

CHEMISTRY
of the
HYDRIDES

HURD

An Introduction to the
CHEMISTRY
of the
HYDRIDES

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Preface

During recent years chemists have become increasingly aware of the real need for a book which coordinates the widely diversified field of hydride chemistry. The fundamental importance of certain hydrides in life processes and in our economy is well recognized. Numerous books describing the properties and reactions of water, the hydrocarbons, ammonia, and the hydrogen halides are to be found on our library shelves. Nevertheless, the relationship of these compounds as hydrides to the salt-like hydrides of the alkali metals, to the obscure hydrides of gallium, bismuth, and tellurium, and to the metallic hydrides of the transitional elements generally has been overlooked. In truth, there are but few general classes of chemical compounds that exhibit as well as the hydrides the variations in physical and chemical properties that accompany the periodic variations in size, valence, and electronegativity of the different chemical elements.

It is particularly appropriate that a book on the chemistry and applications of the hydrides should be presented at this time. The field of hydride chemistry is undergoing a rapid expansion, both in the scope of academic research and in the extent of industrial application. Hydride compounds considered as laboratory curiosities only a few years ago are now being produced industrially on a large scale. Outstanding advances in the theoretical and descriptive aspects of hydride chemistry are being made in university laboratories. Exciting new avenues for research and investigation are being uncovered.

This book is not intended to be a "catch-all" reference book. My principal interest is in a critical and coordinated presentation of the theory, the properties, and the reactions of the hydrides that will be of value to the chemist. To industrial and academic chemists alike, I hope to convey the magnitude of a field unusually rich in possibilities for exploitation.

I have tried, insofar as possible, to maintain a balance in the treatment of the various phases of hydride chemistry. It obviously would be neither practical nor desirable to include in this book the complete chemistry of well-investigated hydrides like water or ammonia, yet a discussion of their places in the family of hydrides and their reactions as hydrides must not be excluded. The amount of space allotted to the discussion of unique hydride systems, such as the boron hydrides,

is in my opinion primarily a function of their relative value rather than an expression of my own particular interest.

In conclusion, I wish to express my sincere gratitude and appreciation to Professor Eugene G. Rochow of Harvard University for reviewing the manuscript and for encouraging me in this project; to Dr. Thomas R. P. Gibb, Jr., formerly of Metal Hydrides, Inc., for general encouragement as well as for specific data on certain hydride systems; to Professor W. C. Fernelius of Pennsylvania State College for reviewing the chapter on nomenclature; to Dr. A. L. Marshall and Dr. A. E. Newkirk of the General Electric Research Laboratory for reviewing the manuscript, in particular the chapter on the boron hydrides, and for helpful suggestions; to Professor Egon Wiberg of the University of Munich, Germany, for much valuable information on hydride compounds; and to Professor A. W. Laubengayer of Cornell University, who first aroused my interest in the hydrides and who introduced me to the fascinating study of modern inorganic chemistry.

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Introduction to the Hydrides

Hydrogen not only is the lightest of the chemical elements, but, considering its chemical behavior, it certainly is one of the most unique elements. It is considerably distinguished from other chemical elements by its versatility as a chemical partner and by the remarkable variety of properties it assumes in its different chemical compounds. Furthermore, hydrogen will enter into chemical combination with almost all the known chemical elements; thus it is present as a constituent in a very large number of chemical compounds.

Certain of the compounds of hydrogen, in particular the binary compounds of hydrogen with other elements, are known as the *hydrides*, and, as such, are the subject of this book. The term *hydride* is used in a very general sense; strictly speaking, *hydride* should be applied only to those relatively few compounds in which hydrogen is present as a negative ion, that is, a *hydride ion*. Some authorities in the field of hydrogen chemistry feel that the term *hydride* should be applied to compounds, and only to such compounds, in which hydrogen is bonded chemically to a *metallic* element. This rule obviously excludes the hydrogen compounds of the non-metallic elements like nitrogen, oxygen, sulfur, and the halogens; it also raises questions concerning the definition of a metal. However, it is not likely that one can get an adequate view or comprehension of hydride chemistry as a whole without considering, at least briefly, the hydrogen compounds of the non-metallic elements as well as those of the metallic elements. Therefore, it is most convenient for the purpose of discussion to use the term *hydride* as a general name for any binary compound comprising one other element and hydrogen. We also shall employ the term *hydride*, again for convenience, in naming complex derivatives of certain of the binary hydrides. These compounds may be called *complex* or *secondary* hydrides to distinguish them from the *simple* or *binary* hydrides. In discussing the hydrides, we shall denote as the *parent element* that element with which hydrogen is combined.

