Inorganic Reactions and Methods

Volume 1
The Formation of Bonds to Hydrogen (Part 1)

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Contents of Volume 1

How to Use this Book xiii
Preface to the Series xix
Editorial Consultants to the Series xxiii
Contributors to Volume 1 xxv

1. The Formation of Bonds to Hydrogen (Part 1) 1

1.1. Introduction 2

1.2. The Formation of Hydrogen 3

1.2.1. Introduction 3
1.2.2. by Reactions of Hydride Ions 3
1.2.2.1. with Hydrogen Halides. 3
1.2.2.2. with OH Groups and Acids in OH Systems. 5
1.2.2.3. with SH and SeH Groups and Acids in SH and SeH Systems. 11
1.2.2.4. with NH Groups and Acids in NH Systems. 12
1.2.2.5. with PH and AsH Groups and Acids in PH and AsH Systems. 14
1.2.3. by Reactions of Complex Hydrides 16
1.2.3.1. with Hydrogen Halides. 16
1.2.3.2. with OH Groups and Acids in OH Systems. 18
1.2.3.3. with SH and SeH Groups and Acids in SH and SeH Systems. 21
1.2.3.4. with NH Groups and Acids in NH Systems. 22
1.2.3.5. with PH and AsH Groups and Acids in PH and AsH Systems. 25
1.2.4. by Reactions of Metals 27
1.2.4.1. with Hydrogen Halides. 27
1.2.4.2. with OH Groups and Acids in OH Systems. 29
1.2.4.3. with SH and SeH Groups and Acids in SH and SeH Systems. 33
1.2.4.4. with NH Groups and Acids in NH Systems. 34
1.2.4.5. with PH and AsH Groups and Acids in PH and AsH Systems. 37
1.2.5. by Reactions of Nonmetals and Semimetals 38
1.2.5.1. with Hydrogen Halides. 38
The Formation of Hydrogen

by Reactions of Nonmetals and Semimetals

1.2.5.2. with OH Groups and Acids in OH Systems. 39
1.2.5.3. with SH and SeH Groups and Acids in SH and SeH Systems. 43
1.2.5.4. with NH Groups and Acids in NH Systems. 43
1.2.5.5. with PH and AsH Groups and Acids in PH and AsH Systems 45
1.2.6. by Electrolytic Reduction 46
1.2.6.1. of Hydrogen Halides. 46
1.2.6.2. of OH Systems. 49
1.2.6.3. of SH and SeH Systems. 51
1.2.6.4. of NH Systems. 52
1.2.6.5. of PH and AsH Systems. 55
1.2.7. by Reactions of Water 57
1.2.7.1. with Carbon. 57
1.2.7.2. with Saturated Hydrocarbons. 57
1.2.7.3. with Unsaturated Hydrocarbons. 59
1.2.7.4. with CO. 60
1.2.7.5. Involving Water Splitting 64
1.2.7.5.1. in Electrochemical Reactions. 64
1.2.7.5.2. in Chemical Reactions Involving Main-Group Elements. 65
1.2.7.5.3. in Chemical Reactions Involving Transition and Inner-Transition Metals. 67
1.2.7.6. with Other OH-Containing Compounds. 68
1.2.8. by Partial Oxidation of Hydrocarbons. 68
1.2.9. Isotopes: Deuterium—Chemical Preparation of D₂ and D₂O 69
1.2.9.1. by Interconversion of Deuterated Compounds 69
1.2.9.1.1. in Reactions between D₂O and Active Metals. 69
1.2.9.1.2. in Electrolyses of Salts Dissolved in D₂O. 69
1.2.9.1.3. in HD Synthesis. 70
1.2.9.2. by Isotopic Enrichment 70
1.2.9.2.1. Principles and Reactions 70
1.2.9.2.2. Catalysis of Hydrogen–Water Isotope Exchange 73
1.2.9.2.3. Catalysis of Hydrogen–Ammonia (Amine) Exchange 74
1.2.9.2.4. Other Processes 75

1.3. The Formation of Hydrogen–Halogen Bonds 77

1.3.1. Introduction 77
1.3.2. by Reactions of Hydrogen 79
1.3.2.1. with Fluorine. 79
1.3.2.2. with Chlorine. 79
1.3.2.3. with Bromine. 80
1.3.2.4. with Iodine. 81
1.3.3. by Reactions of Protonic Acids 82
  1.3.3.1. with Fluoride Ions. 82
  1.3.3.2. with Chloride Ions. 84
  1.3.3.3. with Bromide Ions. 85
  1.3.3.4. with Iodide Ions. 86
  1.3.3.5. with Complex Halides. 87
1.3.4. by Hydrolysis 88
  1.3.4.1. of Fluorides. 88
  1.3.4.2. of Chlorides. 90
  1.3.4.3. of Bromides. 92
  1.3.4.4. of Iodides. 94
  1.3.4.5. of Complex Fluorides. 95
1.3.5. by Industrial Processes. 96
1.3.6. in Syntheses of Deuterium Halides. 98
1.3.7. in Syntheses of Hydrogen Astatide. 100

