Modern inorganic chemistry

AN INTERMEDIATE TEXT

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The periodic table

DEVELOPMENT OF IDEAS

METALS AND NON-METALS

We now know of the existence of over one hundred elements. A century ago, more than sixty of these were already known, and naturally attempts were made to relate the properties of all these elements in some way. One obvious method was to classify them as metals and non-metals; but this clearly did not go far enough.

Among the metals, for example, sodium and potassium are similar to each other and form similar compounds. Copper and iron are also metals having similar chemical properties but these metals are clearly different from sodium and potassium—the latter being soft metals forming mainly colourless compounds, whilst copper and iron are hard metals and form mainly coloured compounds.

Among the non-metals, nitrogen and chlorine, for example, are gases, but phosphorus, which resembles nitrogen chemically, is a solid, as is iodine which chemically resembles chlorine. Clearly we have to consider the physical and chemical properties of the elements and their compounds if we are to establish a meaningful classification.

ATOMIC WEIGHTS

By 1850, values of atomic weights (now called relative atomic masses) had been ascertained for many elements, and a knowledge of these enabled Newlands in 1864 to postulate a *law of octaves*. When the elements were arranged in order of increasing atomic weight, each

successive eighth element was 'a kind of repetition of the first'. A few years later, Lothar Meyer and Mendeléef, independently, suggested that the *properties of elements are periodic functions of their atomic weights.* Lothar Meyer based his suggestion on the physical properties of the elements. He plotted 'atomic volume'—the volume (cm^3) of the

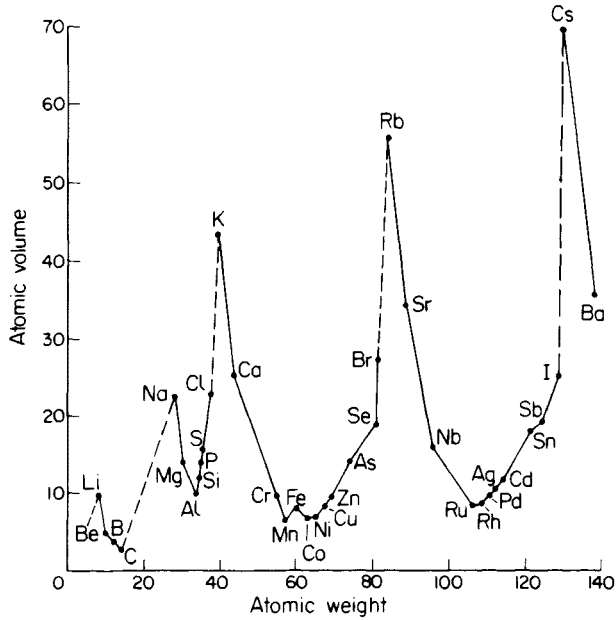


Figure 1.1. Atomic volume curve (Lothar Meyer)

atomic weight (g) of the solid element—against atomic weight. He obtained the graph shown in *Figure 1.1.* We shall see later that many other physical and chemical properties show periodicity (p. 15).

'VALENCY' AND CHEMICAL PROPERTIES

Mendeléef drew up a table of elements considering the chemical properties, notably the valencies, of the elements as exhibited in their oxides and hydrides. A part of Mendeléef's table is shown in *Figure 1.2*—note that he divided the elements into vertical columns called *groups* and into horizontal rows called *periods* or *series.* Most of the groups were further divided into sub-groups, for example Groups

IA. IB as shown. The element at the top of each group was called the 'head' element. Group VIII contained no head element, but was made up of a group of three elements of closely similar properties, called 'transitional triads'. Many of these terms, for example group, period and head element, are still used, although in a slightly different way from that of Mendeléef.

Group	I	II III IV V VI VII	VIII
	Li		–
	Na		–
A sub-group	K		Fe Co Ni
	Rb		Ru Rh Pd
	Cs		Os Ir Pt
	Fr*		
B sub-group	Cu		
	Ag		
	Au		

* Francium, unknown to Mendeléef, has been added

Figure 1.2. Arrangement of some elements according to Mendeléef

The periodic table of Mendeléef, and the physical periodicity typified by Lothar Meyer's atomic volume curve, were of immense value to the development of chemistry from the mid-nineteenth to early in the present century, despite the fact that the quantity chosen to show periodicity, the atomic weight, was not ideal. Indeed, Mendeléef had to deliberately transpose certain elements from their correct order of atomic weight to make them 'fit' into what were the obviously correct places in his table; argon and potassium, atomic weights 39.9 and 39.1 respectively, were reversed, as were iodine and tellurium, atomic weights 126.9 and 127.5. This rearrangement was later fully justified by the discovery of isotopes. Mendeléef's table gave a means of recognising relationships between the elements but gave no fundamental reasons for these relationships.

ATOMIC NUMBER

In 1913 the English physicist Moseley examined the spectrum produced when X-rays were directed at a metal target. He found that the frequencies ν of the observed lines obeyed the relationship

$$\nu = a(Z - b)^2$$

where a and b are constants. Z was a number, different for each metal, found to depend upon the position of the metal in the periodic table.

It increased by one unit from one element to the next, for example magnesium 12, aluminium 13. This is clearly seen in *Figure 1.3*. Z was called the *atomic number*; it was found to correspond to the charge on the nucleus of the atom (made up essentially of protons and neutrons), a charge equal and opposite to the number of extra nuclear

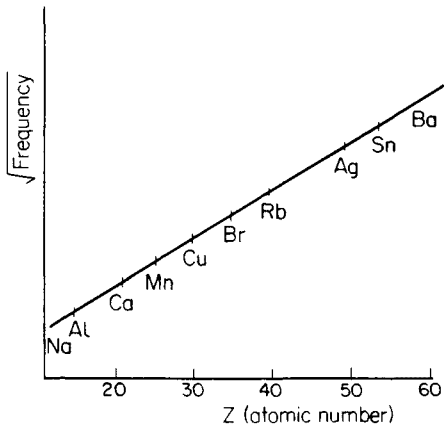


Figure 1.3. Variation of $(frequency)^{\frac{1}{2}}$ *with* Z

electrons in the atom. Here then was the fundamental quantity on which the periodic table was built.

