

## 5 PERIODIC PROPERTIES OF ELEMENTS

One of the greatest intellectual achievement in chemistry is the periodic table of the elements. The periodic table can be printed on a single sheet of paper, but what it contains and can teach us is enormous and beyond measure.

The periodic table is the outcome of continuous effort, beginning in ancient Greece, to understand the true nature of matter. It can rightly be called the Bible of chemistry. The value of the periodic table is not only in its organization of known information, but also in its ability to predict unknown properties. The true greatness of the periodic table lies in that ability.

### 5.1 Periodic table

#### (a) Proposals before Mendeleev

The concept of elements is very old, dating back to ancient Greece. According to the Greek philosophers, matter was made up of four elements: earth, water, fire and air. That view gradually declined, and in the 17<sup>th</sup> century, the definition of elements by the British chemist Robert Boyle (1627-1691) replaced it. Boyle stated that **elements** are substances that cannot be decomposed into simpler substances.

Lavoisier proposed a list of elements in his principal work “*Traite Elementire de Chemie*”. Though he included light and heat in the list, the other members of the list were what we accept as elements today. In addition, he added to the list some elements that had not yet been detected but whose existence he presumed. For instance, chlorine had not yet been isolated, but he added it to the list as the radical of muriatic acid<sup>a)</sup>. Similarly, sodium and potassium were listed.

In the early 19<sup>th</sup> century, these elements were isolated by means of electrolysis, and the list of elements gradually expanded. In the middle of the 19<sup>th</sup> century, spectroscopic analysis, a new method of detecting elements was introduced and accelerated the expansion of the list. Although welcomed by chemists, new problems arose. One was the question “Is there any limitation on the number of elements?” and the other was “Should we expect any kind of regularity in the properties of elements?”

The discovery of new elements catalysed such discussions. When iodine was discovered in 1826, the German chemist Johann Wolfgang Döbereiner (1780-1849) noticed the similarity between this new element and the already known elements chlorine and bromine. He also detected other trios of similar elements. This is the “**triad**” theory of Döbereiner.

**Table 5.1** Triads by Döbereiner

lithium (Li)	calcium (Ca)	chlorine (Cl)	sulfur (S)	manganese (Mn)
sodium (Na)	strontium (Sr)	bromine (Br)	selenium (Se)	chromium (Cr)
potassium (K)	barium (Ba)	iodine (I)	tellurium (Te)	iron (Fe)

#### (b) Predictions by Mendeleev and their fulfillment

Many other ideas were proposed but nonesatisfied the scholarly world of that day. However, the theory proposed by the Russian chemist Dmitrij Ivanovich Mendeleev (1834-1907), and independently by the German chemist Julius Lothar Meyer (1830-1895) differed from other theories and was more persuasive. Their common viewpoint is stated below.

#### The viewpoint of Mendeleev and Meyer

- (1) The list of elements known at that time is not necessarily complete.
- (2) It is expected that the properties of elements vary systematically. Hence the properties of unknown elements can be predicted.

<sup>a)</sup> the old name of hydrochloric acid

Initially the theory of Mendeleev failed to attract much attention. In 1875, however, it was shown that a new element gallium discovered by the French chemist Paul Emile Lecoq de Boisbaudran (1838-1912) was none other than *eka*-aluminum whose existence and properties had been predicted by Mendeleev. Thus, the significance of the theory of Mendeleev and Meyer was gradually accepted. Table 5.2 gives the properties predicted by Mendeleev for the unknown element *eka*-silicon and those for germanium discovered by the German chemist Clemens Alexander Winkler (1838-1904).

**Table 5.2** Predictions of properties by Mendeleev and comparison with actual results

property	eka-silicon	germanium
atomic weight	72	72.32
specific gravity	5.5	5.47
atomic volume	13	13.22
valence	4	4
specific heat	0.073	0.076
specific gravity of dioxide	4.7	4.703
boiling point of tetrachloride (°C)	<100	86

Mendeleev published a table that might be regarded as the origin of the modern periodic table. In preparing the table, Mendeleev initially arranged the elements in the order of their atomic weights, as his predecessors had. However, he pointed out the periodicity of properties, and sometimes rearranged the elements, thus reversing the order based on atomic weights.

Furthermore, the situation was complicated because the procedure for determining the atomic weights had not yet been standardized, and sometimes chemists might use different atomic weights for one and the same element. This troublesome dilemma was gradually improved after the 1<sup>st</sup> International Chemical Congress<sup>a)</sup> which Mendeleev attended, yet difficulties still remained.

By depending on valence in determining atomic weights, Mendeleev circumvented the problem to some extent (Table 5.3).

**Table 5.3** Early periodic table by Mendeleev (1869)

			K = 39	Rb = 85	Cs = 133	—	—
			Ca = 40	Sr = 87	Ba = 137	—	—
			—	? Yt = 88?	? Di = 138?	Er = 178?	—
			Ti = 48?	Zr = 90	Ce = 140?	? La = 180?	Th = 231
			V = 51	Nb = 94	—	Ta = 182	—
			Cr = 52	Mo = 96	—	W = 184	U = 240
			Mn = 55	—	—	—	—
			Fe = 56	Ru = 104	—	Os = 195?	—
			Co = 59	Rh = 104	—	Ir = 197	—
			Ni = 59	Pd = 106	—	Pt = 198?	—
			Cu = 63	Ag = 108	—	Au = 199?	—
			Zn = 65	Cd = 112	—	Hg = 200	—
			—	In = 113	—	Tl = 204	—
			—	Sn = 118	—	Pb = 207	—
			As = 75	Sb = 122	—	Bi = 208	—
			Se = 78	Te = 125?	—	—	—
			Br = 80	J = 127	—	—	—
Typische Elemente							
H = 1	Li = 7	Na = 23					
	Be = 9,4	Mg = 24					
	B = 11	Al = 27,3					
	C = 12	Si = 28					
	N = 14	P = 31					
	O = 16	S = 32					
	F = 19	Cl = 35,5					

### (c) Periodic table and electron configuration

The periodic table continuously expanded after the proposal of Mendeleev. Meanwhile

<sup>a)</sup> The Congress was held in 1860 at Karlsruhe, Germany. The purpose of the Congress was to discuss the problem of the unification of atomic weight. On this occasion Cannizzaro introduced the theory of Avogadro.

