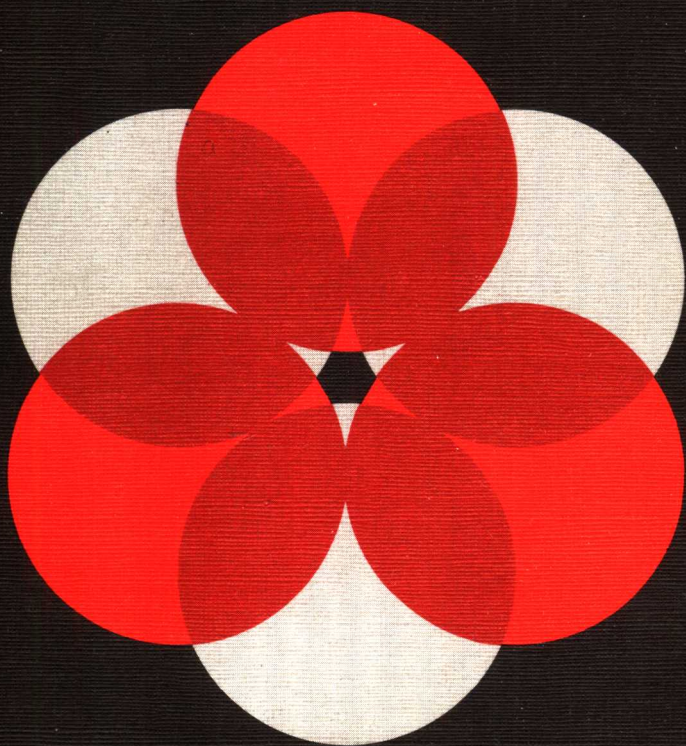


A. Holderness

Advanced Level
Inorganic
Chemistry



Advanced Level Inorganic Chemistry

A. Holderness

A new edition of the *Inorganic* section of *Inorganic and Physical Chemistry* revised by

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and a companion to *Advanced Level Physical Chemistry*



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Preface

The subjects which we study do not have their boundaries defined by God but by men. We take the totality of experience and (for various excellent reasons) call some parts of it 'science'. Science is divided, largely for the convenience of students, teachers, and users, into the disciplines of biology, physics, chemistry, and so on. Chemistry itself is further divided into the major areas of physical, inorganic, organic, and analytical chemistry. Those who practise and use science are crossing the barriers between subjects with increasing frequency and to increasing effect: for examples one has only to think of molecular biology and semi-conductors. The social and economic consequences of scientific activity transcend subject boundaries. But the boundaries and subdivisions still prove useful for the purposes of teaching and learning.

This book is a new edition of the inorganic section of Albert Holderness's *Inorganic and Physical Chemistry*. It uses, as any book on inorganic chemistry must do, very many of the ideas developed in the companion volume on physical chemistry (*Advanced Level Physical Chemistry* by A. Holderness, revised by J. N. Lazonby). It is assumed that this can easily be referred to by the reader, and there are frequent references in this text to the physical chemistry volume.

It is always difficult to revise an established classic. Such is the pace of advance in chemical theory and practice that the new book has to incorporate discussion of ideas and techniques which were either totally unknown, or only dimly perceived, when the book was last revised. A conscious attempt has been made to retain as much as possible of the flavour and philosophy of the previous edition, while at the same time ensuring that the present work is a thoroughly up-to-date textbook. The material has been rearranged, and there have been major deletions and additions. SI units are used, and nomenclature is based on the recommendations of the Association for Science Education and the Examining Boards.

This book contains rather more descriptive and preparative material than is customary in contemporary inorganic chemistry texts at Advanced and Scholarship level, while at the same time covering the syllabus requirements for a theoretical background. It is hoped that this will

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enable the volume to be useful as a reference for both facts and ideas.