ATOMIC SPECTRA

Studies of atomic spectra confirmed the basic periodic arrangement of elements as set out by Mendeléef and helped to develop this into the modern table shown in the figure in the inside cover of this book. When atoms of an element are excited, for example in an electric discharge or by an electric arc, energy in the form of radiation is emitted. This radiation can be analysed by means of a spectrograph into a series of lines called an *atomic spectrum*. Part of the spectrum of hydrogen is shown in *Figure 1.4*. The lines shown are observed in the visible region and are called the Balmer series after their

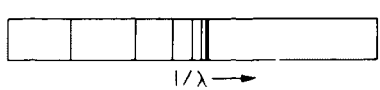


Figure 1.4. A part of the atomic spectrum of hydrogen (λ = *wavelength*)

discoverer. Several series of lines are observed, all of which fit the formula

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

where R is a constant (the Rydberg constant), λ the wavelength of the radiation, and n_1 and n_2 have whole number values dependent upon the series studied, as shown below:

Series	n_1	n_2
Lyman	1	2, 3, 4, . . .
Balmer	2	3, 4, 5, 6, . . .
Paschen	3	4, 5, 6, 7, . . .
Brackett	4	5, 6, 7, 8, . . .

The spectra of the atoms of other elements also consist of similar series, although much overlapping makes them less simple in appearance.

THE BOHR MODEL

To explain these regularities, the Danish physicist Bohr (again in 1913) suggested that the electrons in an atom existed in certain definite *energy levels*; electrons moving between these levels emit or absorb energy corresponding to the particular frequencies which appear in the spectrum. As a model for his calculations, Bohr envisaged an atom as having electrons in circular orbits, each orbit corresponding to a particular energy state. The 'orbit' model accurately interpreted the spectrum of hydrogen but was less successful for other elements. Hydrogen, the simplest atom, is made up of a proton (nucleus) and an electron. The electron normally exists in the lowest energy state E_1, but may be excited from this lowest state, called the ground state, by absorption of energy and reach a higher energy state $E_2, E_3 \ldots$, always such that the energy change E_n is given by $E_n = constant/n^2$ where n is a whole number called a *quantum number*. In Bohr's model, the n values corresponded to different orbits, an orbit with radius r_1 corresponded to $n = 1$, r_2 to $n = 2$ and so on.

Improved spectroscopic methods showed that the spectrum of hydrogen contained many more lines than was originally supposed and that some of these lines were split further into yet more lines when

the excited hydrogen was placed in a magnetic field. An attempt was made to explain these lines using a modified Bohr model with elliptical orbits but this was only partially successful and the model was eventually abandoned.

WAVE-MECHANICS

With the failure of the Bohr model it was found that the properties of an electron in an atom had to be described in wave-mechanical terms (p. 54). Each Bohr model energy level corresponding to $n = 1, 2, 3, \ldots$ is split into a group of subsidiary levels designated by the letters *s*, *p*, *d*, *f*. The number n therefore became the number of a quantum level made up of a set of *orbitals* (p. 54). Interpretation of the effect of a magnetic or electric field on the spectra required that the *p*, *d* and *f* orbitals must also be subdivided so that finally each 'subdivision energy level' can accommodate only two electrons, these being described by the symbols ↑ and ↓ (representing electrons of opposite spin). Each electron can have, therefore, a unique description, its spin and its energy level or orbital. We can summarise the data for the first three quantum levels briefly as shown in *Table 1.1*.

Table 1.1
ELECTRONS IN THE FIRST THREE QUANTUM LEVELS

Orbital	*Quantum level*		
	1	2	3
s	↑↓	↑↓	↑↓
p		↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓
d			↑↓ ↑↓ ↑↓ ↑↓ ↑↓
Total	2	8	18

Note. The maximum number of electrons that any quantum level can accommodate is seen to be given by the formula $2n^2$ where n is the number of the quantum level, for example $n = 3$: the maximum number of electrons is therefore 18.

An orbital is characterised by having a single energy level able to accommodate two electrons. The three *p* orbitals and five *d* orbitals are given symbols to differentiate them, for example p_x, p_y, p_z representing three orbitals at right angles each capable of containing two electrons.

THE MODERN PERIODIC TABLE

The close similarity of the atomic spectra of other atoms to that of hydrogen indicates that, as we progressively increase the number of protons in the nucleus and the extranuclear electrons in the atom for a series of elements of increasing atomic number, the additional electrons enter orbitals of the type originally suggested by wave-mechanics for hydrogen. The orbitals are filled in order of ascending energy and when several equivalent energy levels are available, each is occupied by a single electron before any pairing of electrons with opposed spin occurs.

The order of increasing energy for the orbitals can be deduced from the modern periodic table although for elements of high atomic number (when the electron energy levels are close together) the precise positioning of an electron may be rather uncertain. The filling of the energy levels for the first ten elements, hydrogen to neon, atomic numbers 1–10 is shown in *Table 1.2*.