**Table 5.4a** Electron configuration of atoms ( ${}_1\text{H}$ - ${}_{54}\text{Xe}$ )

period	element	K		L		M			N			O				
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	
1	1 H	1														
	2 He	2														
2	3 Li	2	1													
	4 Be	2	2													
	5 B	2	2	1												
	6 C	2	2	2												
	7 N	2	2	3												
	8 O	2	2	4												
	9 F	2	2	5												
	10 Ne	2	2	6												
	3	11 Na	2	2	6	1										
		12 Mg	2	2	6	2										
13 Al		2	2	6	2	1										
14 Si		2	2	6	2	2										
15 P		2	2	6	2	3										
16 S		2	2	6	2	4										
17 Cl		2	2	6	2	5										
18 Ar		2	2	6	2	6										
4		19 K	2	2	6	2	6	1								
		20 Ca	2	2	6	2	6	2								
	21 Sc	2	2	6	2	6	1	2								
	22 Ti	2	2	6	2	6	2	2								
	23 V	2	2	6	2	6	3	2								
	24 Cr	2	2	6	2	6	5	1								
	25 Mn	2	2	6	2	6	5	2								
	26 Fe	2	2	6	2	6	6	2								
	27 Co	2	2	6	2	6	7	2								
	28 Ni	2	2	6	2	6	8	2								
	29 Cu	2	2	6	2	6	10	1								
	30 Zn	2	2	6	2	6	10	2								
	31 Ga	2	2	6	2	6	10	2	1							
	32 Ge	2	2	6	2	6	10	2	2							
	33 As	2	2	6	2	6	10	2	3							
	34 Se	2	2	6	2	6	10	2	4							
	35 Br	2	2	6	2	6	10	2	5							
	36 Kr	2	2	6	2	6	10	2	6							
5	37 Rb	2	2	6	2	6	10	2	6					1		
	38 Sr	2	2	6	2	6	10	2	6					2		
	39 Y	2	2	6	2	6	10	2	6	1				2		
	40 Zr	2	2	6	2	6	10	2	6	2				2		
	41 Nb	2	2	6	2	6	10	2	6	4				1		
	42 Mo	2	2	6	2	6	10	2	6	5				1		
	43 Tc	2	2	6	2	6	10	2	6	6				1		
	44 Ru	2	2	6	2	6	10	2	6	7				1		
	45 Rh	2	2	6	2	6	10	2	6	8				1		
	46 Pd	2	2	6	2	6	10	2	6	10						
	47 Ag	2	2	6	2	6	10	2	6	10				1		
	48 Cd	2	2	6	2	6	10	2	6	10				2		
	49 In	2	2	6	2	6	10	2	6	10				2	1	
	50 Sn	2	2	6	2	6	10	2	6	10				2	2	
	51 Sb	2	2	6	2	6	10	2	6	10				2	3	
	52 Te	2	2	6	2	6	10	2	6	10				2	4	
	53 I	2	2	6	2	6	10	2	6	10				2	5	
	54 Xe	2	2	6	2	6	10	2	6	10				2	6	

several problems arose. One important problem was how to deal with rare gases, transition elements and **rare earth elements**. All these problems were nicely solved and made the periodic table more valuable. The periodic table, being the Bible of chemistry, should be consulted frequently.

The new entry for the unreactive rare gases was conveniently inserted between the very reactive positive elements, the alkaline metals (group 1) and the very reactive negative elements, halogens (group 7).

Transition metal elements were accommodated in the periodic table by introducing the **long period** though the rationale was not quite clear. The real problem was the lanthanoids. They were treated as “extra” elements and were placed marginally out of the main body of the periodic table. However, in fact that procedure did not solve the main problem. First of all, why such extra elements existed was not clear at all; even more puzzling was the question: as to whether there was any limitation on the number of elements? Since very similar elements existed, it was very difficult to judge how many elements could exist.

The Bohr theory and experiments by Moseley yielded theoretical solution of these problems. The explanation of the periodic table from the 1<sup>st</sup> period to the 3<sup>rd</sup> period could be explained by the theory of electron configuration described in Ch. 4. The 1<sup>st</sup> period ( ${}_1\text{H}$  and  ${}_2\text{He}$ ) corresponds to the

process in which electrons are going to occupy the 1s orbital. Similarly the 2<sup>nd</sup> period (from <sub>3</sub>Li to <sub>10</sub>Ne)

**Table 5.4b** Electron configuration of atoms (<sub>55</sub>Cs-<sub>103</sub>Lr)

period	element	K		L			M			N				O				P			Q
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s		
6	55 Cs	2	2	6	2	6	10	2	6	10	2	6			2	6			1		
	56 Ba	2	2	6	2	6	10	2	6	10	2	6			2	6			2		
	57 La	2	2	6	2	6	10	2	6	10	2	6		1	2	6			2		
	58 Ce	2	2	6	2	6	10	2	6	10	1	2	6	1	2	6			2		
	59 Pr	2	2	6	2	6	10	2	6	10	3	2	6		2	6			2		
	60 Nd	2	2	6	2	6	10	2	6	10	4	2	6		2	6			2		
	61 Pm	2	2	6	2	6	10	2	6	10	5	2	6		2	6			2		
	62 Sm	2	2	6	2	6	10	2	6	10	6	2	6		2	6			2		
	63 Eu	2	2	6	2	6	10	2	6	10	7	2	6		2	6			2		
	64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1	2	6			2		
	65 Tb	2	2	6	2	6	10	2	6	10	9	2	6		2	6			2		
	66 Dy	2	2	6	2	6	10	2	6	10	10	2	6		2	6			2		
	67 Ho	2	2	6	2	6	10	2	6	10	11	2	6		2	6			2		
	68 Er	2	2	6	2	6	10	2	6	10	12	2	6		2	6			2		
	69 Tm	2	2	6	2	6	10	2	6	10	13	2	6		2	6			2		
	70 Yb	2	2	6	2	6	10	2	6	10	14	2	6		2	6			2		
	71 Lu	2	2	6	2	6	10	2	6	10	14	2	6	1	2	6			2		
	72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2	2	6			2		
	73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3	2	6			2		
	74 W	2	2	6	2	6	10	2	6	10	14	2	6	4	2	6			2		
75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5	2	6			2			
76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6	2	6			2			
77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7	2	6			2			
78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9	1	2	6		1			
79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10	1	2	6		1			
80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6			2			
81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1		2	1		
82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2		2	2		
83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	3		2	3		
84 Po	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	4		2	4		
85 At	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	5		2	5		
86 Rn	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	6		2	6		
7	87 Fr	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6			2	6	
	88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6			2	6	
	89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1		2	6	
	90 Th	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2		2	6	
	91 Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1		2	6	
	92 U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6		2	6	
	93 Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6		2	6	
	94 Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2	6	
	95 Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2	6	
	96 Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2	6	
	97 Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2	6	
	98 Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	9	2	6	1	2	6	
	99 Es	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	1	2	6	
	100 Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	1	2	6	
101 Md	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	1	2	6		
102 No	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	1	2	6		
103 Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2	6		

corresponds to the occupation of the 1s, 2s and 2p orbitals by electrons, and the 3<sup>rd</sup> period (from <sub>11</sub>Na to <sub>18</sub>Ar) to the occupation of the 1s, 2s, 2p, 3s and 3p orbitals.

