

COMPREHENSIVE INORGANIC CHEMISTRY

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COMPREHENSIVE INORGANIC CHEMISTRY

IN FIVE VOLUMES

Volume 1

H
He, Ne, Ar, Kr, Xe, Rn
Li, Na, K, Rb, Cs, Fr
Be, Mg, Ca, Sr, Ba, Ra
B, Al, Ga, In, Tl
C, Si

Volume 1. H, Noble Gases, Group IA, Group IIA, Group IIIB, C and Si

Volume 2. Ge, Sn, Pb, Group VB, Group VIB, Group VIIB

Volume 3. Group IB, Group IIB, Group IIIA, Group IVA, Group VA, Group VIA, Group VIIA, Group VIII

Volume 4. Lanthanides, Transition Metal Compounds

Volume 5. Actinides, Master Index

PREFACE

THE Editorial Board of Comprehensive Inorganic Chemistry planned the treatise to fill a gap in the literature. There was no work that provided more information than could be found in single volumes but was not so large as to put it out of reach of all but a few central libraries.

The Editorial Board drew up and incorporated in instructions to authors a scheme that would make the best possible use of about five thousand pages. It was envisaged that the treatise would be of service to a wide range of readers many of whom would not be professional chemists. Convenience for all classes of reader was of paramount importance so that if a conflict arose between brevity and ease of use, the latter was preferred. Nevertheless the arrangement of the treatise is so systematic that such conflicts rarely occurred. The convenience of the reader has been further ensured by the adoption of a consistent arrangement of material within the chapters on the elements. The editors have been very gratified to observe that authors have not found the imposed pattern unduly restrictive. It has certainly helped to keep the accounts coherent and to preserve the intended balance between the chapters. The editors are very sensible to the effort that authors have made to collaborate.

The section of the book devoted to the survey of topics, particularly those relating to the transition elements, was a special interest of Sir Ronald Nyholm, whose death after most chapters were in proof saddened many chemists. We hope that those chapters which bear repeated evidence of his intellectual influence will be judged to be one of the many worthy memorials that he left behind him.

A. F. TROTMAN-DICKENSON

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Master Index

1. THE ELEMENT HYDROGEN, ORTHO- AND PARA-HYDROGEN, ATOMIC HYDROGEN

K. M. MACKAY
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1. INTRODUCTION

In this article, the properties of elemental hydrogen are detailed, together with those of its various forms. The heavier isotopes, and species containing them such as HD, are treated in Chapter 2, and hydrogen compounds are reviewed in Chapter 3. More detailed accounts of individual hydrides are given under each element and major sections are devoted to boron hydrides and related compounds and to hydrido-complexes of the transition elements. The proton, protonic acids, and the hydrogen bond are treated later.

The first record of hydrogen probably dates back to Paracelsus in the sixteenth century who observed an "air" formed by the action of acids on iron which was inflammable. Observations on this air were made by a number of seventeenth-century chemists, including Boyle and de Mayerne, but the first isolation of pure hydrogen was not achieved until 1766 by Cavendish, who distinguished it from other inflammable gases. In later work (1784), Cavendish showed that hydrogen burned in oxygen to form water, and the decomposition of water into hydrogen and oxygen by an electric current was demonstrated a few years later. The name *hydrogen* was given by Lavoisier, who demonstrated the formation from steam by the action of red hot iron.

Combined hydrogen is abundant on earth and it is estimated to form just under 1% by weight, or 15.4% by atoms, of the outermost kilometre of the earth's crust (including the oceans and atmosphere). In the Universe, hydrogen is of course the most abundant element and the source of all others by fusion processes in the stars. The common forms of combined hydrogen are water and hydroxyl, and as organic compounds. Much smaller amounts occur combined with nitrogen, sulphur or the halogens, and these mainly in special cases such as volcanic gases and juvenile water.

Free hydrogen is rare, forming about one part in 10^7 of the atmosphere. It is produced in volcanic gases and is also found in inclusions in minerals, in natural gas, and as a product of a few anaerobic fermentation processes such as that of starch by *B. subtilis*. However, its lightness leads to a high mean velocity of 1.84 km sec^{-1} , which is a sufficiently large fraction of the escape velocity of 11.2 km sec^{-1} to mean that hydrogen is rapidly lost from the atmosphere.

Hydrogen is important to the chemist in many ways. It is the simplest element, combines with every other element except the rare gases and one or two of the heavier radioactive elements, and is found in a larger number of compounds than any other element. This simplicity and ubiquity combine to present a major challenge to theoretician and experimentalist alike. It is found in electrovalent, covalent, and metallic bonding, delocalized

polycentred sigma bonds were first invoked to account for a hydride, B_2H_6 , and the hydrogen bond in all its varieties adds further to its range of behaviour.

The most detailed modern account of the properties of hydrogen is that given by Pascal¹, though the data should be used with caution. More abbreviated discussions are given in the slightly older textbooks of inorganic chemistry, especially by Remy and Emeléus and Anderson², but the modern successors give little on the element itself. The books on hydrides by Shaw³ and Mackay⁴ give brief accounts of the element.

2. PREPARATION AND PRODUCTION

Hydrogen is readily available commercially and laboratory preparations are now rarely used except for demonstration purposes. Methods used divide essentially into reductions of the solvated proton (action of metals on water or acid, action of carbon on steam), oxidations of hydride or complex hydride ions, and thermal decomposition of hydrogen compounds (hydrocarbons, water). The more convenient laboratory preparations are as follows.

Active Metal + Water

Use of sodium, as the amalgam for greater control, or calcium is preferred.

Metal + Acid

For the metal, zinc is most convenient and iron is the classic choice. Hydrochloric acid is preferred, but sulphuric acid may be used provided it is sufficiently dilute (or SO_2 is formed). Impurities in the metal give rise to phosphine, arsine, and sometimes hydrogen sulphide.

In the first two preparations many other metals may be used under appropriate conditions. Magnesium and hot water react rapidly and this may be a useful route in special cases.

Metal + Alkali

The most convenient choices are aluminium or silicon (as ferrosilicon) used with caustic soda. Other amphoteric metals may be substituted.

Hydride + Water

LiH , CaH_2 or $LiAlH_4$ may all be used and react in a controllable manner with water. This is an expensive method, but it does give a comparatively pure product and, as half the hydrogen comes from the water, it gives a large amount of hydrogen for unit weight of reagent. This has advantages in the field, for example in filling balloons used for meteorological observations.

¹ *Nouveau Traité de Chimie Minérale*, Vol. I, p. 565, Masson et Cie, Paris (1956).

² H. Remy, *Treatise on Inorganic Chemistry* (translated by J. S. Anderson), Vol. I, p. 21. Elsevier (1956); H. J. Emeléus and J. S. Anderson, *Modern Aspects of Inorganic Chemistry*, 3rd ed., p. 383, Routledge & Kegan Paul, London (1960).

³ B. L. Shaw, *Inorganic Hydrides*, Pergamon (1967).

⁴ K. M. Mackay, *Hydrogen Compounds of the Metallic Elements*, E. & F. N. Spon, London (1966).