Table 1.2
ELECTRONIC CONFIGURATIONS OF THE ELEMENTS HYDROGEN TO NEON

	1*s*	2*s*	2*p*		
H	↑				
He	↑ ↓				
Li	↑ ↓	↑			
Be	↑ ↓	↑ ↓			
B	↑ ↓	↑ ↓	↑		
C	↑ ↓	↑ ↓	↑	↑	
N	↑ ↓	↑ ↓	↑	↑	↑
O	↑ ↓	↑ ↓	↑ ↓	↑	↑
F	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑
Ne	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓

We notice here that the first energy level, quantum number $n = 1$, is complete at helium and there is only one orbital the 1*s* (first quantum level, *s* type orbital). When this is full ($1s^2$), we may call it the helium core. Filling of the quantum level begins at lithium; at beryllium the 2*s* orbital is filled and the next added electron must go into a 2*p* orbital. All three 2*p* orbitals have the same energy in the absence of a magnetic or electric field and fill up singly at first—elements boron to nitrogen—before the electrons 'pair up'. (The effect of pairing on the ionisation energy is further discussed on page 16.) The $n = 2$ quantum level is completed at neon, and again we may use 'neon core' for short.

For the next elements, sodium to argon, the $n = 3$ quantum level fills up in the same way as the $n = 2$ quantum level. This is shown in *Table 1.3*.

Reference to the modern periodic table (p. *(i)*) shows that we have now completed the first three periods—the so-called 'short' periods. But we should note that the $n = 3$ quantum level can still accommodate 10 more electrons.

Table 1.3
ELECTRONIC CONFIGURATIONS OF THE ELEMENTS SODIUM TO ARGON

Atomic number	*Element*	1s	2s	2p	3s	3p	*Notation*
11	Na	↑↓	↑↓	↑↓↑↓↑↓	↑		Ne core $3s^1$
12	Mg	i.e. neon core			↑↓		Ne core $3s^2$
13	Al				↑↓	↑	Ne core $3s^2 3p^1$
14	Si				↑↓	↑↑	Ne core $3s^2 3p^2$
15	P				↑↓	↑↑↑	Ne core $3s^2 3p^3$
16	S				↑↓	↑↓↑↑	Ne core $3s^2 3p^4$
17	Cl				↑↓	↑↓↑↓↑	Ne core $3s^2 3p^5$
18	Ar				↑↓	↑↓↑↓↑↓	$1s^2 2s^2 2p^6 3s^2 3p^6$

The element of atomic number 19 is potassium, strongly resembling both sodium and lithium in its physical and chemical properties. The atomic spectrum of potassium also confirms its position as a Group I element with an electronic configuration resembling that of sodium. These facts indicate that the extra electron in potassium must be placed in a new quantum level and it is therefore ascribed the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ (i.e. 2, 8, 8, 1). Similar reasoning leads to calcium being given an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ (i.e. 2, 8, 8, 2).

The following series of 10 elements, atomic numbers 21–30 inclusive, are all metals, indicating that they probably have the outer electronic configuration of a metal, i.e. 4 or less outer electrons. This is only possible if these electrons are placed in the inner $n = 3$ quantum level, entering the vacant *3d* orbitals and forming a series of 'transition' metals. We should note that at zinc, atomic number 30, the $n = 3$ quantum level is complete and filling of the $n = 4$ quantum level is resumed with electrons entering the *4p* orbitals. The electronic configurations for elements atomic numbers 19–36 are shown in *Table 1.4*.

Krypton is found to be an extremely unreactive element indicating that it has a stable electronic configuration despite the fact that the $n = 4$ quantum level can accommodate 24 more electrons in the *d* and *f* orbitals.

Table 1.4

ELECTRONIC CONFIGURATION OF THE ELEMENTS POTASSIUM TO KRYPTON

Atomic number	*Element*	1s 2s 3s 3p	3d	4s	4p
19	K			↑	
20	Ca			↑↓	
21	Sc		↑	↑↓	
22	Ti		↑ ↑	↑↓	
23	V		↑ ↑ ↑	↑↓	
*24	Cr		↑ ↑ ↑ ↑ ↑	↑↓	
25	Mn		↑ ↑ ↑ ↑ ↑	↑↓	
26	Fe		↑↓ ↑ ↑ ↑ ↑	↑↓	
27	Co	Argon	↑↓ ↑↓ ↑ ↑ ↑	↑↓	
28	Ni	core	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓	
*29	Cu		↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	
30	Zn		↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	
31	Ga		↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑
32	Ge		↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑ ↑
33	As		↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑
34	Se		↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑
35	Br		↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑
36	Kr		↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓

* The tendency to attain either a half filled or fully filled set of *d* orbitals at the expense of the outer *s* orbital is shown by both chromium and copper and should be noted. This apparent irregularity will be discussed in more detail in Chapter 13.

Note. The electronic configuration of any element can easily be obtained from the periodic table by adding up the numbers of electrons in the various quantum levels. We can express these in several ways, for example electronic configuration of nickel can be written as $1s^2 2s^2 2p^6 3s^6 3d^8 4s^2$, or more briefly ('neon core') $3d^8 4s^2$, or even more simply as 2. 8. 14. 2.

Chemical properties and spectroscopic data support the view that in the elements rubidium to xenon, atomic numbers 37–54, the 5*s*, 4*d* 5*p* levels fill up. This is best seen by reference to the modern periodic table p. (*i*). Note that at the end of the fifth period the $n = 4$ quantum level contains 18 electrons but still has a vacant set of $4f$ orbitals.

The detailed electronic configurations for the elements atomic numbers 55–86 can be obtained from the periodic table and are shown below in *Table 1.5*.

Note that the filling of the $4f$ orbitals begins after lanthanum (57) and the 14 elements cerium to lutetium are called the *lanthanides* (Chapter 15). The electronic configuration of some of the newly discovered elements with atomic numbers greater than 95 are uncertain as the energy levels are close together. Filling of the $5f$ orbitals does begin after actinium (89) and the remaining elements are generally referred to as *actinides* (Chapter 15).