The long period begins with the 4<sup>th</sup> period. The explanation for it is that the shape of d orbitals differ greatly from a circle, and hence the energy of 3d electrons is even higher than that of 4s electrons. As a result, in the 4<sup>th</sup> period, electrons will occupy the 4s orbital (<sub>19</sub>K and <sub>20</sub>Ca) immediately after occupying the 3s and 3p orbitals, skipping over the 3d orbital. Then electrons begin to occupy the five 3d orbitals. This process corresponds to the ten elements from <sub>21</sub>Sc to <sub>30</sub>Zn. The process of the occupation of the 4p orbitals that then ensued corresponds to the six elements from <sub>31</sub>Ga to <sub>36</sub>Kr. This is the reason why the 4<sup>th</sup> period contains eighteen elements rather than eight. The energy of electrons in the 4f orbitals is much higher than that in 4d orbitals and hence 4f electrons do not play any role in the 4<sup>th</sup> period.

The 5<sup>th</sup> period resembles the 4<sup>th</sup> period. The electrons will occupy the 5s, 4d and 5p orbitals in that order. Consequently the 5<sup>th</sup> period will have eighteen elements. The 4f orbitals are not involved yet and this is the reason why the number of elements in the 5<sup>th</sup> period is eighteen.

The number of elements included in the 6th period is now thirty-two because the  $7 \times 2 = 14$  elements corresponding to the occupation of the 4f orbitals are included. At first electrons occupy the 6s orbital (<sub>55</sub>Cs and <sub>56</sub>Ba). Though there is some exception, the elements from <sub>57</sub>La to <sub>80</sub>Hg

correspond to the occupation of the 4f and then the 5d orbitals. The **lanthanoid** (to  ${}_{71}\text{Lu}$ ) series of rare earth elements correspond to the occupation of the 4f orbitals. After this process, six main group elements ( ${}_{81}\text{Tl}$  to  ${}_{86}\text{Rn}$ ) follow which corresponds to the occupation of the 6p orbitals.

The 7<sup>th</sup> period starts from the occupation of the 7s orbital ( ${}_{87}\text{Fr}$  and  ${}_{88}\text{Ra}$ ) followed by the filling of the 5f orbitals to yield the **actinoid** series of rare earth elements (from  ${}_{89}\text{Ac}$  to element no. 103). The world of elements is going to expand a little further, but among naturally occurring elements, the element with the largest atomic number is  ${}_{92}\text{U}$ . Elements beyond  ${}_{92}\text{U}$  are artificial elements with very short half-lives. It is not easy to foretell the extent of the list of such elements, but it is most likely that new elements will have very short half-lives.

In Table 5.5, the relation between the periodic table and electron configuration is summarized.

**Table 5.5** Electron configuration of each period

period	orbitals filled	number of elements
1 (short)	1s	2
2 (short)	2s, 2p	2 + 6 = 8
3 (short)	3s, 3p	2 + 6 = 8
4 (long)	3d, 4s, 4p	2 + 6 + 10 = 18
5 (long)	4d, 5s, 5p	2 + 6 + 10 = 18
6 (long)	4f, 5d, 6s, 6p	2 + 6 + 10 + 14 = 32

### Sample exercise 5.1 Electron configuration of lawrencium

The electron configuration of  ${}_{89}\text{Ac}$  is  ${}_{86}\text{Rn}.6d^17s^2$ . Propose the electron configuration of lawrencium  ${}_{103}\text{Lr}$ .

#### Answer

Lawrencium has fourteen more electrons as compared with actinium. Since these electrons will occupy the 5f orbitals, the electron configuration of  ${}_{103}\text{Lr}$  is  ${}_{86}\text{Rn}.5f^{14}6d^17s^2$ .

As previously described, Moseley's law states that there is the following relation between the wavelength  $\lambda$  of the characteristic X-ray of the element and the electric charge of its nucleus  $Z$  (*i.e.*, atomic number):

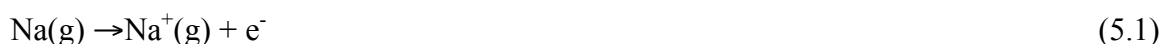
$$1/\lambda = c(Z - s)^2 \quad (2.11)$$

Thanks to Moseley's law, the elements can now be roll-called by atomic number. We are now able to know the exact number of elements in nature.

## 5.2 Periodic nature of the properties of simple bodies

### (1) First ionization energy

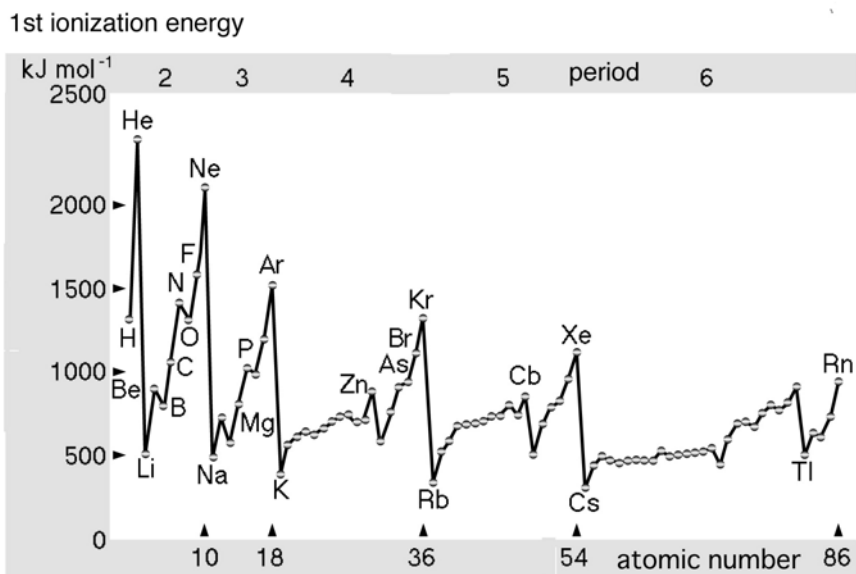
When the elements were arranged according to their atomic weights, the properties of simple bodies or compounds exhibited some periodicity, and this observation led to the discovery of the periodic law. The electron configuration of elements influences not only the chemical properties of elements but also their physical properties. The periodicity is clearly demonstrated because the ionization energy of atoms is directly governed by the electron configuration. The **ionization energy** is defined as the heat of reaction required to remove an electron from a neutral atom, for example, sodium:



The **1<sup>st</sup> ionization energy**, the energy required to remove the 1<sup>st</sup> electron, shows a remarkable periodicity as is clearly shown in Fig. 5.1. For any period, the ionization energy increases as the

atomic number increases to reach the maximum value that for the rare gas. In the same group, the ionization energy decreases as the atomic number increases. Such tendencies can be explained in terms of the number of valence electrons, the nuclear charge, and the number of inner shell electrons.