1.4. The Formation of Bonds between Hydrogen and Elements of Group VIB (O, S, Se, Te, Po) 102

  1.4.1. Introduction 102
    1.4.1.1. Scope 102
    1.4.1.2. Classification 102
    1.4.1.3. Safety and Toxicity 103
  1.4.2. by Reactions of Elemental Hydrogen 104
    1.4.2.1. with Elemental Oxygen 104
      1.4.2.1.1. in the Gas Phase. 104
      1.4.2.1.2. in the Gas Phase under Irradiation or Electrical Discharge Giving Hydrogen Peroxide. 106
    1.4.2.1.3. under Metal Catalysis Giving Hydrogen Peroxide. 108
    1.4.2.1.4. under Metal Catalysis Giving Water. 109
  1.4.2.2. with Elemental Sulfur 111
    1.4.2.2.1. Kinetics 111
    1.4.2.2.2. Equilibrium Constants 112
    1.4.2.2.3. The Influence of Catalysts on the Formation of Hydrogen Sulfide 115
    1.4.2.2.4. Induction by Radiation 117
  1.4.2.3. with Elemental Selenium and Tellurium 118
    1.4.2.3.1. The Formation of Hydrogen Selenide 118
    1.4.2.3.2. The Formation of Hydrogen Telluride 119
  1.4.2.4. with Elemental Polonium 119
The Formation of Bonds between Hydrogen and Elements of Group VI B (O, S, Se, Te, Po)

by Reactions of Elemental Hydrogen with Elemental Oxygen

1.4.2.4.1. The Questionable Existence and Stoichiometry of a Polonium Hydride
119
1.4.2.4.2. Reaction of Dihydrogen with Polonium
120
1.4.2.4.3. Reaction of Nascent Hydrogen with Polonium
120
1.4.2.5. with Oxygen Compounds
120
1.4.2.5.1. in Reductions of Metal Oxides
120
1.4.2.5.2. in Reductions of Metal Sulfates
124
1.4.2.5.3. in Reductions of Main-Group Compounds Other than Carbon Oxides
127
1.4.2.5.4. in Reductions of Oxides of Carbon
128
1.4.2.5.5. in the Reverse Water-Gas Shift Reaction
130
1.4.2.5.6. in the Formation of Methanoic Acid
133
1.4.2.5.7. in Methanation Reactions
133
1.4.2.5.8. in the Formation of Methanol by Heterogeneous Catalysis
137
1.4.2.5.9. in the Formation of Methanol and Other Alcohols by Homogeneous Interactions
140
1.4.2.6. with Sulfur Compounds
143
1.4.2.6.1. in Reductions of Metal Sulfides
143
1.4.2.6.2. in Reductions of Sulfur Dioxide
146
1.4.2.6.3. in Reductions of Carbon Disulfide
146
1.4.2.6.4. in Reductions of Sulfur Halides
147
1.4.2.6.5. in Reductions of Salts of Sulfur Oxyacids
148
1.4.2.7. with Selenium and Tellurium Compounds
149
1.4.2.7.1. in Reductions of Selenides
149
1.4.2.7.2. in Reductions of Tellurides
150
1.4.2.8. with Polonium Halides
150
1.4.3. by Reactions of Hydrogen-Containing Compounds
150
1.4.3.1. with Elemental Oxygen
150
1.4.3.1.1. in Heterogeneously Catalyzed Oxidations
150
1.4.3.1.2. in the Formation of Hydrogen Peroxide and Hydroperoxo Species
151
1.4.3.2. with Elemental Sulfur
152
1.4.3.2.1. in Reactions of Compounds Containing the Hydrogen–Carbon Bond
152
1.4.3.2.2. in Reactions of Compounds Containing the Hydrogen–Oxygen Bond
154
1.4.3.2.3. in Reactions of Compounds Containing Bonds Other than Carbon–Hydrogen or Oxygen–Hydrogen
156
1.4.3.3. with Elemental Selenium and Tellurium 157
1.4.3.3.1. in Cleavage of the Carbon–Hydrogen Bond by Selenium. 157
1.4.3.3.2. in Cleavage of the Oxygen–Hydrogen Bond by Selenium. 158
1.4.3.3.3. in Cleavage of the Carbon–Hydrogen Bond by Tellurium. 158
1.4.4. by Reactions of Aqueous Acids 158
1.4.4.1. with Oxides 158
1.4.4.1.1. in the Preparation of Hydrogen Peroxide from Metal Peroxides. 158
1.4.4.1.2. in the Cathodic Reduction of Dioxygen in Aqueous Solution. 159
1.4.4.2. with Sulfides 161
1.4.4.2.1. in the Preparation of Hydrogen Sulfide. 161
1.4.4.2.2. in Preparations of Higher Sulfanes. 164
1.4.4.2.3. in the Formation of Hydrogen Sulfide in Cathodic Reductions. 166
1.4.4.2.4. in the Formation of Higher Sulfanes in Cathodic Reductions. 167
1.4.4.3. with Selenides and Tellurides 167
1.4.4.3.1. in Preparations of Hydrogen Selenide from Acids and Metal Selenides. 167
1.4.4.3.2. in the Preparation of Hydrogen Selenide by Cathodic Reduction. 168
1.4.4.3.3. in the Formation of Diselenane. 169
1.4.4.3.4. in Preparations of Hydrogen Telluride from Acids and Metal Tellurides. 169
1.4.4.3.5. in the Preparation of Hydrogen Telluride by Cathodic Reduction in Acid Electrolyte. 170
1.4.4.4. in the Cathodic Reduction of Polonium. 172
1.4.5. by Reactions of Protonic Acids 172
1.4.5.1. with Oxides 172
1.4.5.1.1. in Preparations of Sulfonic Acids. 172
1.4.5.1.2. in the Formation of Other Compounds Containing Hydrogen–Oxygen Bonds. 173
1.4.5.2. with Sulfides 174
1.4.5.2.1. in Preparations of Hydrogen Sulfide and Sodium Hydrogen Sulfide. 174
1.4.5.2.2. in Preparations of the Higher Sulfanes. 174
1.4.5.2.3. in Preparations of Anhydrous Acids of Sulfur. 175
1.4.5.3. with Selenides Giving Hydrogen Selenide. 176
1.4.6. by Reactions of Covalent Hydrides 176
1.4.6.1. with Oxygen Compounds 176
1.4.6.1.1. in the Hydrolysis of Peroxodisulfate Giving Hydrogen Peroxide. 176
The Formation of Bonds between Hydrogen and Elements of Group VIB (O, S, Se, Te, Po)

