

**MODERN  
CHEMISTRY  
SERIES**

**INORGANIC  
CHEMISTRY THROUGH  
EXPERIMENT**

**G.F. LIPTROT**

**MILLS & BOON**

# Inorganic Chemistry Through Experiment

BY

G. F. LIPTROT, M.A., Ph.D.

*Head of the Chemistry Department, Eton College*

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## Preface

Over the past twenty or so years there has been a steady advance in the methods of presentation of inorganic chemistry and a shift of emphasis has taken place, away from the traditional preparation and analysis of compounds for their own sake, towards a search for underlying patterns of behaviour. The author hopes that this book may indicate how practical inorganic chemistry can be taught within the broad framework of the Periodic Table and how additional physiochemical data, such as redox potentials, might profitably be employed to correlate chemical behaviour.

The emphasis has been placed on the use of rapid test-tube reactions and the conventional volumetric analysis, which employs burettes and pipettes, has been replaced by a dropping tube technique, as and when it has been felt desirable to illustrate the stoichiometric nature of some important reaction in solution. While the bulk of the experiments can be performed on a small scale, thus economising on chemicals, the conventional larger scale preparative work has not been neglected altogether; in particular, a number of preparations illustrating transition metal chemistry has been included. In addition, some experiments illustrating various unrelated aspects of an element's behaviour have been felt worthy of attention.

It is hoped that the book will prove useful to pupils studying both the new and the more traditional syllabuses at A-level and National Certificate level; to this end, a blend of experiments ranging from those of an 'open-ended' nature to those of a more didactic kind have been included, and it is hoped that a reasonable balance has been achieved.

*Eton College 1974*

G. F. LIPTROT

## Acknowledgements

This book is the result of many years' experience in teaching inorganic chemistry at sixth form level, and the experiments have been accumulated over a long period of time; consequently the origin of many of these has now become rather obscure. However, I have been influenced considerably by recent changes in the shift of emphasis in inorganic chemistry and I should like to pay tribute to the Nuffield Advanced Chemistry Course which has proved to be a rich source of ideas, many of which have filtered through into this book. I am also grateful to Dr. D. J. Waddington for providing me with the details of the experiments on cobalt(III) complexes in Section 11.5, pages 170–173.

Finally I should like to thank Mr. D. Hughes for providing the three plates and for allowing me to draw on his many years of practical experience, Dr. D. J. Waddington and Mr. G. W. Walker for reading the whole of the book in proof and for being constructive in their criticism of certain parts, my wife who as usual undertook the trying task of typing the original manuscript, and my publishers for help at all stages in the production of this book.

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(Plates by courtesy of D. Hughes)

Groups	1A	2A	3A	4A	5A	6A	7A	8	8	8	1B	2B	3B	4B	5B	6B	7B	O
Periods	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	I H																	2 He
2	3 Li	4 Be															9 F	10 Ne
3	11 Na	12 Mg															17 Cl	18 Ar
4	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
5	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
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac															

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Mv	102 No	103 Lw

The non-metallic elements

TABLE 1A The Periodic Table

# 1

## THE PERIODIC CLASSIFICATION OF ELEMENTS

### 1.1 Introduction

Once relative atomic masses (atomic weights) became available in the early nineteenth century, attempts were made to discover if there was any pattern between these figures and the properties of the elements. The most important step in developing a periodic classification was taken in 1869, when the Russian chemist, Mendeléeff, studied the relationship between the relative atomic masses of elements and their properties. He was led to the conclusion that 'the properties of the elements are in periodic dependence on their relative atomic masses'. A modern version of the Periodic Table is shown in Table 1A, the ordering of the elements being based on atomic numbers (the number of protons in the nucleus of the atom) rather than on relative atomic masses.