The 2<sup>nd</sup> and 3<sup>rd</sup> ionization energies are defined as the energies required to remove the 2<sup>nd</sup> and 3<sup>rd</sup> electrons.



**Figure 5.1** First ionization energy of atoms

For every period, the energy is a minimum for the alkaline metal, and a maximum for the rare gases.

### Sample Exercise 5.2 Ionization energy

Three atoms have the electron configurations shown below.

- (1)  $1s^2 2s^2 2p^6$
- (2)  $1s^2 2s^2 2p^6 3s^1$
- (3)  $1s^2 2s^2 2p^6 3s^2$

Which of the three atoms has the highest 1<sup>st</sup> ionization energy? Propose which atom may have the highest 2<sup>nd</sup> ionization energy?

#### Answer

Atom (1) has the closed electron shell, and should have the highest ionization energy. Atoms (2) and (3) are sodium and magnesium, respectively. The second electron to be removed is a 2p electron for Na but a 3s electron for Mg. You can surmise that the outer electron is easier to remove as compared with the inner electron.

### (b) Electron affinity and electronegativity

Electron affinity is defined as the heat of reaction in which an electron is added to a gaseous neutral atom, *e.g.*,



A positive value indicates an exothermic reaction, a negative value an endothermic reaction. Since there are not many atoms, that can add an electron in the gas phase, the available data is limited as compared with that for ionization energies. Table 5.6 indicates that the electron affinity is in general larger for nonmetals than for metals.

**Table 5.6** Electron affinity of atoms

H 72.4	C 122.5	F 322.3
Li 59.	O 141.8	Cl 348.3
Na 54.0	P 72.4	Br 324.2
K 48.2	S 200.7	I 295.2

The magnitude of (electron) negativity is defined by **electronegativity** (Table 5.7), which is a measure of an atom's ability to hold electrons. The American chemist Robert Sanderson Mulliken (1896-1986) defined **electronegativity** as proportional to the arithmetic mean of the ionization energy and the electron affinity.

**Table 5.7** Electronegativity of main group elements (Pauling)

H 2.1						
Li 0.97	Be 1.5	B 2.0	C 2.5	N 3.1	O 3.5	F 4.1
Na 1.0	Mg 1.2	Al 1.5	Si 1.7	P 2.1	S 2.4	Cl 2.8
K 0.90	Ca 1.0	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.7
Rb 0.89	Sr 1.0	In 1.5	Sn 1.72	Sb 1.82	Te 2.0	I 2.2
Cs 0.86	Ba 0.97	Tl 1.4	Pb 1.5	Bi 1.7	Po 1.8	At 1.9

Pauling defined the difference of electronegativity between two atoms A and B as the difference in bond energies of the diatomic molecules AB, AA and BB. Suppose  $D(A-B)$ ,  $D(A-A)$  and  $D(B-B)$  are the bond energies for AB, AA and BB, respectively.  $D(A-B)$  is larger than the geometric mean of both  $D(A-A)$  and  $D(B-B)$ . This is because hetero-diatomic molecules are in general more stable than homo-diatomic molecules due to the contribution of ionic structure. Consequently,  $\Delta(A-B)$ , as defined below, is positive.

$$\Delta(A-B) = D(A-B) - \sqrt{D(A-A)D(B-B)} > 0 \quad (5.3)$$

$\Delta(A-B)$  will be larger as the ionic character of the bond is larger. Using these values, Pauling defined the electronegativity  $x$  as a measure of an atom's ability to attract electrons.

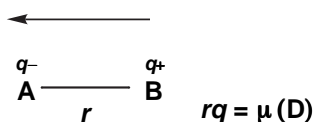
$$|x_A - x_B| = \sqrt{D(A-B)} \quad (5.4)$$

where  $x_A$  and  $x_B$  are the electronegativities of atoms A and B, respectively.

Regardless of which of two electronegativity scale one chooses, it is clear that the electronegativity increases going from left to right across a period and decreases going down the group for the main group elements. Electronegativity is very useful in understanding the chemical properties of the elements.

Much more useful information can be drawn from Table 5.7. The difference between the electronegativity of two bonding atoms can be, though only semi-quantitatively, correlated with such properties of chemical bonds as the dipole moment or the bond energy.

Suppose there is an unequal charge distribution in the A-B bond ( $x_A > x_B$ ). Pairs of positive and negative charges  $\pm q$  separated by distance  $r$  form, (electric) **dipoles**.



The direction of the dipole can be represented by an arrow pointing towards the negative charge center with the tail of the arrow at the positive center of the charge. The magnitude of the dipole,  $rq$ , is called the **dipole moment**. The dipole moment is a vector with the magnitude  $\mu$  and a direction. The magnitude can be determined by experiment but the direction cannot.

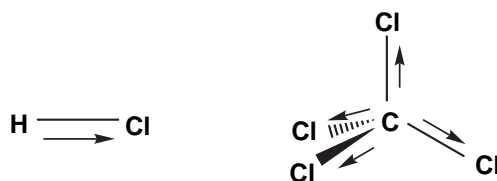
The dipole moment of a molecule (**molecular dipole moment**) is the vector sum of the dipole moment of each bond (**bond dipole moment**). If there is symmetry in the molecule, large bond dipole moments may cancel each other so that the molecular dipole moment will be small or even zero.

### Sample Exercise 5.3 Bond dipole moment and molecular dipole moment

- (a) Answer the following questions on hydrogen chloride HCl and carbon tetrachloride  $\text{CCl}_4$ . Show the direction of the bond dipole moment for each compound. Propose whether these have molecular dipole moments or not.
- (a) Carbon dioxide  $\text{CO}_2$  and sulfur trioxide  $\text{SO}_3$  do not have molecular dipole moments. Propose the molecular structures of these compounds based on these observations.

#### Answer

- (a) The direction of the bond dipole moment is shown below. HCl should have a molecular dipole moment while  $\text{CCl}_4$  should not because the bond dipole moments cancel each other.



- (a) Both compounds should have symmetry in order that the large C-O and S-O bond dipole moments cancel each other. Hence,  $\text{CO}_2$  is linear while  $\text{SO}_3$  is a triangle.

### (c) The oxidation number of atoms

There is a clear relation between the **oxidation number** (or **oxidation state**) of each atom and its position in the periodic table. Oxidation numbers of the atoms in a covalent compound are defined as the imaginary charges the atoms would have if the shared electrons were divided equally between identical atoms bonded to each other or, for different atoms, were all assigned to the atom in each bond that has the greater attraction for electrons.