The Classes of Hydrides. The binary compounds of hydrogen may be classified or divided into three principal categories according

to broad differences in their structures, physical properties, and chemical behavior.

I. *The ionic hydrides* are salt-like compounds in which the hydrogen is present as the negatively charged *hydride ion*, H^- . This ion comprises a hydrogen nucleus, or proton, associated with a pair of electrons, and it is formally analogous to a halide ion. Hydrogen, by virtue of its single valence electron and its valence shell which can become saturated by the addition of one extra electron, may be considered formally either as the lightest member of the alkali metal group or as the lightest member of the halogen group. In combination with strongly positive elements, such as the alkali metals or alkaline earth metals, hydrogen appears to be strongly negative in character and acts as a pseudo-halide ion. Thus, the ionic halides of the strongly positive alkali and alkaline earth metals are typical ionic crystals which are quite similar to the ionic halides in their structures and physical properties. These compounds have high melting points, high heats of formation, a high degree of thermal stability, and they are able to conduct electricity if they are melted.

In combination with strongly negative elements, such as the halogens, hydrogen will be relatively positive in nature. However, the electrical properties of the hydrogen atom resemble those of the halogens more than they do those of the alkali metals; salt-like compounds containing hydrogen as the positive ionic component are not known, although in a few reactions hydrogen may behave as though it were a positive ion.

II. *The covalent hydrides* are volatile gases, liquids, and (in a few cases) solids in which the chemical bonding is primarily of the non-polar, electron-pair-sharing type. This class of compounds comprises a major proportion of the known hydrides. There are considerable variations in the chemical properties of the covalent hydrides, but these compounds have much in common in their physical properties. They are similar in many ways to the organometallic compounds for, in many instances, hydrogen appears to behave as the most simple, or prototype, organic radical.

III. *The transitional metal hydrides* are the hydrides of the transitional elements; that is, those elements lying in the center of the long-form Periodic Table and in which incomplete electron shells underlying the valence shells become progressively occupied and expanded from element to element across the Periodic Table (Figure 1). These compounds are considered as a group largely out of convenience since there are wide variations in the nature and properties of the transitional metal hydrides. A few of the transitional metal hydrides appear to

[illegible]

FIGURE 1. Long-Form Periodic Table of the Elements Showing Distribution of Hydride Types.

comprise little more than molecular hydrogen physically adsorbed in rifts or defects in the structure of the metal. Others of the transitional metal hydrides appear to be formally analogous to alloys; that is to say, the hydrogen behaves as though it, too, were a metal. It assumes definite positions in the metal lattice structure, and the properties of the "compound" remain metallic.

Certain of the transitional metal hydrides resemble the ionic hydrides to a considerable degree. These compounds have high heats of formation and unique crystal structures which differ considerably from those of elements from which they are derived. In the formation of these hydrides, the metallic character of the element is lost and the hydrides appear definitely to be chemical compounds. However, their chemical compositions are variable, depending upon the method by which they are synthesized, and they seldom approach a stoichiometric content of hydrogen. Not all the transitional elements are known to form hydrides.

In addition to the three principal classes of hydrides, there is a group of hydrides which we may designate as the *borderline hydrides*. These compounds are known only as transient or, at best, relatively unstable compounds which appear to have properties intermediate between those of the covalent hydrides and those of the transitional hydrides.

It is of interest to observe the relationships between the various classes of hydrides as outlined above. Figure 1 shows the long-period arrangement of the chemical elements blocked out according to the type of hydride that each element forms. It should be emphasized that there are no sharp dividing lines between the different classes of hydrides except at the ending of each period with an inert gas.

It will be noted that the positive or negative character of each element plays an important role in determining the type of hydride which that element will form. It will become apparent also that there is a gradual transition in hydride type across the periodic arrangement of the elements, although in some places this transition may become somewhat obscure and confused.