1.4.6. by Reactions of Covalent Hydrides

1.4.6.1. with Oxygen Compounds

1.4.6.1.2. in the Formation of Water by Reactions Involving Hydrogen Sulfide. 178

1.4.6.1.3. in the Formation of Water by Thermal Decomposition of Ammonium Salts. 180

1.4.6.2. with Sulfur Compounds 182

1.4.6.2.1. in Hydrolyses of Metal Sulfides. 182

1.4.6.2.2. in Hydrolyses and Ammonolyses of Carbon Sulfides. 183

1.4.6.2.3. in Hydrolyses of Organosulfur Compounds. 186

1.4.6.2.4. in the Reduction of Sulfur Dioxide by Methane. 186

1.4.6.2.5. in Reductions of Sulfur Compounds by Hydrogen Iodide. 188

1.4.6.2.6. in Reductions of Sulfur Compounds by Other Main-Group Hydrides. 191

1.4.6.3. with Selenium and Tellurium Compounds 192

1.4.6.3.1. in the Formation of Hydrogen Selenide by Hydrolysis of Selenides. 192

1.4.6.3.2. in the Formation of Selenols by Hydrolysis of Selenolates. 192

1.4.6.3.3. in Reductions of Selenium(IV) Species. 193

1.4.6.3.4. in the Formation of Hydrogen Telluride by Hydrolysis of Tellurides. 193

