for a given compound though such a procedure can be misleading and should only be used as a first rough guide. Extrapolation has also frequently been used, and to good effect, though it too can be hazardous and unreliable particularly when new or unsuspected effects are involved. Perhaps the classic example concerns the dissociation energy of the fluorine molecule which is difficult to measure experimentally: for many years this was taken to be $\sim 265 \text{ kJ mol}^{-1}$ by extrapolation of the values for iodine, bromine, and chlorine (151, 193, and 243 kJ mol^{-1}), whereas the

⁸ K. D. SEN and C. K. JØRGENSEN (eds.), *Structure and Bonding* 66 *Electronegativity*, Springer-Verlag, Berlin, 1987, 198 pp. J. Mullay, *J. Am. Chem. Soc.* **106**, 5842-7 (1984). R. T. Sanderson, *Inorg. Chem.* **25**, 1856-8 (1986). R. G. Pearson, *Inorg. Chem.* **27**, 734-40 (1988).

most recent experimental values are close to 159 kJ mol^{-1} (see Chapter 17). The detection of such anomalous data from periodic plots thus serves to identify either inaccurate experimental observations or inadequate theories (or both).

2.3.2 Trends in chemical properties

These, though more difficult to describe quantitatively than the trends in atomic and physical properties described in the preceding subsection, also become apparent when the elements are compared in each group and along each period. Such trends will be discussed in detail in later chapters and it is only necessary here to enumerate briefly the various types of behaviour that frequently recur.

The most characteristic chemical property of an element is its valence. There are numerous measures of valency each with its own area of usefulness and applicability. Simple definitions refer to the number of hydrogen atoms that can combine with an element in a binary hydride or to twice the number of oxygen atoms combining with an element in its oxide(s). It was noticed from the beginning that there was a close relation between the position of an element in the periodic table and the stoichiometry of its simple compounds. Hydrides of main group elements have the formula MH_n where n was related to the group number N by the equations $n = N$ ($N \leq 4$), and $n = 18 - N$ for $N > 14$. By contrast, oxygen elicited an increasing valence in the highest normal oxide of each element and this was directly related to the group number, i.e. M_2O , MO , M_2O_3 , . . . , M_2O_7 . These periodic regularities find a ready explanation in terms of the electronic configuration of the elements and simple theories of chemical bonding. In more complicated chemical formulae involving more than 2 elements, it is convenient to define the "oxidation state" of an element as the formal charge remaining on the element when all other atoms have been removed as their normal ions. For example, nitrogen has an oxidation state of -3 in ammonium chloride [$\text{NH}_4\text{Cl} - (4\text{H}^+ + \text{Cl}^-) = \text{N}^{3-}$] and manganese

has an oxidation state of $+7$ in potassium permanganate {tetraoxomanganate(1-)} [$\text{KMnO}_4 - (\text{K}^+ + 4\text{O}^{2-}) = \text{Mn}^{7+}$]. For a compound such as Fe_3O_4 iron has an average oxidation state of $+2.67$ [i.e. $(4 \times 2)/3$] which may be thought of as comprising 1Fe^{2+} and 2Fe^{3+} . It should be emphasized that these charges are formal, not actual, and that the concept of oxidation state is not particularly helpful when considering predominantly covalent compounds (such as organic compounds) or highly catenated inorganic compounds such as S_7NH .

The periodicity in the oxidation state or valence shown by the elements was forcefully illustrated by Mendeleev in one of his early forms of the periodic system and this is shown in an extended form in Fig. 2.5 which incorporates more recent information. The predictive and interpolative powers of such a plot are obvious and have been a fruitful source of chemical experimentation for over a century.

Other periodic trends which occur in the chemical properties of the elements and which are discussed in more detail throughout later chapters are:

- (i) The "anomalous" properties of elements in the first short period (from lithium to fluorine) — see Chapters 4, 5, 6, 8, 11, 14 and 17.
- (ii) The "anomalies" in the post-transition element series (from gallium to bromine) related to the d-block contraction — see Chapters 7, 10, 13, 16 and 17.
- (iii) The effects of the lanthanide contraction — see Chapters 21–30.
- (iv) Diagonal relationships between lithium and magnesium, beryllium and aluminium, boron and silicon.
- (v) The so-called inert pair effect (see Chapters 7, 10 and 13) and the variation of oxidation state in the main group elements in steps of 2 (e.g. IF , IF_3 , IF_5 , IF_7).
- (vi) Variability in the oxidation state of transition elements in steps of 1.
- (vii) Trends in the basicity and electropositivity of elements — both vertical trends

within groups and horizontal trends along periods.