In combination with the strongly positive metals of the first and second groups, hydrogen is, relatively speaking, strongly negative; the hydride compounds are predominantly ionic, exhibiting definite crystalline structures, high heats of formation, and relatively high decomposition temperatures. In the second and third periods, there are no transitional elements. In these periods, the hydrides of beryllium and magnesium form a "bridge" between the ionic hydrides

and the covalent hydrides, and these compounds exhibit properties intermediate between those of the two groups.

In the higher periods, there is a transition in hydride type from the ionic hydrides through the first groups of the transitional metal hydrides, including the rare earth hydrides, in which the hydride compounds are also relatively stable solids with definite crystal structures and large positive heats of formation. However, these compounds differ from the ionic hydrides of the alkali metals and alkaline earth metals in several respects. During the formation of a hydride in this group, an expansion of the crystal structure, or lattice, of the metal occurs rather than the lattice contraction which accompanies hydride formation with the metals of Groups I and II, and the compounds do not have exact formulas; that is, they are of variable and indefinite composition.

Toward the end of the transitional series the hydrides become much less well defined, less like chemical compounds in the conventional sense, and behave more like alloys or interstitial solutions of hydrogen in the metal lattices. In the extreme cases, hydrogen adsorption may be limited to physical adsorption on the surface, or in rifts or defects in the metal structure.

The gap between the last of the transitional metal hydrides and the first of the covalent hydrides is bridged by the relatively unstable or "borderline" hydrides in Groups IB and IIB. Since these elements have completed electron shells underlying their valence electron shells, they are in some ways more closely related to the alkali metals than they are to the transitional elements. However, in the formation of chemical bonds by these elements, electrons may be removed from the completed lower shells into the valence shell, and thus the chemical properties of these elements in their compounds may resemble those of the adjacent transitional elements. The group of "borderline" hydrides belonging to this classification actually should be divided into two subgroups. (1) Copper and zinc form hydrides that appear to be intermediate in properties between those of the covalent hydrides and the hydrides of the alkali metal or alkaline earth metals. (2) The other elements, silver, gold, cadmium, and mercury act more like the transitional elements in the matter of hydride formation. Indium and thallium probably should be included in this classification also.

The remaining elements in Groups III and IIIB through VII and VIIB form volatile covalent hydrides which resemble one another considerably in their gross physical properties. Even the most highly polar of the covalent hydrides, hydrogen fluoride, behaves like a pre-

dominantly covalent compound in its normal state. Thus, the covalent hydrides stand together as a well-defined group on the basis of their physical properties. The chemical properties of the various covalent hydrides depend on the atomic size and weight of the parent element and on the group that the parent element occupies in the Periodic Table.

After the covalent hydrides, the sequence of hydride compounds in a given period is interrupted by the occurrence of a rare gas. With the next period, the sequence just described begins again with an alkali metal hydride.

It may be pointed out that, in addition to the normal hydrides, hydrides of a special sort have been observed for most of the chemical elements. These are transient molecules, usually of the type MH (where M denotes the parent element atom), which are observed by their spectra under the high-temperature conditions of an electric discharge. Such hydrides may be, or may have been, of importance in cosmological processes such as those occurring during the formation of planetary systems. They are of considerable importance in the investigation of the physics of molecular structure, such as, for example, determinations of interatomic bond distances.

GENERAL REFERENCES

- Emeléus and Anderson, *Modern Aspects of Inorganic Chemistry*, Routledge, London, 1938.
Sidgwick, *Chemical Elements and Their Compounds*, Oxford, London, 1950.
Ephraim, *Inorganic Chemistry*, Nordeman, New York, 1939.

Chemical Bonding and the Structure of Hydrides

To understand and interpret the behavior of hydrogen in its reactions with the various chemical elements, and the compounds that hydrogen forms with these elements, we should have an adequate working knowledge of the principles of chemical bonding and valence. It would be much beyond the scope of this book to present a detailed explanation of these principles. The reader interested in refreshing his knowledge of chemical bonding and valence should consult one or more of the many treatises on this subject.* However, it is considered appropriate to include with this discussion of hydrogen and its chemical bonding a brief resume of the principal types of chemical bonding and the influence of factors, such as electron affinity and atomic size, on chemical behavior.