1.4.6.3.5. in the Alcoholysis of Aluminum Selenide and Telluride. 193

1.4.7. by Reactions of Binary Metal Hydrides 193

1.4.7.1. with Oxygen Compounds 193

1.4.7.1.1. in Reductions of Carbon Oxides and Carbonates. 193

1.4.7.1.2. in Reductions of Metal Oxides. 194

1.4.7.2. with Sulfur Compounds and Elemental Sulfur. 196

1.4.8. by Reactions of Complex Hydrides 196

1.4.8.1. with Oxygen Compounds 196

1.4.8.1.1. in Reductions of Carbon Oxides and Oxyhalides. 196

1.4.8.1.2. in Reductions of Organic Compounds to Hydroxy Species. 199

1.4.8.1.3. in Reductions of Metal Oxides. 200

1.4.8.2. with Sulfur Compounds 200

1.4.8.2.1. in Reductions of Oxy Compounds of Sulfur. 200
<table>
<thead>
<tr>
<th>Subheading</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4.8.2.2. in Reductions of Halides of Sulfur.</td>
<td>201</td>
</tr>
<tr>
<td>1.4.8.2.3. in Reductions of Other Compounds of Sulfur.</td>
<td>202</td>
</tr>
<tr>
<td>1.4.8.2.4. in Reductions of Elemental Sulfur.</td>
<td>203</td>
</tr>
<tr>
<td>1.4.8.3. with Selenium and Tellurium Compounds</td>
<td>204</td>
</tr>
<tr>
<td>1.4.8.3.1. in Reductions of the Elements by Tetrahydroborate.</td>
<td>204</td>
</tr>
<tr>
<td>1.4.8.3.2. in Reductions of Oxy Compounds of Selenium and Tellurium by Complex Hydrides.</td>
<td>205</td>
</tr>
<tr>
<td>1.4.8.4. with Polonium Halides.</td>
<td>206</td>
</tr>
<tr>
<td>1.4.9. by Industrial Processes</td>
<td>206</td>
</tr>
<tr>
<td>1.4.9.1. Involving Oxygen Compounds</td>
<td>206</td>
</tr>
<tr>
<td>1.4.9.1.1. in the Production of Hydrogen Peroxide.</td>
<td>206</td>
</tr>
<tr>
<td>1.4.9.1.2. in Methanation Reactions.</td>
<td>209</td>
</tr>
<tr>
<td>1.4.9.1.3. in the Production of Methanol.</td>
<td>210</td>
</tr>
<tr>
<td>1.4.9.2. Involving Sulfur Compounds</td>
<td>212</td>
</tr>
<tr>
<td>1.4.9.2.1. in the Hydrogenation of Sulfur or Sulfides Giving Hydrogen Sulfide.</td>
<td>212</td>
</tr>
<tr>
<td>1.4.9.2.2. in the Formation of Hydrogen Sulfide by Hydrodesulfurization.</td>
<td>213</td>
</tr>
<tr>
<td>1.4.9.2.3. in the Reduction of Sulfur Dioxide to Hydrogen Sulfide.</td>
<td>215</td>
</tr>
<tr>
<td>1.4.9.2.4. in the Production of Hydrogen Sulfide from Hydrocarbons.</td>
<td>216</td>
</tr>
<tr>
<td>1.4.9.2.5. in the Production of Hydrogen Sulfide from Alkaline-Earth Sulfides.</td>
<td>218</td>
</tr>
<tr>
<td>1.4.9.3. Involving Selenium and Tellurium: The Hydride Method of Refining the Elements.</td>
<td>219</td>
</tr>
<tr>
<td>1.4.10. in Syntheses of Deuterium Derivatives</td>
<td>220</td>
</tr>
<tr>
<td>1.4.10.1. by Interconversion of Deuterated Compounds.</td>
<td>220</td>
</tr>
<tr>
<td>1.4.10.1.1. with Oxygen Compounds.</td>
<td>220</td>
</tr>
<tr>
<td>1.4.10.1.2. with Sulfur Compounds.</td>
<td>221</td>
</tr>
<tr>
<td>1.4.10.1.3. with Selenium and Tellurium Compounds.</td>
<td>222</td>
</tr>
<tr>
<td>1.4.10.2. by Isotopic Enrichment Using Chemical Reactions</td>
<td>222</td>
</tr>
<tr>
<td>1.4.10.2.1. with Oxygen Compounds.</td>
<td>222</td>
</tr>
<tr>
<td>1.4.10.2.2. with Sulfur Compounds.</td>
<td>227</td>
</tr>
<tr>
<td>1.4.10.2.3. with Selenium and Tellurium Compounds.</td>
<td>228</td>
</tr>
</tbody>
</table>

List of Abbreviations                           231  
Author Index                                   237  
Compound Index                                 263  
Subject Index                                  317  

How to Use this Book

1. Organization of Subject Matter.

1.1. Logic of Subdivision and Add-On Chapters.

This volume is part of a series that describes all of inorganic reaction chemistry. The contents are subdivided systematically and so are the contents of the entire series. Using the periodic system as a correlative device, it is shown how bonds between pairs of elements can be made. Treatment begins with hydrogen making a bond to itself in H₂ and proceeds according to the periodic table with the bonds formed by hydrogen to the halogens, the groups headed by oxygen, nitrogen, carbon, boron, beryllium and lithium, to the transition and inner-transition metals and to the members of group zero. Next it is considered how the halogens form bonds among themselves and then to the elements of the main groups VI to I, the transition and inner-transition metals and the zero-group gases. The process repeats itself with descriptions of the members of each successive periodic group making bonds to all the remaining elements not yet treated until group zero is reached. At this point all actual as well as possible combinations have been covered.