I am very grateful to John Lazonby for his detailed and helpful criticism of the text. Any errors and imperfections which remain are solely my responsibility. I am also grateful to Graham Taylor, Hamish MacGibbon, and Katherine Ross of Heinemann Educational Books for much encouragement and help. Above all, I am grateful to my wife and children for putting up with me during a task which proved tougher and longer than I had bargained for.

June 1979

Martyn Berry

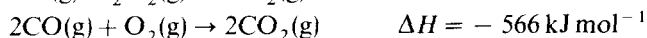
Important note

All melting and boiling points are, unless otherwise stated, quoted for a pressure of $101\,325\text{ N m}^{-2}$.

Where great accuracy is not essential, e.g. in industrial processes, pressures are often quoted in 'atmospheres', abbreviated to 'atm' ($1\text{ atm} \approx 10^5\text{ N m}^{-2}$).

Equations involving energy changes are written with the enthalpy change in the form $(\text{energy}) \times (\text{amount of substance})^{-1}$. The units for ΔH will thus be kJ mol^{-1} . The use of ' mol^{-1} ' does *not* imply 'per mole of any particular material formed or used up,' but 'per molar quantities as indicated by the equation.'

Hence, for example:



(See e.g. Cvitaš and Kallay, *Chemistry in Britain*, June 1978, p. 290.)

About the questions

Most of the questions in this book are of the 'essay' type, although there are also many problems. Readers should remember that the chemistry examinations of an increasing number of Boards require an ability to cope with fixed response questions, usually in the form of an 'objective test' paper and a 'structured' paper. Considerations of space mean that there are no questions of these kinds in this book.

Thanks are due to the Oxford Delegacy of Local Examinations(O), the University of Cambridge Local Examination Syndicate(C), the Joint Matriculation Board(JMB), the University of London University Entrance and Schools Examination Council(L), and the Associated Examination Board (AEB) for permission to reproduce questions.

ELECTRONIC ARRANGEMENTS IN ELEMENTS (1)

	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d	6s 6p 6d	7s
1 H	1						
2 He	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				
11 Na	2	8	1				
12 Mg	2	8	2				
13 Al	2	8	2	1			
14 Si	2	8	2	2			
15 P	2	8	2	3			
16 S	2	8	2	4			
17 Cl	2	8	2	5			
18 Ar	2	8	2	6			
19 K	2	8	8	1			
20 Ca	2	8	8	2			
21 Sc	2	8	8	1	2		
22 Ti	2	8	8	2	2		
23 V	2	8	8	3	2		
24 Cr	2	8	8	5	1		
25 Mn	2	8	8	5	2		
26 Fe	2	8	8	6	2		
27 Co	2	8	8	7	2		
28 Ni	2	8	8	8	2		
29 Cu	2	8	8	10	1		
30 Zn	2	8	8	10	2		
31 Ga	2	8	18	2			
32 Ge	2	8	18	2	2		
33 As	2	8	18	2	3		
34 Se	2	8	18	2	4		
35 Br	2	8	18	2	5		
36 Kr	2	8	18	2	6		
37 Rb	2	8	18	8		1	
38 Sr	2	8	18	8		2	
39 Y	2	8	18	8	1	2	
40 Zr	2	8	18	8	2	2	
41 Nb	2	8	18	8	4	1	
42 Mo	2	8	18	8	5	1	
43 Tc	2	8	18	8	6	1	
44 Ru	2	8	18	8	7	1	
45 Rh	2	8	18	8	8	1	
46 Pd	2	8	18	8	10		

ELECTRONIC ARRANGEMENTS IN ELEMENTS (2)