Table 1.5

ELECTRONIC CONFIGURATIONS OF THE ELEMENTS CAESIUM TO LAWRENCIUM

Element	*Atomic number*	1*s*	2*s* 2*p*	3*s* 3*p* 3*d*	4*s* 4*p* 4*d* 4*f*	5*s* 5*p* 5*d* 5*f*	6*s* 6*p* 6*d* 6*f*	7*s*
Cs	55	2	2 6	2 6 10	2 6 10	2 6	1	
Ba	56	2	2 6	2 6 10	2 6 10	2 6	2	
La	57	2	2 6	2 6 10	2 6 10	2 6 1	2	
Ce	58	2	2 6	2 6 10	2 6 10 (2)	2 6	(2)	
Pr	59	2	2 6	2 6 10	2 6 10 (3)	2 6	(2)	
Nd	60	2	2 2	2 6 10	2 6 10 (4)	2 6	(2)	
Pm	61	2	2 6	2 6 10	2 6 10 (5)	2 6	(2)	
Sm	62	2	2 6	2 6 10	2 6 10 6	2 6	2	
Eu	63	2	2 6	2 6 10	2 6 10 7	2 6	2	
Gd	64	2	2 6	2 6 10	2 6 10 (7)	2 6 (1)	2	
Tb	65	2	2 6	2 6 10	2 6 10 (8)	2 6 (1)	2	
Dy	66	2	2 6	2 6 10	2 6 10 (10)	2 6	(2)	
Ho	67	2	2 6	2 6 10	2 6 10 (11)	2 6	(2)	
Er	68	2	2 6	2 6 10	2 6 10 (12)	2 6	(2)	
Tm	69	2	2 6	2 6 10	2 6 10 13	2 6	2	
Yb	70	2	2 6	2 6 10	2 6 10 14	2 6	2	
Lu	71	2	2 6	2 6 10	2 6 10 14	2 6 1	2	
Hf	72	2	2 6	2 6 10	2 6 10 14	2 6 2	2	
Ta	73	2	2 6	2 6 10	2 6 10 14	2 6 3	2	
W	74	2	2 6	2 6 10	2 6 10 14	2 6 4	2	
Re	75	2	2 6	2 6 10	2 6 10 14	2 6 5	2	
Os	76	2	2 6	2 6 10	2 6 10 14	2 6 6	2	

Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt	78	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	(1)	(2)
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	(2)	(2)
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	(2)	2	6	(1)	(2)
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	(3)	2	6	(1)	(2)
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	(5)	2	6		(2)
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	(6)	2	6		(2)
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	(7)	2	6		(2)
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	(7)	2	6	(1)	(2)
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	(8)	2	6	(1)	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	(10)	2	6		2
Es	99	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2

FEATURES OF THE PERIODIC TABLE

1. Chemical, physical and spectroscopic data all suggest a periodic table as shown on p. *(i)*.

2. The maximum number of electrons which a given quantum level can accommodate is given by the formula $2n^2$ where n is the quantum level number.

3. Except for the $n = 1$ quantum level the maximum number of electrons in the outermost quantum level of any period is always eight. At this point the element concerned is one of the noble gases (Chapter 12).

4. Elements in the *s* and *p* blocks of the table are referred to as *typical elements* whilst those in the *d* block are called '*transition elements*' and those in the *f* block are called *actinides* and *lanthanides* (or 'rare earth' elements).

5. The table contains vertical *groups* of elements; each member of a group having the same number of electrons in the outermost quantum level. For example, the element immediately before each noble gas, with seven electrons in the outermost quantum level, is always a halogen. The element immediately following a noble gas, with one electron in a new quantum level, is an alkali metal (lithium, sodium, potassium, rubidium, caesium, francium).

6. The periodic table also contains horizontal *periods* of elements, each period beginning with an element with an outermost electron in a previously empty quantum level and ending with a noble gas. Periods 1, 2 and 3 are called *short* periods, the remaining are *long* periods; Periods 4 and 5 containing a series of transition elements whilst 6 and 7 contain both a transition and a 'rare earth' series.

7. Comparison of the original Mendeléef type of periodic table (*Figure 1.2*) and the modern periodic table (p. *(i)*) shows that the original group numbers are retained but Group I, for example, now contains only the alkali metals, i.e. it corresponds to the top two Group I elements of the Mendeléef table together with Group IA. At the other end of the table, Group VII now contains only the halogens, i.e. the original Group VIIB. The transition elements, in which the inner *d* orbitals are being filled, are removed to the centre of the table and the 'rare earth' elements, in which the *f* orbitals are being filled, are placed, for convenience, at the bottom of the table, eliminating the necessity for further horizontal expansion of the whole table.

The original lettering of the transition metal groups, for example VIB, VIIB and so on is still used, but is sometimes misleading and clearly incomplete. However, we may usefully refer, for example, to

Group IIB and know that this means the group of elements zinc, cadmium and mercury, whilst Group IIA refers to the alkaline earth metals beryllium, magnesium, calcium, barium and strontium.

When Mendeléef devised his periodic table the noble gases were unknown. Strictly, their properties indicate that they form a group beyond the halogens. Mendeléef had already used 'Group VIII' to describe his 'transitional triads' and the noble gases were therefore placed in a new Group O.

8. The transition or *d* block elements, in which electrons enter inner *d* orbitals, form a well-defined series with many common and characteristic features. They are all metals; those on the right of the block are softer and have lower melting points than those on the left (*Table 13.2*, p. 360). Many are sufficiently resistant to oxidation, corrosion and wear to make them useful in everyday life. They have similar ionisation energies (*Figure 1.6*), often give ions of variable valency, and readily form complexes (pp. 46, 362) many of which are coloured. However, regular gradations of behaviour, either across a series or down a group are much less apparent than in the typical *s* and *p* block elements. The elements at the end of each transition series—copper and zinc in Period 4, silver and cadmium in Period 5 and gold and mercury in Period 6—have *d* orbitals which are filled. When copper and silver form the copper(I) ion Cu^+ and the silver ion Ag^+ respectively, and zinc and cadmium the ions Zn^{2+} and Cd^{2+} respectively, the inner *d* orbitals remain filled. Are these elements and ions properly called 'transition' elements and ions? We shall see in Chapters 13 and 14 that their properties are in some respects intermediate between those characteristic of a transition metal and a non-transition metal. Thus zinc, for example, is like calcium in some of its compounds but like a transition metal in others. Again, silver has some properties like an alkali metal but also has 'transition-like' properties.