The focus is on the primary formation of bonds, not on subsequent reactions of the products to form other bonds. These latter reactions are covered at the places where the formation of those bonds is described. Reactions in which atoms merely change their oxidation states are not included, nor are reactions in which the same pairs of elements come together again in the product (for example, in metatheses or redistributions). Physical and spectroscopic properties or structural details of the products are not covered by the reaction volumes which are concerned with synthetic utility based on yield, economy of ingredients, purity of product, specificity, etc. The preparation of short-lived transient species is not described.

While in principle the systematization described above could suffice to deal with all the relevant material, there are other topics that inorganic chemists customarily identify as being useful in organizing reaction information and that do not fit into the scheme. These topics are the subject of eight additional chapters constituting the last four books of the series. These chapters are systematic only within their own confines. Their inclusion is based on the best judgment of the Editorial Advisory Board as to what would be most useful currently as well as effective in guiding the future of inorganic reaction chemistry.
1.2. Use of Decimal Section Numbers

The organization of the material is readily apparent through the use of numbers and headings. Chapters are broken into divisions, sections and sub-sections, which have short descriptive headings and are numbered according to the following scheme:

1. Major Heading
1.1. Chapter Heading
1.1.1. Division Heading
1.1.1.1. Section Heading
1.1.1.1.1. Subsection Heading

Further subdivision of a five-digit “slice” utilizes lower-case Roman numerals in parentheses: (i), (ii), (iii), etc. It is often found that, as a consequence of the organization, cognate material is located in different chapters but in similarly numbered pieces, i.e., in parallel sections. Section numbers, rather than page numbers, are the key by which the material is accessed through the various indexes.

1.3. Building of Headings

1.3.1. Headings Forming Part of a Sentence

Most headings are sentence-fragment phrases which constitute sentences when combined. Usually, a period signifies the end of a combined sentence. In order to reconstitute the context in which a heading is to be read, superior-rank titles are printed as running heads on each page. When the sentences are put together from their constituent parts, they describe the contents of the piece at hand. For an example, see 2.3 below.

1.3.2. Headings Forming Part of an Enumeration

For some material it is not useful to construct title sentences as described above. In these cases hierarchical lists, in which the topics are enumerated, are more appropriate. To inform the reader fully about the nature of the material being described, the headings of connected sections that are superior in hierarchy always occur as running heads at the top of each page.

2. Access and Reference Tools

2.1. Plan of the Entire Series (Front Endpaper)

Printed on the inside of the front cover is a list, compiled from all 18 reaction volumes, of the major and chapter headings, i.e., all headings that are preceded by a one- or two-digit decimal section number. This list shows in which volumes the headings occur and highlights the contents of the volume that is at hand by means of a gray background.
2.2. Contents of the Volume at Hand

All the headings, down to the title of the smallest decimal-numbered subsection, are listed in the detailed table of contents of each volume. For each heading the table of contents shows the decimal section number by which it is preceded and the number of the page on which it is found. Beside the decimal section numbers, successive indentations reveal the hierarchy of the sections and thereby facilitate the comprehension of the phrase (or of the enumerative sequence) to which the headings of hierarchically successive sections combine. To reconstitute the context in which the heading of a section must be read to become meaningful, relevant headings of sections superior in hierarchy are repeated at the top of every even-numbered page of the table of contents. The repetitive occurrence of these headings is indicated by the fact that decimal section and page numbers are omitted.

2.3. Running Heads

In order to indicate the hierarchical position of a section, the top of every page of text shows the headings of up to three connected sections that are superior in hierarchy. These running heads provide the context within which the title of the section under discussion becomes meaningful. As an example, the page of Volume 1 on which section 1.4.9.1.3 “in the Production of Methanol” starts, carries the running heads:

1.4. The Formation of Bonds between Hydrogen and O,S,Se,Te,Po
1.4.9. by Industrial Processes
1.4.9.1. Involving Oxygen Compounds

whereby the phrase “in the Production of Methanol” is put into its proper perspective.

2.4. List of Abbreviations

Preceding the indexes there is a list of those abbreviations that are frequently used in the text of the volume at hand or in companion volumes. This list varies somewhat in length from volume to volume; i.e., it becomes more comprehensive as new volumes are published.

Abbreviations that are used incidentally or have no general applicability are not included in the list but are explained at the place of occurrence in the text.