The table is divided into a number of vertical Groups and 7 horizontal Periods. The Groups 1 to 7 are subdivided into A and B, and Group 8 contains three elements in a given Period. It should not be thought that there is any special resemblance between the sub-groups, except perhaps one of valency; indeed the chemical differences between the sub-groups are often so great that they are best considered separately. Furthermore, there is no special significance in, say, iron, cobalt and nickel being placed in Group 8; these three elements are best treated as members of the first transition series extending from scandium to copper. The division into sub-groups, etc., is merely the method used by Mendeléeff in his original table and there is little need to alter it.

### 1.2 Some Physical Properties of the Elements

#### (a) Density

Plot the densities of the solid and liquid elements given in Table 1B (p. 9) against atomic number (go as far as the element bismuth). Study the features of the graph you obtain and relate them as far as possible with the Periodic Table (Table 1A). In particular note what kind of elements appear:



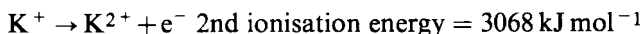
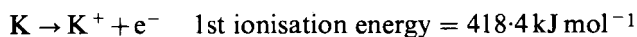
- (i) at the minima
- (ii) on the ascending portions of the graph
- (iii) on the descending portions of the graph.

### (b) Melting points

Plot the melting points of the elements given in Table 1B against atomic number (go as far as bromine). Discuss the main features of the graph in relationship to the Periodic Table (Table 1A).

### (c) Ionisation energies

The energy required to remove an electron completely from an atom of an element is known as the first ionisation energy; the second ionisation energy is similarly the energy needed to remove completely the second electron from the singly charged ion and so on. The values are quoted in  $\text{kJ mol}^{-1}$ , and for the potassium atom they are:



Notice the large difference between the two values, due to the fact that it is obviously more difficult to ionise an atom if the atom already bears a positive charge. The simple device below can be used to determine the first ionisation energy of neon (Fig. 1.1).

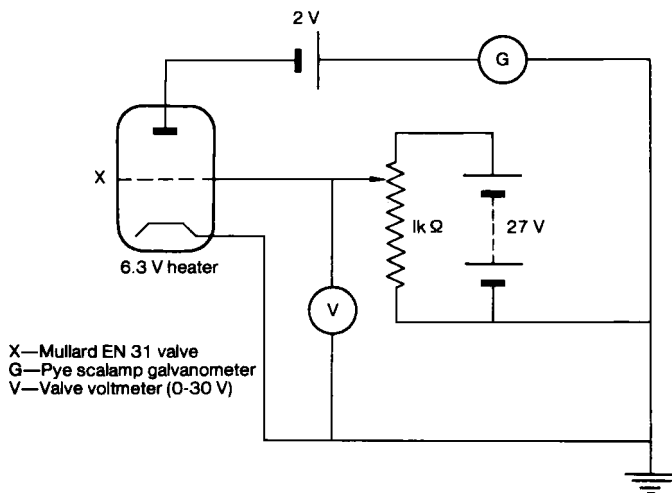


Fig. 1.1  
Determination of the first ionisation energy of neon.