	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d	6s 6p 6d	7s
47 Ag	2	8	18	8 10	1		
48 Cd	2	8	18	<u>8 10</u>	2		
49 In	2	8	18	18	2 1		
50 Sn	2	8	18	18	2 2		
51 Sb	2	8	18	18	2 3		
52 Te	2	8	18	18	2 4		
53 I	2	8	18	18	2 5		
54 Xe	2	8	18	18	<u>2 6</u>		
55 Cs	2	8	18	18	8	1	
56 Ba	2	8	18	18	8	2	
57 La	2	8	18	18	8	1	2
58 Ce	2	8	18	18 1	8 1	2	
59 Pr	2	8	18	18 2	8 1	2	
60 Nd	2	8	18	18 3	8 1	2	
61 Pm	2	8	18	18 4	8 1	2	
62 Sm	2	8	18	18 5	8 1	2	
63 Eu	2	8	18	18 6	8 1	2	
64 Gd	2	8	18	18 7	8 1	2	
65 Tb	2	8	18	18 8	8 1	2	
66 Dy	2	8	18	18 9	8 1	2	
67 Ho	2	8	18	18 10	8 1	2	
68 Er	2	8	18	18 11	8 1	2	
69 Tm	2	8	18	18 12	8 1	2	
70 Yb	2	8	18	18 13	8 1	2	
71 Lu	2	8	18	<u>18 14</u>	8 1	2	
72 Hf	2	8	18	32	8 2	2	
73 Ta	2	8	18	32	8 3	2	
74 W	2	8	18	32	8 4	2	
75 Re	2	8	18	32	8 5	2	
76 Os	2	8	18	32	8 6	2	
77 Ir	2	8	18	32	8 7	2	
78 Pt	2	8	18	32	8 8	2	
79 Au	2	8	18	32	8 10	1	
80 Hg	2	8	18	32	<u>8 10</u>	2	
81 Tl	2	8	18	32	18	2 1	
82 Pb	2	8	18	32	18	2 2	
83 Bi	2	8	18	32	18	2 3	
84 Po	2	8	18	32	18	2 4	
85 At	2	8	18	32	18	2 5	
86 Rn	2	8	18	32	18	<u>2 6</u>	
87 Fr	2	8	18	32	18	8	1
88 Ra	2	8	18	32	18	8	2
89 Ac	2	8	18	32	18	8 (1)	(2)
90 Th	2	8	18	32	18	8 (2)	(2)
91 Pa	2	8	18	32	18	8 (3)	(2)
92 U	2	8	18	32	18	8 (4)	(2)

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Introduction to inorganic chemistry

What is inorganic chemistry?

At the start of his classic textbook *Inorganic Chemistry* (New York: John Wiley, 1952), Professor Therald Moeller wrote:

'As opposed to organic chemistry, inorganic chemistry is properly a study of all chemical materials other than the hydrocarbons and their derivatives. Not only does inorganic chemistry embrace the properties and modes of preparation of such materials, but it goes beyond and seeks to account for and explain specific characteristics and observed similarities, differences, and trends in observed behaviours. Modern inorganic chemistry, unlike classical inorganic chemistry, is more than a descriptive science. It attempts to relate the properties of chemical substances to their structures, which in turn are related to the structures of the particles which combined to make those substances. Modern inorganic chemistry employs, therefore, both the experimental and theoretical approaches and requires familiarity with each. It is concerned with all the elements and with all the combinations in which these elements are found.'

This passage repays careful re-reading. It defines inorganic chemistry, and points out how the structures and properties of materials depend on the structures of the atoms of the elements of which they are composed. In the years since Professor Moeller's book, much progress has been made in *explaining* the myriad properties, similarities, differences, and trends which are observed in inorganic materials. Although we are very far from a complete interpretation and explanation of chemical behaviour, there is now a strong framework of theory which can be used both to hang the observed facts on and to make predictions. Most of the theory needed for our purposes can be found in the companion volume to this book, *Advanced Level Physical Chemistry*, and will be

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referred to and developed later in this chapter. Although it is not necessary to master *all* the theory before embarking on a study of inorganic chemistry—indeed, the immediate opportunity for a wide range of experiments and observations is one of the attractions of the subject—the reader is strongly advised to develop a knowledge and understanding of the unifying theory as soon as possible. This will lessen the need for memorizing many isolated details of factual information. It must be realized, though, that chemical theory is *not* fixed for ever, and that through research it improves with time; so that the reader should be prepared for change during the lifetime of this book. (For an important example of the way in which new observations can force theories to change, see p. 26).