2.5. Author Index

The author index is compiled by computer from the lists of references. Thus it tells whose publications are cited and in that respect is comprehensive. It is not a list of authors, beyond those cited in the references, whose results are reported in the text. However, as the references cited are leading ones,
consulting them, along with the use of appropriate works of the secondary literature, will rapidly lead to the complete literature related to any particular subject covered.

Each entry in the author index refers the user to the appropriate section number.

### 2.6. Compound Index

The compound index lists individual, fully specified compositions of matter that are mentioned in the text. It is an index of empirical formulas, ordered according to the following system: the elements within a given formula occur in alphabetical sequence except for C, or C and H if present, which always come first. Thus, the empirical formula

\[
\begin{align*}
\text{Ti(SO}_4\text{)}_2 & \quad \text{is } O_8S_2Ti \\
\text{BH}_3\text{NH}_3 & \quad \text{BH}_6N \\
\text{Be}_2\text{CO}_3 & \quad \text{CBe}_2\text{O}_3 \\
\text{CsHBr}_2 & \quad \text{Br}_2\text{CsH} \\
\text{Al(\text{HCO}_3}_3 & \quad \text{CsH}_3\text{AlO}_9
\end{align*}
\]

The formulas themselves are ordered alphanumerically without exception; i.e., the formulas mentioned above follow each other in the sequence BH\text{\textsubscript{6}}N, Br\text{\textsubscript{2}}CsH, CBe\text{\textsubscript{2}}O\text{\textsubscript{3}}, C\text{\textsubscript{3}}H\text{\textsubscript{3}}AlO\text{\textsubscript{9}}, O\text{\textsubscript{8}}S\text{\textsubscript{2}}Ti.

A compound index constructed by these principles tells whether a given compound is present. It cannot provide information about compound classes, for example, all aluminum derivatives or all compounds containing phosphorus.

In order to open this route of access as well, the compound index is augmented by successively permuted versions of all empirical formulas. Thus the number of appearances that an empirical formula makes in the compound index is equal to the number of elements it contains. As an example, C\text{\textsubscript{3}}H\text{\textsubscript{3}}AlO\text{\textsubscript{9}}, mentioned above, will appear as such and, at the appropriate positions in the alphanumeric sequence, as H\text{\textsubscript{3}}AlO\text{\textsubscript{9}}*C\text{\textsubscript{3}}, AlO\text{\textsubscript{9}}*C\text{\textsubscript{3}}H\text{\textsubscript{3}} and O\text{\textsubscript{9}}*C\text{\textsubscript{3}}H\text{\textsubscript{3}}Al. The asterisk identifies a permuted formula and allows the original formula to be reconstructed by shifting to the front the elements that follow the asterisk.

Whenever an empirical formula does not show how the elements are combined in groups, it is followed by a linearized structural formula, which reveals the connectivity of the compound(s) underlying the empirical formula and serves to distinguish substances which are identical in composition but differ in the arrangement of elements (isomers). As an example, the empirical formula C\text{\textsubscript{4}}H\text{\textsubscript{10}}O might be followed by the linearized structural formulas (CH\text{\textsubscript{3}}CH\text{\textsubscript{2}})_2O, CH\text{\textsubscript{3}}(CH\text{\textsubscript{2}})_2OCH\text{\textsubscript{3}}, (CH\text{\textsubscript{2}})_2CHOCH\text{\textsubscript{3}}, CH\text{\textsubscript{3}}(CH\text{\textsubscript{2}})_2OH, (CH\text{\textsubscript{2}})_2CHCH\text{\textsubscript{2}}OH and CH\text{\textsubscript{2}}CH\text{\textsubscript{2}}(CH\text{\textsubscript{3}})CHOH to identify the various ethers and alcohols that have the element count C\text{\textsubscript{4}}H\text{\textsubscript{10}}O.
The nonpermuted empirical formulas are followed by keywords. They describe the contexts in which the compound(s) represented by the empirical formulas are discussed. Section numbers direct the reader to relevant positions in the book.

2.7. Subject Index

The subject index provides access to the text by way of methods, techniques, reaction types, apparatus, effects and other phenomena. Also, it lists compound classes such as organotin compounds or rare-earth hydrides which cannot be expressed by the empirical formulas of the compound index.

For multiple entries, additional keywords indicate contexts and thereby avoid the retrieval of information that is irrelevant to the user's need.

Again, section numbers are used to direct the reader to those positions in the book where substantial information is to be found.

2.8. Periodic Table (Back Endpaper)

Reference to periodic groups avoids cumbersome enumerations. Section headings in the series employ this kind of nomenclature.