TABLE 1B

Element	Density/g cm <sup>-3</sup>	Melting point/K	First ionisation energy/kJ mol <sup>-1</sup>	Atomic radius/nm
H		13.9	1313	0.032
He		3.5	2372	
Li	0.54	453.8	520	0.133
Be	1.84	1556	899	0.089
B	2.53	2300	800	0.080
C	2.22*	3700	1091	0.077
N		24.6	1400	0.074
O		54.4	1312	0.074
F		53.6	1679	0.072
Ne		24.6	2080	
Na	0.97	371.0	494	0.157
Mg	1.74	923	738	0.136
Al	2.70	932	578	0.125
Si	2.42	1683	782	0.117
P	1.83*	317.5	1062	0.110
S	2.07*	392.1	1003	0.104
Cl		173	1254	0.099
Ar		83.8	1519	
K	0.87	336.6	418	0.203
Ca	1.54	1123	589	0.174
Sc	3.19	1673	633	0.144
Ti	4.50	1950	661	0.132
V	5.69	2190	649	0.122
Cr	7.10	2176	653	0.117
Mn	7.42	1517	717	0.117
Fe	7.86	1812	762	0.116
Co	8.98	1768	757	0.116
Ni	8.90	1728	736	0.115
Cu	8.94	1356	745	0.117
Zn	7.13	692.7	906	0.125
Ga	5.90	303	578	0.125
Ge	5.46	1210	762	0.122
As	5.73	sublimes 886	946	0.121
Se	4.80	490	941	0.117
Br	3.12	266	1142	0.114
Kr		115.9	1351	
Rb	1.53	312	403	0.216
Sr	2.58	1043	549	0.191
Y	5.51	1773	615	0.162
Zr	6.44	2225	661	0.145
Nb	8.55	2770	664	0.134
Mo	10.20	2890	686	0.129
Tc		2400	703	
Ru	12.53	2700	711	0.124
Rh	12.44	2229	720	0.125
Pd	12.20	1823	803	0.128
Ag	10.50	1234	731	0.134
Cd	8.65	594	868	0.141
In	7.28	429	558	0.150
Sn	7.31	505	708	0.141
Sb	6.70	903	834	0.141
Te	6.25	723	870	0.137
I	4.94	387	1009	0.133
Xe			1170	

\* These density values are for graphite, white phosphorus and rhombic sulphur respectively.

A small negative potential of 2 volts is applied to the anode of the valve. Gradually increase the positive potential on the grid until a small deflection is shown by the galvanometer. No current will flow until the potential on the grid is sufficient to produce singly ionised neon  $\text{Ne}^+$ . The potential in volts is converted into  $\text{kJ mol}^{-1}$  by multiplying by the conversion factor 96.51.

Plot the first ionisation energies of the atoms of the elements given in Table 1B against atomic number. Discuss the main features of the graph in relationship to the Periodic Table (Table 1A).

Can you suggest a reason for the large drop in ionisation energy in going from helium to lithium, neon to sodium, and argon to potassium?

Ignoring the slight irregularities at the positions occupied by beryllium, nitrogen, magnesium and phosphorus, attempt to explain why the ionisation energy rises from lithium to neon and from sodium to argon (refer to the table of atomic radii).

#### (d) Atomic radii

Atomic radii have been determined using X-ray and electron diffraction techniques. For metals, the inter-nuclear distance in the crystal has been shown to be approximately the same as that for a single metal-metal covalent bond, where compounds containing the latter type of bonds are known. Half the inter-nuclear distance is the atomic radius of the element in question. It is essential to realise that bond lengths in covalent compounds are dependent upon the number of covalent bonds linking two atoms together; for example, there is a decrease in bond length along the series  $\text{C}-\text{C}$ ,  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ , and compounds containing single covalent bonds must be used to compute atomic radii. For solids, inter-nuclear distances and hence atomic radii do depend to some extent on the way the atoms are arranged in the crystal.

Using the values of atomic radii given in Table 1B, discuss the general trends that occur in:

- (i) descending a particular Periodic Group
- (ii) traversing a particular Period, e.g. lithium to neon
- (iii) traversing the first transition series (scandium to copper).

Is there any obvious correlation between first ionisation energy values and atomic radii?

### 1.3 Investigation of some Chemical Properties

#### (a) Action of water on some elements (lithium, magnesium, calcium)

Place some distilled water in a small evaporating dish and then carefully invert in it a test-tube half-full of distilled water. Add a small freshly cut piece of lithium to the water and then quickly place the test-tube over it. Collect the gas given off and show that it is hydrogen by placing the mouth of the test-tube near a Bunsen burner flame (since a hydrogen/air mixture is present in the test-tube a sharp squeak should be heard). Test the resulting solution in the evaporating dish with red litmus paper and then write an

equation for the reaction. **The reaction of water with sodium and potassium is violent and should on no account be attempted.**

Repeat the experiment as above using magnesium turnings in place of lithium. What do you observe?

Repeat again with small pieces of calcium.