The Mechanism of Chemical Bonding. It is convenient to describe chemical bonding in terms of *atomic* and *molecular orbitals*. Each chemical element atom has a certain number of orbitals, or *energy levels*, which can be occupied by electrons or electron pairs. These orbitals are grouped into general energy levels which usually are called *electron shells*. If we begin with an atomic nucleus that has been stripped of electrons and then add electrons to it in stepwise fashion, we observe that the process of occupying the vacant orbitals, first by single electrons and eventually by electron pairs, releases energy until a sufficient number of electrons has been added to just balance the positive charge on the atomic nucleus. In this electron

* Several references may be suggested. Since the viewpoints presented will differ slightly, it may be desirable to consult several of these to obtain a broader concept of chemical bonding: Pauling, *Nature of the Chemical Bond*, Cornell University Press, Ithaca, N.Y., 1940. Sidgwick, *Electronic Theory of Valence*, Oxford, London, 1946. Rice, *Electronic Structure and Chemical Bonding*, McGraw-Hill, New York, 1940. Lewis, *Valence and the Structure of Atoms and Molecules*, American Chemical Society Monograph, 1923. A short but excellent description of basic principles may be found in Luder and Zuffanti, *The Electronic Theory of Acids and Bases*, Wiley, New York, 1946.

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addition process, the levels of lower energy are filled first, then levels of higher energy, until the valence shell is reached. The electronic configuration in the highest general energy level normally occupied, that is, the *valence shell* of the atom, will depend on the different energy sublevels within the valence shell; with most uncombined atoms there will be both unpaired electrons and vacant or partially occupied orbitals within the valence shell.

Once the positive nuclear charge of the atom is balanced, the insertion of additional electrons into vacant orbitals will be hindered by the repulsion of the electronic charge. For most elements, this process requires more energy than will be liberated by the process of orbital occupancy and electron pairing. However, if the electronic charge can be balanced in some other way, considerable amounts of energy may be released by the addition of extra electrons to fill vacant orbitals. That is, if a means is available whereby the atom can acquire additional electrons, either to pair with single electrons in valence shell orbitals or to occupy vacant orbitals, and still maintain a favorable electrical balance, the atom will do so since this process releases energy. It is possible for electrons to occupy orbitals on more than one atom, and unfilled orbitals on one atom may be filled by electrons from another atom. This is the basis for the formation of chemical bonds between atoms.*

* A rule that often is used for predicting the valences, and to some extent the chemical behavior, of relatively simple elements like the alkali metals, the halogens, and most of the elements in the first two rows of the Periodic Table, is the rule of "eight or two." Simply stated, this rule predicts that an atom will tend to gain or lose electrons in the formation of its chemical compounds so that it can assume as closely as possible a stable electronic configuration like that of the closest inert gas. For the elements in the first row of the Periodic Table, the stable configuration of the outermost electron shell may correspond to that of helium (two electrons) or to that of neon (eight electrons). Thus, in the formation of lithium fluoride, for example, the lithium atom can lose its one valence electron to expose an underlying structure of two electrons in a closed shell, and the lithium ion has the same electronic configuration as the inert gas helium. The fluorine atom can acquire the electron lost by the lithium atom and add it to its incomplete shell of seven electrons. The fluoride ion thus formed has a completed "octet" of electrons, and its electronic configuration resembles that of the inert gas neon. By this reasoning, we might expect that the hydrogen atom could lose its one electron to become the equivalent of a positive alkali metal ion, or gain one electron to resemble the helium atom and become the equivalent of a negative halide ion.

We know, however, that the rule of "eight or two" is a considerable oversimplification applicable only in rather special cases, and that there are many exceptions to this rule. For example, sulfur forms a very stable compound, *sulfur hexafluoride*, SF_6 , in which there are apparently twelve electrons in the valence shell of the sulfur atom. The rule breaks down also when one tries to apply it to atoms which can show a variety of valence structures, such as those of the transitional elements.