Unfortunately, however, there is at the present time no general agreement on group designations. In fact, the scheme that is most widely used (combining a group number with the letters A and B) is accompanied by two mutually contradictory interpretations. Thus, titanium may be a group IVA or group IVB element depending on the school to which one adheres or the part of the world in which one resides.

In order to clarify the situation for the purposes of the series, a suitably labeled periodic table is printed on the inside back cover of each volume. All references to periodic group designations in the series refer to this scheme.
Preface to the Series

Inorganic Reactions and Methods constitutes a closed-end series of books designed to present the state of the art of synthetic inorganic chemistry in an unprecedented manner. So far, access to knowledge in inorganic chemistry has been provided almost exclusively using the elements or classes of compounds as starting points. In the first 18 volumes of Inorganic Reactions and Methods, it is bond formation and type of reaction that form the basis of classification.

This new route of access has required new approaches. Rather than sewing together a collection of review articles, a framework has had to be designed that reflects the creative potential of the science and is hoped to stimulate its further development by identifying areas of research that are most likely to be fruitful.

The reaction volumes describe methods by which bonds between the elements can be formed. The work opens with hydrogen making a bond to itself in H₂ and proceeds through the formation of bonds between hydrogen and the halogens, the groups headed by oxygen, nitrogen, carbon, boron, beryllium and lithium to the formation of bonds between hydrogen and the transition and inner-transition metals and elements of group zero. This pattern is repeated across the periodic system until all possible combinations of the elements have been treated. This plan allows most reaction topics to be included in the sequence where appropriate. Reaction types that do not arise from the systematics of the plan are brought together in the concluding chapters on oxidative addition and reductive elimination, insertions and their reverse, electron transfer and electrochemistry, photochemical and other energized reactions, oligomerization and polymerization, inorganic and bioinorganic catalysis and the formation of intercalation compounds and ceramics.

The project has engaged a large number of the most able inorganic chemists as Editorial Advisors creating overall policy, as Editorial Consultants designing detailed plans for the subsections of the work, and as authors whose expertise has been crucial for the quality of the treatment. The conception of the series and the details of its technical realization were the subject of careful planning for several years. The distinguished chemists who form the Editorial Advisory Board have devoted themselves to this exercise, reflecting the great importance of the project.

It was a consequence of the systematics of the overall plan that publication of a volume had to await delivery of its very last contribution. Thus was the defect side of the genius of the system revealed, as the excruciating process of extracting the rate-limiting manuscripts began. Intense editorial effort was
required in order to bring forth the work in a timely way. The production process had to be designed so that the insertion of new material was possible up to the very last stage, enabling authors to update their pieces with the latest developments. The publisher supported the costs of computerized bibliographic searching of the literature and a second one for updating.

Each contribution has been subjected to an intensive process of scientific and linguistic editing in order to homogenize the numerous individual pieces, as well as to provide the highest practicable density of information. This had several important consequences. First, virtually all semblances of the authors’ individual styles have been excised. Second, it was learned during the editorial process that greater economy of language could be achieved by dropping conventionally employed modifiers (such as very) and eliminating italics used for emphasis, quotation marks around nonquoted words, or parentheses around phrases, the result being a gain in clarity and readability. Because the series focuses on the chemistry rather than the chemical literature, the need to tell who had reported what, how and when could be considered of secondary importance. This has made it possible to bring all sentences describing experiments into the present tense. Information on who published what is still to be found in the reference lists. A further consequence is that authors have been burdened neither with identifying leading practitioners, nor with attributing priority for discovery, a job that taxes even the talents of professional historians of science. The authors’ task then devolved to one of describing inorganic chemical reactions, with emphasis on synthetic utility, yield, economy, availability of starting materials, purity of product, specificity, side reactions, etc.

The elimination of the names of people from the text is by far the most controversial feature. Chemistry is plagued by the use of nondescriptive names in place of more expository terms. We have everything from Abegg’s rule, Adkin’s catalyst, Admiralty brass, Alfven number, the Amadori rearrangement and Andrussov oxidation to the Zdanovskii law, Zeeman effect, Zincke cleavage and Zinin reduction. Even well-practiced chemists cannot define these terms precisely except for their own areas of specialty, and no single source exists to serve as a guide. Despite these arguments, the attempt to replace names of people by more descriptive phrases was met in many cases by a warmly negative reaction by our colleague authors, notwithstanding the obvious improvements wrought in terms of lucidity, freedom from obscurity and obfuscation and, especially, ease of access to information by the outsider or student.