From the results of these two experiments try to predict what would happen if similar small pieces of barium were added to water. Would you expect the reaction to be more or less violent than with calcium?

### (b) Action of steam on magnesium

Set up the apparatus as shown in Fig. 1.2 and make sure that the steam is freely issuing from the hole in the boiling-tube before you heat the magnesium ribbon. Once the magnesium is burning, place a Bunsen burner flame near the hole in the boiling-tube. Hydrogen is evolved which burns.

Find out from a reference book three more metals that react with steam to give hydrogen.

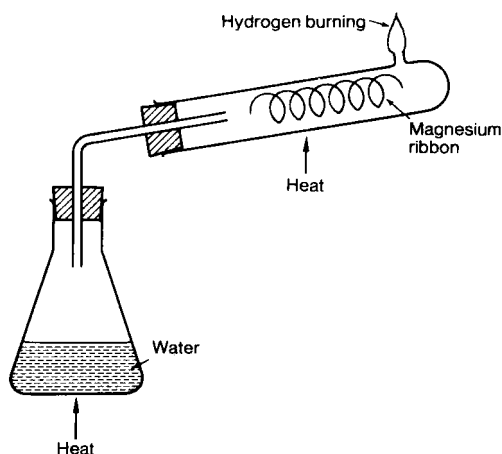


Fig. 1.2  
The action of steam on magnesium.

### (c) Action of steam on some non-metals (Demonstration)

The non-metals boron, carbon and silicon decompose steam at high temperatures to give hydrogen. The experiment is best carried out in the apparatus shown in Fig. 1.3 (p. 12) which employs an electric furnace.

Allow time for the electric furnace to warm up fully, then heat the water and allow the steam to pass over the hot carbon (granular form). After allowing for the displacement of air, collect some of the gas in a boiling-tube. If the gas burns quietly without exploding it is safe to collect it in gas jars. Apply a lighted splint to a gas jar full of the gas and note the colour of the flame. Add lime water, shake and observe what happens. Do the same test on an unburnt sample of the gas, note and explain the difference this time.

Repeat the experiment with silicon and collect the gas in boiling-tubes. Apply a lighted splint to the gas and observe what happens.

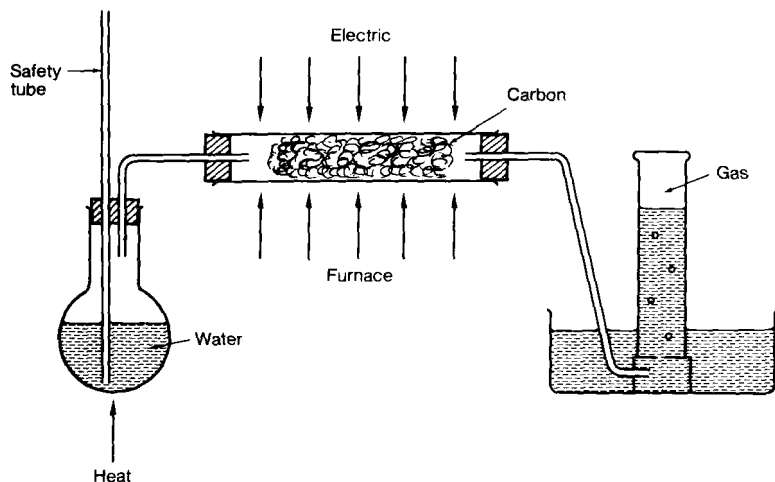


Fig. 1.3  
The action of steam on carbon.

#### (d) Action of hydrochloric acid on some elements

Treat small samples (about 0.5 g) of the following metals separately with approximately 2 M hydrochloric acid: aluminium, bismuth, copper, chromium, iron, lead, magnesium, nickel, tin and zinc and collect any gas evolved as in Fig. 1.4. **Note:** The reaction between magnesium and dilute hydrochloric acid is so rapid that a lighted splint should be applied to the top of the test-tube as soon as the acid has been added to the metal.