- (viii) Trends in bond type with position of the elements in the table and with oxidation state for a given element.
- (ix) Trends in stability of compounds and regularities in the methods used to extract the elements from their compounds.
- (x) Trends in the stability of coordination complexes and the electron-donor power of various series of ligands.

2.4 Prediction of New Elements and Compounds

Newlands (1864) was the first to predict correctly the existence of a “missing element” when he calculated an atomic weight of 73 for an element between silicon and tin, close to the present value of 72.61 for germanium (discovered by C. A. Winkler in 1886). However, his method of detecting potential triads was unreliable and he predicted (non-existent) elements between

rhodium and iridium, and between palladium and platinum. Mendeleev’s predictions 1869–71 were much more extensive and reliable, as indicated in the historical panel on p. 21. The depth of his insight and the power of his method remain impressive even today, but in the state of development of the subject in 1869 they were monumental. A comparison of the properties of eka-silicon predicted by Mendeleev and those determined experimentally for germanium is shown in Table 2.1. Similarly accurate predictions were made for eka-aluminium and gallium and for eka-boron and scandium.

Of the remaining 26 undiscovered elements between hydrogen and uranium, 11 were lanthanoids which Mendeleev’s system was unable to characterize because of their great chemical similarity and the new numerical feature dictated by the filling of the 4f orbitals. Only cerium, terbium and erbium were established with certainty in 1871, and the others (except promethium, 1945) were separated and identified in the period 1879–1907. The isolation of the (unpredicted) noble gases also occurred at this time (1894–8).

Table 2.1

| Mendeleev’s predictions (1871) for eka-silicon, M | Observed properties (1995) of germanium (discovered 1886) | | |
|---|--|---|---------------|
| Atomic weight | 72 | Atomic weight | 72.61(2) |
| Density/g cm ⁻³ | 5.5 | Density/g cm ⁻³ | 5.323 |
| Molar volume/cm ³ mol ⁻¹ | 13.1 | Molar volume/cm ³ mol ⁻¹ | 13.64 |
| MP/°C | high | MP/°C | 945 |
| Specific heat/J g ⁻¹ K ⁻¹ | 0.305 | Specific heat/J g ⁻¹ K ⁻¹ | 0.309 |
| Valence | 4 | Valence | 4 |
| Colour | dark grey | Colour | greyish-white |
| M will be obtained from MO ₂ or K ₂ MF ₆ by reaction with Na | | Ge is obtained by reaction of K ₂ GeF ₆ with Na | |
| M will be slightly attacked by acids such as HCl and will resist alkalis such as NaOH | | Ge is not dissolved by HCl or dilute NaOH but reacts with hot conc HNO ₃ | |
| M, on being heated, will form MO ₂ with high mp, and <i>d</i> 4.7 g cm ⁻³ | | Ge reacts with oxygen to give GeO ₂ , mp 1086°, <i>d</i> 4.228 g cm ⁻³ | |
| M will give a hydrated MO ₂ soluble in acid and easily reprecipitated | | “Ge(OH) ₄ ” dissolves in conc acid and is reprecipitated on dilution or addition of base | |
| MS ₂ will be insoluble in water but soluble in ammonium sulfide | | GeS ₂ is insoluble in water and dilute acid but readily soluble in ammonium sulfide | |
| MCl ₄ will be a volatile liquid with bp a little under 100°C and <i>d</i> 1.9 g cm ⁻³ | | GeCl ₄ is a volatile liquid with bp 83°C and <i>d</i> 1.8443 g cm ⁻³ | |
| M will form MEt ₄ bp 160°C | | GeEt ₄ bp 185°C | |

The isolation and identification of 4 radioactive elements in minute amounts took place at the turn of the century, and in each case the insight provided by the periodic classification into the predicted chemical properties of these elements proved invaluable. Marie Curie identified polonium in 1898 and, later in the same year working with Pierre Curie, isolated radium. Actinium followed in 1899 (A. Debierne) and the heaviest noble gas, radon, in 1900 (F. E. Dorn). Details will be found in later chapters which also recount the discoveries made in the present century of protactinium (O. Hahn and Lise Meitner, 1917), hafnium (D. Coster and G. von Hevesey, 1923), rhenium (W. Noddack, Ida Tacke and O. Berg, 1925), technetium (C. Perrier and E. Segré, 1937), francium (Marguerite Perey, 1939) and promethium (J. A. Marinsky, L. E. Glendenin and C. D. Coryell, 1945).

