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Practical Inorganic Chemistry

Preparations, reactions and instrumental methods

SECOND EDITION

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Preparations, reactions and instrumental methods

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SECOND EDITION



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Preface to the Second Edition

In revising the text opportunity has been taken to introduce SI units throughout. An Appendix has been included which contains tables of SI units and a table of conversion factors for use when consulting data in non-SI units. Chapter 19 now includes experiments demonstrating the use of ion-exchange and solid-liquid chromatography. Exercises involving colorimetry have been included in Chapter 17. These techniques are introduced as part of a complementary exercise where their relevance is seen as part of a complete piece of work. Minor improvements have been made to some of the experimental procedures and we are grateful to those who have made helpful suggestions in this respect.

G. PASS
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Preface to the First Edition

The student of inorganic chemistry is fortunate in having a wide choice of textbooks covering the descriptive and theoretical aspects of the subject. There is no comparable choice of textbooks covering practical inorganic chemistry. Moreover, there is a tendency for many students to draw an unfortunate distinction between chemistry taught in the lecture room, and laboratory work. Consideration of these points prompted the preparation of this book, in which we have attempted to emphasize the relationship between theory and practice.

The experimental work described in this text has been selected with a view to covering most of the principles of inorganic chemistry discussed in an undergraduate course. Each chapter or section is preceded by a theoretical discussion which, it is hoped, will provide a thread of continuity between lecture room and laboratory. This discussion is in outline only and amplification through lectures and standard textbooks is necessary. Much of the experimental work described is of a preparative nature. Each preparation is followed by a set of complementary exercises which must be completed in order to gain maximum benefit from the work. The complementary work includes questions and practical exercises.

Analytical chemistry is seen in correct perspective when used on real, rather than artificial systems. Consequently, the complementary work frequently requires the student to analyse the compound which he has prepared. This may involve the techniques of volumetric or gravimetric analysis, and a student can develop his knowledge of analytical chemistry by devising an analytical method for a particular purpose. Alternatively, more sophisticated instrumental methods of analysis may be used, details of which are given in the later chapters of the book. Satisfactory answers to the complementary questions can often only be given after a certain amount of library work. This

study will lead the student back to the theoretical introduction or to some related topic. In this way it is hoped to emphasize the unity between theory and practice. References are provided at the end of an experiment to assist with this library work. The bibliographies at the end of the chapters and the General Bibliography at the end of the book will provide background reading. The connexion between theory and practice may be more fully emphasized if the theoretical introduction, preparation, and complementary work are taken as headings for an essay.

In addition to illustrating theoretical aspects of the subject, an attempt has been made to demonstrate the diversity of techniques used in inorganic chemistry. Such diversity of method is inevitable in a subject which covers the whole of the periodic table. A representative selection of techniques has been included, but an exhaustive coverage has not been attempted. Some preparations and techniques have been omitted because they present a potential hazard in student hands. Where experiments do involve a possible hazard, suitable safety precautions are given.

The book is suitable for use parallel to a lecture course for an honours degree in chemistry, or its equivalent. The material is arranged in an approximate order of increasing complexity, but it is not suggested that this order must be rigidly followed. A selection of material dependent on the students' current lecture course is advocated. Suitable selection will also enable the text to be used for chemistry courses at a lower level. Some experiments could well be included in more than one chapter, but to avoid duplication of the text, while allowing full correlation of such experiments, cross-references have been given to other sections of the book.

The experimental details have been drawn from a wide range of sources and all have been used in the form in which they are described. Some are from original papers, some we have devised, and some have been adapted from *Inorganic Syntheses*, *Experimental Inorganic Chemistry* by W. G. Palmer, *Inorganic Preparations* by H. F. Walton, *Handbook of Preparative Inorganic Chemistry* by G. Brauer, and *Inorganic Preparations* by A. King.

Finally, our thanks are due to colleagues with whom we have discussed chapters of the book, and in particular to those who have read the manuscript and made many useful suggestions.

G.P.

H.S.

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1 Typical elements

These elements have by definition no incompletely filled *d* or *f* orbitals, and the valence electrons are located in *s* and *p* orbitals. The reactions included are designed to illustrate points in the chemistry of a given subgroup of the periodic table and to demonstrate more general theoretical considerations.

Ion size effects

The preparation of caesium dichloroiodide

The formation of polyhalides AB_n^- depends on the combination of a central halide ion with a halogen or interhalogen molecule, where the atomic weight of A > atomic weight of B. No polyhalides are known where fluorine acts as the central atom. The oxidation state of A depends on the halogen B with which it is combined; increasing oxidation states occur with decreasing atomic weight of B and increasing atomic weight of A. Only large cations with low charge give a stable ionic lattice with the large polyhalide ions. With a small cation, such as sodium, polarization of the polyhalide ion would occur, resulting in the formation of a more stable sodium halide lattice.

The preparation of caesium dichloroiodide

Materials required: Caesium chloride
Iodine
Chlorine

This experiment must be carried out in a fume cupboard.