Why study inorganic chemistry?

The fact that our environment consists very largely of inorganic materials would surely be reason enough for inorganic chemistry to be a worthwhile field of study. But, in addition, a great many important human activities depend on the application of inorganic chemical knowledge. Examples include the extraction and working of all metals; the construction industries of all kinds; semi-conductors; nuclear fuel technology; the supply of safe drinking water; the control and possible elimination of corrosion and pollution. Fossil fuels are not the only materials which are bound to become scarcer; the easily-discovered and easily-worked deposits of the ores of many metals have already been used up. The detection, winning, efficient use of, and recycling of metals form only one region of many fields in which an understanding of inorganic chemistry will become increasingly important. The social and economic impacts which result from the *right* (and, regrettably, sometimes the *wrong*) use of chemical knowledge should never be underestimated.

Sources of inorganic materials

Most inorganic materials of economic importance occur in the solid state as components of the Earth's crust. Most metals are found in combination with oxygen or sulphur. Only the most unreactive (e.g. gold) are found in the free state. A mass of rock which contains an unusually high proportion of a particular metal or group of metals is known as an *ore*. The ways in which the ores were deposited, and their detection and mining, are beyond the scope of this book. However, it should be pointed out that the extraction of metals from concentrated ore is a process of *reduction*. The ores, which are usually oxides or sul-

phides, contain metal ions; these must receive electrons to become free metal. Examples of ways in which this can be done include the extractions of iron (p. 432), copper (p. 456), and aluminium (p. 118).

Other solid materials of economic importance obtainable from the Earth's crust include calcium carbonate (p. 93), silica (p. 116), and sulphur (p. 310).

Many salts, particularly those of the alkali metals, are soluble in water. Such materials will be washed into the sea over many years. (This process may be observed occurring in the Dead Sea.) The main sources of sodium, potassium, and magnesium are either the sea or salt deposits formed by evaporation of sea-water in the distant past (see e.g. p. 43 and p. 69). Halide ions are also found in high concentration in rock salt and sea-water, which are therefore the main sources of chlorine (p. 50) and bromine (p. 371) respectively.

The atmosphere provides the industrially vital gas oxygen (p. 276). 'Fixation' of atmospheric nitrogen by the Haber process (p. 216) is essential for the production of fertilizers.

It is instructive to consider the composition of the Earth's crust, shown in Table 1.1.

Table 1.1 Composition of the Earth's crust, including waters and the atmosphere

<i>Element</i>	<i>Mass per cent</i>	<i>Element</i>	<i>Mass per cent</i>
Oxygen	49.5	Magnesium	1.9
Silicon	25.7	Hydrogen	0.88
Aluminium	7.5	Titanium	0.58
Iron	4.7	Chlorine	0.19
Calcium	3.4	Phosphorus	0.12
Sodium	2.6	Carbon	0.09
Potassium	2.4	All others	0.42

From Table 1.1 it can be seen that not only are many metals of major importance included within the 'all others' percentage of 0.42, but so also are the apparently common non-metals nitrogen and sulphur. Many rocks are roughly describable as 'aluminosilicates', that is materials containing aluminium, silicon, and oxygen. The final product of their weathering, as observed on sea shores, is often more or less impure silicon dioxide, i.e. sand.

The Periodic Table and its relation to atomic structure

The historic development of the Periodic Table is described in *Advanced Level Physical Chemistry*, pp. 58–61.

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Table 1.2 The Periodic Table of the elements, showing the s-, p-, d-, and f-blocks

1		2												
H		He												