The number of general energy levels will depend, of course, on the particular atom. In hydrogen and helium, the normal electronic configuration involves only one such level and, at most, two electrons; in the second-period elements, proceeding from lithium to neon, occupancy of the four orbitals in the second general energy level, or electron shell, occurs until a maximum of eight electrons (four electron pairs) has been reached; in the third-period elements, from sodium to argon, the third electron shell is progressively occupied although not completely filled. In the higher periods, the system of orbital occupancy is more complicated. The energy relationships in the complex electronic structures of the heavier elements are such that some overlapping of electron shells can occur. Certain orbitals in the valence shell may be occupied before all the underlying shells are completely occupied.

It will be apparent that the light elements, with relatively few valence electrons and valence orbitals, will tend to be rather restricted in their chemical behavior as compared with the heavier elements, which have many outlying orbitals in which there are only slight differences in energy, and many electrons potentially available for the formation of chemical bonds. The overlapping energy-wise of electron shells is reflected in the chemical properties of the heavier elements, and in many of these elements we can observe several different states of valence and kinds of chemical behavior. The heavier elements do, in fact, fall into several different groups, for example, the *transitional metals* and the *rare earths*, depending upon their electronic configurations and chemical properties.

We designate the *relative* tendency of an atom within a molecule to attract and hold extra electrons from other atoms as its *electronegativity*. This value is related to the *electron affinity* of the atom, that is, the amount of energy released in the addition of an electron to a normally vacant valence shell orbital, but it also depends on other factors, such as the size of the atom and the extent to which the cloud of electrons surrounding the nucleus can be distorted by other atoms. The electronegativity value has a very important bearing on the chemical behavior of the element and its chemical compounds; repeated references will be made to electronegativity throughout this book.

The Principal Types of Chemical Bonds. There are several ways in which an atom can acquire additional electrons in the formation of chemical bonds: by outright transfer of electrons from another atom or atoms; by the reciprocal sharing of one or more electrons with another atom or atoms; and by the acceptance in a share in an electron or an electron pair donated by another atom or atoms.*

* On theoretical grounds it may be shown that two atoms may be bonded by one electron occupying normally vacant orbitals in each of the atoms, that is, a *one-*

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An *ionic bond* involves (in theory, at least) the complete transfer of electrons from one atom to another. This is a process that can occur only between atoms of widely different electronegativity, and in which one or, at the most, two electrons are involved in the electron transfer between atoms. For example, in *sodium hydride* the energy released by the pairing of the odd electron in the valence shell of the hydrogen atom to form a *hydride ion* is more than sufficient to compensate for the removal of the lone valence electron of the sodium atom to form a positive sodium ion. Consequently, the combination of sodium and hydrogen to form sodium hydride releases energy. This does not imply that the sodium atom has no tendency to retain its valence electron (and certainly not that the sodium atom has a tendency to lose this electron), only that such tendency is relatively weak as compared to the strong tendency of the hydrogen atom to acquire an additional electron. (We shall examine this tendency in more detail further on.) Although the hydrogen atom acquires a charge of -1 in the process of electron transfer, the hydride ion is surrounded by positively charged sodium ions, and vice versa, and the system as a whole, that is, the crystal of sodium hydride, is in electrical balance. Under these conditions, the hydride ions and the sodium ions will behave as stable entities.

Because of the strong electrostatic forces holding the aggregate of positive and negative ions together, considerable amounts of energy are required to separate the component ions of an ionic crystal. Consequently, ionic compounds generally are solids that exhibit high melting points and are soluble only in highly polar solvents.

A *covalent bond* is formed by the *reciprocal sharing* of electrons between atoms. This is the basic type of bonding responsible for the existence of a majority of the known chemical compounds, as well as for the dimeric form of most of the elemental gases. It is entirely possible for an electron pair to occupy orbitals in both of two atoms or, for that matter, to occupy orbitals in more than two atoms if the compound is complex.* True covalence, or the *completely reciprocal*

electron bond. It is necessary, however, that the two atoms have closely similar electronegativities for such bonding to be possible, and the one-electron bond is normally expected to occur only between like atoms. Only a few examples are known in which the presence of a one-electron bond is obvious. One of these is the *hydrogen molecule ion*, H_2^+ , and it is certain that the one-electron bond is much weaker than a normal electron pair bond.

* The occupancy of orbitals in more than one atom by an electron pair can be described quantum-mechanically either in terms of *molecular orbitals* or as a combination of the separate *atomic orbitals*.