#### (1) Main group elements

For main group elements, the oxidation numbers are in most cases the number of electrons the atom will lose or gain to attain the closed shell state,  $ns^2np^6$  (except in the 1<sup>st</sup> period) or  $nd^{10}$  electron configuration (Fig. 5.2).

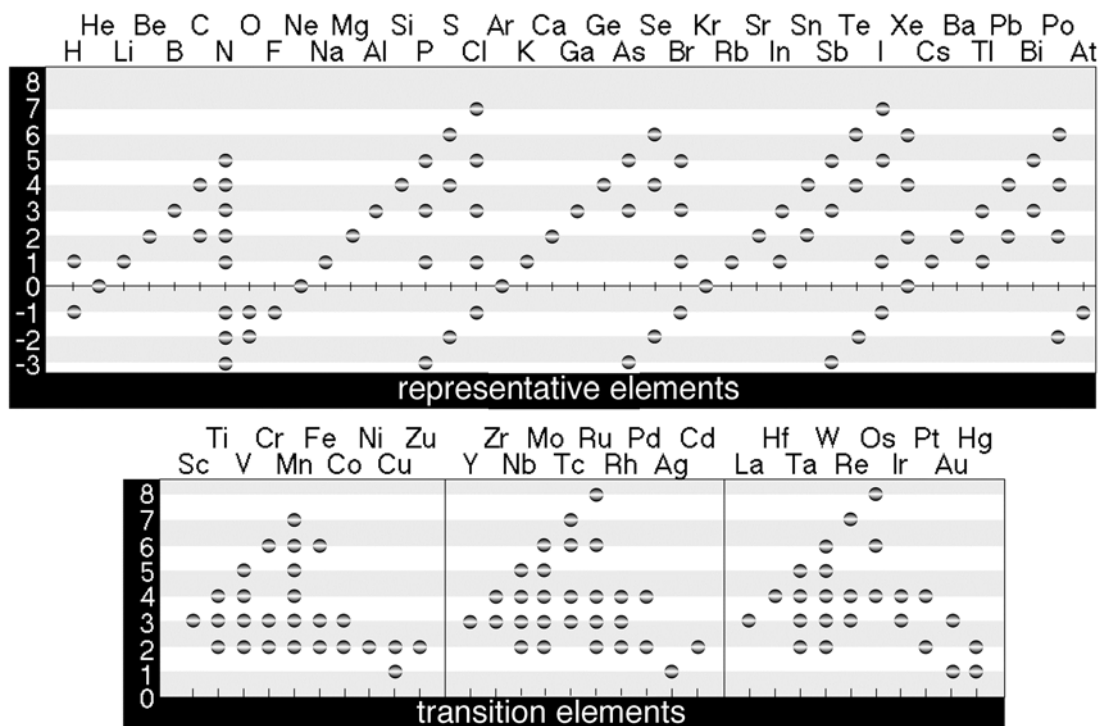
This is clear for the low period elements belonging to the 1<sup>st</sup>, 2<sup>nd</sup> and 13<sup>th</sup>-18<sup>th</sup> groups. For high period elements, these tend to have oxidation numbers corresponding to the electron configuration in which  $ns$  electrons are retained but  $np$  electrons are lost. For instance, tin Sn and lead Pb, both group 14 elements, have the oxidation number +2 by losing  $np^2$  electrons but retaining  $ns^2$  electrons, in addition to the oxidation number +4. The same reason is applied for the fact that phosphorous P and bismuth Bi, both group 15 elements with  $ns^2np^3$  electron configuration, have the oxidation numbers +3 and +5.

Generally speaking, the importance of the oxidation state in which  $ns^2$  electrons are retained will become more and more important for the higher period elements. For nitrogen and phosphorus compounds, the oxidation number of +5 is important, while for bismuth the oxidation number of +3



is dominant, and that of +5 is rather rare.

Metals and semimetal elements (silicon Si or germanium Ge) seldom have negative values, but these are common for nonmetal elements. In hydrides of nitrogen and phosphorus,  $\text{NH}_3$  and  $\text{PH}_3$ , the oxidation number of N and P are  $-3$  for each. The higher period elements lose this property and bismuth Bi does not have any negative oxidation number. Among group 16 elements, the oxidation number of  $-2$  is important as is the case with oxygen O. This tendency again gradually decreases among higher period elements. For instance oxygen has only negative oxidation numbers but sulfur S has positive oxidation numbers such as  $+4$  and  $+6$  which are significant.



**Figure 5.2** Oxidation numbers of elements

The number and values of oxidation number an element can have are various, but the highest oxidation number does exhibit periodicity.

#### Sample Exercise 5.4 Oxidation numbers of atoms

Find the oxidation numbers of the elements indicated below.

- (1)  $\text{MnSO}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{MnO}_4^-$ ,  $\text{MnO}_4^{2-}$  (Mn)
- (2)  $\text{As}_2\text{O}_3$ ,  $\text{AsO}_2^-$ ,  $\text{AsO}_4^{3-}$ ,  $\text{AsH}_3$  (As)
- (3)  $\text{I}^-$ ,  $\text{IO}^-$ ,  $\text{IO}_3^-$ ,  $\text{I}_2$ ,  $\text{ICl}_3$ ,  $\text{ICl}_2^-$  (I)

#### Answer

- (1)  $+2$ ,  $+3$ ,  $+4$ ,  $+7$ ,  $+6$
- (2)  $+3$ ,  $+3$ ,  $+5$ ,  $-3$
- (3)  $-1$ ,  $+1$ ,  $+5$ ,  $0$ ,  $+3$  (electronegativity of Cl is larger than that of I)

#### (2) Transition elements

Though transition elements have several oxidation numbers, a regularity can be recognized. The highest oxidation number of atoms which have five electrons as a maximum in the d orbital corresponds to the state where all of these d electrons (in addition to an s electron) are lost. Thus, in the case of scandium which has an electron configuration of  $(n-1)d^1ns^2$ , the highest oxidation number is 3. Manganese has an electron configuration of  $(n-1)d^5ns^2$ , and hence the highest oxidation number is  $+7$ .

If the number of d electrons exceeds 5, the situation is changed. For iron Fe with the electron

configuration of  $(n-1)d^6ns^2$ , the principal oxidation numbers are +2 and +3. Very rarely is the oxidation number +6. The highest oxidation number of important transition elements such as cobalt Co, Nickel Ni, copper Cu and zinc Zn is lower than the oxidation number of atoms which has lost all of their  $(n-1)d$  and  $ns$  electrons. Among the elements belonging to the same group, the higher oxidation number is more important for the elements belonging to the higher period.