Dissolve caesium chloride (3.5 g) in 35 cm³ of water and add iodine (2.6 g). Heat to just below the boiling point and bubble chlorine into the hot solution until the iodine just dissolves. The solution is conveniently contained in a boiling tube. Avoid excess chlorine, otherwise caesium tetrachloroiodide may be formed. Cool and filter the precipitated caesium dichloroiodide. Record the yield.

Complementary work:

- (1) What is the structure of the ICl_2^- ion? How does this compare with the structure of xenon difluoride?
- (2) Study the effect of heat on the dry product and compare this with the effect of heat on potassium iodide. Identify the volatile product and comment.

The preparation of barium peroxide

Within the subgroups of alkali metals, and alkaline-earth metals there is a decreasing tendency with increasing cation size for the oxide M_2O or $\text{M}^{\text{II}}\text{O}$ to be formed by direct combination of the elements. As described on p. 3, the small Li^+ cation will form a more stable crystal lattice with a small anion than will a larger alkali metal cation. With increasing size of the cation a more stable crystal structure is obtained by expanding the lattice, and increasing the separation of the cations. This may be achieved by replacing the oxide ion O^{2-} by a larger anion such as peroxide, O_2^{2-} or superoxide O_2^- ions. The peroxide ion O_2^{2-} is larger than the oxide ion, O^{2-} . It should be noted that for lithium the most stable lattice is achieved with a small ion, as in Li_2O . For a larger cation such as Ba^{2+} or K^+ the most stable lattice is achieved with the larger anion, O_2^{2-} as in BaO_2 or K_2O_2 .

The experimental details for the preparation of barium peroxide are given on p. 34.

Lattice energy effects

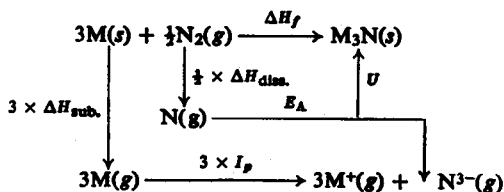
The preparation of lithium nitride

One of the reactions in which lithium differs from the other alkali metals, but resembles magnesium, is the formation of a nitride Li_3N ,

an example of the so-called 'diagonal relationship' in the periodic table. The reaction



may be represented in terms of a Born-Haber cycle



$$\text{therefore } \Delta H_f = 3 \times \Delta H_{\text{sub.}} + 3 \times I_p + \frac{1}{2} \Delta H_{\text{diss.}} + E_A - U.$$

The dissociation energy of nitrogen ($\Delta H_{\text{diss.}}$) and the electron affinity E_A for the formation of N^{3-} are both endothermic terms, and are independent of the alkali metal M . The ionization energy (I_p) and the sublimation energy ($\Delta H_{\text{sub.}}$) are also endothermic and decrease down the group from $\text{Li} \rightarrow \text{Cs}$. The only energetically favourable term in the cycle is the lattice energy (U). The fact that lithium forms a nitride, while sodium does not, demonstrates that the lattice energy of lithium nitride is greater than the lattice energy of the hypothetical sodium nitride. This decrease in lattice energy with increasing size of the cation is a general effect, but is more pronounced with a small highly charged anion e.g. N^{3-} , O^{2-} . The effect is readily noticed in the case of the nitride since it results in the distinct change from compound formation to no compound formation.

The experimental details for the preparation of lithium nitride are given on p. 33, under high temperature reactions.

Ionization energy

The preparation of a cationic iodine compound

Across any period in the periodic table the ionization potential required to form a given cation M^{n+} generally increases. Within a given group in the periodic table the ionization potential generally decreases with increasing atomic weight. As a consequence there is little tendency for the halogens to form M^{n+} cations, but within the group the maximum tendency to form such cations is found with

iodine. Astatine should have the greatest tendency to form M^{n+} cations. However, a knowledge of the chemistry of astatine is limited because the longest lived isotope has a half-life of only 8.3 hours. In practice, a limited number of cationic compounds (as opposed to compounds, such as potassium iodate, in which iodine has a formal positive oxidation state), of iodine have been prepared. The number of cationic bromine and chlorine compounds is even more restricted.

The preparation of dipyridineiodine(I) nitrate

Materials required: Iodine
Silver nitrate
Pyridine

Dissolve silver nitrate (1.7 g) in 5 cm³ of pyridine, and iodine (2.5 g) in 50 cm³ of chloroform. Add the chloroform solution slowly to the pyridine solution, stirring well. Allow to stand, and filter off the yellow precipitate, which can be discarded. To the filtrate add 50 cm³ of diethyl ether, shake, and allow to stand. Filter off the yellow crystals with suction, wash with ether, and suck dry.

Complementary work:

- (1) Dissolve a portion of the product in dilute hydrochloric acid and record your observations.
- (2) Dissolve a portion of the product in dilute sodium hydroxide and record your observations.
- (3) To each of the above solutions add a solution of potassium iodide. Comment on your observations.
- (4) Devise a method for the quantitative determination of iodine in the compound.
- (5) Dissolve a portion of the product in 4M sodium hydroxide solution, and boil until no more volatile material can be detected. Now add a little zinc dust to the solution and boil. Comment on the reactions which have occurred.

Reference

Arotky, J. and Symons, M. C. R., *Quart. Rev.*, (1962), 16, 282.