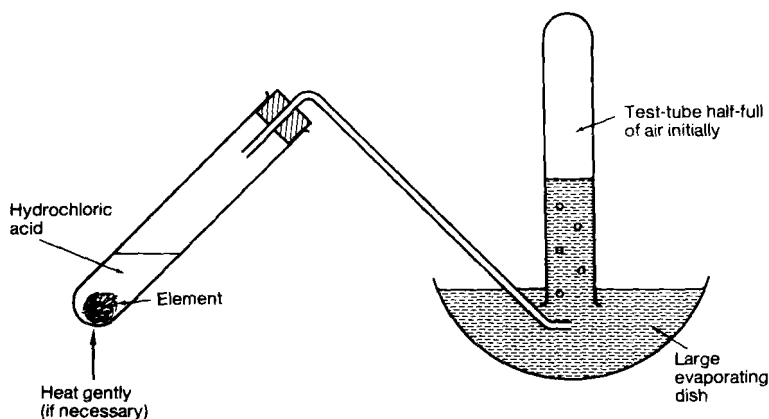


Fig. 1.4  
The action of hydrochloric acid on some elements.

If there appears to be little or no reaction in the cold, try warming the test-tube gently; if there is still little or no gas evolved try increasing the concentration of the acid. Make a list of the metals that do and do not evolve hydrogen under these conditions. Also note whether heat has to be applied and whether the acid is dilute or concentrated.

Try the effect of hydrochloric acid on the three non-metals boron, carbon and silicon. Do they evolve any hydrogen under these conditions?

### (e) Action of water on some oxides and hydroxides

To about  $2\text{ cm}^3$  of distilled water in a test-tube add a small quantity of calcium oxide ( $0.3\text{ g}$  is sufficient). Now add 2 drops of Universal Indicator solution and note the colour of the indicator.

Repeat the experiment with aluminium oxide (obtained by heating aluminium nitrate until no further change takes place), boron trioxide, iodine(V) oxide, lithium oxide (obtained by heating lithium nitrate until no further change occurs), magnesium oxide, phosphorus(V) oxide (**care: the reaction is violent**), silicon(IV) oxide and zinc oxide. Which of the above oxides give acid and which give alkaline solutions? Can you find any relationship between this behaviour and the position of the various elements in the Periodic Table?

Repeat the experiment with carbon dioxide (obtained by heating copper(II) carbonate) and sulphur dioxide (from a syphon).

Repeat the experiment again, but this time use the following hydroxides:  $\text{B}(\text{OH})_3$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{KOH}$  (one pellet),  $\text{NaOH}$  (one pellet),  $\text{P}(\text{OH})_3$ . **Caution: KOH and NaOH are caustic to the skin.** Which hydroxides give alkaline and which give acid reactions in water?

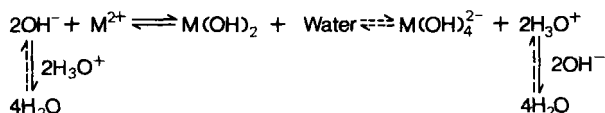
### (f) Precipitation of metallic hydroxides

You will be provided with a number of aqueous solutions of salts in which the concentration of the particular cation is approximately  $0.1\text{ mol dm}^{-3}$  (convenient solutions to use are aluminium sulphate, barium chloride, calcium chloride, chromium(III) sulphate, cobalt(II) chloride, copper(II) sulphate, iron(II) sulphate, iron(III) chloride, lead(II) nitrate, manganese(II) sulphate, nickel sulphate, potassium chloride and zinc sulphate). Take about  $2\text{ cm}^3$  of each solution in a test-tube and add approximately 2M sodium hydroxide solution gradually drop by drop. Observe any colour changes, the appearance and colour of any precipitate and whether the precipitate dissolves in an excess of the sodium hydroxide solution. In addition, note any change in colour of the precipitates of cobalt(II) hydroxide and manganese(II) hydroxide on standing. Summarise your results in the form of a table overleaf.