#### (d) The size of atoms and ions

When Meyer plotted the **atomic volume** defined as the volume of 1 mole of the given element (atomic weight/density) against the atomic number he obtained a saw-toothed plot. This is clear evidence that the atomic volume shows a periodicity. Since it is rather difficult to determine the atomic volume of all elements with an identical standard, this correlation has to remain more or less qualitative. However, Meyer's contribution in attracting attention to the periodicity of atomic size is noteworthy.

There remains necessarily some ambiguity if you want to determine the size of an atom itself because the electron cloud does not have a distinct boundary. For the size of a metal atom, we can determine its **atomic radius** by dividing the interatomic distance measured by X-ray crystallographic analysis by two. It must be pointed out that the value thus obtained depends on the crystal form (*e.g.*, simple cubic lattice or face-centered cubic lattice, *etc.*) and this will cause some ambiguity. The same problem remains in the determination of the **ionic radius** as determined by the X-ray crystallographic analysis of ionic crystals.

The general periodicity is evident as is shown in Fig. 5.3 which shows the atomic and ionic radii of main atoms and ions. For example, ionic radii of cations belonging to the same group decrease as the atomic number increases. This is reasonable since a larger nuclear charge will attract electrons more strongly. As for the ionic radii, the higher the period, the larger is the ionic radius.

#### Sample Exercise 5.5 The size of atoms and ions

Choose the smallest one from each group of atoms or ions.

(1) Li, Na, K (2) P, Sb, As (3) S, Cl, Ar (4)  $O^+$ , O,  $O^-$

**Answer**

(1) Li (2) P (3) Cl (4)  $O^+$

group								
period	族 1	2	13	14	15	16	17	18
1	H 0.030							He 0.140
2	Li 0.152	Be 0.111	B 0.081	C 0.077	N 0.074	O 0.074	F 0.072	Ne 0.154
	Li <sup>+</sup> 0.090	Be <sup>2+</sup> 0.059				O <sup>2-</sup> 0.126	F <sup>-</sup> 0.119	
3	Na 0.186	Mg 0.160	Al 0.143	Si 0.117	P 0.110	S 0.104	Cl 0.099	Ar 0.188
	Na <sup>+</sup> 0.116	Mg <sup>2+</sup> 0.086	Al <sup>3+</sup> 0.068			S <sup>2-</sup> 0.170	Cl <sup>-</sup> 0.167	
4	K 0.231	Ca 0.197	Ga 0.122	Ge 0.122	As 0.121	Se 0.117	Br 0.114	Kr 0.202
	K <sup>+</sup> 0.152	Ca <sup>2+</sup> 0.114	Ga <sup>3+</sup> 0.076	Ge <sup>4+</sup> 0.067		Se <sup>2-</sup> 0.184	Br <sup>-</sup> 0.182	
5	Rb 0.247	Sr 0.215	In 0.163	Sn 0.141	Sb 0.145	Te 0.137	I 0.133	Xe 0.216
	Rb <sup>+</sup> 0.166	Sr <sup>2+</sup> 0.132	In <sup>3+</sup> 0.094	Sn <sup>4+</sup> 0.083		Te <sup>2-</sup> 0.207	I <sup>-</sup> 0.206	
6	Cs 0.266	Ba 0.217	Tl 0.170	Pb 0.175	Bi 0.156			
	Cs <sup>+</sup> 0.181	Ba <sup>2+</sup> 0.149	Tl <sup>3+</sup> 0.103	Pb <sup>4+</sup> 0.092				

**Figure 5.3** Atomic and ionic radii of main atoms and ions  
Because of transition elements, the change between the 3<sup>rd</sup> and 4<sup>th</sup> periods is rather large.

### 5.3 Periodicity of the properties of simple compounds

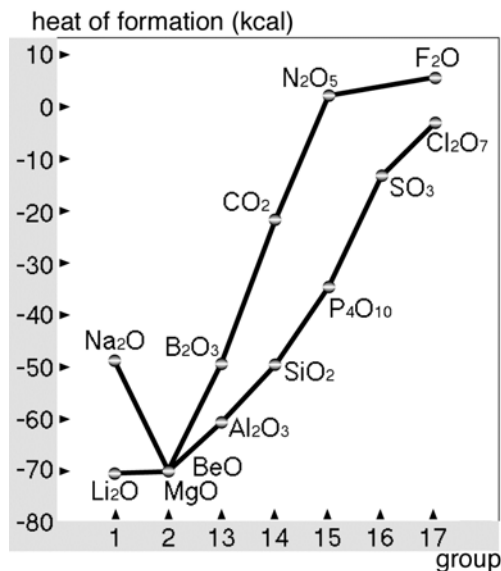
#### (a) Periodicity of the properties of oxides

Oxygen can form compounds (oxides) with almost all elements except a few of the rare gases. This is the reason why oxygen was once used as the standard for atomic weights. When the procedure for determining the atomic weight had not yet fully established, it was convenient and dependable to use “equivalent”, that is, the quantity of a substance that is just enough to react with a given amount of oxygen. Even today, comparing the properties of oxides is important as a measure for comparing the properties of elements.

Most heats of formation of oxides, that is, the heat of reaction in which a simple body reacts with oxygen, are large and negative. This indicates that there is at least one stable oxide. There are only a few oxides, such as those of the halogens or rare gases, that have a positive value of the heat

of formation.

In order to ascertain whether or not these values show periodicity, the heat of reaction in which the element reacts with a given amount (*e.g.*, 8 g) of oxygen should be considered rather than the heat of reaction per mole. The schematic representation of these values is given in Fig. 5.4. In all periods, the absolute value of the heat of formation tends to decrease as the atomic number increases.



**Figure 5.4** Heat of formation obtained from a reaction with a given quantity of oxygen. Periodicity is evident except for the alkaline metals.

It is convenient to classify oxides according to their acidity or basicity since almost all oxides are either acidic or basic. This will also help in understanding Ch. 9 where acidity and basicity are treated.

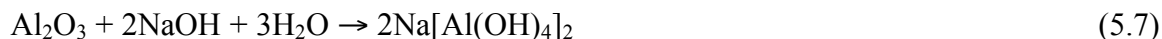
The reaction products between oxides and water generally have a hydroxy group. As will be discussed later, many oxides are acidic even if these do not have any hydrogen. In the case of the reaction product between an **acidic oxide** and water, the hydrogen of a hydroxy group tends to be dissociated as a proton. Thus, an acid in which acidic hydrogen is bonded to oxygen is called **oxoacid**. On the other hand, the reaction product between a basic oxide and water is named a hydroxide in which the hydroxy group tends to be dissociated as the hydroxide ion OH<sup>-</sup>.

Oxides of alkaline metals and alkaline earth metals are more or less soluble in water and exhibit basicity. Sodium oxide Na<sub>2</sub>O is a typical basic oxide. Thus,



where (aq) indicates an aqueous solution. Even if barely soluble in water, an oxide is a basic oxide if it can react with an acid.