The elements gold and mercury show little resemblance to any non-transition metals, but their 'transition-like' properties are not much like those of other transition metals either. In the older Mendeléef form of the periodic table, the elements copper, silver and gold—often called the 'coinage' metals—occupied Group IB, and zinc, cadmium and mercury Group IIB, these being subdivisions of Groups I and II respectively. However, there are no really very good grounds for treating these two trios as groups; copper, silver and gold have few resemblances, and Group IB does not resemble Group IA—the alkali metals. These six elements obviously present a problem; usually they are treated as transition metals or separately as 'the B metals'.

9. The lanthanides and the subsequently discovered actinides do

not fit into the Mendeléef table and can only be fitted into the modern table by expanding it sideways to an inconvenient degree. They are, therefore, placed separately at the bottom of the table. These two series of elements are now recognised as being *inner* transition elements, when electrons enter a quantum level two units below that of the outer. Many properties depend upon the outer electronic configurations and hence we can correctly predict that the lanthanides and actinides are two series of closely similar elements.

10. In noting changes of properties down the typical element groups I–VII of the periodic table, it soon becomes apparent that frequently the top or *head element* in each group does not fall into line with the other elements below it. This is clearly seen when we consider the melting points and boiling points of elements and their compounds (p. 17), and when we come to look at the properties of the individual groups in detail we shall see that the head element and its compounds are often exceptional in both physical and chemical properties. It will be sufficient to note here that *all* the head elements in Period 2, namely lithium, beryllium, boron, carbon, nitrogen, oxygen and fluorine, have one characteristic in common—they cannot expand their electron shells. The elements of Periods 3 onwards have vacant *d* orbitals, and we shall see that these can be used to increase the valency of the elements concerned—but in Period 2 the valency is limited.

Unlike 'typical element' groups the 'transition metal' groups do not have head elements.

11. Although the head element of each group is often exceptional in its properties, it does often show a resemblance to the element one place to its right in the period below, i.e. Period 3. Thus lithium resembles magnesium both physically and chemically. Similarly beryllium resembles aluminium and boron resembles silicon but the resemblances of carbon to phosphorus and nitrogen to sulphur are less marked. Oxygen, however, does resemble chlorine in many respects. These are examples of what is sometimes called the *diagonal relationship* in the periodic table.

12. By reference to the outline periodic table shown on p. (*i*) we see that the metals and non-metals occupy fairly distinct regions of the table. The metals can be further sub-divided into (a) 'soft' metals, which are easily deformed and commonly used in moulding, for example, aluminium, lead, mercury, (b) the 'engineering' metals, for example iron, manganese and chromium, many of which are transition elements, and (c) the light metals which have low densities and are found in Groups IA and IIA.

IMPORTANT PROPERTIES WHICH SHOW A PERIODIC FUNCTION

IONISATION ENERGY

Reference has already been made to Lothar Meyer's plot of 'atomic volume' against atomic weight as a demonstration of a physical property of the elements and *Figure 1.5* shows a modern plot of 'atomic volume' against atomic number. Although regularities are clearly observable 'atomic volume' has no single meaning for all the elements—certainly it does *not* measure atomic size, a quantity which depends on the state of aggregation of the element. There are, however, more fundamental physical properties which show periodicity.

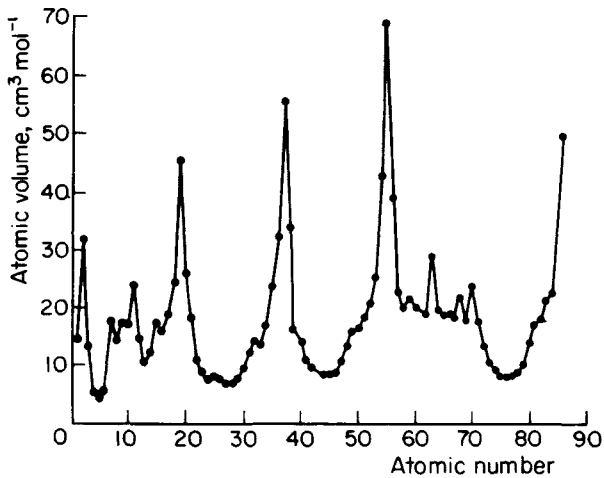


Figure 1.5. Atomic volume and atomic number

One of these is the first ionisation energy. This is the energy needed to remove one electron from a free atom of the element, i.e. for the process:

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

where M is the element atom. A plot of first ionisation energy against atomic number is shown in *Figure 1.6* (units of ionisation energy are kJ mol^{-1}).