A further group of elements, the transuranium elements, has been synthesized by artificial nuclear reactions in the period from 1940 onwards; their relation to the periodic table is discussed fully in Chapter 31 and need not be repeated here. Perhaps even more striking today are the predictions, as yet unverified, for the properties of the currently non-existent superheavy elements.⁽⁹⁾ Elements up to lawrencium ($Z = 103$) are actinides (5f) and the 6d transition series starts with element 104. So far only elements 104–112 have been synthesized,⁽¹⁰⁾ and, because there is as yet no agreement on trivial names for some of these elements (see pp. 1280–1), they are here referred to by their atomic numbers. A systematic naming scheme was approved by IUPAC in 1977 but is not widely used by researchers in the field. It involves the use of three-letter symbols derived directly from the atomic number by using the

following numerical roots:

| | | | | | | | | | |
|-----|----|----|-----|------|------|-----|------|-----|-----|
| 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| nil | un | bi | tri | quad | pent | hex | sept | oct | enn |

These names and symbols can be used for elements 110 and beyond until agreed trivial names have been internationally approved. Hence, 110 is un-un-nilium (Uun), 111 is un-un-unium (Uuu), and 112 is un-un-bium, (Uub). These elements are increasingly unstable with respect to α -decay or spontaneous fission with half-lives of less than 1 s. It is therefore unlikely that much chemistry will ever be carried out on them though their ionization energies, mps, bps, densities, atomic and metallic radii, etc., have all been predicted. Element 112 is expected to be eka-mercury at the end of the 6d transition series, and should be, followed by the 7p and 8s configurations $Z = 113$ –120. On the basis of present theories of nuclear structure an “island of stability” is expected near element 114 with half-lives in the region of years. Much effort is being concentrated on attempts to make these elements, and oxidation states are expected to follow the main group trends (e.g. 113: eka-thallium mainly + 1). Other physical properties have been predicted by extrapolation of known periodic trends. Still heavier elements have been postulated, though it is unlikely (on present theories) that their chemistry will ever be studied because of their very short predicted half-lives. Calculated energy levels for the range $Z = 121$ –154 lead to the expectation of an unprecedented 5g series of 18 elements followed by fourteen 6f elements.

In addition to the prediction of new elements and their probable properties, the periodic table has proved invaluable in suggesting fruitful lines of research in the preparation of new compounds. Indeed, this mode of thinking is now so ingrained in the minds of chemists that they rarely pause to reflect how extraordinarily difficult their task would be if periodic trends were unknown. It is the ability to anticipate the effect of changing an element or a group in a compound which enables work to be planned effectively, though the prudent chemist is always alert to the possibility of

⁹ B. FRICKE, Superheavy elements, *Structure and Bonding* **21**, 89 (1975). A full account of the predicted stabilities and chemical properties of elements with atomic numbers in the range $Z = 104$ –184.

¹⁰ R. C. BARBER, N. N. GREENWOOD, A. Z. HRYNKIEWICZ, M. LEFORT, M. SAKAI, I. ULEHLA, A. H. WAPSTRA and D. H. WILKINSON, *Progr. in Particle and Nuclear Physics*, **29**, 453–530 (1992); also published in *Pure Appl. Chem.* **65**, 1757–824 (1993). See also §31.4.

new effects or unsuspected factors which might surprisingly intervene.

Typical examples taken from the developments of the past two or three decades include:

- (i) the organometallic chemistry of lithium and thallium (Chapters 4 and 7);
- (ii) the use of boron hydrides as ligands (Chapter 6);
- (iii) solvent systems and preparative chemistry based on the interhalogens (Chapter 17);

(iv) the development of the chemistry of xenon (Chapter 18);

(v) ferrocene — leading to ruthenocene and dibenzene chromium, etc. (Chapters 19, 25 and 23 respectively);

(vi) the development of solid-state chemistry.

Indeed, the influence of Mendeleev's fruitful generalization pervades the whole modern approach to the chemistry of the elements.