The oxides of group 13 elements are reactive to both an acid and a base and are named **amphoteric oxides**. A well-known example is aluminum oxide Al<sub>2</sub>O<sub>3</sub>.



Most of the oxides of nonmetal elements are acidic. Their strength as acids increases going from left to right across a period of the periodic table. In other words, the acidity is stronger as the nonmetal property increases. As for group 14 elements, carbon has two oxides, CO and CO<sub>2</sub>, and the

acidity of  $\text{CO}_2$  is weak ( $\text{H}_2\text{CO}_3$  is a weak acid). Oxides of carbon are gaseous but oxides of silicon and of elements below silicon are solid.  $\text{SiO}_2$  is not soluble in water, but it is an acidic oxide since it reacts with a base.

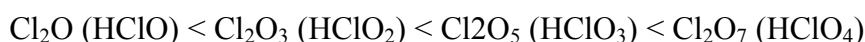


In contrast, many oxides of group 15 and 16 elements are soluble in water.  $\text{SO}_3$  and  $\text{P}_4\text{O}_{10}$  are acidic oxides since these react with water to give protons. For these elements, there are several oxides corresponding to different oxidation numbers. There are two oxides of sulfur with the oxidation numbers of +4 and +6. A typical example would be the oxides of nitrogen. In Table 5.8, a series of oxides of nitrogen and its hydride are listed. They will be discussed later.

**Table 5.8** Oxidation numbers of various nitrogen compounds

oxidation number of nitrogen	compound	molecular formula	Lewis structure
-3	ammonia	$\text{NH}_3$	$\begin{array}{c} \text{H} - \ddot{\text{N}} - \text{H} \\   \\ \text{H} \end{array}$
-2	hydrazine	$\text{N}_2\text{H}_4$	$\begin{array}{c} \text{H} - \ddot{\text{N}} - \ddot{\text{N}} - \text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
-1	hydroxylamine	$\text{NH}_2\text{OH}$	$\begin{array}{c} \text{H} - \ddot{\text{N}} - \ddot{\text{O}} - \text{H} \\   \\ \text{H} \end{array}$
0	nitrogen	$\text{N}_2$	$:\text{N} \equiv \text{N}:$
+1	dinitrogen oxide	$\text{N}_2\text{O}$	$:\ddot{\text{N}} = \text{N} = \ddot{\text{O}}:$
+2	nitrogen oxide	$\text{NO}$	$:\ddot{\text{N}} = \ddot{\text{O}}:$
+3	dinitrogen trioxide	$\text{N}_2\text{O}_3$	$\begin{array}{c} \ddot{\text{O}} \\ \diagdown \\ \text{N} - \ddot{\text{N}} = \ddot{\text{O}} \\ \diagup \\ \ddot{\text{O}} \end{array}$
+4	nitrogen dioxide	$\text{NO}_2$	$:\ddot{\text{O}} - \ddot{\text{N}} = \ddot{\text{O}}:$
+5	nitric acid	$\text{HNO}_3$	$\begin{array}{c} \ddot{\text{O}} - \text{N} - \ddot{\text{O}} - \text{H} \\    \\ \text{O} \end{array}$

When an element has more than one oxide, the oxides with higher oxidation numbers have larger acidities than those with lower oxidation numbers. For sulfur,  $\text{SO}_2$  (oxoacid;  $\text{H}_2\text{SO}_3$ ) is a weak acid but  $\text{SO}_3$  ( $\text{H}_2\text{SO}_4$ ) is a strong acid. The acidities of oxides of chlorine increase in the order shown below.



The acidity of  $\text{Cl}_2\text{O}$  ( $\text{HClO}$ ) is very weak while  $\text{Cl}_2\text{O}_7$  ( $\text{HClO}_4$ ) is one of the strong acids.

Table 5.9 gives the oxides with the highest oxidation number among main group elements and the periodicity of their acidity/basicity. Note that the amphoteric oxides are located from the upper left-hand corner to the lower right-hand corner of the table.

### b) Periodicity of properties of hydrides

Most of main group elements produce hydrides by reacting with hydrogen, but the stability of hydrides depends on the location of the element in the periodic table. Hydride of electropositive group 1 and 2 elements and electronegative group 16 and 17 elements are stable, while some of the

**Table 5.9** Acidity and basicity of oxides of main group elements

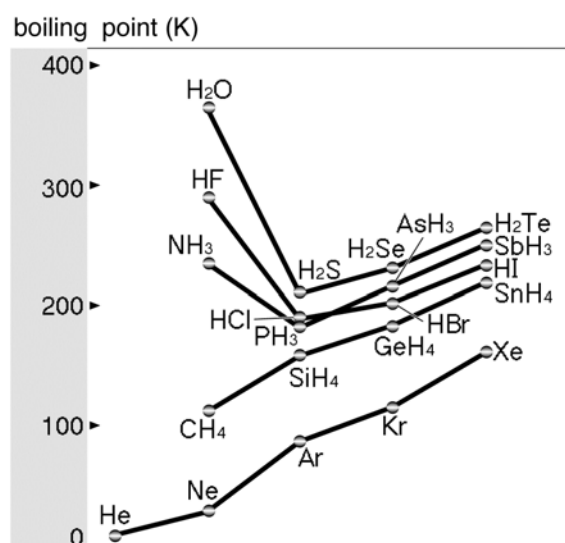
↑ basicity increases	Li <sub>2</sub> O	BeO	B <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub>	N <sub>2</sub> O <sub>5</sub>		F <sub>2</sub> O
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>10</sub>	SO <sub>3</sub>	Cl <sub>2</sub> O <sub>7</sub>
	K <sub>2</sub> O	CaO	Ga <sub>2</sub> O <sub>3</sub>	GeO <sub>2</sub>	As <sub>2</sub> O <sub>5</sub>	SeO <sub>3</sub>	Br <sub>2</sub> O
	Rb <sub>2</sub> O	SrO	In <sub>2</sub> O <sub>3</sub>	SnO <sub>2</sub>	Sb <sub>2</sub> O <sub>5</sub>	TeO <sub>3</sub>	I <sub>2</sub> O <sub>5</sub>
	Cs <sub>2</sub> O	BaO	Tl <sub>2</sub> O <sub>3</sub>	PbO <sub>2</sub>	Bi <sub>2</sub> O <sub>5</sub>		
	→ acidity increases						

hydrides of group 13, 14 and 15 heavy metal elements are sometimes difficult to prepare.

Hydrides of the alkaline and alkaline earth metal elements are colorless crystals, and by molten salt electrolysis these give hydrogen at the anode. This fact suggests in such metal hydrides, for instance in sodium hydride, it exists as Na<sup>+</sup>H<sup>-</sup>, *i.e.*, as a salt-like crystal. All of these hydrides are strong bases.