Clearly the general tendency is for metals to have low ionisation energies and non-metals to have rather high ionisation energies. We should also note that the first ionisation energies *rise* as we cross a

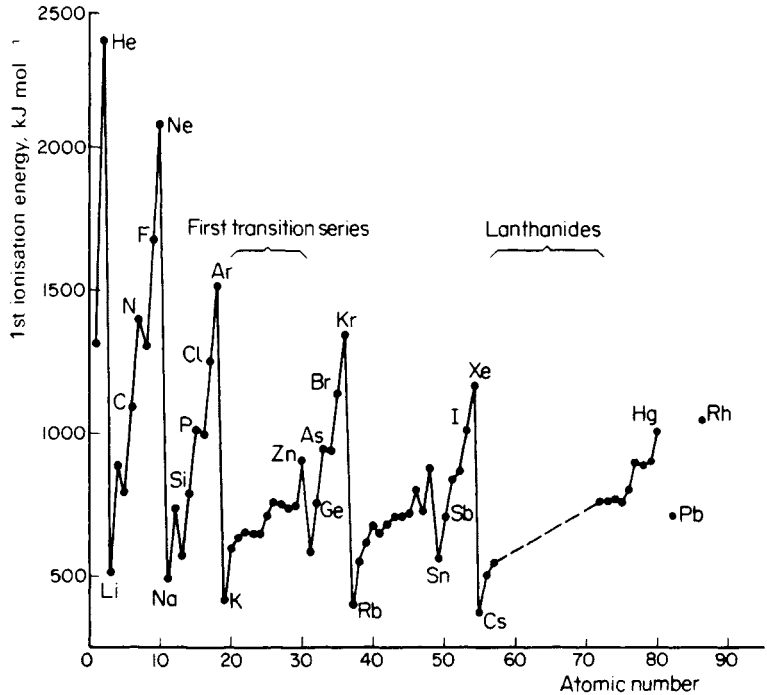


Figure 1.6. First ionisation energies of the elements

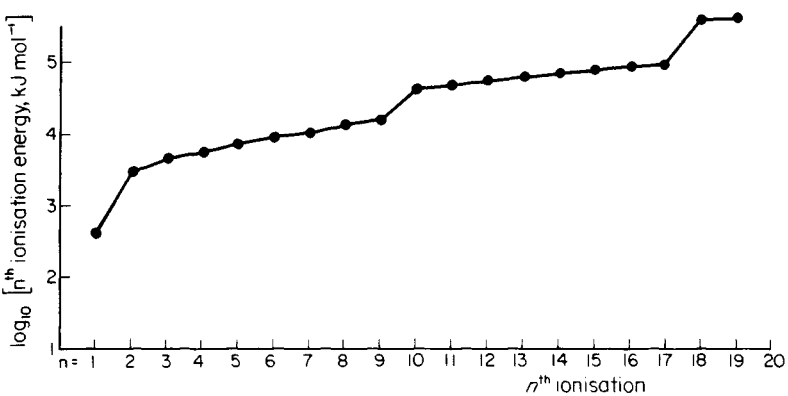
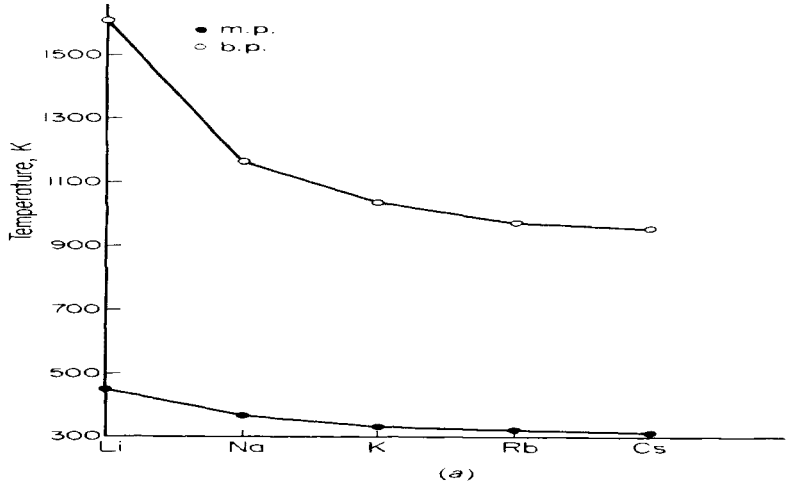


Figure 1.7. Successive ionisation energies for potassium

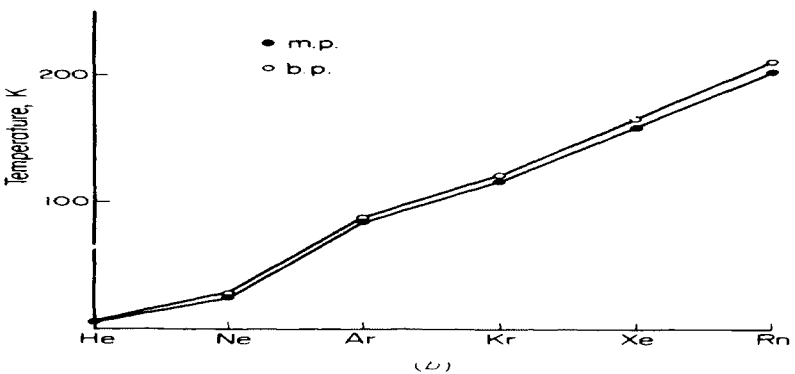
period, although not quite regularly, and *fall* as we descend a group, for example lithium to caesium. The fall in ionisation energy as we descend a group is associated with the change from non-metallic to metallic character and is very clearly shown by the Group IV elements, carbon, silicon, germanium and tin. Here then is a link between the physico-chemical property ionisation energy and those chemical properties which depend on the degree of metallic (electropositive) character of the elements in the group.

If we consider the *successive* (first, second, third . . .) ionisation energies for any one atom, further confirmation of the periodicity of the electron quantum levels is obtained. *Figure 1.7* shows a graph of $\log_{10}$ (ionisation energy) for the successive removal of 1, 2, 3, . . . 19 electrons from the potassium atom (the log scale is used because the changes in energy are so large). The stabilities of the noble gas configurations at the 18 (argon), 10)neon) and 2 (helium) levels are clearly seen. The subject of ionisation energies is further discussed in Chapters 2 and 3.