Cation in aqueous solution	Colour of original solution	Colour of the hydroxide precipitate (if any)	Solubility of the precipitate (if any) in excess sodium hydroxide solution
$\text{Al}^{3+}$ $\text{Ba}^{2+}$ $\text{Ca}^{2+}$ $\text{Cr}^{3+}$ $\text{Co}^{2+}$ $\text{Cu}^{2+}$ $\text{Fe}^{2+}$ $\text{Fe}^{3+}$ $\text{Pb}^{2+}$ $\text{Mn}^{2+}$ $\text{Ni}^{2+}$ $\text{K}^{+}$ $\text{Zn}^{2+}$			

Where do the metals that form coloured salts and coloured hydroxide precipitates appear in the Periodic Table? Similarly, where do the metals that form precipitates, which dissolve in an excess of sodium hydroxide solution, appear in the Periodic Table?

All metallic hydroxides dissolve in dilute acid (and this can be confirmed by adding approximately 2 M nitric acid to the precipitates formed above). However, a few metallic hydroxides also dissolve in an excess of sodium hydroxide solution and such hydroxides are said to be amphoteric. This behaviour is easily explained by assuming an equilibrium to be set up in solution; thus if  $\text{M}(\text{OH})_2$  represents the amphoteric metallic hydroxide:



The addition of an acid drives the equilibrium to the left as the  $\text{H}_3\text{O}^+$  ions remove the  $\text{OH}^-$  ions to form water and the metallic hydroxide  $\text{M}(\text{OH})_2$  dissolves. Similarly the addition of a strong alkali drives the equilibrium to the right as the  $\text{OH}^-$  ions combine with the  $\text{H}_3\text{O}^+$  ions to form water and the metallic hydroxide again dissolves, this time in the form of  $\text{M}(\text{OH})_4^{2-}$  ions.

#### (g) Action of water on some hydrides

To about 25 cm<sup>3</sup> of distilled water in a small beaker add about 0.2 g of lithium hydride (**caution: the reaction is violent**). Note the evolution of a gas; what do you think it is? Add a few drops of Universal Indicator solution to the resulting solution and note the colour of the solution formed.

Repeat the experiment using calcium hydride.

Mix together about 0.5 g of ammonium chloride and 0.5 g of calcium hydroxide and place the mixture in a test-tube. Warm gently and allow the ammonia gas to come into contact with moist Universal Indicator paper held near the mouth of the test-tube. Note any change in colour of the Universal Indicator paper.

To about 0.5 g of sodium chloride in a test-tube add about 1 cm<sup>3</sup> of concentrated sulphuric acid (**caution: concentrated sulphuric acid is corrosive**). Do the reaction in a fume cupboard and note the evolution of a strongly fuming gas, hydrogen chloride. Allow this gas to come into contact with moist Universal Indicator paper held near the mouth of the test tube and note any change in colour of the Universal Indicator paper.

Repeat the experiment using sodium bromide and concentrated sulphuric acid. This reaction produces the strongly fuming gas hydrogen bromide, together with much free bromine.

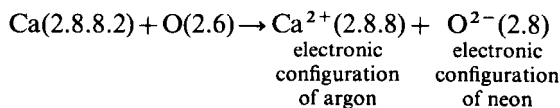
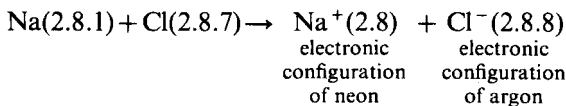
From the results obtained in the above experiments with  $\text{Li}^+\text{H}^-$ ,  $\text{Ca}^{2+}(\text{H}^-)_2$ ,  $\text{NH}_3$ ,  $\text{HCl}$  and  $\text{HBr}$ , write balanced chemical equations for the reaction of these hydrides with water. Remember that an acidic reaction is due to the presence of  $\text{H}_3\text{O}^+$  ions and an alkaline reaction is due to  $\text{OH}^-$  ions.