Further steps toward universality are taken by the replacement of element and compound names wherever possible by symbols and formulas, and by adding to data in older units their recalculated SI equivalents. The usefulness of the reference sections has been increased by giving journal-title abbreviations according to the Chemical Abstracts Service Source Index, by listing in each reference all of its authors and by accompanying references to patents and journals that may be difficult to access by their Chemical Abstracts cita-
Mathematical signs and common abbreviations are employed to help condense prose and a glossary of the latter is provided in each volume. Dangerous or potentially dangerous procedures are highlighted in safety notes printed in boldface type.

The organization of the material should become readily apparent from an examination of the headings listed in the table of contents. Combining the words constituting the headings, starting with the major heading (one digit) and continuing through the chapter heading (two digits), division heading (three digits), section heading (four digits) to the subsection heading (five digits), reveals at once the subject of a "slice" of the plan. Each slice is a self-contained unit. It includes its own list of references and provides definitions of unusual terms that may be used in it. The reader, therefore, through the table of contents alone, can in most instances quickly reach the desired material and derive the information wanted.

In addition there is for each volume an author index (derived from the lists of references) and a subject index that lists compound classes, methods, techniques, apparatus, effects and other phenomena. An index of empirical formulas is also provided. Here in each formula the element symbols are arranged in alphabetical order except that C, or C and H if present, always come first. Moreover, each empirical formula is permuted successively. Each permuted formula is placed in its alphabetical position and cross referenced to the original formula. Therefore, the number of appearances that an empirical formula makes in the index equals the number of its elements. By this procedure all compounds containing a given element come together in one place in the index. Each original empirical formula is followed by keywords describing the context in which the compound is discussed. All indexes refer the user to subsection rather than page number.

Because the choice of designations of groups in the periodic table is currently in a state of flux, it was decided to conform to the practice of a leading inorganic text. To avoid confusion, an appropriately labeled periodic table is printed on the back endpaper.

From the nature of the work it is obvious that probably not more than two persons will ever read it in its entirety: myself and the publisher's copy editor, Dr. Lindsay S. Ardwin. She, as well as Ms. Mary C. Stradner, Production Manager of VCH Publishers, are to be thanked for their unflagging devotion to the highest editorial standards. The original conception for this series was the brainchild of Dr. Hans F. Ebel, Director of the Editorial Department of VCH Verlagsgesellschaft in Weinheim, Federal Republic of Germany, who also played midwife at the birth of the plan of these reaction volumes with my former mentor, Professor Alan G. MacDiarmid of the University of Pennsylvania, and me in attendance, during the Anaheim, California, American Chemical Society Meeting in the Spring of 1978. Much of what has finally emerged is the product of the inventiveness and imagination of Professor Helmut Grünwald, President of VCH Verlagsgesellschaft. It is a pleasure to
acknowledge that I have learned much from him during the course of our asso-
ciation. Ms. Nancy L. Burnett is to be thanked for typing everything that
had to do with the series from its inception to this time. Directing an opera-
tion of this magnitude without her help would have been unimaginable. My
wife Rose stood by with good cheer while two rooms of our home filled up
with over 10,000 manuscript pages of text, their copies and attendant corre-
spondence.

Finally, and most important, an enormous debt of gratitude toward all
our authors is to be recorded. These experts were asked to prepare brief sum-
maries of their knowledge, ordered in logical sequence by our plan. In addi-
tion, they often involved themselves in improving the original conception by
recommending further refinements and elaborations. The plan of the work as
it is being published can truly be said to be the product of the labors of the
advisors and consultants on the editorial side as well as the many, many au-
thors who were able to augment more general knowledge with their own de-
tailed information and ideas. Because of the unusually strict requirements of
the series, authors had not only to compose their pieces to fit within narrowly
constrained limits of space, format and scope, but after delivery to a short
deadline were expected to stand by while an intrusive editorial process homogen-
ized their own prose styles out of existence and shrunk the length of their
expositions. These long-suffering colleagues had then to endure the wait for
the very last manuscript scheduled for their volume to be delivered so that
their work could be published, often after a further diligent search of the liter-
ature to insure that the latest discoveries were being cited and that claims for
facts now proved false were eliminated. To these co-workers (270 for the reac-
tion volumes alone), from whom so much was demanded but who continued
to place their knowledge and talents unstintingly at the disposal of the proj-
et, we dedicate this series.

J. J. ZUCKERMAN

Norman, Oklahoma

July 4, 1985
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<tr>
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1. The Formation of Bonds to Hydrogen (Part 1)
1.1. Introduction

The elaboration of the plan of this work begins with the formation of the bonds to hydrogen, first with hydrogen itself in \( \text{H}_2 \) and its isotopomers, and then to the halogens and the elements of group VIB (O, S, Se, Te, Po), in Volume 1, followed by the rest of the groups and elements in Volume 2.

(J.J. ZUCKERMAN, ED.)