MELTING AND BOILING POINTS


m.p.
b.p.
Temperature, K
1500
1300
1100
900
700
500
300
Li
Na
K
Rb
Cs

(a)


m.p.
b.p.
Temperature, K
200
100
He
Ne
Ar
Kr
Xe
Rn

(b)

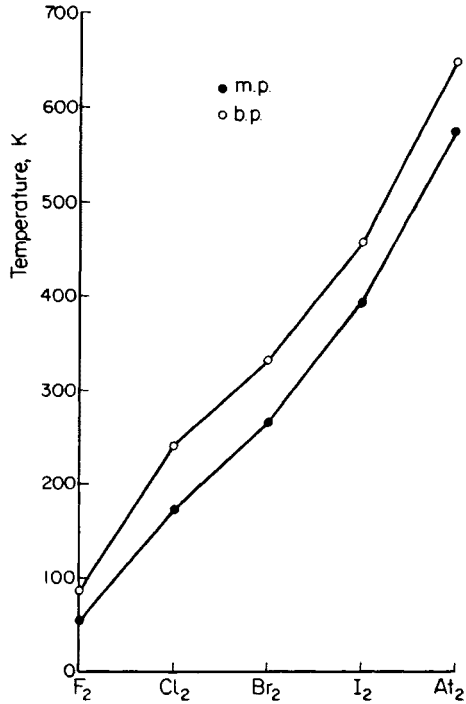


Figure 1.8. (*a*) *M.p. and b.p. of Group IA metals,* (*b*) *m.p. and b.p. of Group O elements,* (*c*) *m.p. and b.p. of the halogens*

Table 1.6
PERIOD 3

Group	I	II	III	IV	V	VI	VII
Fluorides	NaF	MgF_2	AlF_3	SiF_4	PF_5	SF_6	ClF_3
Oxides	Na_2O	MgO	Al_2O_3	SiO_2	$(P_2O_5)_2$	SO_3	Cl_2O_7
Hydrides	NaH	MgH_2	(AlH_3)	SiH_4	PH_3	SH_2	ClH

Table 1.7
PERIOD 4

Group	I	II	III	IV	V	VI	VII
Fluorides	KF	CaF_2	GaF_3	GeF_4	AsF_5		
Oxides	K_2O	CaO	Ga_2O_3	GeO_2	$(As_2O_5)_2$	SeO_3	
Hydrides	KH	CaH_2	GaH_3	GeH_4	AsH_3	SeH_2	BrH

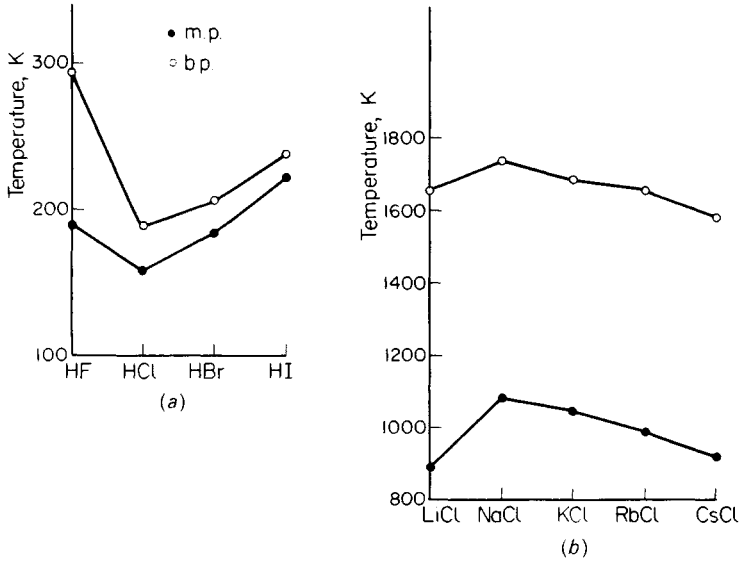


Figure 1.9. (a) M.p. and b.p. of the halogen hydrides HX. *(b) m.p. and b.p. of the Group IA chlorides*

VALENCY

Mendeléef based his original table on the valencies of the elements. Listed in *Tables 1.6* and *1.7* are the highest valency fluorides, oxides and hydrides formed by the typical elements in Periods 3 and 4.

From the tables it is clear that elements in Groups I–IV can display a valency equal to the group number. In Groups V–VII, however, a group valency equal to the group number (x) can be shown in the oxides and fluorides (except chlorine) but a lower valency ($8 - x$) is displayed in the hydrides. This lower valency ($8 - x$) is also found in compounds of the head elements of Groups V–VII.

CHEMICAL CHARACTER

In any group of the periodic table we have already noted that the number of electrons in the outermost shell is the same for each element and the ionisation energy falls as the group is descended. This immediately predicts two likely properties of the elements in a group: (a) their general similarity and (b) the trend towards metallic behaviour as the group is descended. We shall see that these predicted properties are borne out when we study the individual groups.

Increasing metallic—electropositive—behaviour down a group also implies a change in the character of the oxides. They will be expected to become more basic as we descend the group and a change from an acidic oxide, i.e. an oxide of a non-metal which readily reacts with OH^- or oxide ions to give oxoacid *anions*, to a basic oxide, i.e. one which readily yields *cations*, in some groups. The best example of such a change is shown by the Group IV elements; the oxides of carbon and silicon are acidic, readily forming carbonate and silicate anions, whilst those of tin and lead are basic giving such ions as Sn^{2+} and Pb^{2+} in acidic solution. Metallic character diminishes across a period and in consequence the oxides become *more* acidic as we cross a given period. This is clearly demonstrated in Period 3:

Na_2O MgO	Al_2O_3	SiO_2 $(P_2O_5)_2$ SO_3 Cl_2O_7
← Basic	Amphoteric	← Acidic →

Similar trends are shown by all periods except Period 1.