## 1.4 Physical Nature of Oxides, Hydrides and Chlorides

The melting points (Kelvin scale) of the oxides, hydrides and chlorides of the first two short periods are plotted in Fig. 1.5 (p. 16). Where a particular element forms more than one oxide, or hydride, or chloride, only one of them is given. The horizontal line drawn at 288 K (average room temperature) clearly shows which compounds are solids (those above the horizontal line) and those which are either liquids or gases (those below the horizontal line). In one or two cases decomposition occurs before the melting-points are reached and the decomposition temperatures are plotted.

Although a full discussion of chemical bonding is beyond the scope of this book, some reference to it is essential.

There are two main types of chemical bonding (excluding the metallic bond), namely electrovalency and covalency. In electrovalency, one or more electrons (rarely more than two) are transferred from the metallic atom to the non-metallic atom. The ions so formed often have the electronic configurations of a noble gas, thus:





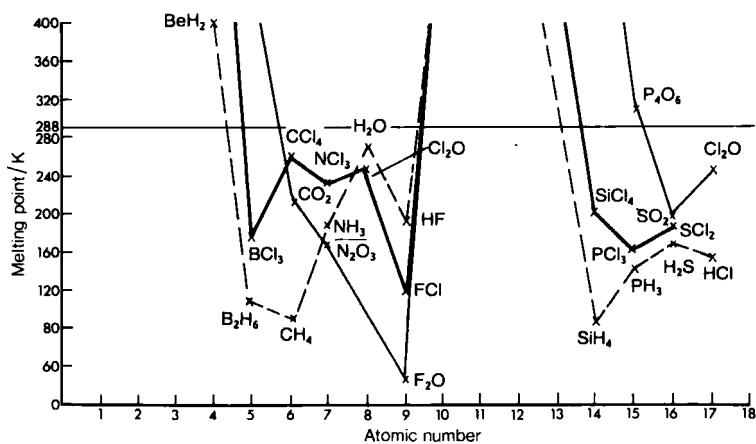
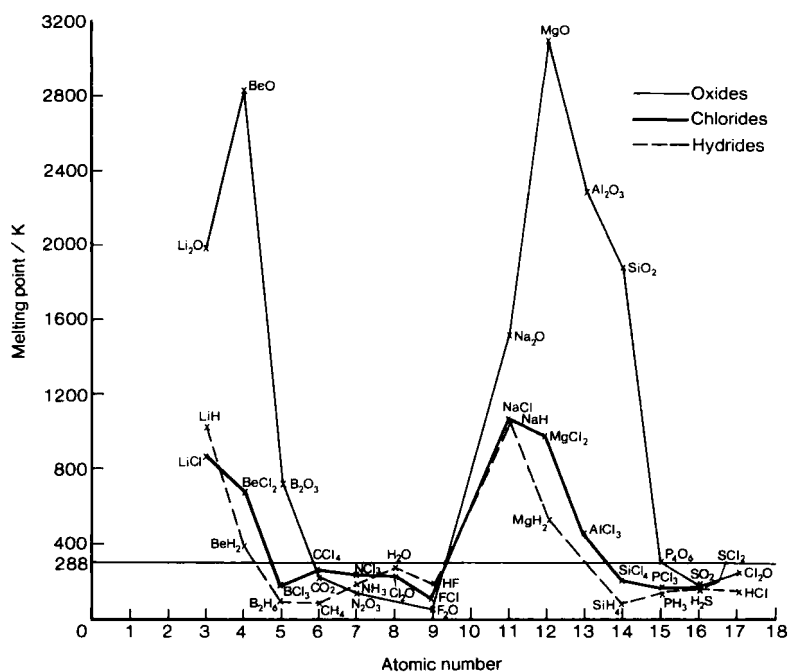


Fig. 1.5

The melting points of the oxides, hydrides and chlorides of elements of the first two short Periods.