Some group 13 and 14 elements have more than one hydride. For instance, for the hydrides of carbon, there are not only methane CH<sub>4</sub>, but also carbene CH<sub>2</sub>, although it is difficult to isolate CH<sub>2</sub> because of excessive instability. All hydrides of group 14 elements including methane are covalent molecules. In going from left to right on the periodic table, the covalent character of hydrides decreases and the ionic character increases. The O-H bond of water and the Cl-H bond of hydrogen chloride, for example, are considerably polar, and dissociate to some degree in water to produce H<sup>+</sup>. In contrast, the acidity of methane is essentially negligible.

In general the hydrides of main group elements are molecules; they have distinct boiling and melting points, and exhibit periodicity. However, hydrides of 2<sup>nd</sup> period elements behave less so. For example, the boiling points are much higher than those of 3<sup>rd</sup> period elements (Fig. 5.5).

**Figure 5.5** Boiling points of hydrides of main group elements.

The periodicity observed for the rare gases and the hydrides of group 14 elements is not evident for hydrides of group 15, 16 and 17 elements.

Since the boiling points of the hydrides of 3<sup>rd</sup> period elements, and thereafter, continue to become higher, and show vivid periodicity, it is clear that the behavior of the hydrides of 2<sup>nd</sup> period elements is exceptional. It is well known that the reason for this is the characteristic formation of hydrogen bonds in the hydrides of 2<sup>nd</sup> period elements.

Hydrogen bonds take place in the compounds which have a bond between hydrogen and electronegative elements. The H-X bond polarizes into H<sup>+</sup>-X<sup>-</sup>. The attractive interaction between the dipoles thus formed is the driving force of hydrogen bonds.

Physical properties of elements such as boiling and melting points show periodicity to some extent. Among the elements belonging to the same group, this periodicity is sometimes clear. For instance, among halogens, the element changes from the gaseous state to liquid, and from liquid to solid. The change is not necessarily uniform. Nitrogen is a gas, but phosphorus and other atoms are all solid. Some discontinuity is evident.

### Exercise

#### 5.1 Electron configuration of atoms

Without consulting the periodic table, write down the electron configuration and the group number in the periodic table for the elements with the atomic numbers shown below.

3, 8, 14, 17, 32, 37, 56

#### Answer

Check your answers with the aid of the periodic table.

#### 5.2 Energy levels of atomic orbitals

Choose the orbital from each pair that has the higher energy.

(a) 3d, 4s (b) 4p, 5s (c) 4s, 4p

#### Answer

(a) 3d (b) 5s (c) 4p

#### 5.3 Electron affinity

From each set of three chemical species, choose the one with the maximum electron affinity and the one with the minimum electron affinity.

(a) Ge, Si, C (b) Cl, Cl<sup>-</sup>, Cl<sup>+</sup>

#### Answer

(a) C, Ge (b) Cl<sup>+</sup>, Cl<sup>-</sup>

#### 5.4 Ionization energy

The 2<sup>nd</sup> ionization energies are defined as the energy required to remove the second electron from the atom. The 3<sup>rd</sup> and 4<sup>th</sup> ionization energy is defined in a similar manner. Select from among elements X, Y and Z the one that will most clearly exhibit the properties (a), (b) and (c) given below.

(a) to form a monovalent ionic compound with chlorine

(b) to form a covalent bond with chlorine.

(c) To have the oxidation number of +2 in most cases.

Atom/ionization energy	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>
X	738	1450	7730	10550
Y	800	2427	3658	25024
Z	495	4563	6912	9540

#### Answer

X belongs probably to an alkaline metal group since both 1<sup>st</sup> and 2<sup>nd</sup> ionization energies are small. You can surmise Y is a group 13 element and Z a group 1 element.

(a) Z (b) Y (c) X

#### 5.5 The size of atoms and ions

Arrange each of the following quartet of four chemical species in the order of increasing the radius.

(a) Ar, Cl<sup>-</sup>, K<sup>+</sup>, S<sup>2-</sup> (b) C, Al, F, Si (c) Na, Mg, Ar, P (d) I<sup>-</sup>, Ba<sup>2+</sup>, Cs<sup>+</sup>, Xe

#### Answer

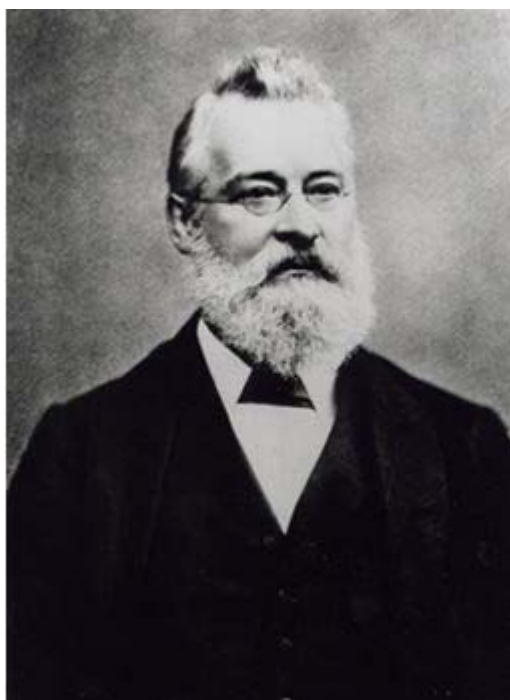
(a) K<sup>+</sup> < Cl<sup>-</sup> < S<sup>2-</sup> < Ar (b) F < C < Si < Al (c) P < Mg < Na < Ar (d) Ba<sup>2+</sup> < Cs<sup>+</sup> < I<sup>-</sup> < Xe

## Coffee-break

### An unrecognized pioneer

There were quite a few chemists who were interested in the periodicity of the properties of elements. The British chemist John Alexandere Reina Newlands (1837-1898) was one of them. Around 1865, he arranged in the order of atomic weight some 60 elements known at that time, and put these in a table with eight rows and six columns. To his surprise, he noticed that the 1<sup>st</sup> element and the 8<sup>th</sup> element and moreover, the 8<sup>th</sup> element and the 15<sup>th</sup> element had similar properties. In other words, an element with similar properties appears at every eighth position in the table. This appearance at every eighth position was very similar to that of musical notes. He announced his findings at a scientific meeting, and called his rule the **law of octaves**. British scientists at that time made fun of him, asking what would happen if one arranges the elements in an alphabetical order.

For many years Newlands was ignored. Finally in 1887, more than ten years after the achievement of Mendeleev was recognized, the Chemical Society (of England) awarded him a prize.



John Newlands (1837-1898)