USES OF THE PERIODIC TABLE

The most obvious use of the table is that it avoids the necessity for acquiring a detailed knowledge of the individual chemistry of each element. If, for example, we know something of the chemistry of (say) sodium, we can immediately predict the chemistry of the other alkali metals, bearing in mind the trends in properties down the group, and the likelihood that lithium, the head element, may be unusual in certain of its properties. In general, therefore, a knowledge of the properties of the third period elements sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine and argon, is most useful in predicting the properties of the typical elements below Period 3.

As regards the transition elements, the first row in particular show some common characteristics which define a substantial part of their chemistry; the elements of the lanthanide and actinide series show an even closer resemblance to each other.

One of the early triumphs of the Mendeléef Periodic Table was the prediction of the properties of elements which were then unknown. Fifteen years before the discovery of germanium in 1886, Mendeléef had predicted that the element which he called 'ekasilicon' would be discovered, and he had also correctly predicted many of its properties. In *Table 1.8* his predicted properties are compared with the corresponding properties actually found for germanium.

Until relatively recently there were other obvious gaps in the

periodic table, one corresponding to the element of atomic number 87, situated at the foot of Group IA, and another to the element of atomic number 85, at the foot of the halogen group (VIIB). Both of these elements were subsequently found to occur as the products from either natural radioactive decay or from artificial nuclear reactions. Both elements are highly radioactive and even the most stable isotopes have very short half lives; hence only minute quantities of the compounds of either francium or astatine can be accumulated.

Table 1.8
PREDICTED PROPERTIES OF GERMANIUM

Property	*Predicted for Ekasilicon (Es) 1871*	*Found for Germanium 1886*
Relative atomic mass	72	72.32
Density ($g\ cm^{-3}$)	5.5	5.47_{293K}
Colour	Dirty grey	Greyish-white
Heat in air	White EsO_2	White GeO_2
Action of acids	Slight	None by HCl(aq)
Preparation	$EsO_2 + Na$	$GeO_2 + C$
Tetrachloride	b.p. 373 K, density 1.9 $g\ cm^{-3}$	b.p. 360 K, density 1.89 $g\ cm^{-3}$

Taking francium as an example, it was *assumed* that the minute traces of francium ion Fr^+ could be separated from other ions in solution by co-precipitation with insoluble caesium chlorate (VII) (perchlorate) because francium lies next to caesium in Group IA. This assumption proved to be correct and francium was separated by this method. Similarly, separation of astatine as the astatide ion At^- was achieved by co-precipitation on silver iodide because silver astatide AgAt was also expected to be insoluble.

It is an interesting speculation as to how much more difficult the isolation of these two elements might have been if the periodic classification had not provided us with a very good 'preview' of their chemistries.

QUESTIONS

1. What do you regard as the important oxidation states of the following elements:

(a) ~~chlorine~~. Iodine
(b) ~~lead.~~ Potassium

(c) sulphur.
(d) iron?

Illustrate, for each valency given, the electronic structure of a compound in which the element displays that valency.

Discuss, as far as possible, how far the valencies chosen are in agreement with expectations in the light of the position of these elements in the Periodic Table. (L, S)

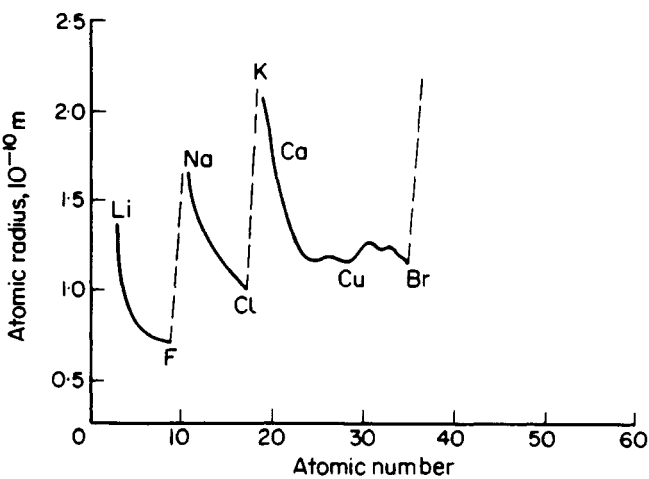
2. How, and why, do the following vary along the period sodium to argon:

(a) the relative ease of ionisation of the element,
(b) the physical nature of the element,
(c) the action of water on the hydrides? (C, A)

3. A century ago, Mendeléef used his new periodic table to predict the properties of 'ekasilicon', later identified as germanium. Some of the predicted properties were: metallic character and high m.p. for the element; formation of an oxide MO_2 and of a volatile chloride MCl_4.

(a) Explain how these predictions might be justified in terms of modern ideas about structure and valency.
(b) Give as many other 'predictions' as you can about the chemistry of germanium, with reasons. (Liverpool B.Sc., Part I)

4. The following graph shows the variation in atomic radius with increasing atomic number:



(a) What deduction can you make from this graph?
(b) Continue the graph to element 60(Nd), and mark on it the approximate positions of the elements
  (i) Ag (element 47),
  (ii) I (element 53),
  (iii) Ba (element 56)
(c) Explain briefly
  (i) the decrease in atomic radius from Li to F,
  (ii) the increase in atomic radius from F to Br,
  (iii) the very large atomic radii of the alkali metals, Li to K.

(JMB, A)

5. Give the electronic configurations of elements with atomic numbers, 7, 11, 17, 20, 26, 30 and 36.

In each case give the oxidation state (or states) you expect each element to exhibit.

6. Explain the terms,

(a) typical element
(b) transition element,
(c) rare earth element,
(d) group,
(e) period,
(f) diagonal relationship,

as applied to the periodic table of elements.
In each case give examples to illustrate your answer.